

LONG TERM BEHAVIOUR OF THE RADIOACTIVE WASTE PACKAGES IN THE NEAR FIELD OF A DEEP GEOLOGICAL DISPOSAL MOCK UP EXPERIMENTS

Patrick LOCOGE ⁽¹⁾ - Hughes PEYCELON ⁽²⁾

⁽¹⁾ Commissariat à l'Energie Atomique - DCC/DESD/SESD/LGEM - Centre d'études de Cadarache.

⁽²⁾ Université d'EVRY Laboratoire d'analyse et d'environnement U.M.R .172 - 91025 EVRY Cedex.

ABSTRACT

For the last three years, the CEA has developed mock-up experiments to contribute to the design basis and validation of a radioactive waste disposal concept. The aim consists in identifying the main mechanisms and in giving typical times concerning the long term evolution of the waste packaging and of the near-field, taking their interactions into account.

It has been established that this evolution is greatly influenced by the environment. Control of the boundary conditions imposed on the system by the near-field is essential.

In this context, a pilot plant, called « Water Module » has been built. The aim of this facility is to deliver natural water, representative of the deep granitic medium (stability of the chemical composition, geo-chemical equilibrium, reducing character, conservation of the main dissolved gases). The method used consists in re-equilibrating pressurized water, sampled from a borehole. This stabilisation is obtained by circulating the sampled water in several triaxial columns (to avoid any depressurization), filled with crushed alterate granitic materials taken from deep sampled fissures.

The experimental plant, which has been operational for 15 months, yields 4 cm³ an hour. The delivered water has the following characteristics : stable reducing redox potential and pH (respectively, -350 mV/N.H.E. and 8.3), stable chemical composition, good state of equilibrium facing mineral phases of the granite material, preservation of the dissolved gases (H₂, N₂, CH₄, CO₂).

At present, this facility is used to supply two equipped mock-ups. The first one concerns the study of the steel container corrosion when these are confined in a compacted clay barrier. The second concerns the study of the influence of the buffer effect in a clay barrier material on the geo-chemistry of the near-field.

INTRODUCTION

The program « Near Field Mock-Up » is one of the experimental parts of the project : Long-Term Behavior of the Radioactive Waste Packages in the Near Field of a deep geological disposal, developed by the CEA (Commissariat à l'Energie Atomique). The main objectives of this project are :

- to elaborate a set of tools permitting the simulation of the long-term evolution of the package and of the near field while taking their interactions into account,
- to build facilities that can qualify these tools,
- to collect and organize a complete and validated database,

- to be able to contribute, working along side with the ANDRA (Agence Nationale pour la Gestion des Déchets RADIOactifs), to the performance assessment of waste packages for a defined concept of storage,

The influence of the environment on the long-term behavior of packages has now been clearly established. The studies relative to this behavior must integrate effects due to the evolution of the near field and to the boundary conditions imposed by the distant geological medium.

Within this framework, the device : « Near Field Mock-Up » has been developed in order to qualify geochemical and transport models and to verify experimentally the functional performances assigned to the materials chosen for the manufacturing of engineered barriers which will be used in the storage sites. Experimentations on a reduced scale (mock-up), to design and test different configurations of near field, permits us to break away from the limitations of laboratory tests (a much too simplified approach) and of in situ experimentations (an environment too complex, and uncontrolled parameters).

For this mock-up, a modular structure has been adopted, in order to be able to replicate some of the subsystems of the near field. Currently three modules have been developed :

- the « Corrosion Module » which permits the study of the corrosion phenomena for the metals used in the manufacture of waste package containers and overcontainers,
- the « Buffer Effect Module » which studies the geochemical evolution of the aqueous phase in the Near Field, while taking into account the buffer effect of an engineered clayey barrier,
- the « Bitumen Module » which is devoted to the studies of the influence of pressure and of temperature on the leaching, under a dynamic flux condition, of a coated bitumen matrix.

These three subsets are organized around the central module of the mock-up : the « Water Module ». Its vocation is to supply them with reference water. This water has the following characteristics : strong reducing character, stable chemical composition, representativity of water circulating in a deep granitic geological medium. The aim of this facility is the simulation of the presence of a distant geological field.

THE « WATER MODULE » FACILITY

THE ADOPTED PROCESS

The « Water Module » of the « Near Field Mock-Up » is an experimental facility that delivers controlled water the composition of which is representative of a deep granitic water.

Processes of deep granitic water equilibration result from numerous interactions [1]. On the one hand mineral : between water and rock, and on the other hand, microbiological : between bacteria and the available substrata (role of catalyst for the oxidation-reduction processes). Any experiments aimed at reproducing representative synthetic water with a controlled and stable composition are difficult to perform due to the complexity of mechanisms intervening in the natural environment. Therefore, the choice was made to design a device based on the use of natural water, coming from a granitic site. The « Water Module » has been designed to take into account the fragility of waters sampled from their natural environment (fast evolution of their chemistry). Its aim is to maintain or to restore a state of equilibrium between water sampled from

a borehole and the constituent minerals of fractures in which it circulated before its sampling, in order to obtain a stabilized water, representative of a reference geological environment at our disposal.

THE REFERENCE SITE.

Several potential sites have been examined. Some with a remarkable hydrogeology, and therefore a particular geochemistry, have been excluded. Among the potentially acceptable sites, a final choice has been made, mainly on logistic criteria :

- presence of deep boreholes with diameters up to 75 mm,
- infrastructures of existing laboratories,
- sufficient knowledge on the geology of the area,
- possibility to have a borehole at our disposal for more than ten years.

The reference site chosen for the sampling of water is located in a granitic formation, at the periphery of the uranium bearing deposit of the Bernardan mine, near Limoges (France).

Among the drills, made during the different phases of the mining prospection, a borehole of 110 mm in diameter and 754 m in depth has been selected to carry out the sampling. This borehole goes through granites of which the weathering degree and the fracturation density are variable. It successively crosses weakly hematized granite levels, zones of épi-sénites and a large vein of lampophyres. A large formation of a relatively sound granite appears between –600 m and –700 m. The weathering products that fill fractures have been characterized. An exploration by the use of diagraphies (pH, Eh, conductivity and temperature profiles) has shown the presence of two layers of stratified water, separated by a transitional zone with 40 m in thickness. The waters of the upper aquifer appear to be clearly influenced by atmospheric contributions (pH close to neutrality, oxidizing redox potential), while the lower layer is constituted by older waters issued from deep circulations. The temperature profile shows a relatively constant gradient. Diagraphies in temperature and in resistance have shown the existence of discharging fractures. The selected sampling zone is located between level –630 m and level –650 m.

Water intended for filling and supplying the re-equilibration cells of the « Water Module » is taken out of the borehole once a month. At each campaign, 5 samples of 2 liters are performed. The average composition of waters appears in Table 1. The values are given for two campaigns achieved at the end of 1997 and in the middle of 1998.

Table 1: Physico-chemical characteristics of waters sampled from the borehole of the Bernardan site (depth = – 630m).

Concentration (mol.l⁻¹) Standard deviation : $\pm 5\%$	November 1997	July 98
Al ³⁺	$3.70.10^{-6}$	$1.04.10^{-6}$
Fe ²⁺	$9.67.10^{-7}$	$6.45.10^{-7}$
Mn ²⁺	$1.00.10^{-6}$	$5.35.10^{-7}$
Zn ²⁺	$1.41.10^{-6}$	$7.65.10^{-8}$
Ca ²⁺	$2.00.10^{-4}$	$1.55.10^{-4}$
K ⁺	$7.67.10^{-5}$	$5.37.10^{-5}$
Li ⁺	$4.90.10^{-5}$	$4.80.10^{-5}$
Mg ²⁺	$9.47.10^{-5}$	$7.82.10^{-5}$
Na ⁺	$5.78.10^{-3}$	$5.91.10^{-3}$
Cl ⁻	$1.52.10^{-3}$	$1.79.10^{-3}$
F ⁻	$3.79.10^{-4}$	$3.37.10^{-4}$
HCO ₃ ⁻	$4.39.10^{-3}$	$4.61.10^{-3}$
SO ₄ ²⁻	$5.83.10^{-6}$	$1.94.10^{-5}$
HS ⁻	$6.05.10^{-5}$	$1.15.10^{-4}$
SiO ₂ (aq)	$2.95.10^{-4}$	$3.68.10^{-4}$
Temperature (°C)	28 (± 0.5)	25 (± 0.5)
pH	8.20 (± 0.25)	7.90 (± 0.25)
Eh (mV/n.h.e.)	-105 (± 25)	-220 (± 25)

THE DEVELOPMENT OF THE « WATER MODULE ».

The balancing of the sampled natural water is ensured by percolation of the latter through several cells filled with weathered granitic materials from drill hole cuttings.

In order to reproduce as accurately as possible the conditions in which waters circulate in the natural geological medium, triaxial type cells have been chosen. This type of equipment induces a circulation of the water at a fixed pressure (corresponding to the piezometric pressure in the borehole at the sampling depth), in a porous medium on which another pressure replicating the lithostatic pressure can be applied.

The role of this facility, on which the relevance of the downstream connected experiments depends, is of utmost importance. Its adjustment required many technical and technological developments, in order to continuously control and guarantee the quality of the fluid from its sampling to its delivery in the different experimental modules.

These developments concern the following key points :

The sampling and the conservation of the natural water.

To avoid any modification of the waters during their sampling and their transportation to the triaxial cells of the « Water Module » a particulate sampling system, called PVV (Préleveur Volume Variable) and developed by the CEA [2], has been used. The design of this tool prevents, at the time of a sampling in a deep borehole (until 1000 m of depth), :

- any depressurization (even partial) of the sample,
- the loss of dissolved gases,
- any chemical pollution (including that induced by trace elements).

The probe (Figure 1), which is 4.5 m long and about 45 kg in weight, consists of 3 different parts :

- the first part contains various devices involved in the opening and closing processes for the multi-channel water intake valve which is protected from particles larger than 40 μm by a Teflon frit. The device operates by a motor step by step. This part is equipped with 23 mm filters to remove or retain suspended materials,
- the second part consists of an interchangeable 2 liter tank (1150 mm long with an inner diameter of 50 mm). Each tank is equipped with manual valves at both ends, to guarantee that the samples are confined and isolated as soon as the probe reaches the surface. Inside the tank, an unconfined piston flushes the distilled water contained in the lower chamber by means of a capillary that guarantees a constant pressure drop,
- the final part consists of a more than 2 l tank, equipped with some one-way valves, in which the flushed distilled water flows after being displaced by the piston during the sampling process. The upper chamber is gradually refilled by displacement.

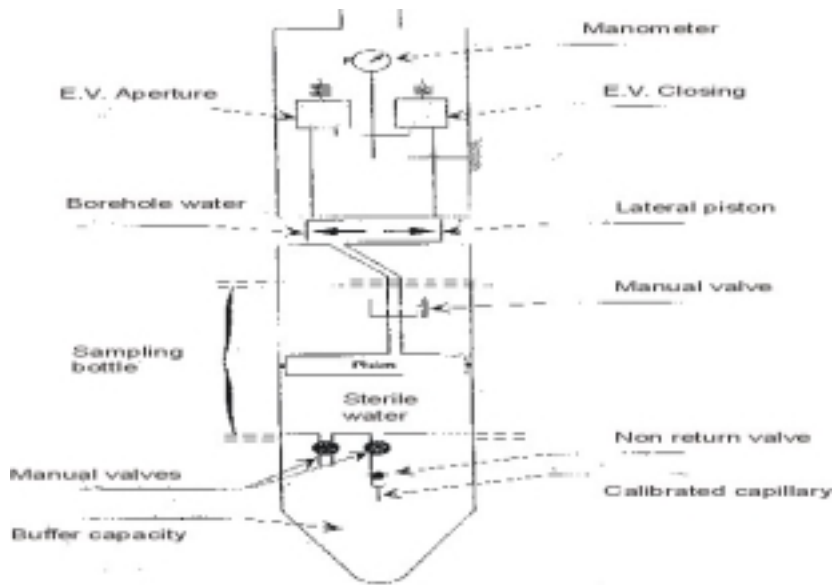


Figure 1 : PVV probe for sampling groundwater

« Water Module » operation

The difficulties encountered were related to :

- obtaining a very accurate regulation (tolerance lower than 2.5%) of the flow rates for very small values (1 to 5 ml/h). Considering the use of triaxial cells with large dimensions, this involved a very accurate regulation (better than ± 50 mbar) of the different pressures (at the entry and the exit of all the cells) in an operating range included between 30 bar and 50 bar. Another difficulty was to achieve a chemically

inert system. To solve this problem, specific valves with very thin glass inserted PEEK membranes, were designed and made,

- guaranteeing that all the elements of the installation in contact with water (pumps, valves, électro-valves, tubing, filters,...) presented a complete chemical inertia and a perfect gas tightness. For that reason, all the hydraulic parts were made in PEEK, except for the electromagnetic sluice gate (manufactured with titanium) and the internal part of the triaxial cells (silicone membranes).

Process control.

The continuous control of the process required :

- the development of micro-samplers manufactured with PEEK, based on the same technology as that of the PVV. They are used to take, during the different steps of the process, fluid samples dedicated to chemical determinations. In fact, all the sampling operations must be done without any disturbances (lost of dissolved gases, chemical pollution, reoxydizing by contact with the atmospheric environment).
- the development of micro-detectors measuring the continuous pH and redox potential in very small volumes of water and under more than 30 bar of pressure.

THE ELEMENTS OF THE SYSTEM

The approach used to ensure the equilibration of the water by the « Water Module » consists in percolating a natural water, sampled from a borehole with an appropriate sampler (the PVV) through triaxial cells filled with granitic materials of different weathering rates. All the parts of the facility (Figure 2 and Figure 3) are maintained at a nominal temperature of 28°C by a system of thermoregulation. This temperature is that of the water at the time of its sampling.

The « Water Module » is made of three parts :

- a barrel containing 6 PVV type bottles used for water supply,
- a set of 2 triaxial cells filled with a « slightly » weathered granitic material,
- a set of 2 triaxial cells filled with a weathered granitic material.

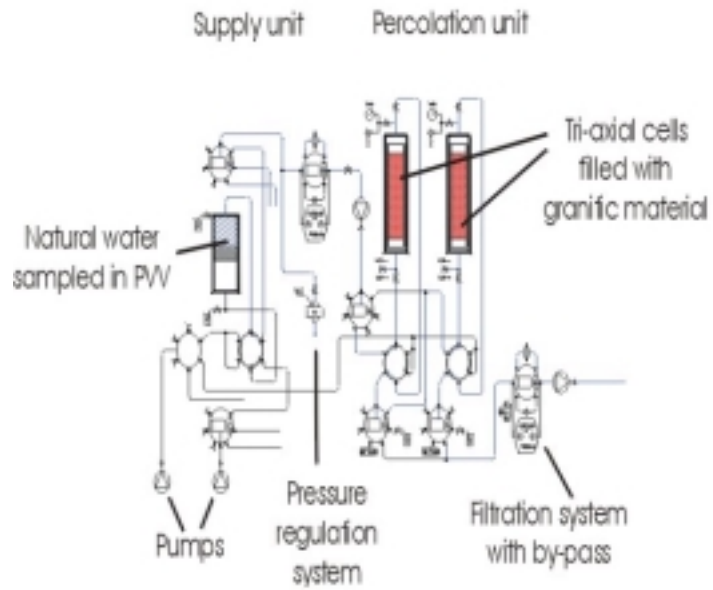


Figure 2 : simplified diagram of the « Water Module ».



Figure 3 : photographs of the facilities : supervision system, tri-axial cells and supplying unit.

A supervision system completes the installation. Its aim is the automation of the different operations in order to facilitate continuous operations over long periods of time.

The automaton controls the following tasks :

- the automatic by-pass of the different filtration units when plugging occurs,
- the regular sampling on different points of the circuit,
- the data acquirement and storage in real time for the nominal operating parameters (pressure, temperature, flow rate),
- the data acquirement and storage concerning the physico-chemical characteristics of the water at the different steps of the requilibration process.

All of the tubes used in this facility are small diameter tubing (either 1/16 in. or 1/8 in.) made with PEEK material

The granite used to fill the triaxial cell comes from core samples of a fractured zone in the reference site. This selected fractured zone is at the same depth as the one in which the water sampling is made.

The first group of cells is filled with a poorly weathered crushed granite. The particle size distribution range is between 500 μm and 1 mm. It is intended to ensure the first step of the rééquilibration with a simulation of a water circulation in a fracture network with a great permeability.

The cells of the second group are filled with a more weathered granitic material whose particle size distribution is between 0.45 μm and 1 mm. Their aim is to refine the rééquilibration process of the water with a simulation, this time, of a percolation within the secondary fracturation network (weakly permeable fractures, filled with more clayey minerals).

The compositions of these two materials are given in the Tables 2 and 3.

Table 2: Spectrometric analysis of the granitic materials used to fill the cells – Composition of main elements

Oxides (%)	Poorly weathered granite	More weathered granite
SiO ₂	72.57	70.97
TiO ₂	0.25	0.30
Al ₂ O ₃	14.86	14.49
Fe ₂ O ₃	0.20	0.99
FeO	1.09	0.83
Fe ₂ O ₃ total	1.40	1.91
MnO	0.03	0.04
MgO	0.43	0.77
CaO	0.69	1.01
Na ₂ O	3.22	2.45
K ₂ O	4.77	5.41
P ₂ O ₅	0.22	0.27
H ₂ O ⁺	0.94	1.72
H ₂ O ⁻	0.02	0.30
TOTAL	99.29	99.55

Table 3 : Mineralogical composition for the main minerals of the granitic samples used in the « Water Module » cells.

Type of mineral (%)	Poorly weathered granite	More weathered granite
Quartz	34.5	32.0
Albite	27.2	20.7
Orthose	18.7	28.8
Muscovite	13.6	4.5
Kaolinite	2.3	8.7
Dolomite	1.1	3
Calcite	0.9	1.2
Others minerals	1	0.7
TOTAL	99.3	99.6

OPERATING NOMINAL PARAMETERS.

Each of the filling loads is confined in a flexible double envelope (the first one, in contact with the granite, is made of silicon to ensure chemical inertness. The second one is made of viton to ensure the tightness to gases). All of these envelopes placed in a confinement built with corrosion-resistant steel. Outside the double envelop, the pressure is regulated at 63 bar in order to simulate the lithostatic pressure. The pressure applied to the water which circulates in the mineral assembly is maintained at 33 bars, an adjusted value equal to that of the natural water in the borehole before its sampling.

All the triaxial cells used in the installation are identical. They have the following characteristics :

- total dimensions : L = 1500 mm - ϕ = 450 mm.
- Inner envelop dimensions : L = 1100 mm - ϕ = 100 mm
- maximum working pressure : 100 bar
- maximum working temperature : 80 °C

Cells filled with « poorly weathered » granite contain 20 kg of ore and their porous volume is equal to 4.8 l. Cells filled with « weathered » granite can contain 22 kg of granitic material and have a porous volume equal to 2.9 l.

The circulation flow rate of the water in the different cells has been set at 4 ml.h⁻¹. This choice results from a compromise between different constraints:

- to minimize the pressure drops due to the low permeability of the environment,
- to ensure a sufficient flow rate of balanced water in order to supply the downstream experimentations of the « Near Field Mock-ups » system,
- to respect a low enough circulation speed with regard to the different kinetics of the different reactions governing the reequilibration processes.

INSTALLATION OPERATION

This installation was started up in July 1996. Two months and half of operation were necessary to establish stationary operating conditions. During the last 14 months, the delivered water presented a stable chemical composition and constant physico-chemical characteristics.

Figure 4 to Figure 8 show the evolution of these features since the beginning of the experimentation :

- the main cations : Ca^{2+} , Na^+ , K^+ , Mg^{2+} ,
- the main anions : Cl^- , SiO_2 , SO_4^{2-} , S tot , F^- , HCO_3^- ,
- the metallic ions : Zn^{2+} , Al^{3+} , Fe^{2+} , Li^+ ,
- the pH, the Eh (continuous measurements at the outlet of the cells),
- the pressure and the flow rate at the outlet of the system.

In the Table 4 is presented an average chemical composition of the water produced by the « Water Module ».

Table 4 : chemical composition of the « Water Module » outlet water in 1997 and 1998.

Concentrations (mol.l-1) Standard deviation : $\pm 5\%$	09/97 Outlet water	06/98 outlet water
Al^{3+}	$1.04.10^{-6}$	$2.5.10^{-6}$
Fe^{2+}	$3.76.10^{-7}$	$1.08.10^{-6}$
Mn^{2+}	$5.45.10^{-6}$	$4.9.10^{-6}$
Zn^{2+}	$7.6.10^{-8}$	$7.6.10^{-8}$
Ca^{2+}	$4.63.10^{-4}$	$5.75.10^{-4}$
K^+	$7.6.10^{-4}$	$1.48.10^{-3}$
Li^+	$6.3.10^{-5}$	$6.2.10^{-5}$
Mg^{2+}	$2.51.10^{-4}$	$2.39.10^{-4}$
Na^+	$5.96.10^{-3}$	$6.83.10^{-3}$
Cl^-	$1.66.10^{-3}$	$1.42.10^{-3}$
F^-	$5.16.10^{-4}$	$4.42.10^{-4}$
HCO_3^-	$5.0.10^{-3}$	$7.51.10^{-3}$
HS^-	$7.03.10^{-5}$	$6.14.10^{-5}$
SO_4^{2-}	$5.31.10^{-6}$	$1.04.10^{-5}$
SiO_2	$2.13.10^{-4}$	$1.16.10^{-4}$
PH	8.35 (± 0.25)	8.20 (± 0.25)
Eh (mV/n.h.e.)	-335 (± 25)	-345 (± 25)

ANALYSIS OF THE CHEMICAL AND PHYSICO-CHEMICAL DATA

case of the physical data.

Concerning the electro-chemical measurements, pH and Eh, conducted in a continuous way without depressurization (33 bar), a good stability of the values can be observed.

The pH value increases slightly during the phase of reequilibration : it increases from 8,05 to 8,35. However, the phase of reequilibration in the « Water Module » greatly affects the value of the redox potential.

The water from the borehole presents a slightly negative potential in relation to hydrogen (-80mV/E.N.H.). It comes out of the installation with a value smaller than -350mV/n.h.e. Then, it has a distinctly reducing signature.

The temperature, the pressure and the flow rate have been perfectly controled during the entire experiment.

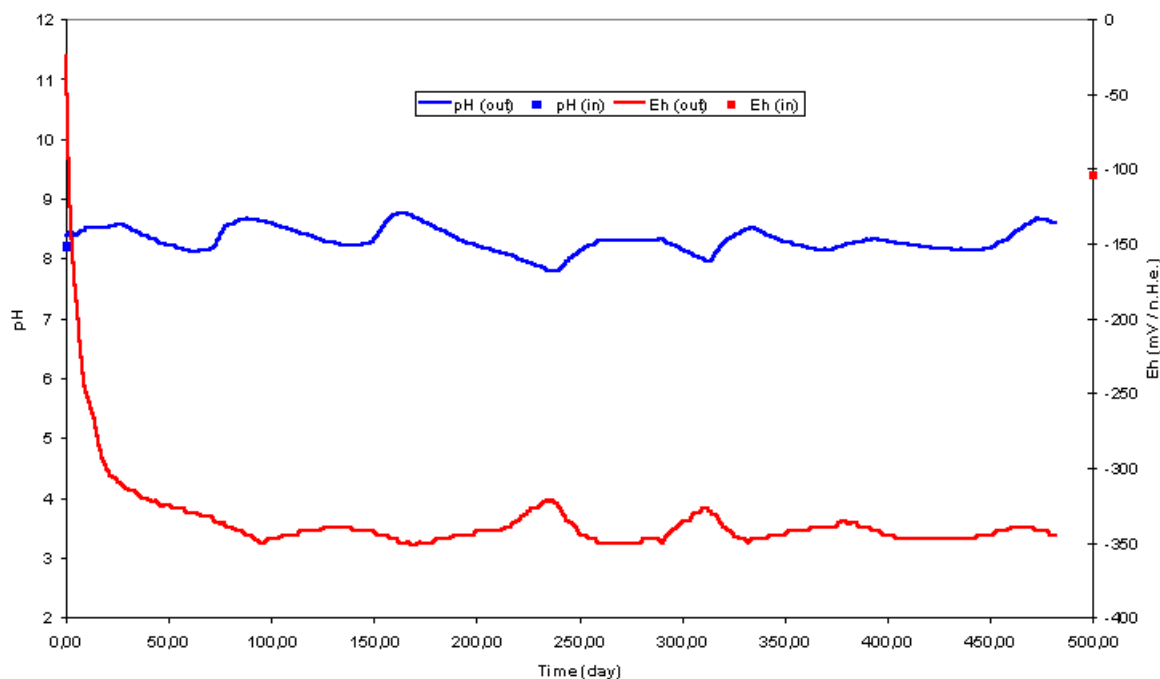


Figure 4 : evolution of pH and Eh at the outlet of the « Water Module ».

Case of metals

A great scattering of the values has been observed at the beginning of the experiment. The first samples were only filtered up to 0,45 μm . In view of the results, filtrations at 10 nm on the aliquots dedicated to the dosage of the metallic species have been achieved. From then on, the scattering of values decreased appreciably. However, metallic element concentrations of water at the outlet of the « Water Module » are slightly higher than those of the natural water used for its supply. This phenomenon is due to the strong reduction of the redox potential.

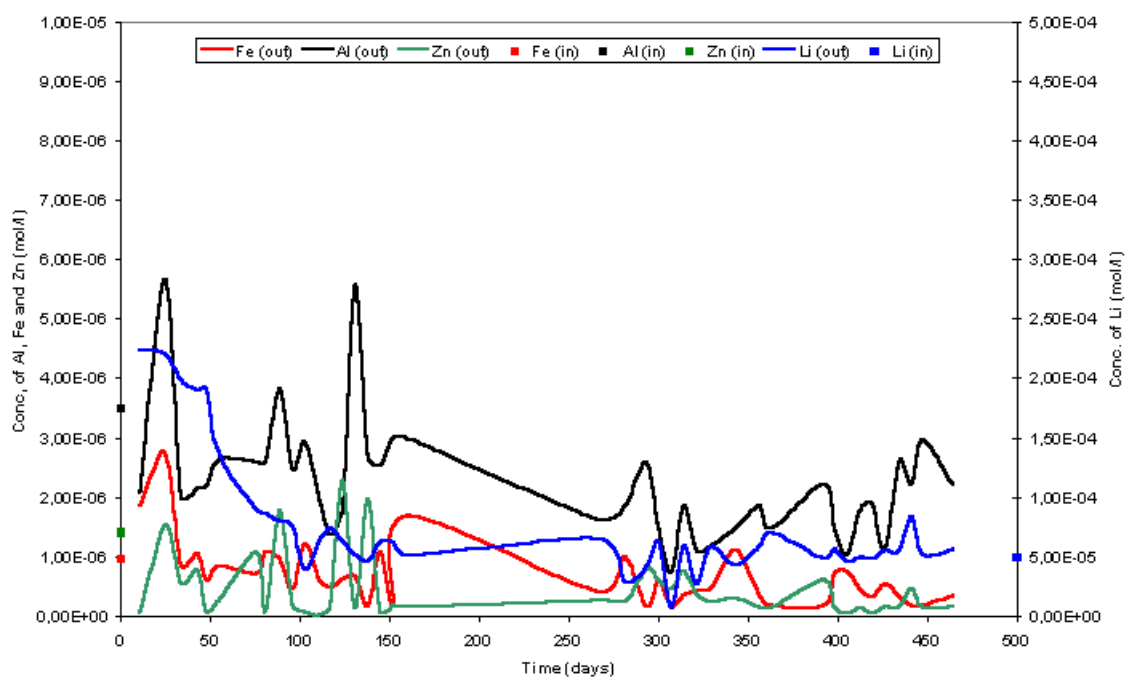


Figure 5: evolution of the metallic species concentrations at the outlet of the « Water Module ».

Case of cations

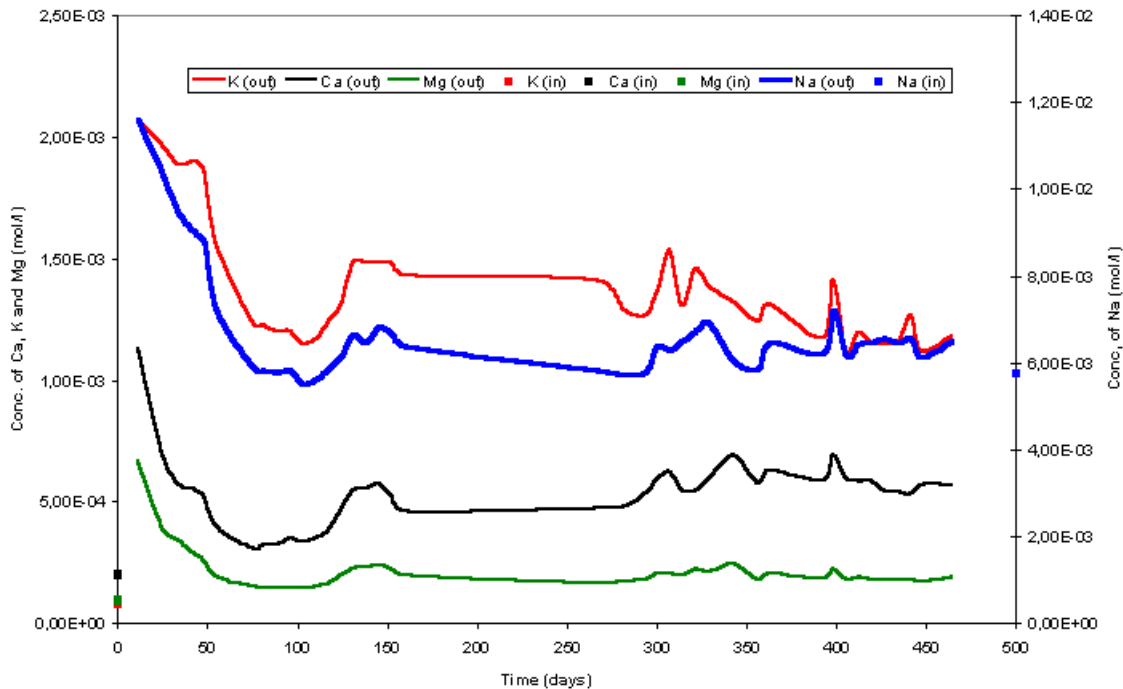


Figure 6 : evolution of the main cationic species concentrations at the outlet of the « Water Module ».

The water produced by the « Water Module » presents a stable composition concerning the sodium and lithium ions. What is more, the measured concentrations are nearly equal to those determined in the inlet water.

The potassium content is also stabilized but about ten times more than the concentration of the water of the borehole. This increase could mean a reequilibration with the K - Feldspar present in great quantities in the columns of the « Water Module » facility.

Magnesium and calcium contents increase very slightly and regularly. This phenomenon could reflect a slow leaching of smectites or of other phases containing Ca-Mg combinations.

Case of anions

Chlorides, silica and carbonate contents are stable and close to the values presented by the inlet water.

With regard to sulphates, the content at the outlet of the cells is very stable but appreciably lower to the one of the water in entry. This phenomenon can be linked to the great decrease of the redox potential. This would mean a reduction of sulphates (contained in the borehole water) in the sulphides or intermediate species. Presently, a survey on the speciation of sulfur species in the water is in progress.

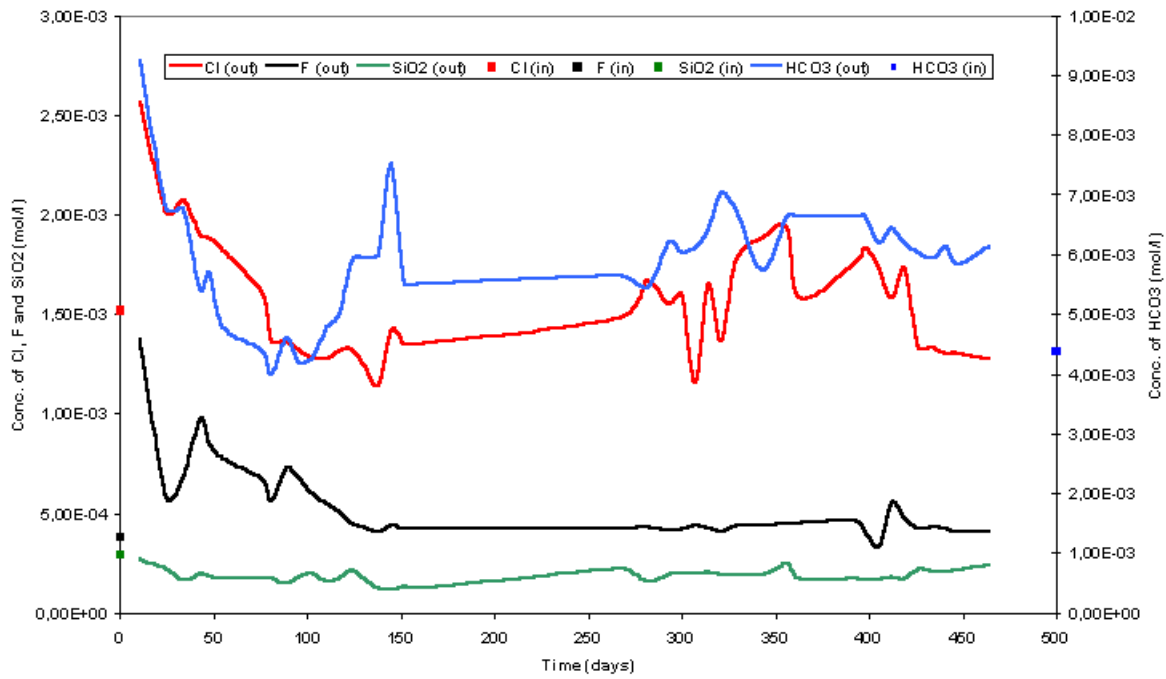


Figure 7 : evolution of the main anionic species concentrations at the outlet of the « Water Module ».

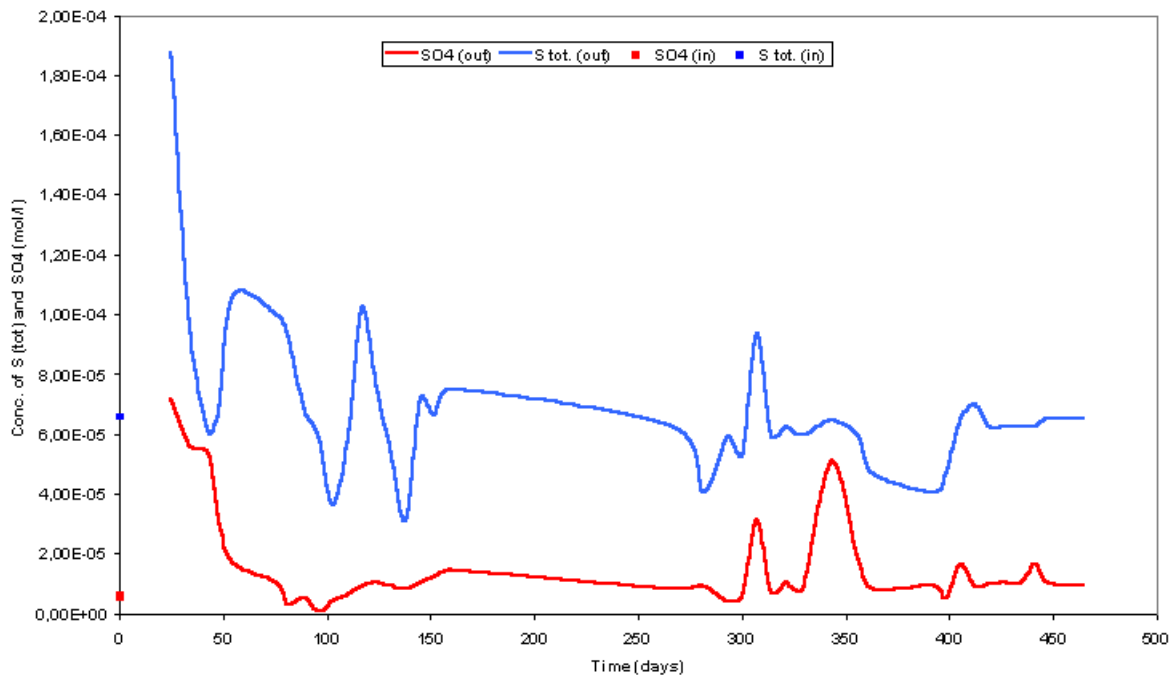


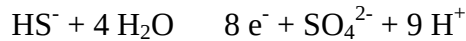
Figure 8 : evolution of the sulphates and total sulfur concentrations at the outlet of the « Water Module ».

CHARACTERIZATION OF WATERS

The inlet waters

Waters sampled in the borehole have HCO_3^- , Na^+ , Ca^{2+} , Mg^{2+} and Cl^- contents and a pH in agreement with a water characteristic of a deeply altered granitic rock (-100 m to -400 m) [3]. The calculated CO_2 partial pressures are respectively $10^{-2.77}$ and $10^{-2.47}$ for the water sampled in 1997 and 1998. These waters present a low salinity with Na^+ , Cl^- and F^- concentrations of 5 mmol.l^{-1} , 1 mmol.l^{-1} and 0.3 mmol.l^{-1} .

The *in situ* redox potentials measured ($E_h = -105$ mV for 1997 and -221 mV for 1998) show the reducing character of these waters. Chemical analyses give concentrations in SO_4^{2-} and HS^- . These concentrations allow the calculation of a potential versus the redox couple $\text{HS}^-/\text{SO}_4^{2-}$. The redox reaction corresponds to :



The corresponding Eh/pH relation is:

$$E_h(\text{V}) = E_0 + \frac{0.0059}{8} \log \frac{[\text{SO}_4^{2-}][\text{H}^+]^8}{[\text{HS}^-]} \quad \text{with } E_0 = 0.249 \text{ V}$$

The calculated potentials are -298 mV for the water sampled in 1997, and -284 mV for the one sampled in 1998. These values must be compared with those measured *in situ* : -105 mV for 1997 and -221 mV for 1998. A great gap exists between the measured and the calculated potentials, particularly for the 1997 sample. This could be due to :

- the analytical difficulties to measure *in situ* correct redox potential [4],
- The different redox couples are not equilibrated, the measured redox potential corresponds to a partial redox equilibrium state of the solution [5].

The calculated values show a greater reducing character of these waters than the measured redox potentials.

Equilibrium state versus the mineral phases

A geochemical speciation calculation has been achieved with the CHESS code [6] for the two representative waters. These calculations allow the estimation of the chemical form and distribution of the different elements in the solution and to calculate the equilibrium states of the solution according to the solid phases. The sampled waters are super-saturated in relation to minerals constituting the granitic rock (Table 3). Saturation indexes are given for the 1997 sample in Table 5. Saturation indexes for the representative water of 1998 are of the same order.

Table 5 : Saturation indexes for mineral phases of representative granitic rock for low and high temperatures.

Mineral	T = 25 ° C	T = 60 ° C
Muscovite	6.9	2.23
Kaolinite	4.1	0.83
K-feldspath	2.6	0.23
Albite	1.5	-0.41
Quartz	0.4	-0.08
Dolomite	1.0	2.1
Calcite	-0.3	0.53

Compared to granitic minerals, these waters are closer to the equilibrium for a temperature of 60°C with saturation indexes that vary between 0.8 and -0.4 except for muscovite and dolomite (over-saturation state).

Waters sampled in the drilling correspond to a deep reducing water with a temperature close to 60° C. When compared to the mineral phases of the granite, these waters sampled at 28 °C, are not yet equilibrated at low-temperature.

outlet water - effects of the transition through the« Water-Module » facility

Analyses of outlet waters of the "water-module" are given in Table 4. The comparison with the representative waters sampled in the borehole and supplying the "water-module" shows, in a first approach, that the global features of the inlet water are preserved, particularly for the pH. The measured potentials are more reducing than those measured and calculated for the inlet waters. Analyses of HS^- and SO_4^{2-} concentrations allow as before the calculation of a redox potential. The calculated values are -314 mV and -305 mV. The measured potential associated to these values is respectively -335 mV and -345 mV. Differences between the measured and calculated potentials are less significant than for the inlet water. The weak differences observed for the outlet water can be due to :

- an equilibrium of redox couples in the solution after the transfer in the installation, the measured potential corresponds to an equilibrium state for all the redox couples in the solution
- a more reliable measurement of the potential in laboratory.

For the main elements, an important difference is located on the concentration of K^+ that is distinctly greater at the exit. The minor phases of the granite, such as biotites or phlogopites were less exposed in the massive granite. The weathering of these phases in the "water-module" can explain part of the increase of concentration in K^+ . Calculations of speciation done on the inlet waters show that these phases present subsaturation indexes and are therefore likely to be destroyed. Concentrations of the other elements associated to the K^+ in these phases are Mg^{2+} , Al^{3+} , SiO_2 and also show weak variations but do not allow us to justify the complete of the increase in K^+ observed.

CONCLUSIONS ET PERSPECTIVES.

The « Water Module » facility is now working in its nominal configuration. During this year, an other line has been built. The chemical composition of the water delivered by this last one is very close to those delivered by the first line.

At now, the other experimental modules : « Corrosion Module » and « Buffer Effect Module » have been achieved and connected to the « Water Module ». They will allow to get informations about :

- the hydrogen production due to the corrosion of iron materials by action of a reducing water
- the chemical composition evolution of the water at the contact with the waste package after its passage through a clay barrier material.

REFERENCES

- [1] MICHARD G., ALLAUX-NEGREL G., TOULHOAT P., BEAUCAIRE C. and OUZOUNIAN G., « Major and trace elements regulation in natural granitic waters. Application to deep radioactive waste disposals », HLWR Management Proc., 2nd Annual Int. Conf., Las Vegas, (1991).
- [2] PEYRUS J.C., VINSON J.M., FERNANDEZ J.M., LOCOGE P., « Hydrochemical and isotopic characterization of the groundwater from the El Berrocal site, Spain » E.U.C. contract n° F12W/CT91/0080, Topical reports vol.2, pp 207-354, (1996)
- [3] AQUILINA L., PAUWELS H. GENTER A. FOUILLAC C., « Water-rock interaction processes in the triassic sandstone and the granitic basement of the rhine graben : geochemical investigation of a geothermal reservoir », Geochimica et cosmochimica acta, vol. 61 , no 20 , pp. 4281 – 4295 (1997)
- [4] VAN DER LEE J., PhD thesis, Ecole des Mines de Paris, France (1997)
- [5] STUMM W. and MORGAN J.J., Aquatic chemistry 2nd ed. John Wiley & Sons, New York, 780 pp, (1981)
- [6] LINDBERG and RUNNELLS, « Ground water redox reactions: an analysis of equilibrium state applied to Eh measurement and geochemical modeling. » Science 225, 925-927, (1984).