

ACID DISSOLUTION OF REDUCED-CHARGE Li- AND Ni-MONTMORILLONITES

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Abstract—Reduced-charge samples were prepared from Li⁺- and Ni²⁺-saturated SAz-1 montmorillonite by heating at 150 and 300°C for 24 h. X-ray diffraction analysis showed interstratification of non-swelling and swelling interlayers in LiS150, while fully expandable interlayers were found in NiS150. Heating at 300°C caused collapse of the interlayers in LiS300 in contrast to NiS300, for which some expandable layers were interstratified in the pseudo-pyrophyllite structure. The infrared (IR) spectra of heated Li-SAz showed new OH-stretching and overtone bands near 3670 cm⁻¹ and 7170 cm⁻¹ (1395 nm), respectively, indicating creation of local trioctahedral domains containing Li(I) in the previously vacant octahedra. No evidence of OH groups in trioctahedral coordination was found in the spectra of heated Ni-SAz. Nickel is supposed to be trapped in the hexagonal holes of the tetrahedral sheets. Reduction of the layer charge substantially affected the extent of the dissolution of SAz-1 montmorillonite in HCl. The MIR and NIR spectra of unheated Li- and Ni-SAz showed a substantial degradation of their structure after acid dissolution. New bands observed at 3744 cm⁻¹ and 7314 cm⁻¹ (1367 nm) were assigned to the vibrations of Si-OH groups formed upon acid treatment. These bands are a means of checking the extent of acid attack on smectites, even in cases when no differences are observed in the 1300–400 cm⁻¹ spectral region (traditionally used to monitor this process). Both the IR spectra and solution analysis revealed that development of non-swelling interlayers in heated montmorillonites substantially reduced dissolution of these samples. The results obtained confirmed that acid attack of the smectite structure occurred at both interlayer surfaces and edges. If the accessibility of the layers for protons is low due to non-swelling interlayers, the dissolution was slower and took place mainly from the particle edges.

Key Words—Dissolution, Fixation of Cations, Layer Charge, MIR and NIR Spectroscopy, Montmorillonite.

INTRODUCTION

Smectites are widely used in many industrial processes, either in their natural form or after appropriate modification. The structure of smectites may be considerably altered in the course of different treatments, and frequently the layer charge of smectites is an important parameter influencing the extent of their modification. For example, acid activation is a common process applied to produce adsorbents, catalysts or catalyst supports. The acid dissolution of smectites involves the exchange reaction between the interlayer cations and surrounding acid solution, followed by dissolution of octahedral sheets as well as tetrahedral Al ions. The final product of smectite dissolution is an amorphous, partly protonated silica phase (Tkáč *et al.*, 1994). The extent of dissolution depends on various factors such as clay type and reaction conditions (Vicente-Rodríguez *et al.*, 1996; Breen *et al.*, 1995). To determine the influence of the layer charge of smectites on their dissolution rate, reduced-charge samples prepared from the same parent Li-montmorillonite by heating at various temperatures were investigated (Komadel *et al.*, 1996). Different experimental techniques such as X-ray diffraction (XRD),

high-resolution transmission electron microscopy (HRTEM) and IR spectroscopy revealed that Li fixation caused collapse of some smectitic, *i.e.* expandable interlayers, and the development of pseudo-pyrophyllite layers. As a consequence of this structural modification, samples with non-swelling interlayers dissolved more slowly than samples with expandable layers.

Modification of smectites is often studied by IR spectroscopy. This technique is very efficient for investigation of the structural changes of reduced-charge montmorillonites (Calvet and Prost, 1971; McBride and Mortland, 1974; Heller-Kallai and Mosser, 1995; Madejová *et al.*, 1999, 2000a) or for observing changes occurring upon acid treatment (Breen *et al.*, 1995; Komadel *et al.*, 1996; Vicente-Rodríguez *et al.*, 1996; Madejová *et al.*, 1998; Gates *et al.*, 2002). In most cases the middle infrared (MIR) region was used. Utilization of the near infrared (NIR) region (11000–4000 cm⁻¹), however, has greatly increased in recent years and has been applied to studies of interlayer water molecules in smectites with different interlayer cations (Bishop *et al.*, 1994), structural changes occurring in Li-saturated dioctahedral smectites upon heating to 300°C (Madejová *et al.*, 2000b) and site occupancies by Fe in nontronites (Gates *et al.*, 2002). Petit *et al.* (2002) showed that reasonable spectra of clay minerals could also be obtained in the 5000–2500 cm⁻¹ range (MIR region) by FTIR spectrometry. This adjustment allowed

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spectra to be obtained in both the combination (NIR) and OH-stretching (MIR) regions simultaneously from a sample prepared as a deposit on a glass slide.

The structural changes of acid-treated smectites are usually followed by IR spectroscopy in the 1300–400 cm^{-1} region, with emphasis on the Si–O-stretching and bending vibrations. However, as far as we know, no NIR evidence has been presented for acid-treated smectites. The aims of this study were: (1) to compare the properties of smectite heated at 150 and 300°C with two different interlayer cations (Li^+ , Ni^{2+}); and (2) to explore how layer-charge reduction influences the extent of Li- and Ni-SAz dissolution in hydrochloric acid. In addition to the MIR spectra, the extended NIR region (11000–3000 cm^{-1}) was applied to study the acid-treated clays.

MATERIALS AND METHODS

The Mg-rich montmorillonite SAz-1 (Cheto, Arizona) obtained from the Source Clays Repository of The Clay Minerals Society was used in this study. The clay was suspended in distilled water, Ca saturated by repeated treatment with 1 M CaCl_2 , and the <2 μm fraction was collected. Dispersion of Ca-saturated fine fraction was placed in dialysis tubes and ion exchanged with a 1 M solution of LiCl or NiCl₂. The Li- and Ni-forms obtained (LiS and NiS, respectively) were washed with distilled water until free of chloride ions, dried at 60°C, and ground to pass a 0.2 mm sieve. To prepare reduced-charge montmorillonites, the samples were heated for 24 h at 150 or 300°C. These samples are referred to as LiS150, LiS300, NiS150 or NiS300.

X-ray diffraction patterns of unheated and heated samples were obtained from oriented specimens prepared by sedimentation of the clay suspension onto a glass slide. Both air-dried and ethylene glycol-saturated samples were analyzed using a Philips diffractometer with $\text{CuK}\alpha$ radiation.

The layer charge of the samples was determined by the alkylammonium method following Olis *et al.* (1990), utilizing expansion of the interlayer with dodecylammonium ions. Depending on the magnitude of the layer charge of the smectite, the alkylammonium ions can form either a monolayer (13.6 Å), a bilayer (17.6 Å), or a pseudotrilyer (22 Å) configuration. The preparation of the alkylammonium derivatives follows the recommendation of Lagaly (1994).

For acid dissolution reaction, a 500 mg portion of each sample was mixed with 100 mL of 6 M HCl at 80°C. The mixture was reacted, with occasional stirring, for 1, 2, 4, 6 or 8 h. After acid treatment the sample was filtered and washed with distilled water. The filtered liquid was analyzed for Al and Mg by atomic absorption spectroscopy (AAS). Dissolution curves were constructed by plotting the undissolved fraction of the respective cation *vs.* time. The solid reaction products

obtained after drying at room temperature were analyzed by IR spectroscopy, using a Nicolet Magna 750 FTIR spectrometer. To obtain IR spectra in the MIR region (4000–400 cm^{-1}), a DTGS detector, a KBr beam splitter, and KBr pressed-disk technique (1 mg of sample and 200 mg KBr) were used. For the extended NIR region (11000–3000 cm^{-1}), a PbSe detector, CaF_2 beam splitter, and the DRIFT technique were used. For each sample 128 scans were recorded with a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

Reduction of the layer charge

X-ray diffraction analysis provides evidence for differences in basal spacings of the montmorillonites after heating to 150 and 300°C. The 001 basal reflection of LiS (air-dried sample) gave a d value of 15.1 Å. The d_{001} decreased to 11.9 and 9.7 Å for LiS150 and LiS300, respectively (Table 1). After ethylene glycol saturation the XRD patterns of LiS, NiS and NiS150 showed intensive 001 reflections as well as less pronounced 002 and 003 basal reflections (Figure 1). The pattern of the LiS150 sample displayed a broad reflection at ~9.2 Å, which is characteristic of collapsed and expanded interstratified interlayers. In addition, two broad shoulders occurred at ~26.9 and 13.5 Å. It is reasonable to assume that ordered mixed layers with expanded (16.9 Å) and collapsed (10 Å) interlayers gave a 1st reflection (superstructure) at 26.9 Å, and a 2nd order at 13.5 Å. The reason the peaks are so poorly defined is that the coherent scattering domain (CSD) size is small, as expected for Li-saturated and heated smectite (Figure 1). According to the peak positions and with reference to simulated XRD patterns (Moore and Reynolds, 1997), the fraction of collapsed interlayers would be ~0.50. For the LiS300 sample, the value of 9.7 Å (air-dried sample) is close to that of pyrophyllite, a non-expandable mineral with no layer charge. Significant differences were observed in the XRD pattern of NiS150 compared to LiS150. The 001 basal reflections of NiS and NiS150 (air-dried samples) gave d

Table 1. d_{001} values for air-dried and dodecylammonium-saturated samples of smectite SAz-1 and the mean layer charge (per half unit-cell) calculated from the peak position of the dodecylammonium-saturated sample.

Sample	Air-dried	Alkylammonium method	
	d_{001} (Å)	d_{001} (Å)	Mean layer charge (Eq/O ₁₀ (OH) ₂)
LiS	15.1	17.6	0.37
LiS150	11.9	13.4	0.24 or less
LiS300	9.7	12.7	0.24 or less
NiS	15.5	17.6	0.37
NiS150	15.3	17.1	0.34
NiS300	9.7	13.5	0.24 or less

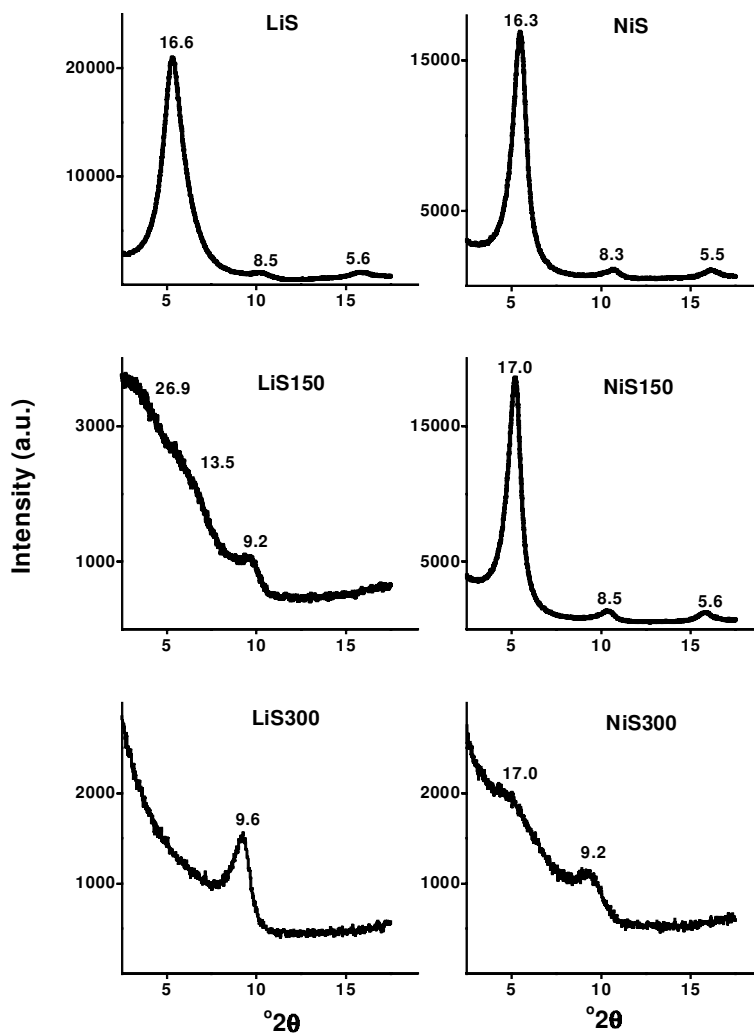


Figure 1. XRD patterns of unheated and heated LiS and NiS samples after ethylene glycol saturation; spacings in Å, CuK α radiation.

values of 15.5 and 15.3 Å, respectively, indicating fully expandable interlayers (Table 1). This is confirmed by the full expansion (16.3 and 17.0 Å) of the samples following solvation with ethylene glycol (Figure 1). The XRD pattern of air-dried LiS150 shows that heating to 150°C causes migration of Li⁺ ions into the layers and reduction of the layer charge. In contrast, water molecules are still coordinated to Ni²⁺ cations in NiS150 and hinder the penetration of the exchangeable cations into the layers. The more negative hydration energy of Ni²⁺ compared to Li⁺ (Güven, 1992) signifies that heating to higher temperatures is needed to cause migration of Ni²⁺ into the structure.

The d_{001} value for air-dried NiS300 is the same as that of LiS300 (9.7 Å, Table 1). However, a high background intensity level at small 2θ angles (before the reflection at 17.0 Å) and a shift of the peak position toward a lower d value (9.2 Å) after saturation with ethylene glycol indicates some expandable layers interstratified with the pseudo-pyrophyllite structure in

NiS300 (Figure 1). This suggests that in Ni-SAz montmorillonite a charge deficit of the octahedral sheet was not completely balanced by Ni(II) after heating to 300°C for 24 h.

The alkylammonium method was used to determine the layer charge of unheated and heated samples. The mean layer charge is determined by the relative proportions of bilayers to monolayers as indicated from the peak migration curve analysis of interstratified spacings (Olis *et al.*, 1990). The XRD data for dodecylammonium-saturated samples are given in Table 1. The d_{001} value of 17.6 Å indicates the presence of a bilayer alkylammonium complex in both LiS and NiS samples. The calculated value of the mean layer charge is 0.37 per half unit-cell (Table 1). The lower d_{001} value found for LiS150 (13.4 Å) indicates a monolayer complex as a result of the charge reduction. The value of the mean layer charge is then 0.24, or less, per half unit-cell, depending on whether the monolayer sheet is complete or not. The XRD pattern of alkylam-

monium-saturated NiS150 shows only a slight decrease of the d_{001} value, demonstrating a minor change in the mean layer charge (0.34 per half unit-cell).

The d_{001} values for alkylammonium-saturated LiS300 and NiS300 are 12.7 and 13.5 Å, respectively, which reveals interstratification of the monolayer complex and collapsed layers (Table 1). However, determination of the mean layer charge according to Olis *et al.* (1990) is inappropriate in this case because charge calculation is based on the peak position of interstratified monolayer and bilayer complexes, but the monolayer sheet may be incomplete.

Infrared spectroscopy in the OH-stretching (MIR) and OH-overtone (NIR) regions was used to follow structural changes occurring in Li- and Ni-saturated SAz-1 upon heating. The spectra of unheated LiS and NiS samples showed the absorption band near 3620 cm^{-1} assigned to stretching vibrations of structural OH groups coordinated to octahedral cations (Figure 2). Upon heating, the interlayer cations penetrated into the layers of the mineral. A small shift of the OH-stretching band position ($\Delta\nu = 4 \text{ cm}^{-1}$) was observed for LiS150, while only a negligible change, if any, was detected for NiS150 (Figure 2). Heating for 24 h at 300°C caused a pronounced shift of the OH-stretching band to 3639 and 3636 cm^{-1} for LiS300 and NiS300, respectively. An upward shift of the OH-stretching band correlates with a layer charge decrease. If dehydrated interlayer cations migrate into the structure upon heating to compensate for the charge deficit, only a limited residual negative charge remains on the apical oxygens (O_{ap}) of the tetrahedra and thus no feasible H-bonding between OH

group and O_{ap} occurs. As a consequence, the O–H bond strength increases and the absorption is observed at higher wavenumbers (Madejová *et al.*, 2000a).

In addition to the observed shift of the structural OH band, a new component near 3670 cm^{-1} appeared in the spectra of LiS150 and LiS300. This band was reported as evidence of local trioctahedral domains and was assigned to the AlMgLiOH vibration (Calvet and Prost, 1971). No such band, however, was observed in the MIR spectra of NiS150 and NiS300, so Li(I) and Ni(II) evidently produce different environments for structural OH groups.

Figure 3 shows the NIR spectra of Li- and Ni-SAz in the OH-overtone region. The band near 7060 cm^{-1} is complex, containing both the overtone ($2\nu_{\text{OH}}$) of the structural OH-stretching mode ($\nu_{\text{OH}} = 3620 \text{ cm}^{-1}$) and the first overtone of water ($2\nu_{\text{w}}$) weakly hydrogen-bonded to surface oxygens of the tetrahedral sheets ($\nu_{\text{w}} = 3610\text{--}3630 \text{ cm}^{-1}$; Farmer, 1974). Comparison of the spectra given in Figure 3 (NIR) and Figure 2 (MIR) reveals that the OH-overtone region is more sensitive to modifications of the clay structure upon heating than the OH-stretching region. For example, shifts in the OH-stretching band, observed in the MIR spectra of LiS150 and NiS150, are small ($\Delta\nu = 4$ and 1 cm^{-1} , respectively), but, the corresponding shifts in the OH-overtone in the NIR are large for LiS150 ($\Delta\nu = 46 \text{ cm}^{-1}$) and moderate for NiS150 ($\Delta\nu = 7 \text{ cm}^{-1}$). If a shift of the OH overtone reflects a layer charge decrease, as it does with the OH-stretching band, then pronounced reduction of the layer charge is observed in LiS150 while only a small decrease is detected in NiS150. The NIR spectra of

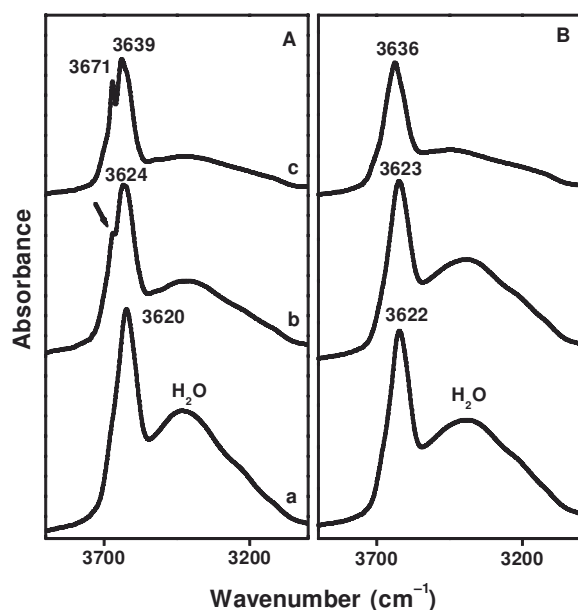


Figure 2. MIR spectra of LiS (A) and NiS (B) in the OH-stretching region: unheated (a), and heated at 150°C (b) and 300°C (c) for 24 h.

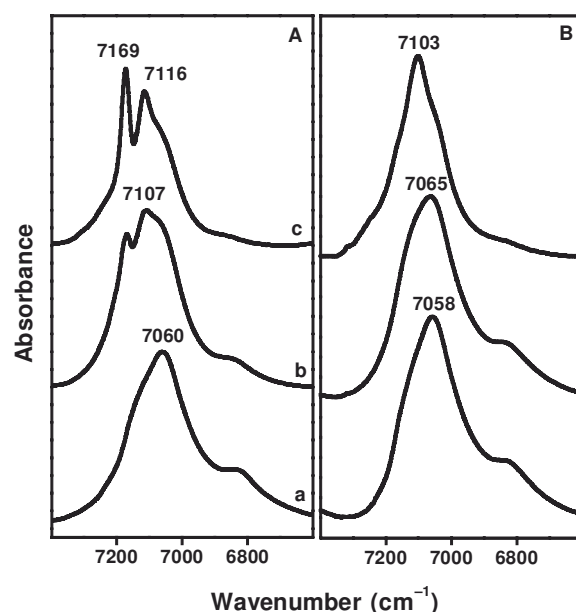


Figure 3. NIR spectra of LiS (A) and NiS (B) in the OH-overtone region: unheated (a), and heated at 150°C (b) and 300°C (c) for 24 h.

Li- and Ni-SAz heated for 24 h at 300°C show the overtone band at 7116 and 7103 cm^{-1} , respectively, and indicate substantial reduction of the layer charge.

The NIR spectrum of LiS150 shows a new OH overtone at 7169 cm^{-1} , corresponding to the OH-stretching mode at 3670 cm^{-1} . This band proves the presence of Li(I) in the previously vacant octahedra. Its intensity increases with temperature of heating due to increasing amount of fixed Li(I). The intensity of this OH overtone is significantly greater than the corresponding OH-stretching component (compare Figures 2 and 3), which demonstrates that the NIR region can be used more effectively to reveal the presence of Li(I) in trioctahedral domains.

Both MIR and NIR spectra of heated Li-SAz showed a new trioctahedral OH component indicating the appearance of Li(I) in previously vacant octahedra. However, no such component was found in the spectra of Ni-SAz heated to 150 or even 300°C. Although Li^+ and Ni^{2+} have similar ionic radii, the lower charge of Li(I) facilitates its penetration into the previously vacant octahedra, while Ni(II) is supposed to be fixed in the hexagonal holes of the tetrahedral sheet. The present study confirms that the extent and type of fixation varies depending on the nature of the interlayer cations, *e.g.* size and charge.

Acid dissolution

Dissolution of smectites in acids causes significant degradation of their structure. Protons penetrating into the layers attack the OH groups and the octahedral atoms are subsequently leached. Only minor differences were observed in the shapes of the acid dissolution curves for Al and Mg dissolved from unheated LiS and NiS (Figure 4). The octahedral atoms were substantially dissolved within 8 h; only 11% of total Mg and near 15% of Al remained insoluble after treatment in 6 M HCl. Pronounced differences were found, however, in the extent of the LiS150 and NiS150 dissolution. While 73 and 76% of total Mg and Al, respectively, was undissolved from LiS150 after 8 h, only 19% of Mg and 26% of Al remained in the solid phase of NiS150. The

d_{001} value of air-dried NiS150 indicates fully expandable interlayers, in contrast with LiS150 in which ~50% of the interlayers are collapsed (Table 1). The number of expandable interlayers affected the accessibility of the sheets to protons, and thus, the reaction rate. The considerable degree of swelling of NiS150 is the main reason for its faster dissolution compared with LiS150. Heating of Li- and Ni-SAz to 300°C resulted in development of collapsed interlayers (Table 1). The swelling ability of these samples was very low and thus dissolution of these samples was minimal. Up to 87% and 86% of Mg and Al, respectively, was found to be insoluble in LiS300 after 8 h. The lower octahedral cation content of the solid phase of NiS300 (75% of Al and 79% of Mg) suggests a greater extent of dissolution of this sample, although the d_{001} spacing of both air-dried samples heated at 300°C was the same. This observation indicates that the number of layers retaining their ability to swell is slightly greater in NiS300 than in LiS300, which agrees well with XRD data of ethylene glycol-saturated samples (Figure 1).

The IR spectra provide a sensitive measure of the changes of the smectite structure due to acid treatment. The OH- and Si–O–M-bending bands (where M is the octahedral atom) are most frequently chosen to follow the extent of acid dissolution. The utilization of this region (1300–400 cm^{-1}), however, fails to follow acid treatment of smectites if the number of leached octahedral atoms is too small (Komadel *et al.*, 1997). The results given above, however, show that the NIR region is frequently more sensitive to the changes in the environment of the OH groups than the MIR region. Therefore, in addition to the measurements in the 1300–400 cm^{-1} region, the FTIR spectrometer was adjusted for the extended NIR region (11000–3000 cm^{-1}) to obtain information simultaneously on both OH stretching and overtone regions.

The IR spectrum of untreated LiS shows the OH-stretching band at 3616 cm^{-1} overlapping a broad band of water near 3400 cm^{-1} (Figure 5B). The corresponding OH overtone was found at 7060 cm^{-1} (Figure 5A). The spectrum of LiS treated with 6 M HCl for 1 h (LiS-1)

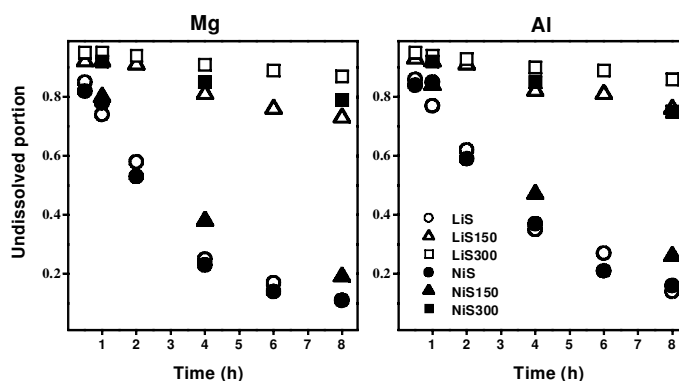


Figure 4. Dissolution of Mg and Al from unheated and heated Li- and Ni-SAz-1 in 6 M HCl at 80°C.

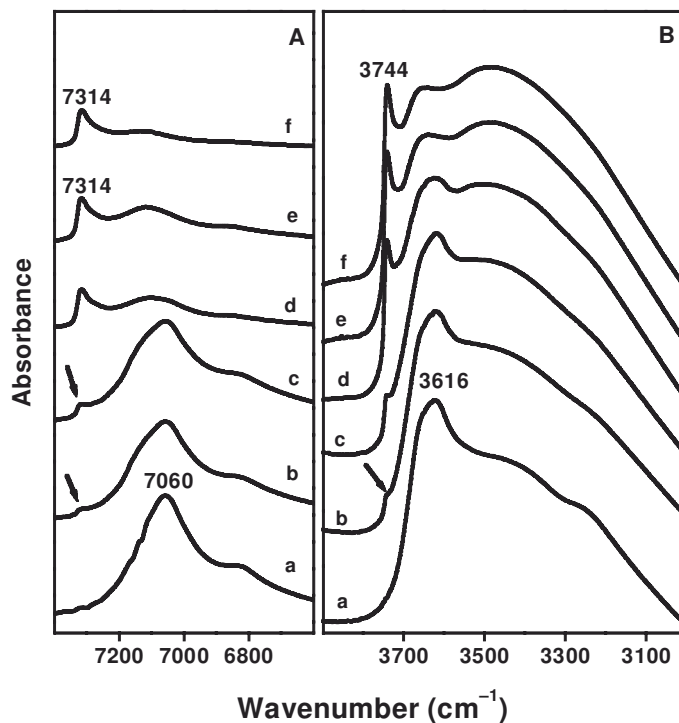


Figure 5. IR spectra of LiS in the OH-overtone (A) and OH-stretching (B) regions: untreated (a), and treated in 6 M HCl for 1 (b), 2 (c), 4 (d), 6 (e) and 8 (f) h.

shows a new component near 3744 cm^{-1} (Figure 5B,b), assigned to the OH-stretching vibrations of Si-OH groups (Parke, 1974; Daniel *et al.*, 2000). This band is very weak in IR spectra taken from KBr pellets (frequently used for MIR measurements) due to the low concentration of smectite in the KBr matrix. However, the DRIFT technique, in connection with the extended NIR region, allows identification of not only the Si-OH-stretching band, but also the corresponding Si-OH overtone at 7314 cm^{-1} (Figure 5A,b). The intensities of both of these Si-OH bands indicate only minimal alteration of the structure under these conditions. As the treatment time progresses (2–8 h), the Si-OH overtone increases in intensity, while a pronounced decrease is observed in the intensity of the OH overtone near 7060 cm^{-1} , related to the vibrations of octahedral cations.

In addition to the OH-stretching and overtone regions, the gradual dissolution of the octahedral atoms and contemporary transformation of the tetrahedral sheet was followed by changes in the $1300\text{--}400\text{ cm}^{-1}$ region (Figure 6). The spectrum of LiS-1 (Figure 6b) shows a slight shift and broadening of the Si-O-stretching band near 1030 cm^{-1} assigned to the vibration within the layers and a weak shoulder near 1082 cm^{-1} due to the vibrations of the reaction product (amorphous SiO_2). The 1030 cm^{-1} component decreases, while that near 1100 cm^{-1} increases in intensity with prolonged time of treatment. Another characteristic band of amorphous silica near 800 cm^{-1} increased in intensity as well. The

Al-O-Si band near 520 cm^{-1} is a very sensitive indicator of the layers remaining in the solid residue after acid

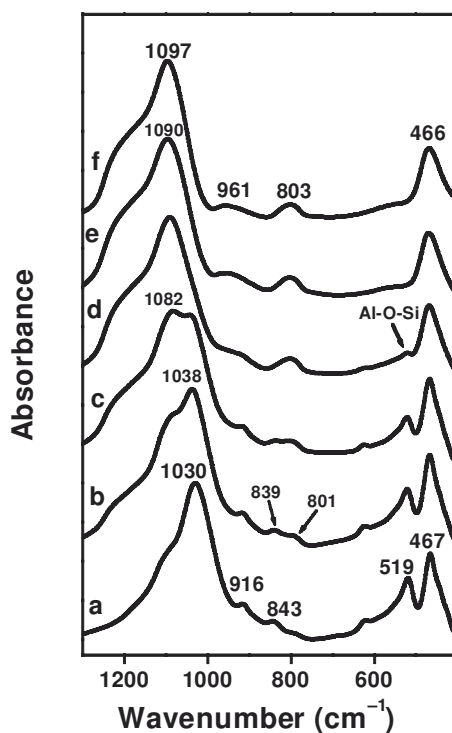


Figure 6. MIR spectra of LiS: untreated (a), and treated in 6 M HCl for 1 (b), 2 (c), 4 (d), 6 (e) and 8 (f) h.

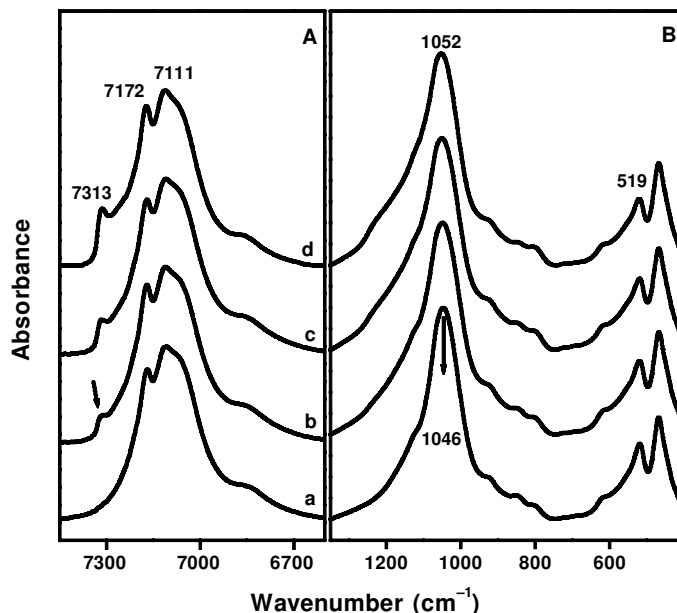


Figure 7. IR spectra of LiS150 in the OH-overtone (A) and 1300–400 cm^{-1} (B) regions: untreated (a), and treated in 6 M HCl for 1 (b), 4 (c) and 8 (d) h.

dissolution. The intensity of this band gradually decreases with time of treatment, and no such band was observed in the spectrum of LiS-8 (Figure 6f). The absorption bands characteristic of smectite are absent from this last spectrum and only the bands of amorphous silica at 1097, 803 and 466 cm^{-1} are observed. The broad band near 961 cm^{-1} is due to vibrations of SiOH groups (Moenke, 1974), which are present in the three-dimensional product, formed as the octahedral sheet in the smectite layer becomes substantially depleted.

The reduction of the layer charge connected with development of non-swelling layers upon heating of Li-SAz montmorillonite significantly influenced the extent of its dissolution in HCl. The MIR spectra of untreated LiS150 and samples acid treated for different time intervals (up to 8 h) are almost the same and indicate negligible degradation of the samples (Figure 7B). On the contrary, the Si-OH overtone at 7313 cm^{-1} is clearly visible even in the spectrum of LiS150-1 (Figure 7A,b) and increases in intensity with the time of treatment

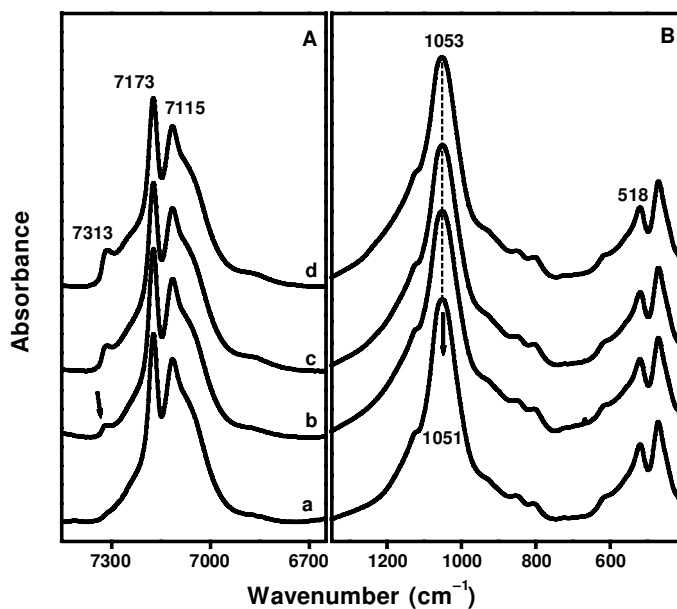


Figure 8. IR spectra of LiS300 in the OH-overtone (A) and 1300–400 cm^{-1} (B) regions: untreated (a), and treated in 6 M HCl for 1 (b), 4 (c) and 8 (d) h.

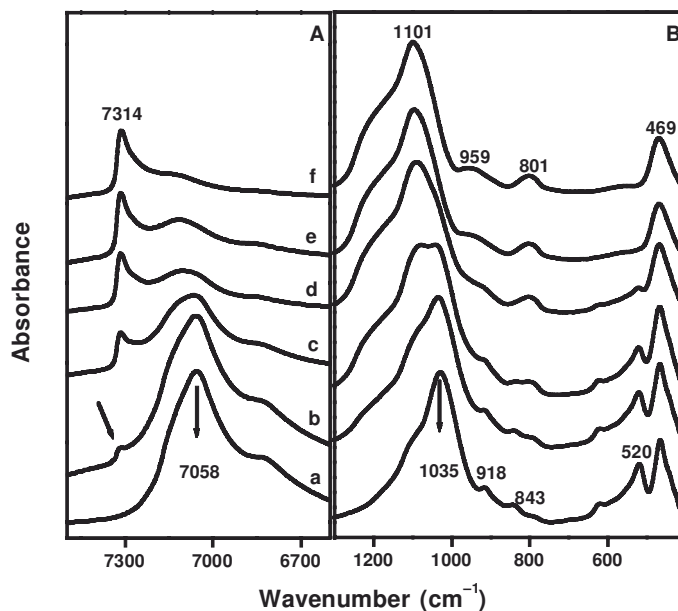


Figure 9. IR spectra of NiS in the OH-overtone (A) and 1300–400 cm^{-1} (B) regions: untreated (a), and treated in 6 M HCl for 1 (b), 2 (c), 4 (d), 6 (e) and 8 (f) h.

(Figure 7A). Similar results were observed for LiS300 after acid treatment (Figure 8). The spectrum of LiS300-8 in the 1300–400 cm^{-1} region is nearly identical to that of untreated LiS300, which indicates minor or no structural changes in the acid-treated sample (Figure 8B). Also, in this case the OH-overtone region is more sensitive for detection of the structural changes due to the acid attack and shows the presence of Si-OH groups the number of which increase with extended periods of treatment as indicated by the increased intensity of the Si-OH overtone at 7313 cm^{-1} (Figure 8A).

The IR spectra of the OH-overtone and 1300–400 cm^{-1} regions of acid-treated NiS are presented in Figure 9. The changes in the spectra in both regions are comparable with those of LiS, indicating that the character of the interlayer cation does not influence dissolution rate of unheated SAZ in hydrochloric acid. On the contrary, the IR spectra of NiS150 (Figure 10) are different from those of LiS150 (Figure 7). While the course of structural modification in LiS150 is similar to that of LiS300 (Figure 8), the spectrum of NiS150 is similar to that of NiS (Figure 9). Pronounced changes in

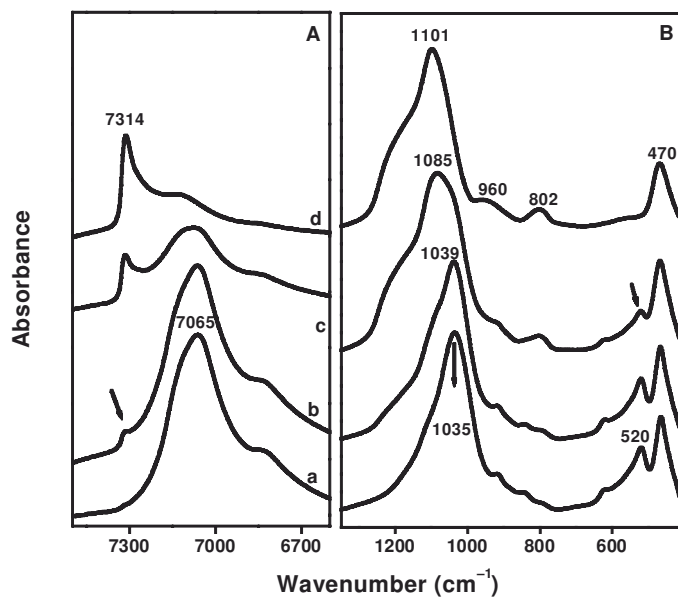


Figure 10. IR spectra of NiS150 in the OH-overtone (A) and 1300–400 cm^{-1} (B) regions: untreated (a), and treated in 6 M HCl for 1 (b), 4 (c) and 8 (d) h.

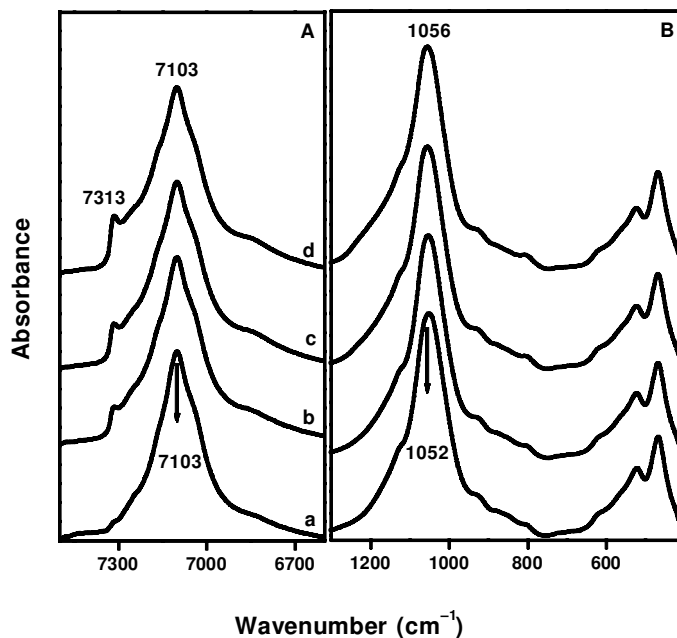


Figure 11. IR spectra of NiS300 in the OH-overtone (A) and 1300–400 cm^{-1} (B) regions: untreated (a), and treated in 6 M HCl for 1 (b), 4 (c) and 8 (d) h.

the NIR and MIR spectra of NiS150 (Figure 10) indicate dissolution of the octahedral atoms (decrease of the 7065 and 520 cm^{-1} band intensities) and creation of the reaction product, *i.e.* protonated amorphous silica (7314, 1101, 960, 802 and 470 cm^{-1}). More dissolution of NiS150 than of LiS150 is due to the greater swelling ability of the former. While a part of Li(I) is fixed in LiS150 and the sample contains interstratified non-swelling and swelling layers, the *d* value of air-dried NiS150 (15.3 Å) indicates only fully expandable interlayers.

As observed for LiS300, the NIR and MIR spectra of acid-treated NiS300 showed no significant changes in the 1300–400 cm^{-1} region after 1, 4 and 8 h of treatment in 6 M HCl at 80°C (Figure 11). The OH-overtone region, however, revealed a mild modification of the structure. The Si-OH overtone at 7313 cm^{-1} , superimposed on the strong OH overtone (7103 cm^{-1}), gradually increased in intensity proving the enhanced level of SAZ dissolution over the less treated samples.

The extent of dissolution of unheated and heated SAZ samples in HCl observed by IR spectroscopy correlates very well with XRD results and proves that the amount of swelling interlayers substantially affects this process. Most dissolution occurred for LiS, NiS and NiS150, *i.e.* for the samples with fully expandable interlayers (Table 1). The *d* value of air-dried LiS150 (11.9 Å) implies interstratification of expandable and non-expandable interlayers, while the interlayers of LiS300 and NiS300 are almost fully collapsed (9.7 Å, Table 1). The collapsed interlayers hinder acid attack of the clay structure from the interlayers. Thus, insignificant changes, if any, were observed in the 1300–400 cm^{-1}

region, *i.e.* in the region where absorption bands due to the vibrations of tetrahedral- and octahedral-sheet cations occur. The appearance of small, though clearly resolved Si-OH overtone in the spectra of acid-treated LiS150, LiS300 and NiS300 indicates, however, that the attack of the clay structure occurs mainly from the particle edges and/or from the layers on the surface of the crystals.

CONCLUSIONS

Heating of Li- and Ni-saturated SAZ montmorillonite at 150 and 300°C for 24 h caused migration of interlayer cations into the previously vacant octahedra and/or hexagonal holes of the tetrahedral sheets. The d_{001} value of 9.7 Å for samples heated at 300°C indicated the collapse of smectitic, *i.e.* swelling, interlayers and the creation of pyrophyllite-like layers. The alkylammonium method showed a layer charge decrease as a result of Li(I) and Ni(II) fixation. The NIR and MIR spectra revealed an upward shift of the OH-stretching and overtone bands due to the reduction of the layer charge, and the appearance of new bands near 3670 cm^{-1} and 7170 cm^{-1} in the spectra of Li-SAZ heated at 150 and 300°C proved the presence of Li(I) in previously vacant octahedra. No evidence for OH groups in trioctahedral coordination was found in the spectra of heated Ni-SAZ. Ni(II) is supposed to be fixed in the hexagonal holes of the tetrahedral sheets.

Acid dissolution of unheated Li- and Ni-SAZ and NiS150 samples caused extensive destruction of their structures. The slower dissolution of LiS150 and both samples prepared at 300°C was related to the develop-

ment of non-swelling interlayers due to the fixation of interlayer cations in the structure. The FTIR spectrometer adjusted for the extended NIR region provided new evidence for the creation of Si-OH groups upon acid treatment. The Si-OH-stretching vibration at 3741 cm^{-1} and Si-OH overtone at 7314 cm^{-1} permitted the extent of acid attack of smectites to be followed by IR spectroscopy, even in the case when no differences were observed in the $1300\text{--}400\text{ cm}^{-1}$ region, which is traditionally used to monitor this process. The results confirmed that acid attack of the clay structure occurs at both the interlayer surfaces and the edges. If the accessibility of the sheets for protons due to the development of non-swelling layers is limited, a little dissolution occurs, mainly from the particle edges.

The use of the NIR region significantly extends the application of IR spectroscopy in the study of clay minerals. The high sensitivity of NIR to the OH-group environment yields new information on the coordination of OH groups in heated samples as well as on the creation of Si-OH groups in acid-treated smectites.

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