

TECHNICAL REPORT 94-22

Physico-Chemical Characterisation and Calculated In Situ Porewater Chemistries for a Low Permeability Palfris Marl Sample from Wellenberg

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ABSTRACT

Wellenberg (Gemeinde Wolfenschiessen, NW) has been chosen by Nagra as a repository site for short lived low- and medium-level radioactive waste. In certain regions of this Palfris marl formation, foreseen as actual locations for the repository, the water flow rates are so low that reliable water samples for chemical analysis were not obtainable. A sample of Palfris marl (SB1-535.83) was provided from such a region and a physico-chemical characterisation technique, developed and tested in previous work, was applied. The measurements, coupled with a geochemical modelling study, yielded a NaCl type porewater with an ionic strength of ~ 0.12 M. In addition, a matrix marl porosity of $\sim 1.5\%$ was deduced using the chloride concentrations in the calculated porewater and measurements on the chloride content of marl.

ZUSAMMENFASSUNG

Der Wellenberg (Gemeinde Wolfenschiessen, NW) wurde von der Nagra als potentieller Standort für ein Endlager für schwach- und mittelaktiven Abfall gewählt. Das Endlager wird sich in der Palfris-Formation, einem Mergel befinden. Aus den bisherigen Sondierbohrungen in diesen hydraulisch sehr dichten Bereichen der Palfris-Formation konnten nur wenige Grundwasserproben, die zudem noch stark durch Bohrspülung kontaminiert waren, gewonnen werden. Deshalb wurden an einer Gesteinsprobe (SB1-535.83) physikalisch-chemische Untersuchungen vorgenommen, um die Beschaffenheit des Grundwassers zu bestimmen. Die verwendeten Untersuchungsmethoden und Techniken wurden schon in früheren Arbeiten entwickelt und getestet. Die Messungen, zusammen mit geochemischen Modellierungen ergaben einen NaCl Grundwassertyp mit einer Ionenstärke von ~ 0.12 M. Aus den modellierten Chlorid-Konzentrationen des Grundwassers und den Chlorid-Gehalten im Mergel kann auf eine Porosität der Mergelmatrix von ca. 1.5% geschlossen werden.

RÉSUMÉ

Le Wellenberg (Commune de Wolfenschiessen, NW) a été choisi par la Cédra comme site de dépôt final pour les déchets de faible et moyenne activité à vie courte. Dans certaines régions de cette formation de marnes de Palfris, effectivement prévues pour l'implantation du dépôt final, la circulation d'eau est si faible qu'il n'est pas possible d'y prélever des échantillons d'eau fiables pour analyse chimique. Un échantillon de marnes de Palfris provenant d'une telle zone (SB1-535.83) a été soumis à une technique de caractérisation physico-chimique développée et testée lors de travaux antérieurs. Les mesures effectuées, combinées avec une étude de modélisation géochimique, ont montré que l'eau interstitielle est de type NaCl et de force ionique de ~ 0.12 M. On a de plus déduit une porosité matricielle de la marne de $\sim 1.5\%$ en utilisant les concentrations de chlorures dans l'eau interstitielle calculée et des mesures de teneurs de chlorures de la marne.

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1 INTRODUCTION

Nagra has selected Wellenberg (Gemeinde Wolfenschiessen, NW) as a repository site for short lived low- and medium-level radioactive waste. The current proposal is to construct the repository in a region of the Palfris marl formation where groundwater flow rates are very low. The hydraulic conductivity in these selected regions is so low that reliable water samples for chemical analysis could not be collected during the last drilling campaign (NAGRA 1993).

The groundwater chemistry in the host rock formation surrounding the repository constitutes an important basic data set in safety analysis studies. Since this information could not be obtained from in situ water sampling campaigns and since it was necessary to close this gap in our knowledge of the geochemical conditions at Wellenberg, a laboratory study was undertaken to deduce an in situ porewater composition. This study was based on physico-chemical characterisation procedures developed in some previous work on samples of Valanginian marl obtained from the Seelisberg Tunnel region at Oberbauenstock (BAEYENS & BRADBURY 1991).

2 MATERIALS AND METHODS

2.1 Mineralogy of Sample SB1-535.83

The sample used in these experiments was taken from cores obtained from borehole SB1 drilled at Wellenberg in March 1991 and provided in the form of a ball milled whole rock powder (particle size < 63 μm) by Dr. M. Mazurek, University of Bern, in April 1994. During the interval between these two dates, no special precautions regarding storage were taken other than that the whole cores were stored under dry conditions. The crushing and milling operations were carried out under atmospheric conditions.

The shaly marl specimen was taken from unfractured matrix rock, away from water conducting features, in the Palfris-Formation. The mineralogical composition of the sample obtained from X-ray-diffraction data and coulomat measurements is given in Table 1.

Table 1: Mineralogical composition of marl sample SB1-535.83
(MAZUREK, pers. comm.)

Mineral	Weight %
Calcite	40
Dolomite/ankerite	5
Quartz	9
K-feldspars	< 1
Albite	<1
Pyrite	1.5
Organic carbon	1.0
<u>Sheet silicates:</u>	
Illite	18
Illite/smectite mixed layers	15
Chlorite	10

2.2 Analytical Methods

Aqueous concentrations of Na, K, Mg, Ca, Sr and Ni were determined by plasma-emission spectroscopy (Applied Research Laboratory ARL 3410D ICP-AES).

The anions F⁻, Cl⁻ and SO₄²⁻ were analysed using an ion chromatograph (Dionex DX500). Alkalinity measurements were made on a Metrohm Titroprocessor 660.

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

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

The O₂ and CO₂ contents in the atmosphere controlled glove boxes were measured on line with gas analysers supplied by Teledyne and Servomex, respectively. The O₂ and CO₂ levels in the glove boxes were generally below 5 ppm.

3 BRIEF OVERVIEW OF THE METHOD

A physico-chemical characterisation procedure for determining porewater chemistries in argillaceous rocks has been developed (BAEYENS & BRADBURY 1991). 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. The first consists of an aqueous extraction, in which crushed rock samples are contacted with de-ionised water at a series of high solid to liquid 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 (if any) present in the marl, 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 marl.

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.

4 AQUEOUS EXTRACTION TESTS

4.1 Experimental Procedure

The aqueous extractions were carried out in glove boxes under an inert N₂ atmosphere in order to avoid any oxidation of pyrite present in the marl (see Table 1). In a separate study (BAEYENS & BRADBURY, unpublished results) it was clearly demonstrated that extractions made under atmospheric conditions led to extensive oxidation of pyrite.

Crushed marl samples were dispersed in de-ionised water at the four different solid to liquid (S:L) ratios given in Table 2.

Table 2: Solid to liquid ratios in the aqueous extraction tests

S:L ratio (gram litre ⁻¹)	Amount of marl (gram)	Volume of water (ml)
2000	40	20
1000	25	25
750	22.5	30
500	15	30

Extraction tests were performed in duplicate for equilibration times of 1, 3, 7 and 28 days. The marl/water suspensions were agitated on an end-over-end shaker. After the required contact times the individual samples were centrifuged (1 hr at 95,000 g max.) and transferred to a glove box for pH measurements. The samples were then re-centrifuged before aliquots were taken and sent for cation and anion analyses in accord with the methods listed in section 2.2.

4.2 Results and Discussion

4.2.1 Aqueous Extract Compositions

The results from the analyses of the aqueous extracts of marl for each of the four S:L ratios are summarised in Tables 3a to 3d where the data are expressed in terms of solution concentrations.

Averaged values of the duplicate samples for each time interval at the different S:L ratios are given in the tables. Concentrations in the duplicate solutions generally agreed to better than 10%.

Comparison of the 1, 3, 7 and 28 day data sets indicates that there were no significant kinetic effects w.r.t. the ion concentrations and constant values were reached after one day. Consequently, for each S:L ratio the duplicate measurements over the four time intervals were averaged and these data are given in the final column of the tables together with calculated standard deviations (s dev). The ion balances at the different S:L ratios are better than 2%.

It is interesting to note that the water generated in these aqueous extraction experiments is essentially a low ionic strength Na-HCO₃ type water. In systems containing calcite and clay minerals with significant Na occupancies, this will always be so. Such a water results as a consequence of contacting marl with relatively large volumes of water (compared with the porewater volume) and the subsequent mineral dissolution/cation exchange reactions (BRADBURY et al. 1990). As will be shown later, the composition of the aqueous extracts have little or nothing to do with the actual porewater composition.

Table 3a: Ion concentrations (meq litre⁻¹) in aqueous extracts of marl after different contact times at a solid to liquid ratio of 2000 gram litre⁻¹

Element	1 day	3 days	7 days	28 days	Mean (s dev)
Na	14.3	13.9	15.0	15.7	14.7 (0.8)
K	0.29	0.31	0.28	0.25	0.28 (0.03)
Mg	0.051	0.053	0.066	0.065	0.059 (0.008)
Ca	0.133	0.120	0.124	0.123	0.125 (0.010)
Sr	0.006	0.006	0.007	0.007	0.007 (0.0005)
Σ Cations	14.8	14.4	15.5	16.1	15.2 (0.8)
F ⁻	1.00	0.96	0.97	0.92	0.96 (0.04)
Cl ⁻	1.44	1.45	1.48	1.26	1.40 (0.11)
SO ₄ ²⁻	4.15	4.19	4.58	4.30	4.30 (0.21)
Alkalinity	8.32	8.05	8.67	8.05	8.27 (0.30)
Σ Anions	14.9	14.7	15.7	14.5	14.9 (0.66)
pH	9.0	8.9	8.9	8.6	8.8 (0.2)

Table 3b: Ion concentrations (meq litre⁻¹) in aqueous extracts of marl after different contact times at a solid to liquid ratio of 1000 gram litre⁻¹

Element	1 day	3 days	7 days	28 days	Mean (s dev)
Na	10.4	10.5	10.6	11.1	10.6 (0.3)
K	0.21	0.23	0.21	0.22	0.22 (0.02)
Mg	0.031	0.033	0.044	0.043	0.038 (0.007)
Ca	0.099	0.084	0.093	0.100	0.094 (0.009)
Sr	0.004	0.004	0.004	0.004	0.004 (0.0005)
Σ Cations	10.7	10.9	11.0	11.5	11.0 (0.3)
F ⁻	0.82	0.84	0.83	0.81	0.82 (0.02)
Cl ⁻	0.70	0.73	0.71	0.60	0.68 (0.06)
SO ₄ ²⁻	2.11	2.29	2.34	2.09	2.21 (0.12)
Alkalinity	6.97	7.02	7.16	7.10	7.07 (0.19)
Σ Anions	10.6	10.9	11.0	10.6	10.8 (0.4)
pH	9.2	9.2	9.0	8.9	9.1 (0.2)

Table 3c: Ion concentrations (meq litre⁻¹) in aqueous extracts of marl after different contact times at a solid to liquid ratio of 750 gram litre⁻¹

Element	1 day	3 days	7 days	28 days	Mean (s dev)
Na	8.9	8.8	9.0	9.5	9.1 (0.3)
K	0.21	0.20	0.19	0.21	0.20 (0.01)
Mg	0.027	0.028	0.033	0.036	0.031 (0.004)
Ca	0.086	0.082	0.075	0.090	0.083 (0.008)
Sr	0.003	0.003	0.003	0.004	0.003 (0.0005)
Σ Cations	9.2	9.1	9.3	9.8	9.4 (0.3)
F ⁻	0.73	0.74	0.75	0.74	0.74 (0.03)
Cl ⁻	0.54	0.52	0.52	0.47	0.51 (0.03)
SO ₄ ²⁻	1.67	1.66	1.68	1.56	1.64 (0.06)
Alkalinity	6.52	6.36	6.42	6.50	6.45 (0.12)
Σ Anions	9.5	9.3	9.4	9.3	9.3 (0.2)
pH	9.3	9.3	9.1	9.0	9.2 (0.2)

Table 3d: Ion concentrations (meq litre⁻¹) in aqueous extracts of marl after different contact times at a solid to liquid ratio of 500 gram litre⁻¹

Element	1 day	3 days	7 days	28 days	Mean (s dev)
Na	7.3	7.2	7.6	8.0	7.5 (0.3)
K	0.20	0.18	0.17	0.17	0.18 (0.02)
Mg	0.022	0.022	0.029	0.030	0.025 (0.005)
Ca	0.070	0.071	0.068	0.084	0.073 (0.01)
Sr	0.003	0.002	0.003	0.003	0.003 (0.0005)
Σ Cations	7.6	7.5	7.9	8.3	7.8 (0.3)
F ⁻	0.62	0.61	0.62	0.59	0.61 (0.02)
Cl ⁻	0.37	0.38	0.36	0.31	0.35 (0.03)
SO ₄ ²⁻	1.13	1.10	1.22	1.02	1.12 (0.08)
Alkalinity	5.64	5.57	5.78	5.65	5.66 (0.09)
Σ Anions	7.8	7.7	8.0	7.6	7.7 (0.2)
pH	9.5	9.4	9.3	9.2	9.3 (0.2)

4.2.2 Speciation Calculations

The chemical speciation in the four aqueous extract solutions (averaged data from Tables 3a to 3d) has been calculated using the geochemical equilibrium code PHREEQE (PARKHURST et al. 1980) and the thermodynamic data base compiled by PEARSON & BERNER (1991). The aim of such calculations is to check the consistency of the analyses and to calculate saturation indices¹ (SI) of minerals which could be present in the system. The results of these model calculations for which the pH in each system was fixed at the experimentally measured value, are given in Table 4.

Table 4: Calculated saturation indices in the aqueous extracts for various minerals

Mineral	S:L Ratio (gram litre ⁻¹)			
	2000	1000	750	500
Calcite	0.20	0.24	0.25	0.26
Dolomite	0.11	0.15	0.13	0.12
Magnesite	-1.1	-1.1	-1.2	-1.2
Strontianite	-0.2	-0.3	-0.3	-0.2
Gypsum	-2.9	-3.3	-3.4	-3.6
Celestite	-2.1	-2.5	-2.7	-2.9
Fluorite	-0.3	-0.5	-0.6	-0.9

The data in Table 4 indicate that the aqueous extracts are undersaturated with respect to magnesite, strontianite, gypsum, celestite and fluorite. None of these minerals were detected in the whole rock mineralogy, Table 1. With respect to the other pure minerals listed, i.e. calcite and dolomite, all aqueous extracts are slightly oversaturated. In some previous work on samples taken from the Valanginian marl formation at Oberbauenstock, similar observations regarding the apparent oversaturation of calcite and dolomite were also made (BAEYENS & BRADBURY 1991).

¹ SI = log(IAP) - logK_{SO}, where IAP is the ion activity product and K_{SO} the solubility product

A key parameter in the speciation calculations is the pH. There is already an uncertainty of ~ 0.2 pH units between the individual measurements given in Tables 3a-3d. Further, it is well known that concentrated soil and clay suspensions exhibit the so-called "suspension effect" (see CREMERS 1972). The measured pH of a concentrated suspension is always lower than in the corresponding supernatant solution after phase separation. pH measurements on suspensions before and after centrifugation indicated that they were always 0.1 to 0.2 units lower. If the above "suspension effect", together with the uncertainty in the individual pH measurements, are taken into account, then the apparent oversaturation of calcite and dolomite in the aqueous extract disappears.

4.2.3 Chloride Extraction Data

Chloride extraction data are important because they can be used in conjunction with the derived porewater composition to estimate the in situ porosity of matrix marl, as will be shown in section 6.2.

Since all chloride salts are highly soluble, the source of chloride in the aqueous extracts can only be the original porewater in the marl. Therefore, a one to one correspondence between Cl^- concentration and dilution at the different S:L ratios would be expected. This 1:1 correspondence is indeed observed, and is illustrated in Figure 1. From the mean values in Tables 3a-3d the quantities of chloride extracted at each solid to liquid ratio can be calculated and the results are summarised in Table 5. To within a very small error, the values expressed in meq kg^{-1} are independent of the S:L ratio. The mean value of 32 individual measurements was $6.9 \pm 0.5 \times 10^{-4} \text{ mol kg}^{-1}$. These results are consistent with the chloride values reported by MAZUREK et al. (1994).

Table 5: Chloride extractions from marl sample SB1-535.83

S:L ratio (gram litre ⁻¹)	Cl ⁻ in aqueous extracts (meq litre ⁻¹)	Cl ⁻ extracted from marl (meq kg ⁻¹)
2000	1.40 (0.11)	0.70 (0.06)
1000	0.68 (0.06)	0.68 (0.06)
750	0.51 (0.03)	0.68 (0.04)
500	0.35 (0.03)	0.70 (0.04)

Values in parentheses are standard deviations of eight individual measurements.

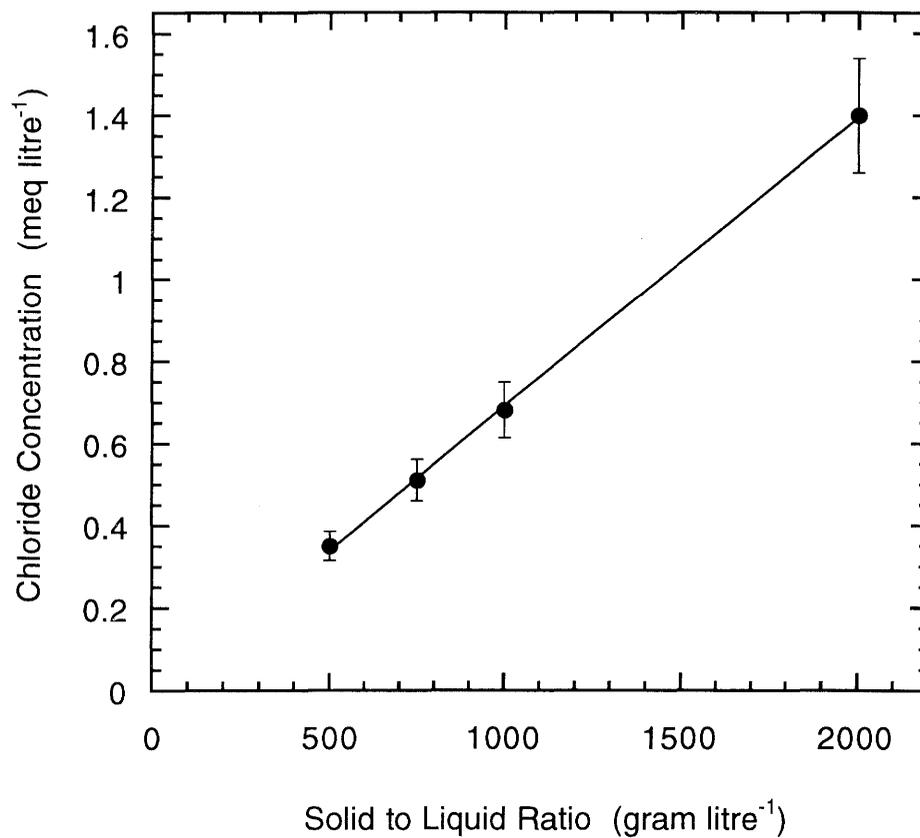


Figure 1: Chloride concentrations measured in the aqueous extracts (mean values from Tables 3a-3d) as function of S:L ratio

4.2.4 Sulphate Extraction Data

If the sulphate data given in Tables 3a-3d are treated in a similar manner to chloride (see Figure 2 and Table 6) it can readily be seen 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 marl of 2.2 ± 0.1 meq kg^{-1} .

Table 6: Sulphate extractions from marl sample SB1-535.83

S:L ratio (gram litre ⁻¹)	SO_4^{2-} in aqueous extracts (meq litre ⁻¹)	SO_4^{2-} extracted from marl (meq kg ⁻¹)
2000	4.30 (0.21)	2.2 (0.1)
1000	2.21 (0.12)	2.2 (0.1)
750	1.64 (0.06)	2.2 (0.1)
500	1.12 (0.08)	2.2 (0.2)

Values in parentheses are standard deviations of eight individual measurements.

The question then arises as to whether the SO_4^{2-} is present as a mineral phase, such as celestite or gypsum, or whether it has arisen via pyrite oxidation during the preparation of the marl samples, see section 2.1. Unfortunately, on the basis of the evidence available from this study alone, we cannot differentiate between these two possibilities. In the latter case, for an undisturbed matrix marl, we would expect to find no sulphate in the porewater, whereas in the former case, the sulphate concentration would be high, reflecting saturation with gypsum/celestite.

A long term down hole water sampling campaign in the SB6 borehole indicated that no SO_4^{2-} is present in the in situ groundwater (DEGUELDRE, pers. comm.). Although the available evidence is inconclusive, it is pointing strongly in the direction of pyrite oxidation alone as being the source of SO_4^{2-} measured in the aqueous extraction experiments. Our conclusion is that SO_4^{2-} is not likely to be present in marl porewaters under the reducing conditions prevailing in an undisturbed marl formation.

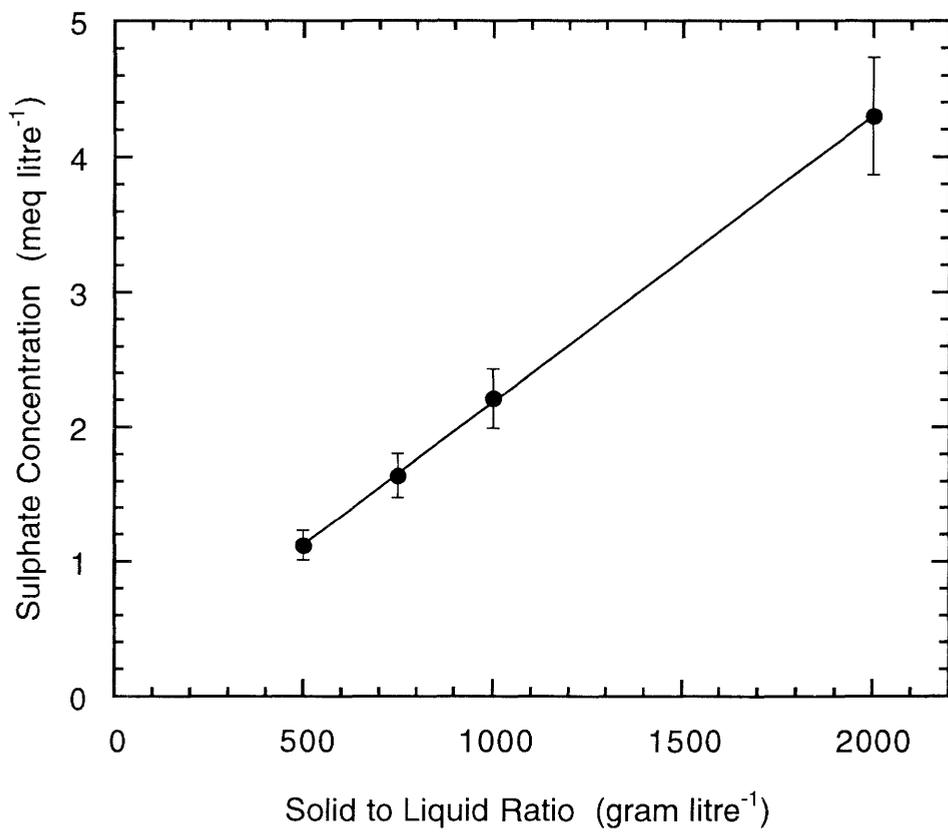


Figure 2: Sulphate concentrations measured in the aqueous extracts (mean values from Tables 3a-3d) as function of S:L ratio

5 NICKEL ETHYLENEDIAMINE EXTRACTION TESTS

5.1 Experimental Procedure

The high selectivity complex solution was prepared by slowly adding ethylenediamine (en) to an 0.2 M Ni(NO₃)₂ solution to obtain a stock solution containing 0.6 M ethylenediamine. Extraction tests with the Ni-en solutions were carried out at four different S:L ratios under exactly the same experimental conditions as described in section 4.1 for the aqueous extraction tests. Experiments were carried out in duplicate and samples were only shaken for one day since previous work had shown this was more than enough time for all cation displacement reactions from the clay to be completed

In such extraction tests it is important to be certain that the high selectivity complex is in sufficient excess to ensure the complete exchange of the cations on the clay. The number of meq of Ni-en in each test was chosen to be about twice that of the exchange capacity of the mass of marl used. (An estimate of the CEC was obtained from some preliminary experiments using solutions spiked with ⁶³Ni, and activity measurements to determine changes in the Ni concentrations.) Consequently, four different standard solutions of Ni-en were prepared corresponding to the calculated amounts required in each of the four S:L ratio extractions.

5.2 Results and Discussion

5.2.1 Ni-en CEC Measurements

The Ni-en cation exchange capacity was calculated for each extract from the difference between the initial and final Ni concentrations and these results at the different S:L ratios are summarised in Table 7. The Ni-en CEC data are consistent, and yield a mean value of 68 ±1 meq kg⁻¹ marl from 8 independent measurements .

Table 7: Ni-en CEC measurements on marl sample SB1-535.83

S:L ratio (gram litre ⁻¹)	Initial Ni conc. (meq litre ⁻¹)	Final Ni conc. (meq litre ⁻¹)	Ni-en CEC (meq kg ⁻¹)	pH
2000	300	168	66	8.7
		166	67	8.7
1000	160	93	67	8.9
		93	67	8.9
750	120	67.5	70	8.9
		69	68	8.9
500	80	46	68	9.1
		45.5	69	9.1

5.2.2 Displaced Cations from Marl in Ni-en Extraction Tests

The cation concentrations measured in the Ni-en extraction solutions at the four different S:L ratios after 1 day contact time are expressed in meq kg⁻¹ marl and are given in Table 8. There is no trend in the data with the S:L ratio and the individual cation measurement generally agree to better than 5%.

In some previous work (BAEYENS & BRADBURY 1991) an elaborate graphical analysis procedure for deducing individual cation occupancies from their measured concentrations in the Ni-en extraction tests at S:L ratios varying from 1000 to 10 gram litre⁻¹ was described. In retrospect, it is clear that such an analysis is not strictly necessary. If the estimates of cation occupancies from the graphical analyses are compared with extracted cation data at the two highest S:L ratios of 1000 and 500 gram litre⁻¹, we see that these two approaches produce estimates that are very close to one another. This is illustrated in Table 9. In this work, Ni-en extractions were only carried out at high S:L ratios (see Table 8) and cation occupancies are deduced directly from this data.

Table 8: Quantities of displaced cations (in meq kg⁻¹) from marl sample SB1-535.83 in Ni-en extraction tests at different S:L ratios

S:L ratio (gram litre ⁻¹)	Na	K	Mg	Ca	Sr	Σ Cations
2000	40.9	3.9	3.2	10.0	0.9	59
	40.9	3.8	3.3	9.4	0.9	58
1000	41.5	4.5	3.5	10.0	0.9	60
	42.6	4.8	3.4	9.8	0.9	62
750	42.3	4.6	3.4	9.9	0.9	61
	40.9	4.8	3.4	9.9	0.9	60
500	41.3	5.2	3.4	10.1	0.9	61
	42.2	4.9	3.4	9.9	0.9	61
Mean (s dev)	41.6 (0.7)	4.6 (0.5)	3.4 (0.1)	9.9 (0.2)	0.9 (0.1)	60 (1)

Table 9: Ion occupancies on Valanginian marl (Oberbauenstock) derived from the graphical analysis and the average of the results of the 1000 and 500 gram litre⁻¹ S:L ratio Ni-en extraction experiments (taken from BAEYENS & BRADBURY 1991)

Cation	Cation occupancies	
	From graphical analysis (meq kg ⁻¹)	From high S:L ratio data (meq kg ⁻¹)
Na	54 (± 2)	55 (± 1)
K	5 (± 2)	5 (± 0.2)
Mg	16 (± 1)	16 (± 0.3)
Sr	2 (± 1)	4 (± 1)

Note: Ca could not be compared since in these Ni-en extraction experiments the Ni-en solutions were saturated with CaCO₃

Before proceeding further, it is interesting to consider why the high S:L ratio extractions should provide the required data. When the Ni-en solution contacts the marl, the cations on the clay mineral components are almost immediately displaced into solution (PLEYSIER et al. 1986). This cation displacement process is much more rapid than solid phase dissolution reactions, see for

example, WOLLAST (1990). Consequently, dissolution takes place against a background of cation concentrations generated by displacement from the clay minerals and these concentrations will depend mainly on the S:L ratio (The higher the S:L ratio the higher the background concentrations of displaced cations.) The consequence of this is that the contribution of cations from dissolving solids to their total concentrations will tend to decrease as the S:L ratio increases because of the common ion effect on the solid phase solubility. In other words, at low S:L ratios the contribution of sparingly soluble solids such as calcite, dolomite/ankerite, to the total concentrations of the individual cations, e.g., Ca, Mg, will be significant. As the S:L ratio increases the concentrations displaced from the clay minerals dominate the solution concentrations.

5.2.3 Estimate of the Ion Occupancies on Marl

Following the above discussion, the monovalent and bivalent cation occupancies can be directly read from the "mean value" row in Table 8. The cation exchange capacity can then be obtained from the sum of the individual occupancies which yields a mean value of 60 ± 1 meq kg⁻¹.

An important point to note is that the sum of extracted cations (Σ cations, Table 8) appears to be ~ 12% less than the CEC determined from the Ni-en measurements, Table 7. This discrepancy is too large to be attributed to measurement errors. In our view the most likely cause of the above is a reaction occurring between Ni-en and the broken bond/edge sites of the >SOH type on the clay minerals in marl. The effect of forming such surface complexes is two fold: (i) Ni would be removed from solution but no cation would be displaced and (ii) the assumption of stoichiometric exchange by the bivalent Ni-en complex would be invalid. The result of such a process would be that the Ni-en determined value for the cation exchange capacity of the planar sites is over-estimated. The inference is that the indirect measurement of the CEC, via the sum of displaced cations, may well be providing the better estimate.

The discrepancy between the Ni-en CEC value and the sum of displaced cations remains an uncertainty in the procedure for deducing an in situ porewater chemistry. Consequently, the porewater modelling described in

Chapter 6 will be carried out with both values to give an idea of the effect of this uncertainty on the calculated aqueous chemistry.

The two possible data sets describing the cation occupancies on the marl which can be derived from the Ni-en extraction results are summarised in Table 10. In the case of data set A, the values are taken from Table 8 (mean values) and the CEC is the sum of cation occupancies. For data set B, where the Ni-en CEC measurement is taken, the Na and K occupancies are again read directly from Table 8. The sum of the bivalent cation occupancies are then calculated to be the difference between the Ni-en CEC and the sum of monovalent cations.

Table 10: Summary of the two possible CEC and cation occupancy data sets derived from Ni-en extractions

Data set A: Taken from Table 8		Data set B: Taken from Table 8 and Ni-en CEC	
Cation	(meq kg ⁻¹)	Cation	(meq kg ⁻¹)
Na	41.6	Na	41.6
K	4.6	K	4.6
Mg	3.4	M = Mg + Ca + Sr	21.6
Ca	9.9		
Sr	0.9		
Σ Cations	60.4	Ni-en CEC	67.8

5.2.4 Calculations of Selectivity Coefficients

In order to calculate a marl porewater composition, the aqueous extract results (section 4.2.1) are used to derive selectivity coefficients for Na and K with respect to the bivalent ions Mg, Ca and Sr. These three bivalent cations are chemically very similar and generally exhibit selectivity coefficients with respect to one another which are close to unity (see for example BRUGGENWERT & KAMPHORST 1982). Consequently we make the assumption that they can be treated as being equivalent, and define selectivity coefficients of Na and K with respect to a bivalent cation, M^{2+} , where $M^{2+} =$

$Mg^{2+} + Ca^{2+} + Sr^{2+}$. The selectivity coefficient for $Na^+ \rightarrow M^{2+}$ exchange, K_{M}^{Na} is defined as:

$$K_{M}^{Na} = \frac{N_{Na}^2}{N_M} \cdot \frac{a_M}{a_{Na}^2} \quad [1]$$

where a_{Na} and a_M are the solution activities of cations Na and M respectively. N_{Na} and N_M are equivalent fractional occupancies defined as the equivalents of Na (or M) sorbed per unit mass divided by the cation exchange capacity, in equivalents per unit mass. (Note that $a_M = a_{Mg} + a_{Ca} + a_{Sr}$ and $N_M = N_{Mg} + N_{Ca} + N_{Sr}$). A similar equation can be written for $K^+ \rightarrow M^{2+}$ exchange. The mass balance equation for the ion exchange phase is then

$$N_{Na} + N_K + N_M = 1 \quad [2]$$

There are three potential sources of Na/K in the system i.e. minerals such as K-feldspar, highly soluble salts (NaCl), and exchangeable Na/K on the clay minerals. Any contribution from minerals can be neglected since the rates of dissolution and solubility limits are very low. If it is assumed that the Cl⁻ extracted from the marl (see section 4.2.3) i.e. $\sim 0.7 \text{ meq kg}^{-1}$, arises from NaCl in the porewater then a simple calculation shows that this represents less than 2% of the total Na measured in the Ni-en extraction experiments. Again this can be neglected. Hence, we conclude that Na and K are predominantly present as exchangeable cations on the clay minerals.

The consequence of the above is that the Na and K occupancies at any S:L ratio in the aqueous extract experiments can be calculated from the difference between their initial occupancies (Table 10) and their equilibrium concentrations in solution, Tables 3a-3d.

As already described in section 5.2.3, because Σ cations is not equal to the CEC determined by the Ni-en measurements, we have the two sets of data given in Table 10 from which selectivity coefficients for Na and K with respect to the sum of bivalent cations can be calculated. The results are given in Tables 11 and 12 where it can be seen that the selectivity coefficients in the

two cases differ by ~ 50%. At first sight such a large difference for only a 12% difference in the CEC may be surprising. However, it should be realised that the 12% higher Ni-en CEC is coupled with a correspondingly higher bivalent cation occupancy, and it is the combination of these two effects which leads to the significant differences in calculated K_C values.

Table 11: Selectivity coefficients calculated from aqueous extract data and cation occupancies using data set A from Table 10

	S:L ratio (gram litre ⁻¹)			
	2000	1000	750	500
<u>Aqueous Extract Data:</u>				
Na extracted in meq kg ⁻¹	7.4	10.6	12.1	15.0
K extracted in meq kg ⁻¹	0.14	0.22	0.27	0.36
<u>Cation occupancies on marl:</u>				
Na (meq kg ⁻¹)	34.2	30.6	29.5	26.6
K (meq kg ⁻¹)	4.5	4.4	4.3	4.2
M (meq kg ⁻¹)	21.6	25.3	26.5	29.5
<u>Fractional cation occupancies:</u>				
N_{Na}	0.567	0.507	0.489	0.441
N_K	0.075	0.073	0.071	0.070
N_M	0.358	0.420	0.440	0.489
<u>Solution concentrations:</u>				
Na (mmol litre ⁻¹)	14.7	10.6	9.1	7.5
K (mmol litre ⁻¹)	0.28	0.22	0.20	0.18
M (mmol litre ⁻¹)	0.096	0.068	0.059	0.051
$\frac{N_{Na}}{N_M} K_C^*$	0.33	0.31	0.33	0.30
$\frac{N_K}{N_M} K_C^*$	13.9	15.0	13.7	11.8

*Selectivity coefficients were calculated using equation 1. Measured concentrations were converted to activities using the Davies equation for the solution activity coefficients (DAVIES 1962)

Table 12: Selectivity coefficients calculated from aqueous extract data and cation occupancies using data set B from Table 10

	S:L ratio (gram litre ⁻¹)			
	2000	1000	750	500
<u>Aqueous Extract Data:</u>				
Na extracted in meq kg ⁻¹	7.4	10.6	12.1	15.0
K extracted in meq kg ⁻¹	0.14	0.22	0.27	0.36
<u>Cation occupancies on marl:</u>				
Na (meq kg ⁻¹)	34.2	30.6	29.5	26.6
K (meq kg ⁻¹)	4.5	4.4	4.3	4.2
M (meq kg ⁻¹)	29.1	32.8	34.0	37.0
<u>Fractional cation occupancies:</u>				
N _{Na}	0.504	0.451	0.435	0.392
N _K	0.066	0.065	0.063	0.062
N _M	0.430	0.484	0.502	0.546
<u>Solution concentrations:</u>				
Na (mmol litre ⁻¹)	14.7	10.6	9.1	7.5
K (mmol litre ⁻¹)	0.28	0.22	0.20	0.18
M (mmol litre ⁻¹)	0.096	0.068	0.059	0.051
$\frac{N_{Na}}{N_{M}K_C}^*$	0.22	0.22	0.22	0.21
$\frac{N_K}{N_{M}K_C}^*$	8.9	10.3	9.5	8.3

*Selectivity coefficients were calculated using equation 1. Measured concentrations were converted to activities using the Davies equation for the solution activity coefficients (DAVIES 1962)

6 MARL POREWATER COMPOSITIONS AND MATRIX POROSITIES

6.1 Calculation of In Situ Marl Porewater Compositions

The information and data required to calculate in situ porewaters for marl have been derived in the preceding sections and are summarised below.

Common Data:

Saturated mineral phases: Calcite
Dolomite
Chalcedony

In situ CO₂ partial pressure: $P_{\text{CO}_2} = 10^{-2}$ bar

From field measurements no reliable pH/ P_{CO_2} data are available. The P_{CO_2} value of 10^{-2} bar used here is a best estimate made by F.J. Pearson, Jr. in 1990.

Data set A:

In situ exchangeable cation occupancies on marl:

Na = 41.6 ± 0.7 meq kg⁻¹
K = 4.6 ± 0.5 meq kg⁻¹
Mg = 3.4 ± 0.1 meq kg⁻¹
Ca = 9.9 ± 0.2 meq kg⁻¹
Sr = 0.9 ± 0.1 meq kg⁻¹
CEC = 60 ± 1 meq kg⁻¹

In situ equivalent fractional ion occupancies:

$N_{\text{Na}} = 0.690$
 $N_{\text{K}} = 0.076$
 $N_{\text{M}} = 0.234$

Selectivity coefficients:

$\frac{N_{\text{Na}}}{N_{\text{M}}} K_{\text{C}} = 0.32 \pm 0.02$
 $\frac{N_{\text{K}}}{N_{\text{M}}} K_{\text{C}} = 13.6 \pm 1.7$

Data set B:

In situ exchangeable cation occupancies on marl:

$$\text{Na} = 41.6 \pm 0.7 \text{ meq kg}^{-1}$$

$$\text{K} = 4.6 \pm 0.5 \text{ meq kg}^{-1}$$

$$\Sigma \text{ Bivalents} = 21.6 \pm 0.3 \text{ meq kg}^{-1}$$

$$\text{CEC} = 68 \pm 1 \text{ meq kg}^{-1}$$

In situ equivalent fractional ion occupancies:

$$N_{\text{Na}} = 0.614$$

$$N_{\text{K}} = 0.068$$

$$N_{\text{M}} = 0.318$$

Selectivity coefficients:

$$\frac{\text{Na}}{\text{M}} K_{\text{C}} = 0.22 \pm 0.01$$

$$\frac{\text{K}}{\text{M}} K_{\text{C}} = 9.30 \pm 1.0$$

The first step in the procedure was to calculate the activities of Ca and Mg in a solution at saturation with calcite and dolomite at a $P_{\text{CO}_2} = 10^{-2}$ bar using the geochemical equilibrium code PHREEQE.

We know that Sr is present on the clay minerals in marl and therefore has to be present in solution. We have assumed that the selectivity coefficient of Sr with respect to Ca is unity. This implies that the Sr/Ca ratio is the same on the solid as in solution. Hence, knowing the initial Sr occupancy on the marl we can fix the Sr activity in solution via the Ca activity. At this stage we have our first estimate of the sum of bivalent cation activities in the liquid phase.

The next step is to calculate the activities of Na and K (as chlorides) in solution which are necessary to maintain the in situ occupancies of Na and K on the clay (Table 10) in the presence of the bivalent cation activities calculated above. Re-arrangement of equation 1 yields

$$a_{\text{Na}} = \left(\frac{1}{\frac{\text{Na}}{\text{M}} K_{\text{C}}} \cdot a_{\text{M}} \cdot \frac{N_{\text{Na}}^2}{N_{\text{M}}} \right)^{1/2} \quad [3]$$

From this relation the activity of Na can be calculated for a given a_M , N_{Na} , N_M and K_C . (A similar expression can be derived for K.) Chloride is used to maintain charge balance in the solution.

A second iteration is now made which is essentially a re-equilibration of the solid phases in the present of the Na and K levels derived at the end of the first iteration. In this manner the dependency of mineral solubilities on ionic strength is taken into account. Iterations of this type are repeated until the difference between the major cation and anion concentrations in successive iterations is < 1%. For this specific case four iterations were sufficient. Fluoride has been measured in the aqueous extracts and this ion should be included in the modelling. Although fluorite is not specifically mentioned as being present in the mineralogical analysis, nevertheless we chose this mineral as being the primary source of F^- and subsequently fixed its level in the porewater by assuming saturation with respect to CaF_2 .

The calculated compositions of the porewater fluids are given in Table 13.

Table 13: Calculated marl porewater composition at a P_{CO_2} of 10^{-2} bar

Parameter	Data set A	Data set B
pH	7.5	7.5
Ionic strength	0.13 M	0.12 M
Temperature	25 °C	25 °C
P_{CO_2}	10^{-2} bar	10^{-2} bar
<u>Total concentrations of elements: (M)</u>		
Na	1.14×10^{-1}	1.05×10^{-1}
K	2.0×10^{-3}	1.9×10^{-3}
Mg	1.3×10^{-3}	1.3×10^{-3}
Ca	1.6×10^{-3}	1.6×10^{-3}
Sr	1.4×10^{-4}	1.4×10^{-4}
Cl	1.16×10^{-1}	1.07×10^{-1}
F	3.1×10^{-4}	3.1×10^{-4}
$C_{inorg.}$	6.1×10^{-3}	6.1×10^{-3}
Si	2.7×10^{-4}	2.7×10^{-4}

The compositions of the porewaters modelled with data sets A and B are very similar, and both yield NaCl waters of moderate ionic strength. The results are essentially insensitive to the uncertainties in cation exchange capacities, cation occupancies and selectivity coefficients discussed in section 5.2.3 and 5.2.4

In order to illustrate the influence of pH on the calculated porewater composition, data set A was taken and the iterative calculations repeated for pH values set at 7 and 8. The results are given in Table 14.

Table 14: Calculated mar porewater compositions at pH = 7 and 8 for data set A

Parameter	pH = 7	pH = 8
Ionic strength	0.17 M	0.09 M
Temperature	25 °C	25 °C
P _{CO₂}	10 ^{-1.3} bar	10 ^{-2.9} bar
<u>Total concentrations of elements: (M)</u>		
Na	1.55 x 10 ⁻¹	8.3 x 10 ⁻²
K	2.6 x 10 ⁻³	1.5 x 10 ⁻³
Mg	2.3 x 10 ⁻³	6.6 x 10 ⁻⁴
Ca	2.9 x 10 ⁻³	8.0 x 10 ⁻⁴
Sr	2.7 x 10 ⁻⁴	7.0 x 10 ⁻⁵
Cl	1.58 x 10 ⁻¹	8.5 x 10 ⁻²
F	2.4 x 10 ⁻⁴	4.0 x 10 ⁻⁴
C _{inorg.}	1.22 x 10 ⁻²	2.9 x 10 ⁻³
Si	2.7 x 10 ⁻⁴	2.8 x 10 ⁻⁴

The system appears to be fairly robust with respect to pH since an uncertainty of 0.5 units about the best estimate value of 7.5 leads generally to only ± 50% changes in the ion concentrations.

It is interesting to consider why a change in pH should influence the calculated NaCl concentration in the manner illustrated by the data in Table 14. The basic reason is that the cation occupancies on the marl are taken to be fixed values. If the pH of the system is lowered, for example, the Ca concentration,

determined by the solubility product of calcite, rises. An increase in the Ca concentration must result in an increase in the Na concentration in order to maintain the cation occupancies on the marl at their fixed values. This can easily be appreciated from the selectivity relation, equation 1, for constant values of N_{Na} and N_M . Because the Na concentration (activity) appears as a squared term in equation 1, any change in the Ca level results in a magnified change in the Na level i.e. the NaCl concentration. The corollary to this is that if the cation occupancies, selectivity coefficients and the NaCl concentration are known, then the pH (P_{CO_2}) can be determined from the Ca concentration calculated from equation 1 and saturation with respect to calcite.

6.2 Estimates of the Matrix Marl Porosity

The chloride concentration in the porewater calculated at a P_{CO_2} of 10^{-2} bar, Table 13, together with the chloride content of the marl (0.7 meq kg^{-1}) given in section 4.2.3, can be used to calculate the "free water" content of the in situ matrix marl assuming that all the available chloride is present in the porewater solution. The procedure is simple and involves calculating in how much water 0.7 meq Cl^- per kg marl must be dissolved to yield the Cl^- concentration given in Table 13. This volume of water can be related to a mass (volume) of marl and hence to a "free water porosity". The porosity value obtained, using a marl density of 2650 kg m^{-3} , is $\sim 1.5\%$. This compares well with the porosity value of $\sim 1\%$ given in MAZUREK et al. (1994). For the Cl^- concentrations presented in Table 14, the corresponding calculated porosities are 1.2% ($\text{pH} = 7$) and 2.0% ($\text{pH} = 8$).

7 SUMMARY

Physico-chemical characterisation techniques, developed in some previous work to deduce in situ porewaters for argillaceous rocks (BAEYENS & BRADBURY 1991), were successfully applied to a sample of Palfris marl from borehole SB1 at Wellenberg (SB1-535.83). The calculated porewater was a Na-Cl type which was saturated with respect to calcite, dolomite, fluorite and chalcedony. The cations Ca, Mg, Sr and K constituted together only a few percent of the Na concentration. The major anion was Cl^- , with C_{inorg} contributing approximately five percent to the total anion concentration. The pH was 7.5 and the ionic strength 0.12 M for the assumed P_{CO_2} of 10^{-2} bar.

The porewater chemistries calculated using data sets A and B (Table 13), which had selectivity coefficients differing by more than 50%, were very similar. Ionic strengths, determined essentially by the NaCl concentrations, differed by less than 10%. This indicates that the method and calculations are fairly robust.

The effects on the calculate porewater composition of varying the pH over the range from 7 ($P_{\text{CO}_2} = 10^{-1.3}$ bar) to 8 ($P_{\text{CO}_2} = 10^{-2.9}$ bar) were significant but not dramatically so. The ionic strength decreased from ~ 0.17 M (pH = 7) to ~ 0.09 M (pH = 8).

The porosity of matrix marl, deduced from the Cl^- content of sample SB1-535.83 in conjunction with the three calculated porewater chemistries, varied over the range from 1.2% to 2.0% which is in good agreement with the values given in MAZUREK et al. (1994).

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