Oral Session 15A

Pore-water chemistry: acquisition and modelling
Chair: Andreas Gautschi - Emmanuel Jacquot
GAS EQUILIBRATION AND PORE WATER SAMPLING EXPERIMENT 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 feasibility 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 deal with the carbonate system and the redox state of the water. Consecutively, the PC-C experiment was initiated in 2003 to reduce these uncertainties using: i) a gas equilibration, and, ii) isobar water sampling.

EXPERIMENTAL CONCEPT
The Porewater Chemistry-C (PC-C) experiment set-up (see Figure 1) is composed of, i) a borehole equipment consisting of packers isolating a test chamber in the investigated rock zone, ii) surface equipment located in the gallery including two modules: a gas circulation unit and a water sampling system, iii) various lines for gas and water movements between the surface equipment and the packed off borehole interval. This innovative concept, i) enables an in-situ equilibration between an injected inert gas (argon) and the rock: the changes in composition of the gas, circulating in a closed circuit in contact with the clay, provide information on dissolved gases in the interstitial water, particularly on the dissolved carbon dioxide, ii) enables to sample water seeping from the borehole without altering its pressure and without contact of this water with other gases than these with which it is in equilibrium in the borehole chamber. A piston pump yielding very low flow rates is used. The formation water samples are taken under isobar conditions sheltered from the atmosphere. This sampling procedure avoids gas loss or exchange between the sampled water and the gallery atmosphere.

FIRST RESULTS
Since the beginning of the experiment (February 2003), an infrared spectrometer included in a bypass of the closed gas circuit allowed for on-line analysis of various components of the circulated gas. Complete gas analysis was carried out using the sampling vials of the gas circuit. The circuit gas composition reflects
exchanges between the argon initially introduced and the gases present in the rock. Consequently, the first objective of the experiment – to acquire knowledge on these gases - is already reached.

After 6 months, a water flow rate into the test chamber close to 3 mL per day is observed allowing for sampling and analysing the water.

This experiment follows the experimental concept developed for the PAC-P experiment to be implemented early 2005 in the Meuse/Haute Marne underground laboratory.

Figure 1: Porewater Chemistry-C (PC-C) experimental setup.

Reference:
DETERMINATION OF POREWATER COMPOSITION AND SPECIES-SPECIFIC TRANSPORT PARAMETERS BY A NEW METHOD USING LABORATORY CORE INFILTRATION: EXAMPLES FROM OPALINUS CLAY (MONT TERRI) AND CALLOVO-OXFORDIAN CLAY (BURE)

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INTRODUCTION
The quantification of transport and water-rock interaction and its rates in very low permeability rocks such as claystone are used to interpret gradients across formations in isotopic, chemical, and gas composition that have evolved over thousands to millions of years. This quantitative understanding allows evaluation of a clay formation as a barrier for deep disposal of radioactive waste. Difficulties in sampling porewater from claystone are due to very low hydraulic conductivities (~10⁻¹³ m/s), the presence of reactive components such as pyrite, carbonate, organics, and in-gassing or degassing of CO₂ during sampling. The aim of our new method is to minimize artifacts and to obtain both chemical and transport information from a single experiment.

EXPERIMENTAL METHOD
The method is forcing displacement of the original porewater contained in a drill core sample by advection of a traced artificial porewater. The feasibility of the method hinges on the well connected porosity and homogeneity of most claystones that result in approximate one dimensional advective-dispersive flow when applying a large hydraulic gradient across the length of a cylindrical sample. Also, the original moisture content has to be physically and chemically preserved during drilling, recovery of the core and sample preparation. The tracers in the infiltrating fluid allow for quantification of mixing with the in-situ porewater, and to observe tracer breakthrough behavior when monitoring the infiltration experiment over a sufficiently long time period. The induced fluid fluxes are low (0.1-0.5 ml/day) and the dispersion is large and dominated by diffusion. Our experience indicates that 10-30 ml of little disturbed original porewater can be extracted from claystones with 10-20 % porosity (4-8 wt % water content). Orientation of forced flow may either be parallel or perpendicular to bedding.

The method is called “porewater extraction by advective displacement” (weeks to few months), and “core infiltration experiment” when monitoring over extended time periods (months to few years) to obtain information on species-specific transport properties. The apparatus is unique and versatile and can be used for porewater extraction as well as transport experiments with focus on chemical rock-water interaction and/or tracer transport and retardation. The strength of the method is to transfer approximate in-situ conditions to the laboratory and minimize unwanted effects due to stress relief, redox processes (pyrite, organics), and reactions within the carbonate system. A single carefully prepared long-term experiment can thus yield a comprehensive data set to constrain rock-water interaction processes as well as transport and retardation properties.
RESULTS FOR OPALINUS CLAY, MONT TERRI
A claystone core of 120 mm length and 79 mm diameter was sealed with Teflon and rubber (outer layer), and fitted with porous Teflon discs at the top and base. The sample was subjected to 65-75 bar confining pressure, and a 40-60 bar infiltration pressure. Temperature was kept at 15°C corresponding to in-situ conditions at Mont Terri. The core was drilled with nitrogen at the Rock Laboratory (borehole BPC-A1, from 10 m depth) and prepared and mounted on-site to minimize drying and exposure to atmosphere. An artificial porewater of a salinity similar to that in-situ and traced with bromide and deuterium was used. The experiment started on March 27, 2002, and is still ongoing as of October 2004.

Initial porewater composition
The first three sample collected are interpreted to be the best representatives of the in-situ porewater extracted by this method (Mäder et al. 2004). The mixing indicators Br and δ2H show progressive admixing contributions from the artificial porewater of no more than 1-3 %. The samples were interpreted using PHREEQC and the Nagra-PSI thermodynamic database to model saturation constraints and processes that may have affected the carbonate system. This interpretation would imply partial pressures of CO₂ of 10⁻².6-10⁻².9 bar at the time of extraction. in-situ pH cannot be rigorously reconstructed. The in-line measured pH of 7.5±0.2 is plausible, and in combination with the associated p(CO₂) is in agreement with multiple lines of evidence for this stratigraphic location (Pearson et al. 2003).

Species-specific transport properties
Tracer breakthrough monitored for Br and deuterium is distinctly species-specific. Fast transport of Br is explained by anion exclusion that reduces transport porosity almost by a factor of 2 relative to deuterium. The physical porosity is close to the water-loss porosity of 16.5% and coincides approximately with the transport porosity for water. Transport during the experiment was approximately 1/3 diffusive and 2/3 advective.

RESULTS FOR CALLOVO-OXFORDIAN CLAY FROM THE BURE SITE
A very similar experiment was performed on a drill core sample from Bure. Analytical work is in progress and results will be presented at the meeting.

References:

ACIDO-BASIC PROCESSES AT THE CLAY-ELECTROLYTE INTERFACE

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Acido-basic sites are located at the broken-bond edges of clay particles, and take the generic form of terminal or bridging hydroxo-groups linked to the metal atoms of the lattice. According to the pH of the medium, these sites undergo protonation/deprotonation and thus confer the particle edges an amphoteric behaviour. In the case of montmorillonite, their abundance is about 10 % of the total charge (i.e. 0.1 meq/g). The structural charge resulting from isomorphic substitutions in the crystal lattice by metals with lower valency (Si⁴⁺/Al⁴⁺, Al⁴⁺/Mg⁡²⁺ ...), represents about 90 % of the total charge (i.e. 1 meq/g), and confers a cation exchange capacity (CEC) to the clay. Dissociable acido-basic sites are generally described as strong energy sites, able to complex metal ions at trace concentration, whereas exchange on the CEC is negligible in such conditions. Therefore, despite their low relative abundance, acido-basic sites of montmorillonite deserve extended study in order to predict the sorption of radionuclides escaping from repositories onto engineered bentonite barriers.

The works devoted to that topic in the past decade have shown that the quantification of the variable charge of 2:1 clays by potentiometric titration is biased by dissolution and ion exchange processes accompanying the targeted dissociation process, and that the choice of proper experimental conditions is crucial. There is therefore a need for a systematic study of the impact of the conditions for preparation, storage, and analysis on the charge/pH curves on montmorillonite. The aim of the present work was to obtain univocal charge/pH curves, in order to allow for determination of dissociation and complexation constants.

Montmorillonite was extracted from the MX80 bentonite, and made homoionic to Na. Potentiometric acid-base titration was used to quantify the surface charge according to the pH and to the electrolyte concentration in different experimental conditions. The examined experimental parameters were: dry vs. wet storage of the purified material, continuous vs. batch titration, cation exchange, and quantification of the dissolved and readsorbed species.

Batch titrations were conducted over 1 to 7 day. Dissolution-readsorption was quantified by analysis of the supernatants at different pH, and desorption experiments, which allowed for quantitative corrections of the titration curves. The continuous titration procedure, which is less subjected to dissolution, was used to quantify the impact of the analytical conditions on the charge/pH curves. As an example, titration curves of dried samples are shifted towards significantly higher pH than wet stored samples. Conversely, wet storage allows solubility equilibria to be established in the suspensions, which alters the titration curves according to the duration of storage (up to 12 months). A standard protocol was thus defined in order to minimize artifacts:

Extraction without strong acidification -> homoionization and washing by centrifugation -> wet storage -> continuous titration and batch titration with analysis of the equilibrium solution.

The net charge curves of MX80 montmorillonite at different ionic strengths, corrected for secondary reactions, do not show a common intersection point which would identify a Point of Zero Charge. Instead, the curves are roughly parallel, and the points of zero net proton consumption (PZNPC) are shifted towards acidic pH according to the ionic strength of the electrolyte. Therefore, the classical surface complexation
models fail to calculate the dissociation constants. Recent theoretical papers introduce a direct or indirect effect of the structural charge on the dissociation equilibria. Calculations from published data show that the shift in PZNPC is proportional to the structural charge for montmorillonites and illites, which confirms the direct contribution of the lattice substitutions to the edge charge.

Preparation of a reduced-charge MX80 montmorillonite by Li-exchange and thermal treatment (Hofmann-Klemen effect) allowed for experimental investigation of the respective contribution of the structural and dissociable charges. The electrokinetic potential (ζ potential) of the treated and untreated samples was measured according to the pH and ionic strength by microelectrophoresis. The electrokinetic behaviour of the untreated montmorillonite is dominated by the structural charge and shows a constant negative potential (around -30 mV) for pH 3 to 10 at ionic strengths from 0.001 to 0.1 mol/l. The reduced-charge montmorillonite shows a pH and ionic strength dependence of the ζ potential, typical for a metal oxide, with an isoelectric point at pH close to 2. This result suggests that the PZC of the montmorillonite edges is probably located at acidic pH, rather than at neutral pH as commonly stated. This hypothesis is supported by the behaviour of the titration curves of the reduced-charge montmorillonite, which are close to the electrokinetic curves.

Calculation of the dissociation constants has been the matter of many attempts in the literature. The models used to that purpose include simple 1site-2pK models, structural-formal charge models (MUSIC) involving up to 27 different surface topographies, or combined Donnan-Double layer models. A simplified representation of the dissociable surface sites of montmorillonite is proposed in the present work. It originates from the observation of two energetic domains on the derivative titration curves, and is based on the two most represented surface groups:

- an OH group linked to the silicium tetrahedra on the outer molecular sheets of the clay platelet, and characterised by unit charge and a single pK:
  \[ \text{SiO}^- + \text{H}^+ = \text{Si-OH}^0 \text{ with } 7<\text{Log}K<10 \]
- an OH group linked to the octahedra of the central sheet, and characterised by a partial charge:
  \[ \text{Me-OH}^{1/2} + \text{H}^+ = \text{Me-OH}_2^{1/2} \text{ with Log}K<5 \text{ (Me = Al > AlSi > Mg > Fe).} \]

However, no common intersection point between titration curves at different ionic strengths was observed in any case, which prevented the determination of the point of zero charge (PZC) according to the classical oxide behavior. Nonetheless, the PZC was estimated lower than pH 5 from the evolution of the initial pH with ionic strength. This result agrees with the electrophoretic behaviour of the Li-montmorillonite. According to these experimental evidences, a simplified model of the acido-basic properties of montmorillonite was proposed, based on two reactive surface sites: a tetrahedral site SiO$^- + \text{H}^+ = \text{Si-OH}^0$ with $7<\text{Log}K<10$ and a octahedral site Me-OH$^{1/2} + \text{H}^+ = \text{Me-OH}_2^{1/2}$ with LogK<5 (Me = Al, AlSi, Mg, Fe, with predominantly Al).
STABLE ISOTOPE COMPOSITION OF POREWATER IN CALLOVIAN-OXFORDIAN ARGILLITES (BURE): INSIGHT FROM CO₂ AND H₂O-VAPOR RELEASED BY CORES

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As part of the joint research programme of BRGM and Andra (Girard et al., 2004), and in relation with the objectives of Andra HAVL-Argile project, work is conducted at BRGM in order to determine the stable isotopic composition (δ¹⁸O-δD) of present-day porewater in Callovo-Oxfordian argillites at Bure, eastern Paris Basin. The ultimate goal of the work is two fold: 1) to gain insight into the nature of porewater and water-rock interactions in the clay formation, and 2) to constrain the mechanism of water and/or mass transfer between argillites and overlying/underlying limestones.

In order to overcome difficulties associated with techniques based on physical or chemical extraction of porewater from clay-rich rocks prior to isotope analysis (see review by Sacchi et al., 2000), a novel and original approach was developed that prevents any significant physical/chemical disturbance to the samples investigated (Girard et al., in press). Application of this new method to the Callovo-Oxfordian argillites from Bure provided encouraging and informative results regarding the origin of porewater and dissolved carbon.

METHODOLOGY

Stainless-steel outgassing cells were specifically designed to collect gases naturally released by core samples under controlled conditions. During drilling operations, a ≈45 cm long segment of argillite core is placed in an outgassing cell within 2-3 hours of coring, following removal of its outer rim by dry sawing. The cell is then sealed with epoxy, flushed with dry N₂ (or He), and evacuated to a pressure in the range of 70-250 mbar. At the laboratory, the outgassing cell is stored at constant temperature (25°C) and gases naturally released by the core are monitored by Gas Chromatography. The liberated gas consists mainly of CO₂ (up to 30%), with traces of alkanes (<1%), and H₂O vapor. Typically, partial pressure of CO₂ in the cell increases gradually and reaches a reproducible plateau within 1-2 months, representing equilibrium with porewater dissolved CO₂.

CO₂-gas and H₂O-vapor released by argillite cores are collected by connecting the outgassing cell to a vacuum line and applying conventional cryogenic separation techniques. CO₂ is further purified from traces of organic volatiles over active charcoals. The δ¹⁸O CO₂ and δ¹³C CO₂ values of purified CO₂ are directly measured by conventional IRMS. The δ¹⁸O H₂O-vap and δD H₂O-vap of recovered water vapor can be determined by water-gas equilibration techniques. Measured δ¹⁸O CO₂ and δ¹³C CO₂ values, combined with appropriate fractionation equations, are used to calculate the oxygen isotope composition of porewater (δ¹⁸O porewater) and the carbon isotope composition of dissolved bicarbonate (δ¹³C diss.HCO₃).

APPLICATION TO CALLOVO-OXFORDIAN ARGILLITES

The methodology outlined above is currently applied to a set of 12 cores of Callovo-Oxfordian argillites from 5 wells. At the present time, the isotopic composition of outgassed CO₂ is available for all samples, while isotope determinations for H₂O vapor are still on-going. The isotopic composition of carbonate minerals (calcite, dolomite) present in the samples investigated was also determined.
CO₂ evolved from cores exhibits δ¹³C CO₂ of -10 to -6 ‰ PDB and δ¹⁸O CO₂ of +30 to +36 ‰ SMOW. Such an isotopic signature is not compatible with an atmospheric, crustal or bacterial origin of CO₂, and is best explained as reflecting isotopic equilibrium with dissolved bicarbonates and porewater. Calculated δ¹³C diss.HCO₃ (-2 to +3 ‰ PDB) is comparable to values expected for HCO₃ in isotopic equilibrium with calcite presently occurring in the samples (δ¹³C calcite = 0 to +3 ‰ PDB), and therefore reflects the primarily inorganic marine source of dissolved carbon. Calculated δ¹⁸O porewater values are markedly negative (-10 to -6 ‰ SMOW), indicating a meteoric nature of present porewater. They are comparable to δ¹⁸O values reported for formation waters in the overlying (Oxfordian) and underlying (Dogger) limestones, which range from -9 to -5 ‰ SMOW. In addition, and in spite of a significant uncertainty (±1 ‰) associated to them, δ¹⁸O porewater values derived from outgassed CO₂ exhibit an asymmetrical bell-type shaped depth trend within the clay formation. This suggests that argillite porewater may have acquired its ¹⁸O isotope composition following a diffusion mechanism, although the lowest δ¹⁸O porewater values of ca. -10 ‰ encountered in the lower-most part of the clay formation remain difficult to explain at this time.

Preliminary data gathered for 2 samples from well EST205 indicate that δ¹⁸O porewater values derived from measurement of δ¹⁸O H₂O-vapor are consistent, within analytical uncertainty, with those derived from outgassed CO₂. If this confirms for other samples, it will further validate the newly-developed methodology put to work in this study and will also permit to constrain the hydrogen isotope composition of porewater from H₂O-vapor data (work underway).

The results reported above have important implications for the reconstruction and geochemical modelling of water-rock interactions in the Callovo-Oxfordian argillites. First, the data indicate that dissolved bicarbonate and CO₂, hence pH, are controlled by mineral equilibria, with no significant influence from organic matter present in the samples (Gaucher et al., this volume). Second, the distinct meteoric isotope signature for porewater throughout the Callovo-Oxfordian argillites and the lack of evidence for any residual seawater imply that significant exchange has occurred with overlying/underlying aquifers, most likely via diffusion.

References:
