



Nuclear waste disposal: I. Laboratory simulation of repository properties



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ABSTRACT

After more than 30 years of research and development, there is a broad technical consensus that geologic disposal will provide for the safety of humankind, now and far into the future. Safety analyses have demonstrated that the risk, measured as the exposure to radiation, will be of little consequence. Still, there is not yet an operating geologic repository for highly radioactive waste, and there remains substantial public concern about the long-term safety of geologic disposal. In the two linked papers we argue for a stronger connection between the scientific data (this paper I) and the safety analysis, particularly in the context of societal expectations (paper II). In the present paper I, we use new experimental data on the properties of clay formations simulating geological disposal conditions to illustrate how one can understand the ability of clay to isolate radionuclides. The data include percolation tests on various intact clay–rock cores with different calcite contents. For the first time, hydrodynamic parameters (anion and cation accessible porosities, permeability, dispersion and diffusion coefficients), as well as retention parameters (sorption behavior of iodine, cesium) and materials interaction parameters (glass dissolution rates, etc.) have been obtained for a series of clay–rock samples of varying mineralogy. Increased calcite content leads to lower permeability and porosity, but the difference between anion and cation accessible porosity diminished. The data confirm very slow radionuclide migration, and a direct extrapolation to repository geometry yields isolation times, for a 70 m clay–rock formation, of many hundreds of thousands of years, even for the most mobile radionuclides such as iodine-129 and chlorine 36 and complete retention for the more radiotoxic, less mobile radionuclides such as the actinides or cesium-137.

In order to assess the meaning of the technical results and derived models for long-term safety, paper II addresses model validity and credibility not only from a technical perspective, but in a much broader historical, epistemological and societal context. Safety analysis is treated in its social and temporal dimensions. This approach provides new insights into the societal dimension of scenarios and risk, and it shows that there is certainly no direct link between increased scientific understanding and a public position for or against different strategies of nuclear waste disposal.

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1. Introduction

Experimental (Abrajano and Bates, 1987; Ames and Rai, 1978; ANDRA, 2005; De Marsily, 1988; Gaucher et al., 2004; Warnecke and Hild, 1988; Wronkiewicz et al., 1996) and field studies (Gaucher et al., 2004; Zito et al., 1989) were carried out for more than 30 years to obtain insight into the isolation process, by studying individual processes or by simulating expected disposal conditions as closely as possible. Scenarios for the long term evolution of the isolation system (NEA/OECD, 2001) were derived to analyze all feature, event and process combinations which might occur in the future and which might compromise the required isolation performance of the disposal sites. Among the key questions which need to be addressed are how long will containers remain ‘water tight’

in the face of inevitable corrosion by groundwater, at which rate will radionuclides be released from the waste into groundwater, whether and to which degree contaminated groundwater will be ‘decontaminated’ by interaction with the surfaces presented by minerals contained in the engineered barrier materials and rocks, and how long will the migration of radionuclides through the rock take, and when and at which rates will they eventually enter the biosphere.

Any assessment of long term waste facility performance requires thorough understanding of the physico-chemical mechanism which govern either retention of radionuclide or their mobilization, of the hydraulic properties of the confinement system, of the temporal evolution of the geochemical and geological system, etc., and this must be represented in detailed mathematical simulation models constrained by, and coherent with, the best available knowledge. Sensitivity and uncertainty analyses must be performed to assess confidence levels.

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An example is the case of disposal of nuclear waste glasses in a repository in deep oxygen free clayrock formations for which a detailed normal evolution scenario¹ can be deduced from the various previous studies as follows: the clayrock pore water will enter the void space around waste containers, driven by hydraulic gradients and corrosion of the steel container will occur at a rate of several micrometers per year (Féron et al., 2008) leading by geomechanical constraints to container breaching after some thousands of years. At this time the decay-generated heat will be much reduced and temperatures will have fallen to some ten degrees above ambient. Water vapor or liquid water will infiltrate into the waste container and chemical corrosion of the glass will begin. Some nanometer to micrometer thick layers of the ~30 cm thick fractured glass block will dissolve, leading to release of soluble radionuclides into the adjacent pore water. Saturation of the pore water system with dissolved silica will rapidly occur, leading to very slow dissolution rates even in permanent presence of water so that it will take more than 200,000 years for complete release of the inventory of soluble radionuclides. During this time, only very small fractions of the highly toxic transuranic elements and Technetium (Tc) become released and they will only migrate a few meters within the clayrock before decay reduces their radioactivity to low levels (Grambow and Giffaut, 2006). Such isolation time scales correspond to the age of homo sapiens.

The principal transport mechanism of dissolved radionuclides in the pluri-nano-meter sized clayrock pores is by molecular diffusion since transport advection in response to groundwater pressure gradients will generally be extremely slow. Furthermore, the strong retention of cationic radionuclide species on clay minerals by ion exchange and/or surface complexation means that they will migrate even more slowly and that most of them will decay very low radioactivities long before they may reach any human accessible environment. Only anionic species such as iodide, chloride or certain types of oxidized selenium species or HSe⁻ show little retention on clayrock. On the other hand, these anions still will move rather slowly (it will take more than 140,000 years until the first anions from the waste migrate all the way through a host clayrock formation of 50 m (Grambow, 2008) and their flux will be limited because the accessible pore space is reduced due to electrostatic repulsion by the negatively charged clay mineral surfaces. Over 30 years of research indicates no dose-related risk for a time period equal to that of the age of homo sapiens and that risks are more than 1000 times lower than those expected from natural radiation for any time period thereafter.

The only problem, but a major one from a societal point of view, is that the large number of processes, models and parameters involved in the formal demonstration of repository safety does not offer any spontaneous indicator which would be understandable to politicians and citizens. Furthermore, due to the long times for which predictions need to be performed, the overall scenario cannot be verified entirely as it is deduced from many individual observations made in many laboratories and by field observations, all of which always simplify certain aspects. This poses a number of questions which will be addressed in the following text: How can one deduce from short-term experimental data measured on centimeter to decimeter scale system the long term behavior of hundreds of meters scale systems? How to be sure that a scientific model or theory derived from experimental data is applicable under repository conditions? What to do if there are different models to explain the same data? How to combine simple models for various individual processes into an overall vision of the performance of the waste isolation system as well as for understanding the performance of individual barriers as a function of time? What are the appropriate indicators for safety and risk? How credible are

predictions for hundreds of thousands of years? Is there any use in carrying out predictions for hundreds of thousands of years, if all data indicate that the risk will be negligible for the next tens of thousands of years? Is there a direct impact of an increase in scientific understanding on the perception of risks from nuclear waste disposal? The challenge of this paper is to contribute to answering some of these questions by combining a natural science approach with safety analyses and a societal approach, considering safety not only as a technical but as well a societal challenge.

The challenge is also that of scientific method. We start from presenting a new experimental approach intended to simulate nuclear waste isolation features of a repository. The natural science approach requires that all data, model hypotheses and experimental conditions are thoroughly documented. The link between the technical data, concepts and derived models with the temporality of risks for multigenerational safety and society is addressed in paper II. Here we show that we need to avoid the easy and self-sufficient shortcut, believing that comparison of model and data assure by themselves credibility and validity for the long term and that temporal scales of hundreds and thousands of years have any self-evident meaning outside of the scientific community and we address validity, credibility and temporality of our models in the much larger historical, epistemological and societal context.

We will use as an example the French nuclear waste repository concept in the Callovo-Oxfordian clayrock formation.

2. Experimental simulation of a nuclear waste repository in the laboratory

Large experimental and field studies are conducted worldwide mainly organized by governmental or nuclear waste management agencies, to assess nuclear waste repository performance. All experimental work in the research on nuclear waste disposal intends to simulate some aspects of the expected behavior of the disposal system, field tests characterize potential disposal sites and test the disposal concept on a realistic spatial scale and some natural analogue studies assess large temporal scales of more than millions of years.

Interactions of radionuclides and nuclear waste disposal materials with the clay host rock are often studied in small batch systems containing ground material at very high water/rock ratios create conditions facilitating observation of chemical phenomena (thorough mixing, easy water analyses, etc.) and minimize the interference of mass transport related effects. Diffusion tests using chemically inert tracers (tritiated water = HTO, chloride) in solid rock allow studies of intrinsic transport properties under realistic water/rock ratios but often require excessively long experimental time frames when the diffusing species interact strongly with the solid matrix (sorption) due to the induced retardation.

In this first presented work, an attempt is made to experimentally simulate in an integral fashion, at the laboratory scale, certain key phenomena responsible for repository isolation performance. For our experimental simulation we used real natural clayrock cores and in order to speed up the mass transfer aspect while still allowing residence times sufficiently long for achieving local equilibrium for fast reaction processes (sorption), the solution was pumped through the pore system at rates more than 10,000 times higher than it would move under natural hydraulic gradients. A similar experimental setup has already been used to simulate and model fluid transfer in compacted bentonite (Samper et al., 2008) or in natural boom clay (Martens et al., 2011). Advection therefore replaced diffusion as the dominant dissolved species transport mechanism. This allows the time needed to observe coupled reaction-transport processes in compact clay media to be reduced significantly.

¹ In the absence of human intrusion.

Advective water displacement by the piston effect allows collection and characterization of the original pore water remaining in the sample. The concentrations of major and trace elements as well as of mobile dissolved organic matter in water can be compared with values obtained from model calculations considering mineral/water interactions and with the composition of water collected in underground laboratory experiments. At the same time, water transfer rates (hydrodynamics) can be assessed in intact clayrock, parameters affecting transport of major anions and cations and of radionuclides can be deduced, and interaction of the pore water and the clayrock with container materials and with nuclear waste glass can be studied. All these processes are expected to occur simultaneously in a real disposal scenario in the confined space and are now studied all together on a number of single natural clayrock samples of different mineralogy for the first time worldwide. The whole experimental program has already lasted seven years.

2.1. Description of the experimental conditions

Representative clayrock with varying mineral compositions (carbonate and clays in particular) were collected under oxygen-free conditions at various depth between –474 m and –501 m in the Callovo-Oxfordian claystone from the location of the French underground research laboratory located in the Meuse and Haute Marne departments. Mineralogy data of the samples are reported in Table 1.

More detailed geochemical and mineralogical information is given by Gaucher et al. (2004). The core samples were transferred to the laboratory, and cylindrical samples were machined to a tolerance of 50 µm to allow tight insertion into various specially designed stainless steel flow-through reactors. In a number of experiments typical nuclear waste materials such as powdered nuclear glass (non-radioactive, in some cases ^{32}Si doped), or iron particles representing container materials were inserted between two adjacent cylindrical clayrock samples. Stainless steel filter plates located at the reactor inlet – and outlet ensured the tight enclosure of the samples. High pressure (HPLC) pumps or a syringe pump with pressures up to 120 bars were used to inject aqueous solutions simulating natural groundwater (clay pore water) composition into the reactor under controlled atmosphere conditions (mixture of N_2/CO_2 at ratios corresponding to natural pCO_2). Sample hydration was done at low pressure before the pressure was increased (10–100 bar) to reach flow rates ranging from 0.02 to 1.2 mL/day. The pCO_2 in the inflowing water was maintained by bubbling a N_2/CO_2 gas mixture through the solution. Re-equilibration of dissolved carbonate with the carbonate minerals of the clayrock is expected along the flow path. In most cases, specific ‘tracer’ substances (radioactive tracers, organic molecules, bacteria, colloidal particles, etc.) were added to the inlet water, either continuously or by pulse injection to observe specific processes and interactions. In certain cases various natural water constituents of interest were omitted to distinguish between preexisting

residual pore water content and injected fluid. Experiments were carried out at temperatures between 20 and 90 °C. A typical experimental setup is shown in Fig. 1.

Out-flowing solutions aliquots were collected in gas-tight sampling vials and analyzed to determine the mass and the chemical composition of the transferred fluids. Comparison with the inlet solutions yielded information on the initial pore water composition and on the interactions of the fluids and radionuclides with the rock. Major and trace elements were analyzed by ICP-MS and ion chromatography, radionuclides by liquid scintillation counting and gamma spectroscopy, total and organic carbon by a COT meter, pH by glass electrodes, oxidation states of few elements before and after injection by ion chromatography. Gas-tightness against air has been tested by proving absence of Fe(II, aq) oxidation in test fluids over a weeklong period. Measured flow rates showed that evolution of sample permeability during the month to years experimental durations was minor. To determine clayrock sample hydrodynamic parameters (permeability, anion and cation accessible porosity, dispersion coefficient), spikes of tritiated water (HTO) solution, ^{36}Cl solution and Sodium Tri-fluoromethane sulfonate NaTFMS solution were injected at different time steps. HTO is used as water tracer, ^{36}Cl as anionic species tracer and TFMS[–] is used to study the effect of molecular size on transport.

In experiments incorporating nuclear glass samples between clayrock cores, glass dissolution rates were followed during the experiments by analyses of the glass constituent boron, but also Li, Cs and Mo in the out-flowing solution. Glass dissolution rates depend strongly on temperature and in order to speed up reaction rates, experiments were performed at 90 °C (much higher than the temperature which will exist when water will contact waste packages in the repository).

After test termination (one or two years) the cylindrical samples were pushed out of the reactor and sliced along the flow axis into mm thick segments. The solid samples were analyzed, by water lixiviation, for their contents of weakly interacting anions (I, Cl, Br), while strongly sorbing radionuclides were analyzed by gamma spectroscopy. These analyses also gave information on the spatial distribution of porosity. The list of test series is given in Table 2.

2.2. Modeling

The above described experiments are more complex than simple batch tests at high water/rock ratios, which means that in many cases different interpretations might exist for a given experimental results. The complex thermodynamic and kinetic interaction of multiple solution components with solid matrix minerals under the presence and absence of other materials, and under the given hydrodynamic and geometric constraints, must ultimately be explainable in terms of a limited set of well-understood variables if a full-scale geochemical/transport coupled models (diffusion/advection equation) is to be used for assessing the space dependent evolution of the pore water composition, of hydrolysis and complexation of aqueous solution species, of the presence, dissolution and precipitation of minerals, of surface charge and surface site distribution and of the speciation of radionuclides.

To do this a geochemical code was used (PHREEQC (Parkhurst and Appelo, 1999)) coupling chemistry and 1D transport processes in a series of completely mixed reaction cells representing the clay slices, filters and inlet and outlet capillaries. Flux boundary conditions were applied at both ends of the flow through reactor and the transport-reaction equation was solved using Fick's second law. Input parameters for low temperature (20 °C) experiments were initial water composition, mineralogy, chloride accessible porosity. It was assumed that calcite (CaCO_3), illite ($\text{K}(\text{H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2(\text{H}_2\text{O})]$), a silica polymorph (SiO_2 ; chalcedony or quartz) and celestine (SrSO_4) were present, and that they

Table 1
Mineralogy of samples taken from the Callovo Oxfordian clay stone formation at the position of the French underground research laboratory.

Sample	Drilling	Depth (m)	Content in clay minerals (%w/w)	Content in carbonate phases (%w/w)	Lithofacies
EST25695	PAC1002	474	60 ± 16	18 ± 4	C2b1
K119	EST205	477	45 ± 3	25 ± 2	C2b1
EST26480	FOR1118	490	53 ± 21	24 ± 5	C2b1
EST27861 (AB)	EST423	501	17 ± 7	37 ± 8	C2c
EST27861 (B)			26 ± 7	17 ± 4	

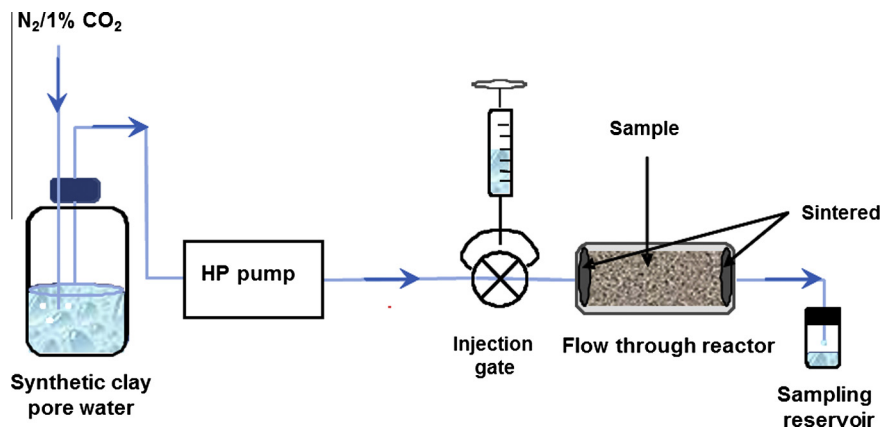


Fig. 1. Schema of flow through reactor used to simulate nuclear waste repository conditions.

Table 2
Conditions and study goals for percolation experiments.

Test notation	Study goals	Injected solution	Description of clay cores and other materials used (see table 1 for details)	Observables	Boundary conditions
W	Clayrock pore water analyses: majors, traces, mobile organics, assess mineral/water equilibria	NaBr solution of reference ionic strength, later composition was changed	a) Oxidized rock b) Anoxic rock Ø= 2 cm, l= 4 cm	Composition of outflowing water as function of change in inlet water. Water flow rate; Concentration gradients in solid	Pressure gradients, T= 20°C pCO2 fixed in inlet solution
H	Validation of Darcy law, determination of anion and cation accessible porosity, dispersion and diffusion coefficients	Synthetic pore water, spikes of water and anion tracers like tritiated water (HTO) and ³⁶ Cl	samples EST 27346, Ø= 60mm, l=15mm EST25695, Ø= 21mm, l=42mm	Water flow rate, outflowing water composition	T=20C, 60°C, 80°C, pCO2 fixed in inlet solution for each temperature
M	Impact of mineralogical composition of clayrock on hydrodynamics	Synthetic pore water	Clayrock samples EST25695 EST27861-B EST27861-AB EST27862 Ø=36mm, l=25mm	Water flow rate, water composition	T=20°C Flow rate 1.2, 0.8, 0.01 mL/d 40–100 bars
T	Effect of temperature at fixed mineralogy	Synthetic pore water	EST25695 Ø= 21mm, l=42mm	Water flow rate	T=20 à 80°C; 0.02 à 0.08 mL/d
R	Radionuclide transport and retention properties	Synthetic pore water and injected radionuclides like ¹³⁷ Cs, ¹³¹ I	Drill core PAC1002 EST423	Evolution of radionuclide concentration in outflowing solution and in sliced clay core	T=20°C
G	Nuclear waste glass dissolution in compact clayrock	Synthetic clay pore water, [Si] = 5–25 mg/L	EST26459 (FOR1118) Ø= 21mm, l=42mm Glass composition: SON68	Water flow rates, concentrations of Li, Mo, B, Cs in outflowing solution,	For 1 month T=20°C to fully hydrate sample at negligible glass corrosion, thereafter T=90°C
S	Steel corrosion with and without SRB microbial activity	Synthetic clay pore water	EST26459 (FOR1118) Steel composition: P235GH	Surface alteration of steel samples at test termination	T=20°C

controlled the concentrations of their constituent elements in the pore water. These minerals are found in mineralogical characterizations of clayrock samples (Gaucher et al., 2004). Typical artificial pore water composition (mmol/L) at 20 °C were Na⁺ 46; K⁺ 1; Ca²⁺ 7.4; Mg²⁺ 6.7; Sr²⁺ 0.2; Cl⁻ 37; SO₄²⁻ 16; CO₃²⁻ 3.3; Br⁻ 4.1; pH 7.1 and log pCO₂ -2.0 (Gaucher et al., 2006). Depending on the rock sample (clay content), the cation exchange capacity was between 1.8 and 24 meq/100 g. Exchange constants (log*k*) for major elements were: NaX: 0.0; KX: 1.0; CaX₂: 0.9; MgX₂: 0.9, SrX₂: 1.0. Formation of electrical double layers was also considered. Retention

coefficients $K_d = C_{solid}/C_{solution}$ (C_{solid} = concentration on solid, $C_{solution}$ = concentration in solution) for Cs were calculated as a function of mineralogical composition of the solid and radionuclide concentration considering ion exchange on three types of site. Radionuclide transport was characterized by a combination of diffusion and advection processes. Due to dominance of advective transport, diffusion coefficients for anions could not be determined with sufficient accuracy and were taken from literature as 2 or $5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. Effective diffusion coefficients of cations and tritium, as well as dispersivity coefficients, were the principal

experimental results and were determined by varying them until a good fit with the experimental data was obtained. The fastest time necessary for radionuclides to diffuse through the argillite cores (or the entire host formation), the so called break-through time t_B , can be estimated on the base of Fick's law using $t_B = d^2/(6D_a)$ (d is the diffusion distance), where $D_a = D_e/(\varepsilon + K_d\rho)$ is the apparent diffusion coefficient, ε the porosity, ρ the density of the medium and K_d is the retention coefficient. In the geological formation ε , ρ and K_d vary within certain limits (see Table 3 below) but the choice of average values may serve for estimations.

Kinetics of glass alteration was typically based upon a first-order rate equation, limited by saturation of a silica phase (chalcedony or amorphous silica).

2.3. Results

The experimental program addresses a large variety of processes of relevance for the isolation properties of a nuclear waste repository in clayrock. For each of the groups of experiments and the different study goals given in Table 2, the results are described separately. Notation of the experiments and studied phenomena are briefly recalled in each case:

H and M Experiments: Hydrodynamics – Validation of Darcy's law, determination of rock permeability anion and cation accessible porosity, dispersion and diffusion coefficient and impact of variation of mineralogy.

Transport of radionuclides as well as water molecules in clay-rock will be driven by both hydraulic gradients (advective transport) and by concentration gradients (diffusion). One might ask the question: Are the experiments meaningful quantifying repository performances if they are performed at hydraulic gradient 10,000 times higher than under realistic conditions? The relation between hydraulic gradient and rate of water transport (flow rate) is given by the law of Darcy (Eq. (1)).

$$Q = K \cdot A \cdot \frac{\Delta h}{L} \quad (1)$$

where Q is the percolation solution flow rate ($\text{m}^3 \text{s}^{-1}$), K the permeability (m s^{-1}), A the cross section (m^2) and $\frac{\Delta h}{L}$ is the hydraulic gradient.

To test this law, the rock core sample was slowly saturated with the solution at percolation rate of 2.8 mL/d. Saturation correspond

to filling of accessible pores by water. Indicator for saturation is that the flow rate of in- and out-flowing water becomes equal. Once saturation is reached, the linearity of Darcy's law (Eq. (1)) was validated for a pressure range from 5 to 45 bar. Detailed results are given in Durce (2011). Hydrodynamic parameters have been determined for a number of clay core samples (see Table 3). We see that carbonated samples are less permeable than clay rich samples.

The kinematic porosity measured by our experiments correspond to the total diffusion accessible porosity since flow rates are very slow (Reynolds number $\ll 1$) and diffusion is sufficiently fast to allow water exchange. Total anion accessible porosity has been determined at test termination by analyses of the chlorine content of the sample, considering absence of sorption and Cl concentrations in pores equal to those of inflowing water. Coherence of modeling (using kinematic porosity) and measured total anion accessible porosity was assured. Anion accessible porosity is always lower than total porosity, since anions are repulsed from negatively charged clay surfaces as for example from interlayers and external basal surfaces of clays. In contrast, HTO exchanges as well with interlayer water. This difference between anionic and total porosities is of course less important for carbonate rich samples.

Experimental and model results for HTO migration in the clay core are shown as an example in Fig. 2, compared with a model curve for ^{36}Cl . Experimental results for ^{36}Cl (not shown) closely agree to the model curve. The corresponding diffusion coefficients are given in Table 3, also for other samples, for which no figure is presented here.

The Peclet number $P = vL/D$ indicates the relative importance of either of advection or diffusion control for solute transport processes, where v is the pore velocity, D is the dispersion coefficient of water as measured by the dispersivity and effective diffusion coefficient D_e for HTO. P values higher than unity indicate advection control, lower values indicate diffusion control. P values ranged between 0.94 and 4.32 for the four clayrock samples which therefore indicates that a mixed diffusion/advection regime occurred under our experimental conditions.

For chloride we used a D_e value of $5 \times 10^{-12} \text{ m}^2 \text{s}^{-1}$ as input parameter. This parameter could not be measured unambiguously due to the strong advective contribution to transport in our experimental setup. Descostes et al. (2008) measured a value for $(4.8 \pm 3.3) \times 10^{-12} \text{ m}^2 \text{s}^{-1}$ for the lithofacies C2b, C2c et C2d

Table 3

Summary of mineralogical, transport and retention properties of the clayrock samples used in this study. Data designated * are input data taken from literature (Descostes et al., 2008) from the same lithofacies and are not derived from the experiments.

Sample name	EST25695	EST27861B	EST27861AB	EST27862
Lithofacies	C2b2	C2c	C2c	C2c
Depth (m)	474	501	501	501
Mineralogy				
%Carbonates	16	19	33	87
%Clay	55	25	15	3
Hydrodynamics				
K (m/s)	$(5.1 \pm 0.2) \times 10^{-14}$	$(8.8 \pm 0.3) \times 10^{-13}$	$(7.4 \pm 0.2) \times 10^{-13}$	$(3.3 \pm 0.4) \times 10^{-15}$
Anion porosity (vol%)	9.8	7.2	10.4	4.3
Total porosity (vol%)	15.6	14.3	16.4	5.7
Fractional anion porosity	0.63	0.5	0.63	0.75
Dispersivity (mm)	3.1	5.8	5.9	6.8
Diffusion coefficient				
D_e (^{36}Cl) (m^2/s)	$5 \times 10^{-12*}$	$5 \times 10^{-12*}$	$5 \times 10^{-12*}$	2×10^{-12}
D_e (I) (m^2/s)	2×10^{-12}	2×10^{-12}	2×10^{-12}	
D_e (HTO) (m^2/s)	$(1.6 \pm 0.3) \times 10^{-11}$	$(3.5 \pm 0.4) \times 10^{-11}$	$(3.1 \pm 0.3) \times 10^{-12}$	$(2.4 \pm 0.3) \times 10^{-12}$
D_e (Cs) (m^2/s)	$(9.2 \pm 0.9) \times 10^{-10}$	$(5.2 \pm 0.5) \times 10^{-10}$	$(3.8 \pm 0.6) \times 10^{-10}$	
Retention				
K_d (I) (mL/g)	0.01	0.14	0.14	
K_d (Cs, trace) (mL/g)		1500	1000	500
K_d (Cs, 0.001 M) (mL/g)		15	8	5

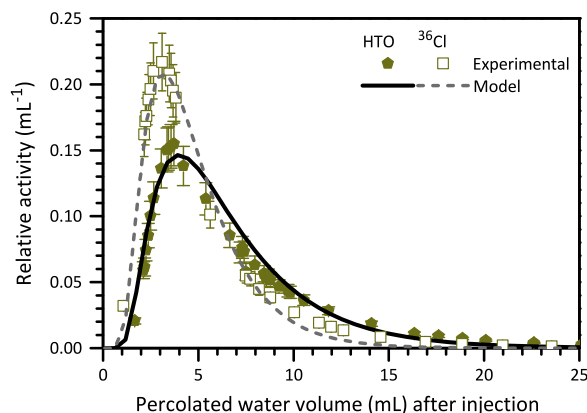


Fig. 2. Breakthrough curve for HTO for the sample EST423-27861(B) (core length = 25 mm, diameter = 36 mm, water flow rate 1.24 mL/day. Relative activity corresponds to the ratio of the outlet volumetric activity (Bq/mL) to the total activity injected (Bq). Comparison to data for ^{36}Cl .

corresponding to our samples. With this value fixed, effective diffusion coefficient of the various other species could be determined for the same sample. D_e values for iodide of $2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ were determined. Also Descostes et al. (2008) observed for these clayrock lithofacies a lower diffusion coefficient of $(2.5 \pm 1.4) \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ for iodide than for chloride. The authors reported accessible porosity values for chloride ions of $(6.7 \pm 2.9)\%$ and for iodide $(9.2 \pm 8.4)\%$ similar to our anion accessible porosity values between 7.2% and 10.4%. The reported (Descostes et al., 2008) slight differences between chloride and iodide accessible porosity are probably due to sample variations, since different samples were used with iodide and chloride, in contrast to our case where these properties were determined on the same sample. D_e values for HTO for clay rich samples between 3.1×10^{-12} and $3.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and HTO accessible porosities (“total porosities”) between 14.3% and 16.4% are slightly lower than the values measured by Descostes et al. (2008) for samples from the same clayrock lithofacies C2c and C2b2 with D_e values between 2 and $5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and porosities between 16% and 22%.

The agreement of diffusion coefficients determined from batch and percolation tests indicates that percolation tests can be used to assess migration properties under repository conditions. Since water flow velocities v are about 10,000 times higher in the percolation experiments than under expected repository conditions due to higher hydraulic gradients and since transport lengths L are about 2000–4000 times larger in the repository (diffusion distance of 70 m in Callovo-Oxfordian clay), the product $v \cdot L$ varies only slightly between field and laboratory, and the Peclet numbers $P = v \cdot L/D$ would be rather similar, indicating that also under realistic repository conditions some mixed diffusion and advection has to be considered for HTO traced water transport.

W/H Experiments: Pore water analyses and controls of composition by mineral interactions.

Fig. 3 shows a typical result of water analyses in outflowing water as function of time. Solution concentrations of SO_4 and Cl (not shown) decrease with time. Modeled curves show close agreement. This approach also allowed analysis of the trace constituents present in the natural pore water. Iodine concentrations in the pore water depended on the degree of oxidation of the clayrock: in case of oxidized clay (sample exposed for years in laboratory atmosphere), I concentrations were about 10^{-7} M , whereas in the samples of this study, protected from oxidation, I concentrations

in the pore water were about $6 \times 10^{-6} \text{ M}$. Speciation analyses by ion chromatography showed that dissolved iodine was essentially in form of iodide.

Dissolved silica concentrations in pore water were $1.8 \times 10^{-4} \text{ M}$. Solution concentrations indicate concentration control by a silica polymorph with solubility close to that of quartz.

A mobile fraction of natural organic matter was observed in the outflowing water. Initially, a dissolved concentration of 0.015 M C was measured in the pore water of anoxic clay. In contrast, in oxidized clay cores, dissolved organic matter (DOM) concentrations were 13 times higher and then decreased rapidly, being flushed out readily with time. The immobile organic matter which is present in about 1000 times larger quantity did not become remobilized over the experimental time frame. The principal compound types observed in DOM (Huclier-Markai et al., 2010) were acidic compounds, fatty acids, aldehydes, amino acids, and lower aging humic compounds, suberic and tiglic acid being a typical of the observed molecules. Organic matter is known to decrease the retention of radionuclides on clay and to increase mobility. A recent study (Vu-Do, 2013) of europium retention in presence of these acids shows that, unlike what one could expect, the presence of small organic acids slightly favors the retention of europium on the argillite: the retention factors in the presence of europium suberates, sorbates and tiglates are respectively 235, 225 and 400 L kg^{-1} . Eu is a homologue to trivalent actinides, hence similar behavior is expected for these actinides. This result indicates that the natural organic matter present in the Callovo-Oxfordian clay-rock should not significantly reduce the retention properties of the clayrock for radionuclides.

T Experiment: Temperature influence on transport properties and control of composition by mineral interactions.

Injection of solutions with various concentration of silicon leads to a constant silicon concentration at 90°C of $6 \times 10^{-4} \text{ M}$. Flow rates increase between 20°C and 80°C from 0.02 mL d^{-1} to 0.08 mL d^{-1} following the change of water viscosity. Diffusion and dispersion coefficients increase by a factor 2–3. Porosity is assumed not to change with temperatures. The pore water composition varies less than predicted from geochemical models. In particular, geochemical models predict the precipitation of dolomite when increasing temperature. Experimental Mg concentrations remain higher than predicted. This may be explained by kinetic constraints. In fact dolomite formation requires the dissolution of about 1 g of minerals per sample to reach dolomite equilibrium. Mineral dissolution rates are probably too slow. Evidently, in a repository in geological formations, there is much more time and dolomite formation at higher temperature may be expected.

R Experiment: Radionuclide transport and retention properties.

As an example of a strongly sorbing radionuclide, we studied the behavior of cesium during migration in the clayrock samples. In contrast to the results for HTO, ^{36}Cl and iodine (see below), all the Cs content of injected water remained fixed in the sample and no Cs could be detected in the outflowing water. Therefore, at test termination, the concentration profile of Cs was determined in the clay core. An example is given in Fig. 4. The derived migration parameter for Cs for the other samples is also included in Table 2. As far as the retention model is concerned, the model takes into account the varying retention as a function of solution concentration. Measured K_d values for 0.001 M and for trace concentration of Cs are included in Table 2. For a detailed description of the model see (Chen et al., submitted for publication).

Corresponding curves for iodine given in Montavon et al. (2014) allowed deriving the corresponding migration parameters in Table 3. Here also a retention factor (K_d) needed to be considered,

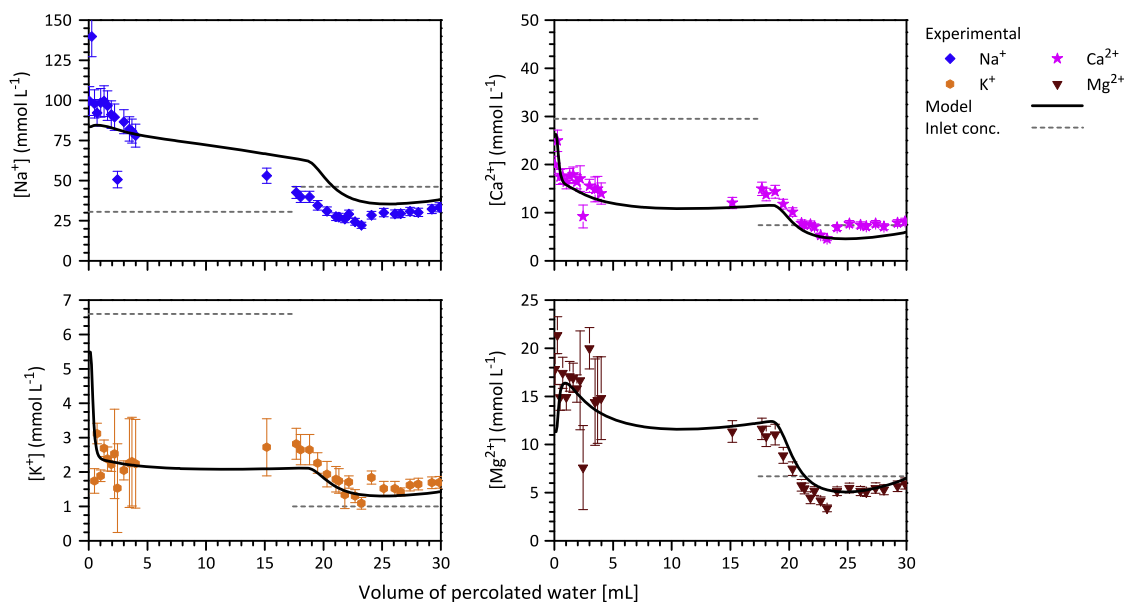


Fig. 3. Evolution of the concentrations of some major ions during percolation of synthetic pore-water through sample EST25695. Dashed lines represent the inlet concentration.

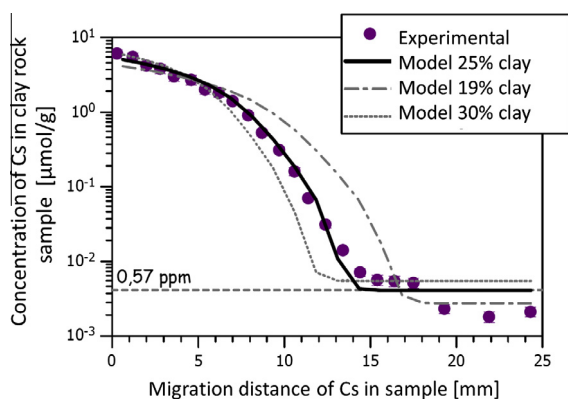


Fig. 4. Concentration profile of Cs in the clay core sample EST423-27861(B) after percolation of 66 mL of a synthesized pore water solution containing 0.95 mmol L⁻¹ of Cs with an average flow rate of 1.4 mL d⁻¹ at 20 °C. The influence of mineralogy is represented considering upper and lower bounds in the clay.

depending on sample between 0.14 and 0.01 L kg⁻¹. In typical safety analyses of ANDRA, a value of zero is used. Despite the low K_d value, an important gain in safety is obtained if the K_d is considered (see below under 3.4).

G Experiments: Impact of clayrock on glass dissolution.

Nuclear waste glasses such as the French R7T7 reference glass slowly dissolve in groundwater, leading to release of soluble elements from the altered surface zone, and leaving sparingly soluble glass constituents and radionuclides behind, bound to the solid glass alteration products. Glass alteration is characterized by fast initial rates (about 0.01 g m⁻² d⁻¹ at 35 °C) and a subsequent slow down by a factor of >1000 to low long term rates depending on accumulation of silicic acid in solution. Presence of clay may influence the accumulation process of silica either by adsorption of dissolved silicic acid or by release of clay bound silicic acid. Experimental results are given in (Neeway, 2011) showing a pH in the outflowing water between 7 and 8 and no hindrance by the clayrock on the achievement of low long term dissolution rates. Long term rates at 35 °C in clay water were measured as low as

6×10^{-5} g_{glass} m⁻² d⁻¹ and since there is about 1 wt% Cs in the glass, Cs release rates should be around 6×10^{-7} g_{Cs} m⁻² d⁻¹. In contrast to typical indicators for glass dissolution (concentrations of boron) which are observed in few days, it takes more than 200 days until some Cs is found in the outflowing water. This is due to the strong retention of Cs on the clay (see also Fig. 4 for Cs retention in the absence of glass).

S Experiments: Impact of clay rock on container corrosion with and without presence of SRB bacteria.

Container steel was positioned in the flow through reactor between two clayrock cores to study corrosion behavior. Results are presented in (El Hajj et al., 2010). Corrosion rates were about twice as high in presence of sulfate reducing bacteria (SRB) compared to sterile conditions. In a geological repository with high amounts of hydrogen produced from steel corrosion, the water activity may remain low enough so as to inhibit development of microbial biofilms. In this case, the role of microorganisms on canister or cladding corrosion may be very minor.

3. Discussion

To assess migration properties of radionuclides in clay rock, the percolation tests have shown some advantages with respect to typical tests using static diffusion cells. Though diffusion cells provide more reliable diffusion data for mobile radionuclides, without interference of advective processes, the drawback is that for each radionuclide typically a new rock sample has to be used. No data have been published where diffusion properties of various radionuclides have been studied on a single sample. In contrast, in our percolation tests, diffusion properties of different nuclides were measured on a single sample. The drawback of our method is that diffusion coefficients of different nuclides were only determined in relative terms. Determination of absolute values of diffusion coefficients relies on the independent measurement of ³⁶Cl diffusion in diffusion cells or on measurements at different flow rates. We used published values for this purpose. Hence, our approach is not an alternative but a complement to diffusion cell measurements. In percolation experiments (experiment R) like in diffusion cells diffusion properties of strongly sorbing radionuclides like Cs require

the post-mortem analyses of the concentration profiles of the radionuclide in the rock sample. However diffusion cell samples are typically mm sized, percolation test samples are cm sized.

Finally, not only can diffusion properties for various radionuclides be analyzed consistently in relative terms on a single sample, one can also determine for the sample the natural pore water composition or one can condition the pore water composition prior to studying radionuclide migration properties. This is an important advantage to diffusion cell approaches if one wants for example to study the effect of water composition on diffusion. For example, to study salinity effects on diffusion properties, typical approaches consist in increasing the salinity in the water reservoirs adjacent to the rock sample. This would either lead to salinity gradients in the rock sample and difficult interpretation of radionuclide diffusion data or one would have to consider long equilibration times prior to injecting radionuclides.

From the experiments H one can predict for natural hydraulic gradients of Callovo-Oxfordian clay that diffusion dominates over advective water flow. To calculate the breakthrough time for radionuclides to migrate from the waste via the clay rock to overlaying geological formations, the diffusion distance to consider is the half the thickness of the about 140 m of the Callovo-Oxfordian clayrock formation (assuming the waste emplacement in the center of the formation).

To know the maximum amount of radionuclides which can be transported by water in clayrock, one need to know the radionuclide concentration at the source (potentially solubility controlled), the distribution ratio (K_d) of the radionuclide between the clayrock and the pore water (experiments R), the diffusion coefficient and accessible porosity (experiments H).

The breakthrough times are calculated according to the formulas given under “modeling”. They are very different for the different radionuclides of the wastes:

Iodine 129: With an effective diffusion coefficient for iodine of $2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ (Table 3) an anionic porosity of 0.05 and a K_d of zero, a breakthrough time of >650,000 years is calculated. Of course, diffusion coefficients have uncertainties. If the larger diffusion coefficient for anions like those determined by Descostes et al. (2008) in the upper limits for the Callovo-Oxfordian clayrock formation of $5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ are used and considering again conservatively for K_d a value of zero, the break through times are still larger than 250,000 years. Sorption of Iodine strongly increases the breakthrough times. Even the lowest experimentally measured K_d of 0.01 mL g^{-1} (Table 3, (Montavon et al., 2014)) increases them to at least 500,000 years. After this very long time, maximum iodine concentrations in the human accessible environment are calculated to be thousands times lower than radiological thresholds.

Cesium 135: For Cs the question may be posed whether one uses the high K_d for low Cs concentrations or the low K_d for high Cs concentrations (see Table 3). High Cs concentrations are not possible since the rate of Cs release from the glass is sufficiently slow that diffusive transport removes all Cs from the glass surface. Already after 4 cm in our experiments, solution concentrations in the outflowing pore water of the clayrock sample are sufficiently low (they are actually below the detection limit), that the K_d value for trace concentrations (Table 3) needs to be used. This corresponds to hypothetical breakthrough times of hundreds of millions of years. Hence, despite of its half-life of 2.3 million years, ^{135}Cs cannot become released from the clay host formation. This conclusion is not modified even if K_d values would be 10 times lower than measured.

Uranium: This element needs some special consideration since its principal isotope ^{238}U has a half-life of 4.5 Mrd yr and secular equilibrium with its daughter products is expected in a very confined space like the pore water of a clay rock. We can make some

very general statements: Analytical precision and accuracy have allowed by multicollector ICP-MS to demonstrate a state of radioactive equilibrium $^{234}\text{U}/^{238}\text{U}$ in Callovo-Oxfordian argillite (Descamps, 2004). This result indicates the immobility of the uranium in this geological formation and, consequently, demonstrates a chemically inactive and closed environment. The situation is different in the overlaying and underlying geological formations (at a distance of about 70 m from the waste): Here, imbalances ($^{234}\text{U}/^{238}\text{U}$) were consistently observed in areas subject to processes of pressure-dissolution (stylolites) in the enclosing carbonate formations of the Oxfordian and Bathonian. These imbalances reflect a discrete remobilization of uranium in the last two million years and therefore active transport process within these formations.

What is the risk of dispersion of uranium from the waste? The most dispersed state is that which exists already today, since the Callovo-Oxfordian formation contains natural uranium within a narrow distribution between 0.7 and 2.3 ppm (Descamps, 2004). Considering the emplacement area of the disposal site of the French project CIGEO of 600 ha and a thickness of the Callovo-Oxfordian formation of 140 m, this corresponds to about 2000 tons of dispersed uranium (and additionally its decay products) already present today in the formation. Yet despite the fact of the presence of this uranium for the age of the formation of about 150 Mio years, no risk of uranium in surface waters has been observed. This argument of analogy does not replace a full scale analysis of uranium behavior, but the outcome is expected to be low.

Transuranium elements: For transuranium actinides, the amount (concentration) of radionuclide adsorbed on the clay is often thousand to ten thousand times higher than the amount which remains in the water. An actinide cation like Am^{3+} has a K_d larger than 5000 mL g^{-1} in smectite clay (Grambow et al., 2006) indicating that a 1 m, thick clayrock barrier will be sufficient to block any Am release. The fractional inventory flux across the barrier can be calculated in a simplifying conservative manner by using Fick's 1st law and expressing concentrations at the waste form/bentonite interface in terms of inventory fractions. For Am a fractional release across the clay barrier of less than 10^{-14} yr^{-1} has been calculated (Grambow and Giffaut, 2006). Sorption and solubility constraints provide redundant barriers against safety relevant release. A typical solubility value for Am in water at the glass/clay interface is 10^{-9} M (Rai et al., 2011). Taking a K_d of 5000 mL g^{-1} , and using the measured dispersion coefficient of 0.01, a pore diffusion coefficient of $10^{-10} \text{ m}^2 \text{ s}^{-1}$ a porosity of 20% a permeability of $10^{-13} \text{ m s}^{-1}$ and a hydraulic gradient of 0.5 m m^{-1} one obtains in 1 m migration distance across the clayrock after 1000 years and a maximum Am concentration of $<10^{-29} \text{ M}$ well below drinking water standards and for longer times Am concentrations will vanish due to radioactive decay. If we consider an extreme case of a rock location with only 10% clay, the K_d would then “only” be 500 mL g^{-1} and maximum Am concentrations in 1 m distance from the clay would still remain always lower than 10^{-25} M . The case of Plutonium is similar: typical Pu concentrations at the glass/water interface under reducing conditions expected in a nuclear waste repository in clay formations are 10^{-9} M (Rai et al., 2011) like for Am and K_d values in clayrock are higher than 500 L kg^{-1} (Latrille et al., 2006). Half-lives of Pu are longer than those of Am and Pu, but even after 500,000 years and 1 m of migration distance in clay, solution concentrations of Pu would remain lower than $2 \times 10^{-15} \text{ M}$, much lower than drinking water standards. Beyond this time, Pu concentrations vanish due to radioactive decay.

Glass dissolution in compact clay: The glass dissolution rate of $6 \times 10^{-5} \text{ g}_{\text{glass}} \text{ m}^{-2} \text{ d}^{-1}$ measured in contact to clay rock (Neeway, 2011) in experiment G needs to be seen in the overall context research of the last 30 years to have some meaning on glass performance in the repository. This research has allowed to develop

physical chemical laws to describe the diminishing rate of glass dissolution as a function of environmental parameter such as water flow rate or solution volume and surface area by an affinity term (effect of solution saturation by silicic acid dissolved from the glass) and by diffusion processes (Frugier et al., in press; Grambow and Muller, 2001). Glass dissolution and environmental influences became thus predictable. Even after saturation of solution by silicic acid, dissolution continues, though with a very low rate. This long term rate often decreases with the square root of time, indicating control of corrosion by a diffusion process through a growing layer (Grambow et al., 1992; Grambow and Muller, 2001). Extrapolation of the measured rate value of $6 \times 10^{-5} \text{ g}_{\text{glass}} \text{ m}^{-2} \text{ d}^{-1}$ with a square root of time rate law would allow predicting glass stability for many millions of years, but such a prediction would be over-optimistic, since the diffusion layer may become brittle. A much more robust extrapolation can be done if one ignores the potential decrease of reaction rate with time and makes the hypothesis that the lowest observed rates remain constant and do not decrease further. This is a bounding case extrapolation and a linear extrapolation is in this respect conservative. Credibility of the conservatism (of the bounding character) of such an extrapolation is given by the fact that (1) essentially all available experimental data indicate absence of increase of rates for the experimental conditions simulating repository behavior, (2) that also natural glass alteration data show very low reaction rates in confined space (Grambow et al., 1986) and (3) that a detailed physical–chemical law has been developed explaining the low linear long term rate law by formation of secondary phases (Grambow and Muller, 2001). The results of the G experiment increase credibility in statements of long-term glass stability in a repository as they show that the long term glass dissolution rates observed in the absence of clayrock remain low in confined clayrock.

4. Conclusions

The simulation by percolation tests of some key safety features of a geological disposal site has provided important indicators for the safety for clayrock:

- (1) In accordance to experimental observation, our clay pore water model provides information non-trivial evolution of solution concentrations and pH, indicating the pertinence of the model. As far as the main and some minor components are concerned, the calculated water composition is within the variability of the composition of the pore water observed in the Callovo-Oxfordian clayrock formation, see also (Gaucher et al., 2006).
- (2) The fact of having determined similar diffusion coefficients for our percolation setup than those reported from pure diffusion cells (Descostes et al., 2008) increases the credibility of our approach. Peclet numbers in our experiments will be rather similar to those under field conditions, indicating mixed diffusion/advection control of radionuclide migration. Hence, percolation tests are a useful tool to simulate hydrodynamics of large scale repository performance.
- (3) Migration times for the fastest moving radionuclides through intact clayrock are very slow, our models indicate that it will take some hundreds of thousands of years for the transfer over 70 m from the waste to the next geological formation.
- (4) Glass corrosion rates in compact clay are similarly low to rates in confined silica rich solutions.
- (5) Mobile organic matter in clay pores consists of small molecules of the type of diacids.

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