

## LOW TEMPERATURE EXPERIMENTAL INVESTIGATION OF THE EFFECT OF HIGH pH NaOH SOLUTIONS ON THE OPALINUS SHALE, SWITZERLAND

J. A. CHERMAK

Mineralogisch-Petrographisches Institut, Universität Bern, Baltzerstrasse 1, CH - 3012 Bern, Switzerland

**Abstract**—Batch reactor experiments were performed at 150°C, 175°C, and 200°C to determine the effect of high pH NaOH solutions on the mineralogy of the Opalinus shale. In these experiments, the change in solution quench pH at 25°C, solution composition, and mineralogy were monitored as a function of time for up to ≈40 days. Runs were performed in 50 ml titanium hydrothermal reactor vessels. Each reactor was charged with 0.5–5.0 g of the 80–200 mesh size fraction of Opalinus shale, and 25 ml of solution (0.1 and 0.01 M NaOH). The general sequence of reaction products observed under these high pH conditions include first the formation of analcime, followed by vermiculite, and finally Na-rectorite formation.

**Key Words**—Analcime, Experimental investigation, High pH, Na-rectorite, Opalinus shale, Vermiculite.

### INTRODUCTION

High pH solution-mineral reactions occur naturally in a variety of geological environments and also where the environment has been modified by various engineering projects. Two common engineered high pH environments include emplaced concrete (Andersson *et al.*, 1989; Lunden and Andersson, 1989) and alkaline flooding of sandstone reservoirs (Novosad and Novosad, 1984; Mohnot *et al.*, 1987). In the case of concrete, high pH fluids enter the host rock significantly alter the *in situ* pH, solution composition, and mineralogy of the surrounding rock (McCulloch *et al.*, 1985; Chapman and Flowers, 1986). The interaction of this high pH plume with the host rock is now a major area of study (Savage *et al.*, 1991; Berner, 1990). The minerals formed under high pH conditions in natural environments include zeolites and clay minerals. Their precipitation has also been documented in the laboratory using many different starting materials (Barrer, 1982), although very little experimental data exists on the effects of the interaction of high pH solutions with shales. This present experimental investigation examines the effect of high pH NaOH solutions on the Opalinus shale (middle Jurassic, Mont Terri, Northern Switzerland).

The breakdown of concrete in natural environments produces high pH conditions. The pore fluids associated with cement range in pH from 12.5–13.5, have high ionic strengths, and are dominated by Na and K in concentrations ranging from 300–4200 ppm and from 100–7500 ppm, respectively (Andersson *et al.*, 1989; Lunden and Andersson, 1989). Ca concentrations in these pore fluids are much lower and range in concentration from 20–130 ppm. The release of this high pH plume to the surrounding media has been modeled

(Haworth *et al.*, 1989; Reardon, 1990; Jefferies *et al.*, 1988; Berner, 1990; Vieillard and Rassinoux, 1992) and shows first a period of NaOH and KOH release (pH > 13), followed by a solution composition controlled by portlandite (CaOH<sub>2</sub>) solubility (pH to 12.5 at 25°C), and finally a solution controlled by calcium-silicate-hydrate (CSH) gels (pH to 9–10).

Concrete and cement are proposed as matrix material, backfill material, and as structural components of radioactive waste repositories (Bath *et al.*, 1987). The amount of concrete and cement associated with these repositories, especially in low-level waste facilities is often quite large (e.g.,  $8.2 \times 10^5$  m<sup>3</sup>, Karlsson *et al.*, 1986). Surrounding these repositories will be a series of engineered barriers known as the multiple barrier approach (Bredhoeft *et al.*, 1978; Hoffman and Choppin, 1986). The final barrier will be the host rock. Shales, due to their high sorption properties and low permeabilities, are considered as suitable rocks for low- and high-level radioactive waste repositories (Brookins, 1987; Chapman and McKinley, 1987; Hollister *et al.*, 1981; Krauskopf, 1986; 1988). The interaction of the high pH fluid associated with the concrete and the shales needs to be considered to determine the effects of this high pH fluid on host rock mineralogy and radionuclide sorption (Karlsson *et al.*, 1986; Allard *et al.*, 1985).

Natural analogs can be used to determine transformations that occur when minerals are exposed to high pH fluids (Alexander *et al.*, in press; Khoury *et al.*, 1985; Khoury *et al.*, in press). In the natural system, high pH fluids that produce zeolites occur in six general regimes (Hay 1978, 1986). The type of zeolite that forms is highly dependent on source material, chemistry of the pore fluids, temperature, and time. The five

most abundant naturally occurring zeolites are analcime, phillipsite, clinoptilolite, heulandite, and laumontite (Hay, 1978). The formation of analcime (Moncure *et al.*, 1981) is important in the present experimental study.

The precipitation of clay minerals in nature under mid- to high pH conditions has been observed (Pevear *et al.*, 1980; Velde, 1985), but has not been intensively studied. Clay mineral transformations in shales are observed during burial diagenesis in response to increased temperature and changing solution composition as well as in the weathering environment. Precipitation and transformation of the expandable phases vermiculite and smectite are quite common. Increasing temperature associated with burial diagenesis of shales often leads from smectite to random illite/smectite alteration and then to the formation of a rectorite-like mineral (R1 ordered) and finally to illite (Hower *et al.*, 1976). In hydrothermal alteration zones the formation of smectite and rectorite has also been observed (Pevear *et al.*, 1980). In this regime, the volcanic glass first alters to smectite and later to rectorite (temperatures = 145°–160°C). Also the formation of high charge vermiculites from chlorite has been widely observed (Velde, 1985).

High pH fluid-mineral reactions producing zeolites and clays have been studied quite extensively in the laboratory (Barrer, 1982). Both zeolite and clay minerals have been synthesized using different starting materials and over a range of temperatures, solution compositions and pHs. Under high solution pH conditions similar to those expected in the cement-shale system, varying types of zeolites have been observed to grow and precipitate (Donahoe *et al.*, 1984; Donahoe and Liou, 1985; Hawkins, 1981; van Aardt and Visser, 1977). Especially applicable to this study are those experiments conducted in the Na hydroxide systems (Barth-Wirshing and Höller, 1989), where the starting material used was rhyolitic glass and the precipitation of analcime was observed. Experimental clay mineral transformations in shales have also been widely studied in the laboratory (Eberl, 1978; Velde, 1985; Whitney and Northrop, 1988). Directly applicable to this study is the work of Eberl (1978) and Matsuda and Henmi (1983) where the transformation of smectites and kaolinite to rectorite was observed. The effects of high solution pH on silicate dissolution rates have been studied by Brady and Walther (1989), who showed that minerals in contact with high pH solutions have increased dissolution rates due to mineral surface speciation.

To investigate mineralogical alterations when shales are in contact with high pH NaOH solutions, experiments were conducted at 150°C, 175°C, and 200°C using the Opalinus shale. In these experiments both solids and solutions were monitored as a function of time to determine changes that occur in the solution and in the mineralogy of the shale.

## EXPERIMENTAL METHODS

Batch experiments were run in 50 ml titanium hydrothermal reactor vessels whose details and design are given in Chermak and Rimstidt (1990). These reactors were sealed and placed onto a rotisserie unit (8 rpm) inside an oven set at temperatures of 150°C, 175°C, or 200°C for reaction times up to 42 days. Each reactor was charged with variable amounts (0.5–5.0 g) of the 80–200 mesh size fraction of Opalinus shale, and 25 ml of solution of varying NaOH composition (0.1–0.01 M). The specific surface area of the starting solid was calculated from a N<sub>2</sub> desorption BET isotherm to be 14.7 m<sup>2</sup>/g. The total organic matter in the shale is <0.5 wt. %. Individual reactors were removed at specific intervals, quenched in cold water, and opened. The solution pH was measured at 25°C using a Ross combination pH electrode, and the solids were separated from the solution by centrifugation and then decanting the solution. The solution was filtered through a 0.45 μm filter and saved for further analysis. The solids were then washed with distilled/deionized water and saved for X-ray diffraction analysis.

Dissolved Na and Si concentrations were determined for all samples, and Ca, Mg, Al, and Fe were determined for select runs. Na concentration in solution was determined by atomic adsorption spectrophotometry (AAS) using a CsCl ionization buffer (Varian, 1979). In select samples (the 175°C run), Na was determined by ion chromatography (IC) and differed from the AAS values by <3%. IC was also used to determine Mg and Ca concentrations for all samples in the 175°C run. Mg values were below 5 ppm for all samples. Silica concentrations were determined colorimetrically using the molybdate blue method (Govett, 1961; Gieskes and Peretsman, 1986). Al concentration in solution was determined (at 2, 10, and 30 days at 175°C) by ion coupled plasma spectrophotometry (ICP) and was very low and close to the detection limit of the instrument (0.5 ppm). In select samples, Fe in solution was measured by the Dipiridal colorimetric method (E. Merck AG, 1966) and was found to be below detection limits (0.2 ppm).

The Opalinus shale was characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), and surface area analysis. Reaction products were examined by XRD and SEM. The Ca saturated, <4 μm fraction, which appeared to have the largest amount of reaction products, was prepared by the millipore method (Moore and Reynolds, 1989) and utilized for XRD analysis. Patterns were collected for air-dried, glycolated, and heat-treated (550°C for one hour) samples. To characterize the nature of the expandable phase, further diffraction patterns were collected after Mg saturation and exposure to both glycol and glycerol. XRD determination of the amount of quartz and calcite was done on the bulk

Table 1. Oxide composition as determined by XRF of the starting Opalinus shale. The amount of FeO in the starting shale was determined colorimetrically and is = 1.90%.

Chemical component	Weight percent
SiO <sub>2</sub>	67.38
Al <sub>2</sub> O <sub>3</sub>	10.83
Fe <sub>2</sub> O <sub>3</sub>	4.90
CaO	10.92
MgO	1.95
MnO	0.06
TiO <sub>2</sub>	0.71
Na <sub>2</sub> O	0.83
K <sub>2</sub> O	2.09
P <sub>2</sub> O <sub>5</sub>	0.36
Total	100.03
Loss on ignition	15.97

shale using LiF internal standard mixture (Brindley, 1980) and semi-quantitative analysis of the <4 $\mu$ m fraction was determined by comparing patterns to those of standard clay mineral mixtures (Snyder and Bish, 1989; Brindley, 1980; Pawloski, 1985). Quantitative determination of mineral phases in shales is quite difficult, and in this study only relative changes in mineral proportions are discussed (i.e., total disappearance of diffraction peaks and appearance of new peaks). Mineral composition of the starting shale is approximately: 40% quartz, 20% kaolinite, 15% muscovite (illite), 15% calcite, 5% chlorite, 3% mixed layer illite/smectite, 2% siderite and a trace of pyrite. These values were comparable to estimates derived by optical microscopy. Table 1 gives the chemical composition of the starting Opalinus shale as determined by XRF (reduced iron was determined by the method of E. Merck AG, 1966). SEM was used to examine crystal habit and morphology and to aid in confirming reaction products.

## RESULTS

Table 2 gives the quench pH at 25°C, Na, Ca (175°C only) and Si concentration vs time data at 150°C, 175°C, and 200°C for six experiments. These experiments evaluate the effect of temperature (150°C, 175°C and 200°C with 0.5 g solid and 25 ml of 0.1 M NaOH solution), solid/solution ratio, (200°C with 0.5, 1.5, and 5.0 g of solid) and solution composition (200°C with 0.5 g solid and 25 ml of 0.1 and 0.01 M NaOH solution) on the transformations occurring as a function of time in the Opalinus shale. Figure 1 shows a plot of quench pH at 25°C versus time at 150°C, 175°C, and 200°C. In the 150°C and 175°C experiments the pH dropped to a value of 11.70 and 11.33 after 26 and 17 days, respectively and was constant for the remainder of the experiments. Notice the large effect that the amount of shale has at 200°C with 0.5, 1.5, and 5.0 g of solid on the solution pH, indicating a substantial buffering capacity (Table 2).

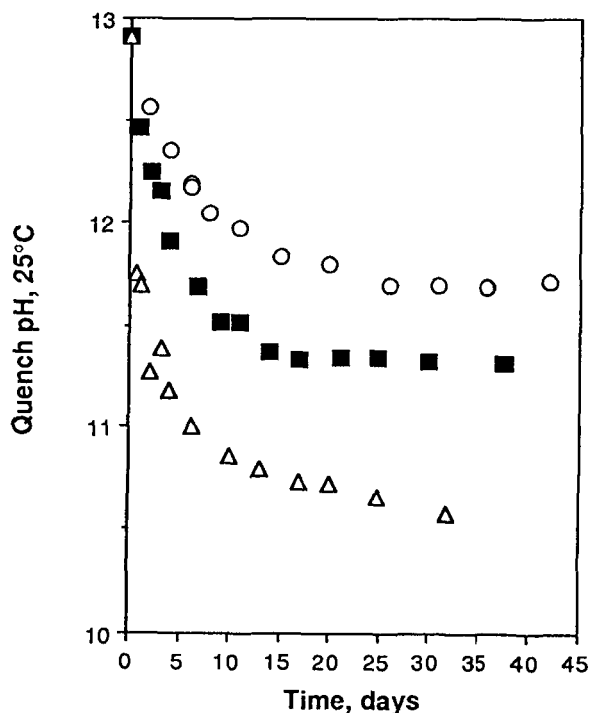


Figure 1. A plot of quench pH at 25°C vs time in days for 0.1 M NaOH experiments at 150°C (open circles), 175°C (solid squares), and 200°C (open triangles).

The determined Na and Si values (see Table 2) showed errors in reproducibility of <2% using AAS and <3% using colorimetric methods, respectively. In the lower temperature runs (150°C and 175°C, Table 2), a general decreasing trend can be observed although the Na data is a bit erratic. This can possibly be explained by the presence of poorly crystalline vermiculite and Na-rectorite with the ability to exchange Na. Silica data for 150°C, 175°C, and 200°C runs are plotted in Figure 2 and show a range of values from 400–1275 ppm; interpretation of this data will be given in the discussion section.

Along with the changes in solution composition with time, mineralogical transformations were monitored. Reaction products found in experiments in the <4 $\mu$ m fraction as determined by XRD are given in Table 3. A general sequence of events observed at all temperatures include first the precipitation of analcime, followed by vermiculite precipitation, and finally by Na-rectorite precipitation. Figure 3 shows three XRD patterns of the Ca saturated, ethylene glycol solvated <4 $\mu$ m fraction of the starting Opalinus clay and products at 175°C after 1 and 38 days. The first observed expandable phase was Ca saturated and exposed to glycol and expanded to  $\approx$ 16.1Å. This phase was Mg saturated and exposed to both glycol and glycerol and showed no evidence of expansion (d(001) peak at 14.1 Å), and thus called vermiculite (see review, Brindley,

Table 2. Quench pH at 25°C, Na, Si, and Ca (175°C only) concentration versus time data at 150°C, 175°C, and 200°C.

Time, days	pH 25°C	Na, ppm	Silica, ppm
150°C, 0.1 M NaOH, 0.5 g			
0.000	12.91	2300	0
1.937	12.56	2016	557
4.000	12.35	2006	1205
6.000	12.19	1975	1154
6.000	12.17	1957	1149
7.896	12.04	1921	1029
11.000	11.97	1873	940
14.980	11.83	1872	940
20.052	11.80	1835	909
26.031	11.70	1863	878
30.875	11.70	1849	897
35.771	11.69	1791	859
41.948	11.71	1850	892

Time, days	pH 25°C	Na, ppm	Silica, ppm	Ca, ppm
175°C, 0.1 M NaOH, 0.5 g				
0.000	12.91	2300	0	0
1.000	12.46	1976	856	290
2.000	12.24	1911	1275	180
3.000	12.15	1939	1262	370
4.000	11.91	1885	1022	4.0
6.760	11.69	1866	923	23.0
8.990	11.51	1826	918	4.0
11.010	11.51	1787	900	3.0
13.865	11.37	1850	882	12.0
17.000	11.33	1859	882	4.0
21.000	11.34	1917	891	4.0
24.792	11.34	1724	847	5.0
30.000	11.32	1786	874	4.0
37.700	11.31	1796	864	2.0

200°C, 0.1 M NaOH, 0.5 g			
0.000	12.91	2300	0
0.833	11.75	1868	1021
1.083	11.70	1848	1038
2.062	11.27	1837	990
3.125	11.39	1841	950
4.000	11.18	1806	854
6.125	11.00	1789	897
9.916	10.86	1769	878
12.927	10.79	1761	806
16.917	10.73	1743	717
19.917	10.72	1751	756
24.771	10.66	1735	710
31.750	10.57	1504	651

200°C, 0.1 M NaOH, 1.5 g			
0.000	12.91	2300	0
0.875	11.28	1309	751
1.833	10.78	1262	624
2.948	10.69	1242	528
4.166	10.50	1235	436
6.979	10.41	1181	355
12.167	10.37	1233	341
17.021	10.26	1213	319
24.000	10.20	1175	304
33.104	10.11	1064	237

Table 2. Continued.

Time, days	pH 25°C	Na, ppm	Silica, ppm
200°C, 0.1 M NaOH, 5 g			
0.000	12.91	2300	0
0.875	9.53	927	31.0
2.000	8.07	831	70.0
2.020	8.06	839	69.1
3.125	7.81	776	70.1
5.792	7.66	678	63.2
12.833	7.58	672	57.0
16.958	7.53	693	60.8
33.104	7.60	799	59.1
33.114	7.65	—	—
200°C, 0.01 M NaOH, 0.5 g			
0.000	11.88	265	0
0.792	9.41	258	40.9
1.917	8.95	245	59.6
4.771	7.63	227	70.1
8.730	6.96	230	71.7
13.719	6.77	184	78.9
20.750	6.76	177	81.9
23.708	6.75	216	76.1
34.875	6.68	175	73.2

—, not determined.

1966). The second expandable phase showed similar characteristics to Na-rectorite (Ca saturated air-dried and glycolated d(001) at  $\approx 22.5\text{\AA}$  and  $\approx 24.8\text{\AA}$ , respectively) and collapsed to  $19.6\text{\AA}$  after one hour at  $550^\circ\text{C}$

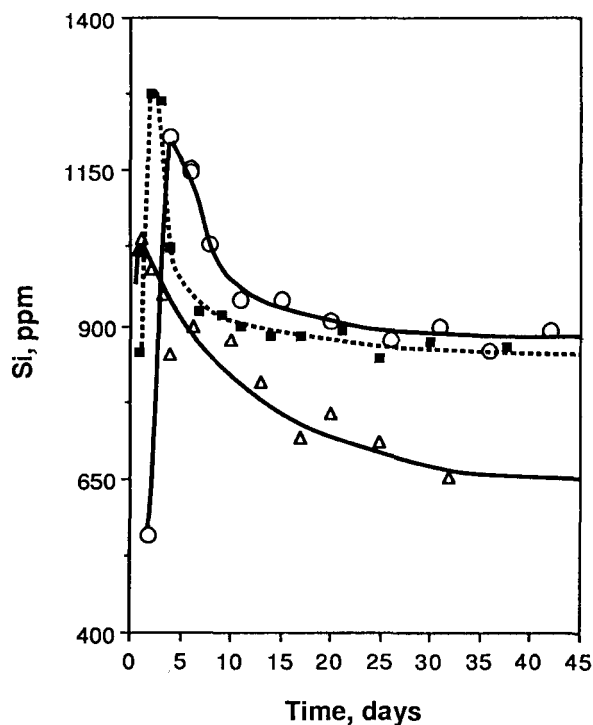


Figure 2. A plot of Si concentration, ppm vs time in days for 0.1 M NaOH experiments at 150°C (open circles), 175°C (solid squares), and 200°C (open triangles).

Table 3. Reaction products of the  $<4\mu$  fraction versus time data at 150°C, 175°C, and 200°C as determined by XRD.

Time, days	Reaction products
	150°C, 0.1 NaOH, 0.5 g
1.937–4.000	analcime
6.000–41.948	analcime, vermiculite, Na-rectorite
	175°C, 0.1 NaOH, 0.5 g
1.000	analcime
2.000–3.000	analcime, vermiculite
4.000–37.700	analcime, vermiculite, Na-rectorite
	200°C, 0.1 NaOH, 0.5 g
0.833–12.927	analcime, vermiculite, Na-rectorite
16.917–24.771	analcime, vermiculite, Na-rectorite, paragonite/paragonite
31.750	analcime, vermiculite, paragonite/paragonite
	200°C, 0.1 NaOH, 1.5 g
0.875–33.104	analcime, vermiculite, Na-rectorite
	200°C, 0.1 NaOH, 5 g
0.875–12.833	analcime
16.958–33.114	analcime, vermiculite
	200°C, 0.01 NaOH, 0.5 g
0.792	no change
1.917–34.875	analcime

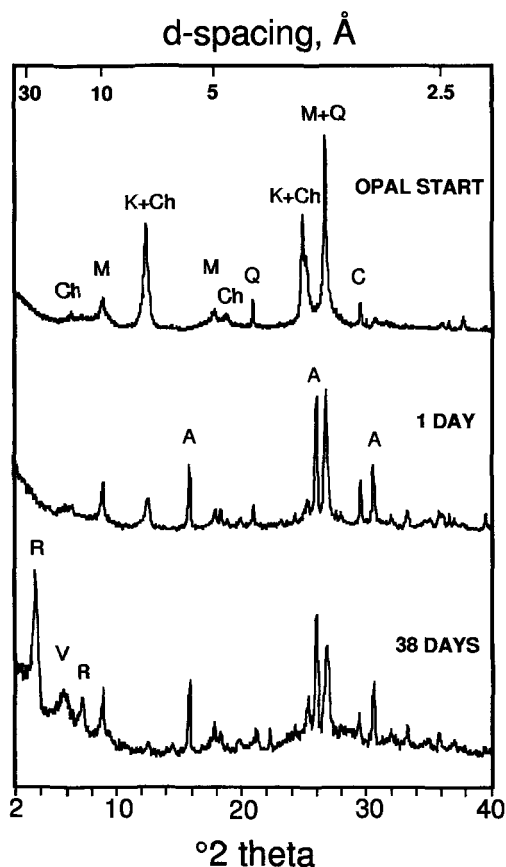


Figure 3. X-ray diffraction patterns of the Ca saturated, ethylene glycol solvated  $<4\mu$  fraction of the Opalinus shale. The

(Kodama, 1966). The behavior of the expandable layer showed no expansion with Mg saturation and exposure to both glycol and glycerol ( $d(001)$  at  $\approx 21.8 \text{ \AA}$ ). The expandable layer in the Na-rectorite mineral behaves similarly to the vermiculite during the different cation saturations. The effect of different cation saturations and the exposure to organic molecules on rectorites is an area where not much data exists in the literature.

Figure 4 shows SEM photographs of the reaction products in the 175°C experiment after 1.00,  $\approx 7$  and  $\approx 25$  days. The progression of reaction products is shown in these SEM photos: after 1 day, the pervasive precipitation of analcime cubes (a–b); followed by the precipitation of vermiculite after 7 days (c); and finally, after 25 days, the Na-rectorite phase (d). In the 0.5 g, 200°C experiment at times longer than  $\approx 17$  days the precipitation of a mixed-layer mica/mica mineral composed of two types of mica is observed. It seems reasonable to assume that both mica layers are paragonite or paragonitelike because the solution chemistry is dominated by Na. Figure 5 shows a X-ray diffraction pattern of this mineral after 31.75 days (this mineral does not expand when treated with ethylene glycol).

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top pattern is the starting Opalinus shale, and the middle and bottom patterns are the shale reacted with 0.1 M NaOH solution after 1 and 38 days, respectively. Labels on the X-ray diffraction peaks correspond to Ch = chlorite, K = kaolinite, Q = quartz, C = calcite, V = vermiculite, A = analcime, and R = Na-rectorite.

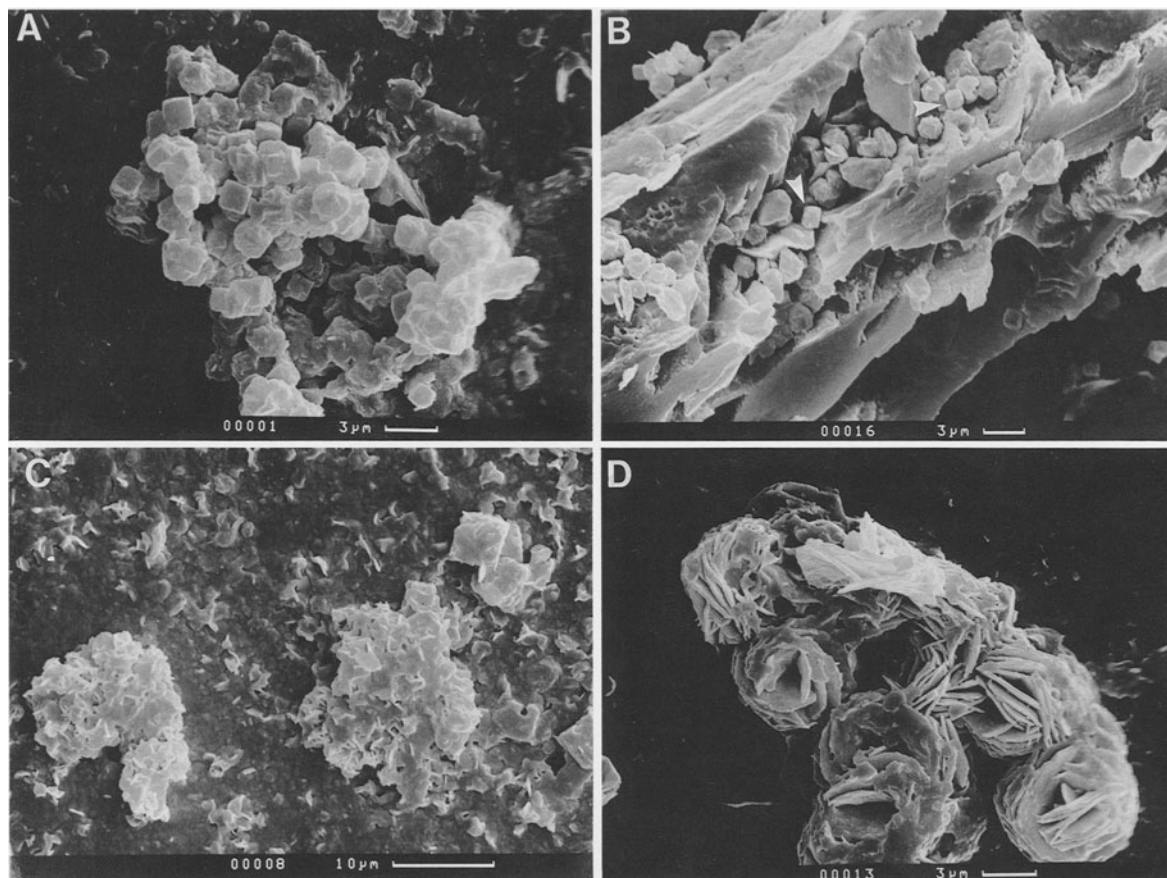
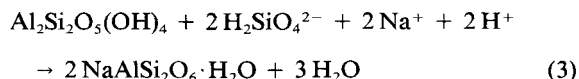
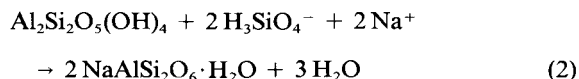
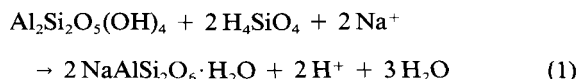


Figure 4. SEM photographs of reaction products at 175°C in contact with 0.1 M NaOH solutions: (A) analcime cubes that precipitated after 1 day; (B) dissolution of a quartz grain and the presence of analcime cubes (white arrows) after 1 day; (C) vermiculite grains that precipitated after  $\approx 7$  days; (D) Na-rectorite grains after  $\approx 25$  days.

The mineral is identified as a mixed-layer mica/mica because of the presence of a  $\approx 19.8\text{\AA}$  peak, which is interpreted as a compositional superlattice probably resulting from a significantly different Fe content of the two mica types. A theoretical diffraction pattern was generated using Newmod© (Reynolds, 1985) and is shown in Figure 5.

#### DISCUSSION

Combining the solution and solid data brings several details of the mineral transformations into focus. The first reaction product formed in these experiments is analcime. The precipitation of analcime and the corresponding decrease in the reactants kaolinite and quartz suggest that the first important reaction is kaolinite + quartz  $\rightarrow$  analcime. An experiment reacting only quartz and kaolinite in 0.1 M NaOH solutions at 175°C produced analcime. The distribution of silica is critical in determining if this reaction has an effect on solution pH. Three of the possible reactions in this system include:



Notice in reaction (1), analcime precipitation would correspond to  $\text{Na}^+$  consumption and  $\text{H}^+$  production, and thus to a large corresponding drop in pH. This large drop in pH is not observed in the 150°C, 175°C, and 200°C, 0.1 M NaOH experiments (Figure 1). The formation of analcime from kaolinite and quartz when  $\text{H}_3\text{SiO}_4^-$  is the dominant species (2) is independent of pH and is probably the important reaction initially in these experiments. In reaction (3) with analcime precipitation an increase in pH could possibly be observed. Analcime precipitation is pervasive in these

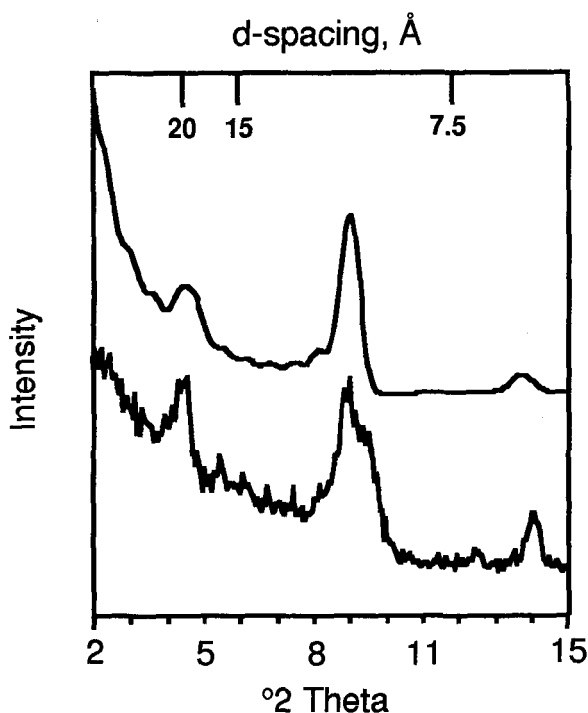


Figure 5. X-ray diffraction patterns of the Ca saturated, ethylene glycol solvated  $<4 \mu$  fraction of the Opalinus shale at  $200^\circ\text{C}$  after 31.75 days showing the paragonite/paragonite mineral (bottom pattern), note also the presence of a discrete muscovite phase. The top diffraction pattern is a Newmod© simulation of the mineral using  $d(001) = 9.66$  for both micas and full octahedral iron occupancy for one mica, and Reichweite = 1.

experiments but does not affect the pH when starting with a 0.1 M NaOH solution. Analcime precipitation under the conditions of reaction (1) could be pH controlling in the 0.01 M NaOH and 5.0 g experiments at  $200^\circ\text{C}$  as suggested by a large drop in pH and associated low silica values (Table 2).

The second mineral phase that precipitated in these experiments was vermiculite. The appearance of vermiculite coincided with a decrease in the amount of chlorite. The details of this reaction are complex and poorly understood at present, although transformations of this nature have been observed by other authors (e.g., Velde, 1985). After the development of vermiculite, the silica values in solution increase until the precipitation of a third mineral phase, Na-rectorite, is observed. The decrease in the solution silica values in the  $150^\circ\text{C}$  and  $175^\circ\text{C}$  (Figure 2) experiments corresponds to the precipitation of Na-rectorite (Table 3). In the  $150^\circ\text{C}$  and  $175^\circ\text{C}$  experiments, the products analcime, vermiculite, and Na-rectorite remain until the termination of the experiment. In the 0.5 g,  $200^\circ\text{C}$  experiment after  $\approx 17$  days the Na-rectorite phase begins to transform into a paragonite/paragonite phase. This reaction continues until the Na-rectorite totally

transforms to paragonite/paragonite (Figure 5) after  $\approx 32$  days.

The overall trend in clay mineral transformations from an expandable phase to Na-rectorite has also been observed by Eberl and Hower (1977) and Eberl (1978) and has been described as the "mica trend". Eberl also speculated that the Na-rectorite should further transform to paragonite. In Eberl's hydrothermal experiments temperatures ranged from  $260^\circ\text{C}$ – $400^\circ\text{C}$ , and starting reactants included gels of smectite composition and smectites that transform to Na-rectorite. The corresponding quench pH values ranged between 4 and 5. It is interesting to note that the same general trends are observed in these experiments although the temperatures are much lower ( $150^\circ\text{C}$ – $200^\circ\text{C}$ ) and the pHs much higher. It seems that these high pH conditions greatly increase reaction rates in this system.

There is a large effect of the amount of Opalinus shale used on the quench pH values (Table 2), although there seems to be no simple relationship between surface area of the solid and the corresponding pH value. The details of reactions such as these are fairly complex and are presently being modeled with irreversible thermodynamic models (Lichtner, 1985, 1988). Initial attempts at modeling pH values at lower temperatures have produced good agreement between the observed pH and the modeling results (Chermak and Lichtner, 1991), although, at  $75^\circ\text{C}$ , reaction products in experiments could not be observed after 60 days. More experimental data are required in these high pH environments to evaluate the ability of shales to affect the solution pH and to determine corresponding changes in mineralogy.

## CONCLUSIONS

The main purpose of this experimental investigation was to determine the effect of high pH NaOH solutions on the Opalinus shale. These high pH solutions are similar to those found in the pore waters of concrete, and these laboratory conditions simulate interactions that could occur in a repository environment where pore waters from the concrete interact with a host shale. Reactions of these solutions with the Opalinus shale reduce the pH and significantly changes the mineralogy of the shale. The general sequence of reaction products observed included first the precipitation of analcime; followed by vermiculite precipitation; and, finally, Na-rectorite precipitation. Starting minerals that were found to react include kaolinite, quartz, and chlorite.

Experiments conducted in the shale-high solution pH system can be used to constrain existing thermodynamic and kinetic models presently used in nuclear waste disposal. Experiments under these high pH conditions seem to show similar changes in mineralogy as found in other low pH, higher temperature studies, although reaction rates in the high pH environments are much faster.

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