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SORPTION PROPERTIES OF REDUCED-CHARGE MONTMORILLONITES

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Abstract: Four series of reduced-charge montmorillonites, with ranges in layer charge, were prepared from parent Ca-montmorillonites of various chemical compositions. Fine fractions of bentonites from Otay (USA), Ivančice (Czech Republic), Sarigus (Armenia) and Kriva Palanka (Macedonia) were used. The extent of ion exchange, 62–89 % of CEC covered by Li^+, was dependent on the mineral and on the Li^+ concentration in the liquid phase. Different levels of charge reduction were achieved via Li-fixation by heating the samples for 24 h at 110–300 °C. Li^+ ions were fixed in the layers of all four montmorillonites, but incomplete Li^+ for Ca^{2+} exchange diminished the extent of charge reduction. Heating the samples at temperatures up to 140 °C caused Li-fixation and reduction in relative cation-exchange capacity (CEC) values by 32 to 48 % but only a decrease by 17 to 24 % in the sorption of water and by 4 to 14 % of ethylene glycol monoethyl ether. The greatest changes in these properties were observed among the samples prepared at 130–200 °C, while higher temperatures had little effect. The most extensive reduction in CEC, by 81 % after preparation at 300 °C, was obtained for the Otay montmorillonite, the mineral with the highest octahedral and the lowest tetrahedral charge and the greatest level of Li^+ for Ca^{2+} exchange. Higher tetrahedral charge and a lower level of Li^+ for Ca^{2+} exchange negatively affected the decrease in the cation exchange capacities, the specific surface areas and the water uptake capabilities of the prepared reduced-charge montmorillonites.

Key words: water sorption, EGME specific surface area, cation-exchange capacity, Li-fixation, montmorillonite.

Introduction

The abundance of montmorillonitic bentonite deposits has led to extensive studies of its properties and industrial applications. Montmorillonites are common in many soils, sediments and hydrothermal alteration products. The minerals of this group have an expandable lattice, which has a variable c-axis dimension depending on the number of layers of water molecules hydrating the inorganic exchange cation between silicate layers. Montmorillonites have interesting plastic, colloidal, and other properties, which are frequently quite different from one sample to another (Grim & Kulbicki 1961).

The layer charge and its distribution are among the most important characteristics of montmorillonites and indicate the capacity of a mineral to retain and to release cations and to adsorb water and various polar organic molecules (Mermut 1994). The negative charge of the layers arises mainly from the replacement of Al(III) by Mg(II) in the octahedral sheet. Charge neutrality is achieved through the presence of hydrated cations in the interlayer space. These cations can be relatively easily replaced in the laboratory with other cations, such as Li^+, in order to obtain a homoionic form of the mineral. Upon the thermal treatment of Li-saturated montmorillonite, Li^+ cations move towards the negative charge centres in the layers and become irreversibly fixed. Such cation fixation lowers the cation exchange capacity of the clay (Hofmann & Klemen 1950; Bujdák et al. 1991). Preparation of reduced-charge montmorillonites provides a possibility to investigate the properties of these materials that relate to the layer charge (Brindley & Ertem 1971; Clementz et al. 1974; Bujdák et al. 1992, 2000).

The amount of water present in smectite powders is very variable. It depends strongly on several factors, such as relative humidity, kind and amount of exchangeable cations, size and shape of the particles, and structural or crystal-chemical constraints. For example, in the structurally related muscovites, two-thirds of the octahedral positions, and one-fourth of the tetrahedral positions, are occupied by Al(III). The resultant 2*e* charge per unit cell is compensated by two K^+ ions, which do not hydrate and the physical properties of mica do not depend on the water vapour pressure in the ambient atmosphere. On the other hand, the Li-montmorillonites, where the layer charge is generally less than 1*e* per unit cell, are particularly susceptible to swelling by water and their physical properties are accordingly affected (Bidadi et al. 1988).

With certain cations at interlayer exchange sites, smectites readily adsorb water and polar molecules, resulting in a marked expansion of their interlayers (Hendricks et al. 1940). Because of the layer structure and charge of montmorillonite, the sorption of vapours on the mineral can occur by different mechanisms, depending on the molecular properties of the vapour. For polar molecules on montmorillonite the overall vapour sorption may reflect both surface adsorption and other effects (Monney et al. 1952). Chiou & Rutherford (1997) studied the effects of layer charge and of Ca^{2+}, Na^+, K^+, Cs^+ and tetramethylammonium exchangeable cations on the sorption of water and EGME (ethylene glycol monoethyl ether) vapours on two montmorillonites. With the same exchangeable cation,

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the high-charge SAz-1 mineral showed a higher water capacity than the low-charge SWy-1. The hydration of the tetrahedral sheets of the minerals was found to be relatively weak. The water uptake was enhanced by the increased charge in the SAz-1 clay for all exchanged cations and at all p/p^0 (RH) due to generally more gain in the energy of cation hydration than in the energy of layer attraction when the clay is exposed to water vapour.

The purpose of this study was to determine how the sorption characteristics of water, at various relative humidities, and of EGME, were affected by layer charge in four series of reduced-charge montmorillonites.

Materials and methods

Four series of reduced-charge montmorillonites were used. The parent < 2 μm fractions were separated from the bentonites from Kriva Palanka (KP, Republic of Macedonia), Sarigus (Sa, Republic of Armenia), Ivančice (Iv, Czech Republic) and Otay (Ot, USA). Most of the exchangeable cations were replaced with Li^+ using 5–7 times repeated washings with 1 M LiCl during ion exchange in dialysis tubing and LiCl solutions. Iv was ion-exchanged differently, with 0.1–1 M LiCl solutions. This technique allowed elimination of spinning of big volumes of dispersions at high rotations; however, full ion exchange was not achieved. Their layer charge, given as multiples of charge of one electron, $e = 1.6018.10^{-19}$ C, per structural unit $O_{20}(OH)_4$, distribution and structural formulae are listed in Table 1. One specimen of each parent material remained unheated, while the others were heated for 24 h at 110, 120, 130, 140, 150, 160, 180, 200, 250 and 300 °C to evoke different levels of Li^+ ion fixation. The details of separation and samples preparation are described (Hrobáriková et al. 2001).

The cation-exchange capacities (CECs) were determined by repeated saturation of the samples with 1 M solution of ammonium acetate at pH = 7. All extracts obtained from the same sample were combined and analysed for Ca and Li by atomic absorption and emission spectroscopy, respectively. Infrared (IR) spectra in the 4000–400 cm^{-1} spectral range with a resolution of 4 cm^{-1} were obtained on KBr pressed disks (0.4 mg sample and 200 mg KBr), using a Nicolet Magna 750 FTIR spectrometer equipped with a DTGS detector.

The relative total specific surface area was determined by ethylene glycol monoethyl ether (EGME) adsorption, following the method of Novák & Čičel (1970). The samples were dried under vacuum in a desiccator over P_2O_5 for 48 h and weighted afterwards. A few drops of EGME were added in several minor portions to each sample (~250 mg) until a slight excess of EGME was achieved. The point when the clay became unable to accept more EGME was clearly visible. Afterwards the samples with EGME were stored in a vacuum desiccator over ignited $CaCl_2$. They were weighed every 90 minutes until constant mass was achieved and the total specific surface area was then calculated according to Novák & Čičel (1970).

Sorption and desorption isotherms of water vapour were determined under static conditions. Briefly, ~250 mg of the samples were dried at 60 °C overnight; then kept at 25 °C for 48 hours in a desiccator above P_2O_5, at which time the amount of adsorbed water at 0 % RH was determined gravimetrically. The samples were then stored under the next higher RH for the following 48 hours. On the basis of the previous skills of Bujdák et al. (1992) with similar amounts of samples and experiments, this period of time was considered sufficient to obtain the equilibrium. This procedure was repeated in dessicators above the saturated solutions of $CaCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, $BaCl_2$ or above H_2O, for RHs of 20, 43, 52, 66, 88 and 100 %, respectively. The results were collected and the sorption curves plotted. Then, the samples were stored under gradually decreasing RHs to obtain the corresponding desorption curves. All the data were measured in triplicates; the relative error was generally < 3.2 % of the measured value.

Results and discussion

Montmorillonite with Al-rich octahedral sheets was found to be the dominant mineral in all four separated samples. No admixtures were detected in KP, but minor amounts of pyrophyllite were found in Ot, amorphous SiO_2 in Iv and opal-CT in Sa (Hrobáriková et al. 2001). Opal-CT, the commonest form of hydrous silica, is composed of disordered stacking of cristobalite-like and tridymite-like sequences (Jones & Segnit 1971).

Cation-exchange capacity (CEC) is a directly measurable property dependent on the layer charge. Higher temperature during preparation caused greater Li^+ fixation, greater layer charge reduction and thus, a more extensive decrease in relative CEC in all four series (Fig. 1). Preparation below 140 °C decreased significantly the CEC in all four series. The same order, $CEC_{Ot} < CEC_{KP} < CEC_{Sa} < CEC_{Iv}$, was retained in relative CEC reduction for the samples prepared ≥ 140 °C. The CEC values decreased systematically with increasing temperature of preparation up to 250 °C, but further decreases were negligible for the materials prepared at 300 °C (Fig. 1). The most extensive CEC reduction occurred in the Ot series, with the parent montmorillonite of the highest octahedral and the

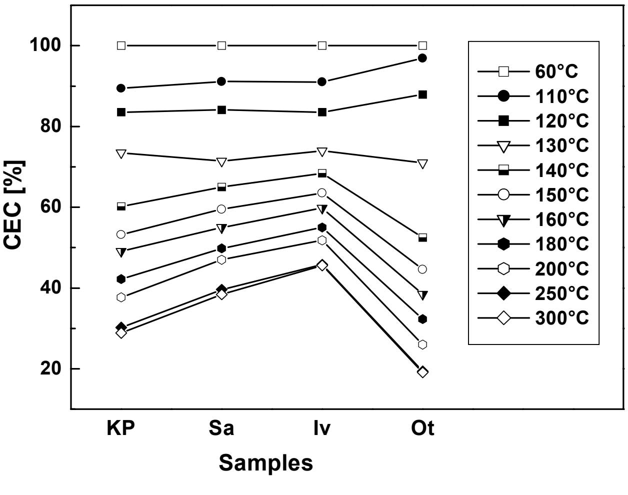

Fig. 1. Relative cation exchange capacities for series of reduced-charge montmorillonites prepared by heating for 24 hours at indicated temperatures.

lowest tetrahedral charge (Table 1). After heating this sample at 300 °C, the CEC decreased to 19 % of the value obtained for the unheated Ot. The second greatest decrease was observed in the KP series, yielding a CEC of 27 % of its original CEC after heating at 300 °C. The KP montmorillonite has a lower octahedral charge (–0.72 $e/\mathrm{O_{20}(OH)_4}$) than Ot as well as a slightly higher tetrahedral charge (–0.15 $e/\mathrm{O_{20}(OH)_4}$). Relative CEC values decreased considerably less (to 38 % of the original) in the Sa series, and were presumably affected by the negative contribution of the relatively high tetrahedral charge, partially compensated by possibly unexchangeable $\mathrm{K^+}$ cations. The least extensive decrease in relative CECs occurred in the Iv series (Fig. 1) with the lowest $\mathrm{Li^+}$ for $\mathrm{Ca^{2+}}$ substitution (Hrobáriková et al. 2001). Relative CEC was reduced only to 45 % of CEC of unheated sample presumably due to lower excess of $\mathrm{Li^+}$ in the used solutions.

The relative EGME specific surface areas (SSAs) obtained for the four series of reduced-charge montmorillonites are shown in Fig. 2. The values for the parent, unheated montmorillonites were 745, 796, 706 and 799 $\mathrm{m^2.g^{-1}}$ for samples Ot, KP, Sa and Iv, respectively. The presence of opal-CT and the high tetrahedral charge of –0.43 $e/\mathrm{O_{20}(OH)_4}$ together with the relatively high $\mathrm{K^+}$ content saturating 18 % of the negative charge, suggest possible presence of illitic, non-swelling interlayers (Hrobáriková et al. 2001) in Sa and explain its lowest SSA. The SSAs in all series decreased only slightly with increasing temperature of preparation up to 130 °C. This decrease was by 10 % in KP, 8 % in Sa, 3 % in Ot and 1 % in Iv (Fig. 2). Presumably the interlayer space was fully accessible to EGME molecules for the montmorillonitic minerals in each sample.

Higher temperatures of preparation resulted in further decreases in SSA and presumably led to the formation of low charged pyrophyllite-like layers. The enhanced $\mathrm{Li^+}$ fixation at these temperatures, accompanied by reduction of the negative layer charge, is known to decrease the swelling ability of reduced-charge montmorillonite (Komadel et al. 1996). The bands near 1120 and 420 $\mathrm{cm^{-1}}$, assigned to absorption of pyrophyllite-like layers (Farmer 1974; Madejová et al. 1999) can be distinguished in the IR spectra of Iv, KP, Ot and Sa samples prepared at ≥150 °C (Fig. 3). The original fine fraction of Ot bentonite contained an admixture of pyrophyllite, thus the IR spectra of all Ot samples in the series displayed absorption bands at these wavenumbers. Increasing intensity of these bands confirmed increasing content of pyrophyllite-like layers in the Ot samples prepared at ≥150 °C (Hrobáriková et al. 2001). EGME molecules could not penetrate into the non-swelling interlayer spaces. This was reflected in decreased EGME SSAs obtained for the samples prepared at ≥150 °C (Fig. 2).

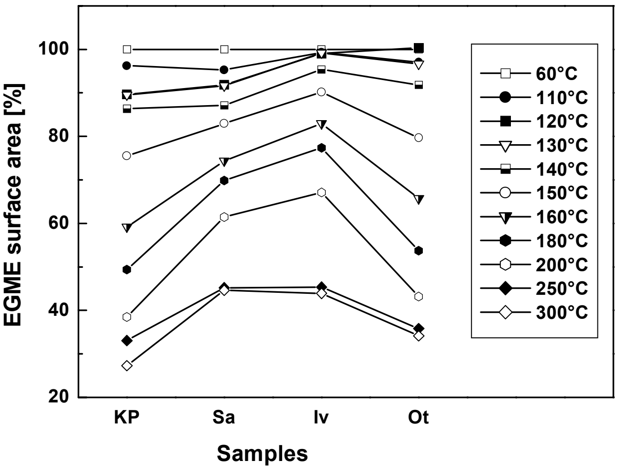

Fig. 2. Relative EGME specific surface areas for series of reduced-charge montmorillonites prepared by heating for 24 hours at indicated temperatures.

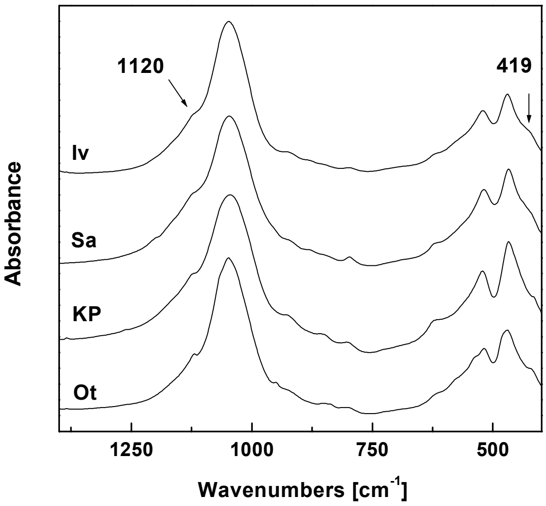

Fig. 3. Infrared spectra of samples Iv, Sa, KP and Ot prepared by heating for 24 hours at 150 °C.

The effect of heating at 150–200 °C on the samples was clearly different (Fig. 2). The relative EGME SSA decrease

Table 1: Tetrahedral, octahedral and total charges and structural formulae of parent Li-montmorillonites.

montmorillonite	charge ($e/\mathrm{O_{20}(OH)_4}$) tetrahedral	octahedral	total	structural formula
Kriva Palanka	−0.15	−0.72	−0.87	$\mathrm{[Si_{7.85}Al_{0.15}][Al_{2.96}Fe_{0.32}Mg_{0.72}]Ca_{0.07}K_{0.03}Li_{0.68}O_{20}(OH)_4}$
Sarigus	−0.43	−0.73	−1.16	$\mathrm{[Si_{7.57}Al_{0.43}][Al_{2.36}Fe_{0.91}Mg_{0.73}]Ca_{0.11}K_{0.21}Li_{0.71}O_{20}(OH)_4}$
Ivančice	−0.21	−0.74	−0.95	$\mathrm{[Si_{7.79}Al_{0.21}][Al_{2.84}Fe_{0.42}Mg_{0.74}]Ca_{0.17}K_{0.02}Li_{0.58}O_{20}(OH)_4}$
Otay	−0.05	−0.93	−0.98	$\mathrm{[Si_{7.95}Al_{0.05}][Al_{2.77}Fe_{0.15}Mg_{1.17}]Ca_{0.05}K_{0.05}Li_{0.81}O_{20}(OH)_4}$

was more pronounced for the KP and Ot series than for the Sa or Iv series, as was observed for the relative CEC values (Fig. 1). The relative SSAs of the samples prepared at 200 °C decreased to 38, 43, 61 and 68 % of the values obtained for the parent KP, Ot, Sa and Iv samples, respectively. The exact reason for this behaviour remains unclear, however, possible differences in the homogeneity of the layer charge distribution in the parent samples could be one of the explanations. As was observed for CEC, differences between the samples in the same series prepared at 250 and 300 °C were minor, proving that heating of Li-montmorillonites beyond 250 °C results in little further change to their properties (Madejová et al. 1999). For the samples prepared at 300 °C the values obtained were 27, 34, 45 and 44 % for KP, Ot, Sa and Iv (Fig. 2). The final extent of reduction in relative SSAs reflected the negative influence of the highest tetrahedral charge in Sa and the lowest Li^+ for Ca^{2+} substitution in Iv.

Comparison of relative CECs and relative EGME SSAs for four series of reduced-charge montmorillonites is shown in Fig. 4. It demonstrates clearly that CEC was affected to a greater extent than SSAs at low and intermediate preparation temperatures; indicating that decreases in layer charge had a greater effect on the exchange capacity than the total surface area available for the sorption of EGME molecules. This effect is most significant for the Ot series, i.e. for the mineral of the highest octahedral charge, in which the relative charge decrease was the greatest before the substantial decrease in relative EGME surface area could be observed (Fig. 4).

Representative water sorption-desorption curves (SDCs) of the Sa series are illustrated in Fig. 5. The shapes of the SDCs for the other three reduced-charge montmorillonite series (not shown) were similar. The inclination of isotherms was influenced by the layer charge reduction. The irregular shapes of both the adsorption and desorption branches of the isotherms suggested complex water adsorption mechanisms. More water remained on all the samples during desorption, i.e. when the drying parts of the sorption/desorption curves were measured. Such hysteresis was reported to occur due to more extensive water adsorption mainly on the external surfaces of the montmorillonite particles throughout the drying rather than wetting experiments (Ormerod & Newman 1983; Bujdák et al. 1992). The amount of water sorption was dependent on RH, as is often the case for swelling clay minerals (Cases et al. 1992). As was expected from the high hydration energy of the Li^+ cation, hydration of the interlamellar space of reduced-charge samples started at very low relative pressures. The samples prepared at the lowest temperatures of 110 and 120 °C had a higher affinity for water (Fig. 5, data for 120 °C are not shown, they overlap with those for 110 °C) than the untreated samples. Higher water uptake by these samples, in comparison to the parent Li-montmorillonites, could be caused by lower hydration of their interlayer cations brought about via more extensive dehydration upon preparation at increased temperatures of 110 or 120 vs. 60 °C.

The samples prepared at 130–300 °C were less hydrated at all investigated RHs. Water content in these samples gradually decreased with decreasing layer charge and with decreasing surface area. The effect of charge reduction on hydration was better observed at high relative humidity: at a high RH, more water was adsorbed, but differences between samples were greater; as the RH decreased, both the total amount of water adsorbed and differences between the materials decreased. At high RH, above ~80 %, the water vapour hydrated interlayer cations and condensed more effectively in the micropores and interlayer voids by wicking, resulting in saturation of water sorption capacities of the samples (Güven 1992). The water molecules filled the interlayers as well as the spaces between the mineral particles.

Relative water sorption data obtained at 100 % RH for four series of reduced-charge montmorillonites are shown in Fig. 6. All samples prepared at 110 and 120 °C adsorbed a similar amount of water to their parent counterparts. Preparation at higher temperatures, resulting in Li^+ fixation and layer charge reduction as well as more extensive dehydration of the remaining Li^+ cations in the interlayers, led to materials of gradually decreased water uptake ability. The data for the samples prepared at 250 and 300 °C overlapped, again confirming the sim-

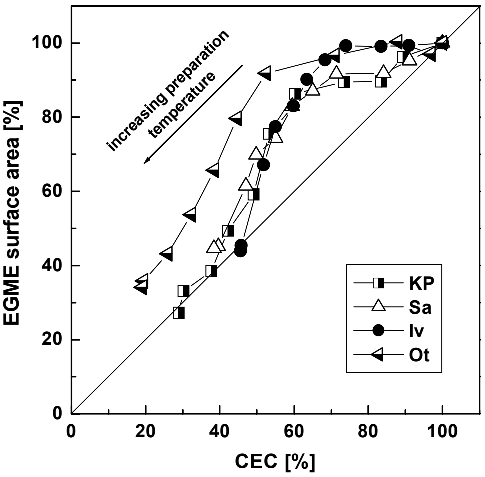

Fig. 4. Comparison of relative cation exchange capacities and relative EGME specific surface areas for four series of reduced-charge montmorillonites.

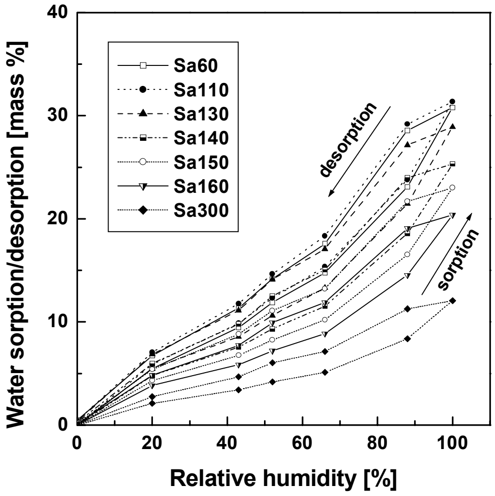

Fig. 5. Effect of preparation temperature on water sorption and desorption of the Sa series at various relative humidities.

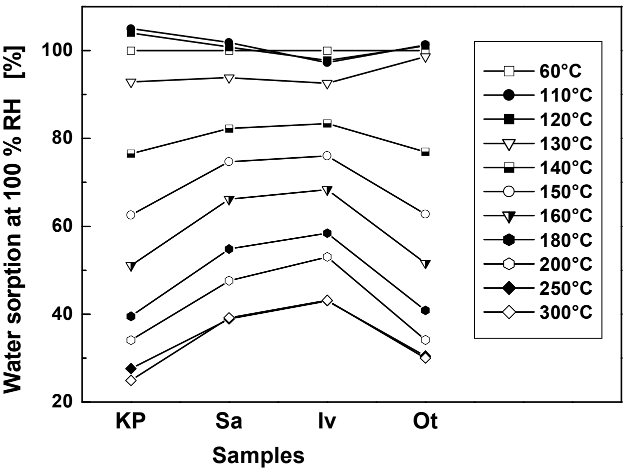

Fig. 6. Relative water sorption data at 100 % relative humidity for series of reduced-charge montmorillonites prepared by heating for 24 hours at indicated temperatures.

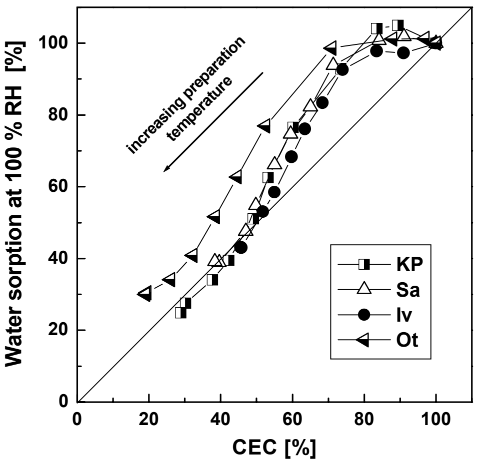

Fig. 7. Comparison of relative cation exchange capacities and relative water sorption at 100 % RH for four series of reduced-charge montmorillonites.

ilarity in hydration properties of these pairs of samples. The changes in water sorption within the series (Fig. 6) and among the series were similar to those observed for the relative EGME specific surface areas (Fig. 2), showing the negative effect of the increasing number of pyrophyllite-like layers on sorption properties of all four series investigated. This information along with IR and RTG results shows the negative effect of the increasing number of non-expandable layers on the water uptake. Comparison of the relative cation exchange capacities and the relative levels of water sorption at 100 % RH is made in Fig. 7 for all four series of reduced-charge montmorillonites. As was observed for EGME uptake, the relative water uptake decreased at a lower rate that the decrease of relative CECs for sample preparation below 200 °C. Heating of the samples for 24 hours at temperatures <200 °C evoked more pronounced decreases in the relative CECs than in the relative amount of water sorbed. Similarly to EGME sorption (Fig. 4), the effect is most pronounced for the Ot series, where the most extensive reduction of the relative CEC was observed before the relative water sorption effectively decreased from its initial value (Fig. 7).

Conclusions

Four series of reduced-charge montmorillonites with gradually decreasing cation exchange capacity were prepared from different parent Li-montmorillonites by heating at 110–300 °C. Preparation at 110–130 °C produced materials with significantly decreased CEC, but with rather minor modification in both the total specific surface area as well as water and EGME sorption capabilities. All investigated properties of the products prepared at higher temperatures were more significantly modified, presumably due to the development of collapsed and non-swelling pyrophyllite-like interlayers. Negligible differences in properties of materials prepared at 250 and at 300 °C proves that heating at 250 °C for 24 hours is sufficient to achieve a maximal extent of Li^+ fixation and layer charge reduction.

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