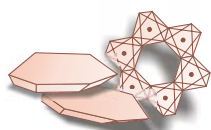# SMECTITE REACTIVITY IN ALKALINE SOLUTIONS

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Abstract: Bentonite and alkaline solutions were reacted in batch experiments at 90 °C during 365 days to determine the effect of the chemical composition and pH of the solution in stability of the smectite. Bentonite and concrete are considered for use as backfilling and sealing materials in a deep geological repository of high level radioactive waste. The pH of the pore-water leached from concrete during degradation is above 11 for a long period of time. In these alkaline conditions, reactions take place in smectite, affecting the properties of bentonite. The aim of this work is to identify crystalchemical changes in smectite resulting from its interaction with synthetic cement pore water, taking into account the temperature effect in order to consider the thermal impact originated by radioactive decay. The bentonite used comes from the "La Serrata de Níjar" deposit (Almería, Spain). The bentonite comprised mainly high-charge montmorillonite. Alkaline solutions are representative of cement pore water leached from concrete during the first stages of degradation. Crystalchemistry characterization of smectite (< 0.5 μm fraction of bentonite) was performed before and after the experiments by differential thermal analysis, X ray diffraction (Hofmann & Klemen test, simplified alkylammonium method), infrared spectroscopy and chemical analysis. The results suggest a preferential dissolution of some smectite layers, more specifically octahedrally-charged layers.

Introduction

Bentonite and cement will be used as engineered barriers in the final disposal for the high level radioactive waste in crystalline rock. The cement's degradation produces alkaline solutions, which affect the smectite crystalchemistry and, therefore, the properties of the bentonite. Because of the main role of bentonite in the safety of the system, the effect of the alkaline conditions on the smectite stability has been studied for several years. Some works focussed on the collapse of expandable smectite layers and, more specifically, on the formation of illite or illite/smectite mixed-layers. Eberl et al. (1993) using Wyoming bentonite observed the increase of the proportion of illite layers up to 25 % after reacting for 9 months at 35 °C in potassium hydroxide solution (KOH 3 M). Likewise, a random mixed-layer containing non-expandable layers was also obtained using a sodium hydroxide solution (NaOH 0.5 M) at 35 °C. In general, the formation of non-expandable layers, both in potassic and sodic solutions, depends on solution concentration rather than on temperature and reaction duration. According to Bauer & Berger (1998) and Bauer & Velde (1999), the smectite reacts with a potassic alkaline solution to form an illite/smectite mixed-layer. The formation of mixed-layer phases was seen as an intermediate step in a series of dissolution-precipitation processes. These authors propose three steps in the alteration of Ceca and Ibeco smectites in potassium hydroxide solution (KOH up to 4 M). Initially, there is dissolution of tetrahedral and octahedral sheets in smectite. Further, the illite content increases up to 40 % at 35 °C and up to

90 % at 80 °C. Finally, new phases precipitate in the following sequence: discrete mica, KI-zeolite (Barrer 1982), phillipsite, K-feldspar and quartz. Recently, Rassineux et al. (2001) studied Wyoming bentonite reaction with pH 13.5 solutions at 35 and 60 °C up to 730 days. In spite of an apparent invariability of the chemical composition and crystal structure of the smectite layer, as determined by IR spectroscopy, a slight increase of the expandability after octahedral charge neutralization was observed. To explain this fact, the authors proposed the re-organization of the layer stacking during the reaction, so that the number of charged tetrahedral sheets, adjacent to the same interlayer space, increases.

According to these results it seems necessary to investigate in detail the chemical and crystal structure of smectites which have experienced the alkaline reaction. The objective of the present work is to study the crystalchemistry of the smectite in the Spanish bentonite after alteration in alkaline conditions at 90 °C in order to consider the effects of (1) solutions leached out from cement and (2) heat generated by the radioactive decay.

Materials and methods

The bentonite used was extracted from the "Cortijo de Archidona" deposit ("La Serrata de Níjar", Almería, Spain), which is the Spanish reference material for the high-level radioactive waste disposal. Powder X-ray diffraction (XRD) patterns indicate that the bentonite is composed of 93 ± 3 % smec-

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tite, 2±0.5 % quartz, 3±1 % feldspars, 2±0.2 % cristobalite, 1±0.7 % calcite and 1.5±0.1 % rhyodacitic volcanic glass (average values from Cobeña et al. 1998; Linares et al. 1993).

Characterization by XRD was carried out using oriented Ca^{2+} saturated and ethylene-glycol solvated samples. XRD data were obtained with a PHILIPS 1729 diffractometer with a Fe filtered Co tube operated at 40 mA and 40 kV. The diffractometer is associated with a Socabim DACO-MP recorder system controlled by the DiffracAt software.

The IR spectra were obtained using a Nicolet 510 Fourier transform IR spectrometer (FTIR) equipped with the OMNIC software to measure the integrated intensity of the absorption bands. Spectra were recorded in the 4000–400 cm^{-1} range with a resolution of 4 cm^{-1}. Measure was made from dried KBr pellets, which were prepared by mixing and pressing 1 mg of sample with 150 mg KBr.

Major elements were determined by X-ray fluorescence (XRF) using a PHILIPS PW-1404 X-ray Spectrometer with a Sc/Mo tube and operated at 30 kV and 80 mA.

The DTA analyses were performed on 20 mg sample, using a Netzsch STA 409 EP at a heating rate of 10 °C/min from 20 °C to 1100 °C. Samples were loaded into platinum crucibles and run in air atmosphere.

Experimental

Bentonite was altered in batch experiments carried out in tightly-closed Teflon reactors during 365 days at 90 °C. The solid/solution ratio was 1/3: 80 g of < 1 mm sieved bentonite and 240 ml solution. These experiments are part of a series detailed in Vigil et al. (2001) and Ramírez et al. (2001).

Alkaline solutions are representative of the cement pore-water leached out during the first stages of concrete degradation. According to Anderson et al. (1989), the pH of the cement pore-water varies from 12.4 to 13.5, Na^+ and K^+ being the main cations in the solution. The Na^+ and K^+ concentrations range between 0.05 and 0.3 mol/dm³ while the Ca^{2+} concentration is below 2.5×10^{-3} mol/dm³. The chemical compositions of alkaline working solutions used in the experiments are shown in Table 1. Alkaline solutions were standardized by titration with a potassic phtalate solution (stock solutions) or with a sulphuric acid solution (working solutions).

At the end of the reaction time, the reactor was cooled to room temperature. Then, control of reactors weight was performed. No significant weight loss was observed. The solids were separated from the solution by centrifugation. The solids were dried in a glove-box, in CO_2 free atmosphere and sieved to < 1 mm. Mineralogy of bulk samples is reported in Ramírez et al. (2001) and Vigil et al. (2001). According to semi-quantitative XRD analyses and SEM observations, the main mineralogical changes after the sodic-potassic alteration tests are the formation of zeolite and dissolution of poorly crystallized minerals, especially feldspars and volcanic glass. Under SEM, no dissolution features were observed on calcite crystals. To characterize the crystalchemistry in both initial and treated samples, the < 0.5 μm fraction was separated by centrifugation and Ca^{2+} saturated. This fraction is characterized as nearly a pure smectite by XRD and FTIR analyses. The structural for-

**Table 1:** Chemical composition of initial solutions.

solution	Na⁺ (mol/dm³)	K⁺ (mol/dm³)	Ca²⁺ (mol/dm³)	pH
a	-	-	223×10^{-4}	12.6
b	0.08	0.17	8.52×10^{-4}	13.2
c	0.17	0.33	4.07×10^{-4}	13.5

mulas were calculated from chemical analyses. For evaluating amount and localization of the layer charge, the following methods were used: (1) the simplified alkylammonium procedure of Olis et al. (1990) using XRD and (2) cation exchange capacity (CEC) evaluation using IR spectroscopy from NH_4^+-saturated samples (Petit et al. 1998, 1999). Evaluation of layer charge was made before and after using the Hofmann & Klemen treatment (Hofmann & Klemen 1950), so octahedral charge was evaluated separately. The lithium saturation was performed on calcium saturated samples by one week dialysis against LiCl 1 M solutions. In order to assure complete saturation with Li^+, LiCl dialysis solutions were renewed every 48 hours. Then, the samples were heated at 250 °C in Pt crucible for 12 hours.

Results

XRD patterns of Ca^{2+}-saturated and ethylene-glycol solvated samples exhibit the basal reflections of a smectite with two ethylene glycol layers in the interlayer space (Fig. 1): intense peak at 16.97×10^{-1} nm and higher order peaks at $8.39-8.50 \times 10^{-1}$ nm, $5.54-5.57 \times 10^{-1}$ nm and $3.34-3.35 \times 10^{-1}$ nm. The presence of small amounts of 10×10^{-1} nm collapsed layers in a random mixed-layer, in both initial and treated samples, was deduced from the irrationality of the diffraction patterns and from the broad $d(001)$ reflection with a high low-angle shoulder (Moore & Reynolds 1989). The percentage of illite like layers, interstratified with smectite layers, was quantified using the procedure described by Inoue et al. (1989). According
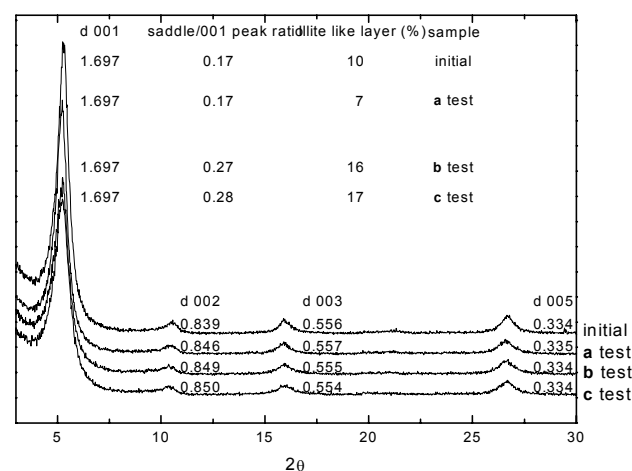
Fig. 1. XRD patterns of samples before and after the alteration experiment. Basal reflection (in nm), saddle/001 peak intensity ratio and percentage of illite like layers randomly interstratified with the smectite layer.

to this method, the saddle/001 peak intensity ratio is correlated with the proportion of illite in a random mixed-layer I/S. The calibration curve for the saddle/001 peak intensity ratio versus the percentage of 10×10^{-1} nm collapsed layers was constructed from calculated XRD patterns using NEWMOD© (Reynolds 1985). The average (δ) and maximum crystallite sizes (N_{max}) are defined by the parameters $\delta = 4$ and $N_{max} = 10$, respectively. These values were selected because they produce the best fit with experimental XRD patterns. In the initial sample, 10 % of 10×10^{-1} nm collapsed layers are found interstratified with 90 % of 17×10^{-1} nm expanded layers. After alteration by alkaline treatments only slight changes in the saddle/001 peak intensity ratio were observed, and attributed to a decrease of crystallite size rather than change in the percentage of interstratified illite-like layers.

After neutralization of the octahedral charge (Hofmann & Klemen treatment), expandability decreases for all samples (Fig. 2). However, a broad and poorly defined peak near 17.30×10^{-1} nm indicates the presence of expandable layers and, consequently, layers having a tetrahedral charge. The sample treated with the calcic solution (**a** experiment) shows a diffractogram similar to that of the initial sample. The increase of the 17.30×10^{-1} nm reflection intensity, as well as the shift of $d(002)$ reflections to higher angles, are evident after the sodic-potassic treatment (**b** and **c** experiments). The $d(002)$ reflection position reveals a mixed-layer with expanded layers (8.57×10^{-1} nm, second order) and collapsed layers (9.6×10^{-1} nm). That is indicative of the increase in the proportion of tetrahedrally-charged expanded layers. From simulated diffractograms obtained with NEWMOD©, about 40 % of expanded layers are present in the initial sample after neutralization of the octahedral charge whereas about 50 % were found for the treated samples in **b** and **c** experiments.

The XRD patterns of the initial and treated samples after intercalation with $C_{12}H_{25}NH_4^+$ are shown in Fig. 3A. Alkylammonium ions in the interlayer space of the clay may adopt either a monolayer (13.6×10^{-1} nm), a double-layer (17.7×10^{-1} nm) or a pseudotrimolecular layer (21.7×10^{-1} nm) complex depending on the magnitude of the layer charge (Olis et al. 1990). The
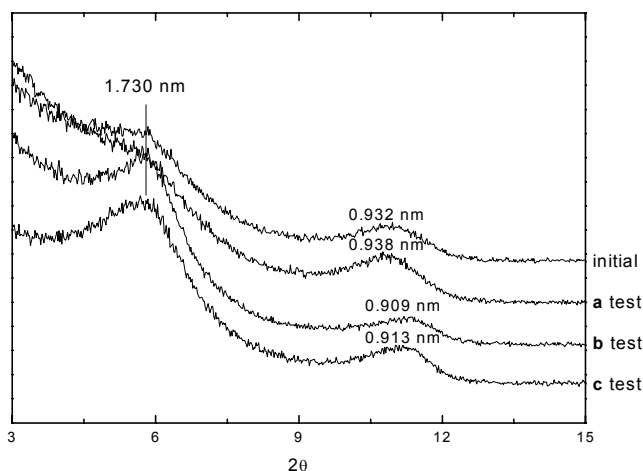

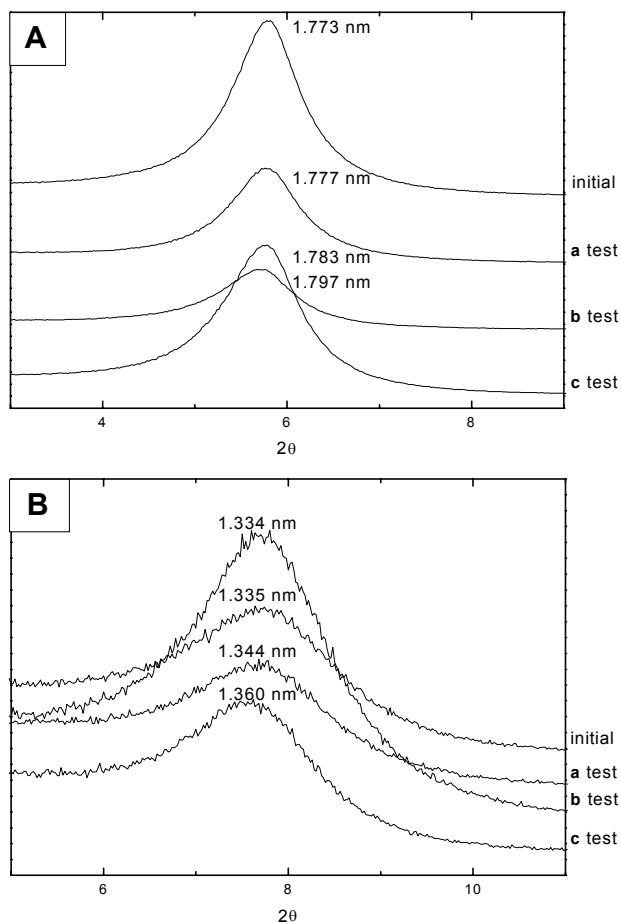**Fig. 2.** XRD patterns of the initial and treated samples after the Hofmann & Klemen treatment.

Fig. 3. XRD patterns of the initial and treated samples after intercalation with the alkylammonium cation (nC = 12) before (**A**) and after (**B**) the Hofmann & Klemen treatment.

$d(001)$ position points out the formation of an alkylammonium double-layer in both the initial and altered samples from **a** experiment. A slight shift of peak position toward lower angles is shown in the samples treated with sodic-potassic solution (**b** and **c** experiments) up to 17.97×10^{-1} nm and 17.83×10^{-1} nm, respectively. This slight shift would be induced by a decrease of the coherent scattering domain size (Moore & Reynolds 1989). Actually, delamination of smectite clay particles is often observed when clays are treated with alkaline and sodic solutions (Lagaly 1981). For the initial sample, and after neutralization of octahedral charge (Hofmann & Klemen treatment; Fig. 3B), the position of the $d(001)$ reflection is slightly lower than 13.6×10^{-1} nm. This would indicate an interstratification between collapsed layers (9.6×10^{-1} nm) and monolayer alkylammonium complex (13.6×10^{-1} nm). Collapsed layers are assumed to have no tetrahedral charge, whereas layers which accept intercalation of alkylammonium cations must have a minimal tetrahedral charge. The position of the $d(001)$ reflection in the treated samples was not significantly affected, which would indicate that no significant change in the amount of tetrahedral charge was induced by the treatments.

Recently, Petit et al. (1998, 1999) have proposed a method for evaluation of the layer charge in NH_4^+-clays by IR spectros-
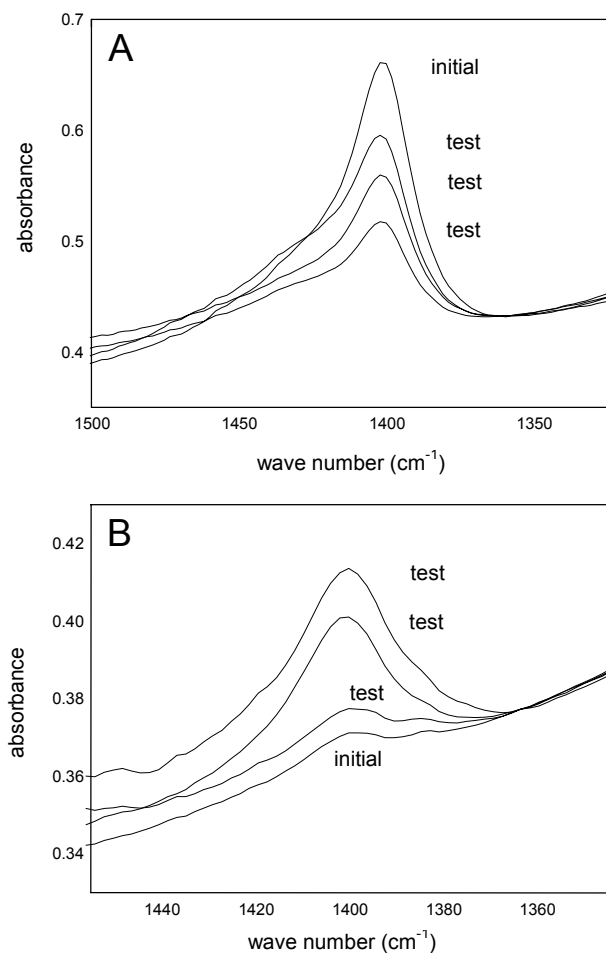
Fig. 4. ν_4 NH_4^+ band in the IR spectra of the initial and treated samples before **(A)** and after **(B)** the Hofmann & Klemen treatment.

copy. In order to compare the samples on the same quantitative basis, normalization of the spectra was performed using the Si-O band at 1000 cm^{-1} as an internal reference band. The ν_4 NH_4^+ band in the IR spectra of the initial and treated samples is shown in Fig. 4. Measurements were made before and after the Hofmann & Klemen treatment and, consequently, the cation exchange capacity (CEC) obtained is assumed to result from permanent plus variable charges and tetrahedral plus variable charges, respectively. The difference between the two CEC values corresponds to the octahedral charge (Table 2). In the sample treated with calcic solution (**a** experiment) the percent-

Table 2: Normalized integrated intensity of the ν_4 NH_4^+ band (S NH_4^+) in the IR spectra before and after the Hofmann & Klemen treatment (HK) and octahedral charge associated in the initial and treated samples.

|	S NH_4^+ (arbitrary units)		octahedral charge (%)
	before HK	after HK	
initial	8.26	0.17	98
a experiment	7.12	0.23	97
b experiment	6.21	1.28	79
c experiment	4.67	1.06	77

age of octahedral charge is similar to the initial one, while after sodic-potassic solution treatments (**b** and **c** experiments) the octahedral charge decreases from 98 % to 77 % of the total charge.

Structural formulas (Table 3) were calculated from the chemical analysis of the Ca^{2+} saturated < 0.5 μm fraction. According to XRD data, the chemical analysis does not correspond to a single homogeneous phase, but to heterogeneously charged smectite layers. Nevertheless, the obtained data were used to compare cationic distribution between the treated and initial samples. After the experiment, the increase in Mg^{2+} assigned to the octahedral sheet is evidenced. The amount of octahedral Mg^{2+} cation increases with initial pH of experimental solutions. After **a** experiment (calcic solution at pH 12.6), the Mg^{2+} content is 0.92 per unit cell, close to the initial value, while in sodic-potassic solution at pH 13.5 (**c** experiment) it rises up to 1.04 per unit cell. Simultaneously, the amount of octahedral Al^{3+} decreases from 2.68 in the initial sample to 2.55 in the **c** treated sample.

Table 3: Structural formula before and after alteration experiment calculated from the chemical analysis of the calcium saturated < 0.5 μm fraction.

	structural formula (O$_{20}$(OH)$_4$ anion basis)
initial	(Si$_{7.72}$ Al$_{0.28}$)^{IV} (Al$_{2.68}$ Fe$_{0.39}$ Mg$_{0.85}$ Ti$_{0.01}$)^{VI} Ca$_{0.62}$ K$_{0.09}$
a experiment	(Si$_{7.77}$ Al$_{0.23}$)^{IV} (Al$_{2.68}$ Fe$_{0.38}$ Mg$_{0.92}$ Ti$_{0.01}$)^{VI} Ca$_{0.55}$ K$_{0.07}$
b experiment	(Si$_{7.71}$ Al$_{0.29}$)^{IV} (Al$_{2.67}$ Fe$_{0.38}$ Mg$_{0.99}$ Ti$_{0.02}$)^{VI} Ca$_{0.50}$ K$_{0.08}$
c experiment	(Si$_{7.75}$ Al$_{0.25}$)^{IV} (Al$_{2.55}$ Fe$_{0.40}$ Mg$_{1.04}$ Ti$_{0.01}$)^{VI} Ca$_{0.55}$ K$_{0.18}$

The DTA patterns of the samples are shown in Fig. 5. At low temperatures, the curves show a strong endothermic peak at nearly 100 °C corresponding to the loss of pore water and another endothermic peak at about 170 °C due to the elimination of interlayer water. The dehydroxylation peak at about 630 °C is characteristic of dioctahedral smectites (Mackenzie 1970). In addition, another endothermic peak is observed at high temperature. As the initial pH of the experiment increases, the temperature of this peak decreases: 859 °C in the initial sample and 851, 847 and 837 °C after the 12.6, 13.2 and 13.5
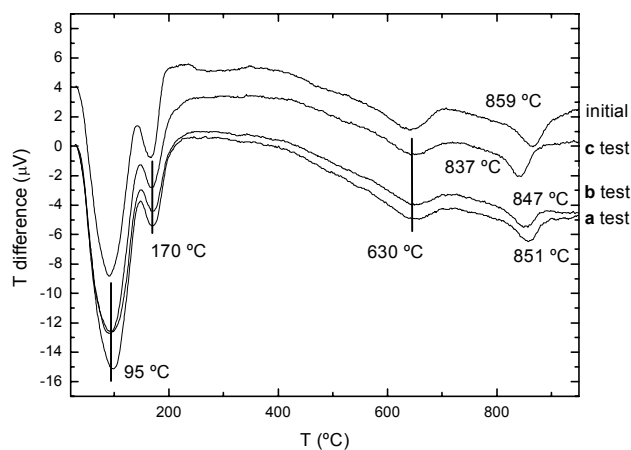
Fig. 5. Differential thermal analyses (DTA) of samples before and after the alteration experiment.

pH experiment, respectively. This peak is correlated with the breakdown of the clay-lattice and formation of amorphous phases from the dioctahedral smectites (Grim & Brandley 1940; Mackenzie 1970). The decrease of the temperature of lattice breakdown suggests that the smectite structure has been weakened by the treatments.

The IR spectra of the treated samples do not show any significant structural alteration with regard to the initial sample. The OH stretching region before and after the Hofmann & Klemen procedure is shown in Fig. 6. The band at 3630 cm^{-1} attributed to the vibration of Al$_2$OH in octahedral sheets is observed. After Hofmann & Klemen treatment, the shift of this band up to 3635 cm^{-1} and the appearance of a vibration attributed to AlMgLiOH band at 3670 cm^{-1} evidences the migration

Fig. 6. OH stretching region in the IR spectra of the initial and treated samples before **(A)** and after **(B)** the Hofmann & Klemen treatment.

of Li$^+$ from the interlayer into the previously vacant octahedral positions (Madejová et al. 2000).

Discussion and conclusions

Changes in the chemical composition and crystalchemistry characterization indicate contrasted behaviour according to the
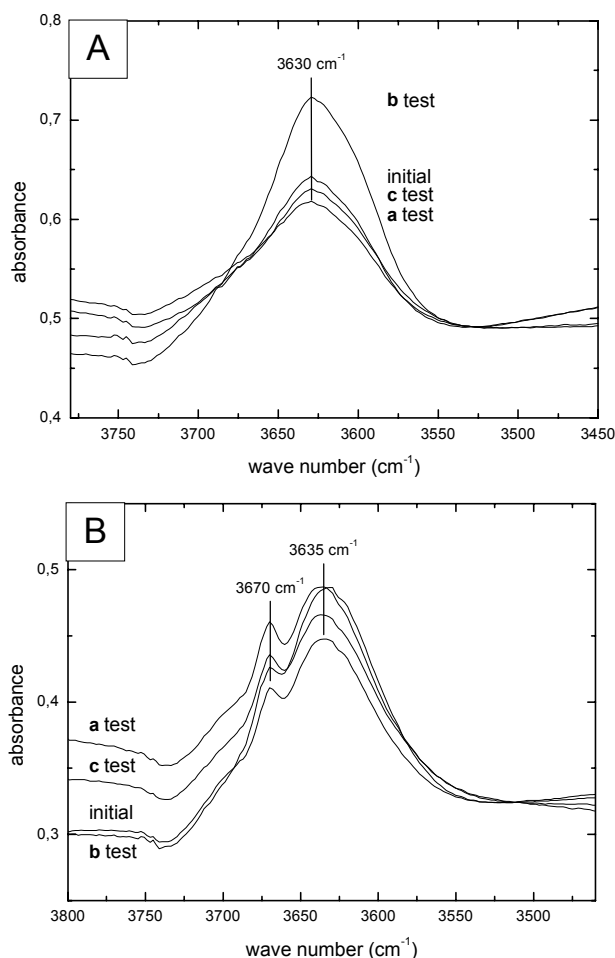
chemistry of altering solutions. No changes were observed for the sample treated with solution **a**. Consequently, the Spanish smectite is considered to be stable in Ca(OH)$_2$ saturated solution at 90 °C. For samples treated with solution **b** and **c**, a relative increase of magnesium with reference to aluminum in the octahedral sheet is observed. Milodowski et al. (1990) found the same results after reaction of bentonite (Wyoming and Calcigel) and cement pastes at ambient temperature. In order to explain this fact, these authors considered the preferential leaching of aluminum. In the present experiment, aluminum is actually released to the solution during smectite alteration and consumed for crystallization of zeolite (Ramírez et al. 2001; Vigil et al. 2001), of the average chemical composition (Na$_{2.47\pm1.61}$K$_{0.58\pm0.28}$Ca$_{1.88\pm0.48}$Mg$_{0.25\pm0.10}$)(Al$_{5.06\pm0.17}$Fe$_{0.07\pm0.03}$Ti$_{0.05\pm0.02}$) Si$_{10.24\pm0.36}$ O$_{32}$ ·12 H$_2$O.

Changes observed on XRD patterns of ethylene glycol solvated and alkylammonium saturated samples were attributed to a reduction of the coherent scattering domain size. Preferential dissolution of some smectite layers would contribute to that reduction. Actually, susceptibility to alteration may vary according to the crystalchemistry of smectite layers. Righi et al. (1998) have demonstrated that montmorillonitic smectites are more susceptible to weathering in soils with alkaline pH (≈ 9) than beidellitic smectites.

Changes in CEC measured by IR spectroscopy are not fully understood. According to the results, total CEC decreases from the initial sample to the **a**, **b** and **c** treated samples. Probably the alkaline treatments have dramatically altered the surface of clay particles and consequently, it is likely that large changes in the amount of variable charge have occurred. In such a situation it is difficult to evaluate accurately the eventual alteration of the permanent charge. If we assume that Hofmann & Klemen treatment does not alter the proportion of permanent and variable charges, the difference between CEC before and after the Hofmann & Klemen treatment allows an evaluation of the octahedral charge. With reference to the total charge, relative amount of octahedral charge decreases with the **b** and **c** treatments. This would suggest that the more octahedrally-charged layers are preferentially altered by the treatments.

The transformation of smectite to illite-like layers has been frequently proposed as an alteration process in an alkaline medium (Eberl et al. 1993; Bauer & Berger 1998; Bauer & Velde 1999). The illitization process is generally described by the formation of high tetrahedrally-charged layers and, according to Cuadros & Altaner (1998), is associated with the increase of aluminum and decrease of magnesium in the octahedral sheets. This chemical evolution was not observed in the present work. Actually, IR spectroscopy does not show any structural transformation of the reacted smectite. Furthermore, the results are better explained by preferential dissolution of some smectite layers, more specifically octahedrally charged layers.

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