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DEHYDRATION AND REHYDRATION OF MONTMORILLONITE FROM IVANČICE (CZECH REPUBLIC)

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Abstract: The processes of dehydration and rehydration appear quite different for natural Ca-montmorillonite (Ca-MMT, for short) and its sodium saturated form (Na-MMT). During dehydration the d_{001} values of Ca-MMT sample drop continuously from 15.36 Å to 10.20 Å with increasing temperature of dehydration (from 25 to 300 °C), but the relation breaks down at 200 °C, above which the position remains equal to 10.2 Å. The mass loss $\Delta m_{200^{\circ}}$ corresponds to 9.5 water molecules per one interlayer cation. In contrast to Ca-MMT, the dehydration process of Na-MMT can be divided into three stages: (1) At temperatures ≤ 70 °C there is a small shift of d_{001} from 12.90 Å to 12.48 Å; (2) At temperatures between 80 and 110 °C, there is a significant shift of the d_{001} value to 10.95 Å; (3) Collapsed Na-MMT structure (10.2 Å) appears at above 150 °C. The mass loss $\Delta m_{150^{\circ}}$ corresponds to 4.9 water molecules per one interlayer cation. In the rehydration process of both Ca-MMT and Na-MMT two stages can be recognized. The first corresponds to temperature ranges from 25 to 200 °C (Ca-MMT) and from 25 to 150 °C (Na-MMT); there the rehydration ability drops to 61 % for Ca-MMT and 88 % for Na-MMT, however no significant collapse of the interlayer of rehydrated samples is observed. The second stage corresponds to temperatures between 200 °C (150 °C for Na-MMT) and 500 °C, where the rehydration ability drops significantly and so do the d_{001} values.

Key words: Dehydration, rehydration, montmorillonite, XRD analysis.

Introduction

Early studies of smectites (e.g. Bradley et al. 1937; Méring 1946), showed a continuous variation of layer thickness with water content. Bradley et al. (1937) also showed that water molecules could be sorbed in the interlayer of montmorillonite as one, two, three, and four water molecular sheets. Mooney et al. (1952) showed how the water content is related to the saturating cations. Méring (1946) and Bradley & Grim (1948) reported the range of the layer thickness of Ca-montmorillonite between 14 and 15 Å at different relative humidities. Glaeser & Méring (1968) and Suquet et al. (1975) showed the effect of interlayer cations and relative humidities on the basal spacings of smectites (e.g. the spacing ranged between 12.5 and 15.5 Å for Na-saturated montmorillonite).

According to MacEwan & Wilson (1980), the hydration of smectites is controlled by three interrelated factors: (i) the magnitude of the negative charge on the clay mineral interlamellar surface, (ii) the exchangeable cations which occur between the interlamellar surfaces and balance the overall negative charge on the layer surface and (iii) the interaction of the water molecules with the cations and with the clay mineral interlamellar surface. The type of exchangeable cations and their tendency to hydrate determines the arrangement of the water molecules and ultimately the thickness of the water layer.

According to Odom (1984), most molecular (adsorbed) water is interlayer water, and liberated at low temperatures 100–200 °C. The structure is able to rehydrate and accepts back some of the adsorbed water, the amount depending on the relative humidity of ambient air and the properties of the clay. Smectites containing primarily exchangeable Ca and Mg usually rehydrate more rapidly than smectite clays containing exchangeable Na. When smectite clays are heated only slightly above 200 °C, they tend to rehydrate completely in the presence of liquid water, but certain properties such as swelling and/or dispersion do not return to their original values. In the presence of liquid water, smectite clays will generally rehydrate to some degree even after heating to temperatures 500–700 °C. In such cases, the degree of rehydration depends mainly on the degree of structural damage brought about by loss of OH.

The amount of adsorbed water lost depends on the quality of the interlayer cation(s) and to a lesser degree on the structure of the smectite (Farmer & Russell 1971). When Na is the predominant interlayer cation, adsorbed water is usually lost during a single stage, but when Ca and Mg dominate, the adsorbed water is sometimes lost in two temperature stages.

Using X-ray diffraction, Grim & Kulbicki (1961) studied montmorillonite clay minerals during heating. Two different types of montmorillonites were found, Cheto and Wyoming, which differ primarily in the population of the octahedral sheet. In the Cheto-type, relatively more octahedral aluminum is substituted by magnesium, thus increasing the net layer charge. The Cheto-type shows a greater loss of water in the 100–500 °C temperature interval than the Wyoming-type. The accompanying changes of intensities of the 001 reflections are more pronounced for the Wyoming-type than for the Cheto-type.

Koster van Groos & Guggenheim (1990) suggested that calcium has a greater ability to offset partially the charge on the residual oxygen than a univalent cation. Using structural models of thermal decomposition, Koster van Groos & Guggenheim (1990) and Guggenheim (1990) suggested that calcium can asymmetrically position itself in the interlayer cation site upon the formation of a residual oxygen. The results of thermal gravimetric analyses enabled them to estimate the number of water molecules per interlayer cation for different montmorillonites (Table 1). As we can see from Table 1, montmorillonites containing primarily exchangeable Ca and Mg exhibit significantly more water molecules than those containing exchangeable Na and K.

Skipper et al. (1991) predicted possible arrangements of water molecules in Mg and Na saturated montmorillonites using the Monte Carlo computer simulation procedure. The simulation cells contained 16 and 8 water molecules per one interlayer Mg^{2+} and Na^{+}, respectively, supposing 79 % relative humidity. The calculated equilibrium layer spacing was 14.7 Å with interlayer Mg^{2+} and 14.2 Å with interlayer Na^{+}. They concluded that the interlayer cations in Mg-smectite lie midway between the layers, and are octahedrally coordinated to form $Mg^{2+}(H_2O)_6$ complexes. Additional water is either hydrogen-bonded to a clay surface or occupies a tetrahedral ring site within a clay layer. In contrast to Mg-smectite, the interlayer cations in hydrated Na-smectite have a tendency to bind to the clay surface. Coordination of these cations is completed by interlayer water. The remaining water is highly hydrogen bonded to other water molecules and to the clay surfaces. Some water molecules also occupy tetrahedral ring sites.

Chorom and Rengasamy (1996) investigated the effects of heating to 400 °C on charge reduction, swelling and dispersion of a smectite saturated with different cations. Thermal treatment apparently affects the bonding and authors concluded that the smaller cations (Li, Mg and Al) migrate to octahedral vacant sites and form covalent bonds and reduce the negative charge. Larger cations Na, K and Ca apparently do not migrate on thermal treatment. Upon heating to 400 °C the interlayer cations are still exchangeable at a reduced level in limited hydration (see also Calvet & Prost 1971).

The aim of this paper is, (1) to determine and compare the rehydration ability of the "low-temperature phases" arising after dehydration of Ca-, and Na-montmorillonites and (2) to determine the changes in the shape and position of 001 XRD powder profiles after dehydration and rehydration.

Materials and methods

Samples

Natural montmorillonite (Ca-MMT, the dominant cation in the interlayer is Ca) from Ivančice (Czech Republic) was used for the experiments. The original sample contains less than 5 % quartz. This sample was ground in an agate mortar and the fraction with grain size less than 5µm was prepared by sedimentation. The content of quartz in the fraction was less than 3 %. A saturated sodium form of montmorillonite (Na-MMT) was prepared from this fraction by multiple overnight saturation (shaking) with 1 Mol/l NaCl solution. The sample was then washed with deionized water and air dried.

The chemical analyses for major elements in Ca-MMT and Na-MMT were performed on the X-ray fluorescence spectrometer (XRF). Calcium, sodium, magnesium and potassium in montmorillonites were determined by the ICP method. The following crystallochemical formulas were calculated for both montmorillonite samples from the bulk chemical analyses (Rieder 1977):

Ca-montmorillonite

$[(Al_{1.25}\,Mg_{0.50}\,Fe^{3+}{}_{0.23}\,Ti_{0.02})\ (Si_{3.99}\,Al_{0.01})\ O_{10}\,(OH)_2]\ (Na_{0.09}\,K_{0.03}\,Mg_{0.07}\,Ca_{0.12})$

Na-montmorillonite

$[(Al_{1.31}\,Mg_{0.39}\,Fe^{3+}{}_{0.25}\,Ti_{0.02})\ (Si_{3.99}\,Al_{0.01})\ O_{10}\,(OH)_2]\ (Na_{0.40}\,K_{0.02}\,Ca_{0.01})$

The Brunauer-Emmett-Teller (BET) surface area (external surface area only) was determined by N_2 gas adsorption for Ca-MMT and Na-MMT as 132 m^2/g and 110 m^2/g , respectively.

Dehydration in high-temperature XRD camera ("D")

Powder samples were heated in a standard holder of the X-ray diffraction high-temperature camera. X-ray patterns were taken 15 minutes after reaching the following temperatures: 25°, 50°, 60°, 70°, 80°, 90°, 100°, 110°, 130°, 150°, 200°, 250°, 300 °C using diffractometer SIEMENS D500 (CoKα radiation). Temperatures 100° and 300 °C were omitted for Na-MMT. The X-ray camera was not evacuated during exposure because vacuum dehydrates the samples and would cause changes similar to those induced by heating.

Rehydration in laboratory conditions ("R")

Powder samples were heated in a muffle furnace to 50°, 60°, 70°, 80°, 90°, 100°, 110°, 130°, 150°, 200°, 250°, 300°, 350°, 400°, 450°, 500 °C, and kept for 60 minutes at each temperature. After dehydration at individual temperatures, the mass of the sample (m_D) was recorded gravimetrically under laboratory conditions (RH = 48 %). After rehydration when a stable equilibrium between the sample and atmosphere was established, the mass of the sample (m_R) were recordered again. Samples were analyzed after rehydration by the X-ray powder diffractometer INEL with a curved position-sensitive detector CPS120 (CuKα radiation, Ge-monochromator).

Results and discussion

Mass change during dehydration and rehydration

The dehydration curves (Fig. 1) show that the mass loss of samples heated to 100 °C is higher for Ca-MMT (10.67 wt. %) than that for Na-MMT (9.02 wt. %) and the difference increases with increasing temperature. The mass loss Δm at 500 °C is 17.25 wt. % and 12.96 wt. % for Ca-MMT and Na-MMT, respectively. From Fig. 1, we can see two stages of the dehydration process in Ca-MMT, the mass loss increases more rapidly above 300 °C than it does below. On the contrary, the mass loss for Na-MMT increases monotonously throughout the whole temperature range.

The mass loss can be converted into the number of water molecules per one interlayer cation. If one assumes that the composition of the residual sample of Ca-MMT which had lost 12.32 wt. % of water during heating to 200 °C is described by its crystallochemical formula, we can calculate formula weight amounts equal to 375.53 g. This weight represents 87.68 % of the weight of the hydrated sample, then 2.93 molecules of water to the formula weight of the dehydrated sample can be calculated [(12.32 × 375.53 : 87.68) :18]. Relating this water to the number of interlayer cations per formula unit (0.31), one obtains 9.46 water molecules per one interlayer cation. The same approach was used for Na-MMT when water contents of 2.16 molecules per formula unit and 5.01 molecules per one interlayer cation were found (see Table 2).

Table 1: Dehydration mass loss (Δm) and estimated number of water molecules per one interlayer cation based on thermal gravimetric analyses (according to Koster van Groos & Guggenheim 1990).

Cations	Total Δm (wt. %)	Total H_2O molecules
Na	9	4–5
K	6	3–4
Ca	16	13
Mg	16	13–14

Table 2: Dehydration mass loss (Δm) and corresponding number of water molecules for both montmorillonite samples heated to 100–200 °C.

Temperature	Δm (wt. %)	number of H_2O molecules	
		A	B
Ca-MMT			
100 °C	10.67	8.04	9.27–9.89
150 °C	11.25	8.53	
200 °C	12.32	9.46	
Na-MMT			
100 °C	9.02	4.82	4.16–5.14
150 °C	9.13	4.88	
200 °C	9.35	5.01	

A = per one interlayer cation, calculated from Δm using the crystallochemical formula.

B = predicted for corresponding interlayer composition of the sample using data given in Table 1.

The rehydration ability (%) of heated montmorillonite samples was calculated according to the formula:

$$(1 - \Delta m_R/\Delta m_D).100,$$

where Δm_D is mass loss after dehydration of the sample heated to the corresponding temperature and Δm_R is the mass loss after its rehydration under laboratory conditions. The rehydration capabilities of both montmorillonite samples heated to the temperatures chosen are compared in Fig. 2. It is seen that the ability to rehydrate is significantly lower for Ca-MMT samples heated above 150 °C than that for Na-MMT samples. The most significant differences appear for 250°, 300° and 350 °C. These differences can be explained by the following reasons:

1. Different abilities to form shells of water molecules for Na and Ca, and consequently different arrangements of cations and water molecules in the structure of interlayers.

2. Different negative layer charges for Na-MMT and Ca-MMT. Kawano & Tomita (1991) concluded that the rehydration ability of dioctahedral smectite increases when octahedral negative charge decreases. We should like to note, that our Ca-MMT is electrically neutral, however, there is a change in the composition of the octahedral layer after Na-exchange and the negative charge of the layer decreases.

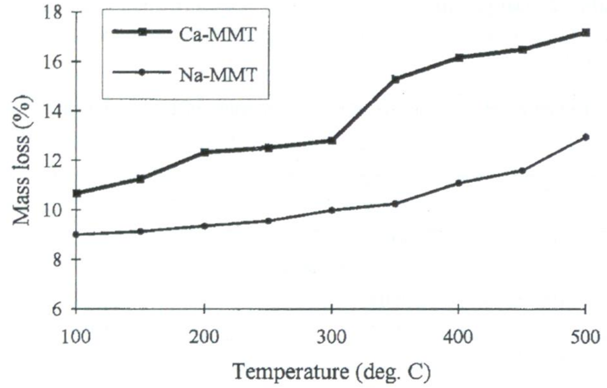

Fig. 1. Mass loss (Δm) for Ca-, and Na-montmorillonite samples heated at 100–500 °C.

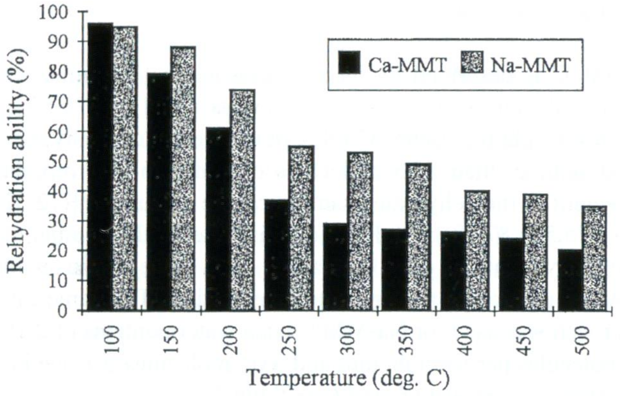

Fig. 2. The rehydration ability of Ca-, and Na-montmorillonite samples heated to 100–500 °C.

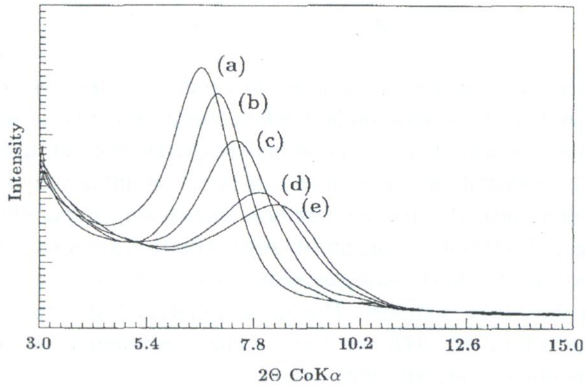

Fig. 3. XRD profiles of 001 diffraction of Ca-MMT taken on a high-temperature camera at (a) 25 °C, (b) 50 °C, (c) 70 °C, (d) 90 °C, and (e) 110 °C.

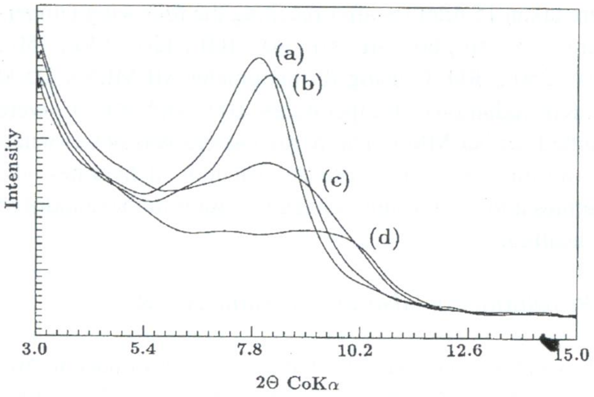

Fig. 4. XRD profiles of 001 diffraction of Na-MMT taken on a high-temperature camera at (a) 25 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C.

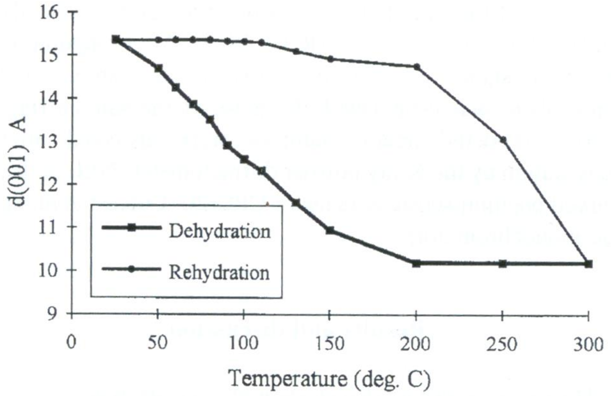

Fig. 5. Changes in d_{001} of Ca-montmorillonite during dehydration and after rehydration in laboratory conditions.

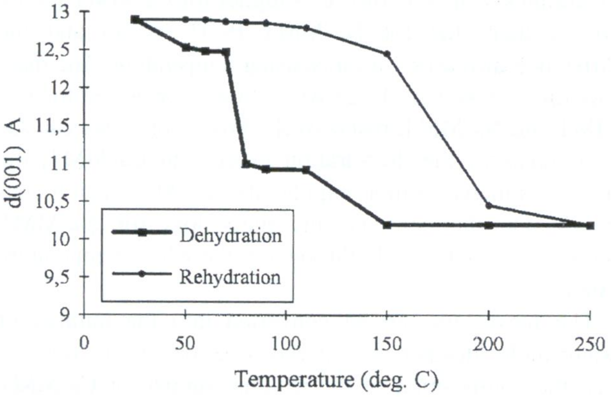

Fig. 6. Changes in d_{001} of Na-montmorillonite during dehydration and after rehydration in laboratory conditions.

X-ray diffraction patterns

Profiles of the first basal diffraction (001) of Ca-MMT and Na-MMT recorded on an XRD temperature camera exhibit significant changes induced by dehydration (Figs. 3 and 4). There is a decrease of the profile intensity and a shift of the maximum (uncorrected profiles) from 15.36 Å to 10.20 Å and 12.90 Å to 10.17 Å as the temperature increases from 25° to 200 °C and 25° to 150 °C for Ca-MMT and Na-MMT, respectively. After reaching 150 °C for Ca-MMT and 90 °C for Na-MMT, the profiles become very diffuse. The profiles were not corrected for angular dependence of the Lorentz-polarization factor, for the structure factor, surface roughness effects or for specific features of low-angle geometry (see Janeba et al. 1998).

An analysis of XRD powder patterns of rehydrated montmorillonite samples (R) shows that profiles of the first basal diffraction (001) of both montmorillonite samples also exhibit a decrease of the profile intensity, a modulation of the profile and a shift of maximum as the temperature of dehydration increases. However, particularly at higher temperatures, the changes become more pronounced than we can observe for dehydrated (D) samples (preceding paragraph). Corresponding dehydrated samples already exhibit contraction of their interlayer at low temperatures in contrast to rehydrated ones. Processes of dehydration and rehydration for Ca-, and Na-montmorillonites are compared in Figs. 5 and 6 using position of the profile maximum (d_{001}).

It appears that processes of dehydration and rehydration are quite different for Ca-MMT and Na-MMT. The mass loss during dehydration for Ca-MMT is greater than that for Na-MMT whereas the rehydration ability is lower.

The d_{001} of dehydrated Ca-MMT samples drops continuously (Fig. 5) with increasing dehydration temperature (from 25° to 300 °C), but the relation breaks down at 200 °C, above which the position remains equal to 10.2 Å. 200 °C is the first temperature at which the collapsed interlayer structure can be observed and, therefore, we can deduce that the mass loss Δm_{200^o} corresponds to the 9.46 water molecules per one interlayer cation for Ca-MMT. If we consider the content of interlayer cations in the present Ca-MMT sample and the predicted number of water molecules according to Koster van Groos & Guggenheim (1990) we get 9.27-9.89 water molecules per one interlayer cation.

The rehydration process of Ca-MMT can be divided into two stages (Figs. 2 and 5). The first corresponds to temperatures between 25° and 200 °C where the rehydration ability drops to 61 %, but where no significant collapse of the interlayer of rehydrated samples can be observed (a decrease of d_{001} from 15.36 Å to 14.76 Å). The second stage corresponds to temperatures between 200° and 500 °C where the rehydration ability drops significantly (37-20 %) and so does d_{001}, from 14.76 Å to 10.2 Å.

In contrast to Ca-MMT, the d_{001} of dehydrating Na-MMT samples does not drop continuously (Fig. 6) with increasing temperature of dehydration (from 25° to 250 °C). The dehydration process of Na-MMT can be divided into three stages:

The first stage corresponds to temperatures 25-70 °C, where only a small shift of d_{001} from 12.90 Å to 12.48 Å can be observed.

In the second stage, between 80° and 110 °C, a significant drop of d_{001} (10.95 Å) can be observed.

The third stage represents Na-MMT structure collapsed after reaching 150 °C (10.2 Å). The mass loss Δm_{150^o} corresponds to 4.88 water molecules per one interlayer cation. If we consider the content of interlayer cations determined in our Na-MMT sample and the number of water molecules predicted according to Koster van Groos & Guggenheim (1990), we get 4.16-5.14 water molecules per one interlayer cation.

Similarly to Ca-MMT, the rehydration process of Na-MMT can be divided into two stages (Figs. 2 and 6). The first stage corresponds to temperatures 25-150 °C, where the rehydration ability drops to 88 % and where no significant reduction of basal spacings of rehydrated samples is observed (there is a decrease of d_{001} from 12.90 Å to 12.46 Å). The second stage corresponds to temperatures 150-500 °C, there the rehydration ability drops slowly (74-35 %), but the d_{001} drops significantly (from 12.46 Å to 10.2 Å).

Conclusions

1. The behaviour of Ca-MMT and Na-MMT during dehydration and rehydration appears to be quite different. Mass loss during dehydration for Ca-MMT is greater than that for the Na-MMT (Fig. 1) but their rehydration ability is the opposite (Fig. 2). 200 °C for Ca-MMT and 150 °C for Na-MMT are the first dehydration temperatures at which their collapsed interlayer structure appears (10.2 Å). Mass losses Δm_{200^o} for Ca-MMT and Δm_{150^o} for Na-MMT correspond to the 9.46 water molecules per one interlayer cation for Ca-MMT and the Δm_{150^o} corresponds to 4.88 water molecules per one interlayer cation for Na-MMT. These values are in agreement with the limit for those estimated by Koster van Groos & Guggenheim (1990) — c.f. data in Table 2.

2. The dehydration process of Ca-MMT appears to be continuous with increasing temperature of dehydration from 25° to 200 °C (the values d_{001} drop continuously from 15.36 Å to 10.20 Å — see Fig. 5) whereas the dehydration process of Na-MMT is non-continuous and it can be divided into three stages: (1) At temperatures ≤ 70 °C (d_{001} ranges from 12.90 Å to 12.48 Å); (2) At temperatures between 80° and 110 °C (d_{001} value drops to 10.95 Å); (3) Collapsed Na-MMT structure (10.2 Å) appears at above 150 °C (Fig. 6).

3. In the rehydration process of both Ca-MMT and Na-MMT two stages can be recognized: (1) Rehydration at temperature ranges from 25° to 200 °C (Ca-MMT) and from 25° to 150 °C (Na-MMT); there the rehydration ability drops to 61 % for Ca-MMT and 88 % for Na-MMT, however no significant collapse of the interlayer of rehydrated samples is observed. (2) Rehydration at temperatures between 200 °C (150 °C for Na-MMT) and 500 °C, where the rehydration ability drops significantly (37-20 % for Ca-MMT and 74-35 % for Na-MMT) and so do the d_{001} values.

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