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Addendum to

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

M. H. Bradbury, B. Baeyens, F. J. Pearson, U. Berner

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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 Cooperative 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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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).

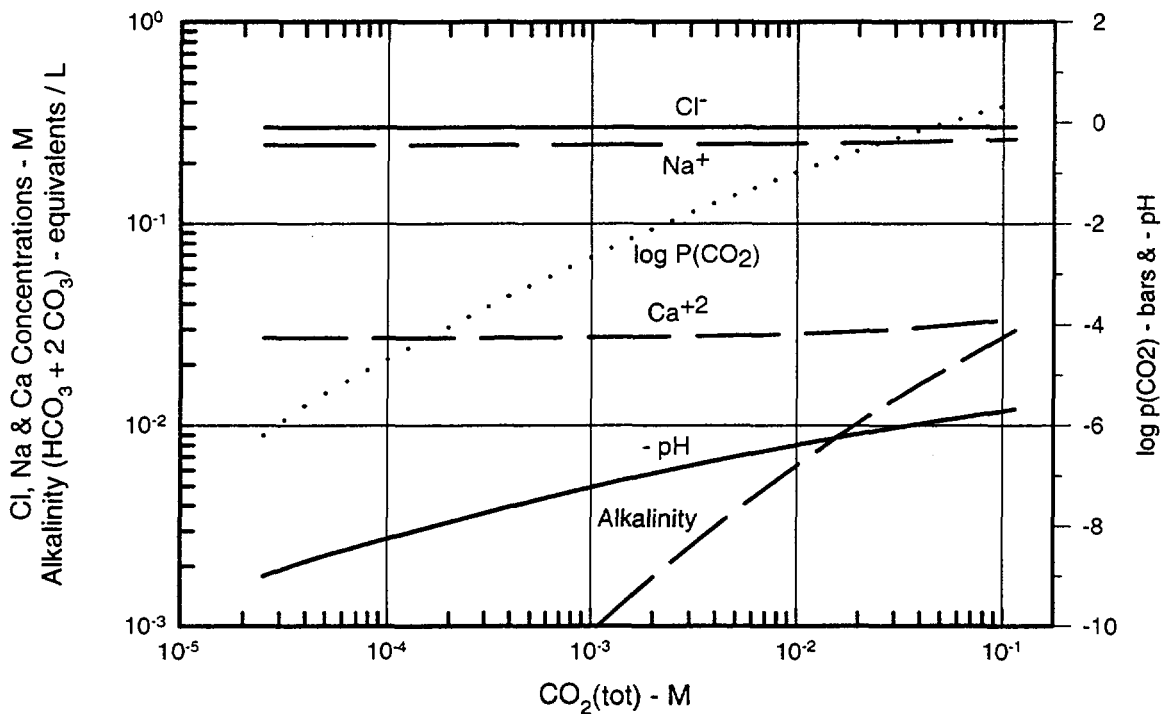


Figure 1: Range of compositions of water based on geochemical modelling described in section 3.

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 CaCl_2 or from NaCl or CaCl_2 solutions with arbitrary quantities of NaHCO_3 . 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 $\text{CO}_2(\text{tot})$ concentration on the system and led to only a single water composition. In the MINSORB modelling, the source of all Ca^{2+} 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 $\text{CO}_2(\text{tot})$ into the system fixing its concentration. Determining $\text{CO}_2(\text{tot})$ 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 pH/ P_{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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