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Modification of layer charge in smectites by microwaves

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Abstract

The layer charge reduction of two Li-saturated montmorillonites is referred to application of microwave radiation at 2.45 GHz for dispersions and 30.0 GHz for the solid powders. Efficiency of these treatments was compared to the same conditions applying conventional heating. The samples were heated in the temperature and time windows corresponding to 190–270 °C and 30–120 min, respectively. Changes in the mean layer charge were monitored by the determination of cation exchange capacity values using exchange of triethylene tetraamino copper ions. The charge reduction of the montmorillonites in aqueous dispersions was rather low (<30%) despite the fact, that high Li^+ concentration dissolved in solution was selected (1 mol L^{-1}). This behaviour was attributed to the very high water content in used dispersions and high hydration enthalpy of Li^+ cations. Nevertheless, the microwave heated dispersions (2.45 GHz) showed detectable layer charge reduction as compared to conventionally heated dispersions, where no significant changes were found.

Solid powders with different content of exchangeable lithium ions were prepared with solutions having different molar fraction of Li^+ and Na^+ cations (0%, 20%, 40%, 60%, 80%, 100% of Li^+). Final composition of interlayer cations was analysed with ICP-OES. In contrary to dispersions, the microwave treatment of the prepared powders revealed high layer charge reduction, which was much higher than for conventionally heated powders. The efficiency was enhanced with increasing interlayer lithium content but reached a limiting value depending on the montmorillonite used. Migration of the lithium into the structure of the montmorillonite supported with microwaves was extremely fast, finished probably within the few minutes of the treatments. The exchangeable Li^+ cations are accelerated through alternating electric field of microwaves and highly efficient layer charge neutralisation occurs. Infrared spectroscopy showed that the products obtained with microwave treatments correspond to the materials heated conventionally for much longer periods of time. Hence, applying microwaves the time and energy requirement can be significantly reduced. The X-ray diffraction showed that montmorillonite layers were able to swell in ethyleneglycol upon charge reduction, if the cation exchange capacity was not reduced more than 20–40%.
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1. Introduction

The layer charge of smectites related to the cation exchange capacity of the silicate framework is one of the most important properties of these type minerals

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(Lagaly, 1994; Laird, 1994; Mermut, 1994). Typically, the layer charge affects several physical–chemical properties of clays such as hydration of interlayer cations, swelling and/or sedimentation volumes, coagulation, rheology etc. (Güven, 1992a,b; Sposito, 1992; Low, 1992; van Olphen, 1992; Lagaly et al., 1997). It is well-known that layer charge distribution of smectites originating from different deposits differs significantly (Lagaly and Weiss, 1971, 1975). The research was focused recently on the modification and characterisation of one parent smectite used for the preparation of the series of layer charge modified materials (Hrobáriková et al., 2001; Komadel et al., 2003, 2005). This treatment can result in the alteration of the required properties of the parent clay for its variable utilization, e.g. in: carbon less copy papers, adjustment of the rheological properties of clay slurries, modification of the clay surface wettability.

The modification of the layer charge of smectites is known as Hofmann–Klemen effect. Upon exchange of the exchangeable cations of dioctahedral smectite for Li^+ cations, the material heated to 100–200 °C for about 21 days revealed the loss of cation exchange capacity and the ability to swell. The loss of the cation exchange capacity and the re-hydration of interlayer cations were interpreted by these authors as result of the solid state reaction (Hofmann and Klemen, 1950). Hence, under those conditions are the lithium cations able to migrate into the structural vacant octahedral positions of dioctahedral smectites and thus reduce the layer charge density of the minerals (Calvet and Prost, 1971; Maes et al., 1979; Jaynes and Bigham, 1987; Malla and Douglas, 1987). The reports can be found in the literature, that cations with small radius such as magnesium, copper, nickel, etc. can be fixed within the layers depending on the treatment conditions (Farmer and Russell, 1967; Prost and Calvet, 1969; Calvet and Prost, 1971; McBride and Mortland, 1974; Karakassides et al., 1999). The localisations of layer charge within the elementary layers, e.g. tetrahedral vs. octahedral affects this process significantly too (Malla and Douglas, 1987; Hrobáriková et al., 2001; Komadel et al., 2003).

In every case an intensive thermal treatment such as heating at 100–300 °C during 24 h was required for instance to obtain reasonable series of modified materials for spectroscopic investigations (Madejová et al., 1999, 2000a,b). To lower the time requirements and the costs connected with production of charge modified smectites, we have tested an alternative-microwave heating to produce layer charge modified materials. It is known that microwave assisted processing is fast, clean, simple and often energetically more efficient than conventional heating. Microwave energy can be directly transferred into the volume of the dielectric materials where it is absorbed and transferred into heat by different absorption mechanisms such as dipolar relaxations or ionic conduction (Schiffmann, 1997; Rao et al., 1999).

Heating with microwave energy is determined by dielectric properties of the material, prescribed as complex dielectric permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) which in general depends on frequency of the electromagnetic energy as well as on temperature. The real part of the permittivity (ε') is characterizing the polarizability of the materials as well as the propagation of microwaves into the material. The loss factor (ε'') indicates the ability of the material to dissipate electric energy. Very often in literature the absorption properties of materials are discussed in terms of the dielectric loss tangent $\tan\delta$ which corresponds to the ratio of the loss factor to the relative dielectric constant ($\tan\delta = \varepsilon'' / \varepsilon'$) For optimum coupling, a balanced combination of moderate ε', to permit adequate penetration and high loss (high ε'' and $\tan\delta$) are required (Bogdal et al., 2003).

The power P absorbed inside the material is proportional to the installed microwave power, the angular frequency ω and the dielectric loss factor ε''. It can be estimated as follows. $P = \frac{1}{2}\omega\varepsilon_0\varepsilon'' |E|^2$ With respect to this knowledge we have tested the effect of two microwave frequencies corresponding to 2.45 GHz, an ISM frequency (industrial–scientific–medical) usually used in domestic devices and 30 GHz. Higher frequency processing may improve uniformity of electromagnetic energy and thus temperature gradients and enhances the radiation absorption (Bykov et al., 2001). This paper presents for the first time the results concerning the investigation of the Hofmann–Klemen effect with the application of microwave technique.

2. Experimental

2.1. Materials

The fine fractions smaller than 2 μm from a two sodium saturated bentonites (Volclay—Wyoming, USA and Calcigel—Bayern, Germany) obtained from Süd-Chemie, Germany, were used in this study. The bentonites were fractionated according to the method of Stul and van Leemput (1982) revised by Tributh and Lagaly (1986a,b) to obtain a sodium form of the smectite dispersions. This procedure includes removal of carbonates, iron oxohydroxides, organic matter such as humic material and fractionation. The dispersion of sodium saturated fine fraction of each bentonite was divided into three parts.

The first one was treated as non-modified sample in the sodium form, which was washed from excess salt until the conductivity of supernatant was below 10 μS cm^{-1}, freeze-dried, crushed in an agate mortar and stored in a PE flask.

The X-ray diffraction and IR analysis detected that Volclay was pure montmorillonite, however, Calcigel contained still significant admixtures of quartz, illite and possibly kaolinite. RFA analysis of silicon was combined with the ICP-OES analysis of the chemically digested samples to achieve chemical composition of both materials. The data are presented in the Table 1. Calculation of structural formula for Volclay from the data shown in Table 1 indicate that this montmorillonite has negligible isomorphous substitutions in the tetrahedral sheets, unfortunately, the admixtures present in the Calcigel disable to get an reasonable estimate of structural formula for this sample. In comparison to Volclay has Calcigel certainly some isomorphous substitutions in the tetrahedral sheets.

The second part of dispersion was at least seven times washed with 1 M LiCl solution to ensure preparation of Li-saturated form of montmorillonite. Samples were used as dispersion prepared in 1 M LiCl solution for the experiments preformed at 2.45 GHz and with conventional heating. The solid content used was about 10 wt.%. Upon heating treatment, the dispersions were washed by deionised water in the ultracentrifuge Sorvall® Ultra Pro® 80 (Kendro Laboratory Products, Connecticut USA), until the supernatant conductivity was under the 10 μS cm^{-1}. The samples were stored as dispersions and the solid content was determined gravimetrically.

Finally, the third part was used for preparation of the powders with different molar content of sodium–lithium cations applying the mixed solutions of NaCl and LiCl with final ionic strength of 1 M and lithium fraction 0, 20, 40, 60, 80 and 100 M % (Table 2). The excess salts were washed out with ethanol until AgNO$_3$ test with the supernatant was negative. The samples were dried at 60 °C, crushed in the agate mortar and stored in the PE flask. Powders prepared in this series were used for experiments with microwaves performed at 30.0 GHz and using conventional heating. The water content determined gravimetrically was ≤5%. All microwave treatments (Mw) were preformed in accord to selected experimental scheme using treatment times 30, 60 and 120 min with final temperatures 190, 230 and 270 °C. To compare the efficiency of microwaves parallel experiments applying conventional heating treatments (Ct) under the same conditions were made.

Table 2
Content of exchangeable cations in used montmorillonites upon lithium saturation with solutions of different Li$^+$ content

Sample (%)	x_{Li}^{S}/ %	x_{Li}^{A}/ %	Element/mmol g^{-1}				Σ/ mval g^{-1}
			Li	Na	K	Ca	
VO 0	0	0	0.00	0.93	0.02	0.00	0.95
VO 20	20	12	0.12	0.90	0.02	0.00	1.04
VO 40	40	26	0.25	0.72	0.02	0.00	0.99
VO 60	60	43	0.44	0.57	0.02	0.00	1.03
VO 80	80	66	0.67	0.34	0.02	0.00	1.03
VO 100	100	97	0.95	0.03	0.02	0.00	1.00
CA 0	0	0	0.01	0.74	0.30*	0.05	0.85§
CA 20	20	10	0.09	0.80	0.35*	0.02	0.93§
CA 40	40	21	0.17	0.65	0.38*	0.03	0.88§
CA 60	60	36	0.30	0.53	0.38*	0.02	0.87§
CA 80	80	58	0.47	0.34	0.34*	0.02	0.85§
CA 100	100	91	0.72	0.07	0.37*	0.02	0.83§

^{S}Lithium molar fraction used in the treatment solutions containing only the Li$^+$ and Na$^+$ cations, ^{A}lithium molar fraction including only the Li and Na content as analysed by ICP-OES, * indicates non-exchangeable portion of K$^+$ cations present in the illite/smectite and/or feldspar admixture. §Sum of exchangeable cations without K.

For this purpose we used High Pressure Asher (AP Paar Kuerner Analysentechnik, Rosenheim, Germany) allowing heating of dispersions or the powders in a quartz vessel equipped with tightly closing quartz caps applying an external gas pressure. The treatment times indicated refer to the time used for keeping of sample at given temperature. The ramp time required to reach this temperature was at microwave systems 5 min, however, conventional heating at the equipment used in our experiment required ramp times between 10 and 25 min. In the cooling phase was the temperature 100 °C reached at any equipment within 5–10 min. To estimate the variance among samples at least two replicas were prepared for each montmorillonite and any treatment.

2.2. Microwave systems

Commercially available microwave system MLS-Ethos (MLS GmbH, Leutkirch, Germany) operating at 2.45 GHz with maximum output power 1 kW was used for treatment of montmorillonite dispersions in 1 M solution of LiCl. The temperature was controlled in one of the 80 ml tightly closed reaction vessel made from Teflon® equipped with

Table 1
Chemical composition of Volclay (VO) and Calcigel (CA) samples upon saturation with sodium cations as found by ICP OES and RFA analysis

Sample	Percentage of oxide content (w/w)								
	SiO$_2$*	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	TiO$_2$	l.i.
VO	62.4	19.8	3.53	2.24	0.03	3.03	0.09	0.15	8.75
CA	55.6	20.2	5.77	2.87	0.29	2.27	1.78	0.40	10.8

* — Silicon content as determined by RFA, l.i. — loss of ignition.

thermocouple. We used 2–4 vessels which were filled with 10 ml of the corresponding dispersion. This volume ensured sufficient contact with the thermocouple. Applied temperature profile included 5 min heating phase to the required temperature followed with defined holding time and cooling phase.

The powders were treated within a compact gyrotron microwave system operating at 30.0 GHz (Bykov et al., 1995), with an installed output power of up to 15 kW, however, less than 1 kW was used at our work conditions. The temperature was controlled with a k-type thermocouple stuck in about 1 g of powder in a glass vessel. The temperature treatment profile was similar as in the case of 2.45 GHz experiments.

2.3. Methods

The cation exchange capacity (CEC) of all samples was determined with the copper-triethylenetetramine complex method proposed by Meier and Kahr (1999) using UV–VIS spectrophotometer (UV 1201, Shimadzu) at 570 nm. About 80–100 mg of each sample was used for the determination. The water content was determined gravimetrically by drying of the samples to the constant weight at 105 °C. Estimated variance of CEC determination is indicated in all figures dealing with changes of cation exchange capacity from independent replicas.

The IR spectra were obtained on the Bruker IFS 66 Fourier transform infrared (FTIR) spectrometer equipped with DTGS detector and the Golden Gate single reflection diamond attenuated total reflectance (ATR) cell from Graseby Specac, over a spectral range 4000–400 cm^{-1} with 4 cm^{-1} resolution. About 100 mg of solid powder was spread on the diamond crystal surface and pressed to the surface using a torque key with a force of 70 N cm^{-1}. Collected FTIR spectra were evaluated with Bruker Opus software.

The X-ray diffraction patterns were collected by a Bragg–Brentano goniometer Siemens D5000 (CuKα_1 radiation, $\lambda = 1.5405$ nm) equipped with a graphite secondary beam monochromator with a step-size of 0.02° 2θ and at least 2 s/step at room temperature. Patterns were recorded over a 2–62° 2θ range for montmorillonite and/or for ethyleneglycol saturated samples. Ethylene glycol (EG) saturation was performed with p.a. quality substance (Merck, Germany) added to the sample material to form 25% (w/w) dispersion. The samples were stored in a tightly closed flask at 60 °C for 4 days. The positions of the basal reflections were determined using Bruker evaluation programme Diffrac^plus.

3. Results and discussion

3.1. Changes of cation exchange capacity

The CEC values of non-modified montmorillonites determined by exchange of triethylene tetraamino copper ions revealed 0.95±0.04 mmol g^{-1} for the

Volclay (VO) and 0.69±0.05 mmol g^{-1} for the Calcigel (CA) sample. Dispersions of these samples prepared in 1 M LiCl solutions were supposed to absorb efficiently microwave radiation, as this is enhanced by increasing ionic strength of the aqueous solutions at 2.45 GHz (Schiffmann, 1997). The high ionic strength was used at the same time to ensure the compression of the diffuse double layer and thus increase the concentration of Li^+ cations at the montmorillonite surface.

Fig. 1 shows relative CEC values of the VO dispersion treated 60 min at different temperatures using 2.45 GHz microwaves (Mw) and conventional heating (Ct). Slight increase in the efficiency of the charge reduction was found for the VO dispersion heated at 270 °C. On the other hand no significant changes in CEC were found for the VO dispersion treated by conventional heating. For comparison, the effect of 2.45 GHz microwaves on the CEC change of both VO and CA dispersions treated at 230 °C during different periods of time are shown in the Fig. 1. The relative CEC values compared to non-modified sample showed that changes between 5% and 15% reductions of CEC was achieved under these conditions for the VO and CA montmorillonites. The 5% reduction of CEC is at the detection limit with exchange of triethylene tetraamino copper ions.

Microwave treatment of the dispersions results clearly in more efficient charge reduction than applying the conventional heating. Nevertheless, only rather modest layer charge reduction was achieved (<30% of CEC). One can suppose that the reason may be the very high water content in used dispersions. The hydration enthalpy of Li^+ cations is the highest one from the
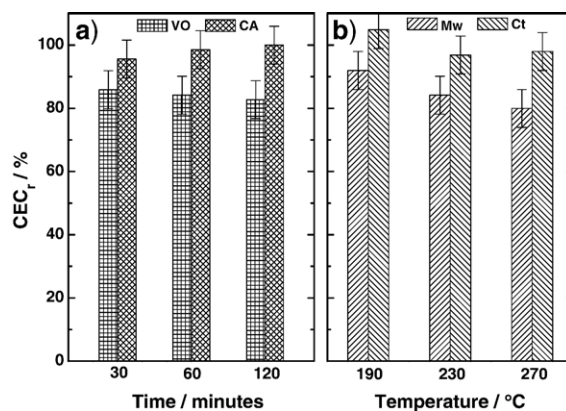

Fig. 1. Changes of relative cation exchange capacity of: a) VO and CA dispersions as function of time during microwave treatment at 230 °C; b) VO sample as function of heating temperature for Mw (2.45 GHz) and Ct heating treatments after 60 minutes. Dispersions with 1 mol L^{-1} Li^+ cations.

alkaline cations and equals to -522 kJ mol^{-1} (Güven, 1992a). Hydrated Li$^+$ cations adsorbed at the surface of montmorillonite must lose their hydration shell (dehydrate) prior they are able to penetrate into the vacant octahedral positions in the structure. Therefore high water content means barrier for effective layer charge reduction due to re-hydration of Li$^+$ cations at montmorillonite surface. By the other words, the high water content means at the same time higher probability of water molecules collisions with dehydrated Li$^+$ cations located on the montmorillonite surface. Based on these results and the fact that changes detected by spectroscopic methods require almost 40–50% reduction of CEC (Hrobáriková et al., 2001) further characterisation of these layer charge modified samples was omitted.

The effect of 30 GHz microwaves on the CEC change of both VO and CA powders treated with solutions of 20, 40, 60 and 80 M % of Li$^+$ cations (see also Table 2) compared to conventional heating treatment are shown in Figs. 2 and 3, respectively. The results of CEC changes with application of Mw are striking in comparison to Ct samples. Already at 190 °C and 60 min treatment time significant changes of CEC can be observed for Mw treated samples. The CEC further decreased by increasing molar content of

exchangeable Li$^+$ cations in used materials and reached about 1/5 and 1/2 of CEC of non-treated VO and CA, respectively. The layer charge reduction was further less affected by the treatment time and the temperature of treatment.

On the contrary, the Ct samples revealed at 190 °C and 60 min treatment no significant changes in CEC. Only increase of temperature and/or treatment time resulted in detectable changes of CEC. For instance the heating of the sample at 270 °C and 60 min during Ct revealed comparable CEC reduction as Mw treatment at 190 °C during 60 min (Fig. 2c vs. a; Fig. 3c vs. a). The efficiency of layer charge reduction was enhanced by both temperature increase and by duration of treatment. CEC further decreased by increasing molar content of interlayer Li$^+$ cations. Anyhow, this effect was less pronounced for Mw treated samples, where similar efficiency for layer charge reduction was observed.

It is supposed that this finding is decisive for understanding of interactions between lithium saturated montmorillonites and microwave radiation. The Fick's law can describe the diffusion of the Li$^+$ cations in the solid where the diffusion coefficient depends on the temperature of diffusion. In our experiments was the final treatment temperature used for Mw and Ct treatments identical hence an additional mechanism
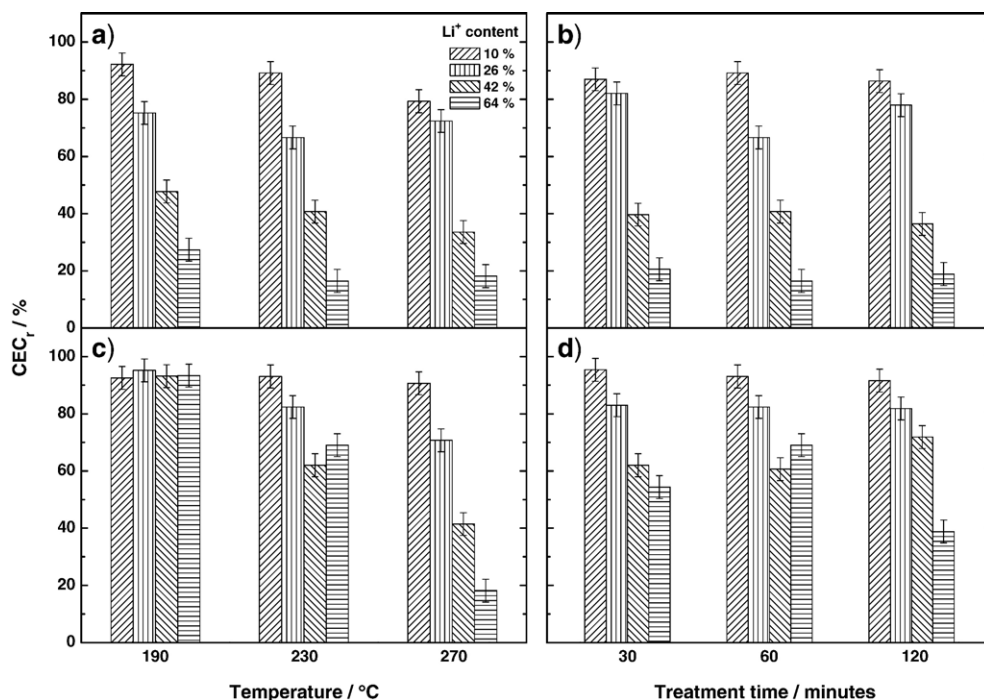

Fig. 2. Effect of treatment temperature and time on relative cation exchange capacity of VO powders as function of interlayer Li$^+$ content. a), b) — treated by Mw (30.0 GHz); c) d) — treated by Ct. Temperature at varying time 230 °C, time at varying temperature 60 min.
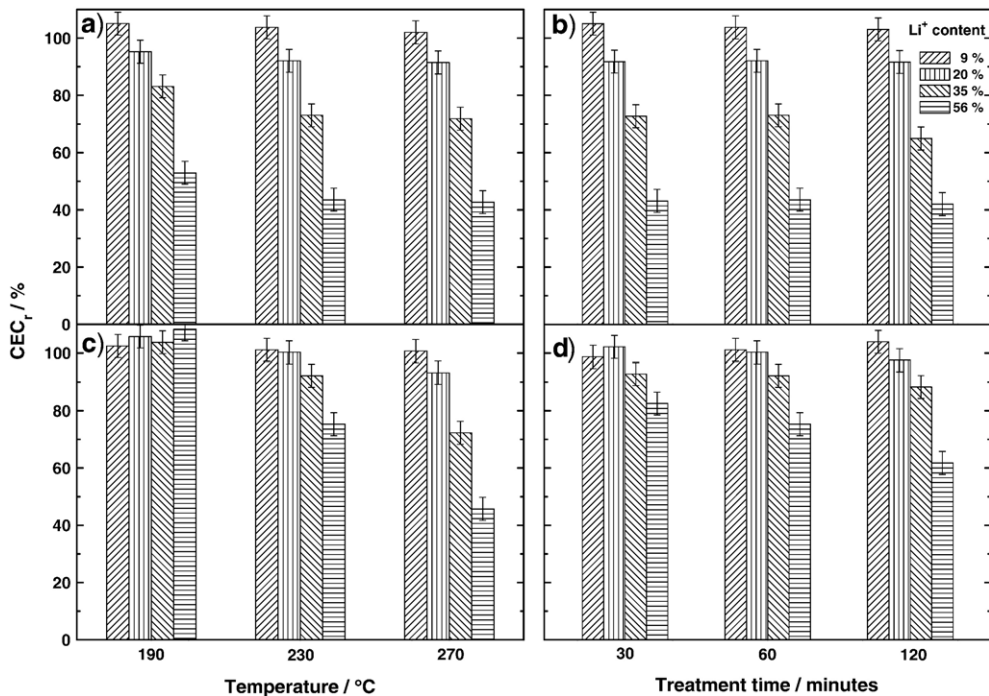
Fig. 3. Effect of treatment temperature and time on relative cation exchange capacity of CA powders as function of interlayer Li^+ content. a), b) — treated by Mw (30.0 GHz); c), d) — treated by Ct. Temperature at varying time 230 °C, time at varying temperature 60 min.

must be acting for layer charge neutralisation with Mw. It is highly probable that the exchangeable Li^+ cations present in the interlayer space of montmorillonite are accelerated through alternating electric field of microwaves such as in the case of ionic conduction (Schiffmann, 1997; Rao et al., 1999). The accelerated Li^+ cations can much more easily enter the octahedral cavity present in dioctahedral smectites where they are

entrapped and neutralise the layer charge. This is in good correlation with the tendency found for enhanced layer charge neutralisation by increasing Li^+ content in the interlayer, as the higher concentration means higher probability of Li to locate in octahedral cavities.

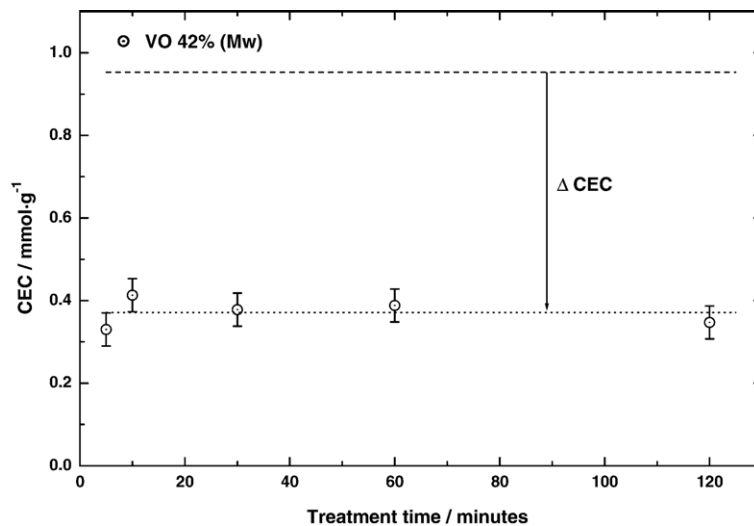The values of relative CEC of VO and CA samples treated with Mw strongly indicates that detected CEC

Fig. 4. Change of cation exchange capacity depending on treatment time with Mw (30.0 GHz) of VO 42% sample.

varied only within the frame of experimental errors and were less affected by the selected parameters like treatment time and temperature (Figs. 2 and 3). The reaction kinetics of the layer charge neutralisation process within selected parameters was much better pronounced by Ct heated samples. To response fundamental question, at which time scale the kinetic effect of layer charge neutralisation using Mw could be observed, treatment time was shortened to 5 min. The results found for the sample VO with 43% of exchangeable Li are shown in the Fig. 4. It is striking that despite application of extremely short treatment times, CEC changed to the extend corresponding with experiments at longer time scales (30–120 min). This means that the layer charge neutralisation of powders using Mw is an extremely fast process. It can be supposed that this process is finished within the first few minutes hence the reaction kinetics should be observable only on the second time scale.

The changes of total CEC of VO and CA samples treated at 230 °C during 60 min by Mw or Ct as function of the Li^+ molar content in the interlayer space are
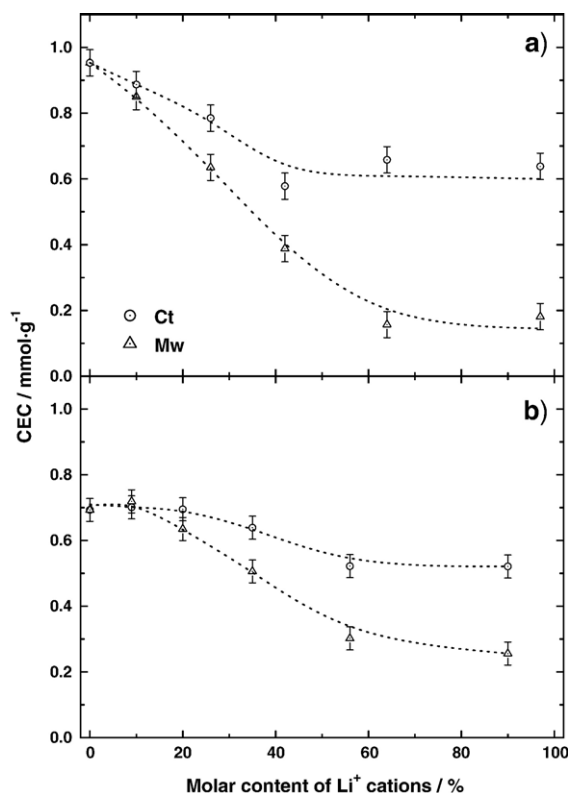

Fig. 5. Change of cation exchange capacity as function of interlayer Li^+ content as detected by ICP-OES analysis (see Table 1). a) — VO, b) — CA sample treated by Mw (30.0 GHz) and Ct at 230 °C for 60 minutes.

shown in the Fig. 5. The non-modified sample in the sodium form represents the CEC values for 0% of the Li^+ cations. Enhanced efficiency of Mw treatment is clearly demonstrated by this figure despite the fact that significant change of CEC by Ct was detected. In both cases the Li^+ content affected the final CEC, however, higher layer charge reduction was observed for VO sample. This difference may be explained by the dissemblance in the chemical composition of both montmorillonites and localisation of structural isomorphous substitutions—tetrahedral vs. octahedral (Green-Kelly, 1955; Hrobáriková et al., 2001).

3.2. ATR–FTIR spectra

Spectroscopic investigations were used to prove migration of the lithium into the sheets of montmorillonite upon Mw and Ct heating treatments and to compare the resulting products. The vibrations of OH groups in smectites are sensitive to the local environment of the structural cations and affected by the Hofmann–Klemen effect. Therefore the changes in the positions of the absorption bands related to the stretching vibrations of the structural OH groups ($3750–3500$ cm^{-1}) and of bands related to the OH-bending and Si–O vibrations ($1200–500$ cm^{-1}) are usually investigated (Madejová et al., 1999, 2000a,b).

The ATR–FTIR patterns of VO and CA samples treated by Mw or Ct as function of the Li^+ molar content in the interlayer space are shown in Figs. 6 and 7, respectively. The non-modified sample represents the spectra with 0% of the Li^+ cations. Typical spectra for aluminium rich montmorillonites were found in the case of VO and CA sample (Farmer, 1974; Madejová et al., 1998; Madejová and Komadel, 2001). Infrared spectroscopy detected an admixture of silica in the form of quartz in both VO and CA samples with an absorption bands detectable at about 796, 690 cm^{-1} and with weak shoulder at 780 cm^{-1}. Possible admixture of feldspars is indicated by weak absorption bands at 720–760 cm^{-1} and a shoulder at 605 cm^{-1}. The admixture of quartz was detected for CA by X-ray diffraction experiments but not for VO sample. Additionally, small admixture of kaolinite can be expected in the CA sample as the OH stretching band of kaolinite at about 3695 cm^{-1} was detected (Madejová et al., 2002).

Structural stretching vibrations of OH groups for the non-modified montmorillonite samples were detected near 3620 cm^{-1}. Bending vibrations of montmorillonite OH groups reflect well the chemical composition of its octahedral sheets (Farmer, 1974; Madejová et al., 1998; Madejová and Komadel, 2001). The AlAlOH bending
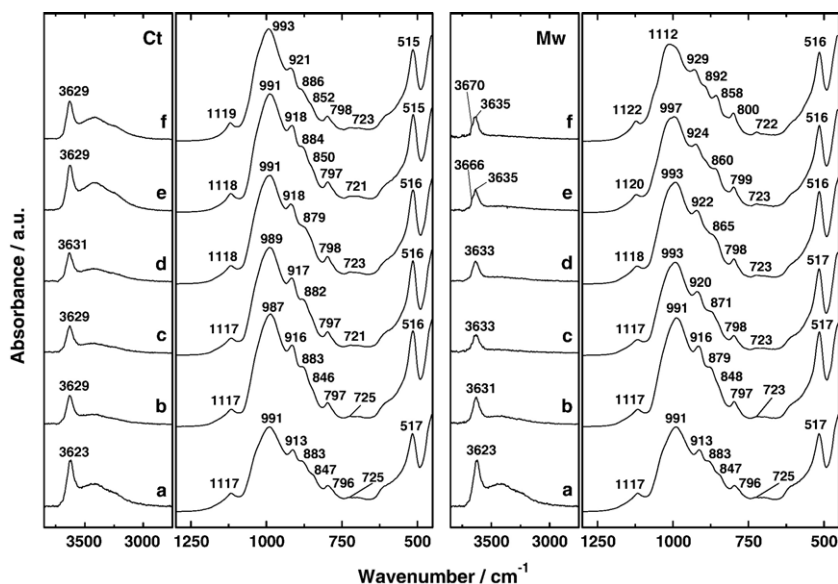
Fig. 6. Infrared spectra of VO samples as function of interlayer Li$^+$ content as detected by ICP-OES analysis a) — 0%, b) — 12%, c) — 26%, d) — 43%, e) — 66% f) — 97%. Treated by Mw (right) and Ct (left) at 230 °C for 60 min.

vibration is detected as the most intense band, at 912 cm^{-1}, confirming the high octahedral Al content in both VO and CA samples. The presence of structural iron in the octahedral sheets of montmorillonite is clearly detected by the bending adsorption of AlFeOH at about 880 cm^{-1} for VO and CA montmorillonite. The AlMgOH bending band at 844 cm^{-1} was found for VO but not for CA sample and indicate lower octahedral Mg content in the CA sample. On the other hand, the CA sample showed band at 833 cm^{-1} which indicate an admixture with high tetrahedral layer charge, e.g. illite. The Si–O in-plane vibrations for sodium form of montmorillonite were observed at about 1116 cm^{-1} with complex Si–O stretching vibrations at 991 (VO) and 983 cm^{-1} (CA). The bending Si–O–Al vibration can be seen for both samples at about 516 cm^{-1}.
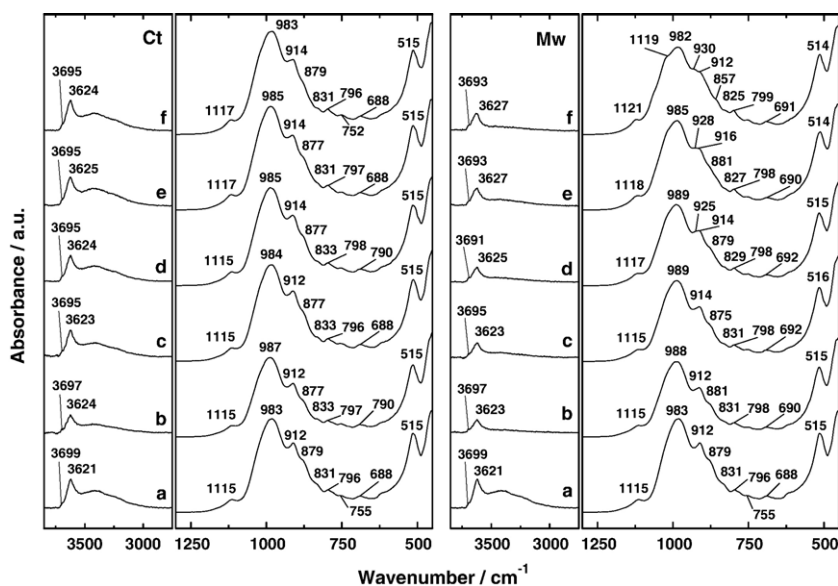

Fig. 7. Infrared spectra of CA samples as function of interlayer Li$^+$ content as detected by ICP-OES analysis a) — 0%, b) — 10%, c) — 21%, d) — 36%, e) — 58%, f) — 91%. Treated by Mw (right) and Ct (left) at 230 °C for 60 min.

The changes of the ATR–FTIR patterns as function of the Li^+ molar content in the interlayer space of starting material and treatment procedure (Mw or Ct) of VO and CA treated at 230 °C during 60 min are shown in Figs. 6 and 7. While increasing the lithium content in the starting material the Ct treatment affected only slightly the OH stretching vibrations of VO sample. At the same time slight shifts of OH-bending bands in the VO sample (Fig. 6) and inconsiderable changes in the CA series (Fig. 7) were observed. For instance the position of the AlAlOH bending band for VO sample revealed a shift of 8 cm^{-1} to higher wave numbers, and small shifts for AlFeOH or AlMgOH were observed. In the case of CA sample, only the decrease of the AlFeOH band intensity at 879 cm^{-1} was observed. These results are in good agreement with the efficiency of the layer charge reduction determined by CEC as the Ct treatment revealed about 35% reduction of VO but only about 25% of CA sample at the highest Li^+ content.

On the contrary, Mw treatment led to considerable changes in the IR spectra which was systematically enhanced by increasing Li^+ content (Figs. 6 and 7). For instance, the OH stretching vibrations revealed a shift for 12 cm^{-1} of VO and for about 6 cm^{-1} of CA sample to higher wave numbers. New stretching band corresponding to vibration of AlMgLiOH at 3670 cm^{-1} appeared for VO, known as pyrophillite-like band in lithium reduced charge montmorillonites (Hrobáriková et al., 2001). In the case of CA sample this band is very weak and possibly not well resolved due to the admixture of kaolinite with OH stretching band at about 3695 cm^{-1}. However, the observed intensities of the OH stretching bands are relatively low due to measurements with the single reflection ATR technique, which is not optimal for OH stretching region as the depth of wave penetration into the sample depends on the wavelength and is proportional to the number of reflections.

The OH-bending bands exhibit strong perturbation of the OH vibrations due to presence of Li(I) in the structure. We found typical shift of AlAlOH vibrations to higher wave numbers in the case of VO sample (Fig. 6), but in the case of CA sample this characteristic vibration split to the doublet at 930 and 912 cm^{-1} (Fig. 7). The AlFeOH band shifted systematically to lower wave numbers, while AlMgOH band to higher wave numbers and both bands have been merged at about 40–60% of Li^+ cations in the VO starting material. Further increase in lithium content resulted in the development of two well defined absorption bands at 892 and 858 cm^{-1} (Fig. 6). The intensity of the AlFeOH band in the CA sample decreased significantly after Mw treatment and the position was difficult to estimate. At the highest interlayer Li^+ content in the starting CA material, well defined absorption at 857 cm^{-1} comparable to the VO sample at 858 cm^{-1} was found (Fig. 7). We suppose that this behaviour could be helpful for the assignment of the OH-bending bands upon fixation of Li (I) in the structure of dioctahedral smectites as it reflects the chemical composition of the octahedral network.

Indeed, the splitting of AlAlOH vibrations of CA sample upon heating to the bands at 930 and 912 cm^{-1} can be explained by the presence of kaolinite admixture. The band near 930 cm^{-1} is band of montmorillonite which shifted to higher wavelength similarly to VO sample. The band at 912 cm^{-1} is AlAlOH vibration of kaolinite. These two bands are overlapping in the untreated sample, however, after Mw treatment splitting is observed because OH groups of kaolinite are not influenced by Li migration.

The Si–O complex stretching vibration of VO at 991 and of CA at 983 cm^{-1} was affected inconsiderably by Ct treatment. The Mw treatment of VO resulted in the shift of Si–O stretching band maximum to higher wave numbers for 12 cm^{-1} accompanied with the change of the peak symmetry for starting sample by highest content of exchangeable lithium ions. In comparison the Si–O stretching band of CA showed clearly shoulder development finally located at 1119 and original vibration at 982 cm^{-1}. The Si–O in-plane vibrations revealed a significant shift to higher wave numbers only upon Mw treatment with about 5 cm^{-1} for VO and about 6 cm^{-1} for CA. The bending Si–O–Al vibration at about 516 cm^{-1} remains unaffected by the migration of Li^+ cations into the montmorillonite structure.

Spectral changes induced by Mw treatment of used montmorillonites are similar to those already known in the literature (Madejová et al., 1999; Hrobáriková et al., 2001). Nevertheless, some of the detected spectral features of VO and CA samples used for investigation may be attributed to their specific crystalochemical composition and ATR technique resolving very well the OH-bending and Si–O vibrations in spectral range of 1200–500 cm^{-1}. This means that the prepared materials correspond to the products obtained by Ct treatments, but the time and energy requirement were significantly reduced as shown from the investigation of CEC.

3.3. XRD and expandability upon ethylene glycol saturation

The detection of expandability upon saturation of samples with ethylene glycol is important for practical

utilisation of layer charge reduced samples. The interlayer space of such samples can be in such way modified with EG as guest molecules. The XRD measurements of VO and CA samples shown in Table 2 revealed the d_{001} diffraction between 1.20 and 1.40 nm, which is typical for this type of materials with various portions and quality of interlayer cations present in the interlayer space (MacEwan and Wilson, 1980; Hrobáriková et al., 2001; Komadel et al., 2002; Komadel et al., 2005). Significant amount of admixtures such as illite, kaolinite and quartz were detected in the CA sample (Fig. 8a).

Ethylene glycol saturated species of sodium forms VO and CA showed typical expansion of the interlayer space detected with d_{001} diffraction at 1.74 nm (Calvet and Prost, 1971; Malla and Douglas, 1987). Similar behaviour was found for all Ct samples where the d_{001} diffractions changed from 1.20–1.40 to 1.74 nm. The Mw treatment caused almost full collapse of interlayer space as d_{001} diffractions at 0.96 nm were detected (Fig. 8b). The ethylene glycol saturation of the samples with lower lithium content, e.g. VO and CA 0–80% resulted in expansion of all layers and d_{001} diffraction at 1.74 nm was found (Fig. 8d,e). However, samples with higher lithium content (VO and CA 90–100%) showed two d_{001} diffractions at 1.74 nm corresponding to ethylene glycol expanded fraction of layers and those at 0.91 nm corresponding to fully collapsed layers (Fig. 8c).

Similar results were found for the ethylene glycol vapour sorption experiments (up to 20 days) performed at room temperature. The X-ray diffraction data indicate that there can be a limiting level of the charge reduction at which non-expansible layers for EG molecules are formed.

4. Conclusions

Only a low layer charge reduction of the samples treated in dispersions despite high Li^+ concentration can be achieved. This behaviour can be attributed to the very high water content and high hydration enthalpy of Li^+ cations. Nevertheless, the microwave (2.45 GHz) heated dispersions showed slightly higher layer charge reduction than conventionally heated samples where no significant changes of the layer charge were observed.

On the other hand, a series of solid powders with different interlayer lithium content treated with microwaves (30.0 GHz) revealed high layer charge reduction. The charge reduction was much higher than for conventionally heated powders as the efficiency was enhanced by increasing interlayer lithium content. We found out that the lithium migration into the structure of the montmorillonite supported by microwaves through ionic conduction is an extremely fast process probably finished within the first few minutes of the treatments. The infrared spectra of prepared materials showed that the products obtained with microwave treatments correspond well to the samples heated
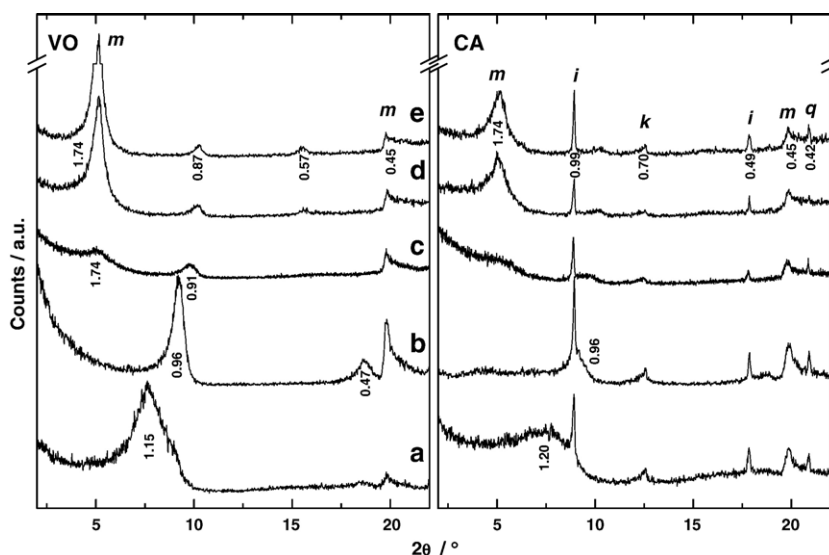

Fig. 8. X-ray diffraction patterns of VO and CA samples a) — Na-form, b) — upon 100% Li exchange (see Table 1) and Mw (230 °C/60 min) treatment, c) — sample as b) than in EG dispersion (60 °C/4 days), d) — upon 80% Li and Mw (230 °C/60 min) treatment, than in EG dispersion (60 °C/4 days), e) — upon 60% Li and Mw (230 °C/60 min) treatment, than in EG dispersion (60 °C/4 days), m — montmorillonite, i — illite, k — kaolinite, q — quartz (*d* values in nm).

conventionally for longer periods of time, however, the time and energy requirement can be significantly reduced applying microwaves. The montmorillonite layers were able to swell in ethyleneglycol upon charge reduction if the cation exchange capacity was not reduced more than 80%.

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References

Bogdal, D., Penczek, P., Pielichowski, J., Prociak, A., 2003. Microwave assisted synthesis, crosslinking, and processing of polymeric materials. Adv. Polym. Sci. 163, 193–263.

Bykov, Yu., Eremeev, A., Flyagin, V., Kaurov, V., Kuftin, A., Luchinin, A., Malygin, O., Plotnikov, I., Zapevalov, V., Feher, L., Kuntze, M., Link, G., Thumm, M., 1995. Gyrotron Installation for millimeter-wave processing of materials. Vakuumelektronik Displays form VDE-Verlag GmbH, Berlin Offenbach, vol. 132, pp. 103–108.

Bykov, Yu.V., Rybakov, K.I., Semenov, V.E., 2001. High-temperature microwave processing of materials. J. Phys., D, Appl. Phys. 34, R55–R75.

Calvet, R., Prost, R., 1971. Cation migration into empty octahedral sites and surface properties of clays. Clays Clay Miner. 19, 175–186.

Farmer, V.C., 1974. The Layer Silicates. In: Farmer, V.C. (Ed.), Monograph, vol. 4. Mineralogical Society, London, pp. 331–363.

Farmer, V.C., Russell, J.D., 1967. Infrared absorption spectrometry in clay studies. Clays Clay Miner. 15, 121–142.

Green-Kelly, R., 1955. Dehydratation of montmorillonite minerals. Mineral. Mag. 30, 604–615.

Güven, N., 1992a. Molecular aspects of clay/water interactions. In: Güven, N., Pollastro, R.M. (Eds.), Clay Water Interface and its Rheological Implications. CMS Workshop Lectures, vol. 4. The Clay Minerals Society, Boulder, CO, pp. 1–79.

Güven, N., 1992b. Rheological aspects of aqueous smectite suspensions. In: Güven, N., Pollastro, R.M. (Eds.), Clay Water Interface and its Rheological Implications. CMS Workshop Lectures, vol. 4. The Clay Minerals Society, Boulder, CO, pp. 81–125.

Hofmann, U., Klemen, R., 1950. Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung. Z. Anorg. Allg. Chem. 262, 95–99.

Hrobáriková, J., Madejová, J., Komadel, P., 2001. Effect of heating temperature on Li-fixation, layer charge and properties of fine fractions of bentonites. J. Mater. Chem. 11, 1452–1457.

Jaynes, W.F., Bigham, J.M., 1987. Charge reduction, octahedral charge, and lithium retention in heated, Li-saturated smectites. Clays Clay Miner. 35, 440–448.

Karakassides, M.A., Madejová, J., Arvaiová, B., Bourlinos, A., Petridis, D., Komadel, P., 1999. Location of Li (I), Cu (II) and Cd (II) in heated montmorillonite: evidence from specular reflectance infrared and electron spin resonance spectroscopies. J. Mater. Chem. 9, 1553–1558.

Komadel, P., Hrobáriková, J., Smrèok, L., Koppelhuber-Bitschnau, J., 2002. Hydration of reduced charge montmorillonite. Clay Miner. 37, 543–550.

Komadel, P., Madejová, J., Hrobáriková, J., Janek, M., Bujdák, J., 2003. Fixation of Li^+ cations in montmorillonite upon heating. Solid State Phenom. 90–91, 497–502.

Komadel, P., Madejová, J., Bujdák, J., 2005. Preparation and properties of reduced-charge smectites — a review. Clay Clays Miner. 53, 313–334.

Laird, D.A., 1994. Evaluation of structural formulae and alkylammonium method of determining layer charge. In: Mermut, A.R. (Ed.), Layer Charge Characteristics of 2 : 1 Silicate Clay Minerals. CMS Workshop Lectures, vol. 6. The Clay Minerals Society, Boulder, CO, pp. 79–104.

Lagaly, G., 1994. Layer charge determination by alkylammonium ions. In: Mermut, A.R. (Ed.), Layer Charge Characteristics of 2 : 1 Silicate Clay Minerals. CMS Workshop lectures, vol. 6. The Clay Minerals Society, Boulder, CO, pp. 1–46.

Lagaly, G., Weiss, A., 1971. Neue Methoden zur Charakterisierung und Identifizierung quellungsfähiger Dreischichttonminerale. Z. Pflanzenernähr. Bodenkd. 130, 9–24.

Lagaly, G., Weiss, A., 1975. The layer charge of smectitic layer silicates. Proc. Int. ClayConf. Mexico, pp. 157–172.

Lagaly, G., Schulz, O., Zimehl, R., 1997. Dispersionen und Emulsionen. Eine Einführung in die Kolloidik Feinverteilten Stoffe einschließlich der Tonminerale. Steinkopff, Darmstadt. 560 pp.

Low, P.F., 1992. Interparticle forces in clay suspensions: flocculation, viscous flow and swelling. In: Güven, N., Pollastro, R.M. (Eds.), CMS Workshop Lectures, vol. 4. The Clay Minerals Society, Boulder, CO, pp. 157–190.

MacEwan, D.M.C., Wilson, M.J., 1980. In: Brindley, G.W., Brown, G. (Eds.), Interlayer and Intercalation Complexes of Clay Minerals. Mineralogical Society, London, pp. 197–248.

Madejová, J., Komadel, P., 2001. Baseline studies of the clay minerals society source clays: infrared methods. Clays Clay Miner. 49, 410–432.

Madejová, J., Bujdák, J., Janek, M., Komadel, P., 1998. Comparative FT-IR study of structural modifications during acid treatment of dioctahedral smectites and hectorite. Spectrochim. Acta A 54, 1397–1406.

Madejová, J., Arvaiová, B., Komadel, P., 1999. FTIR spectroscopic characterisation of thermally treated Cu^{2+}, Cd^{2+} and L^{i+} montmorillonites. Spectrochim. Acta A 55, 2467–2476.

Madejová, J., Bujdák, J., Petit, S., Komadel, P., 2000a. Effects of chemical composition and temperature of heating on the infrared spectra of Li-saturated dioctahedral smectites. (I) Mid-infrared region. Clay Miner. 35, 739–751.

Madejová, J., Bujdák, J., Petit, S., Komadel, P., 2000b. Effects of chemical composition and temperature of heating on the infrared spectra of Li-saturated dioctahedral smectites. (II) Near-infrared region. Clay Miner. 35, 753–761.

Madejová, J., Kečkéš, J., Pálková, H., Komadel, P., 2002. Identification of components in smectite/kaolinite mixtures. Clay Miner. 49, 410–432.

Maes, A., Stul, M.S., Cremers, A., 1979. Layer charge — cation exchange capacity relationship in montmorillonite. Clays Clay Miner. 27, 387–392.

Malla, P.B., Douglas, L.A., 1987. Layer charge properties of smectites and vermiculites: tetrahedral vs. octahedral. Soil Sci. Soc. Am. J. 51, 1362–1366.

Mermut, A.R., 1994. Problems associated with layer charge characterisation of 2:1 phyllosilicates. In: Mermut, A.R. (Ed.), Layer Charge Characteristics of 2:1 Silicate Clay Minerals. CMS Workshop lectures, vol. 6. The Clay Minerals Society, Boulder, CO, pp. 105–127.

McBride, M.B., Mortland, M.M., 1974. Copper (II) interactions with montmorillonite: evidence from physical methods. Proc. - Soil Sci. Soc. Am. 38, 408–414.

Meier, L.P., Kahr, G., 1999. Determination of the cation exchange capacity (CEC) of clay minerals using the complexes of copper (II) ion with triethylenetetramine. Clays Clay Miner. 47, 386–388.

Prost, R., Calvet, R., 1969. Position du lithium dans une montmorillonite Li chauffée. C.R. hebd. Séanc. Acad. Sci. Paris, vol. 269, pp. 539–541.

Rao, K.J., Vaidhyanathan, B., Ganguli, M., Ramakrishan, P.A., 1999. Synthesis of inorganic solids using microwaves. Chem. Mater. 11, 882–895.

Schiffmann, R.F., 1997. Microwaves: Theory and Application in Materials Processing IV. The American Ceramic Society, pp. 41–60.

Sposito, G., 1992. In: Güven, N., Pollastro, R.M. (Eds.), The Diffuse-Ion Swarm Near Smectite Particles Suspended in 1:1 Electrolyte Solutions: Modified Gouy–Chapman Theory and Quasicrystal Formation. CMS Workshop lectures, vol. 4. The Clay Minerals Society, Boulder, CO, pp. 127–155.

Stul, M.S., van Leemput, L., 1982. Particle-size distribution, cation exchange capacity and charge density of deferrated montmorillonites. Clay Miner. 17, 209–215.

Tributh, H., Lagaly, G., 1986a. Aufbereitung und Identifizierung von Boden-und Lagerstättentonen: I. Aufbereitung der Proben im Labor. GIT-Fachzeitschrift für das Laboratorium 30, 524–529.

Tributh, H., Lagaly, G., 1986b. Aufbereitung und Identifizierung von Boden-und Lagerstättentonen: II. Korngrößenanalyse und Gewinnung von Tonsubfraktionen. GIT. Fachzeitschrift für das Laboratorium 30, 771–776.

van Olphen, H., 1992. In: Güven, N., Pollastro, R.M. (Eds.), Particle Associations in Clay Suspensions and their Rheological Implications. CMS Workshop lectures, vol. 4. The Clay Minerals Society, Boulder, CO, pp. 191–210.