Session 5

Pore-water Chemistry

Chair: Pedro Hernan / Catherine Beaucaire
CO₂ DATA ON GAS AND POREWATER SAMPLED IN SITU IN THE OPALINUS CLAY AT THE MONT TERRI ROCK LABORATORY

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INTRODUCTION

The study of the mechanisms governing the composition of the interstitial fluids in clay formations with very low permeability constitutes a part of the scientific programmes associated with the safety analyses of deep repositories for the geological disposal of long-lived radioactive waste. Several in situ geochemical experiments have been performed since 1996 in the Mont Terri Rock Laboratory to develop methods for studying these mechanisms in the Opalinus Clay formation. These experiments enabled to build a conceptual model of the interstitial water in the Opalinus Clay (Pearson et al., 2003). The main uncertainties of this model concern the carbonate system and the redox state of the water. Consecutively, another experiment, called PC-C, was implemented in 2004 to reduce these uncertainties using gas circulation and water sampling. This paper presents the CO₂ data obtained on the gas and porewater samples collected in this experiment and the interpretation of these data.

EXPERIMENTAL CONCEPT

A 15 m long borehole was drilled upwards, perpendicular to the bedding plane of the Opalinus Clay formation, in a niche of the access gallery to the Mont Terri Rock Laboratory. The top 5 meters, constituting the test interval, were drilled with nitrogen to avoid rock oxidation. The borehole equipment was installed as quickly as possible after the drilling. Great care was taken to restrict the development of bacterial activity in the borehole by cleaning the drilling tools. After completion, the test interval was filled with pure argon at a pressure of 1 bar. The borehole equipment allows the circulation of the gas in contact with the rock in a closed circuit and the monitoring of the gas pressure in the open section. Due to the large hydraulic gradient between the test interval and the surrounding rock, the water is flowing freely into the interval and is pumped out at a constant rate. The borehole equipment allows the sampling of interstitial water produced in the test interval.

The gas circulation has been performed over one year. The gas composition was monitored by sampling and with an infrared spectrometer connected on line on the gas circuit (Cailteau et al., 2005; Vinsot et al., 2006). Seepage water has been continuously extracted at a flow rate of 3.5 mL/day over more than three years. Its composition has been monitored by sampling, pH and Eh have been measured on line. Gas and water analyses have been performed by Hydroisotop (Germany).

RESULTS AND DISCUSSION

The composition of the water has been very stable over three years. The collected water shows a low level of chemical disturbance and should be representative of the natural state of the porewater. The measured composition is in agreement with the previous in situ investigations and modelling work (Pearson et al.,
2003). However, it was observed that CO₂ partial pressures measured on the gas phase were lower than those calculated from the porewater composition at the same time.

Data obtained over a few months on the circulating gas have been modelled with PHREEQC (Parkhurst and Appelo, 1999). The modelling involves the diffusion of CO₂ from interstitial water to the circulating gas and its buffering by reaction in porewater.

The drilling of the borehole and equipment installation has disturbed the Opalinus Clay and the porewater in the immediate vicinity of the borehole. The calculation shows that the disturbance is very slowly restored in front of the gas zone of the test interval due to the small diffusion rates. This disturbance is still significant over several centimetres after one year. Consequently, the pH in the porewater in the borehole surrounding is higher than a few centimetres farther in the formation. It is also higher than the pH measured on the seepage water.

These results suggest that the seepage water derives mainly from a continuously saturated zone at the bottom of the test interval and not from the whole surface of the test interval. Therefore, this water seems not to be involved in the exchange reactions with the circulating gas.

CONCLUSION
CO₂ data obtained on both gas and porewater samples show an unexpected discrepancy. CO₂ data obtained on water samples seem to be more representative of the natural porewater than those obtained on the gas phase. CO₂ data on the gas phase have been modelled consistently by taking into account diffusion and rapid interactions with porewater. The experimental and modelling results on the gas phase give information about the processes controlling the CO₂ concentration and about their kinetic. The comparison between gas and porewater experimental results suggests a complex organisation of the water pathway within the partly saturated zone around the test interval. It is foreseen to apply a two phase flow model to improve our understanding.

References


IMPROVEMENTS IN THE MODELLING OF THE POREWATER CHEMISTRY OF THE CALLOVIAN-OXFORDIAN FORMATION

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INTRODUCTION

Within the partnership between the French Geological Survey (BRGM) and the French agency for nuclear waste management (ANDRA), the project THERMOAR (Thermodynamic of water in argillaceous formations) aims at defining the porewater chemistry of the Callovian-Oxfordian formation (ANDRA URL, Bure, France). A first model has been published (GAUCHER et al., 2006) using only the data obtained from core samples from deep scientific boreholes (GAUCHER et al., 2004; GIRARD et al., 2005). The construction of the underground laboratory enabled since 2004, a direct access to the formation. The PAC experiment (VINSOT and DELAY, 2007; VINSOT and METTLER, 2007) has been designed to enable the collection of water and gas of the formation directly in the underground rock laboratory. The drilling under N\(_2\) and the innovative design of the equipment has resulted in a high level of preservation of the samples. The chemical analysis of these water samples made possible a comparison with the previous modelling work. Some discrepancies have been observed especially for Fe\(^{2+}\), K\(^+\), Sr\(^{2+}\) and SO\(_4^{2-}\) (Fig. 1), but pH (7.1) and others elements were satisfactorily modelled. A revision of the model has been undertaken to explain and eliminate the discrepancies between the modelled porewater composition and the measured one. The results of this revision are given in this paper.

REVISION OF THE MODEL

The mineralogical equilibrium constraints have not been changed in the new model. The porewater is considered to be in equilibrium with the clay exchanger cations composition, quartz, pyrite, illite, chlorite, celestite, calcite,

![Figure 1: Chemical composition of the Callovian-Oxfordian porewater. 1. Historical model (closed circles), 2. Chemical analysis of the porewater (~475m, white triangles), 3. New model (gray triangles).](image-url)
dolomite, and siderite. The revision of the database in the framework of the THERMOCHIMIE project resulted in important corrections with regards to celestite and siderite solubility constants. A minor revision of the quartz solubility was also considered. The experimental acquisition of thermodynamic constants for clay minerals resulted also in important improvements (BLANC et al., 2007; GAILHANOU et al., 2007). A complete reinterpretation of the cation exchange selectivity coefficients (TOURNASSAT et al., 2007) has been also undertaken with a strong impact on the K+ concentration. Finally, a new procedure of preservation of the core samples in liquid N2 (TOURNASSAT et al., 2006) has been crucial for the determination of the adsorbed Fe2+ and the its further use in the model. The partial pressure of CO2: (log10pCO2 = -2 bar) established by equilibrium between the porewater and the mineral assemblage is in agreement with the highest values that could be measured on core samples.

CONCLUSION
The figure 1 illustrates the progress made in the modelling of the porewater chemistry. One should note that there is no adjustment parameter in the model, that is to say the model is fully predictive. The mineral assemblage at equilibrium with the porewater composition given in the previous model (GÄUCHER et al., 2006) is then considered to be completely relevant provided that correct solubility constants are considered.

References:


NATURE AND REACTIVITY OF DISSOLVED ORGANIC MATTER IN THE OPALINUS CLAY AND CALLOVO-OXFOORDIAN FORMATIONS

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Argillaceous geological formations are currently investigated for the possible long-term storage and final disposal of high-level radioactive waste in several countries. Two clay rock candidates are the Opalinus Clay (OPA) in Switzerland and the Callovo-Oxfordian (COx) in France. The two potential host rocks mainly consist of clay minerals, carbonate, quartz and feldspars with trace amounts of pyrite. In addition, both rocks contain up to 1% w/w organic carbon (Nagra 2002, Andra 2005). Most of the organic matter is attached to the mineral particles of the rock but a small portion is present as dissolved organic matter (DOM) in the pore water (Pearson et al. 2003, Vinsot and Mettler 2006). Up to now, it is not known to which extent the presence of DOM possibly influences the fate of radionuclides within the rock formation. While the complexation of radionuclides by solid-bound organic matter may retard their transport within the rocks, the DOM may increase their mobility by forming dissolved radionuclide-organic matter complexes. Therefore, knowledge on the nature and reactivity of dissolved organic matter is required to assess its relevance for radionuclides migration in the rocks. Since the amounts of available in-situ pore waters are strongly limited for both rock formations, the aims of the present study were i) to extract and characterize DOM from the rock material under anoxic conditions, ii) to characterize DOM of OPA and COx pore waters and compare pore water DOM with rock-extracted DOM, and iii) to assess the reactivity of the pore water and rock-extracted DOM with respect to proton and metal binding.

The OPA and COx pore waters and rock samples used in this study originated from the Mont-Terri (Switzerland) and the Meuse-Haute Marne (France) rock laboratories, respectively. DOM was extracted from ground OPA and COx rock materials with deionized water, synthetic pore water (SPW, water containing all major ions at pore water concentrations but no organic matter), and 0.1 M NaOH in a glove box (< 1 ppm O₂). The size distribution and the low molecular weight organic acid contents of the isolated DOM were determined by liquid chromatography coupled with an organic carbon detector (LC-OCD) and by ion chromatography. The binding of protons, Eu³⁺ and Cm³⁺ of both pore water and the SPW-extracted DOM was determined with acid-base titrations, voltammetry, and time-resolved laser fluorescence spectroscopy (TRLFS), respectively.

The results of the anoxic rock extractions revealed that approximately 0.02% to 0.05% of the total organic carbon content of both OPA and COx rock materials was released as dissolved organic carbon (DOC). Maximum DOC concentrations in the anoxic OPA extracts ranged from 3.9 ± 0.3 mg/L for SPW extracts to 8.0 ± 2.2 mg/L for 0.1 M NaOH extracts. Slightly higher DOC concentrations (5.1 to 13.7 mg/L) were found in the anoxic COX extracts. In comparison, the pore water of the OPA and COX formations exhibited DOC concentration of 15.5 mg/L and 56.7 mg/L, respectively. The characterization of the pore waters and rock-extracted DOM by LC-OCD indicated that hydrophilic low molecular weight organic compounds (< 500 Da) represented the major part of the DOM for both rocks, namely 55 to 80% of the total DOC. Contrary to the COX argillite, the size distribution of the extracted DOM was strongly affected by the type of solvent for the OPA. For both formations, the DOM in the SPW extracts was most similar to the pore water DOM. Further analyses with ion chromatography indicated that a large fraction of the hydrophilic
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low molecular weight compounds consisted of low molecular weight organic acids (acetate, malate, formate, lactate, propionate), representing approximately 30 % of the DOC in the pore water and the extracts for the OPA. Only 11 to 22 % of the DOC was identified as low molecular weight organic acids in the COx extracts, while the COx pore water DOM was almost exclusively composed of acetate and propionate (88% of the DOC). The differences between the COx anoxic extracts and pore water may arise from the heterogeneity of the rock material, a more effective DOM filtration by the rock formation compared to laboratory extractions, or possibly, bacterial activity in the pore water induced by the borehole disturbance. In general, the results showed that SPW may be the most suitable solvent to extract DOM representative of the in-situ DOM. Consequently, the reactivity of the DOM was investigated using pore water samples and SPW extracts only.

The acid-base titrations revealed that in the pore water and SPW extracts of both rocks, protons were mostly buffered by inorganic compounds, i.e., mainly by carbonates and to a less extent also by ammonium, borate, and silicate in the alkaline pH range and by the identified low molecular weight organic acids in the acidic pH range. Overall, the results indicated that the DOM only contributed to a minor extent of the total proton buffering capacity of OPA and COX pore waters and SPW extracts. In addition, the data suggested that the OPA pore water contained high affinity organic ligands which were not isolated in the OPA SPW extract. The analyses of Eu\(^{3+}\) and Cm\(^{3+}\) complexation by the pore water DOM and SPW-extracted DOM confirmed that the OPA pore water DOM exhibited a higher potential to bind trivalent cations than the corresponding SPW extract and that the aqueous speciation of Eu\(^{3+}\) and Cm\(^{3+}\) was strongly dominated by inorganic complexes for both rock formations.

References:


PH4: A 250M DEEP BOREHOLE IN TOURNEMIRE FOR ASSESSING THE RELIABILITY OF CHLORIDE-, HELIUM AND WATER STABLE ISOTOPES PROFILES IN THE TOARCIAN/DOMERIAN SHALES

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INTRODUCTION

One method to obtain information about fluid flow and solute transport in porous media of low hydraulic conductivity and water content is based on the study of natural-tracer distribution in pore-water. Such an approach has been previously applied to the Tournemire Toarcian/Domerian shales and, based on the profiles of the water stable isotopes and chloride in the pore water, it was concluded that diffusion might be the main transport mechanism in these rocks (Patriarche et al., 2004). However, the low water content (2 to 5 %), the small pore size (few nm) and the charged clay surfaces of such rocks make the determination of such natural tracer concentrations difficult and measurements are easily subject to artefacts that deviate the measured data from that actually present in situ. For example, a comparison of different vacuum distillation and isotope exchange methods to determine the pore water isotopic composition revealed that the vacuum distillation method resulted in systematically lower, geologically difficult explicable, $\delta^{18}O$ and $\delta^2$H values, making the previous studies based on this technique questionable (Altinier et al., 2007).

The present study aims at assessing the reliability of various techniques used for the determination of natural–tracers in pore water by the comparison of several natural tracer profiles (chloride, water stable isotopes and helium) with the tracer data obtained from adjacent samples from the same borehole.

EXPERIMENTAL CONCEPT

Drillcore samples were collected from a 250m-deep vertical borehole drilled in winter 2006/2007 from the tunnel down to the lower calcareous aquifer and penetrated through 220m of Toarcian/Domerian argillite and marls. The borehole was air-drilled throughout in order to prevent contamination of the natural tracers by drilling fluid.

The water stable isotope contents in the pore water have been approached by two methods. At intervals of 10 m, core material was recovered and conditioned on-site (removal of the core rim, crushing, placing in a vapour-tight container together with an isotopically spiked solution) for the vapour exchange method for water isotopes. From the same core piece less than 10cm apart, another sub-sample was prepared for radial diffusion experiments (see Savoye et al., 2006a & 2006b for details). The supernatant solution of these experiments was analysed for its isotopic composition as well as for its Cl concentration. In addition, this
method also allows the derivation of the geochemical porosity of the rock and its diffusion parameters. For the determination of pore-water helium concentrations, about 10 freshly drilled rock samples were conditioned on-site to octahedral helium cylinders by dry-cutting the core rim and were immediately transferred in He-tight stainless steel containers. The containers were repeatedly flushed with nitrogen and evacuated, to remove excess air and finally left under a slight under pressure. Complete outgassing of He is attained after several weeks to a few months and He will be analysed by mass spectrometry. Possible contamination of the samples with air is monitored by the simultaneous measurement of the Ne isotope ratio on the recovered gas. Other core samples were dedicated to on-site petrophysical measurements such as the gravimetric determination of the water content by drying at 150°C to stable weight conditions and still other sample were preserved in aluminium bags under vacuum for their mineralogy.

RESULTS
Although some of the experiments take months until their full equilibration and thus the analytical work has not yet been completed, some first results are already available: The hydrogen isotope ratios of the pore-water derived by the vapour exchange technique describe a profile with a “classical” V-shape: from δ²H values of about -45‰ V-PMOW at the tunnel level, deuterium contents regularly increase up to δ²H values of -30‰ in the lower Toarcian and drop down again to -50‰ in the lower Carixian aquifer. A discrepancy of about 20‰ is observed between the present δ²H values and those obtained by Patriarche et al. (2004) for a part of the present profile. This difference persists along the entire stratigraphic column and must be attributed to the artefacts linked to the applied vacuum distillation technique, as already highlighted by Altinier et al. (2007). Similar is observed for the δ¹⁸O profile showing the same vertical trend the δ²H values, but less accentuated. Although the data acquisition is still in progress, these first findings already show the importance of having a) an improved understanding of artefacts introduce by sample conditioning and methods applied, b) a control on the obtained tracer concentrations by applying complementary methods, and c) a complete multi-tracer profile that extends to the bounding aquifer what will allow a much better constrained modelling of the tracer data.

References:
DEVELOPMENT OF A NEW FACILITY FOR DATING OLD GROUNDWATERS BY USING 81KR

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INTRODUCTION

Groundwater age data are critical for modeling hydrogeologic systems for deep geological nuclear waste repository studies. New developments are in progress for groundwater dating based on 81Kr measurement. This radioactive isotope is only produced by nuclear reactions induced by cosmic rays in the earth’s atmosphere. With a half-life of 229 ky, this isotope is considered as an ideal tracer for dating ancient groundwaters.

In the earth’s atmosphere, the abundance ratio 81Kr/Kr is constant for at least the last million years and is equal to (5.2 ± 0.4) 10^{-13} (Collon et al, 2004). Thermodynamic laws control the dissolution of atmospheric krypton in water at the soil – atmosphere interface. Once the underground water is isolated from the atmospheric reservoir, the abundance ratio 81Kr/Kr starts to decrease due to disintegration of 81Kr. Then the measured 81Kr/Kr ratio gives a direct determination of the mean age of the water on a time scale from 50,000 years to about a million years. The measurement of 81Kr from a groundwater sample was first demonstrated using several isotopic enrichment steps followed by RIS-TOF technique [N. Thonnard et al., 1987; B.E. Lehmann et al., 1991]. Due to the very low abundance of 81Kr in groundwater – 1200 atoms/l in modern water – the dating generally requires large sample volumes. Collon et al., 2000 validated the 81Kr method by dating very old groundwater from the Great Artesian Basin in Australia using an AMS facility, after gas extraction from 16,000 liters of water. More recently, a laser-based atom trap method (Lu and Wendt, 2003; Sturchio, et al., 2004) was used to measure the age of groundwater from the Sahara using 2,000 liters of water per measurement.

A second radioactive isotope exists, 85Kr, with a half-life of 10.76 years. Krypton-85 is a fission product and 85Kr atoms are released from nuclear installations when spent fuel rods are reprocessed. It can be used for dating modern groundwaters or, like in our case, for tracing sample contamination of the investigated sample with atmospheric Kr.

EXPERIMENTAL CONCEPT

Since 2003, in a collaborative work with IRIM, CNAB is developing a set of four instruments or lines in order to measure 81Kr in groundwater using reasonable volume of water (20 l). Each instrument is dedicated to perform essential steps in the dating process and requires a complex technical development.

(1) Special water containers of 20 liters have been developed for high quality sampling and sample storage.

(2) A vacuum line is designed for gas extraction from 20 l of water, Kr separation and purification. It includes a 50 l vaporization tank, 4 gas chromatography columns containing 5A molecular sieves and several getters in order to purify Kr gas.

(3) A first mass spectrometer is dedicated to the 81Kr and 85Kr enrichment process is building. It consists in a modified HR-ICP-MS in order to perform high ionization efficiency, high ion transmission and high mass resolution with large Kr samples. Selected ions are implanted in a thin Al layer on sapphire targets.
(4) A second mass spectrometer has been also built. It includes a Bauer-Signer source, a 60’’ and 12.5 cm radius magnetic sector. It is designed to perform a second enrichment step with low Kr gas pressure implanted during the first enrichment step and released by vaporizing Al layer with a laser beam.

(5) A new facility based on resonance ionization spectroscopy – time of flight mass spectrometry (RIS-TOF) is now operating. It is capable to perform isotopic abundance measurements from samples containing only a few thousands atoms of Kr. Krypton ionization is done by resonant 2 + 1 UV photons at 216 nm. The mass spectrometer also includes an atom buncher device operating at 25K to enhanced ionization efficiency.

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