

## ADSORPTION OF COPPER AND ZINC IONS ON VARIOUS MONTMORILLONITES: AN XRD STUDY

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### ABSTRACT

The adsorption of Cu- and Zn ions on four Na-montmorillonites with rather different mineralogical features and charge characteristics was investigated by XRD in order to observe structural changes during the adsorption. The adsorption capacity of the samples is 0.33–0.38 mol/kg for Cu, and 0.32–0.47 mol/kg for Zn. Zinc adsorption capacity increase with layer charge and CEC, while copper adsorption seems to be independent from these parameters. The basal spacing of metal-adsorbed montmorillonites depends on the type of metal ion, on the starting metal ion concentrations, and on the equilibrium pH-s. Cu-adsorbed montmorillonites have about 13–14 Å basal spacing (two water layer arrangement) in case of small concentration and high pH, while in case of high metal ion concentration and low pH Cu-adsorbed montmorillonites have 12.5 Å basal spacing (one layer water arrangement). Zn-adsorbed montmorillonites tend to have 14–15 Å basal spacing (two water layer). Sharpening of the basal peaks with increasing metal ion concentration indicates increase of domain size, suggesting structural re-building of montmorillonite crystallites during the adsorption. The expansion capacity in ethylene-glycol of the metal-adsorbed montmorillonites did not change, but in case of glycerol solvation loss of expansion capacity can be observed for both metals, but only for the montmorillonites with low layer charge. Upon 250°C heat treatment Cu enter into the silicate sheet of montmorillonites resulting total loss of ability for expansion (Hofmann-Klemen effect). Although ionic radius of Cu<sup>2+</sup> and Zn<sup>2+</sup> are similar, in case of Zn-adsorbed montmorillonites the Hofmann-Klemen effect can not be observed.

**Key words:** metal adsorption, montmorillonite, copper, zinc, XRD, swelling capacity, domain size, pH

### INTRODUCTION

Copper and zinc are two of those elements which are essential in small amount for vital functions, but in high concentrations (e.g. in case of environmental pollution) they are toxic (Siegel 2002). In soils, clay minerals play an indispensable role in chemical and biological processes involving heavy metals by their preferring cation adsorption and exchange capacity. The bioavailability of these trace elements by plants decreases with the clay mineral content in brown forest soils, referring to the strong retention capacity of clay minerals to copper and zinc (Sipos 2003). It has been proved by many studies that among soil clay minerals smectites have the greatest adsorption affinity to copper and zinc (Shukla 2000, Helios-Rybczka et al. 1995). In consequence of environmental changes chemical and physical characteristics (i.e. interlayer composition, layer charge, crystallite size) of the smectites may alter, their adsorption, ion exchange and swelling properties can modify. These changes may influence the chemical and physical properties of the soil itself.

Although, numerous work were presented on the adsorption of copper or zinc (as trace elements or pollutants in soils) on clay minerals (as soil components), only a few papers deal with the effect of these heavy metals on the structure of the clay minerals and with the parameters which influence the structural changes (Brigatti et al. 1995, Heller-Kallai and Mosser 1995, Ma and Uren 1998, He et al. 2001).

The objective of the present study was to determine the adsorption of Cu and Zn on montmorillonites and to characterize the effects of the adsorption on their structural properties, namely the swelling capacity. For these reason the adsorption of copper and zinc ions by four montmorillonites with roughly similar mineralogical and crystallochemical characteristics but from different origin was investigated by X-ray diffractometry.

### ANALYTICAL METHODS

The adsorption experiments were performed by mixing 400 mg of montmorillonite with 40 ml of solutions containing various concentrations of copper and zinc ions. The initial metal concentrations were set to 20, 40, 50, 80, 100, 200, 500, 1000, 1500 and 2000 mg/l. These values seem to be high regarding the natural metal contents of a soil, but they can occur in case of serious contamination. Moreover, these concentration values are expected to be enough to cause changes in the structure of montmorillonites. The samples were shaken for 48 hours at room temperature, then they were centrifuged. The equilibrium concentrations of Cu and Zn were measured by atomic absorption spectrometry (PERKIN ELMER 5000). The amounts of adsorbed metals were calculated from the difference between concentration of the starting and equilibrium solutions. Initial pH of the solutions was set to 4.5–5.0 by adding some drops of dilute HNO<sub>3</sub>.

**Table 1.** Mineralogical characteristics of the montmorillonite samples.

Sample	Origin	Main mineral components	Layer charge/half unit cell (min–max)	CEC (meq/kg)
SWy-2	Wyoming (USA)	montmorillonite	0.25–0.36 octahedral	77
IMB	Hungary	92% montmorillonite, 8 % cristobalite	0.265–0.392 octahedral	103
UVB	Rumania	80–85 % montmorillonite, 15–20% cristobalite	0.265–0.392 octahedral	94
VCB	Rumania	montmorillonite	0.28–0.43 octahedral>>tetrahedral	109

In this pH range the competition between metal ions and  $H^+$  ions is the smallest according to Farrah and Pickering (1979).

The solid phase was washed by distilled water and then sedimented on a glass slide for the XRD analysis. The samples were air dried and stored under controlled humidity conditions ( $RH = 25\text{--}30\%$ ) in a desiccator. The XRD measurements were carried out by a PHILIPS PW 1710 diffractometer, using 45kV accelerating voltage and 35mA current. The speed of scan was  $0,02^\circ 2\theta$ , detecting time was 2 sec. The samples were glycolated in vapour at  $60^\circ\text{C}$  overnight and glycerol solvated at  $95^\circ\text{C}$  overnight. The Hofmann-Klemen effect was tested by heating the untreated and the copper and zinc saturated samples at  $250^\circ\text{C}$  for 16 hours and subsequent glycerol solvation. In all cases the sample thickness was the same ( $3\text{mg}/\text{cm}^2$ ), except the samples prepared for the Hofmann-Klemen test where it was  $8\text{mg}/\text{cm}^2$  to avoid the effect of sodium extraction from the glass slide (Lim and Jackson 1986).

The CEC values were determined on the basis of Ba-exchange. The layer charge of untreated samples was determined by the alkyl-ammonium method of Lagaly (1994).

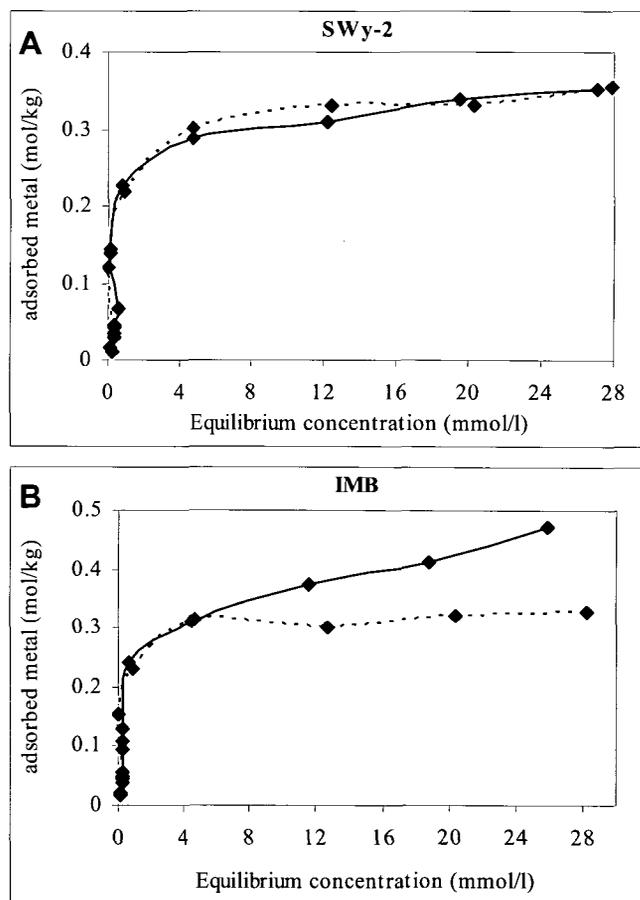
#### MATERIALS STUDIED

The following montmorillonite samples were used: 1) international standard Na-montmorillonite from Wyoming (SWy-2), 2) montmorillonite from the Hungarian "Istenmezeje" bentonite (IMB), and two Rumanian bentonites from 3) Oraşu Nou (UVB) and from 4) Valea Chioarului (VCB). SWy-2 and VCB are pure montmorillonites, the latter is a natural sodium form. IMB is composed by 92% of montmorillonite and 8% of cristobalite, which can not be physically separated from each other. UVB sample is an artificially activated bentonite by soda with high amount of cristobalite (15–20%). The summary of the mineralogical and chemical features of the four montmorillonites are given in Table 1. The amount of mean layer charge follows the  $SWy-2 < IMB = UVB < VCB$  order. The layer charge distribution is heterogeneous for SWy-2 and IMB, more homogeneous for UVB and VCB. Based on the Green-Kelly test nearly the total layer charge of the samples is originated from the octahedral sheet for the samples SWy-2, IMB and UVB, while VCB besides montmorillonite has some percent beidellitic layers also. SWy-2, UVB and VCB are Na-montmorillonites, only IMB montmorillonite was Na-saturated by washing three times with NaCl. The sedimented less than  $2\mu\text{m}$  fraction of the samples was used in the adsorption experiments.

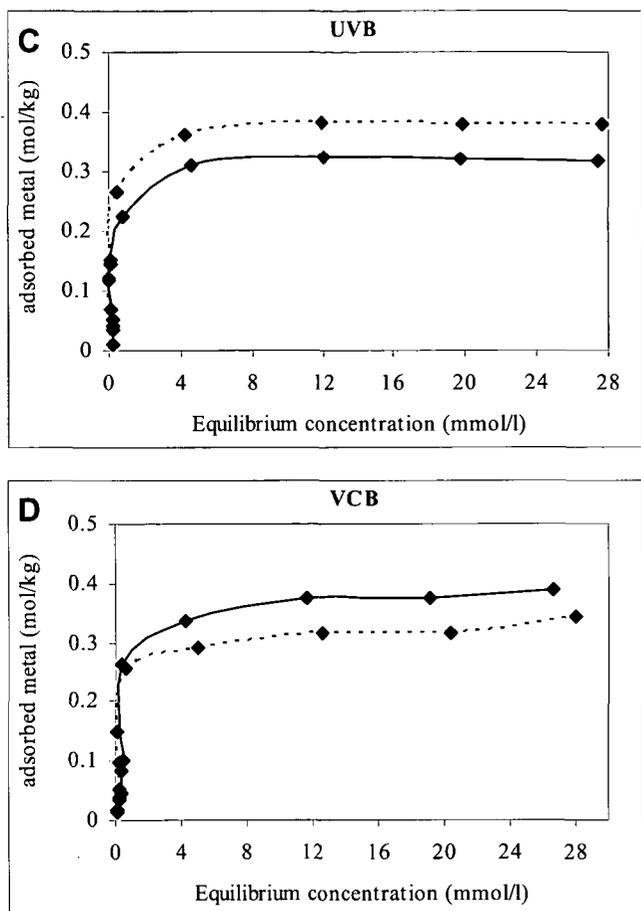
#### RESULTS AND DISCUSSIONS

##### Adsorption isotherms and pH changes

The Cu and Zn adsorption curves are plotted in Fig. 1. Based on the classification of Giles et al. (1960) the shape of isotherms is H-type, which is characteristic for the adsorbents with high affinity to the adsorbate, and suggests chemisorption as mechanism of adsorption. The metal ion uptake was calculated from the Langmuir adsorption isotherms. The maximal adsorption values expressed in mol/kg and in mg/kg (ppm) are shown in Table 2. The adsorbed Cu and Zn amounts are in accordance with the values obtained by Helios-Rybicka et al. (1995) and Vengris et al. (2001) for bentonites and are consistent with adsorption



**Fig. 1.** Adsorption isotherms for Cu and Zn: (A) SWy-2 and (B) IMB montmorillonites. Solid line = Zn, dashed line = Cu. The lines are only used to guide the eye.



**Fig. 1. (continued)** Adsorption isotherms for Cu and Zn: **(C)** UVB and **(D)** VCB montmorillonites. Solid line = Zn, dashed line = Cu. The lines are only used to guide the eye.

**Table 2.** Maximal copper and zinc adsorption of the montmorillonites.

Sample	Maximal Cu adsorption		Maximal Zn adsorption	
	(mol/kg)	(mg/kg)	(mol/kg)	(mg/kg)
SWy-2	0.35	22241	0.35	22880
IMB	0.33	20970	0.47	30724
UVB	0.38	24147	0.32	20918
VCB	0.34	21606	0.40	26148

capacities of natural clayey soil samples (Sipos et al. 2005). As expressed by the percentage of adsorbed Cu and Zn, the montmorillonites show a higher preference for both metal ions at lower concentrations, the increase is the most evident when initially 80 or 100 mg/l metal ion are present in the solution. It corresponds to the 6–7 pH range, and it agrees well with the 6.5 pH value for the maximal Cu adsorption observed by Flor et al. (1995).

Although, the similar chemical and geochemical characteristics of the two metal ions are reflected in the adsorption results also, one can not draw a total parallel between the Cu and Zn experiments. We measured the highest Cu adsorption for UVB and the maximal adsorption of the other montmorillonites can be considered equal, while

Zn adsorption of UVB is relatively low, and VCB and IMB seem to be the best Zn adsorbents. SWy-2 and IMB montmorillonites adsorb about the same amount of Cu and Zn, while UVB shows higher affinity to Cu, and VCB to Zn. The order of affinity for Cu does not follow those of layer charge or cation exchange capacity. However, a tendency of higher the CEC or layer charge the higher the adsorption capacity can be outlined in the case of zinc adsorption. The equilibrium pH-s for Cu and Zn decrease from 8.3 to 4.4, and from 9.3 to 5.9, respectively, with the increase of the metal ion concentration. The turning of pH into more acidic initially is due to the hydrolysis of metal ions and afterwards due to the release of  $H^+$  from the coordinated water molecules of the adsorbed metal cations. Comparison of pH of montmorillonite samples with adsorption capacities suggests an inverse relation, but it can not be considered as a linear regularity.

#### XRD investigation of Cu-montmorillonites

XRD patterns of the montmorillonites saturated with Cu-solutions of different concentrations are shown in Fig. 2. The most frequently observed (001) reflection of Cu-smectites at ambient conditions is around 12.5 Å, indicating one layer water arrangement of Cu in the interlayer space (El-Sayed et al 1970, Pusino et al. 1989, Stadler and Schindler 1993, Heller-Kallai and Mosser 1995, Emmerich et al. 2001). On the contrary, we found that the basal spacing tend to rise from the initial 12.5 Å (Na-montmorillonite) to 14.5 Å at low metal concentrations (SWy-2, IMB: 20–100 or UVB, VCB: 20–200 mg/l starting  $Cu^{2+}$  concentrations) and at pH  $\geq 6$ . Simultaneously, beside the increase of  $d(001)$ , the broadening of basal peak can be considered as well, indicating the decrease of crystallite size and/or interlayering of montmorillonite layers with different basal spacing. This observation enables one to think that Cu formed a two-water layer hydrate in the interlayer space and that the montmorillonite crystallites decomposed. According to the calculated data of Stadler and Schindler (1993) in Cu-Ca-montmorillonite system in this pH range (5–7)  $Cu(OH)^+$  and  $Cu_2(OH)_2^{2+}$  chemical species participate in the ion exchange. Our measurements support rather the existence of divalent ion-pair form of Cu in the interlayer space in this pH range. However, this value is similar also to that obtained at pH 3 to 6 by He et al. (2001) interpreted as the presence of fully hydrated hexaaqua  $Cu^{2+}$  ions in the interlayer space (Morton et al. 2001). For the determination of the form of adsorbed Cu further spectroscopic studies (FTIR, EPR or XPS) are needed.

At higher starting Cu concentrations, above 200 ppm, and at more acidic pH the 001 reflection re-shifted to 12.5 Å and the peaks became sharper. This value agree with those found in the literature cited above and it indicates the full saturation by Cu, as shown by adsorption curves (Fig. 1), and proved directly by analytical electron microscopy (Németh 2003).

Corresponding to the change in basal spacing a dramatic change in equilibrium pH can be observed between 100 and 200 ppm starting Cu concentrations. This phenomenon can be explained by the form of Cu in the interlayer space, which is mostly determined by the pH. To check this hypothesis, we studied VCB smectite with and without adjusting the pH (Fig. 3.). Remarkable differences in basal spacing can be observed even in case of small differences in pH. When pH

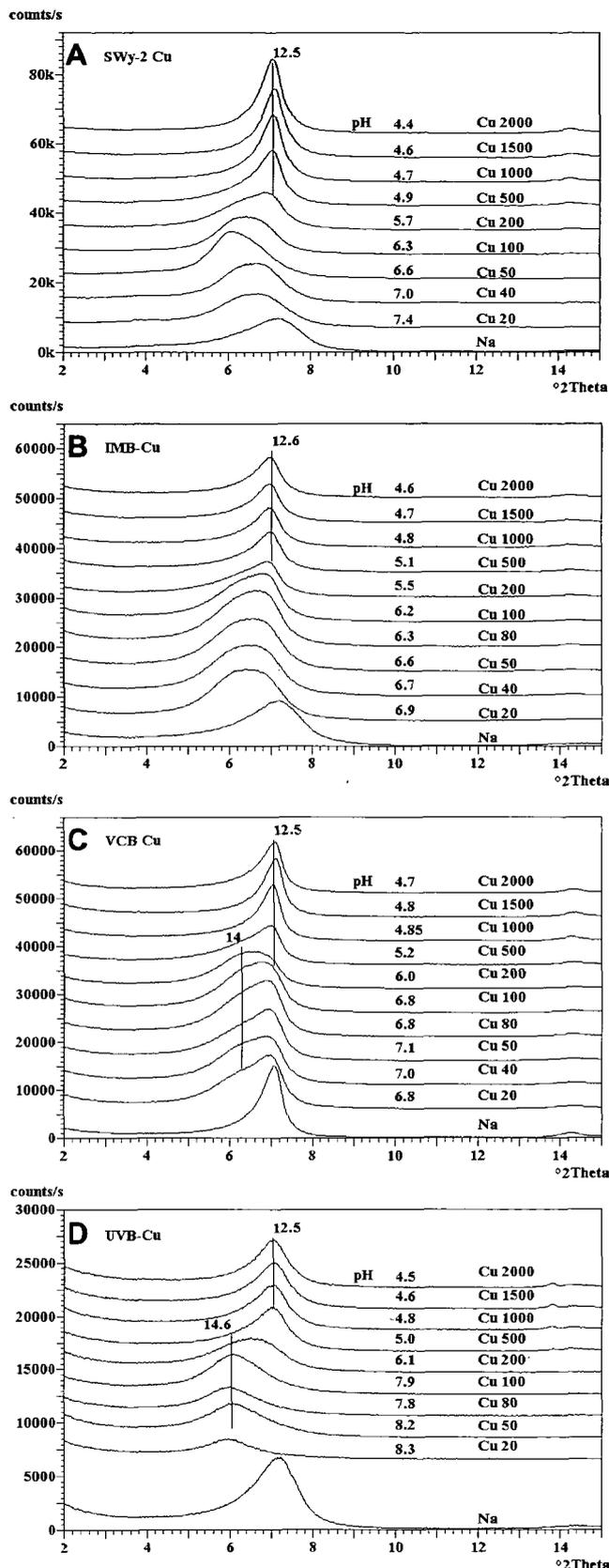


Fig. 2. XRD patterns of Cu-adsorbed (A) SWy-2, (B) IMB, (C) UVB and (D) VCB. The starting metal concentrations and the equilibrium pH-s are shown.

was not been adjusted, the basal spacing around 14 Å appeared at pH = 6.6 (100 ppm starting Cu) and remained only in a narrow pH and concentration range (Fig. 3A).

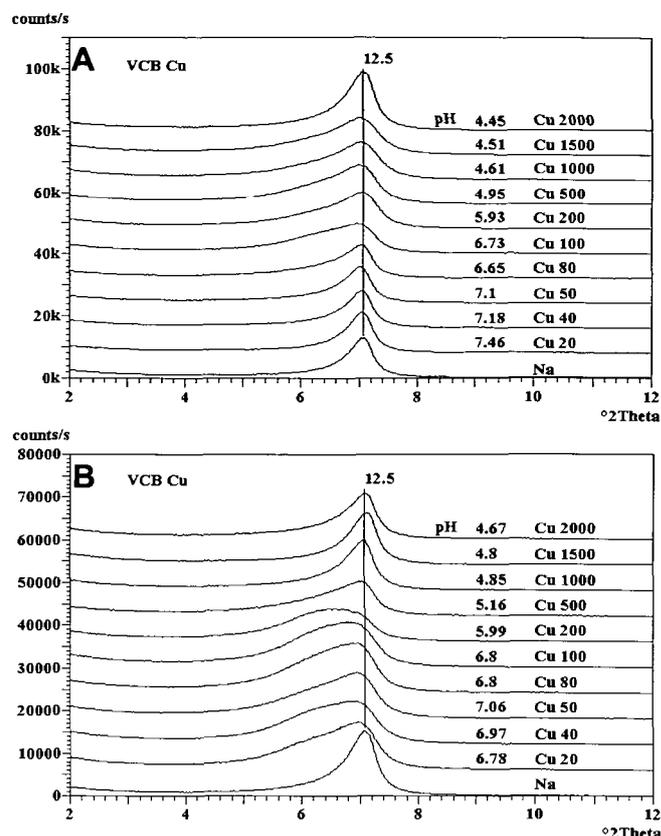


Fig. 3. XRD patterns of Cu-adsorbed VCB smectite (A) without and (B) with pH adjusting.

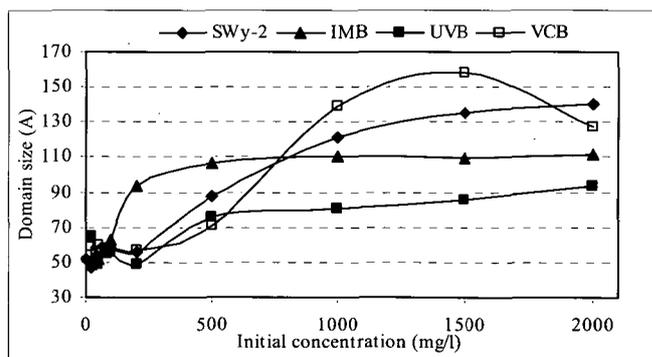


Fig. 4. Domain size (in Å) of Cu-adsorbed montmorillonites in function of initial Cu concentration. The lines are only used to guide the eye.

At other pH-s Cu-montmorillonite is characterised by  $d(001)=12.5$  Å. On the contrary, the 6–7 pH and the basal spacing around 14 Å remained stable in the 20–200 ppm starting Cu concentration range when pH was adjusted (Fig. 3B).

Sharpening of (001) peak indicates structural reordering in the interlayer space and an increase of crystallite size. Fig. 4. shows the variation of calculated domain size of montmorillonites with Cu concentration. Domain sizes vary from about 50 Å to 160 Å. As expected, the soda activated UVB montmorillonite is composed by the thinnest crystallites, while SWy-2 is the thickest one. After the initial decomposition of crystallites at low concentration rate an increase of domain size can be considered for all the four

samples. Similar structural decomposition and reordering was revealed by XRD line profile analysis of Cu-adsorbed IMB montmorillonite in a previous work (Kiss et al. 1997).

#### XRD investigation of Zn-montmorillonites

XRD patterns of the montmorillonites adsorbed by Zn solutions of different concentrations are shown in Fig. 5. The characteristic basal reflection of Na-saturated montmorillonites was progressively shifted to about 14.5 Å and the shape of the peak became sharper. The four montmorillonites behaved similarly but with small differences. In case of SWy-2 the 14.5 Å reflection was achieved with the starting concentration of 100 ppm, while VCB reached the 14.5 Å basal spacing at 200 ppm. Generally, the basal spacing progressively increases with decreasing pH until it reaches the permanent 14.5 Å value at neutral pH. Based on data presented by Ma and Uren (1998) Zn may be in both one- and two water layer arrangement in the interlayer space, depending from its chemical speciation. At higher pH  $\text{ZnOH}^+$  is in the interlayer with one water layer, while in lower pH  $\text{Zn}^{2+}$  occurs with two water layer resulting 12.5 and 15.1 Å  $d(001)$ , respectively. Our results coincide with these observations and show that Zn tends to be in two water layer form in the interlayer space at neutral and lower pH. On the contrary, Brigatti et al. (1995) found 12.8 Å basal spacing for  $\text{Zn}^{2+}$ -saturated Cheto-montmorillonite, but their experiments were carried out under different time and pH conditions. Similarly to copper, Zn adsorption causes also crystal rebuilding and increase of domain size.

#### XRD investigations of solvated Cu- and Zn-montmorillonites

Some typical XRD patterns of Cu- and Zn-montmorillonites saturated with organic compounds, namely ethylene glycol and glycerol are shown in Fig. 6. Upon glycolisation the basal spacings of all the four montmorillonites in case of both the Cu- and the Zn-adsorbed forms were around 17 Å (Fig. 6A, B). This  $d(001)$  value corresponds with that of Heller-Kallai and Mosser (1995). The basal spacing of ethylene-glycol-Cu/Zn-montmorillonite complexes was independent on the metal concentrations, but the intensity of the basal peak progressively and significantly decreased with the adsorbed metal content of the montmorillonites, suggesting that the intercalation of organic compounds into the relatively ordered layer stacking of metal-adsorbed montmorillonite became more difficult.

When SWy-2 was glycerol solvated the starting Na-form swelled to 17,8 Å and this state remains up to 500 ppm added copper. However, above this concentration value a broad reflection occurred between 17,5 and 14,3 Å. With the increase of Cu loading, the maximum of this broad peak shifted to 14,3 Å, suggesting the interlayering of montmorillonite layers containing one and two layer glycerol (Fig. 6C). The occurring of a reflection shoulder at 15 Å for Cu-IMB suggests the same phenomena. In case of Zn-adsorbed SWy-2 this loss of expansion with glycerol solvation can be observed from 100 ppm starting Zn concentration (Fig. 6D). This loss of swelling capacity is not characteristic for all the montmorillonites. Cu- and Zn-VCB, Cu-UVB, Zn-IMB behaved like a normal montmorillonite and swelled. The differences may be due to the real crystal chemical characteristics of the montmorillonites. SWy-2 montmorillonite which has the lowest layer charge

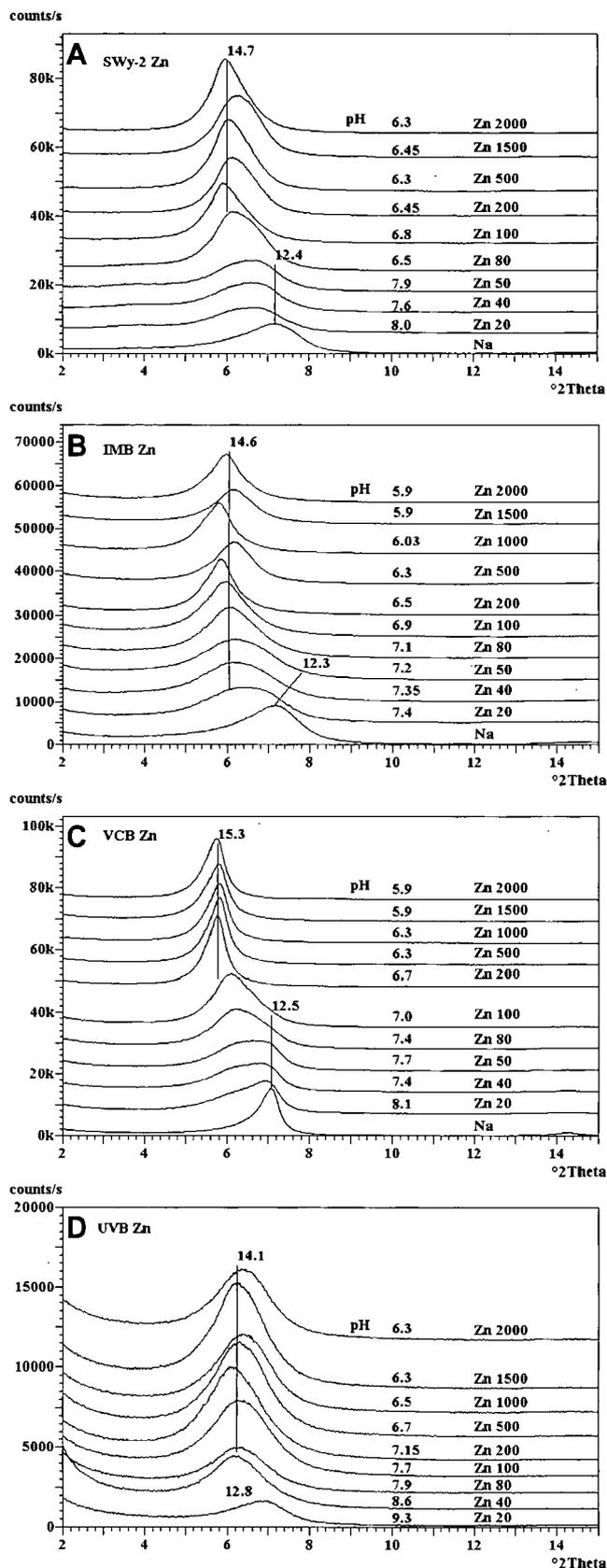


Fig. 5. XRD patterns of Zn-adsorbed (A) SWy-2, (B) IMB, (C) UVB and (D) VCB. The starting metal concentrations and the equilibrium pH-s are shown.

always lost its swelling capacity for glycerol, while the high charged VCB montmorillonite remained expansive even at the highest Cu and Zn concentration.

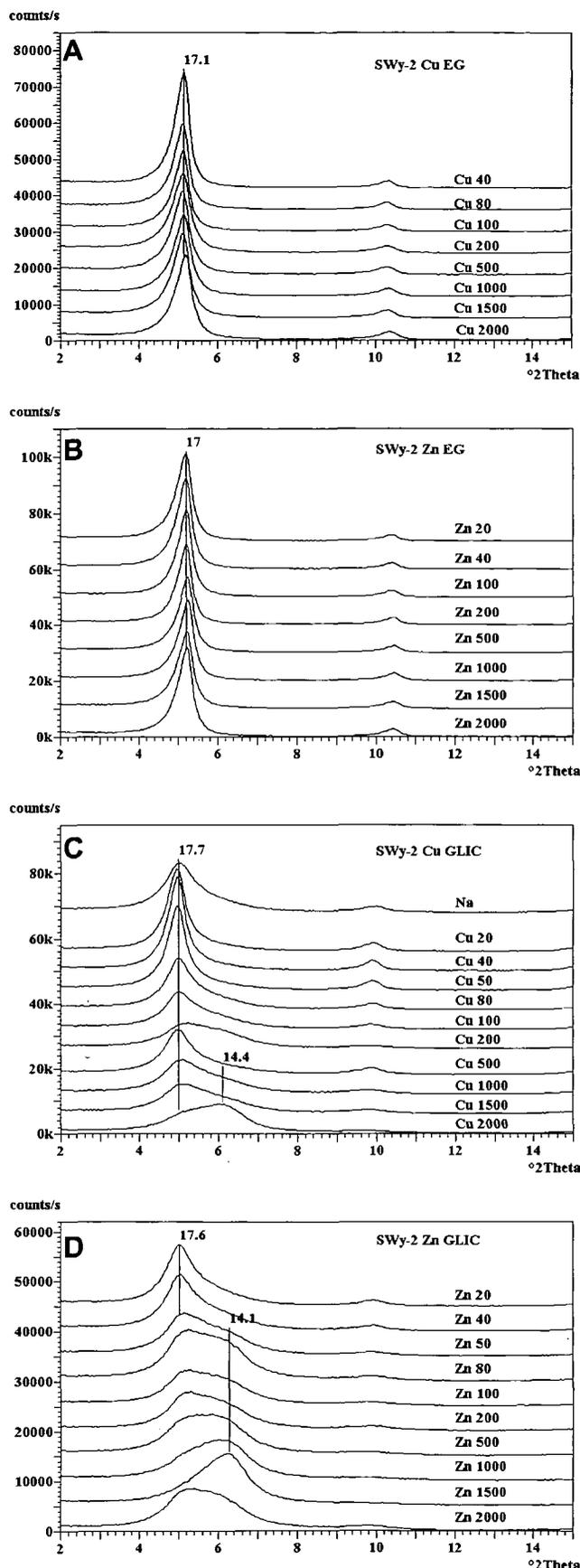


Fig. 6. XRD patterns of (A) ethylene-glycol solvated Cu-adsorbed SWy-2, (B) ethylene-glycol solvated Zn-adsorbed SWy-2, (C) glycerol solvated Cu-adsorbed SWy-2 and (D) glycerol solvated Zn-adsorbed SWy-2.

#### XRD investigation of thermally treated Cu- and Zn-montmorillonites

It is widespread known that lithium saturation and subsequent heating at 250°C deprives montmorillonite of its swelling capacity (Hofmann and Klemen 1950). The three conditions proposed by Srasra et al. (1994) to obtain this so-called Hofmann-Klemen effect are that the cation has ionic radius smaller than 0.7 Å, vacancies are present in the octahedral sheet, and that a part of the layer charge is originated from octahedral isomorphous substitution.

The present investigations were undertaken to test if this effect does work in these montmorillonites possessing octahedral charge, in the presence of copper and zinc ions with around 0.7 Å ionic radius. In case of SWy-2, the untreated Na-saturated sample showed a full re-expansion to 17.8 Å after heating at 250°C and glycerol solvation. The sample saturated with 200 ppm Cu solution still swelled in a small amount, but when 1000 ppm Cu solution was added, SWy-2 totally lost its expansion capacity (Fig. 7A). VCB smectite behaves in a similar way (Fig. 7C). IMB montmorillonite lost its swelling capacity even at 200 ppm (Fig. 7B). The loss of swelling capacity suggests that Cu has migrated into the silicate lattice and remarkably reduced the layer charge. The location of Cu trapped in the 2:1 silicate structure at 300°C may be in the hexagonal cavities in the tetrahedral sheet (Madejová et al. 1999, Heller-Kallai and Mosser 1995), or in the octahedral vacancies (He et al. 2001). The divalent Cu- and Zn ions are nearly of similar size and therefore expected to penetrate similarly into the silicate layer.

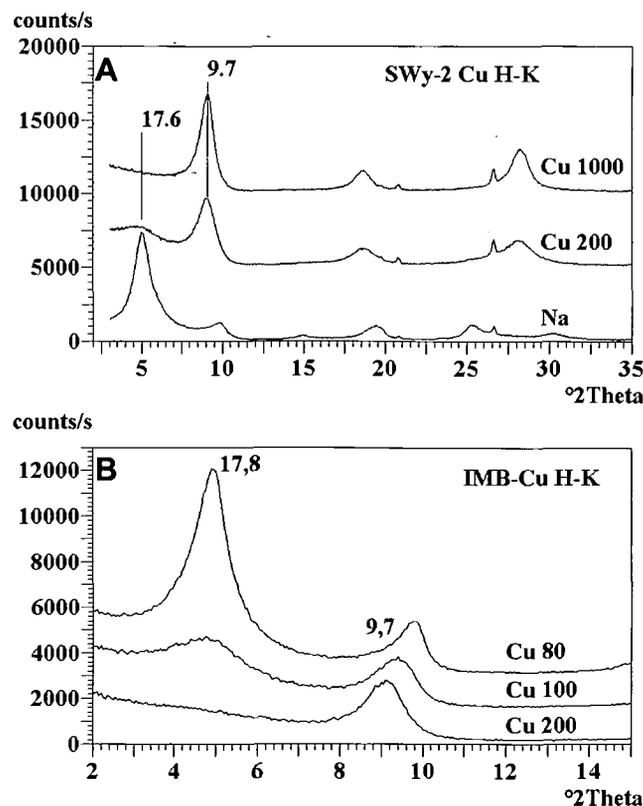


Fig. 7. XRD patterns of (A) Cu-adsorbed SWy-2 and (B) Cu-adsorbed IMB after 250°C heat treatment and subsequent glycerol solvation.

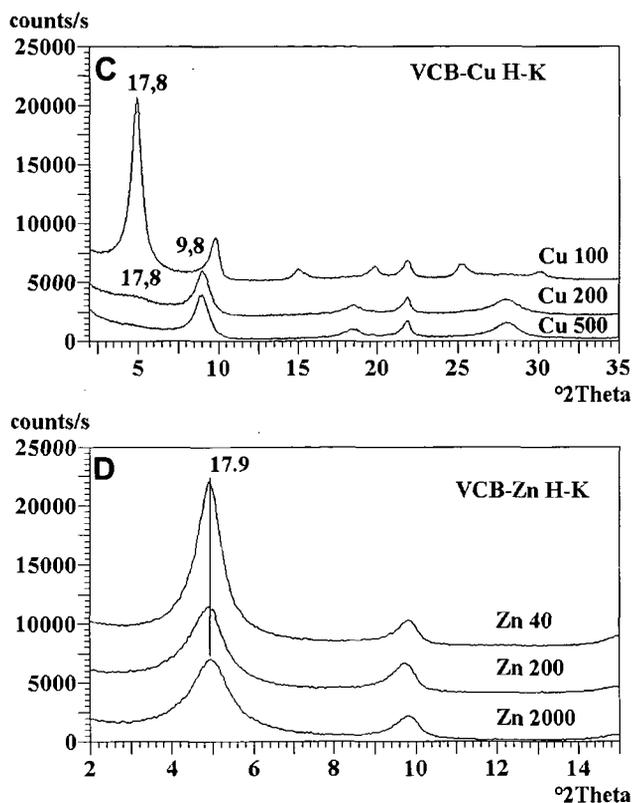


Fig. 7. (continued) XRD patterns of (C) Cu-adsorbed VCB, and (D) Zn-adsorbed VCB after 250°C heat treatment and subsequent glycerol salivation.

However, the Zn-adsorbed montmorillonites preserve their expansion capacity after heat treatment, suggesting that Zn do not enter into the silicate layer at 250°C (Fig. 7D).

#### CONCLUDING REMARKS AND SUMMARY

Montmorillonites with slightly variable characteristics adsorb Cu- and Zn ions in a similar way and of rather similar quantity. However, the adsorbed quantities on the samples may be slightly different from each other. The adsorption capacity may be influenced by layer charge, cation exchange capacity and equilibrium pH of montmorillonites. The basal spacings of montmorillonites change with the starting metal concentrations and with the equilibrium pH-s. Cu-adsorbed montmorillonites have about 13-14 Å basal spacing (two water layer arrangement) in case of small concentration and high pH, while in case of high metal ion concentration and low pH Cu-adsorbed Cu-adsorbed montmorillonites have 12.5 Å basal spacing (one layer water arrangement). Zn-adsorbed montmorillonites tend to have 14-15 Å basal spacing (two layer water). This suggests that the basal spacing of montmorillonites and the speciation of metal ions in the interlayer space depend on the equilibrium pH. Swelling characteristics of montmorillonites in glycerol vapour are influenced by saturation by Cu and Zn solutions in a different way. In case of typical low charged montmorillonites (SWy-2) Cu and Zn cause the loss of expansion capacity, while the high charged one does not loss it. Anyway, it is necessary to take this observation into account when smectites are differentiated from vermiculites

by their swelling in glycerol in copper or zinc polluted soils.

Upon 250°C heat treatment Cu ions enter into the silicate layer of montmorillonites resulting total loss of ability for expansion (Hofmann-Klemen effect). Although ionic radius of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are similar, in case of Zn-adsorbed montmorillonites the Hofmann-Klemen effect can not be observed.

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