Uptake of Ba^{2+} ions by natural bentonite and CaCO$_3$: A radiotracer, EDXRF and PXRD study

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Ba^{2+} uptake by natural bentonite, CaCO$_3$ in addition to a number of bentonite-CaCO$_3$ mixtures with variable compositions as a function of pH and Ba^{2+} concentration was studied. Radiotracer method, EDXRF, and PXRD were used. The results of radiotracer experiments showed that the uptake of Ba^{2+} by CaCO$_3$ was larger than its uptake by natural bentonite samples, particularly at low initial concentrations of Ba^{2+} and higher pH values. This finding was supported by the EDXRF results. According to the sorption data, the apparent $\Delta G°$ values of sorption were in the range -9 ± 1 to -13 ± 3 kJ/mol. The PXRD studies revealed the formation of BaCO$_3$ upon sorption of Ba^{2+} on pure CaCO$_3$ and on some of the bentonite-CaCO$_3$ mixtures.

Introduction

The fact that radionuclides encountered in radioactive waste have a harmful impact on the biosphere makes investigation of the retardation of these radionuclides by various soil fractions an important issue. Barium isotopes include various radionuclides among which is ^{140}Ba ($T_{1/2} = 12.8$ d). Although this radionuclide has a short half-life, it is particularly important because it is formed in high yield (6.24%) during the fission process.[1]

Bentonite is a clay mineral with outstanding sorption characteristics compared with other clay minerals. Its high cation exchange capacity, wide availability, thermal stability and favorable swelling behavior makes it one of the most appropriate clays suggested to be used as backfill material in the radioactive waste repositories.[2] On the other hand, carbonate minerals are usually associated with the clays and consequently affect the sorption properties of those materials. Carbonate minerals play a major role in regulating the aquatic environments via precipitation, dissolution and sorption reactions. These reactions controlled by chemical processes are taking place at the interface between mineral lattice and bulk solution.[3] The widespread distribution of calcite (one form of CaCO$_3$) in the Earth's crust makes it one of the most important minerals to look at in terms of geochemically and environmentally important aqueous-metal partitioning reactions.[4]

This study is aimed of the investigation of the uptake of Ba^{2+} ions by natural bentonite and CaCO$_3$, in addition to mixtures of different proportions of the two solids. Since the carbonate surface is of a dynamic nature being to a large extent subject to pH variations, the experiments were performed using two sets; in one no pH control was attempted, and in the second the pH was kept constant at a high value ($= 9.0$). The effect of initial Ba^{2+} concentration on sorption was investigated using the radiotracer method and γ-ray spectroscopy. Powder

X-ray diffraction (PXRD) was used to elucidate the structural changes that accompany the fixation of Ba^{2+} ions by the sorbent phases. Energy dispersive X-ray fluorescence (EDXRF) was applied to quantify the sorbed amounts of Ba^{2+} by the solids and the 'depleted' amounts of different cations in the solid matrix upon Ba^{2+} sorption.

Experimental:

Natural bentonite samples of white color, relatively rich in calcium content, were obtained from the Turkish General Directorate of Mineral Research and Exploration (MTA). The samples originated from Giresun, situated in the Black Sea region of Anatolia. The particle sizes were <38 μm. The CaCO$_3$ used throughout the study was Merck extra pure CaCO$_3$.

Radiotracer experiments

The batch method was applied throughout the experiments. To each of a 30 mg solid sample placed in preweighed tubes, 3 ml of Ba^{2+} solution containing an appropriate amount of ^{133}Ba ($T_{1/2} = 10.7$ y) radiotracer was added. ^{133}Ba tracer was used because of its long half-life and well resolved prominent γ-peak at 361 keV. The solid samples used in those studies were natural bentonite, CaCO$_3$ and mixtures of both with bentonite percentages of 80, 60, 50, 40, and 20%. The initial concentrations of Ba^{2+} solution used in these experiments were $1.0\cdot10^{-2}$ and $1.0\cdot10^{-6}$M. Tubes were shaken at room temperature for a period of 48 hours in a temperature-controlled environment using a Nuve ST 402 water bath shaker equipped with a microprocessor thermostat. Following shaking, samples were centrifuged and 2 ml portions of the supernatant were counted using a 35 cm^3 HPGe detector connected to a multichannel PGT analyzer. Duplicate experiments were performed to check the reproducibility of the experimental data.

Tubes were vigorously hand-shaken prior to centrifugation to collect any liquid drops or solid particles adhering to the inner surface of each tube. The relative error in activity arising from adsorption by the inner tube surface was estimated to be less than 0.05, i.e., less than 5% of the radioactivity was removed from the sorption system by adsorption on the inner tube wall. The uncertainties in the measurements stemmed principally from those of counting statistics. Other error sources of less importance were those originating from weight and volume measurements. The error in the calculated R_d values was estimated to be less than ±10% in all cases.

PXRD and EDXRF experiments

Throughout the sorption experiments the batch method was used and the initial concentration of Ba^{2+} solution was kept at 0.010M. The amounts of liquid and solid phases were fixed at 250.0 ml and 2.50 g, respectively. A magnetic stirrer was used for mixing and the period of contact was 48 hours at room temperature. Two sets of experiments were prepared. In the first set no pH control was attempted and the sorbent phases were obtained by mixing bentonite with CaCO$_3$. The investigated compositions were 80%, 60%, 40%, and 20% bentonite in addition to pure natural bentonite and pure CaCO$_3$ samples. The measured pH values at the end of mixing in this set of experiments were 4.03, 7.50, 7.69, 7.88, 8.59, and 9.89 for experiments where the solid phase consisted of 100%, 80%, 60%, 40%, and 20% bentonite in addition to pure CaCO$_3$, respectively.

In the second set of experiments, the pH was kept at 9.0±0.1 for all samples. The pH was monitored regularly and adjusted whenever necessary, by adding an appropriate amount of 0.01M of NaOH. The solid phases used in this set of experiment were obtained by mixing bentonite and CaCO$_3$ fractions in the same proportions as given previously. At the end of the mixing, the solid phases were filtered and dried overnight in an evacuated oven kept at 90 °C.

PXRD analysis

Powder X-ray diffraction (PXRD) analysis was carried out using a Rigaku Miniflex model instrument. Samples of natural and Ba-sorbed bentonite, CaCO$_3$ and bentonite-CaCO$_3$ mixtures were analyzed in the powder form. The source consisted of unfiltered Cu Kα radiation, generated in a tube operating at 30 kV and 15 mA. Spectra were recorded with 2 θ values ranging from 2 to 45 degrees in steps of 0.02 degree. The mineralogical compositions of the samples were determined using a search-match procedure.

EDXRF analysis

Energy dispersive X-ray fluorescence (EDXRF) analysis was carried out for the mineral samples before and after Ba^{2+} sorption. The analysis was done using a multi-element analyzer (in the range $_{11}$Na to $_{92}$U), high performance Oxford ED2000 EDXRF system located at the Nuclear Research and Training Center of the Turkish Atomic Energy Authority, Ankara. The samples were analyzed for a total of 27 elements, using the Oxford Geological Majors and Tracers Method. XRF pellets were positioned in front of a Si (Li) detector and irradiated with X-rays originating from an Rh target. The detector was connected to a computer controlled system. The spectra were acquired and analyzed using Oxford Xpert Ease software. The tube power was 50 W and the maximum current was 1000 μA. Each sample was measured under five different conditions; very light element conditions, steel conditions, medium element conditions, heavy trace element conditions, very heavy element conditions. The weights of the samples and standards were approximately 2 g.

Results and discussion

Characterization of the solid samples

Natural bentonite and CaCO$_3$ samples used in this study were characterized using EDXRF, FTIR, and PXRD. The chemical analysis of the untreated samples is given in Table 1. Natural bentonite, which contains a number of oxides with variable proportions, has a very high SiO$_2$/Al$_2$O$_3$ ratio. This stems from the fact that the clay is a heterogeneous mixture of montmorillonite and silica minerals as discussed below. CaCO$_3$ contains tiny amounts of Al and Fe oxides as impurities.

PXRD patterns of natural bentonite, CaCO$_3$, and a mixture of both are given in Fig. 1. Natural bentonite samples are composed of montmorillonite, characterized by the major (001) peak occurring at $d_{001} = 15.15$, in addition to cristobalite (low-type), an allotrope of silica that has the prominent (101) peak at $d_{101} = 4.05$. The PXRD diagram of CaCO$_3$ reveals that it is composed of calcite and aragonite. Calcite and aragonite have, among other peaks, the characteristic (104) and (111) peaks occurring at $d_{104} = 3.03$ and $d_{111} = 3.39$, respectively.

Table 1. Chemical composition of natural bentonite, $CaCO_3$, and their different mixtures obtained by EDXRF technique (in percent composition by weight

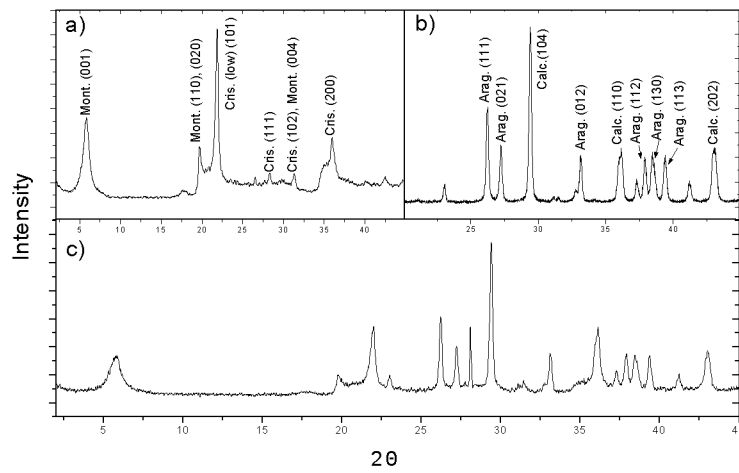| Constituent	100% bentonite	20% CaCO₃ + 80% bentonite	40% CaCO₃ + 60% bentonite	50% CaCO₃ + 50% bentonite	60% CaCO₃ + 40% bentonite	80% CaCO₃ + 20% bentonite	100% CaCO₃
MgO	0.97	0.95	0.62	0.76	0.36	0.26	0.00
Al_2O_3	9.71	8.57	5.94	6.35	3.87	2.01	0.24
SiO_2	85.52	64.65	41.84	43.05	25.45	9.92	0.00
K_2O	0.26	0.17	0.10	0.08	0.07	0.00	0.00
CaO	1.15	23.97	49.73	48.28	68.97	87.06	98.65
TiO_2	0.26	0.23	0.21	0.19	0.15	0.06	0.00
MnO	0.02	0.02	0.02	0.01	0.01	0.01	0.01
Fe_2O_3	1.60	1.43	1.31	1.06	0.91	0.43	0.04
Others	<0.51	<0.10	<0.23	<0.22	<0.21	<0.25	<0.06

Fig. 1. PXRD diffractograms of natural bentonite (a), $CaCO_3$ (b) and a mixture of bentonite and $CaCO_3$ (50:50) (c). Mont.: montmorillonite, Cris.: cristobalite, Arag.: aragonite, Calc.: calcite
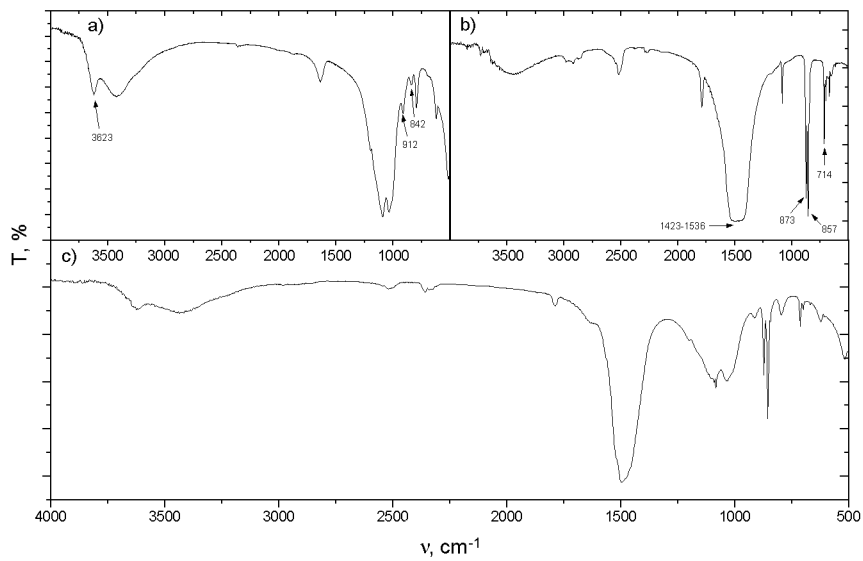

Fig. 2. FTIR spectra of natural bentonite (a), $CaCO_3$ (b), and a mixture of bentonite and $CaCO_3$ (50:50) (c)

The IR spectra of natural bentonite, $CaCO_3$, and a mixture of both are given in Fig. 2. The presence of montmorillonite (Fig. 2a) component in natural bentonite can be identified from the features occurring at 3623, 912, and 842 cm^{-1}. The broad peak at 3625 cm^{-1} forms an envelope for a wide range of AlAlOH and AlMgOH environments, the latter resulting from the isomorphous substitution of Mg for Al in the octahedral sheet of the clay. More characteristic of montmorillonite are the well-resolved deformation bands at 915 cm^{-1} (AlAlOH) and 840 cm^{-1} (AlMgOH). The features at 1423-1576, 872, 857 and 713 cm^{-1} are diagnostic for $CaCO_3$ (Fig. 2b). These bands are indicative that $CaCO_3$ samples are composed of calcite, and aragonite,[5] in line with the PXRD characterization.

Radiotracer studies

The experimental data obtained from radiochemical studies were expressed in terms of the 'distribution ratio', R_d, given as:

$$R_d = \frac{A° - A_1}{A_1} \cdot \frac{V}{M} \qquad (1)$$

where $A°$ is the initial count rate of solution before sorption, (cps)/ml; A_1 is the count rate of solution after sorption, (cps)/ml; V is the volume of solution, ml; and M is the weight of solid material, g.

The R_d values for two different initial concentrations of Ba^{2+} are given in Table 2. While there is no clear trend in the dependence of R_d values on $CaCO_3$ content of the solid mixtures at the higher initial Ba^{2+} concentration, an increase in R_d is obvious as $CaCO_3$ content increases at the lower initial Ba^{2+} concentration. The R_d values reported in Table 2 correspond to the arithmetic mean of the data obtained from duplicate experiments with a relative error ranging within ±2% to 10%.

Table 2. R_d values and the corresponding averaged apparent $\Delta G°$ (calculated at $T = 295$ K) values for two different initial concentrations of Ba^{2+} 10^{-2}M Ba^{2+} (a) and 10^{-6}M Ba^{2+} (b)

$CaCO_3$, %	R_d, ml/g		$\Delta G°$, kJ/mol
	(a)	(b)	
0	20	43	−8 ± 1
20	35	45	−9 ± 1
40	22	58	−9 ± 1
50	29	70	−9 ± 1
60	20	249	−10 ± 3
80	29	326	−11 ± 3
100	45	649	−13 ± 3

Table 3. Relative concentration (in wt%) of sorbed Ba^{2+} on different bentonite–$CaCO_3$ mixtures obtained from EDXRF measurements, no pH control (a) and pH 9.0 (b)

Solid phase composition	(a)	(b)
80% Bentonite + 20% $CaCO_3$	4.59	7.31
60% Bentonite + 40% $CaCO_3$	4.56	9.01
40% Bentonite + 60% $CaCO_3$	4.67	11.71
20% Bentonite + 80% $CaCO_3$	9.50	12.66

The apparent Gibbs free energy values of sorption, $\Delta G°$, were calculated by:

$$\Delta G° = -RT \ln R_d \qquad (2)$$

Here R_d is approximated to be the equilibrium constant. Actually R_d is a function of the initial concentration and as such leads to changes in the corresponding apparent $\Delta G°$ values. In order to obtain $\Delta G°$ values representative over the entire concentration ranges, arithmetic averages of apparent $\Delta G°$ values were calculated for each solid composition at room temperature (295 K). The results are given in Table 2. The negative $\Delta G°$ values in all cases indicate that the Ba^{2+} sorption is spontaneous. The magnitudes of $\Delta G°$ in the 8–16 kJ/mol range indicate that the sorption mechanism is mainly of ion exchange type.[6]

EDXRF studies

The EDXRF technique enabled the chemical analysis of different samples prior to and following sorption. According to EDXRF findings, the weight percentages of sorbed Ba^{2+} increased from 0.043 for the samples of 100% bentonite up to 29.09 for the ones composed of 100% $CaCO_3$. For the bentonite-$CaCO_3$ mixtures, the weight percentages of Ba^{2+} increased, as the samples became richer in $CaCO_3$. This trend is observed for both sample series (a, b) as shown in Table 3. The table shows also that the increase in pH resulted in an increase in sorbed Ba^{2+} amounts for all samples.

The amounts of different constituents of the solid matrix prior to and following the sorption of Ba^{2+} were analyzed. According to the results, a depletion of Ca, Mg, and K is observed upon Ba^{2+} sorption. In order to enable the comparison of the quantities of these elements prior to and following sorption, they were normalized to the Al+Si oxides. Both Al and Si are 'skeletal' elements that can be assumed not to take part in the exchange process. For the samples composed of 100% bentonite, the dominating exchanged cation was Ca^{2+}, for which the $CaO/(Al_2O_3+SiO_2)$ ratio changed from 0.0112 to 0.0025. For $CaCO_3$, this ratio changed from 429 to 75. For samples composed of different bentonite and $CaCO_3$ proportions, the results are given in Table 4. The largest depletion is shown by CaO, which is contained in larger quantities compared with the others.

Table 4. Variation in the relative concentrations of MgO, CaO, and K_2O normalized to $Al_2O_3+SiO_2$ content, obtained from EDXRF analysis of: samples prior to sorption (a), Ba-sorbed samples (no pH control) (b), and Ba-sorbed samples (pH 9.0) (c)

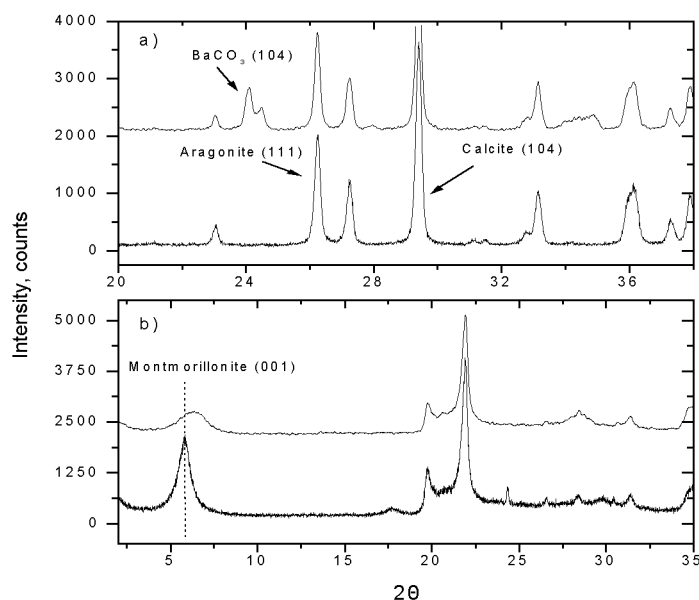| Element	Sample	Element/(Al+Si)			
		80% bentonite + 20% $CaCO_3$	60% bentonite + 40% $CaCO_3$	40% bentonite + 60% $CaCO_3$	20% bentonite + 80% $CaCO_3$
MgO	(a)	0.013	0.012	0.012	0.022
	(b)	0.012	0.012	0.008	N.D.
	(c)	0.013	0.011	0.012	0.011
CaO	(a)	0.32	1.04	2.35	7.30
	(b)	0.20	0.63	2.10	4.40
	(c)	0.20	0.59	1.38	4.67
K_2O	(a)	0.0023	0.0021	0.0020	N.D.
	(b)	0.0018	0.0019	0.0014	N.D.
	(c)	0.0017	0.0015	0.0015	N.D.

N.D.: Not detected.

Fig. 3. PXRD diffractogram of Ba-sorbed $CaCO_3$ (a), and PXRD diffractogram of Ba-sorbed natural bentonite (b)

PXRD studies

The PXRD diagrams of Ba-sorbed bentonite and Ba-sorbed $CaCO_3$ are given in Fig. 3. The sorption of Ba^{2+} on $CaCO_3$ is marked by the formation of $BaCO_3$ features (Fig. 3a) accompanied by a reduction in the other peak intensities. The sorption of Ba^{2+} on natural bentonite (Fig. 3b) leads to a significant intensity reduction of the montmorillonite (001) peak and to a slight change in its peak position from $d_{001} = 15.2$ Å to $d_{001} = 13.3$ Å, corresponding to $\Delta d_{001} = 1.9$ Å. Peak position changes had been reported for sorption of Pb^{2+} and Zn^{2+} on Ca-montmorillonite ($\Delta d_{001} = 2.64$ Å for Pb^{2+},

$\Delta d_{001} = 1.77$ Å for Zn^{2+}) and attributed to changes in the hydration state of the interlayer spacing of the clay upon sorption.[7]

PXRD was also used to analyze the uptake of Ba^{2+} by mixtures of bentonite and $CaCO_3$ with variable compositions. The diffractograms of the samples prepared without any pH control and those prepared while pH was fixed at 9.0 are given in Figs 4a and 4b, respectively. For the sorption experiments carried out without any pH control, where the pH changed from 4.03 to 9.89 depending on the $CaCO_3$ content, $BaCO_3$ formation was observed for mixtures containing at least 60% $CaCO_3$ by composition as shown in Fig. 4a.
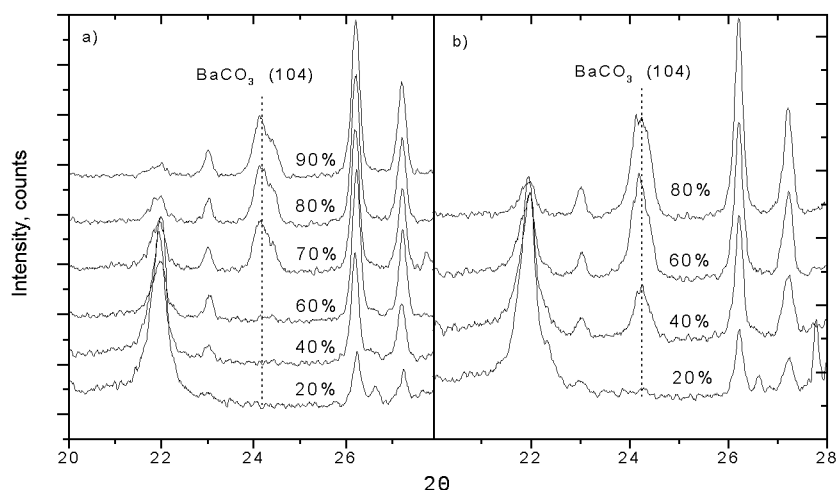
Fig. 4. PXRD diffractogram of Ba-sorbed mixtures of bentonite and CaCO$_3$ (no pH control) (a), and PXRD diffractogram of Ba-sorbed mixtures of bentonite and CaCO$_3$ (pH 9.0) (b)

When the pH was kept constant at 9.0±0.1, the precipitate formation was observed for samples having 20% CaCO$_3$ or higher as given in Fig. 4b. The increase in pH is expected to enhance the role of the CaCO$_3$ fractions in Ba^{2+} fixation. The pH has minimal effects on sorption on bentonite due to the low 'zero point of charge (ZPC)' for such clays, which is generally below ~2.5 pH units.[8] The increased role of CaCO$_3$ fractions in Ba^{2+} sorption is reflected in larger amounts of Ba^{2+} being sorbed when the pH was increased as was previously stated based on the EDXRF measurements.

Conclusions

The uptake of Ba^{2+} by bentonite is enhanced as the quantity of CaCO$_3$ incorporated in the clay increases, particularly, at lower Ba^{2+} concentration and higher pH values of the sorption system. The sorption of Ba^{2+} is spontaneous and is accompanied by a depletion of K$^+$, Mg^{2+} and Ca^{2+} ions originally present within the solid phases. The interlayer spacing of bentonite seems to be affected by Ba^{2+} sorption, as the montmorillonite (001) peak position showed some changes, the thing that might be attributed to a change in the hydration state of the interlayer space of the clay. The role of CaCO$_3$ in Ba^{2+}

fixation is verified by the formation of BaCO$_3$. For a given initial Ba^{2+} concentration, BaCO$_3$ formation is dependent on the amount of CaCO$_3$ present in the solid phase in addition to pH value. BaCO$_3$ presence was detected for bentonite samples containing at least 60% CaCO$_3$ by mass when no pH control was carried out. When the pH was raised to 9.0 and kept constant, BaCO$_3$ formation appeared for bentonite samples containing 20% CaCO$_3$ by mass or larger.

References

1. K. H. LIESER, Radiochim. Acta, 70/71 (1995) 355.
2. M. TAKAHASHI, M. MUROI, A. INOUE, M. AOKI, M. TAKIZAWA, K. ISHIGURE, N. FUJITA, Nucl. Techn., 76 (1987) 221.
3. P. V. CAPPELLEN, L. CHARLET, W. STUMM, P. WERSIN, Geochim. Cosmochim. Acta, 57 (1993) 3505.
4. N. X. MICHAEL, F. HOCHELLA Jr., G. BROWN Jr., A. PARKS, Geochim. Cosmochim. Acta, 60 (1996) 2801.
5. M. J. WILSON, Clay Mineralogy: Spectroscopic and Chemical Determination Methods, Chapman & Hall, London, 1994.
6. F. HELFFERRICH, Ion Exchange, Mc Graw Hill, New York, 1962.
7. M. AUBOIROUX, P. BAILLIF, J. C. TOURAY, F. BERGAYA, Appl. Clay Sci., 11 (1996) 117.
8. J. I. DREVER, The Geochemistry of Natural Waters, Prentice-Hall, New Jersey, 1982.