

TECHNICAL REPORT 97-07

Derivation of In Situ Opalinus Clay Porewater Compositions from Experimental and Geochemical Modelling Studies

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

PREFACE

The Laboratory for Waste Management at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Co-operative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

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ABSTRACT

Many countries are considering argillaceous sedimentary rocks as potential formations for the disposal of high level radioactive waste. One of the main attractions of such formations from a waste management viewpoint are their generally low groundwater flow rates. However, porewater chemistry constitutes an important basic data set for performance assessment studies and the low transmissivities often mean that it is very difficult, or even impossible, to obtain good in situ water samples. This report describes procedures based on physico-chemical characterisation of whole rock samples and geochemical modelling which were developed as an additional tool for determining porewater compositions in low porosity/permeability clay rich systems. The methodology was applied to core samples of Opalinus clay within the framework of an international investigation being carried out at Mt. Terri, Canton Jura, Switzerland. The calculated porewater compositions are described and discussed in relation to experimental data from the analyses of borehole seepage water and water samples obtained from squeezing tests. Because the latter two waters were clearly out of equilibrium, only a comparison based on general aqueous features was attempted. In all three cases the groundwaters were high ionic strength Na-Cl types. The experimentally determined pH values were in the range 7.5 - 8 whereas for the modelled porewater a value near 6 was calculated. This discrepancy was explained by postulating that the sampled waters lost dissolved CO₂ through out-gassing.

ZUSAMMENFASSUNG

In vielen Ländern werden tonige Sedimente als potentielle Gesteinsformationen für die Lagerung von hochradioaktivem Abfall untersucht. Unter dem Gesichtspunkt der Endlagerung liegt ein wesentlicher Vorteil dieser Gesteinsformationen in den geringen Durchlässigkeiten. Aufgrund der geringen Wasserflüssen ist es oft schwierig, wenn nicht gar unmöglich, Wasserproben in ausreichender Menge zu erhalten. Die chemischen Daten des Porenwassers sind jedoch nötig und stellen eine wichtige Grundlage für sicherheitsanalytische Studien dar. Im vorliegenden Bericht wird neben physikalisch-chemischen Charakterisierungsmethoden für Gesteinsproben im Gesamten auch geochemische Modellierung beschrieben. Diese ergänzt die Untersuchungen zur Zusammensetzung des Porenwassers in tonreichen Sedimenten mit geringer Porosität und Permeabilität. Im Rahmen einer internationalen Studie am Mt. Terri im schweizerischen Kanton Jura konnte diese Methode auf Kernproben des Opalinustons angewendet werden. Ausgehend von der berechneten chemischen Zusammensetzung des Porenwassers werden die Ergebnisse mit denjenigen aus Bohrloch-Sickerwasseranalysen und aus Auspressversuchen (squeezing) verglichen. Weil die beiden letzteren Wässer sich eindeutig nicht in einem chemischen Gleichgewichtszustand befinden, wird hier versuchsweise nur ein Vergleich der Hauptmerkmale angestellt. Alle drei Fälle sind dem Na-Cl Typ hoher Ionenstärke zuzuordnen. Die experimentell gemessenen pH Werte befanden sich in einem Bereich zwischen 7.5 und 8. Im Gegensatz dazu wurde für das modellierte Porenwasser ein pH Wert von nahezu 6 berechnet. Dieser scheinbare Widerspruch lässt sich aber mit Hypothese erklären, dass die Wasserproben infolge Ausgasung gelöstes CO₂ verloren hatten.

RESUME

Dans beaucoup de pays, les formations sédimentaires argileuses sont étudiées comme roches d'accueil potentielles pour les déchets radioactifs de haute activité. Dans le cadre des études de stockage, l'un des intérêts majeurs de ces formations réside dans leur faible transmissivité. Cependant, la composition des eaux interstitielles représente une donnée de base essentielle pour les études de démonstration de sûreté. Or, la détermination de la chimie des eaux dans de telles formations est souvent difficile, voire impossible, parce que les écoulements d'eaux y sont si faibles qu'il n'est pas possible d'obtenir des échantillons d'eaux non-perturbées. Ce rapport décrit une méthode permettant de déterminer la composition des eaux interstitielles dans des systèmes argileux de faible perméabilité. Cette méthode s'appuie sur une caractérisation physico-chimique des échantillons de roche dans leur ensemble, combinée à une modélisation géochimique. La méthodologie a été appliquée à des échantillons d'argile de la formation Opalinus obtenus à partir de forages dans le cadre d'une étude internationale effectuée au Mt. Terri (Canton du Jura, Suisse). Les compositions des eaux interstitielles calculées par cette méthode sont décrites et confrontées aux données expérimentales issues des eaux de forage ou des expériences d'extraction d'eau sous pression ("squeezing"). Cette confrontation s'est cependant limitée aux caractéristiques générales de ces eaux car les eaux naturelles récoltées expérimentalement (par forage ou squeezing) sont clairement hors d'équilibre. Dans les trois cas, il s'agit d'eaux salines de type Na-Cl ayant une force ionique importante. Mais les valeurs de pH mesurées varient entre 7.5 et 8 alors que celui de l'eau interstitielle simulée se situe aux alentours de 6. Ce décalage est interprété comme le signe d'un dégazage partiel du CO₂ dissous dans l'eau.

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1 INTRODUCTION

The argillaceous Opalinus clay (OPA) sediment is being considered by Nagra as a potential host rock formation for the disposal of high level radioactive waste. An assessment of the suitability of such a rock type is underway. As part of this work numerous types of investigations are being carried out at, and on samples from, a reconnaissance gallery associated with the Mt. Terri motor way tunnel (Canton Jura) which passes, for part of its length, through the OPA formation (Mt. TERRI PROJECT 1996).

The groundwater chemistry in any host rock formation constitutes an important basic data set in safety analysis studies. Samples of OPA for laboratory investigations were selected from cores drilled up to 20 m into the wall rock of the Mt. Terri reconnaissance tunnel. Special precautions were taken designed to minimise contact with air, see Chapter 2. Adjacent parts of cores were sent to the Paul Scherrer Institut (PSI) and the British Geological Survey (BGS), Keyworth, UK. The aim was that both research institutes should apply different techniques to determine the OPA porewater chemistry and compare the results. A squeezing technique was used by BGS (CAVE et al. 1996) and a procedure based on physico-chemical characterisation and geochemical modelling at PSI (BAEYENS & BRADBURY 1991,1994).

The methodology for the latter approach had been developed previously for determining porewater chemistries in very low porosity/permeability clay-rich systems such as exist in parts of the Valanginian and Palfris marl formations and for which in situ collection of water samples or squeezing techniques were practically impossible. Because of these very factors, an independent verification of the derived porewater chemistries was not possible for the marl system. The OPA core samples, on the other hand, presented a potential opportunity for a verification exercise since this argillaceous rock has porosities in the region of 10 vol.% making them amenable to squeezing. This was an additional incentive for performing this work as well as defining a porewater chemistry.

Fortuitously, before the experimental work began, very small volumes of water, which were nevertheless sufficient for chemical analyses, were obtained from

borehole BWS-A1. As a result, a core sample from this borehole was chosen for the laboratory investigations.

One of the major uncertainties in the water chemistries in very tight formations is the pH (P_{CO_2}). There were some indications from previous experiences in applying the physico-chemical characterisation and geochemical modelling methodology to sedimentary rocks that a good estimate of the in situ pH could be made if the water content (porosity) of the sediment was known (BAEYENS & BRADBURY 1994). This possibility will be specifically addressed here.

2 MATERIALS AND METHODS

2.1 Mineralogy

The material used in these experiments was taken from core obtained from a borehole dry drilled at Mt. Terri in February 1996. The core sample designation was BWS-A1 C12, 13.8 - 14.0 m.

Special precautions were taken to ensure that the core was as pristine as possible and that the contact time with air was minimised (~2 hours). Only sections of cores taken from well beyond the excavation disturbed zone (MÖRI & ADLER 1996) were selected. The surfaces of the chosen parts of the core were wiped clean, placed in aluminium coated plastic bags which were thoroughly flushed with N₂ before evacuating and sealing. Each sealed sample was placed in another plastic bag which was again flushed with N₂, evacuated and sealed. Finally, the packages were loaded into steel cylinders back filled with N₂ for transport to PSI where they were immediately transferred into inert gas glove boxes.

The mineralogical composition of the sample obtained from X-ray diffraction (XRD) data and coulomat measurements is given in Table 1.

The dominant clay minerals in this OPA sample are the 2:1 type illite and illite/smectite mixed layer and the 1:1 type kaolinite. Both types of clays are present in approximately equal proportions.

The best estimate available for the porosity of the samples used in this work is 10 - 12 vol. % (MAZUREK 1996, pers. comm.) and a bulk rock density of 2500 kg m⁻³ was taken from BLÄSI et al. (1991).

2.2 Analytical Methods

Aqueous concentrations of the elements Na, K, Mg, Ca, Sr, Ba, Al, Fe, Mn, Si, S and Ni were determined by plasma-emission spectroscopy (Applied Research Laboratory ARL 3410D ICP-AES).

Table 1: Mineralogical composition of Opalinus clay from Mt. Terri, sample BWS-A1 C12, 13.8 - 14.0 m (MAZUREK 1996, pers. comm.)

Mineral	Weight %
Calcite	11
Dolomite/ankerite	<2
Siderite	4
Quartz	14
K-feldspar	2
Albite	2
Pyrite	1.7
<u>Sheet silicates</u>	
Illite	16-22
Illite/smectite mixed layers	6-12
Chlorite	5-9
Kaolinite	26-32

The anions NO_2^- , NO_3^- , PO_4^{3-} , SO_3^{2-} , Br^- , CH_3COO^- , HCOO^- , F^- , Cl^- and SO_4^{2-} were analysed using a Dionex ion chromatograph. Alkalinity measurements were made on a Methrohm Titroprocessor 660. Inorganic carbon measurements were carried out on the Dohrman Carbon Analyser.

It is estimated that the total analytical errors are less than $\pm 10\%$ for the major ions in all of the above measurements.

pH measurements were taken on a WTW Microprocessor 535 pH meter using an Orion 8103 Ross™ combination pH electrode.

Radiochemical assays of ^{63}Ni (supplied by Amersham, UK) were carried out on a Canberra Packard Tri-Carb 2250 CA liquid scintillation analyser.

The O_2 and CO_2 contents in the atmosphere controlled glove boxes were measured on line with gas analysers supplied by Teledyne and Servomex, respectively and were generally below 5 ppm.

3 BRIEF OVERVIEW OF THE METHOD

A physico-chemical characterisation procedure for determining porewater chemistries in clay rich rocks has been developed and applied to low porosity marl samples (BAEYENS & BRADBURY 1991, 1994). The principle lying behind the method is that the cation occupancies on the clay minerals act as a "fingerprint" for the last solution composition with which they were in equilibrium. If the cation occupancies on undisturbed argillaceous rock samples can be determined, then the way is open to calculate the equilibrium porewater composition.

Basically, two types of ion extraction experiments are performed in inert atmosphere glove boxes in order to avoid any complications due to oxidation effects. The first consists of an aqueous extraction, in which crushed rock samples ($\leq 63 \mu\text{m}$) are contacted with de-ionised water at a series of high solid to liquid (S:L) ratios and allowed to equilibrate. After phase separation, the supernatant solutions are analysed. The aim of these experiments is to quantify the amounts of soluble salts present in the rock (particularly chlorides), and to determine which mineral phases contribute significantly to the composition of the aqueous phase.

A second series of extractions in nickelthylenediamine (Ni-en) solutions are carried out in an analogous manner. Ni-en is a powerful high selective complex which displaces all exchangeable cations from the clay minerals into solution (MAES & CREMERS 1986) and was chosen for the reasons given in BAEYENS & BRADBURY (1991). These experiments provide cation exchange capacity and cation occupancy data for the solid phase. In addition, selectivity coefficients for the major cations can be deduced with the aid of these data combined with the aqueous extraction results.

All the data required to calculate an in situ porewater composition are provided by these two sets of extraction experiments. The detailed procedures are described in the following chapters.

However, the porewater pH (formation P_{CO_2}), which is a very important parameter, is often poorly known in tight rocks with low porosities since direct measurements are impossible. Even in more porous rocks where small volumes

of groundwater may be obtainable, large uncertainties in pH may still exist if the formation P_{CO_2} is high and de-gassing occurs.

In previous work (BAEYENS & BRABDURY 1994), it was noted that if the cation occupancies, selectivity coefficients, the Cl^- concentration and the porosity are known, then for a calcite saturated porewater the pH (P_{CO_2}) can be derived. This "backdoor" approach to defining the system pH represents an exciting new possibility for obtaining an extremely important system parameter which is otherwise inaccessible.

4 AQUEOUS EXTRACTION TESTS

4.1 Aqueous Extraction Tests at Low S:L Ratios

The OPA core was first removed from its protective packaging in the glove box just prior to beginning the preparatory procedures.

The main aim of the first tests was to see whether the sample had suffered any oxidation. Parts of the outer surface of the 6.5 cm diameter core were removed to a depth of <2 mm with an electric drill and spade bit (~1 cm diameter) at slow revolutions. The material so obtained was immediately transferred to weighed polyethylene centrifuge tubes containing de-ionised water and closed. A second set of samples were obtained and treated in a similar manner except that they were taken from the centre of the core. These tests were carried out at 4 different S:L ratios. Both sets of samples were gently shaken in the glove box for 7 days before centrifuging (1 h at 95000*g* max.) and sampling the supernatant solution (again in the glove box) for chemical analyses of total S and SO_4^{2-} . (In addition Cl^- determinations were also carried out and these results are given in section 4.2, Table 4.)

The sulphate concentrations as measured by ion chromatography, and total elemental sulphur determined by ICP-AES, are summarised in Table 2. In general for each S:L ratio the correspondence between sulphate and total S data taken from the inside and outside regions of the OPA borecore is good. This implies that no significant oxidation of the pyrite in the core took place after sampling. Therefore it was concluded that these measurements represent the inventory of sulphate in the OPA and have to be taken into consideration in the calculations of the porewater composition. The effect of S:L ratio on the extraction results are discussed further in section 4.2.

Table 2: Comparison of SO_4^{2-} and S measurements on samples taken from the surface and from the centre of the Opalinus clay bore core (BWS-A1 C12, 13.8 - 14.0 m) at different S:L ratios.

S:L Ratio (kg L ⁻¹)	Sample location	SO_4^{2-} (mmol L ⁻¹)	S (mmol L ⁻¹)
0.030	Surface	0.05	nm*
0.027	Centre	0.06	0.08
0.059	Surface	0.11	0.13
0.058	Centre	0.09	0.09
0.084	Surface	0.15	0.15
0.084	Centre	0.20	0.16
0.113	Surface	0.20	0.17
0.115	Centre	0.25	0.20

* no measurement

4.2 Aqueous Extraction Tests at High S:L Ratios

Aqueous extractions were carried out using crushed whole rock samples ($\leq 63 \mu\text{m}$) obtained from the central 4 cm of the core at solid liquid ratios of 0.25, 0.5, 1 and 1.5 kg L⁻¹. The OPA/de-ionised water suspensions were agitated on an end-over-end shaker inside a glove box for either 7 or 28 days after which centrifugation and sampling followed in the manner previously described. The analytical results are summarised in Table 3. The charge balance of the aqueous extracts were generally better than $\pm 5\%$.

Also, Ba (<d.l.), Al ($\leq 5 \times 10^{-5}$ M), Fe ($\leq 10^{-5}$ M), and Mn ($\leq 5 \times 10^{-7}$ M) were analysed by ICP-AES and NO_2^- ($\leq 4 \times 10^{-5}$ M), NO_3^- ($\leq 4 \times 10^{-5}$ M), PO_4^{3-} (<d.l.), SO_3^{2-} (<d.l.), Br^- ($\leq 3 \times 10^{-5}$ M), CH_3COO^- ($\leq 6 \times 10^{-5}$ M) and HCOO^- ($\leq 4 \times 10^{-5}$ M) by ion chromatography. All of the above species were only below the detection limit (d.l.) or present at trace concentration levels given in brackets.

Table 3: Aqueous extraction data of the Opalinus clay bore core BWS-A1 C12, 13.8 - 14.0 m at high S:L ratios.

S:L Ratio (kg L ⁻¹)	0.25	0.25	0.5	0.5	1	1	1.5	1.5
Time (days)	7	28	7	28	7	28	7	28
pH	9.1	8.9	8.8	8.7	8.6	8.5	8.4	8.3
<u>Conc. (M)</u>								
Na	7.05E-3	7.59E-3	1.06E-2	1.18E-2	1.84E-2	1.92E-2	2.54E-2	2.68E-2
K	2.80E-4	2.20E-4	nm	3.40E-4	4.00E-4	4.30E-4	4.80E-4	5.90E-4
Mg	3.50E-5	3.50E-5	6.50E-5	7.00E-5	1.50E-4	1.70E-4	3.05E-4	2.80E-4
Ca	8.50E-5	7.00E-5	1.20E-4	1.15E-4	2.20E-4	2.55E-4	4.30E-4	3.75E-4
Sr	1.0 E-6	1.0 E-6	2.0 E-6	2.0 E-6	4.5 E-6	6.0 E-6	8.5 E-6	8.5 E-6
F ⁻	1.74E-4	1.64E-4	2.28E-4	2.06E-4	2.13E-4	2.09E-4	1.79E-4	1.75E-4
Cl ⁻	3.27E-3	2.91E-3	6.48E-3	5.44E-3	1.44E-2	1.31E-2	nm	1.85E-2
SO ₄ ²⁻	4.71E-4	5.00E-4	8.46E-4	9.27E-4	1.81E-3	1.85E-3	2.63E-3	2.54E-3
Alkalinity (Eq. L ⁻¹)	3.54E-3	3.84E-3	4.29E-3	4.90E-3	4.23E-3	4.88E-3	3.55E-3	4.33E-3
Σ Cations (Eq. L ⁻¹)	7.57E-3	8.02E-3	1.15E-2	1.25E-2	1.95E-2	2.05E-2	-	2.87E-2
Σ Anions (Eq. L ⁻¹)	7.93E-3	7.93E-3	1.27E-2	1.24E-2	2.24E-2	2.18E-2	-	2.80E-2
Si (M)	2.35E-4	1.98E-4	2.86E-4	2.68E-4	3.25E-4	4.64E-4	3.74E-4	2.93E-4
S (M)	4.87E-4	4.94E-4	1.05E-3	9.76E-4	1.73E-3	1.87E-3	2.68E-3	2.61E-3
Inorg. C (M)	3.45E-3	4.10E-3	4.31E-3	5.68E-3	4.25E-3	4.84E-3	4.01E-3	4.53E-3

nm: no measurement

Inorganic carbon was analysed by 2 different methods. Table 3 includes the results of the inorganic carbon analyses as measured by the Dohrman carbon analyser and the alkalinity measurements obtained from acid titrations. Good agreement was found between the two methods.

SO₄²⁻ and S were measured using the same techniques as described previously, and again good agreement between the two methods was found

(see Table 3) indicating that, within experimental error, all of the sulphur was present as sulphate. Also, no systematic increases in sulphate levels were observed as a function of time indicating that no oxidation of pyrite was occurring in the glove boxes.

There are however trends in the data presented in Table 3, particularly with respect to the pH and alkalinity measurements. For a given S:L ratio, the pH tends to decrease and alkalinity to increase with increasing equilibration time. Also, lower pH values are generally associated with higher S:L ratios. These observations have mainly to do with the dissolution of calcite/dolomite and the kinetics of their equilibration. This is illustrated in Figure 1, where the Ca to Mg activity ratio is plotted as a function of S:L ratio for the 7 and 28 day data. At equilibrium, the Ca:Mg activity ratio should be 1.35. This figure is discussed further in Chapter 8.

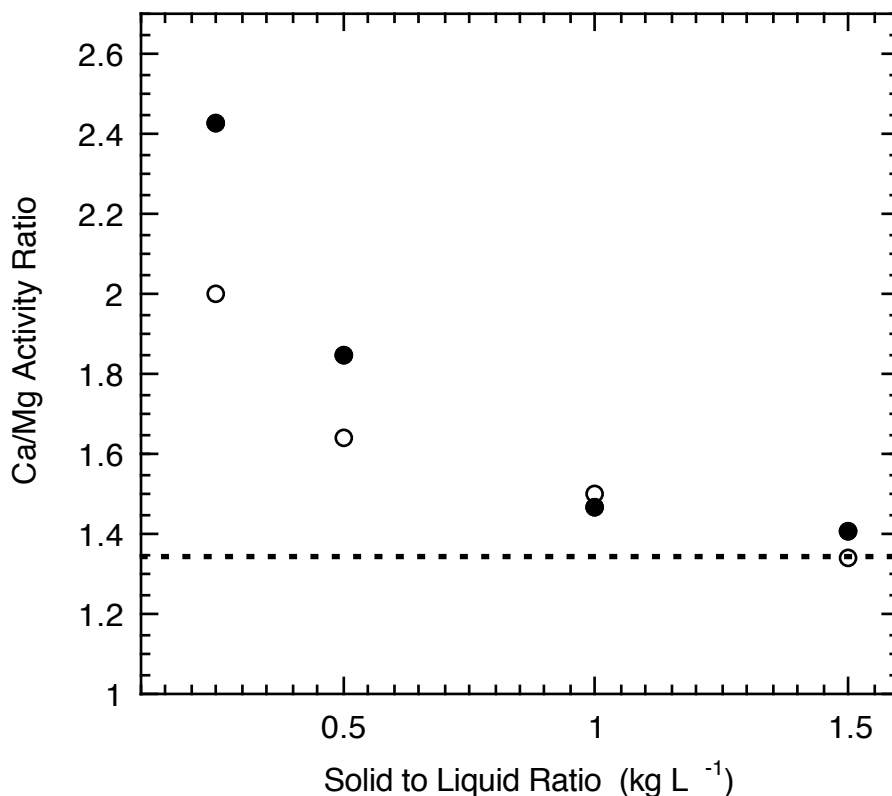


Figure 1: Ca/Mg activity ratios in the aqueous extracts at the different S:L ratios after 7 days (●) and 28 days (○) contact times. (The dotted line represents the aqueous Ca/Mg activity ratio for equilibrium between calcite and dolomite.)

Chloride Extraction Data

Since all chloride salts are highly soluble, the source of chloride in the aqueous extracts can only be the original porewater in the OPA. A summary of the Cl⁻ results from all aqueous extraction experiments is given in Table 4.

Figure 2 illustrates the expected 1:1 correspondence between Cl⁻ concentration and dilution at the different S:L ratios. The mean Cl⁻ content in the BWS-A1 C12, 13.8 - 14.0 m OPA sample from 15 individual measurements was 12.3 (± 1.6) mmol kg⁻¹.

Table 4: Summary of aqueous chloride extraction data.

S:L ratio (kg L ⁻¹)	Cl ⁻ in aqueous extracts (mmol L ⁻¹)	Cl ⁻ extracted from OPA (mmol kg ⁻¹)
0.027	0.38	14.2
0.030	0.34	11.3
0.059	0.63	10.6
0.058	0.60	10.3
0.084	0.90	10.7
0.084	1.28	15.3
0.113	1.18	10.4
0.115	1.52	13.2
0.25	3.27	13.1
0.25	2.91	11.6
0.50	6.48	13.0
0.50	5.44	10.8
1.0	14.4	14.4
1.0	13.1	13.1
1.5	18.5	12.3

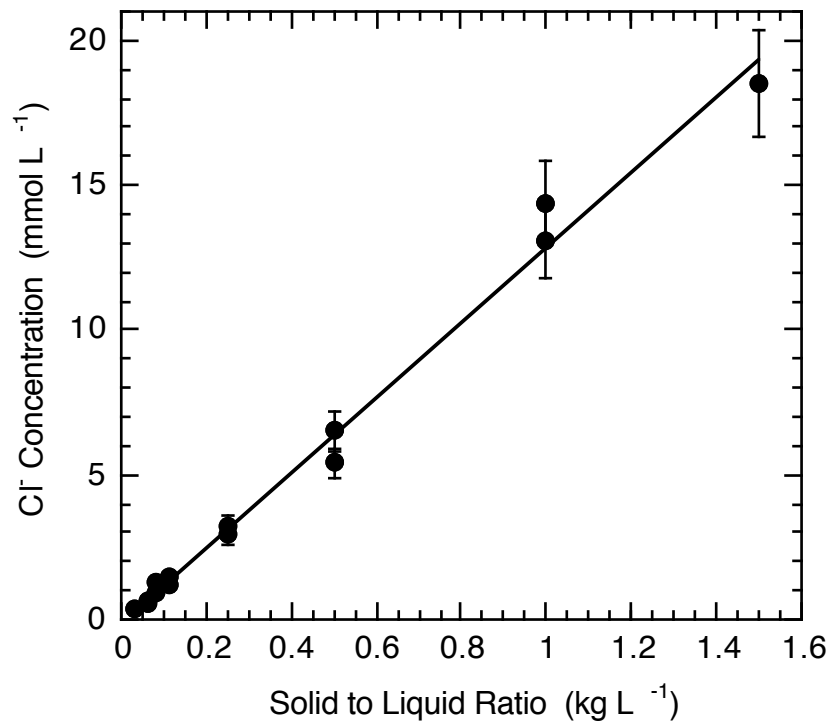


Figure 2: Chloride concentrations measured in the aqueous extracts as function of S:L ratio.

Sulphate Extraction Data

If the sulphate data given in Table 2 and the high S:L extraction results (Table 3) are combined (Table 5) and treated in a similar manner to chloride, it can readily be seen in Figure 3 that the SO_4^{2-} concentrations in the aqueous extracts are also linearly dependent on the S:L ratio i.e. dilution, and are consistent with a SO_4^{2-} content in the BWS-A1 C12, 13.8 - 14.0 m OPA sample of 1.85 ± 0.19 mmol kg⁻¹.

Although SO_4^{2-} behaves similarly to Cl^- , the source of sulphate is unlikely to be a highly soluble sulphate phase but rather a sparingly soluble mineral such as gypsum. The reason that the SO_4^{2-} concentration linearly increases with S:L ratio in Figure 3 is that the volumes of water present are able to dissolve all of the sulphate phase available in the OPA. (Aqueous speciation calculations indicated that gypsum was undersaturated in all the extraction tests.)

Table 5: Summary of aqueous sulphate extraction data.

S:L ratio (kg L ⁻¹)	SO ₄ ²⁻ in aqueous extracts (mmol L ⁻¹)	SO ₄ ²⁻ extracted from OPA (mmol kg ⁻¹)
0.027	0.055	2.04
0.030	0.052	1.74
0.059	0.106	1.80
0.058	0.092	1.58
0.084	0.144	1.71
0.084	0.195	2.32
0.113	0.196	1.74
0.115	0.243	2.12
0.25	0.47	1.88
0.25	0.50	2.00
0.50	0.85	1.69
0.50	0.93	1.85
1.0	1.81	1.81
1.0	1.85	1.85
1.5	2.63	1.76
1.5	2.54	1.70

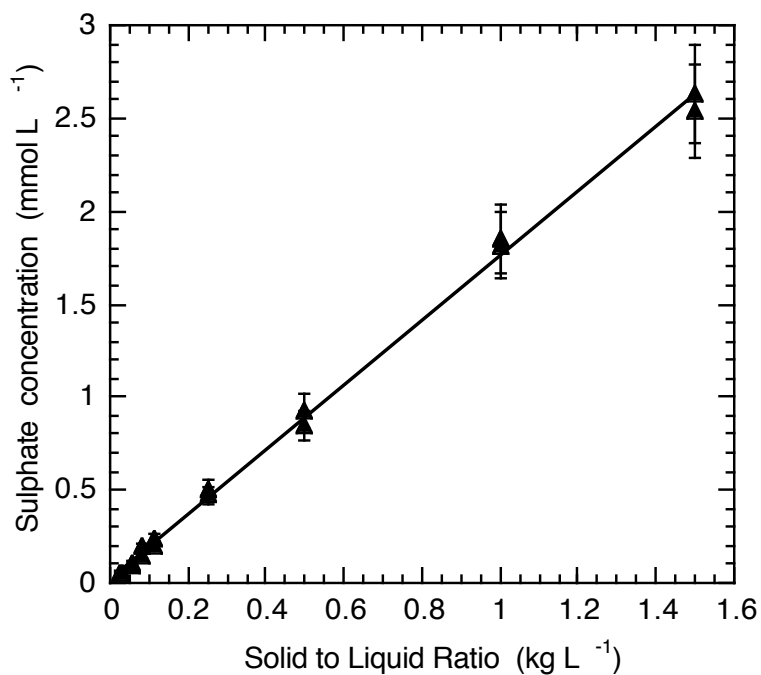


Figure 3: Sulphate concentrations measured in the aqueous extracts as function of S:L ratio.

5 NICKELETHYLENEDIAMINE EXTRACTION TESTS

5.1 Nickelethylenediamine Isotherm Determination

The reasons for choosing nickelethylenediamine (Ni-en) as the high selectivity complex in the extraction tests and the experimental methodology are described in BAEYENS & BRADBURY (1991, 1994), so only an outline of this technique will be given here. An important first step in using Ni-en with any sedimentary rock of unknown cation exchange capacity is to determine the sorption isotherm by measuring its uptake onto the solid as a function of concentration. The isotherm indicates the concentration of Ni-en above which all cations are completely displaced from the exchange sites i.e. the Ni-en cation exchange capacity. Also, in the extraction tests performed as a function of high S:L ratios, the optimum conditions are achieved when the added equivalents of Ni-en are approximately twice the exchange capacity; all cations are displaced and an ~50% reduction in the Ni-en concentration for ease of measurement.

The high selectivity complex was prepared by slowly adding ethylenediamine (en) to a $\text{Ni}(\text{NO}_3)_2$ solution to obtain a stock solution containing 0.01 M Ni and 0.03 M en. The pH of this solution was adjusted to a value of ~8 by using HNO_3 Titrisol™ solutions.

Solutions containing between 2×10^{-4} M and 3×10^{-2} M Ni-en were prepared from the stock solution and added to ~0.9 g lots of OPA, pre-weighed into polypropylene centrifuge tubes, to give an S:L ratio of 25 g L^{-1} . The tubes were closed, shaken end-over-end for 2 days, centrifuged and the supernatant solutions analysed for Ni. The experiments were repeated with ^{63}Ni labelled solutions which were radio assayed using a β liquid scintillation counter.

The Ni-en sorption isotherm for the OPA sample is presented in Figure 4. The uptake of Ni-en is very strong and reaches a plateau at $\sim 125.3 \pm 5.2 \text{ meq kg}^{-1}$ which is the Ni-en exchange capacity. The insert in Figure 4 corresponds to the four lowest Ni-en concentration data points given in the main figure and shows in more detail the highly non-linear sorption behaviour of this complex at low equilibrium concentrations. (Note that this is a linear-log plot.)

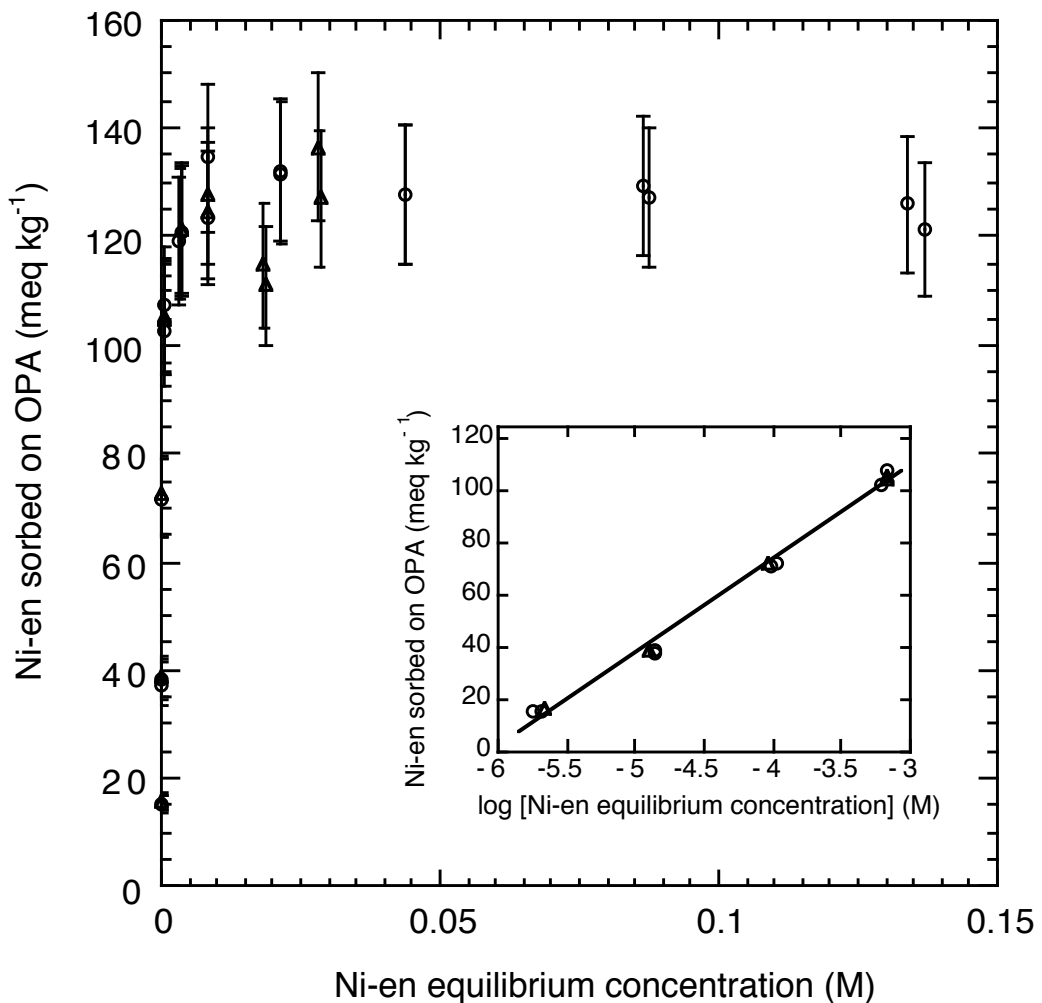


Figure 4: Ni-en sorption isotherm on Opalinus clay. Circles: Inactive Ni data, including Ni-en extract results. Triangles: ⁶³Ni data. (Estimated errors are ±10%.)

5.2 NিকেথিলেনডIAMINE Extracts at High S:L Ratios

For the high S:L ratio extraction tests a Ni-en stock solution was made as described in the previous section except that the concentrations were 0.2 M Ni(NO₃)₂ and 0.6 M ethylenediamine.

Extraction tests with the Ni-en solutions were carried out in duplicate at four different S:L ratios under the same experimental conditions as described in

section 4.2 for the aqueous extraction tests except that samples were only shaken for 7 days. The number of equivalents of Ni-en in each test was chosen to be about twice that of the exchange capacity of the mass of OPA used to ensure that all displacement reactions on the clay minerals went to completion. The cation concentrations measured in the Ni-en extraction solutions are expressed in meq kg⁻¹ in Table 6. With the exception of K (see section 7.1) there are no trends in the data with the S:L ratio and the individual cation measurements generally agree to better than 5%.

Table 6: Ni-en extraction data at high S:L ratios.

S:L ratio (kg L ⁻¹)	Na (meq kg ⁻¹)	K (meq kg ⁻¹)	Mg (meq kg ⁻¹)	Ca (meq kg ⁻¹)	Sr (meq kg ⁻¹)
0.25	66.8	8.8	15.8	28.5	1.0
	64.0	7.8	16.2	29.1	1.0
0.5	58.8	6.7	16.2	28.2	1.0
	58.6	6.8	15.5	28.7	1.0
1.0	57.8	5.8	15.6	30.4	1.0
	57.7	5.8	15.4	30.0	1.0
1.5	60.6	5.3	15.2	29.5	1.0
	59.1	5.4	14.7	28.3	1.0
mean (s. dev.)	60.4 (±3.3)	5.4* (±0.1)	15.6 (±0.5)	29.1 (±0.8)	1.0 -

* Only data taken for S:L = 1.5 kg L⁻¹, see section 7.1

When the Ni-en solution contacts the OPA, the cations on the clay mineral components are almost immediately displaced into solution (PLEYSIER et al. 1986). Such a process is much more rapid than solid phase dissolution reactions, see for example WOLLAST (1990); DREYBRODT et al. (1996). Consequently, the extent of mineral dissolution is reduced via the common ion effect. Thus at high S:L ratios the concentrations of cations displaced from the clay minerals dominate the solution compositions.

6 SATURATED PHASES

The mineralogical analysis indicates the presence of calcite, dolomite, siderite and quartz. Wherever the former two minerals occur in natural systems the groundwaters are almost invariably saturated with respect to them. Siderite, in the presence of calcite, will not contribute to the major ion composition since its solubility product is a factor of ~ 300 times less (PEARSON et al. 1992). Chalcedony is normally taken instead of quartz as being the phase determining silica concentrations in natural systems.

The extraction experiments show F^- to be present, and its concentration in the OPA porewater will be modelled by assuming saturation with fluorite. Although the aqueous extracts were always undersaturated with respect to fluorite, F^- was quickly released into solution. If one assumes that these readily available quantities are also present in the OPA porewaters (OPA porosity ~ 10 vol.%), then they are more than sufficient to result in fluorite saturation.

Although the aqueous extraction experiments showed clearly that the OPA contains ~ 1.85 mmol kg^{-1} of sulphate, see section 4.2, sulphate minerals at such low levels would not be detectable by the XRD and coulomat analytical methods used to determine the mineralogy. Hence, at this stage sulphate cannot be allocated to a solid phase.

There is Sr in the system with an inventory of 0.5 mmol kg^{-1} but because of the uncertainty of its origin it presents certain modelling difficulties. Some Sr certainly arises from the clay minerals but it could also be present as a separate solid phase or as a solid solution or as a combination of all of these. The motivation for attempting to include Sr is one of completeness rather than importance. Its occupancy represents at the most ~ 1 % of the CEC, emphasising the second order contribution of Sr to the overall picture. A proposal for calculating the concentration of Sr in the porewater and its occupancy on the clay minerals is given in section 9.4.

7 ESTIMATES OF IN SITU CATION OCCUPANCIES

In order to calculate an OPA porewater composition, the in situ fractional cation occupancies of Na, K, Mg and Ca on the clay minerals need to be determined. These cation occupancies can be derived from the Ni-en extraction data together with information from the aqueous extraction tests. In the latter, Cl^- and SO_4^{2-} mean inventories of 12.3 and 3.7 meq kg^{-1} respectively were measured. These quantities are also released in the Ni-en extraction tests and a correction needs to be made for them. However, it is not possible to know a priori which cations are associated with these anions. The approach adopted is to try and bound the problem by concentrating on the two most important cations, Na and Ca. Since OPA is a marine sedimentary rock it is more than likely that Cl^- is present as NaCl but SO_4^{2-} could reasonably be associated with either Na or Ca. In the following two cases are considered. In the first case Na is associated with Cl^- and Ca with SO_4^{2-} whereas in the second case both Cl^- and SO_4^{2-} are associated with Na. This leads to two sets of in situ cation occupancies, see Table 7, and two sets of selectivity coefficients, see Table 8. It will be shown in section 9.3 that the OPA porewater compositions calculated from the two data sets are not significantly different.

7.1 Case I: NaCl/CaSO₄

Na occupancy

From the high S:L ratio Ni-en extraction results given in Table 6, the average inventory of Na in the OPA samples was 60.4 ± 3.3 meq kg^{-1} . This quantity is made up of the Na displaced from the exchange sites of the clay minerals and the Na present in the porewater associated with the Cl^- inventory of 12.3 ± 1.6 meq kg^{-1} . Hence the Na occupancy on the clay minerals is the difference between these two values i.e. 48.1 ± 4.9 meq kg^{-1} .

K occupancy

The calculated quantity of K extracted from OPA (expressed in meq kg^{-1}) appears to increase with decreasing S:L ratio (see Table 6). This behaviour is not compatible with K being present as KCl but may be more indicative of the dissolution of a phase containing K. It might be speculated that at sometime during the evolution of the OPA formation, partial oxidation of pyrite led to the formation of jarosite type phases, $\text{KFe}_3(\text{SO}_4)_2\text{OH}_6$, which in the porewater

could control the aqueous K concentration. (This mineral has been identified by XRD in oxidised Boom clay samples, BAEYENS et al. 1985). There are thus intrinsic uncertainties in extracting K inventories, and hence occupancies, from the data available. The K inventory at the highest S:L ratio from Table 3 is selected as being the best approximation to the loading on the clay minerals i.e. the K occupancy is taken to be $5.4 \pm 0.5 \text{ meq kg}^{-1}$. (The relatively large error given reflects the uncertainty.) The actual K occupancy may be lower than this value but is almost certainly not higher because of the trend in K inventories with S:L ratio.

Mg occupancy

As discussed in section 5.2, cation displacement reactions from clay minerals by Ni-en are much more rapid than dissolution reactions and thus tend to suppress any contribution in the aqueous phase of like cations from sparingly soluble solids by the common ion effect. This effect is particularly relevant where the solid phase has a low solubility and the bivalent cation loading on the clay is relatively high. In Ni-en extraction results for the OPA this process applies particularly to Mg and to a certain extent to Ca, see below. The Mg extracted in meq kg^{-1} at the different S:L ratios remains essentially constant with an average value of $15.6 \pm 0.5 \text{ meq kg}^{-1}$ (Table 6), which is taken to represent the Mg loading on the clays.

Ca occupancy

The situation for Ca is slightly more complex than for Mg because of the presence of sulphate. As already mentioned above, for this case study it is assumed to a first approximation that all of the sulphate is associated with Ca. As in the case of Mg, there is no trend in the displaced Ca inventory as a function of S:L ratio. The Ca loading on the clay is therefore the difference between the averaged quantity of displaced Ca, $29.1 \pm 0.8 \text{ meq kg}^{-1}$ (Table 6), and the SO_4^{2-} inventory of $3.7 \pm 0.4 \text{ meq kg}^{-1}$. The in situ Ca occupancy is thus taken to be $25.4 \pm 1.2 \text{ meq kg}^{-1}$.

7.2 Case II, NaCl/Na₂SO₄

The procedure for deriving in situ cation occupancies is the same as described before. Since in this second case study the SO_4^{2-} and the Cl^- inventories are associated with Na, the in situ Na occupancy decreases to $44.4 \pm 5.3 \text{ meq kg}^{-1}$.

For Ca no correction for sulphate is now needed and the in situ occupancy becomes $29.1 \pm 0.8 \text{ meq kg}^{-1}$. The K and Mg occupancies remain the same.

7.3 Summary of Cation Occupancies

The cation occupancies deduced for OPA in the undisturbed in situ state are given in Table 7 for the two cases considered. The cation exchange capacity is taken as the sum of the individual occupancies and yields a mean value of $94.5 \pm 7.1 \text{ meq kg}^{-1}$.

Table 7: In situ cation occupancies on the clay minerals in Opalinus clay.

Cation	CASE I Cation occupancies (meq kg^{-1})	CASE II Cation occupancies (meq kg^{-1})
Na	48.1 ± 4.9	44.4 ± 5.3
K	5.4 ± 0.5	5.4 ± 0.5
Mg	15.6 ± 0.5	15.6 ± 0.5
Ca	25.4 ± 1.2	29.1 ± 0.8
Σ Cations	94.5 ± 7.1	94.5 ± 7.1

An important point to note is that the sum of extracted cations (Σ cations, Table 7) is $\sim 25\%$ less than the Ni-en exchange capacity of $125 \pm 5.2 \text{ meq kg}^{-1}$, section 5.1. This discrepancy is too large to be attributed to measurement errors and is considered to be a real effect whose origin is as yet uncertain.

Proton exchange on the permanent charge sites is not expected to be a significant process in the extraction tests carried out in the pH range from 8 to 9 where the H^+ concentrations are $\sim 10^{-8} \text{ M}$ or less. The Na^+ - H^+ selectivity coefficient for smectites is approximately unity (GILBERT & LAUDELOUT (1965), FOSCOLOS & BARSHAD (1969)). The behaviour of illites and kaolinites with respect to proton exchange is similar (GRIM 1953).

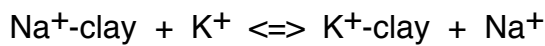
One of the most likely explanations is that the Ni-en not only interacts with the permanent charge sites and displaces all the exchangeable cations but also reacts with the amphoteric SOH type sites at the edges of the clay mineral platelets in OPA (see for example YARIV & CROSS 1979). The effect of forming surface complexes with such sites would be twofold: (i) Ni would be removed from solution and displace predominantly protons and (ii) the assumption of stoichiometric exchange by the bivalent Ni-en complex would be invalid. Thus, while Ni-en can be relied upon to efficiently displace all exchangeable cations, the changes in aqueous Ni concentrations are probably not an accurate reflection of the cation exchange capacity. The indirect measurement of the CEC, via the sum of displaced cations, most probably provides the better estimate and this value has been used in the following calculations.

8 SELECTIVITY COEFFICIENTS

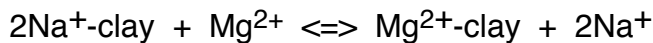
8.1 General

Selectivity coefficients of K, Mg, and Ca are calculated with respect to Na for the OPA system. Na was chosen as the reference cation since it is the most abundant cation present.

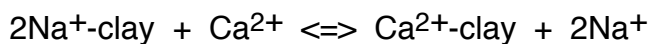
The exchange reactions and the associated mass action equations defining the selectivity coefficients are given below,



$$\frac{N_{\text{K}}}{N_{\text{Na}}} K_c = \frac{N_{\text{K}}}{N_{\text{Na}}} \cdot \frac{a_{\text{Na}}}{a_{\text{K}}} \quad (1)$$



$$\frac{N_{\text{Mg}}}{N_{\text{Na}}} K_c = \frac{N_{\text{Mg}}}{N_{\text{Na}}^2} \cdot \frac{a_{\text{Na}}^2}{a_{\text{Mg}}} \quad \square(2)$$



$$\frac{N_{\text{Ca}}}{N_{\text{Na}}} K_c = \frac{N_{\text{Ca}}}{N_{\text{Na}}^2} \cdot \frac{a_{\text{Na}}^2}{a_{\text{Ca}}} \quad \square\square(3)$$

where "a" represents solution activities and N_{Na} , N_{K} , N_{Mg} and N_{Ca} are equivalent fractional cation occupancies defined as,

$$N_{\text{B}} = \frac{\text{Quantity of cation B on the permanent charge sites of the clay minerals (meq kg}^{-1}\text{)}}{\text{CEC (meq kg}^{-1}\text{)}} \quad (4)$$

where B = Na^+ or K^+ or Mg^{2+} or Ca^{2+} .

As can be seen from the above mass action relations the quantities required to calculate the selectivity coefficients are the same in each case i.e. the

appropriate aqueous cationic activities and fractional cation occupancies on the solid. The important data here are the results from the aqueous extraction tests, see Table 3, and the in situ cation occupancies given in Table 7 which will be used later to derive values for the OPA system.

As indicated in section 4.2, the majority of the aqueous extraction measurements given in Table 3 are non-equilibrium data as far as the calcite/dolomite system is concerned. A combination of long shaking times and high S:L ratios (large surface areas of calcite and dolomite) appear to be required in order to attain equilibrium on a time scale of a month or so. If these minerals are present and in equilibrium, the Ca/Mg activity ratio in solution is fixed at a value of 1.35. This can be appreciated from the thermodynamic solubility constants which are $10^{-8.48}$ and $10^{-17.09}$ for calcite and dolomite respectively (PEARSON & BERNER 1991). Inspection of Figure 1 indicates that this condition is only achieved after 28 days in the aqueous extraction experiments at the highest S:L ratio of 1.5 kg L^{-1} . The fact that the Ca to Mg activity ratio equals exactly 1.35 at equilibrium will be used to calculate the Ca-Mg selectivity coefficient in the next section. Therefore, only the 28 day aqueous extraction data at 1.5 kg L^{-1} are considered.

8.2 Cation Occupancies on the Opalinus Clay in the Aqueous Extraction Tests: S:L = 1.5 kg L^{-1} , 28 Day Equilibration

When de-ionised water is contacted with the OPA samples mineral dissolution and exchange reactions occur simultaneously modifying the original cation occupancies on the clay minerals given in Table 7. For Na and K it is relatively straightforward to calculate the new occupancies, but for Ca and Mg dissolving minerals are present which contain these elements and have to be taken into consideration. As before, Cases I and II have to be considered separately since the initial occupancies calculated in Chapter 7 are different.

8.2.1 Case I, NaCl/CaSO₄

Na occupancies on OPA

The Na in the aqueous extract originates from two sources; the exchangeable Na on the clay and the NaCl in the porewater. The measured Na concentration in the aqueous extract is $2.68 \times 10^{-2} \text{ M}$ (Table 3), which correspond to 17.9 meq

kg⁻¹. The quantity of Na present as NaCl is 12.3 ±1.6 meq (see section 4.2) and thus only 5.6 meq kg⁻¹ is displaced from the clay. Since the original Na occupancy was 48.1 ±4.9 meq kg⁻¹ (Table 7, Case I), the new occupancy in the aqueous extract must be 42.5 ±4.9 meq kg⁻¹ or $N_{Na} = 0.45 \pm 0.05$.

K occupancies on OPA

The exchangeable K on the clay minerals was assumed to be the only source of this element and therefore the quantity remaining on the solid in the aqueous extraction experiment is simply determined from mass balance. The measured K concentration in the aqueous extract is 5.90×10^{-4} M which corresponds to 0.4 meq kg⁻¹. The K occupancy in the aqueous extract is thus 5.0 ±0.5 meq kg⁻¹ or $N_K = 0.05 \pm 0.005$.

Mg and Ca occupancies on OPA

The calculation for bivalent cations occupancies cannot be done in the same manner since solid phases containing these elements are dissolving. Instead, it is noted that the relation

$$N_{Na} + N_K + N_{Ca} + N_{Mg} = 1 \quad (5)$$

must be valid.

Hence, since the K and Na occupancies in the aqueous extracts have been calculated (see above), the sum of the fractional occupancies of Ca and Mg can be found i.e. $N_{Ca} + N_{Mg} = 0.50 \pm 0.05$.

From the thermodynamic considerations discussed previously in section 8.1, the Ca²⁺/Mg²⁺ activity ratio is 1.35 for a system in equilibrium with calcite and dolomite. If this equilibrium is achieved in the aqueous extract then it must also apply to the in situ porewater. The Ca²⁺/Mg²⁺ occupancy ratio on the in situ OPA is 1.63, (see Table 7, Case I). These two results can only be compatible if the selectivity of Ca²⁺ with respect to Mg²⁺ is greater than unity. Substituting the above values into the following mass action equation

$$\frac{a_{Ca}}{a_{Mg}} K_c = \frac{N_{Ca}}{N_{Mg}} \cdot \frac{a_{Mg}}{a_{Ca}} \quad (6)$$

yields a $\frac{Ca}{Mg}K_c$ value of 1.2.

The Ca-Mg selectivity coefficient of 1.2 can be used together with the Ca^{2+}/Mg^{2+} cationic activity ratio of 1.35 and the relation $N_{Ca} + N_{Mg} = 0.50 \pm 0.05$, to calculate the Ca and Mg equivalent fractional occupancies in the aqueous extract experiment from equation 6. These values are 0.31 ± 0.03 and 0.19 ± 0.02 for Ca and Mg respectively.

8.2.2. Case II, NaCl/Na₂SO₄

Na occupancies on OPA

The concentration of Na in the aqueous extract is the same as in Case I (equivalent to 17.9 meq kg^{-1}) but in addition to the quantity of Na arising from NaCl ($12.3 \pm 1.6 \text{ meq kg}^{-1}$), there is also the contribution of $3.7 \pm 0.4 \text{ meq kg}^{-1}$ from Na₂SO₄. Hence only 1.9 meq kg^{-1} is displaced from the clay giving a Na occupancy in the aqueous extract of $42.5 \pm 5.3 \text{ meq kg}^{-1}$ or $N_{Na} = 0.45 \pm 0.06$.

K occupancies on OPA

The K occupancy in the aqueous extract is the same in both cases i.e. $N_K = 0.05 \pm 0.005$.

Mg and Ca occupancies on OPA

The procedure to calculate the Ca and Mg equivalent fractional occupancies in the aqueous extract experiment is the same as for Case I. The different in situ N_{Ca}/N_{Mg} fractional occupancy ratio of 1.87 (Table 7, Case II) yields a $\frac{Ca}{Mg}K_c$ value of 1.4. The calculated Mg and Ca equivalent fractional occupancies are therefore 0.17 ± 0.03 and 0.33 ± 0.04 respectively.

8.3 Calculation of Selectivity Coefficients for K-Na, Ca-Na, and Mg-Na Exchange Equilibria

The fractional cation occupancies calculated for Cases I and II can be used together with the concentrations of Na, K, Mg, and Ca measured in the aqueous extract experiment (S:L=1.5 kg L⁻¹, 28 day equilibration time) expressed in terms of cation activities to calculate selectivity coefficients from equations 1 to

3. The values for $\frac{K}{Na}K_c$, $\frac{Mg}{Na}K_c$ and $\frac{Ca}{Na}K_c$ are summarised in Table 8. (Uncertainties in K_c values are discussed further in section 9.3.)

Table 8: Fractional cation occupancies and corresponding selectivity coefficients for Cases I and II. The values given in parenthesis represent the upper and lower uncertainty ranges of the parameters.

Fractional equivalent cation occupancies on OPA in the 1.5 kg L ⁻¹ aqueous extract.		
	CASE I	CASE II
N _{Na}	0.45 $\left(\begin{smallmatrix} +0.05 \\ -0.05 \end{smallmatrix} \right)$	0.45 $\left(\begin{smallmatrix} +0.06 \\ -0.06 \end{smallmatrix} \right)$
N _K	0.05 $\left(\begin{smallmatrix} +0.005 \\ -0.005 \end{smallmatrix} \right)$	0.05 $\left(\begin{smallmatrix} +0.005 \\ -0.005 \end{smallmatrix} \right)$
N _{Mg}	0.19 $\left(\begin{smallmatrix} +0.02 \\ -0.02 \end{smallmatrix} \right)$	0.17 $\left(\begin{smallmatrix} +0.03 \\ -0.02 \end{smallmatrix} \right)$
N _{Ca}	0.31 $\left(\begin{smallmatrix} +0.03 \\ -0.03 \end{smallmatrix} \right)$	0.33 $\left(\begin{smallmatrix} +0.3 \\ -0.4 \end{smallmatrix} \right)$
Calculated selectivity coefficients (I=0)		
$\frac{K}{Na}K_c$	5.0 $\left(\begin{smallmatrix} +0.7 \\ -0.5 \end{smallmatrix} \right)$	5.0 $\left(\begin{smallmatrix} +0.8 \\ -0.5 \end{smallmatrix} \right)$
$\frac{Mg}{Na}K_c$	3.9 $\left(\begin{smallmatrix} +1.5 \\ -1.1 \end{smallmatrix} \right)$	3.5 $\left(\begin{smallmatrix} +1.9 \\ -1.1 \end{smallmatrix} \right)$
$\frac{Ca}{Na}K_c$	4.7 $\left(\begin{smallmatrix} +1.8 \\ -1.3 \end{smallmatrix} \right)$	5.0 $\left(\begin{smallmatrix} +2.2 \\ -1.6 \end{smallmatrix} \right)$

The selectivity coefficients for Cases I and II are not significantly different, and are in generally good agreement with literature values; $\frac{K}{Na}K_c = 5 - 10$; $\frac{Mg}{Na}K_c = 3.8$; $\frac{Ca}{Na}K_c = 2 - 7$ (BOLT et al. 1963; BAEYENS 1982; BRUGGENWERT & KAMPHORST 1982; BROUWER et al. 1983; BAEYENS & BRADBURY 1991,1994).

9 OPALINUS CLAY POREWATER COMPOSITION CALCULATIONS

9.1 Constraints on the Aqueous Chemistry

In the previous sections, the in situ occupancies of Na, K, Mg and Ca on OPA were determined ("fingerprint" values) together with the corresponding selectivity coefficients. Additionally, the inventories of chloride and sulphate were established and information was presented which indicated that the in situ OPA porewater was saturated with respect to calcite, dolomite, fluorite and chalcedony. From these data one would conclude that the ion concentrations of particular relevance for the derivation of an in situ OPA porewater are those of H, Na, K, Mg, Ca, Cl⁻, SO₄²⁻, F⁻, Si and C_{inorg}.

The constraints on the OPA porewater system as defined above may be usefully examined using the Gibb's phase rule which states:

$$F = C - P + 2 \quad (7)$$

"F" represents the number of degrees of freedom, "C" the minimum number of components necessary for the description of all phases present in the system, and "P" the number of phases in the system. The fact that temperature and pressure can be varied accounts for the "2" in the equation.

There are 10 components in the system (listed above) and five obvious phases; the solution, calcite, dolomite, chalcedony and fluorite. The components which are associated with the latter four phases are C_{inorg}, Mg^{*}, Si and F⁻. Also, following the work of ANDERSON & CRERAR (1993) the fixed fractional cation occupancies on the clay mineral components of the OPA (N_{Na}, N_K and N_{Ca}) can be identified as separate phases. In their derivation of the Gibb's phase rule, these authors defined a "phase" as any entity which can be identified with an equation constraining the aqueous composition. The fractional occupancies

* The Mg concentration can be determined from either dolomite saturation or from the N_{Mg} value via cation exchange. In this case both procedure leads to the same result since the Mg-Na selectivity coefficient was calculated under conditions for which dolomite was saturated, see Chapter 8.

are related to their corresponding aqueous cation activities over the cation exchange equations and the associated selectivity coefficients. Thus, the system has 10 components and 8 phases and hence, according to equation 7, four degrees of freedom. Two of these disappear if conditions of constant temperature and pressure are defined.

On the basis of the above analysis, a unique OPA pore water chemistry cannot be calculated since the system has two degrees of freedom. In order to solve this impasse, additional information is required. There are three remaining components whose concentrations are as yet undetermined, namely the in situ Cl^- , SO_4^{2-} and H concentrations.

Chloride and sulphate inventory values for OPA are available from the laboratory investigations, section 4.2, and these data offer a means of providing in situ concentrations if the porosity, or, more precisely, the $\text{Cl}^-/\text{SO}_4^{2-}$ accessible porevolume in the OPA samples is known. Porosities are quite difficult to determine and the values found often depend on the method used, see for example PEARSON (1997). Porosity data are available for OPA, and even if a range of values has to be taken, this nevertheless provides a means of bounding in situ porewater compositions.

Thus if the appropriate porosity value is known, the Cl^- concentration can be fixed from the inventory data and likewise a maximum sulphate concentration is also fixed. (At high porosities the whole of the sulphate inventory may dissolve whereas at low porosities its concentration will tend to be solubility limited by gypsum.)

The interesting conclusion to emerge from this approach is that the water chemistry is now fully defined (no degrees of freedom) and that all conditions and equations can only be satisfied at one unique pH for each porosity corresponding to the in situ value.

9.2 Calculation Methodology Using MINSORB

The following calculations for the OPA porewater chemistry were performed with the MINSORB code which is based on the geochemical equilibrium code

MINEQL (WESTALL et al. 1976) modified to include cation exchange (see Appendix I). Proton exchange on the planar sites was not included because even at pH values as low as 5.5 the H^+ concentrations are too low to be competitive with other cations such as Na, K, Mg and Ca (see section 7.3 and GORGEON 1994). The thermodynamic data compilations of PEARSON & BERNER (1991) and PEARSON et al. (1992) were used throughout. Redox reactions were not considered.

In any one set of calculations a porosity value was taken which then fixed the initial Cl^- and SO_4^{2-} concentrations. The exchange coefficients, K_{EX} , for K-Na, Mg-Na and Ca-Na required as input parameters in the code, were determined as described in Appendix I. In order to begin with an approximately charge balanced system, the sum of the initial aqueous Na and K concentrations was taken to be equal to the Cl^- concentration. (The Na to K ratio was estimated from equation 1.) Finally, a starting pH was chosen (normally neutral) and the first calculation carried out under the conditions of saturation with respect to calcite, dolomite, fluorite and chalcedony. Adjustments in the Na concentration were used throughout to maintain electrical neutrality in the calculated solutions.# The calculated fractional equivalent cation occupancy values from this first iteration were then compared with the "fingerprint" values given in Table 7. From this comparison the pH for the second iteration was changed in a direction so as to reduce the discrepancy i.e. decreased if the calculated Ca and Mg occupancies were too low or increased if they were too high.

Aqueous K concentrations were also adjusted up or down on the basis of the difference between calculated and "fingerprint" occupancies. Otherwise, the charge balanced output aqueous concentrations from the first iteration were used as input values to the second iteration, in which the whole calculation was repeated. This procedure was continued until the calculated and "fingerprint" fractional equivalent cation occupancies were within 1% of each other which normally required approximately ten iterations.

#A characteristic of MINEQL is that solutions have to be checked for charge balance after each calculation.

9.3 Errors/Uncertainties

There are some intrinsic uncertainties in the data and parameter values arising out of the procedures described in Chapters 4, 5 and 7 and it is important to try to quantify the extent to which such errors may influence the calculated porewater chemistry. Na is the major cation in the system and its occupancies can vary between 53.0 and 43.2 meq kg⁻¹ for Case I, and in Case II from 49.7 to 39.1 meq kg⁻¹ (Table 7). Selectivity coefficients can be calculated corresponding to the above Na occupancy values when the occupancies of the other major cations are adjusted to give a consistent OPA cation exchange capacity. The range of fractional equivalent cation occupancies deduced for the 1.5 kg L⁻¹ aqueous extract data and the calculated selectivity coefficients (see Chapter 8) are summarised in Table 8. The range in the selectivity coefficient values in Table 8 essentially reflects the uncertainties in the Na occupancies and whether the sulphate is taken to be present in the Ca or Na form, Cases I and II respectively.

Porewater compositions calculated over the uncertainty ranges of fractional occupancies and selectivity coefficients given in Table 8, are presented in Table 9. For purpose of these illustrative examples an OPA water content of 0.041 L kg⁻¹ was assumed, which, for a grain density of 2.7 kg L⁻¹ is equivalent to a porosity of ~10.4 vol.%. (See section 9.4 and Table 10.) The values given in parenthesis represent the upper and lower bounds on the variability of the quantity concerned. The chloride concentration was fixed in the calculations from the mean chloride inventory and the water content. Si concentrations are those corresponding to saturation with chalcedony.

The water compositions for Cases I and II are essentially the same within the bounds of the estimated errors. The results show that the calculations are not very sensitive to the exact value taken for the Na occupancy nor to assumptions regarding which cation, Na or Ca, is associated with sulphate, i.e. the model appears to be fairly robust.

Table 9: Calculated Opalinus clay porewater compositions for Cases I and II at a porosity of 10.4 vol.%.

	CASE I	CASE II
pH	$5.8 \left(\begin{smallmatrix} +0.1 \\ -0.1 \end{smallmatrix} \right)$	$5.8 \left(\begin{smallmatrix} +0.1 \\ -0.1 \end{smallmatrix} \right)$
Ionic strength (M)	$0.40 \left(\begin{smallmatrix} +0.01 \\ -0.005 \end{smallmatrix} \right)$	$0.40 \left(\begin{smallmatrix} +0.01 \\ -0.01 \end{smallmatrix} \right)$
P_{CO_2} (bar)	1.3	1.3
<u>Concentration (M)</u>		
Na	$2.6 \left(\begin{smallmatrix} +0.2 \\ -0.2 \end{smallmatrix} \right) \times 10^{-1}$	$2.4 \left(\begin{smallmatrix} +0.2 \\ -0.2 \end{smallmatrix} \right) \times 10^{-1}$
K	$5.8 \left(\begin{smallmatrix} +0.2 \\ -0.3 \end{smallmatrix} \right) \times 10^{-3}$	$5.8 \left(\begin{smallmatrix} +0.1 \\ -0.1 \end{smallmatrix} \right) \times 10^{-3}$
Mg	$2.5 \left(\begin{smallmatrix} +0.4 \\ -0.3 \end{smallmatrix} \right) \times 10^{-2}$	$2.7 \left(\begin{smallmatrix} +0.4 \\ -0.4 \end{smallmatrix} \right) \times 10^{-2}$
Ca	$3.2 \left(\begin{smallmatrix} +0.4 \\ -0.4 \end{smallmatrix} \right) \times 10^{-2}$	$3.6 \left(\begin{smallmatrix} +0.6 \\ -0.4 \end{smallmatrix} \right) \times 10^{-2}$
Sr [#]	$2.6 \left(\begin{smallmatrix} +0.4 \\ -0.4 \end{smallmatrix} \right) \times 10^{-4}$	$3.2 \left(\begin{smallmatrix} +0.4 \\ -0.4 \end{smallmatrix} \right) \times 10^{-4}$
Cl ⁻	3.0×10^{-1}	3.0×10^{-1}
F ⁻	$1.2 \left(\begin{smallmatrix} +0.1 \\ -0.1 \end{smallmatrix} \right) \times 10^{-4}$	$1.2 \left(\begin{smallmatrix} +0.1 \\ -0.1 \end{smallmatrix} \right) \times 10^{-4}$
SO ₄ ²⁻	$2.7 \left(\begin{smallmatrix} +0.3 \\ -0.4 \end{smallmatrix} \right) \times 10^{-2}$	$2.4 \left(\begin{smallmatrix} +0.4 \\ -0.3 \end{smallmatrix} \right) \times 10^{-2}$
HCO ₃ ⁻	$1.9 \left(\begin{smallmatrix} +0.1 \\ -0.1 \end{smallmatrix} \right) \times 10^{-2}$	$1.9 \left(\begin{smallmatrix} +0.1 \\ -0.1 \end{smallmatrix} \right) \times 10^{-2}$
Si	2.8×10^{-4}	2.8×10^{-4}

See section 9.4

9.4 Calculated In Situ Opalinus Clay Porewater Compositions

Since it has been shown that the calculated porewater chemistries are not sensitively dependent upon which of the two data sets in Table 8 are chosen, the mean parameter values given for Case I will be used in the following.

The porosity of OPA, or rather the volume of water accessible to the major anions and cations (the two are not necessarily the same), is a critical parameter for the calculations of in situ porewater compositions. As far as the OPA system is concerned, the uncertainty in this parameter value has the greatest influence on the uncertainty associated with the aqueous chemistry

calculations. Currently available data indicate porosities from ~8 and ~15 vol.%, depending on the measurement method (PEARSON 1997), with the most probable value lying between 10 and 12 vol.%. The in situ porewater calculations given in Table 10 have been carried out at accessible water volumes corresponding to 8, 10, 12 and 14 vol.%. A graphical representation of the concentrations of the major ions is shown in Figure 5.

As stated previously, the inclusion of Sr in the modelling of the in situ porewater presents certain problems. Sr is present in the system at an inventory of 0.5 mmol kg⁻¹ but its origin is unclear. However, in the range of porosities considered in the previous calculations there is sufficient Sr to ensure that celestite (SrSO₄) is saturated, even taking into account exchange of Sr on the clay minerals. Mainly because of this the aqueous concentration of Sr was fixed via saturation with respect to celestite. For each calculation at the different porosities the Sr occupancy on the clay is then determined by this concentration and the assumption that the selectivity coefficient of Sr with respect to Na is the same as that of Ca (BRUGGENWERT & KAMPHORST 1982). (The boundary condition on the calculation is that the inventory of Sr is not exceeded.) This additional calculation for Sr is carried out after the main porewater chemistry has been established. (Note that since the Sr concentration is determined by the inclusion of an additional solid phase (celestite) the phase rule is not violated in the latter calculations and the arguments given previously in section 9.1 are still valid.)

The main features of the OPA porewaters emerging from these calculations are that they are of the NaCl type with relatively high ionic strengths and pH values between 5.6 and 6.1. Figure 5 shows clearly that at increasing porosities all ion concentrations, with the exception of sulphate, decreases. For porosities in the range considered, the measured sulphate inventories lead to the conclusion that the waters are saturated with gypsum which accounts for the rise in sulphate concentrations with increasing porosities. Although stringent precautions were taken, rapid oxidation of a very reactive part of the pyrite cannot be completely ruled out, and part of the SO₄²⁻ levels measured could have come from this source. It should be mentioned in this context that including or excluding SO₄²⁻ in the calculations did not have any significant impact on the concentrations of the other major ions.

Table 10: Calculated Opalinus clay porewater compositions at different Cl⁻ accessible water contents.

Cl ⁻ accessible water content	8 vol.%	10 vol.%	12 vol.%	14 vol.%
pH	5.6	5.8	5.9	6.1
Ionic strength (M)	0.51	0.42	0.36	0.32
P _{CO₂} (bar)	2.5	1.6	1.1	0.7
<u>Concentration: (M)</u>				
Na	3.1 x 10 ⁻¹	2.6 x 10 ⁻¹	2.3 x 10 ⁻¹	2.1 x 10 ⁻¹
K	6.8 x 10 ⁻³	5.9 x 10 ⁻³	5.3 x 10 ⁻³	4.8 x 10 ⁻³
Mg	3.3 x 10 ⁻²	2.6 x 10 ⁻²	2.1 x 10 ⁻²	1.8 x 10 ⁻²
Ca	4.4 x 10 ⁻²	3.4 x 10 ⁻²	2.8 x 10 ⁻²	2.3 x 10 ⁻²
Sr	4.0 x 10 ⁻⁴	3.0 x 10 ⁻⁴	2.4 x 10 ⁻⁴	1.9 x 10 ⁻⁴
Cl ⁻	3.9 x 10 ⁻¹	3.1 x 10 ⁻¹	2.6 x 10 ⁻¹	2.2 x 10 ⁻¹
F ⁻	1.1 x 10 ⁻⁴	1.2 x 10 ⁻⁴	1.2 x 10 ⁻⁴	1.3 x 10 ⁻⁴
SO ₄ ²⁻	2.2 x 10 ⁻²	2.6 x 10 ⁻²	3.0 x 10 ⁻²	3.3 x 10 ⁻²
HCO ₃ ⁻	2.2 x 10 ⁻²	2.0 x 10 ⁻²	1.8 x 10 ⁻²	1.6 x 10 ⁻²
Si	2.8 x 10 ⁻⁴	2.8 x 10 ⁻⁴	2.8 x 10 ⁻⁴	2.8 x 10 ⁻⁴

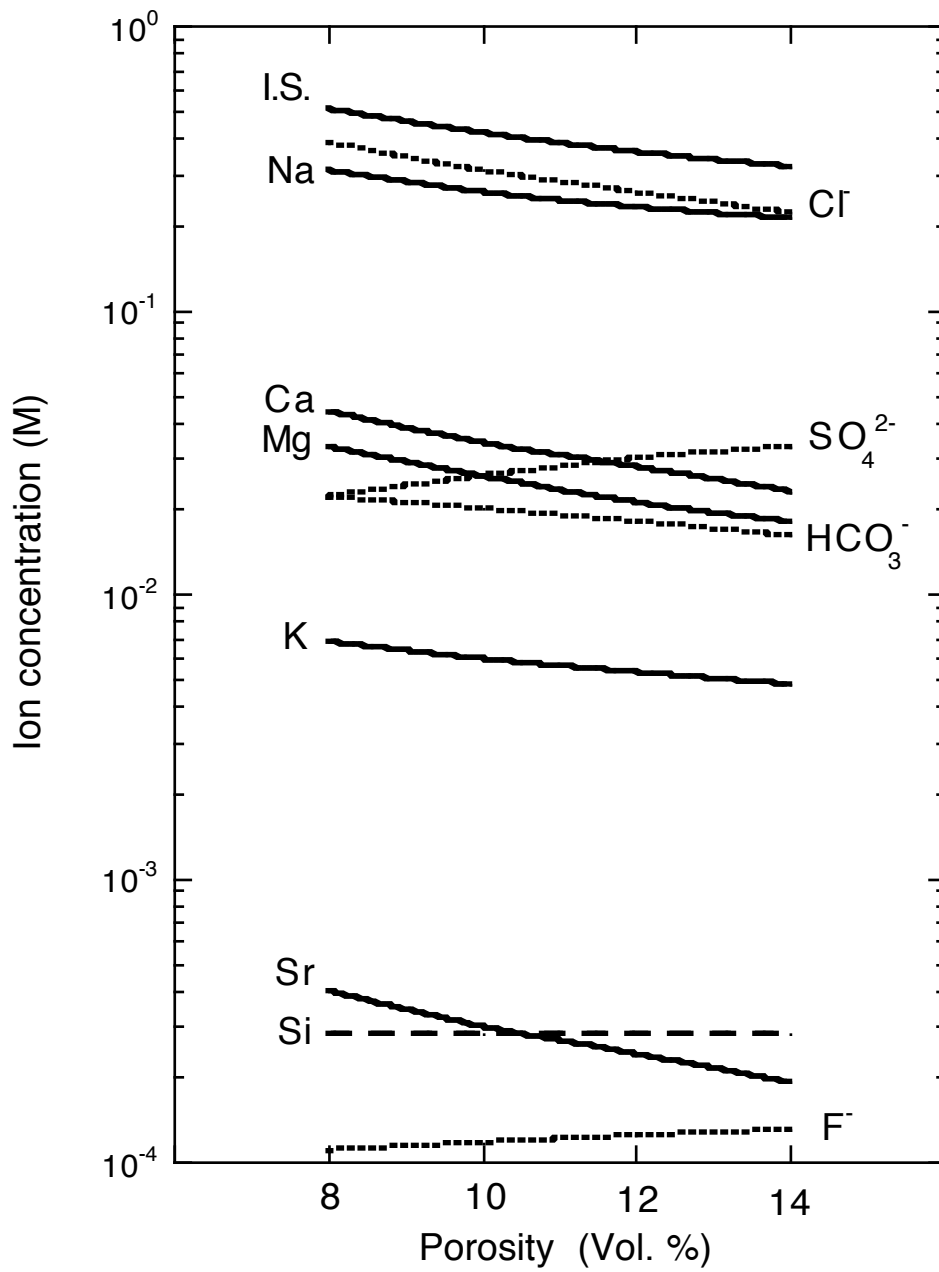


Figure 5: Ionic strength and concentrations of the major ions in the calculated Opalinus clay porewater composition at different Cl⁻ accessible water contents.

10 DISCUSSION OF WATER CHEMISTRY RESULTS FROM THE PHYSICO-CHEMICAL METHOD, SQUEEZING AND BOREHOLE SAMPLING

In Table 11 the pH, P_{CO_2} , ionic strength and major cation/anion concentration ranges for in situ OPA porewater calculated at porosities between 8 and 14 vol.% (Table 10) are presented together with squeezing data from the British Geological Survey (BGS), (CAVE et al. 1996) and the compositions measured on "free flowing" water sampled from borehole BWS-A1. This particular set of squeezing data were chosen because they were derived from a directly adjacent sample to the one used in the laboratory investigations. The water sample taken in the field was at that time the only one obtained from the same borehole as the two samples mentioned above.

For brevity, the PSI calculated ranges will be referred to as "physico-chem" values, the BGS data as "squeezing" values and the Nagra borehole water sample as "borehole" values.

A direct and detailed comparison between the calculated porewater compositions and the experimental data is not considered to be particularly meaningful since the latter two data sets are clearly far away from equilibrium. Thus, one of the original aims of verifying the calculated porewater chemistry against squeezing and borehole data was not possible. Consequently, the discussion will be restricted to the more general aqueous composition features characterising the different waters.

Despite the uncertainty in the OPA porosity, the calculated groundwaters are in all cases high ionic strength, Na-Cl types in which the Na concentrations are always less than those of Cl^- . The experimentally measured water compositions also have exactly the same characteristics with Na and Cl^- concentrations within the calculated ranges. These observations may be seen as a partial verification of the approach which, it should not be forgotten, starts with a "lump of rock".

Table 11: Results of calculated (physico-chem), squeezing and borehole Opalinus clay porewater data.

Method	Physico-chem [*] (PSI)	Squeezing (BGS)	Borehole (Nagra)
Sample	BWS-A1 C12, 13.8 - 14.0 m	BWS A1 C13 14.0 - 14.5 m	BWS A1 Borehole
pH	5.6 - 6.1	7.5	7.7
P _{CO₂} (bar)	2.5 - 0.7	0.002	0.003
Ionic strength (M)	0.5 - 0.3	0.38	0.40
<u>Concentration: (M)</u>			
Na	3.1 - 2.1 x 10 ⁻¹	2.36 x 10 ⁻¹	2.61 x 10 ⁻¹
K	6.8 - 4.8 x 10 ⁻³	7.80 x 10 ⁻⁴	2.00 x 10 ⁻³
Mg	3.3 - 1.8 x 10 ⁻²	2.10 x 10 ⁻²	1.76 x 10 ⁻²
Ca	4.4 - 2.3 x 10 ⁻²	2.01 x 10 ⁻²	2.17 x 10 ⁻²
Sr	4.0 - 1.9 x 10 ⁻⁴	5.50 x 10 ⁻⁴	4.02 x 10 ⁻⁴
Cl ⁻	3.9 - 2.2 x 10 ⁻¹	2.87 x 10 ⁻¹	3.11 x 10 ⁻¹
SO ₄ ²⁻	2.2 - 3.3 x 10 ⁻²	1.72 x 10 ⁻²	1.67 x 10 ⁻²
Si	2.8 x 10 ⁻⁴	2.09 x 10 ⁻⁴	5.77 x 10 ⁻⁵
HCO ₃ ⁻	2.2 - 1.6 x 10 ⁻²	1.89 x 10 ⁻³	4.26 x 10 ⁻³
<u>Mineral Saturation</u>			
<u>Indices:</u>			
Calcite	0 ^{**}	0.36	0.91
Ordered Dolomite	0 ^{**}	0.90	1.89
Gypsum	0 ^{**}	-0.42	-0.40
Celestite	0 ^{**}	0.2	0
Chalcedony	0 ^{**}	-0.1	-0.7

* Data from Table 10 (porosity: 8 - 14 vol.%)

** Saturation indices are zero by definition.

The relatively high sulphate inventory of 1.85 mmol kg⁻¹ was experimentally determined (Figure 3) and led to gypsum saturation in the calculated porewaters. This resulted in sulphate concentrations higher than those in squeezed and borehole waters which are well undersaturated with respect to this mineral (SI = -0.4). Although extensive precautions were taken to avoid any pyrite oxidation effects (sections 2.1 and 4.1) it is nevertheless possible that a

small, very reactive fraction of the pyrite did indeed oxidise rapidly during sample preparation. In some previous work, it was shown that in long term tests (~90 days) in which suspensions of crushed argillaceous rock were shaken in open containers exposed to the glove box atmosphere there were no measurable increases in SO_4^{2-} concentrations with time.

The most significant discrepancies in the porewater compositions lie in the pH, P_{CO_2} and HCO_3^- values and all of these parameters are linked over the pH/calcite/dolomite equilibrium as are the Ca and Mg concentrations. The squeezed and borehole water samples are remarkable for how far away from equilibrium they are with respect to the carbonate minerals. The squeezed water is factors of ~2 and ~8 oversaturated with respect to calcite and dolomite respectively. The borehole water sample is even more out of equilibrium; factors of ~8 and ~80 oversaturated with respect to calcite and dolomite respectively.

The low pH predicted for the physico-chem water, combined with the condition of saturation w.r.t. calcite and dolomite, leads to a high P_{CO_2} of ~1.3 bar. If such a high partial pressure of CO_2 were to exist in the formation, then sampling will certainly be associated with out-gassing of CO_2 from the porewater and a corresponding rise in pH. The response of the solution pH is likely to be relatively rapid, whereas the approach of the system as a whole to equilibrium will be much slower. The precipitation kinetics of dolomite are so slow that for practical purposes no precipitation will occur. Calcite will begin to precipitate slowly, influencing the SO_4^{2-} concentration via the common ion effect with Ca and the solubility of gypsum. Changes in mineral solubilities with an increasing pH will lead to disequilibrium with the cation occupancies on the clay mineral components of OPA and consequently to cation exchange reactions. This too will have an influence on the water composition. Falling Ca concentrations would favour the uptake of Na and Mg thus tending to reduce their concentrations in solution.

The above explanation of the sequence of processes occurring in the development of the water chemistry in an OPA core sample after the degassing of CO_2 is semi-quantitatively compatible with the differences observed between the physico-chem calculated water composition and the two measured water chemistries. In particular it explains the distinct disequilibrium observed

between the three important solid phases; calcite, dolomite and gypsum, and the solution components.

This hypothesis also accounts for the observation that the ionic strengths are nearly the same in all three cases despite the changes described above. The main contributors to the ionic strength are Na and Cl^- from NaCl. The Na and Cl^- concentrations are little effected by the above processes. Other changes will be determined by precipitation reactions. Dolomite will not precipitate at all, the solubility of gypsum is virtually constant over the pH range from 6 to 8 and only calcite is likely to be precipitating slowly and these are all second order effect as far as the ionic strength is concerned. Even the cation exchange reactions are not important here. They will have an influence on the composition of the water but since exchange reactions are stoichiometric they will not have any effects on the ionic strength.

The above process will have occurred in all of the samples extracted from the borehole i.e. the samples received at BGS for squeezing and at PSI will have changed in the same way. Why then are the conclusions concerning the water chemistries so different? The answer lies in what is measured in the two cases. At BGS the squeezed out water was analysed directly, whereas at PSI the porewater chemistry was deduced from physico-chemical measurements on the solid. As described previously, the major changes in pH and HCO_3^- concentration occur rapidly upon sampling, and will be reflected in the aqueous phase analyses. Changes occurring in cation concentrations will only have minor influences on the cation occupancies on the clay minerals because of the high cation capacity of the clay components compared with that of the interstitial water. For example, considering the data in Table 9, a change in Ca concentration from 3.2×10^{-2} M (physico-chem) to 2.0×10^{-2} M (squeezing) represents a change of ~ 1 meq kg^{-1} in the Ca content of the system whereas the Ca capacity arising from the clay minerals is more than 25 meq kg^{-1} .

Finally, it is worth mentioning results from two additional modelling exercises. In the first, a porosity of 30 vol.% was taken and a porewater chemistry calculated with the same basic data set as was used to generate the results given in Table 10. Even at such a high porosity the calculated pH (6.9) was still almost one pH unit below the measured values. (The ionic strength was, of course, low by a factor of ~ 3 .) In the second, the chloride concentration was fixed at 0.3 M and a

porewater composition was calculated at a pH of 7.7 (a measured value). The predicted Na occupancy on the clay minerals in OPA was nearly twice the measured value i.e. 83.6 meq kg⁻¹ as opposed to 48.1 meq kg⁻¹.

The general conclusion is therefore that the apparent consistency of the squeezing and borehole water chemistries may be misleading and should not necessarily be taken as evidence indicating that they are representative of the actual in situ porewater in the OPA formation. In fact quite the reverse may be true since both are interpreted here as being artefact compositions resulting from the same cause i.e. the de-gassing of the high partial pressure of CO₂ existing in the undisturbed porewater and the resulting pH and (time dependent) solubility changes of the major minerals coupled with cation exchange reactions.

11 SIMPLIFIED PROCEDURE FOR POREWATER CHEMISTRY DETERMINATIONS

On the basis of the parameter values given here, and the experimental and modelling procedures described (see also BAEYENS & BRADBURY 1991, 1994), it is possible to propose a simplified methodology for determining porewater chemistries for low porosity sedimentary rocks in which there is little or no free flowing water.

A detailed mineralogical analysis is required.

An aqueous extract and a Ni-en extract at a suitable S:L ratio (1 to 2 kg L⁻¹) measured inside a glove box and allowing sufficient time for equilibration (~30 days for aqueous extracts and ~5 days for Ni-en extracts) provides the chloride (and sulphate) inventory, the loadings on the clay mineral components and the CEC. They also provide additional information on water chemistry determining mineral phases which are present at levels which may not have been detected in the mineralogical analysis e.g. fluorite, gypsum and celestite in OPA.

Finally a porosity determination is required. Perhaps the simplest means of estimating the available water content is from weight difference by heating a pristine core sample to constant weight at 105 °C.

If the selectivity coefficients given in Table 8 are used, all the necessary information is available to calculate the in situ water chemistry in the manner described in Chapter 9.

The short range and long range porewater composition variation within the OPA formation is an important consideration. A quick and easy method of obtaining first estimates of any variability is proposed by measuring the water content of core samples, as described above, and the Cl⁻ inventories of the same samples to give Cl⁻ concentration profiles.

12 SUMMARY AND CONCLUSIONS

Physico-chemical characterisation techniques, developed in some previous work to deduce in situ porewaters for argillaceous rocks (BAEYENS & BRADBURY 1991, 1994), have been applied to a sample of OPA, BWS-A1 C12, 13.8 - 14.0 m, taken from a borehole drilled into the wall rock of a reconnaissance gallery associated with the Mt. Terri motor way tunnel (Canton Jura).

The technique has been extended, allowing the in situ pH of the formation to be deduced. This was achieved by using the physico-chemical characterisation and modelling procedures already developed in conjunction with data on the Cl⁻ accessible water content in the bulk rock. This may be an important new development in understanding and defining the porewater chemistries in tight sedimentary rock formations, such as OPA, where the low porosities and no flowing water implies that the in situ pH will never be known.

The in situ porewater deduced from the study was an NaCl water at pH=5.8, ionic strength ~0.4 M, saturated with calcite, dolomite, gypsum, fluorite, chalcedony and also celestite. The partial pressure of CO₂ associated with this porewater was ~1.3 bar.

One of the aims in this study was to attempt to verify the physico-chemical characterisation approach by comparing the calculated values with the analyses of water squeezed from a core and water which had slowly seeped into and accumulated in one of the boreholes at Mt. Terri. This borehole, BWS-A1, was also the source of samples in the squeezing tests and for the physico-chemical characterisation studies. Comparisons of the data sets indicated that there were areas of very good agreement (ionic strengths) and very poor agreement (pH, P_{CO₂} and HCO₃⁻). The conclusion reached was that the apparent consistency of the squeezing and borehole water chemistries could not be taken as evidence indicating that they were representative of the actual in situ porewater in the OPA formation. Rather, both were considered to be artefact compositions resulting from the same cause i.e. the de-gassing of the high partial pressure of CO₂ existing in the undisturbed porewater and the resulting pH and (time dependent) solubility changes of the major minerals coupled with cation exchange reactions.

On the balance of the currently available evidence, our final conclusion was that the calculations using the physico-chemical data measured for OPA most probably provided the best description of the in situ porewater chemistry. It was possible, starting with the calculated in situ porewater, to explain the evolution of the measured artefact water compositions and also to explain the origin of the internal inconsistencies in these data . However, only more field work directed at in situ measurements of P_{CO_2} and or pH can resolve this issue.

A simplified laboratory methodology for the determination of in situ porewater chemistries in tight, low porosity clay mineral rich sediments was proposed.

Finally, a quick and easy method was proposed for obtaining short and long range chloride profiles through the Mt. Terri OPA formation.

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14 REFERENCES

- ANDERSON, G. M. & CRERAR, D. A. (1993): *Thermodynamics in Geochemistry: The Equilibrium Model*. Oxford University Press. Oxford.
- BAEYENS, B. (1982): *Strontium, Cesium and Europium Retention in Boom Clay: A Potential Repository Site for Nuclear Waste*. Ph.D. Thesis, Katholieke Universiteit Leuven, Belgium.
- BAEYENS, B., MAES, A., CREMERS, A. & HENRION, P.N. (1985): Aging effects in Boom Clay. *Radioactive Waste Management and the Nuclear Fuel Cycle*. Vol. 6 (3-4), pp. 409-423.
- BAEYENS, B. & BRADBURY, M.H. (1991): *A Physico-Chemical Characterisation Technique for Determining the Porewater Chemistry in Argillaceous Rocks*. PSI Bericht Nr. 103. Paul Scherrer Institut, Villigen. Nagra Tech. Ber. NTB 90-40. Nagra, Wettingen.
- BAEYENS, B. & BRADBURY, M.H. (1994): *Physico-Chemical Characterisation and Calculated In Situ Porewater Chemistries for a Low Permeability Palfris Marl Sample from Wellenberg*. PSI Bericht Nr. 94-19. Paul Scherrer Institut, Villigen. Nagra Tech. Ber. NTB 94-22. Nagra, Wettingen.
- BENSON, L.V. (1982): A Tabulation and Evaluation of Ion Exchange Data on Smectites. *Environmental Geology*. Vol. 4, pp. 23-29.
- BLÄSI, H.-R., PETERS, T. & MAZUREK, M. (1991): *Der Opalinus-Ton des Mt. Terri (Kanton Jura): Lithologie, Mineralogie und physico-chemische Gesteinsparameter*. Unpubl. Nagra Internal Report, Wettingen.
- BOLT, G.H., SUMNER, M.E. & KAMPHORST, A. (1963): A Study of the Equilibria between Three Categories of Potassium in an Illitic Soil. *Soil Sci. Soc. Am. Proc.* Vol. 27, pp. 294-299.
- BROUWER, E., BAEYENS, B., MAES, A. & CREMERS, A. (1983): Cesium and Rubidium Ion Equilibria in Illite Clay. *J. Physical Chemistry*. Vol. 87, pp. 1213-1219.

- BRUGGENWERT, M.G.M. & KAMPHORST, A. (1982): Survey of Experimental Information on Cation Exchange in Soil Systems. In: BOLT, G.H. (ed.): Soil Chemistry B. Physico-Chemical Models. Elsevier Science Publishers, Amsterdam.
- CAVE, M. R., REEDER, S., ENTWHISTLE, D. C., BLACKWELL, P.A., TRICK, J. K., WRAGG, J. & VICKERS, B. P. (1996): Chemical Characterisation of Squeezed Porewaters and Aqueous Leachates from Opalinus Clay from the Mt. Terri Tunnel, Switzerland: BGS Technical Report WI796/12C, British Geological Survey, Keyworth.
- DREYBRODT, W., LAUCKNER, J., ZAIHUA LIU, SVENSSON, U. & BUHMANN, D. (1996): The Kinetics of the Reaction $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HCO}_3^-$ as One of the Rate Limiting Steps for the Dissolution of Calcite in the System $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$. *Geochim. Cosmochim. Acta*. Vol. 60, pp. 3375-3381.
- FLETCHER, P. & SPOSITO, G. (1989) The chemical modelling of clay/electrolyte interactions for montmorillonite. *Clay Minerals* Vol. 24, pp. 375-391.
- FOSCOLOS, A.E. & BARSHAD, I. (1969): Equilibrium constants between both freshly prepared and aged H-montmorillonites and chloride salt solutions. *Soil Sci. Soc. Am. Proc.* Vol. 33, pp. 242-247.
- GAINES, G.L. & THOMAS, H.C. (1953): Adsorption Studies on Clay Minerals. II. A Formulation of the Thermodynamics of Exchange Adsorption. *J. Chem. Physics*. Vol. 21, pp. 714-718.
- GILBERT, M. & LAUDELOUT, H. (1965): Exchange properties of hydrogen ions in clays. *Soil Sci.* Vol. 100, pp. 157-162.
- GORGEON, L. (1994): Contribution à la modélisation physico-chimique de la rétention de radioéléments à vie longue par des matériaux argileux. Ph.D. dissertation. Université Paris 6.

- GRIM, R.E. (1953): Ion exchange. In Clay Mineralogy, Chap. 7, Mc Graw Hill.
- MAES, A. & CREMERS, A. (1986): High Selective Ion Exchange in Clay Minerals and Zeolites. In: DAVIS J.A. & HAYES, K.F. (eds.): Geochemical Processes at Mineral Surfaces. ACS Symposium Series 323, pp. 254-295.
- MÖRI, A. & ADLER, M. (1996): Small Scale Mapping of Niches. Mt. Terri Project Technical Note 96-02, Wettingen.
- Mt. TERRI PROJECT (1996): International Research Project in the Mt. Terri Reconnaissance Tunnel for the Hydrogeological, Geochemical and Geotechnical Characterisation of an Argillaceous Formation (Opalinus Clay). Programme Overview, Work Programme of Phase 2, Wettingen.
- PEARSON, Jr., F.J. (1997): What is the Porosity of a Mudrock? Submitted for publication in Proceedings of a Meeting on Mudrocks at the Basin Scale: Properties, Controls and Behaviour. Geological Society of London Special Publication.
- PEARSON, Jr., F.J., & BERNER, U. (1991): Nagra Thermochemical Data Base I. Core Data. Nagra Tech. Ber. NTB 91-17. Nagra, Wettingen.
- PEARSON, Jr., F.J., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Tech. Ber. NTB 91-18. Nagra, Wettingen.
- PLEYSIER, J., JANSSENS, J. & CREMERS, A. (1986): A Clay Suspension Stability End Point Titration Method for Measuring Cation Exchange Capacity of Soils. Soil Sci. Soc. Am. J. Vol. 50, pp. 887-891.
- VANSLOW, A.P. (1932): Equilibria of the Base-Exchange Reactions of Bentonites, Permutites, Soil Colloids and Zeolites. Soil Science. Vol. 33, pp. 95-113.
- WESTALL, J., ZACHARA, J.L. & MOREL, F. (1976): MINEQL: A Computer Programme for the Calculation of Chemical Equilibrium Composition of

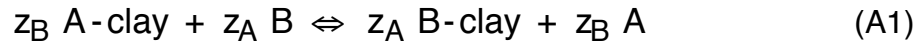
Aqueous Systems. Report Technical Note 18. Massachusetts Institute of Technology, Cambridge.

WOLLAST, R. (1990): Rate and Mechanism of Dissolution of Carbonates in the System $\text{CaCO}_3\text{-MgCO}_3$. In: STUMM, W. (ed.): Aquatic Chemical Kinetics. Wiley Interscience, New York.

YARIV, S. & CROSS, H. (1979): Geochemistry of Colloid Systems. Springer-Verlag, Berlin.

APPENDIX: INTRODUCTION OF CATION EXCHANGE INTO GEOCHEMICAL COMPUTER CODES

A stoichiometric cation exchange reaction involving cations A and B, with valence z_A and z_B respectively, can be written as:



The species in Eqn. A1 are treated in geochemical codes as if they are in the aqueous phase and hence all quantities, including those associated with the solid phase, should be represented in terms of activities. However, since little or no reliable surface activity coefficient data are available, these parameters are normally taken to be unity by convention. The mass action equation corresponding to reaction A1 is then,

$${}^B_A K_{\text{ex}} = \frac{(Q_B)^{z_A}}{(Q_A)^{z_B}} \cdot \frac{(a_A)^{z_B}}{(a_B)^{z_A}} \quad (\text{A2})$$

where K_{ex} is an exchange coefficient, "a" terms are solution activities and "Q" terms are sorbed quantities expressed on a molar scale. It is important to realise that exchange coefficients as defined in Eqn. A2, cannot, a priori, be treated as constants, as will be shown below.

Exchange coefficients (see for example BENSON, 1982; FLETCHER & SPOSITO, 1989) required as input parameters in geochemical codes are most commonly derived from selectivity coefficients (VANSLOW, 1932, GAINES & THOMAS, 1953) determined from cation exchange experiments. Extensive compilations of selectivity coefficient values for a multitude of cation - clay mineral combinations already exist in the open literature (BRUGGENWERT & KAMPHORST, 1982). Also, the selectivity concept is one which has stood the test of time and enabled cation exchange processes to be described and quantified over a wide range of experimental conditions.

Selectivity coefficient values, K_C , defined on a fractional equivalent scale (see section 6.1) are favoured here over those defined on a fractional molar scale because in the former case a constant CEC can be used in the calculations

and exchange coefficients can be simply deduced from selectivity coefficients via Eqn. A7, see below. An implicit assumption in the calculations is that selectivity coefficients as defined in section 6.1 are constants over the ranges of cation occupancies considered. (See for example BRUGGENWERT & KAMPHORST, 1982).

If the selectivity coefficient for Eqn. A1, ${}^B_A K_C$, is defined as (see section 6.1):

$${}^B_A K_C = \frac{(N_B)^{z_A}}{(N_A)^{z_B}} \cdot \frac{(a_A)^{z_B}}{(a_B)^{z_A}} \quad (A3)$$

then a comparison with Eqn. A2 shows that the ${}^B_A K_{ex}$ parameter is obtained by converting sorbed quantities from an equivalent fractional scale to a molar concentration scale.

For a cation exchange capacity of "CEC" equiv. g⁻¹ and a sorbent concentration in the experiment of "S" g L⁻¹, the effective concentration of cation B sorbed on the solid, Q_B, expressed in mol L⁻¹, is then

$$Q_B = N_B \cdot \frac{CEC}{z_B} \cdot S \quad (A4)$$

from which:

$$N_B = Q_B \cdot \frac{z_B}{CEC} \cdot \frac{1}{S} \quad (A5)$$

Similarly:

$$N_A = Q_A \cdot \frac{z_A}{CEC} \cdot \frac{1}{S} \quad (A6)$$

Hence,

$${}^B_A K_{ex} = {}^B_A K_C \cdot \left(\frac{z_A}{z_B}\right)^{z_B-z_A} \cdot \left(\frac{1}{CEC}\right)^{z_B-z_A} \cdot \left(\frac{1}{S}\right)^{z_B-z_A} \quad (A7)$$

Eqn. A7 shows that the exchange coefficients derived from K_C values cannot generally be regarded as constants. They are related to the corresponding selectivity coefficient via the cation exchange capacity of the solid phase, the valences of the exchanging cations and the solid to liquid ratio. The sorbent concentration (S:L ratio) is a parameter required by the codes to carry out the

calculations, and normally its value can be arbitrarily chosen. However, the K_{ex} values must be compatible with the chosen sorbent concentrations as defined in Eqn. A7. In the case of homovalent exchange, the exchange coefficient is equal to the selectivity coefficient and only in this case may its value be taken as a constant.

NAGRA NTB 97-07/ADD

Addendum to

**Derivation of In Situ Opalinus Clay Porewater
Compositions from Experimental and Geochemical
Modelling Studies**

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1 BACKGROUND

Because of the very low permeability of the Opalinus Clay and similar argillaceous formations, samples of porewater cannot be collected by the methods conventionally used for groundwater sampling. The hydrochemical program at Mont Terri has therefore focused on unconventional methods for characterising porewater. Some water samples have been collected for analysis by squeezing porewater from core samples at high pressure and by allowing formation water to seep slowly into sealed sections of boreholes. In addition, a water composition has been proposed based on geochemical modelling using laboratory-determined properties of the Opalinus Clay (BRADBURY & BAEYENS 1997a). A synthesis of this combination of field and laboratory procedures leads to useful understanding of Opalinus Clay porewater chemistry (PEARSON et al. 1998).

The modelled water composition (BRADBURY & BAEYENS 1997a) is notable for having much lower pH values (~6 versus ~8) and higher calculated P_{CO_2} values (~1 bar versus $10^{-3.5}$ bar) than any of the measured water samples. This was attributed to the loss of CO_2 during the slow accumulation of water in the sealed boreholes or during the squeezing process. Based on this modelled water composition, artificial waters used in certain borehole experiments at Mont Terri were designed to have P_{CO_2} values of about 1 bar (PEARSON 1998a).

As part of a synthesis of water chemistry studies at Mont Terri, a re-examination of the modelling method showed that it should lead to a range of water compositions rather than to a single composition. The single composition resulted from two compensating oversights, a theoretical one and a modelling one. These are discussed in this Addendum.

2 THEORY

The basis of the method is the widely accepted and frequently demonstrable concept that the chemistry of a porewater can be usefully considered as the result of chemical equilibrium between the water and the minerals of its host rock. For illustrative purposes, we can consider H^+ (the pH), Na^+ , Ca^{2+} , CO_2 (tot) (total dissolved carbonate), and Cl^- as a minimum group of constituents necessary to define the major porewater chemistry in this system. The Opalinus Clay itself contains calcite ($CaCO_3$) and clay minerals on which Na^+ and Ca^{2+} cation exchange reactions occur. In the original report (BRADBURY & BAEYENS 1997a), the system was explored using the phase rule, but it can also be viewed, with perhaps greater clarity, by directly considering the algebra of equations describing the system.

Solutions must be electrically neutral, so we can write the charge balance equation:

$$m_{H^+} + m_{Na^+} + 2m_{Ca^{2+}} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} + m_{Cl^-} \quad (1)$$

where m_i is the concentration of the dissolved constituent in moles per unit solution.

Several mass-action equations also apply to the solution at equilibrium:

Hydrolysis of water:

$$K_{H_2O} = a_{H^+} \cdot a_{OH^-} \quad (2)$$

Calcite solubility:

$$K_{CaCO_3} = a_{Ca^{2+}} \cdot a_{CO_3^{2-}} \quad (3)$$

Bicarbonate dissociation:

$$K_{HCO_3^-} = \frac{a_{H^+} \cdot a_{CO_3^{2-}}}{a_{HCO_3^-}} \quad (4)$$

Cation exchange:

$$K_{\text{ex}}^{\text{Ca/Na}} = \frac{a_{\text{Ca-X}}}{(a_{\text{Na-X}})^2} \cdot \frac{(a_{\text{Na}})^2}{a_{\text{Ca}}} \quad (5)$$

In these equations, a_{i-X} is the activity of the constituent on the exchanger and, a_i is the thermodynamic activity of the dissolved constituents.

Activities and concentrations of dissolved constituents are related by:

$$a_i = m_i \cdot \gamma_i \quad (6)$$

where γ_i is the activity coefficient. This quantity can be found at any stage of the calculation by the application of, for example, Pitzer theory or an ion-pairing model. If the latter formulation is used, ion pairs such as NaHCO_3^0 must also be included in the charge balance equation. However, for each such ion pair there will be an additional mass action equation. It is also assumed that the values of the equilibrium constants, K , in the mass action equations, are known at the temperature and pressure of the system. Finally, it is assumed that the ratio of the activities of the constituents on the exchanger, $a_{\text{Ca-X}}/(a_{\text{Na-X}})^2$, is the same as the ratios of their equivalent fractional occupancies on the exchanger, $N_{\text{Ca-X}}/(N_{\text{Na-X}})^2$, and that these occupancies are known.

The unknowns in the systems are the concentrations of the seven constituents included in Eq. (1), the charge-balance equation. The system is described by five equations, the charge-balance equation and the four mass action Eqs. (2) through (5). If the Cl^- concentration is specified, the number of unknowns is reduced to six, but there is still one more unknown than there are equations. Thus, the system must be univariant.

We now re-examine the application of the phase rule to the system :

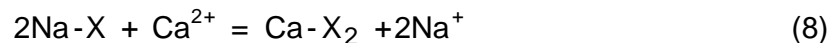
$$F = C - P + 2 \quad (7)$$

where C is the number of components in the system, F is its number of degrees of freedom, and P the number of phases. In this illustrative case, the components are taken to be the same five dissolved constituents H^+ (the pH), Na^+ , Ca^{2+} , CO_2 (tot) (total dissolved carbonate), and Cl^- . In the original report,

four phases were considered: the solution itself, calcite and fixed sodium and calcium occupancies on the Opalinus Clay. This led to a system with three degrees of freedom, two of which can be identified with the temperature and pressure of the solution. The values of these two constraints are known and if the Cl^- content of the porewater is specified, the system has zero degrees of freedom, that is, it is invariant.

The system actually modelled included the additional four dissolved constituents (components): K^+ , Mg^{2+} , SO_4^{2-} and F^- . Each of these additional components was identified with an additional fixed parameter (the SO_4^{2-} concentration) or phase (fluorite, CaF_2 for F^- , dolomite, $\text{CaMg}(\text{CO}_3)_2$ for Mg^{2+} and a fixed loading of K^+ on the exchanger for K^+). Thus it would be only a trivial extension of the argument given here involving five components to cover the full nine components considered in the original report. Note that in the Opalinus Clay, a Mg^{2+} -exchanger could also be chosen as the controlling phase for Mg^{2+} . However, as discussed by BRADBURY & BAEYENS (1997a), the assumption of dolomite saturation was used in developing the Mg^{2+} cation exchange data for the system. Thus, Mg^{2+} exchange and dolomite solubility cannot be considered as separate constraints on the system.

In BRADBURY & BAEYENS (1997a), the Na^+ , Ca^{2+} (and K^+) occupancies were treated as separate phases because, in the derivation of the phase rule from more fundamental thermodynamic equations, a "phase" can be formally identified with a controlling equation (ANDERSON & CRERAR 1993). However, cation exchange reactions are described by equations such as:



on which the mass action Eq. (5) above, is based. But both Na^+ and Ca^{2+} exchange are described by a single equation and together represent only a single phase in the phase rule. Thus, phase rule considerations also lead to the conclusion that the system has one degree of freedom, or is univariant.

3 MODELLING

The equations describing the system are most conveniently solved using one of the geochemical solution modelling programs that have so advanced our understanding of aqueous geochemistry during the past 25 years. The calculations in the original report were made using MINSORB (BRADBURY & BAEYENS 1997b) an extended version of MINEQL (WESTALL et al. 1976). The re-examination described here was prompted by the observation that when the system was modelled with PHREEQC (PARKHURST 1995) the results differed from the MINSORB results. Also, the MINSORB modelling led to a single water composition, consistent with the phase rule considerations in the original report, while the PHREEQC modelling led to a range of solution compositions. The PHREEQC calculations of a range of compositions are consistent with the re-examination of the algebraic and phase rule descriptions of the system given above. To account for the fact that the MINSORB calculations led to a single water composition requires consideration of the details of how that program was used.

Figure 1 illustrates the range of compositions calculated by PHREEQC for the illustrative system: H^+ , Na^+ , Ca^{2+} , CO_2 (tot), and Cl^- . The modelling used the same NAGRA thermochemical data base (PEARSON & BERNER 1991, PEARSON et al. 1992) as used in the original report, and the same system constraints. These include a fixed Cl^- concentration of 0.3 M and populations of exchangeable ions on exchange sites and exchange equilibrium constants as given in Tables 7 and 8 (for Case I) respectively of BRADBURY & BAEYENS (1997a). In Figure 1 the water composition and its pH and $\log P_{CO_2}$ values are plotted against the CO_2 (tot) of the water.

The trends shown in Figure 1 follow directly from the constraints on the system. The Cl^- is specified to be constant at 0.3 M over the entire range of CO_2 (tot) concentrations. Na^+ is the dominant cation and is virtually constant throughout at a concentration slightly below that of Cl^- , as required for solution charge balance. The effect of cation exchange is to keep the ratio $a_{Ca}/(a_{Na})^2$ constant for the fixed measured exchangeable ion occupancies of the formation (Eq. 5).

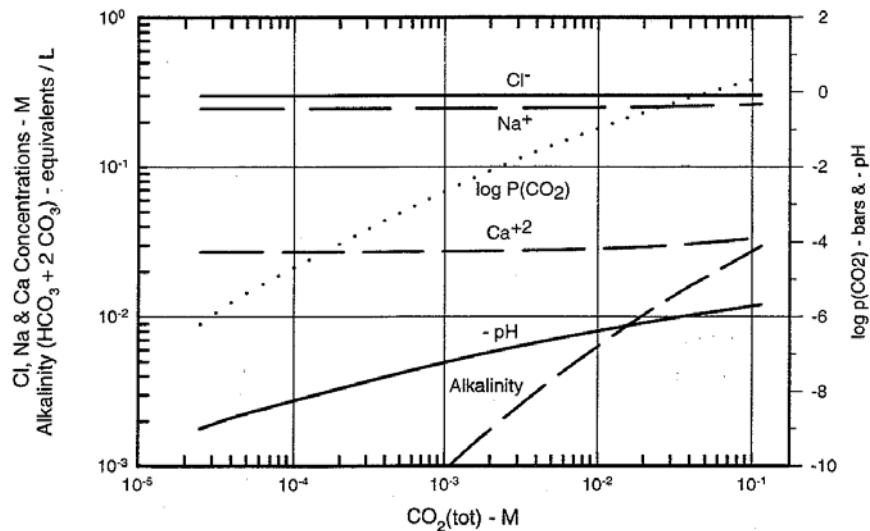


Figure 1: Range of compositions of water based on geochemical modelling described in section 3.

As Na^+ is virtually constant, so is Ca^{2+} , except at the highest $\text{CO}_2(\text{tot})$ values where both increase slightly for the reason given below. Because calcite saturation is specified, a virtually constant Ca^{2+} concentration leads to a virtually constant CO_3^{2-} concentration. A constant CO_3^{2-} exists over a wide range of $\text{CO}_2(\text{tot})$ values if the pH varies to change the proportions of $\text{CO}_2(\text{aq})$, HCO_3^- and CO_3^{2-} which make up the $\text{CO}_2(\text{tot})$.

Higher $\text{CO}_2(\text{tot})$ contents require higher HCO_3^- contents, which lead to lower pH values according to Eq. (4), and to a corresponding increase in P_{CO_2} . At the highest $\text{CO}_2(\text{tot})$ values the alkalinity ($\text{HCO}_3^- + 2 \text{CO}_3^{2-}$) is high enough that one sees the slight increase in Na^+ (and accordingly Ca^{2+}) needed to maintain solution charge balance.

The actual modelling by PHREEQC can be performed in a number of ways. For example, one can begin with a 0.3 M NaCl solution with pH constrained by the requirement for charge balance. This solution can then be brought to equilibrium with calcite and with an excess of a Na/Ca exchanger of the required properties. Adding varying amounts of CO_2 to the solution while maintaining these equilibria and constraining pH by charge balance lead to the range of solutions shown in Figure 1. The same range of solutions can be

calculated from a starting solution of 0.15 M CaCl₂ or from NaCl or CaCl₂ solutions with arbitrary quantities of NaHCO₃. A property of an equilibrium state is that its composition is independent of the path by which it is approached: "All roads lead to Rome."

The modelling described by BRADBURY & BAEYENS (1997a) using MINSORB is apparently identical to that just described for PHREEQC. However, the way MINEQL was actually used forced a specific CO₂(tot) concentration on the system and led to only a single water composition. In the MINSORB modelling, the source of all Ca²⁺ in the system (required to maintain a fixed Na/Ca ratio in the water) was calcite dissolution (and fluorite dissolution in the larger model). This introduced an equivalent amount of CO₂(tot) into the system fixing its concentration. Determining CO₂(tot) this way removed the last degree of freedom of the calculation and led to the invariant water composition. Because the phase rule as originally applied also predicted an invariant composition, there was no reason to question the modelling results.

In a subsequent publication (BRADBURY & BAEYENS 1998) the above considerations were included in the geochemical modelling and the Opalinus Clay/porewater system was treated as being univariant as described in the following section.

4 CALCULATED OPALINUS CLAY POREWATER COMPOSITIONS

The interesting conclusion to emerge from the analysis given above is that even for a system as well characterised as the one described in BRADBURY & BAEYENS (1997a, 1998), a unique Opalinus Clay porewater chemistry cannot be calculated using only the type of laboratory investigations discussed in these reports. Either the H^+ activity or C_{tot} or HCO_3^- or the P_{CO_2} needs to be defined in addition. (Fixing any one of these parameters fixes the others in the calculations.) The carbonate- CO_2 -water equilibrium is critical since it determines the pH. Herein lies a major difficulty. In tight low porosity argillaceous rock formations it may be physically impossible to collect water samples on which reliable pH or carbonate measurements can be made. Even in cases where groundwater samples are available, large uncertainties are often associated with measurements of the above parameters because of effects such as contamination and de-gassing. Thus, some of the most important groundwater parameters are the most difficult to reliably determine and are consequently the least well known.

In the modelling described in section 3, the Cl^- concentration in the system was fixed at the value measured in several samples of Opalinus Clay water taken in the field from sealed boreholes and in the laboratory from high-pressure squeezing of core samples. Even when Cl^- concentrations in the porewater are not known, the calculations described below can still be carried out based on a knowledge of the Cl^- content of the rock and the geochemical porosity (PEARSON 1998b).

In order to calculate an Opalinus Clay porewater chemistry an additional component value is still required. If such a value is absent then the best that can be done is to bound likely Opalinus Clay porewater compositions by taking a range of values for the missing parameter. This is what has been done for the calculated data given in Tables I and II below.

In Table I the porewater compositions are given over a range of porosity values for a fixed P_{CO_2} of 10^{-2} bar. The major cation and anion concentrations, and hence the ionic strength, scale approximately inversely with the porosity, as would be expected. The exceptions to this are the carbonate species and SO_4^{2-} . At a fixed CO_2 partial pressure the HCO_3^- , CO_3^{2-} and total inorganic carbon

concentrations increase with increasing porosity to compensate for the decreasing Ca^{2+} and Mg^{2+} concentrations under the constraint of calcite and dolomite saturation. Note that in the calculations Mg concentrations could either be fixed over dolomite saturation or over the Mg loading in Opalinus Clay and the Mg-Na selectivity coefficient, see BRADBURY & BAEYENS (1997a, 1998)

Table I: Calculated Opalinus Clay porewater compositions at 8, 10, 12 and 14% porosities for a $P_{\text{CO}_2} = 10^{-2}$ bar (BRADBURY & BAEYENS, 1998).

Porosities	8%	10%	12%	14%
pH	6.83	6.90	6.95	7.00
Ionic strength (M)	0.49	0.40	0.34	0.30
<u>Concentration: (M)</u>				
Na	2.95×10^{-1}	2.53×10^{-1}	2.25×10^{-1}	2.04×10^{-1}
K	6.6×10^{-3}	5.7×10^{-3}	5.2×10^{-3}	4.7×10^{-3}
Mg	3.1×10^{-2}	2.3×10^{-2}	1.9×10^{-2}	1.6×10^{-2}
Ca	4.0×10^{-2}	3.1×10^{-2}	2.5×10^{-2}	2.1×10^{-2}
Sr	3.6×10^{-4}	2.7×10^{-4}	2.2×10^{-4}	2.0×10^{-4}
Cl^-	3.94×10^{-1}	3.11×10^{-1}	2.56×10^{-1}	2.16×10^{-1}
F^-	1.1×10^{-4}	1.2×10^{-4}	1.3×10^{-4}	1.3×10^{-4}
SO_4^{2-}	2.3×10^{-2}	2.7×10^{-2}	3.0×10^{-2}	3.3×10^{-2}
HCO_3^-	1.4×10^{-3}	1.6×10^{-3}	1.8×10^{-3}	2.0×10^{-3}
CO_2 (tot)	2.2×10^{-3}	2.4×10^{-3}	2.5×10^{-3}	2.7×10^{-3}
Si	2.8×10^{-4}	2.8×10^{-4}	2.8×10^{-4}	2.8×10^{-4}

The value chosen for the Opalinus Clay porosity in the range considered has only a minor influence on the calculated pH. For porosities from 8 to 14%, the measured sulphate inventories lead to the conclusion that the Opalinus Clay porewaters are saturated with gypsum. However, although stringent precautions were taken to minimise the contact of the samples with air, rapid oxidation of a very reactive part of the pyrite cannot be completely ruled out, and part of the SO_4^{2-} levels measured could have come from this source.

In Table II a best estimate porosity value of 11% is taken and the P_{CO_2} varied from 10^{-3} to 10^{-1} bar. For this range of CO_2 partial pressures, the calculations indicate virtually no influence on the major anion and cation concentrations, but

the pH changes from ~7.4 to ~6.4. While the CO_3^{2-} concentration remains essentially unchanged, since it is fixed by a constant Ca^{2+} concentration and the calcite saturation condition, the HCO_3^- concentration increases ten-fold from $\sim 5 \times 10^{-4}$ to $\sim 5 \times 10^{-3}$ M in response to the increased carbonic acid in the system.

Table II: Calculated Opalinus Clay porewater compositions at a P_{CO_2} of 10^{-1} , 10^{-2} and 10^{-3} bar and a porosity of 11% (BRADBURY & BAEYENS, 1998).

P_{CO_2} (bar)	10^{-1}	10^{-2}	10^{-3}
pH	6.43	6.93	7.43
Ionic strength (M)	0.37	0.37	0.37
<u>Concentration: (M)</u>			
Na	2.39×10^{-1}	2.38×10^{-1}	2.37×10^{-1}
K	5.4×10^{-3}	5.4×10^{-3}	5.4×10^{-3}
Mg	2.1×10^{-2}	2.1×10^{-2}	2.1×10^{-2}
Ca	2.8×10^{-2}	2.7×10^{-2}	2.7×10^{-2}
Sr	2.5×10^{-4}	2.4×10^{-4}	2.4×10^{-4}
Cl^-	2.80×10^{-1}	2.80×10^{-1}	2.80×10^{-1}
F^-	1.2×10^{-4}	1.2×10^{-4}	1.2×10^{-4}
SO_4^{2-}	2.8×10^{-2}	2.9×10^{-2}	2.9×10^{-2}
HCO_3^-	5.5×10^{-3}	1.8×10^{-3}	5.5×10^{-4}
CO_2 (tot)	1.0×10^{-2}	2.5×10^{-3}	7.2×10^{-4}
Si	2.9×10^{-4}	2.8×10^{-4}	2.9×10^{-4}

Thus the physico-chemical characterisation and geochemical modelling approach described in BRADBURY & BAEYENS (1997a,1998) can provide important information on the likely major cation and anion porewater concentrations in argillaceous rocks. The approach may be of particular relevance when, for whatever reason, reliable porewater samples cannot be collected. However, the key system parameters $\text{pH}/P_{\text{CO}_2}$ cannot be determined.

Additional field and laboratory data on the Opalinus Clay have become available from the Mont Terri project which make it possible to constrain the

range of water compositions more tightly than may appear in this report or in BRADBURY & BAEYENS (1997a, 1998). As mentioned, the Cl^- content is now known for water in that part of the formation from which the sample described by BRADBURY & BAEYENS (1997a, 1998) was taken. Likewise, field pH measurements and interpretative modelling, although not unequivocal, strongly indicate that the P_{CO_2} in this region is below $10^{-3.5}$ bar. Finally, consistent differences between modelled and measured values for K^+ concentrations suggest that the population of exchangeable K^+ given in BRADBURY & BAEYENS (1997a, 1998) may not completely match the K^+ population available for water-rock reactions *in situ*. A synthesis of field data and modelling, including the application of the technique presented in BRADBURY & BAEYENS (1997a), is given by PEARSON et al. (1998). This describes the present state of knowledge of the water chemistry in the Opalinus Clay.

Acknowledgements

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5 REFERENCES

- ANDERSON, G. M. & CRERAR, D. A. (1993): Thermodynamics in Geochemistry: The Equilibrium Model. Oxford University Press. Oxford.
- BRADBURY, M.H. & BAEYENS, B. (1997a): Derivation Of In Situ Opalinus Clay Porewater Compositions From Experimental And Geochemical Modelling Studies" PSI Bericht Nr. 97-14. Paul Scherrer Institut, Villigen. Nagra Tech. Ber. NTB 97-07. Nagra, Wettingen.
- BRADBURY, M.H. & BAEYENS, B. (1997b): A Mechanistic Description of Ni and Zn Sorption on Na-Montmorillonite. Part II: Modelling. Journal of Contaminant Hydrology Vol. 27, pp. 223-248.
- BRADBURY, M.H. & BAEYENS, B. (1998): A physico-chemical characterisation and geochemical modelling approach for determining porewater chemistries in argillaceous rocks. Geochimica et Cosmochimica Acta Vol. 62, pp. 783-795.
- PARKHURST, D.L. (1995): PHREEQC - A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations. U.S Geological Survey, Water-Resources Investigations Report 95-4227.
- PEARSON, Jr., F.J., & BERNER, U. (1991): Nagra Thermochemical Data Base I. Core Data. Nagra Tech. Ber. NTB 91-17. Nagra, Wettingen.
- PEARSON, Jr., F.J., BERNER, U. & HUMMEL, W. (1992): Nagra Thermochemical Data Base II. Supplemental Data 05/92. Nagra Tech. Ber. NTB 91-18. Nagra, Wettingen.
- PEARSON, F. J. (1998a): Artificial Waters for Use in Laboratory and Field Experiments with Opalinus Clay: Status June 1998. Paul Scherrer Institut TM 98-44-08.
- PEARSON Jr. F.J. (1998b) What is the porosity of a mudrock? Submitted for publication in Proceedings of a Meeting on Mudrocks at the Basin Scale: Properties, Controls and Behaviour. Geological Society of London Special Publication.

PEARSON, F. J., SCHOLTIS, A. & GAUTSCHI, A. (1998): Hydrochemistry. *In* THURY, M. & BOSSART, P. (eds.): Results of the hydrogeological, geochemical, and geotechnical experiments performed in the Opalinus Clay (1996-1997): Bern, Geologische Bericht der Landeshydrologie und -geologie (*in prep.*)

WESTALL, J., ZACHARA, J.L. & MOREL, F. (1976): MINEQL - A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems. Massachusetts Institute of Technology, Cambridge, Report Technical Note 18.