

DU COMBUSTIBLE NUCLÉAIRE AUX DÉCHETS :
RECHERCHES ACTUELLES

FROM NUCLEAR FUELS TO WASTE: CURRENT RESEARCH

Migration mechanisms of radionuclides from a clay repository toward adjacent aquifers and the surface

Ghislain de Marsily^a, Julio Gonçalves^a, Sophie Violette^a, Maria-Clara Castro^b

^a Université Paris VI, UMR Sisyphe, 4, place Jussieu, 75252 Paris cedex 05, France

^b Department of Geological Sciences, University of Michigan, 2534 C.C. Little Building 425 E, University Ave., Ann Arbor, MI 48109-1063, USA

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Abstract

This article is a critical review of the current understanding of migration processes of solutes in clay. The major migration mechanisms are examined: advection through compaction, thermal convection, migration by hydrocarbon expulsion, gravitational flow, osmosis, molecular diffusion, hydrodynamic dispersion. Examples are taken from the Callovo-Oxfordian clays of the Paris basin in the Meuse/Haute Marne area, near Bure, where France is studying the feasibility of a potential nuclear waste disposal facility. Recent work on the helium distribution in the aquifers of the Paris Basin confirms the importance of molecular diffusion for solute transport in clays. Migration in aquifers is also described, and the major causes of uncertainties for solute migration are discussed. *To cite this article: G. de Marsily et al., C. R. Physique 3 (2002) 945–959.*

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Mécanismes de migration des radionucléides d'un stockage de déchets radioactifs dans l'argile vers la surface

Résumé

Cet article constitue une revue critique des connaissances actuelles sur la migration des éléments en solution dans les milieux argileux. Les principaux mécanismes de migration dans les formations argileuses d'un bassin sédimentaire sont passés en revue : advection par compaction, convection thermique, migration par expulsion des hydrocarbures, mise en charge gravitaire, osmose, diffusion moléculaire, dispersion hydrodynamique. Les argiles du Callovo-Oxfordien du bassin de Paris, aux confins de la Meuse et de la Haute Marne, à Bure, où la France conduit des recherches sur la faisabilité d'un éventuel stockage de déchets radioactifs, sont données en exemple. Des travaux récents sur la distribution de l'hélium dans les aquifères du bassin de Paris permettent de confirmer l'importance du transfert par diffusion dans les séries argileuses. Les transferts dans les aquifères sont également décrits, et les principales causes d'incertitude des migrations sont précisées. *Pour citer cet article : G. de Marsily et al., C. R. Physique 3 (2002) 945–959.*

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E-mail address: gdm@ccr.jussieu.fr (G. de Marsily).

1. Introduction

The migration of radionuclides from a clay repository toward the adjacent more permeable rocks (aquifers) and eventually toward the surface can only start when the canisters containing the wastes have been breached (e.g., by corrosion) and the radionuclides have been dissolved by water and transported away from the waste through the engineered barriers surrounding the canisters (bentonite, which is a natural swelling clay, concrete, etc.). We shall consider here the migration mechanisms in the clay and in aquifers, in its natural undisturbed conditions away from the disposal tunnels and the so-called Disturbed Zone and away from the engineered barriers. Migration mechanisms in these disturbed or engineered media, which could play, e.g., a short-circuit role in the behaviour of a repository, should also be taken into account in a safety assessment, but are not considered here. Radionuclides can be transported by three mechanisms, advection, diffusion and dispersion [1]. Adsorption and chemical interactions with the rocks can also influence their migration, depending on their nature, electrical charges and valence, generally retarding the migration velocity; we will only briefly address this issue here.

2. Advection

Advection is defined as the migration of a solute by the velocity of the water in which it is dissolved, the advective flux Φ_1 [$\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$] of a nuclide is therefore given by: $\Phi_1 = \mathbf{U} \cdot \mathbf{C}$, where \mathbf{U} is the Darcy flux [$\text{m}\cdot\text{s}^{-1}$] and \mathbf{C} is the concentration [$\text{kg}\cdot\text{m}^{-3}$ or $\text{g}\cdot\text{L}^{-1}$]. The Darcy flux is given by $\mathbf{U} = -\mathbf{K} \text{grad} h$, where \mathbf{K} [$\text{m}\cdot\text{s}^{-1}$] is the hydraulic conductivity tensor, and h is the hydraulic head [m]. The actual water velocity in the medium is not the Darcy flux \mathbf{U} , but its ratio to the porosity, \mathbf{U}/ω . The migration equation, if advection is the only mechanism in action, is written, in one dimension:

$$\frac{\partial \mathbf{U}_z \mathbf{C}}{\partial z} = \omega \frac{\partial \mathbf{C}}{\partial t}.$$

The porosity ω to be used needs to be carefully defined. In clay, in particular, the size of the pores can be very small, and the water contained in the pores is often divided into mobile and adhesive water; the fraction of the porosity containing the mobile water is called the kinematic porosity, and can be very small, for example a few percent, when the total porosity is 10–20%. However, solutes can penetrate into the non-mobile water fraction, by molecular diffusion. If this is the case, the porosity accessible to the solute is not the kinematic porosity, but the total porosity. For large molecules, the size of the pores may restrict the accessible porosity; for charged ions, electrostatic effects can also modify the accessible porosity: as clay particles are generally negatively charged, anions are not allowed to access the total porosity, because they are kept away from the clay particle surfaces, and a smaller porosity has to be considered, this is called anionic exclusion. Nevertheless, when an ionic solution migrates through a clay layer, electro-neutrality has to be preserved, and a unique porosity has to be used for both anions and cations.

The first task when studying migration in clay is therefore to determine the advective velocity \mathbf{U} , especially in the vertical direction. It is then necessary to consider not only the individual clay layer where the repository might be built, but also the entire sedimentary basin in which this layer is included, as fluid migration in a basin is the result of several mechanisms affecting the ensemble of layers. Five mechanisms are reviewed here: compaction, thermal convection, hydrocarbon expulsion, gravitational flow and osmosis.

3. Compaction

The formation of a sedimentary basin such as the Paris basin [2], Fig. 1, occurred mostly by successive deposition of different types of sediment in the ocean. Once a layer of sediment has accumulated at the bottom of the ocean, it is slowly compacted by the weight of younger sediment, deposited on top of it. While the layer is compacting, the seawater it contains is released into adjacent horizons, thus creating a hydraulic

head gradient and a Darcy velocity. At early times of basin formation, this is the dominant mechanism for water circulation in a clay layer; for instance, its initial porosity while it is forming on the sea bottom may be as high as 75%; whereas when it becomes buried at a depth of 500 m below the sea bottom, its porosity may be reduced to 30%, and still continue to decrease at greater depths. At the Bure site, for instance, the porosity of the Callovo-Oxfordian clay is now on the order of 10–15%, because, in the past, the maximum burial depth has been around 1000 m, but part of the overburden has been removed by erosion. The compaction mechanism is slow: once a layer has reached a constant depth (i.e., sedimentation has stopped), it may take some million years to reach an equilibrium condition, depending on the hydraulic conductivity of the various layers through which the compaction fluids have to migrate. During compaction, fluids migrate mostly vertically upward, and very rarely in the horizontal direction. The only noticeable exception is when a salt layer (evaporites) is deposited (as occurred during the Triassic in the Paris basin, between Reims and Nancy); in that case, the salt layer is so impervious that fluids can hardly flow through it, and they have to find a horizontal pathway around the salt layer and then, a vertical one toward the surface. If there is no such pathway, so-called ‘abnormal pressures’ and ‘abnormal compaction’ develop: the formation beneath the salt is undercompacted and keeps an abnormally high porosity; the fluids contained in this formation are at a higher pressure than hydrostatic, and can stay so for tens or hundreds of millions of years; this was observed, for example, in the Sahara during drillings for oil, below the Triassic salt layers. Vertical barriers (e.g., impervious faults) have also to exist to prevent fluid migration laterally. In the case of the Callovo-Oxfordian clays at Bure, it is interesting to observe that the head distribution within the formation (based on the few existing pressure measurements) seems to indicate the existence, in the centre of the layer, of

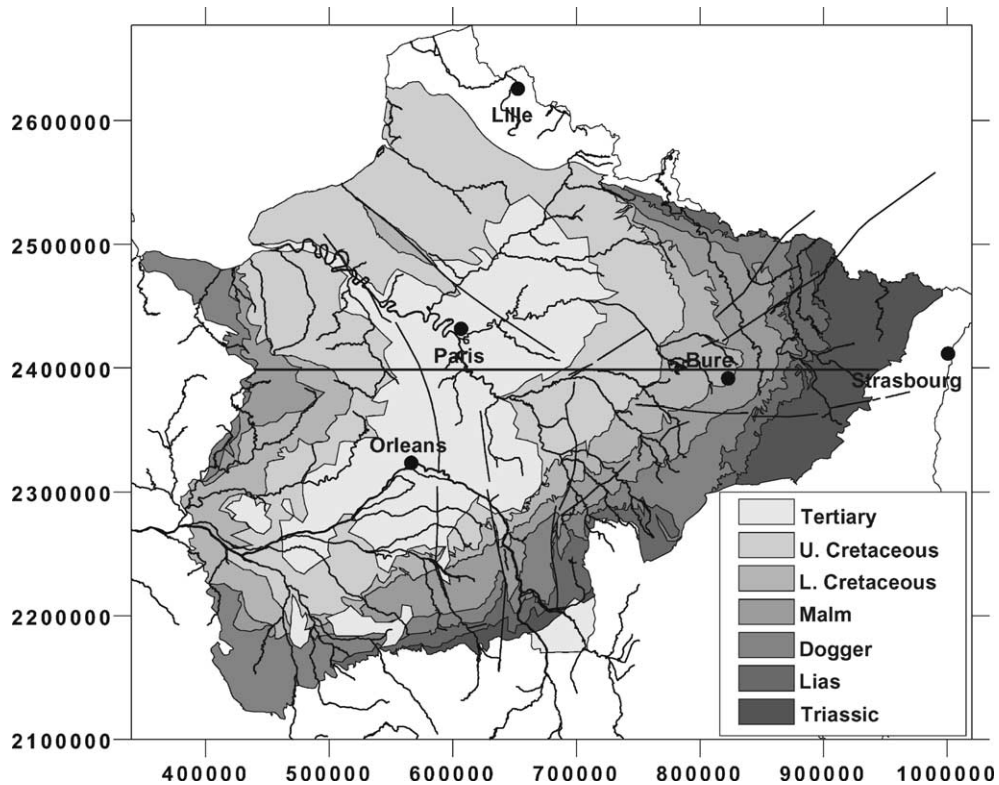


Figure 1. Geological map of the Paris Basin.

Figure 1. Carte géologique du Bassin de Paris.

abnormally high pressures, about 50 m above hydrostatic, which need to be explained and have sometimes been attributed to abnormal compaction. We have built a 3-D numerical model of the formation of the Paris basin [3], from the Triassic to present time, and shown that sedimentation stopped more than 10 million years ago, that the last erosion removed about 300–500 m of sediments overlying the Bure site, and that the absence of any salt layer above the Callovo-Oxfordien and of impervious faults means that an abnormal pressure cannot be maintained in this layer at the present time, if the hydraulic conductivity of the clay is on the order of 10^{-11} – 10^{-13} m·s⁻¹, as measured by injection tests in boreholes and on core samples [4]. Several uplifts and erosions occurred in the basin during its entire history, but it was found that abnormal pressures each time disappear in a few hundred thousand years.

Another compaction mechanism, which could put fluids into motion in a sedimentary basin, is tectonic stress. Due to the Alpine orogeny, compressive forces directed mostly from the SE to the NW gradually deform the Paris basin. Through in situ stress measurements, it is possible to observe that this orogeny, which became active about 20 million years ago, is still active today and that the compressive forces are still present. It is conceivable that horizontal compression is also compacting the basin, thus expelling fluids, and potentially causing the observed abnormal pressures. However, the present strain rate is too low to maintain these abnormal pressures in the Callovo-Oxfordian, assuming that it has the measured hydraulic conductivity.

Advection can occur at two different scales. The first is a microscopic velocity in the pores of the sediments; the hydraulic conductivity K of each formation governs the magnitude of this velocity, as given by Darcy's law. There is, however, a second scale of advection, which might be called 'short-circuit', where the flow takes place in faults or fault zones. Faults are very common features in sedimentary basins and have a large variety of origins. Some are called 'syngenetic' as they are formed at the moment (or slightly after) deposition. They can be the result of mechanical instabilities, slumping, when the sediments are still loose and plastic. Others appear when the basin is deepened through extension. They are called normal faults and are mostly vertical or have a small dip angle from the vertical. Others occur during the compressive stage of the history of the basin, when tectonic forces create an uplift of the basin, and are called reverse faults. They are also mostly vertical. Finally, faults can also occur due to the horizontal displacement of two blocks, separated by a thrust fault; the principal stress orientation can however have an angle with that of the fault. These various faults can affect the entire thickness of the basin (and sometimes the underlying crust), or only a portion of it. This would, for example, be the case of faults created in the past but no longer active and buried by younger layers of sediments, which they do not affect. Some faults can be permeable and serve as fluid conduits; they generally have an orientation parallel to the direction of the major component of the stress tensor, while those orthogonal to this direction are likely to be closed and impervious or, at least, have a lower hydraulic conductivity. But faults can also be sealed by the precipitation of carbonates, silica, and clays and be no longer permeable. In clays, depending on their mechanical properties, faults can be sealed simply by the plastic behaviour of the rock, which may close all openings and maintain the two surfaces of the fault in contact. In the Paris basin, one of the major unanswered questions concerning the Callovo-Oxfordian clay is the presence/absence of faults and fractures in the area selected for the Underground Research Laboratory, and, in the case where faults or fractures would be present, if they are sealed by plastic behaviour or by precipitation of minerals (e.g., calcite). The 3-D seismic survey, which was carried out at the Bure site, showed that, if faults are present, their vertical displacement is less than a few metres, and none have so far been determined in the existing boreholes. The role of the faults, if they exist in the clay, could be crucial because the hydraulic conductivity of a fracture or a fault zone could locally be several orders of magnitude higher than that of the unfractured clay and might serve as a short-circuit for radionuclide transport through the formation. If the faults are pervious, any waste disposal should avoid them by at least several tens of metres. If such faults exist, the description of solute transfer must consider two mechanisms, advection in the more permeable fractures as well as diffusion into the porosity of the two fracture walls, in a direction perpendicular to the advective velocity. Diffusion, as described below, acts as

a sink of the solutes in the immobile water of the porous clay (or almost immobile water, if the hydraulic conductivity of the clay is not neglected compared to that of the fault).

4. Thermal convection

The next important cause of fluid movement in a sedimentary basin is thermal convection. When the basin is still below seawater, and in quasi-hydrostatic conditions, the geothermal flux from the earth's interior (on the order of $60\text{--}80\text{ mW}\cdot\text{m}^{-2}$) induces a temperature gradient directed vertically upward, with typical values on the order of $30\text{ }^{\circ}\text{C}\cdot\text{km}^{-1}$. In case of crustal thinning, or magmatic intrusion, the heat flux can be much higher, up to $300\text{ mW}\cdot\text{m}^{-2}$, and the temperature gradient may reach $150\text{ }^{\circ}\text{C}\cdot\text{km}^{-1}$. It is, however, not believed today that the Paris basin has ever had an abnormal heat flux or temperature gradient. Nevertheless, any given temperature gradient can potentially generate Rayleigh–Taylor instabilities and convective cells may develop. This would be mostly likely to occur in thick permeable layers, not in clay layers. If the layers are horizontal, a critical Rayleigh number can be defined [5], as a function of the temperature gradient, the thickness of the layer, the thermal conductivity and capacity and the hydraulic conductivity; above this number, convection takes place. If the layers have a dip, there is no critical Rayleigh number, and convection can occur in large cells from the lowest part of the layer (syncline) to its highest part (anticline). Above a critical Rayleigh number, additional convective cells may develop on top of the general one, depending, in this case, also on the dip angle. It is, however, not believed today that thermal instabilities have ever played an important role in the Paris basin, given the small heat flux and the relative thinness of the permeable layers. A temperature increase however has a significant effect on the hydraulic conductivity, as it is inversely proportional to the viscosity.

5. Hydrocarbon expulsion

The next cause of fluid flow is expulsion of hydrocarbons. This requires that some of the clay layers in the basin have a significant solid organic-matter content, and that these layers reach the so-called 'oil window', defined by a temperature and a pressure range, where the solid organic matter is transformed into oil and/or gas. These fluids are then expelled from the clay (so-called primary migration) and assemble in adjacent permeable rocks (reservoirs) whence they can either migrate toward the surface or toward an impervious structure, such as an anticline, and be trapped for millions of years (secondary migration). The mechanism of primary migration is not yet fully understood [6], but it seems that the pressure of the hydrocarbons, formed inside the clay layer, is large enough to create small cracks, that eventually connect to the top or bottom of the layer and permit the hydrocarbons to migrate. The Darcian hydraulic conductivity of clay is too low to allow direct hydrocarbon migration within a reasonable time span. It appears that these micro-cracks in the clay become sealed and disappear, at least partly, when the primary migration is completed. However, the properties of the clay (porosity, connectivity of the pores) may have been irreversibly changed. In the Paris basin, the clay layer that generated the hydrocarbons lies below the Callovo-Oxfordian, in the Liassic. It only reached the oil window some 80 million years ago [6] in the centre of the basin, and not in the vicinity of Bure, which was never deep enough. At present, no hydrocarbons are forming in the basin, and this mechanism is not believed to play a role at Bure. The question arises of the possibility that the heat released by the nuclear waste might be high enough to bring the Callovo-Oxfordian clay through the oil window and thus generate a potential migration path. The answer is no, the temperature will be kept below $100\text{ }^{\circ}\text{C}$ and furthermore, the organic-matter content of the Callovo-Oxfordian clay is low, and the duration of the waste thermal pulse is short compared to the time needed to produce hydrocarbons.

High fluid pressures in a clay layer can create 'hydraulic fracturing' of the clay, i.e., the opening of a relatively long fracture in the medium, if the pressure becomes larger than the minimum stress in the medium; the tensile strength of clay is indeed rather small.

6. Gravitational flow

The next fluid-flow mechanism is called gravitational flow. It occurred at each phase of uplift in the basin, and particularly at the end of its formation, when compressive forces began to replace distensive ones. The last two major compressive phases occurred about 70–50 million and 20 million years ago, originating in the south (Pyrenean orogeny) and later in the southeast, where the Alps started to rise, because of the collision between the African and Eurasian plates [2]. The eastern border of the basin started to rise, and meteoric water infiltrated into the outcrops of the permeable layers, circulating downward through these layers, toward the centre of the (now folded) basin, and then up to the outcrops of the layers at a lower altitude, toward the northwest, into the English Channel. Gravity flow is still the principal force driving groundwater flow today: the water infiltrates at a high elevation and flows (as in a U tube) toward the low areas. The major component of the flow is quasi-horizontal and occurs mainly in the permeable layers called ‘aquifers’ (sand, sandstone, limestone) and hardly at all in the clay layers. However, if a low hydraulic conductivity clay layer separates two aquifers, and if the hydraulic head in these two aquifers is different along the same vertical, then the flow may have an almost vertical component crossing the clay layer; this is called ‘leakage’ (drainance in French). This is the flow component that we are interested in for a repository in the clay, Fig. 2. The vertical Darcy flux U can be determined from the vertical hydraulic gradient, given by the head difference between the two aquifers surrounding the clay, divided by the thickness of the clay layer. In most cases, in natural conditions, this Darcy flux is directed upward in the centre of the basin, because generally, the deeper aquifers (which outcrop at a higher elevation on the uplifted margin of the basin) have a higher hydraulic head than the shallower ones; toward the periphery, near the outcrop, the

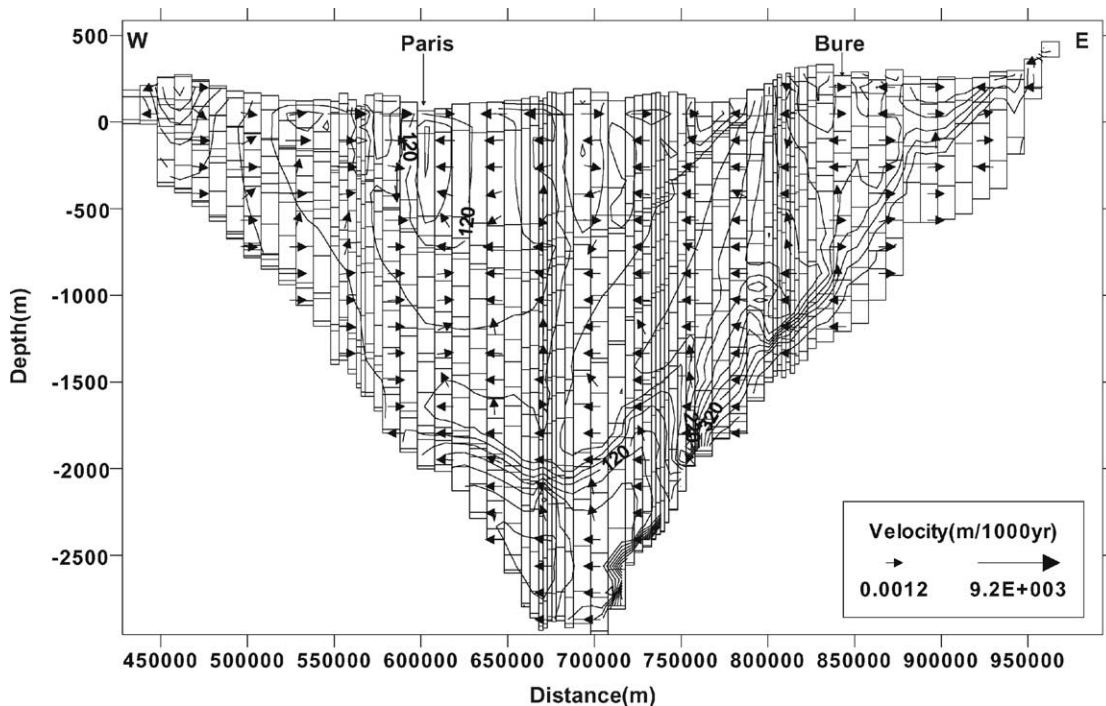


Figure 2. East-West cross-section (see Fig. 1 for position) through the Paris Basin at present time, with the equal-head contour lines, and the direction and magnitude of the porewater velocity vector.

Figure 2. Coupe Est-Ouest dans le bassin de Paris (voir la position Fig. 1) à l’actuel, montrant les lignes d’égal charges et les directions et intensités des vecteurs vitesse de pore.

Dracy flux can be directed downward. Local conditions or exploitation of the aquifers may change this general picture; at the Bure site, the Dogger aquifer directly beneath the Callovo-Oxfordien clay appears to have a lower head than the Calcareous Oxfordian one above the clay (289 m and 317 m, respectively). The Darcy flux should therefore, in principle, be directed downward but the existence of an anomalous head in the middle of the Callovo-Oxfordian, larger than those of the aquifers above and below (around 339–342 m), would tend to indicate a diverging flow from the middle of the layer, upward in the upper section of the clay layer and downward in the lower one. The precise cause of this anomalous head is yet unexplained. If we ignore this anomaly, and want to estimate the time needed for a radionuclide to be transported through half of the Callovo-Oxfordian thickness (60 m), with a head difference of 28 m between the two adjacent aquifers, a hydraulic conductivity of $10^{-13} \text{ m}\cdot\text{s}^{-1}$ for the clay, and a porosity of 10%, one finds a ‘breakthrough’ time of 8×10^6 years, for a non-sorbed nuclide; it would be shorter with a higher hydraulic conductivity, and much longer for a sorbed nuclide (see the section on ‘retardation’ below).

Climate changes, variations in the sea level, and deepening of the valleys by erosion strongly influence this gravitational flow as it changes the boundary conditions and the recharge rates on the outcrops.

7. Osmosis

The last cause of fluid flow, which has been proposed, e.g., by [7], is osmosis. Clay layers can have an osmotic-membrane effect, and if the water they contain has a higher salinity than the adjacent aquifers, water can flow from the aquifers toward the clay. This mechanism is presently one of the proposed explanations of the abnormal pressure in the Callovo-Oxfordian, as it has indeed a higher salinity than the adjacent aquifers. However, coupled to the fluid flow, there is transport of the salt by diffusion, which is directed in the opposite sense to that of the fluid flow. The high pressure in the centre of the Callovo-Oxfordian would therefore result from osmotic pressures, generated from both above and below; the hydraulic gradient generated by the osmotic pressure would exactly compensate the osmotic gradient, and the net water velocity would be zero, while the hydraulic pressure would not be at equilibrium, and diffusion would tend to equilibrate the salinity, and eventually the pressure, albeit only in the very long term, as diffusion is very slow.

Surprisingly, abnormal pressures are not uncommon in thick clay layers. They have been reported, e.g., from the Pierre Shale in Dakota in the US by [7] and in the Opalinus clay in Switzerland (also a tentative host rock for a repository) by [8]. In the latter case, however, the salinity difference is small, and osmotic pressure is not believed to be the main cause of the observed abnormal pressures, which are on the same order of magnitude as at Bure. Mechanical compaction is not a reasonable explanation either, if the measured hydraulic conductivities (on the order of 10^{-12} – $10^{-13} \text{ m}\cdot\text{s}^{-1}$) are used in a compaction equation. One possible interpretation is that clays do not follow Darcy’s law and that there is a hydraulic-gradient threshold below which no flow can occur in clay and which must be exceeded for Darcy’s law to be valid. This idea has been discussed for years, without any final answer being found, but it is often strongly opposed, e.g., by [9]. It is nevertheless puzzling that similar explanations cannot yet be proposed for the same abnormal pressures in relatively similar geological settings.

It is generally considered that other so-called non-diagonal transport mechanisms, such as thermal diffusion, electro-migration, do not need to be taken into account in a clay repository.

8. Diffusion

Let us now turn to diffusion. Fick’s first law applies in porous media: $\Phi_2 = -\omega d \text{ grad } C$, where Φ_2 [$\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$] is the diffusive flux, ω is the porosity, d is the molecular diffusion coefficient in porous media [$\text{m}^2\cdot\text{s}^{-1}$], and C is the concentration [$\text{kg}\cdot\text{m}^{-3}$ or $\text{g}\cdot\text{L}^{-1}$]. The presence of the porosity ω in Fick’s law results from the fact that diffusion takes place only in the liquid phase and not through the solids. As previously mentioned for convection, the accessible porosity for diffusing species may vary according to the size of the molecules, and to their charges. The diffusion coefficient d in porous media is, however,

smaller than that in water d_0 , approximately $0.7d_0$ for sand, and $0.1d_0$ to $0.01d_0$ for clay. The reduction coefficient (0.7 to 0.01) is sometimes called the tortuosity of the medium. In the absence of any fluid flow, radionuclide migration by diffusion could therefore still occur in the clay. Fick's second law, the diffusion mass-balance equation, is written, in one dimension, z being, e.g., the vertical direction:

$$\omega d \frac{\partial C}{\partial z} = \omega \frac{\partial C}{\partial t},$$

where, in this case, the porosity ω can be deleted on both sides.

Assuming a constant concentration C_0 at $z = 0$ (e.g., the solubility limit of a given radionuclide) and a semi-infinite medium in the positive z direction, the solution of this equation is:

$$C(z, t) = C_0 \operatorname{erfc} \left[z \sqrt{\frac{1}{4dt}} \right].$$

Taking, for instance, a diffusion coefficient of $1.5 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, one easily finds that the concentration of a non-sorbing nuclide 60 m above the repository (half the thickness of the Callovo-Oxfordian) would reach 0.1%, 1% or 10% of C_0 after 2.1×10^6 , 3.5×10^6 and 8.3×10^6 years, respectively. With a diffusion coefficient of $1.5 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, these times would be divided by 10. Sorption would on the contrary slow down this transfer.

9. Hydrodynamic dispersion

The third migration mechanism to take into account if both advection and diffusion are occurring is called 'hydrodynamic dispersion'. It is analogous to turbulent diffusion or dispersion in gases or in liquids, at high Reynolds numbers. In porous media, the cause of dispersion is not turbulence, because the Reynolds numbers are always very low and flow is always laminar. However, dispersion results from a similar effect due to the complexity of the microscopic velocity field, which must 'disperse' to flow around the grains and all sorts of material heterogeneities that create variations in the direction and amplitude of the microscopic velocity with respect to the average velocity, expressed by the macroscopic Darcy law. However, empirical evidence and some approximate theories, e.g., [10,11] suggest that hydrodynamic dispersion can be represented by a generalised form of Fick's law, $\Phi_3 = -D \cdot \operatorname{grad} C$, where D is now the dispersion tensor whose principal directions are parallel and orthogonal to the velocity vector. However, the components of the tensor D are related to the velocity:

$$D_L = \alpha_L |\vec{U}|^n \quad \text{and} \quad D_T = \alpha_T |\vec{U}|^n,$$

where the exponent n is very close to one, and L and T stand for the directions parallel (longitudinal) and orthogonal (transverse) to the velocity vector U . The new variable α [m] is called the dispersivity. If the three mechanisms: advection, diffusion and dispersion are acting simultaneously, the transport equation can be written, in one dimension:

$$\frac{\partial}{\partial z} [(\omega d + D_L) \operatorname{grad} C - UC] = \omega \frac{\partial C}{\partial t}.$$

However, if the Darcy velocity is small, as in a clay layer, the dispersion becomes negligible compared to the diffusion, whereas the opposite is generally true in aquifers, where the velocity is large.

The presence of fractures in a medium can create a strong heterogeneity of the velocity, depending on their aperture and connectivity, and thus increase the dispersion.

10. A natural tracer of past migration: helium

To determine if the proposed transport equations hold, it is important to investigate the migration of naturally occurring elements in the basin through some of the mechanisms described above (e.g., gravitational advection, dispersion and diffusion). In the Paris basin, we have used salt produced by the dissolution of evaporites (salt layers) during the Triassic [12] as well as natural noble gases [13,14] as tracers of element transport. Below, we will briefly summarise our findings on the migration of helium, which was measured in 29 deep wells in the basin, and modelled on a 2-D vertical cross-section extending horizontally from Lunéville to Versailles and vertically from the pre-Triassic bedrock to the surface. Helium is interesting as it is non-reactive, and has a large diffusion coefficient given its small molecular size.

Helium has two stable isotopes, ^3He and ^4He , which can be found in solution in groundwater. For old groundwaters, the first source of He is of atmospheric origin where ^3He and ^4He are dissolved in meteoric water that infiltrates into the ground. The second source results from the α -decay of the natural uranium and thorium series, which are present in small amounts in every sedimentary layer, and which produce ^4He (radiogenic origin). In addition, ^3He is produced by secondary α or n reactions on lithium (nucleogenic origin). Radiogenic and nucleogenic production of He can occur inside the sedimentary layers or deeper inside the crust. Finally, small amounts of He resulting from the degassing of the mantle can be present. He of mantle origin contains large amounts of ^3He , thus presenting much higher $^3\text{He}/^4\text{He}$ ratios than the atmospheric ratio of 1.36×10^{-6} [15]. In the Paris basin, the He concentration profiles in the aquifers show a strong gradient from the bottom to the top of the basin (Fig. 3). This is interpreted as evidence of a strong He flux arriving from the deeper part of the crust (i.e., the first 20 km of the crust, which is estimated to be about 40 km deep in the Paris basin) with a possible minor component of mantle He; this He flux is progressively diluted by meteoric water carrying primarily an atmospheric He component. The transfer mechanism of the He flux through the crust is unknown but thought to be diffusion. The flux is estimated to be 4.3×10^{-13} and $4 \times 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$, for ^3He and ^4He , respectively. Once arrived at the bottom of the basin, He

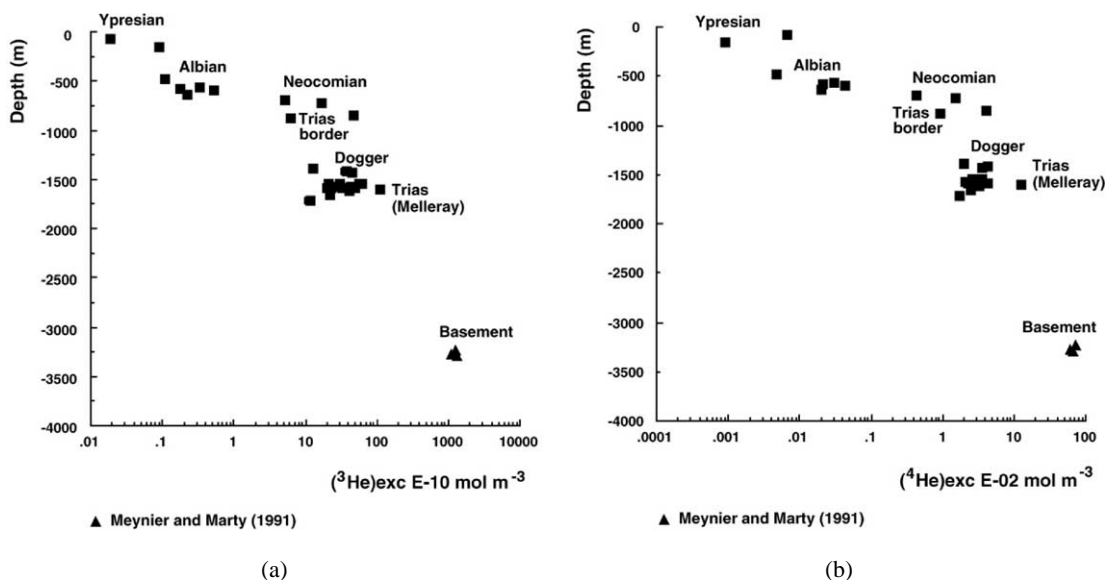


Figure 3. Adapted from [13]. (a) Evolution of measured ^3He concentrations in the water as a function of depth in the Paris Basin; (b) similar evolution of ^4He concentrations.

Figure 3. D'après [13]. Evolution des concentrations mesurées en ^3He (a) et ^4He (b) dans l'eau dans le bassin de Paris en fonction de la profondeur.

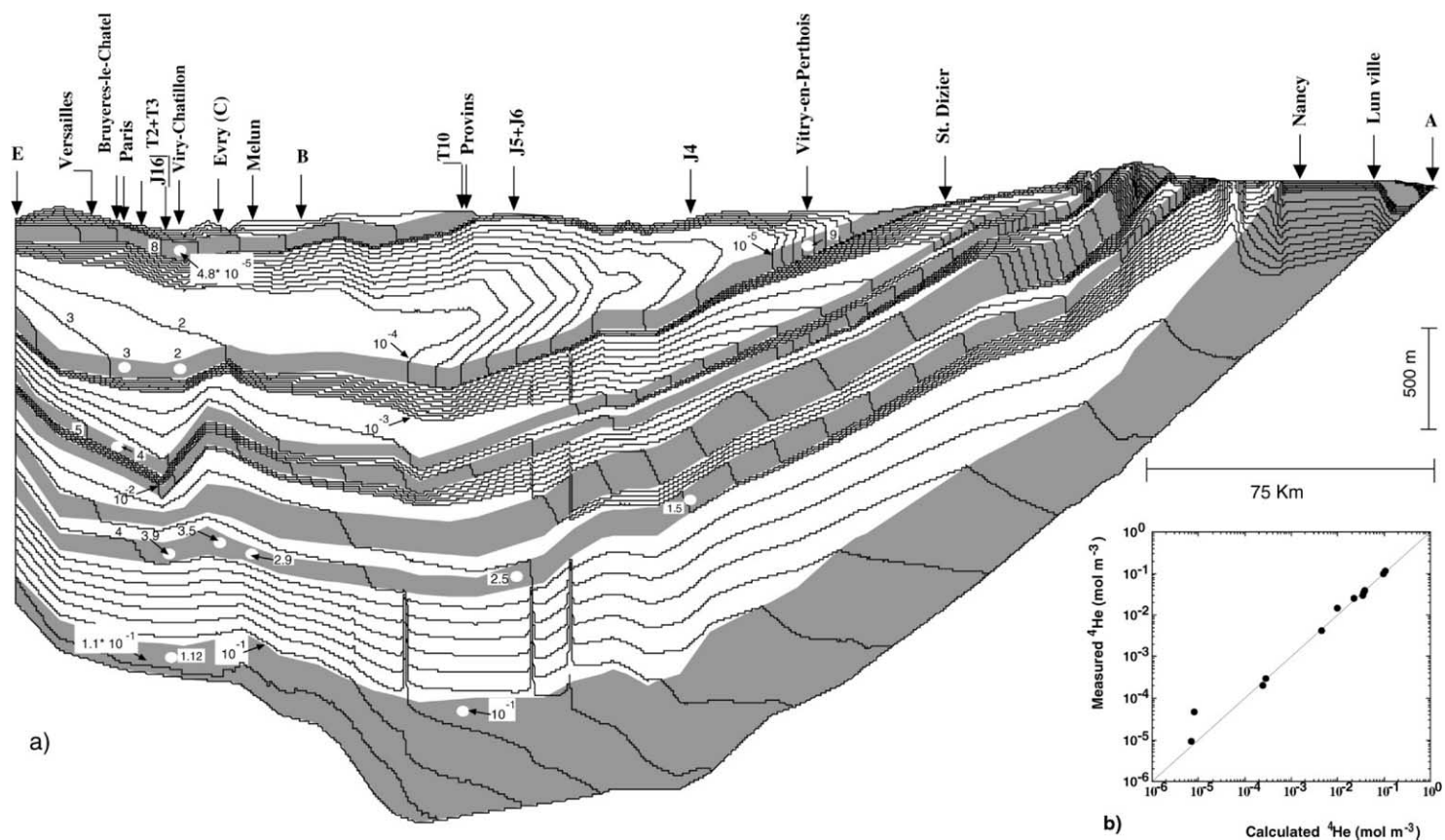


Figure 4. Adapted from [14]. (a) Calculated ${}^4\text{He}$ concentration distribution in $\text{mol}\cdot\text{m}^{-3}$ on the East-West cross-section of the Paris Basin. Contours for values of 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} and 10^{-5} $\text{mol}\cdot\text{m}^{-3}$ are marked. Except for the 1.1×10^{-1} $\text{mol}\cdot\text{m}^{-3}$ contour in the Triassic, all other contours express constant concentration variations of 1 unit inside each order of magnitude. The measured value of each sample is given together with some contours whose values are close to the measured ones. In these cases, only the molar number is given; (b) measured ${}^4\text{He}$ values plotted as a function of calculated values.

Figure 4. D'après [14]. (a) Concentrations calculées en ${}^4\text{He}$ en mol/m^3 sur la coupe Est-Oest du bassin de Paris. Les courbes d'égaies concentrations de 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} et 10^{-5} $\text{mol}\cdot\text{m}^{-3}$ sont indiquées. Excepté pour la courbe $1,1 \times 10^{-1}$ $\text{mol}\cdot\text{m}^{-3}$ dans le Trias, toutes les courbes représentent une variation d'une unité à l'intérieur de chaque ordre de grandeur. Les valeurs ponctuelles mesurées de chaque échantillon sont données; (b) Valeurs des concentrations en ${}^4\text{He}$ mesurées et calculées.

migrates through the aquifers and clay layers (Fig. 4). In the clay, the transfer is mostly vertical upwards and dominated by molecular diffusion (Fig. 5), while in the aquifers, the transfer is mostly advective in the horizontal direction; the He flux is ‘diluted’ in the water flux which circulates horizontally through each aquifer. Vertical advective transfer of He in the basin fault zones is possible, but data are lacking to clearly distinguish this localised advective flux with higher values in limited areas of the basin from a smaller but ubiquitous advective/diffusive flux. The most convincing argument supporting the hypothesis of a dominant diffusive flux through clay layers is the fact that the migration of ^3He and ^4He is slightly different, ^3He is transported slightly faster than ^4He , thus creating a gradual change in the isotopic ratio of the two gases, as shown by samples collected higher up in the basin. A similar and more accentuated phenomenon is also observed between the radiogenic ^4He and ^{40}Ar ratio, which also supports this hypothesis [14]. The diffusion coefficient (assumed constant for all clay layers in the basin) resulting from the fitting of the model on the observed He concentrations in the aquifers is $3.24 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ for ^4He , and 5% more for ^3He . These figures are large, and assume a tortuosity of 0.3. Values of the diffusion coefficient measured on samples in the Callovo-Oxfordian clay are more in the range of $1.5 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, i.e., a tortuosity of about 0.01; the cause of this discrepancy is not yet understood but it could be related to the scale difference of the measurements: at the kilometre scale for the indirect basin tracer measurements and at the centimetre scale in the laboratory experiments. Note that the fitted diffusion coefficient is assumed to be the same for all clay layers of the basin, where in reality it is, most likely, different for each one.

If diffusion is the dominant vertical transfer mechanism, it is possible to show, with the 1-D solution of the diffusion equation and the estimated diffusion coefficients ($3.24 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$), that the equilibration time of the He concentration is about 20 million years. This means that if the basin contained no He and if,

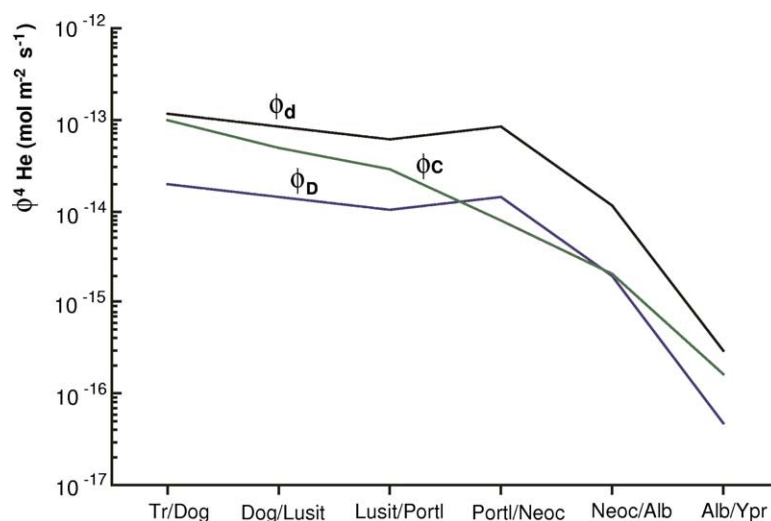


Figure 5. Adapted from [14,20]. Values of diffusive ϕ_d , advective ϕ_c and dispersive ϕ_D fluxes in each aquitard. Values estimated on the same vertical line at the centre of the basin, using ^4He concentrations and vertical velocities obtained by fitting the model. Tr/Dog, Dog/Lusit, Lusit/Portl, Portl/Neoc, Neoc/Alb and Alb/Ypr are the aquitards situated between the aquifers of the same names. For example, Tr/Dog refers to the Liassic aquitard between the Triassic and Dogger aquifers.

Figure 5. D'après [14,20]. Valeurs des flux diffusifs ϕ_d , advectifs ϕ_c et dispersifs ϕ_D au sein de chaque semi-perméable. Ces valeurs sont estimées sur une verticale au centre du bassin, en utilisant les concentrations en ^4He et les vitesses verticales obtenues par calage du modèle. Tr/Dog, Dog/Lusit, Lusit/Portl, Portl/Neoc, Neoc/Alb et Alb/Ypr sont des semi-perméables encadrés par les aquifères du même nom. Par exemple, Tr/Dog désigne le semi-perméable du Lias situé entre les aquifères du Trias et du Dogger.

at time zero, with a fixed aquifer geometry and flow rate, a constant He concentration were prescribed at the bottom of the basin, it would take on the order of 20 million years before the He concentration profile in the basin reached equilibrium. In reality, the geometry of the basin has not been constant over the last 20 million years and many deformations and flow changes in the aquifers (by changes in the boundary conditions) have occurred. On the other hand, the He flux at the bottom of the system was not turned on 20 million years ago as it has been present at approximately the same rate as today since the beginning of the formation of the basin, 240 million years ago. It is, however, unlikely that the He concentration profile is exactly at equilibrium today.

11. Retardation

So far, we have described the migration mechanisms of solutes in a sedimentary basin. An additional component of the transport of radionuclides is their retardation by interactions with the solid phase of the sediments. There are many types of possible interactions but the most common is adsorption, particularly in the case of clay. Additional mechanisms may include chemical reactions (acid-base, redox, precipitation, etc.) as well as reactions of the solute with organic molecules or with mineral colloids naturally present in the groundwater. If radionuclides react with or sorb on such molecules or particles, they may not interact with the solid (no sorption) and be transported faster than expected. The issues of ‘facilitated’ transport are not discussed here but it is worth mentioning that at the Nevada test site, in the US, it has been shown that minute amounts of Pu were transported over relatively long distances by such mechanism [16]. However, this occurred in alluvial sediments, and is not likely to take place in clay.

Sorption on clay particles of positively charged radioactive cations occurs by surface complexation with the major natural cations present in the porewater and forming a sorbed layer around the negatively charged clay particles. Under the assumption of low concentration, sorption is generally assumed to be linearly, reversibly and instantaneously dependent on the concentration in the solution. A ‘linear sorption isotherm’ is defined by $F = K_d C$, where C is the concentration of a given cation in the solution [$\text{g}\cdot\text{L}^{-1}$], and F is the mass concentration of the same cation sorbed on the solid [$\text{g}\cdot\text{g}^{-1}$]. K_d [$\text{L}\cdot\text{g}^{-1}$] is called the distribution coefficient and is different for each cation. It can easily be measured on rock samples in batch experiments. The right-hand side of the transport equation is then modified as follows to include sorption:

$$\frac{\partial}{\partial z} [(\omega d + D_L) \text{grad } C - UC] = \omega \frac{\partial C}{\partial t} + (1 - \omega) \rho_s \frac{\partial F}{\partial t}.$$

If the equilibrium isotherm $F = K_d C$ is reached instantaneously, then $\partial F / \partial t = K_d \partial C / \partial t$ and the transport equation is:

$$\frac{\partial}{\partial z} [(\omega d + D_L) \text{grad } C - UC] = \omega R \frac{\partial C}{\partial t} \quad \text{with } R = 1 + \frac{1 - \omega}{\omega} \rho_s K_d,$$

where R is called the retardation coefficient. The effect of sorption is to slow down the velocity of the cation migration by the factor R ; the apparent porewater velocity is no longer U/ω , but $U/R\omega$. Note that anions are generally not sorbed and migrate at the advective velocity, sometimes even slightly faster as a result of the phenomenon of ‘anion exclusion’, already described, which is the repulsion of the anions by the negatively charged clay particles, making them migrate in a lower porosity than that of cations or uncharged solutes. This sorption model is very simple, and more sophisticated models have been developed to account for more complex interactions [17]; it is, nevertheless, widely used in safety assessments.

12. Transport in aquifers

Whereas the migration of radionuclides through clay is likely to be dominated by diffusion, when the radionuclides reach an aquifer, their transport will be dominated by advection and dispersion. The same

general transport equation is used, including the sorption mechanisms, but the major parameter is now the advective velocity in the aquifers. Aquifers are generally recharged on their outcrops at higher elevations and flow down towards springs or rivers in the valleys. At the Bure site, the outlets of the two aquifers surrounding the Callovo-Oxfordian clay are mainly the Marne and the Meuse rivers. A small fraction of the flow may be directed toward the centre of the basin and eventually into the English Channel. The water velocity in the aquifers is much higher than in the clay, and the migration time to the outlets varies from thousands to millions of years. The effect on humans of the radionuclides depends, of course, on their concentration in the aquifer water. The flux of nuclides arriving by diffusion through the clay is first diluted into the flux of water flowing in the aquifers at the site. The larger this flux of water, the higher this dilution. Therefore, a high water flux in layers adjacent to a clay formation has a positive effect. The radionuclides are further diluted in the aquifers as they migrate by hydrodynamic dispersion and finally, by the water in the outlets, the Marne and Meuse rivers. The highest concentration is therefore likely to occur in the vicinity of the repository, if an artificial outlet is made in the aquifers: this would be the case, for example, of a well drilled into one of the aquifers for water supply. In safety assessments, this is called the ‘well scenario’ and often represents the most severe threat in terms of doses to humans.

13. Conclusion

The safety of a repository constructed in a clay formation depends, in the long term, on the rate of transfer of the radionuclides from the repository to the environment. If, during their transfer, radioactive decay has made the nuclides disappear before they reach the surface, the repository can be considered safe, at least for the ‘normal scenario’ where the confining properties of the geologic barrier are not disturbed. Alternatively, if the flux of radionuclides is diluted in the outlets at the surface so that the dose to humans that can, in the future, result from the consumption of the water at the outlets is well below the permissible limits, then the repository may also be considered safe. Initially, in the short term (e.g., first thousand years), the engineered barriers (canister, bentonite, concrete) may remain effective in preventing radionuclide migration but in the long term, it is reasonable to assume that the natural geologic setting ought to be the dominant barrier to radionuclide migration. The French Safety Rule RFS.III.2.F [18] specifically states, for instance, that in the long term, only the confinement provided by the natural barriers should be considered in safety studies.

In a clay layer, unless there are unsealed fractures, the major migration mechanism is thought to be molecular diffusion. The time needed to transfer significant amounts of radionuclides through a 60 m clay layer depends on the magnitude of the diffusion coefficient, but it is on the order of hundreds of thousands to millions of years. Uncertainties need to be explicitly taken into account, e.g., by Monte Carlo simulations, in all safety analysis. The major uncertainties here are the presence/absence of fractures, the magnitude of the diffusion coefficient and the sorption properties of the clay. Still poorly understood mechanisms are those responsible for the presence of abnormal pressures in clay layers and the difference in magnitude of the diffusion coefficient between values measured on samples and those estimated from the large-scale distribution of environmental tracers, e.g., noble gases. A recent study conducted by the Institut de Radioprotection et de Sûreté Nucléaire (IRSN) in clays at Tournemire, an experimental research facility in Toarcian clays near Roquefort, France, has however shown that the large-scale chlorine concentration profile in the clay can be explained with a diffusion model using the diffusion coefficient measured on clay samples in the laboratory [19].

Once the radionuclides have reached the aquifers above or below the clay layer, their migration in the aquifers toward the natural outlets is dominated by advection and dilution/dispersion and is relatively faster than in the clay. The major uncertainties here are the possible existence of ‘fast pathways’, where the velocity might be higher than elsewhere, and the likelihood that, in the future, a water supply well is drilled in the vicinity of the repository whose existence has been forgotten. Fast pathways may be formed by heterogeneities in the aquifers, e.g., coarse-grained layers in sandstone, fractures, karstic (dissolution) features in limestone, etc. The long-term evolution of the flow system in the aquifers needs to be predicted

(recharge rates, boundary conditions, ...). The minimum dilution achieved in a fast-pathway or well-scenario transfer is important in the safety assessment of a repository and requires measurements and experiments at the planned repository site and towards the natural outlets, in aquifer formations surrounding the host rock, i.e., not in the confining layers of the waste. This is also a difficult task.

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Discussion

Question de Y. Bréchet

Est-ce que la perméabilité du solide poreux évolue en fonction de la quantité d’eau qui a circulé (dissolution, précipitation, ‘colmatage’, ...)?

Réponse de G. de Marsily

Oui, aux échelles de temps géologiques dont nous parlons, la perméabilité des milieux souterrains évolue par ouverture ou fermeture de la porosité. La dissolution augmente en effet la porosité, et la précipitation la réduit. Ces phénomènes sont en général fonction des gradient thermiques dans le milieu, et des vitesses de circulation. Si par exemple un fluide chaud, en équilibre thermique et géochimique avec la roche qu’il traverse, se met à migrer vers le haut et se refroidir, il va précipiter une partie des éléments en solution qu’il contient. C’est le cas pour la silice, pour les argiles néoformées par exemple. Les carbonates au contraire précipitent si la température augmente. Ces phénomènes font partie de ce que l’on appelle les processus de diagenèse des sédiments. La diagenèse argileuse est celle qui fait le plus souvent chuter la perméabilité des réservoirs gréseux pétroliers. On commence à savoir modéliser ces phénomènes, mais la prévision quantitative de ce colmatage en fonction de l’histoire du sédiment est encore très difficile. Il faut non seulement prendre en compte les équilibres thermodynamiques eau-roches, mais aussi les cinétiques, et le rôle des hétérogénéités.

Question de P. Toulhoat

Concernant le transfert de l'hélium, quelle est la possibilité d'un transfert en phase gazeuse, associé à des gaz non condensables (CH₄) connus dans le Bassin Parisien ?

Réponse de G. de Marsily

Quand il existe des hydrocarbures (liquides ou gazeux) en contact avec les eaux du bassin, il y a en effet un équilibre qui s'établit entre la concentration de l'hélium dans l'eau et celle dans l'hydrocarbure. Connaissant ce coefficient de partage, on peut d'ailleurs mesurer la concentration de l'hélium dans l'une des phases et la calculer dans l'autre. En ce qui concerne le cas du méthane, si celui-ci migrait, il pourrait entraîner avec lui un flux d'hélium, qui aurait ainsi une mobilité supplémentaire de l'hélium (non prise en compte dans le modèle que j'ai présenté) par l'entraînement convectif par le gaz qui en contient. Mais aujourd'hui, la production de gaz à partir des roches mères dans le bassin de Paris est arrêtée depuis environ 60 millions d'années, la température du bassin est redevenue trop faible pour fabriquer des hydrocarbures, et ceux qui sont encore présents dans le bassin sont piégés dans des dômes structuraux et ne sont pas mobiles. Il n'y a donc pas, à ma connaissance, de migration d'hélium par ce mécanisme aujourd'hui dans le bassin de Paris.