



Working report 97-62e

Model for diffusion and porewater chemistry in compacted bentonite

Preliminary results of the
porewater chemistry studies

Arto Muurinen
VTT Chemical Technology

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MODEL FOR DIFFUSION AND POREWATER CHEMISTRY IN COMPACTED BENTONITE - PRELIMINARY RESULTS OF THE POREWATER CHEMISTRY STUDIES

ABSTRACT

This report describes the progress of the experimental research on the model of porewater chemistry in bentonite. The research is part of the project "Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency" (Contract No. FI4W-CT95-0012) within the European Commission Nuclear Fission Safety Program (1994 - 1998). The porewater model will be based on the micro- and macro-scale material properties of bentonite and surrounding conditions. The work consists of simulation model development work and supporting experimental studies on porewater chemistry.

Experimental studies of solution-bentonite interactions are underway. The parameters varied are the bentonite density, bentonite-to-water ratio, composition of the solutions, and the composition of bentonite. The bentonite types used in the experiments are commercial MX-80 and artificial bentonites prepared from purified MX-80 in sodium form where CaCO_3 , CaSO_4 and pyrite are added. The report presents the experimental arrangements and the preliminary results of the experiments.

Keywords: Bentonite, montmorillonite, porewater chemistry, solubility

MALLI DIFFUUSIOLLE JA HUOKOSVESIKEMIALLE KOMPAKTOIDUSSA BENTONIITISSA - HUOKOSVESIKEMIAN TUTKIMUKSEN ALUSTAVAT TULOKSET

TIIVISTELMÄ

Tässä raportissa esitetään kuvaus bentoniitin huokosvesikemian kokeellisen tutkimuksen edistymisestä. Tutkimus on osa Euroopan komission Nuclear Fission Safety-ohjelman (1994 - 1998) projektia "Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency" (Contract No. FI4W-CT95-0012). Mallin lähtököhtana ovat bentoniitin mikro- ja makroskaalan materiaaliominaisuudet ja ympäristön olosuhteet. Tehtävä koostuu mallinkehitystyöstä ja sitä tukevasta huokosvesikemian kokeellisesta tutkimuksesta.

Kokeet veden ja bentoniitin välisistä vuorovaikutuksista ovat meneillään. Vaihdeltavat parametrit ovat bentoniitin tiheys, bentoniitti-vesisuhde, liuoksen ioniväkevyys ja bentoniitin koostumus. Kokeissa käytetyt bentoniittityypit ovat kaupallinen MX-80 ja keinotekoiset bentoniitit, jotka valmistettiin puhdistetusta MX-80:stä natrium muodossa lisäämällä siihen CaCO_3 :a ja CaSO_4 :a ja pyriittiä. Raportissa esitetään koejärjestelyt ja alustavat tulokset.

Avainsanat: Bentoniitti, montmorilloniitti, huokosvesikemia, liukoisuus

FOREWORD

Within the European Commission Nuclear Fission Safety Program (1994 - 1998), the research project "Microstructural and Chemical Parameters of Bentonite as Determinants of Waste Isolation Efficiency" (Contract No. FI4W-CT95-0012) has jointly been started by Clay Technology AB in Sweden, VTT Chemical Technology in Finland, Universität Hannover in Germany and Kungliga Tekniska Högskolan in Sweden. Professor Roland Pusch from Clay Technology AB is the co-ordinator of the project. The work in Finland is funded by The European Commission, Posiva Oy and VTT Chemical Technology. The contact person for Posiva Oy is Jukka-Pekka Salo. The work in Finland is concentrated on the development of a model for diffusion and porewater chemistry in compacted bentonite.

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1 INTRODUCTION

The understanding of the diffusion processes and porewater chemistry in bentonite are essential for the prediction of the release of radionuclides from the repository of nuclear waste. This study is part of a project where a model for diffusion and porewater chemistry in bentonite will be developed, and contains experimental studies on porewater chemistry.

The evolution of porewater chemistry is determined by the dissolving components initially present in bentonite together with the ions coming with water from the surroundings. The most important easily-dissolving components in natural bentonites are calcite, gypsum and pyrite. Ion-exchange processes occur between the exchangeable cations of montmorillonite, the main component of bentonite, and the cations in the porewater. In compacted bentonite, where the charged surfaces are close to each other, exclusion effects may be important, too. The small amount of free water in compacted bentonite may also affect the dissolution of sparingly soluble components.

The evolution of porewater chemistry has been studied in solution-bentonite interaction experiments. At the end of the interaction the equilibrating solution, the porewaters squeezed out of the bentonite samples, and bentonites themselves are analysed to give information for the interpretation and modelling of the interaction.

Three experimental series have been initiated. In the first one Volclay MX-80 was used as the bentonite to be studied. The parameters varied in the experiments were the bentonite density, bentonite-to-water ratio and ionic strength of the solution. These experiments have been finished after an interaction period of about 300 days, and the external waters and porewaters squeezed out of the bentonites have been analysed.

In the second series, studies are underway with simulated bentonites prepared from sodium montmorillonite, CaSO_4 and CaCO_3 . The parameters varied in these experiments are the bentonite-to-water ratio and the concentrations of the added accessory minerals. Deionized water is used as the solution. The progress of the interaction of some of the experiments has been monitored by taking samples from the external solutions to see whether equilibrium has been attained.

In the third series, which has just started, simulated bentonite prepared from sodium montmorillonite and ground pyrite (FeS_2) is being studied. The objective of these experiments is to clarify the oxidation of pyrite and its effect on the porewater chemistry. The experiments are performed under aerobic and anaerobic conditions with loose bentonite as well as compacted bentonite. Deionized water is used as the solution.

2 EXPERIMENTAL STUDY ON POREWATER CHEMISTRY

2.1 EXPERIMENTAL ARRANGEMENTS

The evolution of porewater chemistry is studied in solution-bentonite interaction experiments with the experimental apparatus shown in Fig. 1. The size of the bentonite sample is 20 mm in diameter and 9.5 mm in height. The size of the cell for the solutions is varied in view of different bentonite-water ratios (b/w). Bentonite is in contact with the external solution through a steel sinter of pore size 5 micrometers. At the end of the experiment the equilibrating external solution and the porewaters squeezed out of the bentonite samples are analysed to give information for the interpretation and modelling of the interaction.

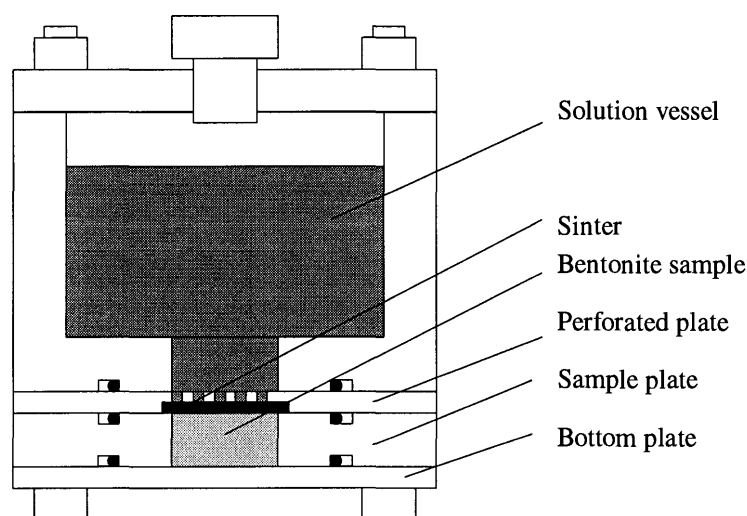


Fig.1. Schematic diagram of apparatus for water-bentonite interaction experiment.

The apparatus used for squeezing porewater from bentonite samples is seen in Fig. 2. It consists of a pressing apparatus that is used to create the necessary long-term compression, and the compaction cell where the porewater is separated from the bentonite and collected in a syringe. The constant long-term force is maintained with a strong spring by adjusting the length of the lower part of the pressing apparatus with nuts. The hydraulic cylinder housed in the upper part of the pressing apparatus presses the lower part to the desired length prior to fixing the nuts in order to maintain the selected length. After adjusting the length, the hydraulic cylinder can be moved to the next pressing apparatus.

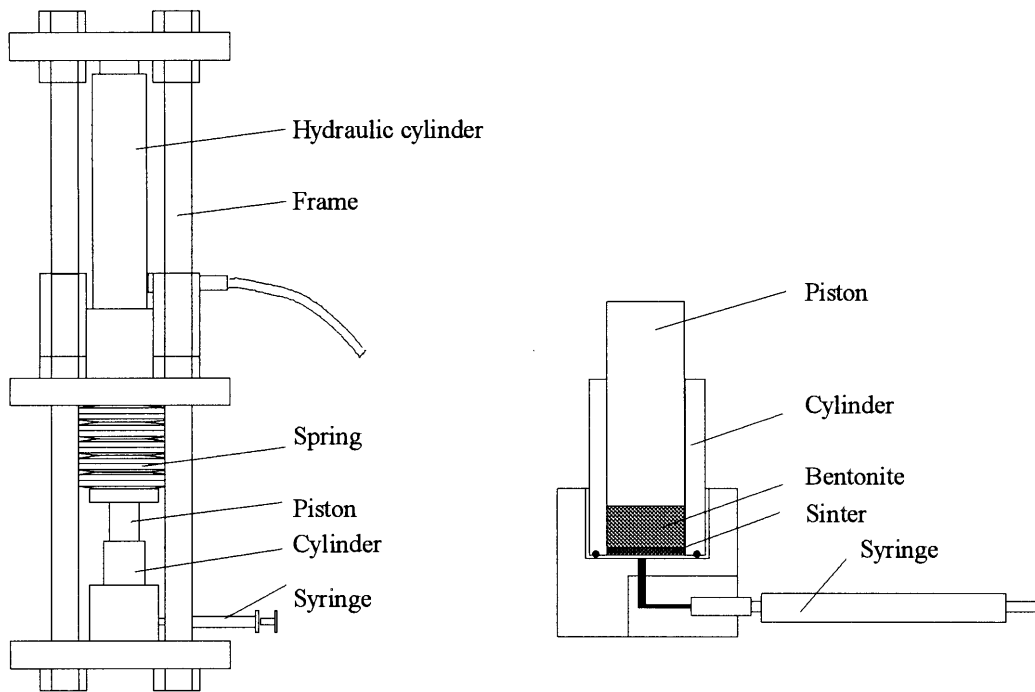


Fig. 2 Pressing apparatus (left) and compaction cell (right).

The compaction cell consists of the base part, syringe, sample cylinder, sinter and piston. The bentonite is pressed with the piston against the sinter on the bottom of the cylinder. The pressure is increased stepwise up to 120 MPa, which typically takes 1 to 2 weeks. The porewater flows through the sinter and the hole in the base part to a syringe. The sample size of 20 mm in diameter and 9.5 mm in height used in the experiments gives porewater samples from about 0.5 ml to 1.5 ml, depending on the density of bentonite. Several successive porewater samples could be squeezed from the bentonite sample of low densities.

The solution-bentonite interaction experiments with MX-80 and Na-montmorillonite + $\text{CaCO}_3/\text{CaSO}_4$ and squeezing of the porewaters were performed at room temperature in a glove-box where the main components were 90 % nitrogen and 10 % hydrogen. The oxygen concentration was about 5 ppm and carbon dioxide concentration 2 to 5 ppm. The interaction experiments with Na-montmorillonite + pyrite and squeezing of the porewaters were performed in a glove-box of a pure nitrogen atmosphere or under aerobic conditions.

The pH values of the small porewater samples were determined before any dilution with a small pH-electrode under the experimental conditions. The sample size used in the pH-measurements varied from 100 μl to 50 μl , depending of the sample volume available. Prior to the chemical analysis, the small porewater samples were diluted under the experimental conditions. The carbonate concentrations were determined by alkalinity titration in the N_2/H_2 -glove-box and the other anions and cations by ion chromatography.

2.2 EXPERIMENTAL RESULTS

2.2.1 Experiments with MX-80 bentonite

The parameters varied in the interaction experiments with MX-80 bentonite were the bentonite density, the bentonite-water ratio and the ionic strength of the solution. The compositions of the solutions used in the experiments are presented in Table 1. The ionic strength of the fresh water (Allard water) was about 3.7 meq/L, and that of the saline water about 415 meq/L. The experimental conditions, together with the results, are presented for the fresh water experiments in Table 2, and for the saline water experiments in Table 3.

Table 1. The compositions of the experimental solutions.

Component	Fresh water (Allard water) Concentration (mmol/L)	Saline water Concentration (mmol/L)
Na ⁺	2.26	209
K ⁺	0.10	0.54
Ca ²⁺	0.464	99.8
Mg ²⁺	0.190	2.3
Sr ²⁺		0.4
SiO ₂		0.055
HCO ₃ ⁻	1.80	0.035
Cl ⁻	1.48	417
Br ⁻		1.3
F ⁻		0.063
I ⁻		0.007
SO ₄ ²⁻	0.10	0.044
B		0.85
pH	9.1	8.2

Figs. 3 - 14 clarify the evolution of the chemistry of the external waters and the porewaters. The left side of the figure presents the chemistry of the external solution as the function of the interaction time. In the case of low b/w values, the solution volume was big enough to allow sampling during the interaction period, while in the case of higher b/w values only the concentrations at the beginning and at the end of the interaction could be analysed. The right side of the figure presents the concentrations in the squeezed porewater fractions as a function of the clay density. The density coupled to each point corresponds to the mean dry density of the bentonite during squeezing of that porewater fraction.

The results of the fresh water experiments (Figs. 3 - 6) show that during the interaction the ionic strengths of the external solutions and porewaters clearly grow, and the obtained concentrations (Figs. 7 - 8) increase with increasing

bentonite-to-water ratio. In many cases the concentrations of the porewater are lower than those in the external water, and it can be assumed that the equilibrium of the quick dissolution and ion-exchange reactions has been obtained (Figs. 3, 5 and 6). It is obvious, however, that in some cases the experiment has not been long enough to allow all the dissolved components to diffuse out (Fig. 4). This concerns especially the high bentonite densities, where the diffusivities are low, and low b/w ratios, where many more ions have to diffuse out than in the case of high b/w values. In those cases the concentrations in the porewater are higher than in the external water and the equilibrium has not yet been reached. The pH values of the external waters and porewaters, presented in Figs. 9 and 10, show a small decrease in pH with increasing b/w. Typical for the successive porewater fractions is a decrease in the concentration as a function of increasing density.

The saline water experiments (Figs. 11 - 14) show a similar increase in the ionic strength of the external solution and porewater, as do the fresh water experiments. The obtained ionic strength also increases with increasing bentonite-to-water ratio. In most cases the concentrations in the porewater are lower than in the external water. Only in the case of the density of 1.8 Mg/m^3 and b/w 0.015 g/mL is the sulphate concentration higher in the porewater than in the external water, which indicates slow diffusion at that density. The difference between porewater and external water increases with increasing initial density. The concentrations in the porewater decrease when the density is increased during squeezing of the porewater.

Table 2. Evolution of external water and porewater chemistry in the interaction experiments with MX-80 and fresh water.

Dry density (Mg/m ³)	Water type	b/w ratio (g/ml)	Exp.time (day)	pH	Na (mmol/L)	K (mmol/L)	Ca (mmol/L)	Mg (mmol/L)	CL (mmol/L)	SO4 (mmol/L)	HCO3 (mmol/L)
0	External w.	0.00	0	9.1	2.3	0.10	0.46	0.19	1.5	0.10	1.8
0.6	External w.	0.5	308	8.8	74	0.61	0.95	0.49	8.3	33	8.6
0.6	Pw. 0.6 - 0.9	0.5	308	8.9	45	0.38	0.40	0.22	7.4	19	5.9
0.6	Pw. 0.9 - 1.1	0.5	308	9.2	35	0.41	0.19	0.00	3.9	15	5.5
0.6	Pw. 1.1 - 1.4	0.5	308	9.4	25	0.23	0.00	0.00	2.7	9.2	5.7
0.6	Pw. 1.4 - 1.5	0.5	308	9.0	18	0.00	0.00	0.00	1.7	4.7	7.0
0.6	External w.	0.015	29	9.4	2.8	--	0.38	0.19	1.7	0.29	1.9
0.6	External w.	0.015	71	9.0	4.0	--	0.34	0.18	1.7	0.75	0.0
0.6	External w.	0.015	141	8.9	4.5	--	0.34	0.20	1.7	0.76	1.9
0.6	External w.	0.015	327	9.0	5.0	0.13	0.18	0.16	1.7	0.72	2.4
0.6	Pw. 0.6 - 0.9	0.015	327	8.9	3.2	0.14	0.00	0.00	1.1	0.15	1.9
0.6	Pw. 0.9 - 1.2	0.015	327	9.6	2.0	0.26	0.00	0.00	0.71	0.09	1.1
0.6	Pw.1.2 - 1.4	0.015	327	9.5	2.2	0.00	0.00	0.00	0.37	0.07	1.1
0.6	Pw. 1.4 - 1.5	0.015	327		2.3	0.00	0.00	0.00	0.72	0.00	1.5
1.2	External w.	1.5	308	8.4	247	1.71	9.06	4.0	5.7	129	3.6
1.2	Pw. 1.2 - 1.4	1.5	308	8.7	104	0.59	1.42	0.78	3.6	52	2.6
1.2	Pw. 1.4 - 1.7	1.5	308	9.0	61	0.25	0.43	0.38	2.8	27	3.1
1.2	External w.	0.015	29	9.9	3.9	--	0.35	0.17	1.8	0.73	2.1
1.2	External w.	0.015	71	9.3	4.1	--	0.33	0.22	1.7	0.70	--
1.2	External w.	0.015	131	9.2	4.4	--	0.24	0.14	1.7	0.71	1.9
1.2	External w.	0.015	308	9.2	4.5	0.17	0.13	0.11	1.8	0.73	1.9
1.2	Pw. 1.2 - 1.5	0.015	308	9.6	5.8	0.00	0.00	0.00	0.54	0.56	4.0
1.2	Pw. 1.5 - 1.7	0.015	308	9.8	4.2	0.11	0.00	0.00	0.54	0.39	3.0
1.2	Pw. 1.7 - 1.9	0.015	308	9.1	3.6	0.74	0.00	0.00	0.85	0.00	2.0

Table 2 (continues). Evolution of external water and porewater chemistry in the interaction experiments with MX-80 and fresh water.

Dry density (Mg/m ³)	Water type	b/w ratio (g/ml)	Exp.time (day)	pH	Na (mmol/L)	K (mmol/L)	Ca (mmol/L)	Mg (mmol/L)	CL (mmol/L)	SO4 (mmol/L)	HCO3 (mmol/L)
1.5	External w.	1.5	308	8.6	189	1.25	4.69	2.4	11.7	98	7.0
1.5	Pw. 1.5 - 1.8	1.5	308	9.2	42	0.43	0.25	0.17	5.2	18	3.7
1.5	Pw. 1.8 -1.9	1.5	308	9.1	22	0.00	0.00	0.00	2.1	8.7	3.1
1.5	External w.	0.5	308	8.7	56	0.41	0.80	0.45	6.1	26	5.3
1.5	Pw.1.5 - 1.8	0.5	308	9.4	17	0.00	0.00	0.00	2.0	3.8	5.5
1.5	Pw.1.8 -1.9	0.5	308	9.3	7.0	0.00	0.00	0.00	1.2	1.1	3.4
1.5	External w.	0.1	320	8.6	13	0.24	0.36	0.28	2.2	4.4	3.3
1.5	Pw. 1.5 - 1.8	0.1	320	9.5	8.4	0.00	0.00	0.00	0.85	1.6	4.3
1.5	Pw. 1.8 - 1.9	0.1	320		4.8	0.00	0.00	0.00	0.87	0.00	2.7
1.5	External w.	0.015	22	9.5	3.2	0.00	0.30	0.19	1.7	0.4	--
1.5	External w.	0.015	64	9.2	3,7	0.00	0.30	0.20	1.7	0.6	1.8
1.5	External w.	0.015	134	8.7	4.0	0.00	0.25	0.15	1.7	0.6	1.6
1.5	External w.	0.015	320	8.8	4.2	0.14	0.15	0.16	1.7	0.7	2.0
1.5	Pw. 1.6 - 1.8	0.015	320	9.1	8.8	0.15	0.00	0.00	0.54	2.6	2.8
1.5	Pw. 1.8 - 1.9	0.015	320		4.0	0.00	0.00	0.00	0.68	0.42	1.7
1.8	External w.	0.015	22	9.6	2.7	--	0.30	0.23	1.7	0.20	1.8
1.8	External w.	0.015	64	9.0	3.1	--	0.28	0.16	1.7	0.30	1.9
1.8	External w.	0.015	134	9.0	3.4	--	0.22	0.14	1.7	0.40	1.6
1.8	External w.	0.015	320	8.7	3.6	0.11	0.20	0.19	1.7	0.47	1.6
1.8	Pw. 1.8 - 2.0	0.015	320	8.8	43	0.37	0.69	0.55	1.2	21.4	2.3

Pw 1.8 - 2.0 = Porewater fraction which corresponds the dry density 1.8 - 2.0 Mg/m³.

Table 3. Evolution of external water and porewater chemistry in the interaction experiments with MX-80 and saline water.

Dry density (Mg/m ³)	Water type	b/w ratio (g/ml)	Exp.time (day)	pH	Na (mmol/L)	K (mmol/L)	Ca (mmol/L)	Mg (mmol/L)	CL (mmol/L)	SO4 (mmol/L)	HCO3 (mmol/L)	Br (mmol/L)
0	External w.	0	0	8.2	209	0.5	100	2.3	417	0.0	0.0	1.3
1.2	External w.	1.5	331	8.1	509	2.9	39	14.0	466	33	1.4	1.7
1.2	Pw. 1.2 - 1.5	1.5	331	8.1	473	2.2	35	14.9	419	32	0.6	1.4
1.2	Pw. 1.5 - 1.8	1.5	331	8.7	232	0.4	12	6.6	243	19	1.4	0.6
1.2	External w.	0.015	15	7.8	195	0.4	90	1.9	419	0.2	--	1.3
1.2	External w.	0.015	57	7.4	196	0.4	90	2.0	423	0.4	--	1.3
1.2	External w.	0.015	127	7.3	194	0.4	87	2.1	422	0.6	0.1	1.1
1.2	External w.	0.015	324	7.7	181	0.5	82	2.1	336	--	0.3	1.1
1.2	Pw. 1.2 - 1.5	0.015	324	7.9	179	0.4	73	2.9	330	0.7	0.3	1.0
1.2	Pw. 1.5 - 1.7	0.015	324	8.5	100	0.0	34	1.9	199	0.4	0.3	0.6
1.5	External w.	1.5	324	8.1	522	2.4	39	13.0	498	34	2.7	1.6
1.5	Pw. 1.5 - 1.7	1.5	324	8.8	266	0.6	14	7.4	262	25	1.1	0.7
1.5	External w.	0.5	336	8.0	349	1.5	47	9.4	398	14	2.1	1.3
1.5	Pw. 1.5 - 1.73	0.5	336	8.6	161	0.2	16	4.2	193	6.8	1.1	0.9
1.5	External w.	0.1	336	7.9	249	1.0	79	5.3	398	3.0	1.2	1.2
1.5	Pw. 1.6 - 1.7	0.1	336	8.5	55	0.0	21	2.4	117	2.6	0.1	0.3
1.5	External w.	0.015	15	7.8	200	0.4	92	1.9	422	0.0	--	1.2
1.5	External w.	0.015	57	7.5	199	0.4	83	2.0	425	0.2	--	1.1
1.5	External w.	0.015	127	7.2	198	0.4	84	2.2	432	0.4	0.0	1.1
1.5	External w.	0.015	336	7.7	207	0.5	95	2.4	390	--	0.3	1.2
1.5	Pw. 1.5 - 1.51	0.015	336	--	320	0.0	122	8.1	560	27	0.0	1.8
1.8	External w.	0.015	15	8.0	199	0.4	94	1.9	422	0.1	--	1.4
1.8	External w.	0.015	57	7.5	195	0.4	83	2.1	418	0.2	--	1.2
1.8	External w.	0.015	127	7.3	199	0.4	92	2.3	423	0.2	0.1	1.1
1.8	External w.	0.015	337	7.5	202	0.4	95	2.4	381	--	0.2	1.0
1.8	Pw. 1.8 - 1.9	0.015	337	8.7	96	0.0	52	2.4	206	16	0.4	0.5

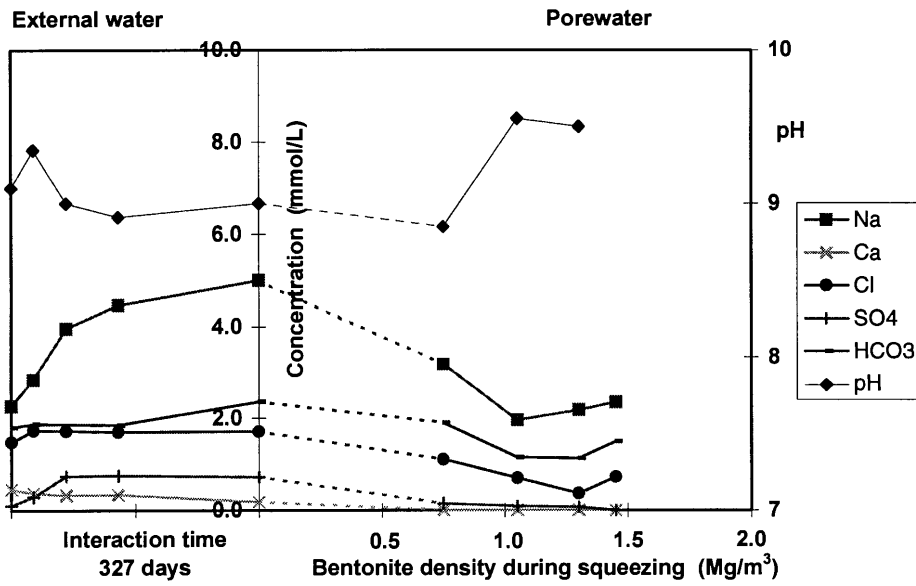


Fig. 3. Evolution of the external water and porewater chemistry during interaction and squeezing respectively. Fresh water experiment, dry density of bentonite 0.6 Mg/m^3 and b/w 0.015 g/mL .

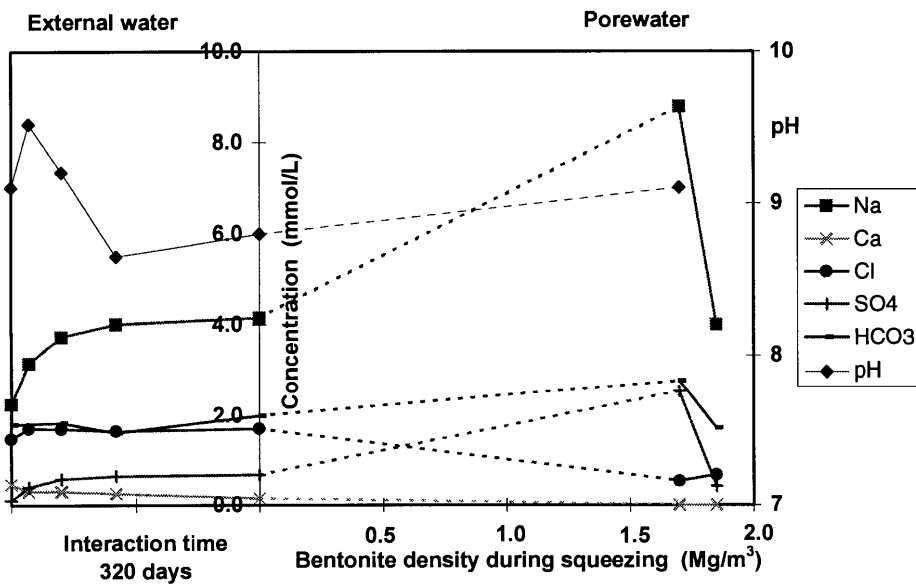


Fig. 4. Evolution of the external water and porewater chemistry during interaction and squeezing respectively. Fresh water experiment, dry density of bentonite 1.5 Mg/m^3 and b/w 0.015 g/mL .

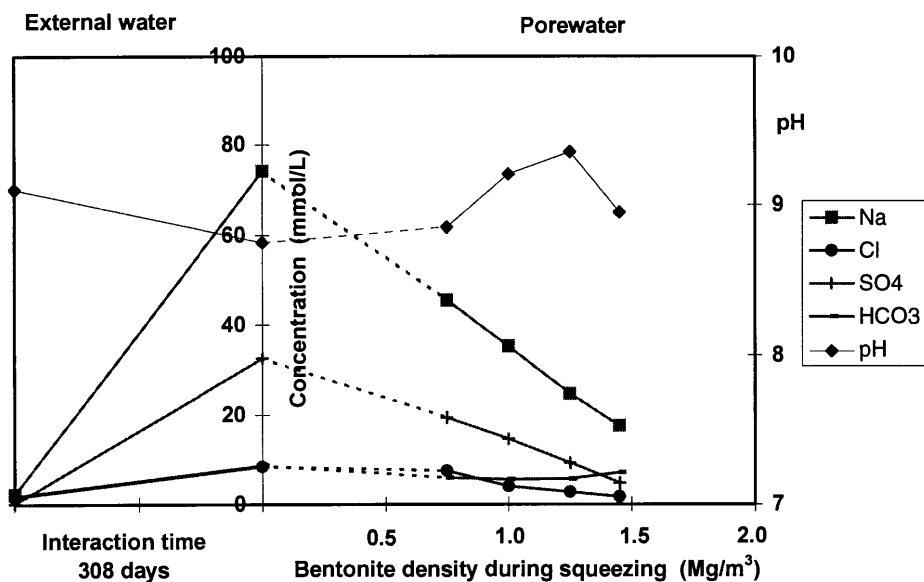


Fig. 5. Evolution of the external water and porewater chemistry during interaction and squeezing respectively. Fresh water experiment, dry density of bentonite 0.6 Mg/m^3 and b/w 0.5 g/mL .

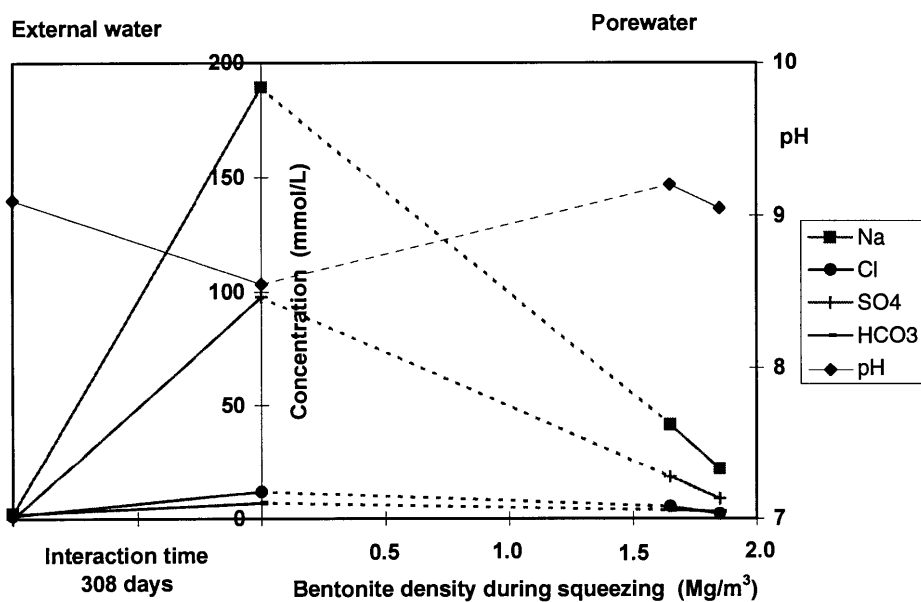


Fig. 6. Evolution of the external water and porewater chemistry during interaction and squeezing respectively. Fresh water experiment, dry density of bentonite 1.5 Mg/m^3 and b/w 1.5 g/mL .

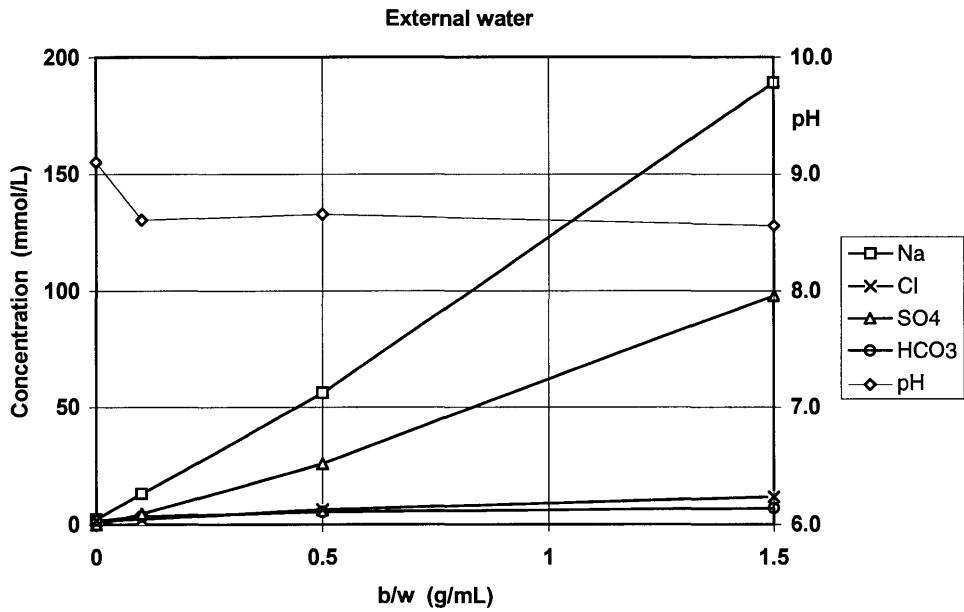


Fig. 7. Final concentrations of the external waters in the fresh water experiments. The dry densities of the samples were 1.5 Mg/m^3 .

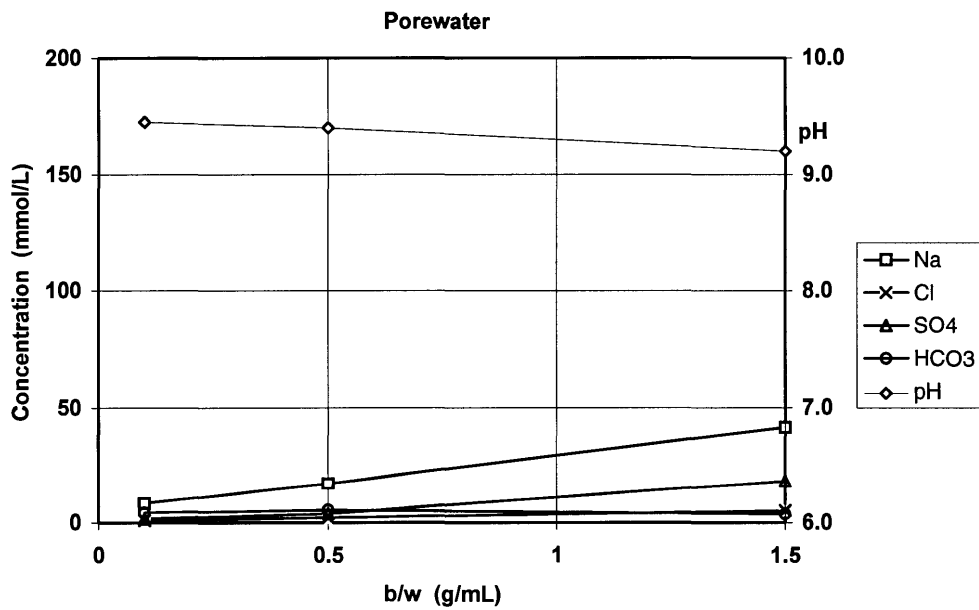


Fig. 8. Concentrations of the porewaters in the fresh water experiments. The dry densities of the samples were 1.5 Mg/m^3 .

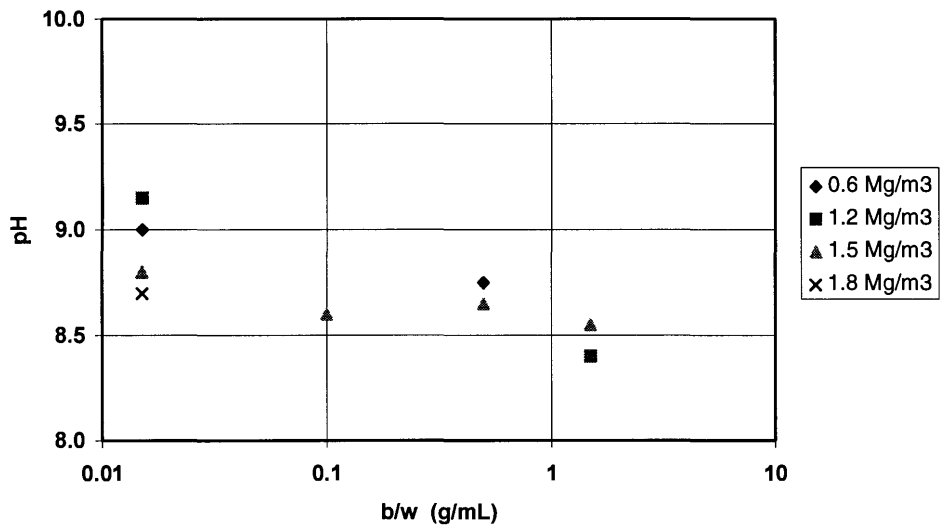


Fig. 9. Final pH values of the external solutions in the fresh water experiments.

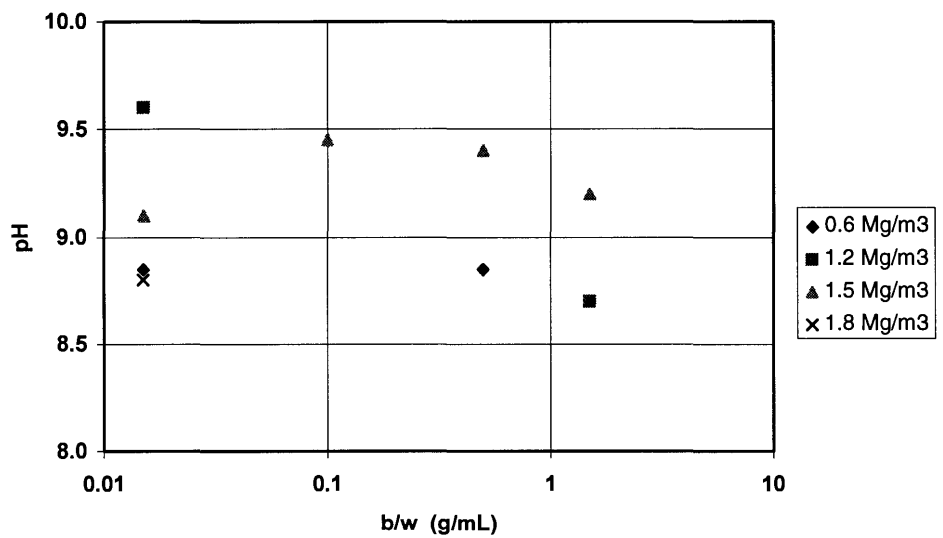


Fig. 10. The pH values of the first porewater fractions in the fresh water experiment.

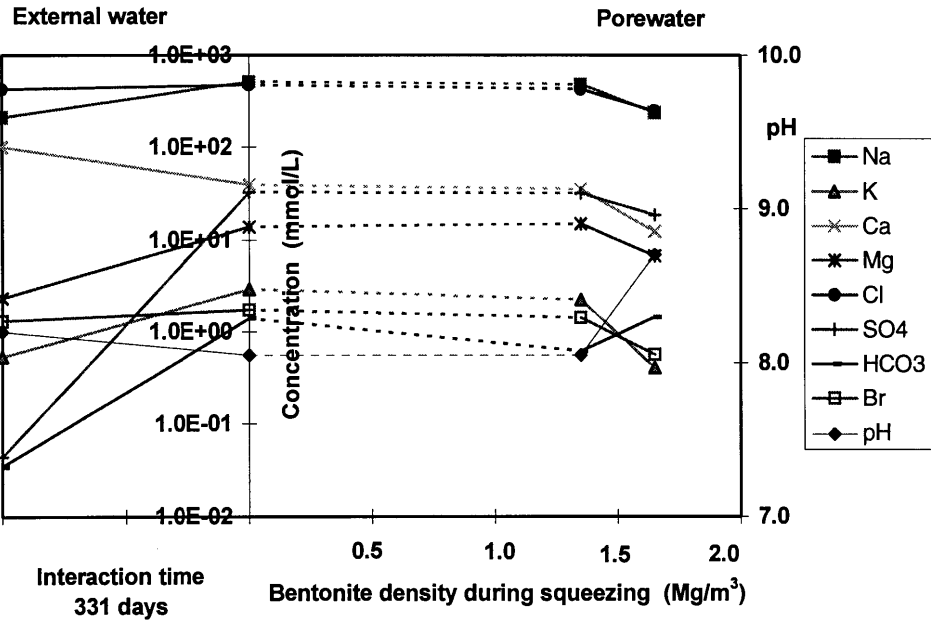


Fig. 11. Evolution of the external water and porewater chemistry during interaction and squeezing respectively. Experiment with saline water, dry density of bentonite 1.2 Mg/m^3 and b/w 1.5 g/mL .

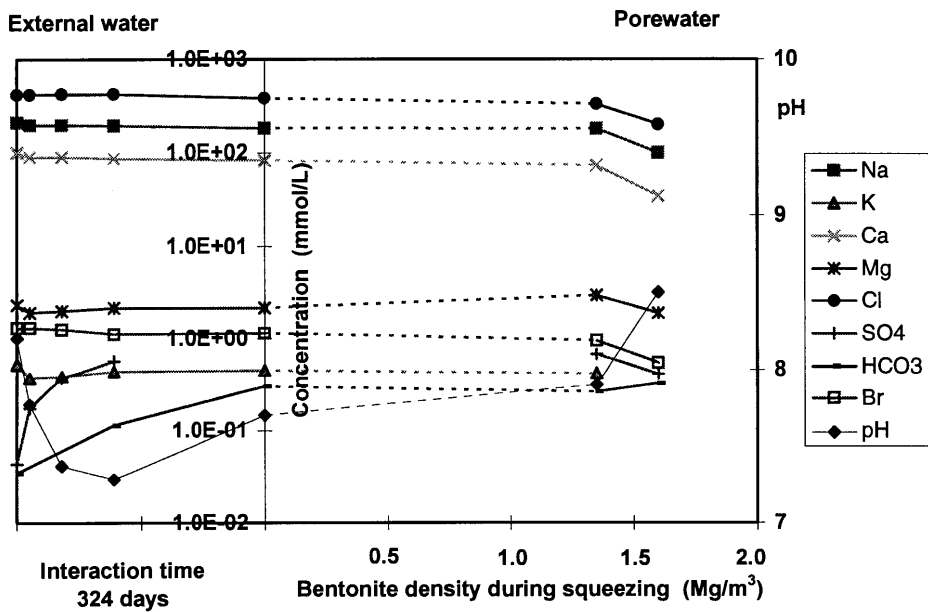


Fig.12. Evolution of the external water and porewater chemistry during interaction and squeezing respectively. Experiment with saline water, dry density of bentonite 1.2 Mg/m^3 and b/w $0,015 \text{ g/mL}$.

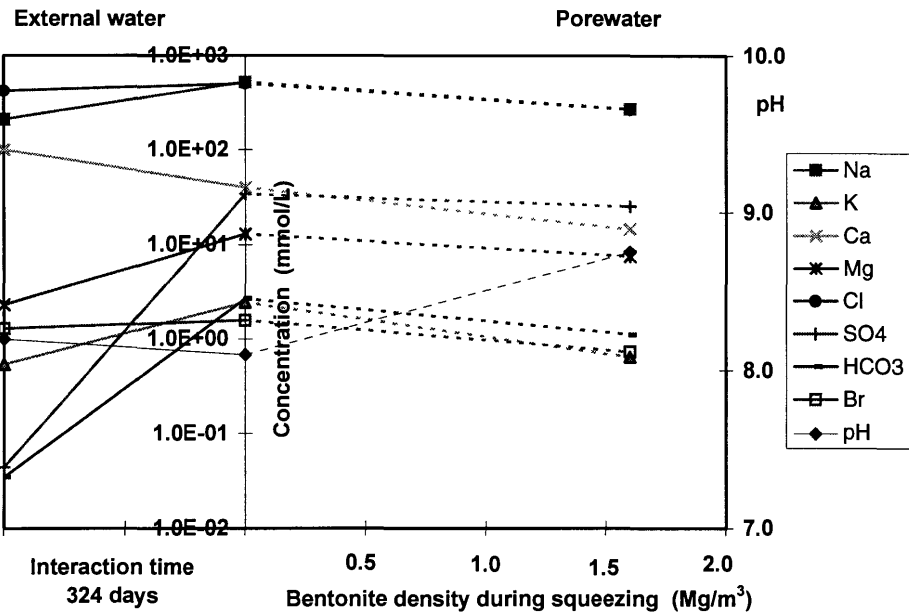


Fig. 13. Evolution of the external water and porewater chemistry during interaction and squeezing respectively. Experiment with saline water, dry density of bentonite 1.5 Mg/m^3 and b/w 1.5 g/mL .

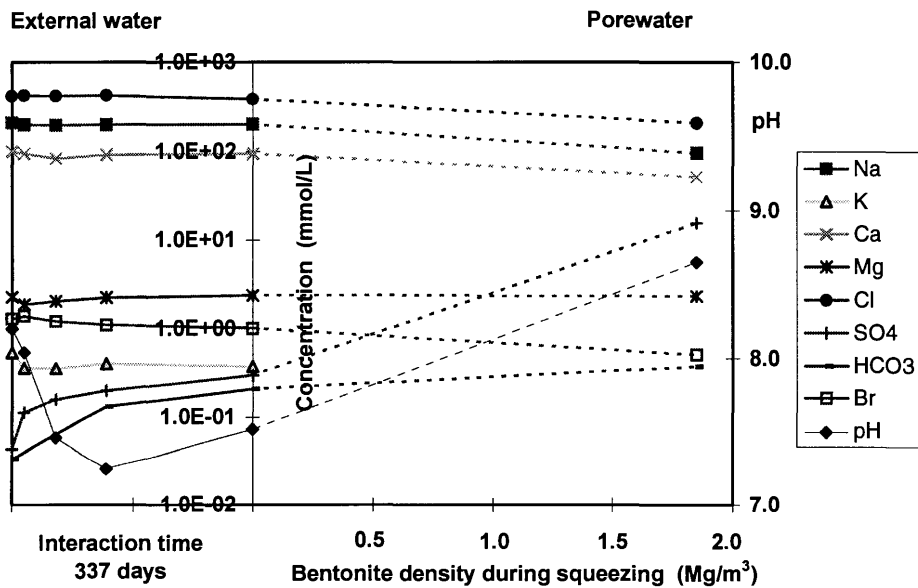


Fig. 14. Evolution of the external water and porewater chemistry during interaction and squeezing respectively. Experiment with saline water, dry density of bentonite 1.8 Mg/m^3 and b/w 0.015 g/mL .

2.2.2 Experiments with the mixtures of montmorillonite, CaCO_3 and CaSO_4

The artificial bentonites were prepared by mixing CaCO_3 or CaSO_4 or both of them with Na-montmorillonite purified from MX-80. The purification procedure was modified from that by Sposito et al. (1981) and included the following steps:

- 450 g of air dry MX-80 bentonite was mechanically mixed with 9 litres of deionized water. The fraction $< 2 \mu\text{m}$ was separated by centrifuging.
- The suspension was flocculated by adding 9 litres of 1 M NaCl solution at pH 3. The bentonite was separated by centrifuging. The washing was repeated 13 times until the pH value was about three.
- Washing was continued with 0.1 M NaCl solution until a pH value of 5.8 was reached. Seven washings with 9 litres of solution was needed.
- The separated bentonite was then washed twice with 9 litres of 0.01 M NaCl solution at pH 5.8.
- The bentonite separated by centrifuging was moved to dialysis bags and dialyzed six times with 25 litres of deionized water until the obtained electrical conductivity of water during 20 hours changed from only $1.5 \mu\text{S/cm}$ to $4.5 \mu\text{S/cm}$. The pH value of the dialysis solution at the end of the process was 6.5.
- The bentonite suspension was vacuum freeze-dried.

The total recovery of the purification process was about 75 % .

The interaction of the artificial bentonites with deionized water was studied with compacted and soft clay samples. Table 4 gives the experimental conditions and the compositions of the clays used in the experiments.

In the experiments where the b/w values were low, the solution volume was big enough to allow sampling during the interaction. The preliminary analysis of the external solutions for the compacted clays with the b/w at 0.015 g/mL are presented in Table 5. The ions found in the solutions are sodium, bicarbonate and sulphate. The calcium released, when CaCO_3 and CaSO_4 dissolve, is not seen in the external water. It has obviously exchanged for sodium of the montmorillonite. The experiments will still continue for about half a year.

The conditions, together with the results for the 100-day-long interaction experiment with soft clay are given in Table 6. The ions found in the water are sodium, calcium, bicarbonate and sulphate. The calcium released, when CaCO_3 and CaSO_4 dissolve, is seen in the water when CaSO_4 content in the bentonite is high. Part of the dissolved calcium is obviously exchanged for sodium of the montmorillonite.

Table 4. Conditions of the interaction experiments with deionized water and mixtures of sodium montmorillonite, CaCO_3 and CaSO_4 .

Na-montmorillonite + CaCO_3

Solution	Density (Mg/m^3)	CaCO_3 (%)	b/w-ratio (g/mL)			
Di. w.	loose	3.0	0.1			
Di. w.	loose	1.0	0.1			
Di. w.	loose	0.4	0.1			
Di. w.	loose	0.2	0.1			
Di. w.	loose	0	0.1			
Di. w.	1.5	3.0	1.5			
Di. w.	1.5	1.0	1.5	0.5	0.1	0.015
Di. w.	1.5	0.4	1.5	0.5	0.1	0.015
Di. w.	1.5	0.2	1.5			
Di. w.	1.5	1.0	3.4	100 % RH		

Na-montmorillonite + CaSO_4

Solution	Density (Mg/m^3)	CaSO_4 (%)	b/w-ratio (g/mL)			
Di. w.	loose	8.1	0.1			
Di. w.	loose	2.4	0.1			
Di. w.	loose	1.0	0.1			
Di. w.	loose	0.4	0.1			
Di. w.	1.5	3.0	1.5			
Di. w.	1.5	1.0	1.5	0.5	0.1	0.015
Di. w.	1.5	0.4	1.5	0.5	0.1	0.015
Di. w.	1.5	0.2	1.5			
Di. w.	1.5	1.0	3.4	100 % RH		

Na-montmorillonite + CaCO_3 + CaSO_4

Solution	Density (Mg/m^3)	CaCO_3 (%)	CaSO_4 (%)	b/w-ratio (g/mL)			
Di. w.	loose	1.0	2.4	0.1			
Di. w.	loose	1.0	1.0	0.1			
Di. w.	loose	1.0	0.4	0.1			
Di. w.	1.5	1.0	1.0	1.5	0.5	0.1	0.015
Di. w.	1.5	1.0	1.0	3.4	100 % RH		

Table 5. Evolution of the chemistry in the external solution of the interaction experiment with deionized water and compacted mixtures of sodium montmorillonite, CaCO₃ and CaSO₄. Bentonite dry density was 1.5 g/cm³ and b/w ratio 0.015 g/mL.

CaCO ₃ (%)	CaSO ₄ (%)	Exp.time (day)	pH	Na (mmol/L)	HCO ₃ (mmol/L)	SO ₄ (mmol/L)
1	0	31	8.1	0.07	0.07	0.00
1	0	106	7.6	0.32	0.25	0.00
0.4	0	31	8.0	0.20	0.16	0.00
0.4	0	106	8.0	0.36	0.49	0.00
0	1	31	6.7	0.54	0.03	0.28
0	1	106	7.8	1.09	0.06	0.50
0	0.4	31	7.8	0.22	0.02	0.12
0	0.4	106	8.0	0.55	0.04	0.26
1	1	31	8.3	0.68	0.12	0.26
1	1	106	8.0	1.95	0.60	0.48

Table 6. Chemical composition of the solutions when deionized water was equilibrated with non-compacted mixtures of sodium montmorillonite, CaCO₃ and CaSO₄. The b/w ratio was 0.1 g/mL and experimental time about 100 days.

CaCO ₃ (%)	CaSO ₄ (%)	pH	Na (mmol/L)	Ca (mmol/L)	SO ₄ (mmol/L)	HCO ₃ (mmol/L)
0.00	0,00	5.5	3,6	0.0	0,5	0.5
3,00	0.00	8,7	15.7	0,3	0.2	24,5
1.00	0,00	8.7	14,3	0.0	0,4	21.3
0,40	0.00	8,4	9.3	0,0	0.3	10,7
0.20	0,00	7.8	4,4	0.0	0,0	3.8
0,20	0.00	7,8	4.3	0,0	0.0	3,7
0.00	7,90	5.2	57,2	12.0	39,0	0.0
0,00	2.37	5,5	35.4	0,9	17.8	0,0
0.00	1,00	5.1	19,9	0.0	8,7	0.0
0,00	0.42	5,3	12.0	0,0	4.9	0,0
1.00	2,40	9.2	30,1	0.7	11,6	9.0
1,00	0.79	9,1	22.5	0,3	5.4	17,6
1.00	0,43	9.1	19,1	0.3	3,5	22.4

2.2.3 Experiments with the mixtures of montmorillonite and pyrite

The interaction of deionized water with artificial bentonites prepared of sodium montmorillonite and pyrite is studied with compacted and soft clay samples. Spanish pyrite was ground to a size of $< 10 \mu\text{m}$. Table 7 gives the conditions and the compositions of the clays used in the experiments. The experiments have just been started and are planned to continue for about one year.

Table 7. The conditions used in the experiments with the mixtures of sodium montmorillonite and pyrite.

Solution	Density (Mg/m ³)	Pyrite content (%)	Surrounding conditions	Liquid conditions	b/w-ratio (g/ml)	Experimental time (months)
Di. w..	loose	3	Aerobic	Free liquid	0.1	1
Di. w.	Loose	3	Aerobic	Free liquid	0.1	3
Di. w.	Loose	3	Aerobic	Free liquid	0.1	6
Di. w.	Loose	3	Aerobic	Free liquid	0.1	12
Di. w.	Loose	3	Anaerobic	Free liquid	0.1	1
Di. w.	Loose	3	Anaerobic	Free liquid	0.1	3
Di. w.	Loose	3	Anaerobic	Free liquid	0.1	6
Di. w.	Loose	3	Anaerobic	Free liquid	0.1	12
Di. w.	1.5	3	Aerobic	Free liquid	0.1	1
Di. w.	1.5	3	Aerobic	Free liquid	0.1	3
Di. w.	1.5	3	Aerobic	Free liquid	0.1	6
Di. w.	1.5	3	Aerobic	Free liquid	0.1	12
Di. w.	1.5	3	Anaerobic	Free liquid	0.1	1
Di. w.	1.5	3	Anaerobic	Free liquid	0.1	3
Di. w.	1.5	3	Anaerobic	Free liquid	0.1	6
Di. w.	1.5	3	Anaerobic	Free liquid	0.1	12
Di. w.	1.5	3	Aerobic	100 % RH	3.4	Saturation
Di. w.	1.5	3	Aerobic	100 % RH	3.4	Saturat. + 3
Di. w.	1.5	3	Aerobic	100 % RH	3.4	Saturat. + 6
Di. w.	1.5	3	Anaerobic	100 % RH	3.4	Saturation
Di. w.	1.5	3	Anaerobic	100 % RH	3.4	Saturat. + 3
Di. w.	1.5	3	Anaerobic	100 % RH	3.4	Saturat. + 6

Di.w. = deionized water

100 % RH = 100 % relative humidity

3 SUMMARY

The evolution of porewater chemistry in bentonite is studied in solution-bentonite interaction experiments. The compacted bentonite is in contact with the external solution through a steel sinter or the sample is saturated in 100 % relative humidity. The experiments are continued until equilibrium between the solution and bentonite is reached or the bentonite is fully water-saturated, respectively. Part of the experiments are performed by mixing soft clay and the solution. The parameters varied are the bentonite density, bentonite-to-water ratio (b/w), ionic strength of the solution, and the composition of bentonite. The bentonite types used in the experiments are commercial MX-80 and artificial bentonites prepared from purified MX-80 in sodium form where CaCO_3 , CaSO_4 and pyrite are added. At the end of the experiment, the equilibrating external solution and the porewater squeezed out of the bentonite samples are analysed to give information for interpretation of the interaction.

The experiments performed with MX-80 bentonite suggest that the evolution of porewater chemistry is determined by the dissolving components initially present in the bentonite together with the ions coming with water from the surroundings. Ion-exchange processes occur between the exchangeable cations of montmorillonite, the main component of the bentonite, and the cations in the porewater. Typical of the experiments with fresh water is diffusion of sodium and sulphate from the bentonite to the external solution, and diffusion of calcium from the solution to the bentonite. The obtained concentrations in the external solution and porewater strongly depend on the b/w used. In the case of low b/w, the dissolving components of the bentonite are diluted, while in the case where the b/w is high, the obtained concentrations in the porewater are high, too.

The ions found in the external waters, when the artificial clay was prepared of sodium montmorillonite, CaCO_3 and CaSO_4 , were sodium, calcium, bicarbonate and sulphate. Calcium is only seen when CaSO_4 content in the bentonite is high. Part of the dissolved calcium is obviously exchanged for sodium of the montmorillonite. These experiments are still to be continued. The experiments with montmorillonite and pyrite have just been started and are planned to continue for about one year.

4 REFERENCES

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