

EFFECTS OF COPPER-ADSORPTION ON THE LINE-PROFILE OF FIRST BASAL REFLECTION OF MONTMORILLONITE

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ABSTRACT

Montmorillonite containing mostly Ca as interlayer cation was used for examining the effects of copper-complex forming and adsorption on the surface of montmorillonite. Exchangeable cations were replaced with ammonium (NH₄⁺) and sodium (Na⁺) ions, thus getting monoionic montmorillonite-forms.

Copper sorption on mineral surface may include several processes with different characteristics. In case of montmorillonite ionexchange in the interlayer region and complexation on the surface hydroxyl groups can be taken into account. The Cu-uptake analysed by Langmuir's adsorption isotherm is the sum of these metal binding reactions.

Starting pH was 4.5 and equilibrium pH was observed. Different concentrations of solutions of CuSO₄ from 0 to 1400 ppm were used.

The place and profile of X-ray diffraction basal reflection d_{001} of montmorillonite is very characteristic and depends on the features and amount of adsorbed cation and water:

As to the X-ray diffraction line-profile analysis, in the function of adsorbed amount of copper a significant change occurred in crystallite size (size of domains coherently scatter X-rays) and degree of deformation even in half-width of the first basal reflection. Our result is that half-width (signed as $\Delta\sin\theta$) does not but the other two variables does indicate the adsorptional process well and their variance correlate with on the adsorption isotherms.

Key words: montmorillonite, copper, adsorption, intercalation, XRD, domain size, deformation.

INTRODUCTION

Copper in soil originates from geological, industrial and agricultural processes, but agricultural origin is more considerable. As a bioessential microelement it is very important, but copper can be even toxic if its concentration is too high. Plants take copper up from the soil (by creating acidic agent where copper-hydroxydes are moveable) thus this element finally gets into the body of human being through food chain. From environmental point of view adsorption processes in the soil can be useful specially near chemical factories because they may not allow copper to get into ground water.

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As the adsorption occurs through clay minerals the more we know about these processes the easier we can avoid environmental contamination. Adsorption of copper was examined on the surface of different forms of montmorillonite as it is an important compound of soil.

Character of adsorptional processes depends on pH. Effects of pH and complex formation on the uptake of Cu-ions by Ca-montmorillonite has been investigated formerly. A comprehensive description of clay-metal interaction must include both ion exchange and surface complexation. Copper is sorbed through coordination to surface hydroxyl ions at the edges of the clay and by sorption at negative sites on the mineral faces (FARRAH and PICKERING, 1976).

SPOSITO (1984) distinguished between two main processes: specific adsorption (complexation on surface hydroxyl groups – formation of inner sphere complexes) and unspecific adsorption (ion exchange at negative sites – outer sphere complexation).

In water-clay systems the reactions are pH-dependent because H^+ like any other cations available in recent solution competes for every possible binding sites with copper.

STADLER and SCHINDLER (1993) found that in the range of pH 3.5–4.5 mainly ion exchange occurred in the interfacial region of Ca-montmorillonite. The pH-dependent adsorption began at pH 4.5 and became more and more important at $pH > 5.5$ based mainly on surface hydroxyls. Copper forms mainly $CuOH^+$ at higher pH.

Further, depending on pH copper exists and can be sorbed in the form of hexa-aqua and penta-aqua-hydroxy species (KOPPELMAN, 1977).

Character of adsorption of different cations and number of water-layers existing in the interlayer-space are determined by the charge and size of the ion. Montmorillonites with different cations in the interlayer-space may have different interlayer distance (shown by d_{001} of X-ray diffraction pattern) (MACEWAN and WILSON, 1980). Changes of the distance and line profile of basal reflection (001) may indicate some processes occurring in the structure during adsorption. Adsorption creates new conditions in the structure of montmorillonite. This process can be observed by the two data: domain size and lattice strain. In this work authors examine changes of structure of montmorillonite during intercalation process, and changes of half-widths (SmC), domains sizes and deformation in the function of Cu-intercalation. Understanding intercalational processes can promote a better knowledge of structure of montmorillonite and other clay minerals as adsorption mostly takes place in the interlayer space.

METHODS

MATERIAL STUDIED. The material used for examination of the effects of copper-adsorption on montmorillonite is a bentonite from the locality of Istenmezeje, NE Hungary. This bentonite is a Wyoming-type bentonite.

Mineral composition of bentonite:

montmorillonite	90%
cristobalite	8%
quartz	2%

Chemical composition of bentonite (from Istenmezeje):

Major components:	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	Na ₂ O
(%)	59.95	12.65	2.00	0.01	3.16	1.75	0.31	0.15

Minor components: Cu
(ppm) 200

Basal reflection (001) of layer silicates is very characteristic. Montmorillonite of bentonite from Istenmezeje has a 15.5 Å basal spacing. Treating with ethylene glycol causes a swelling to 17.0 Å. (Fig. 1.)

Bentonite from Istenmezeje (NE Hungary)

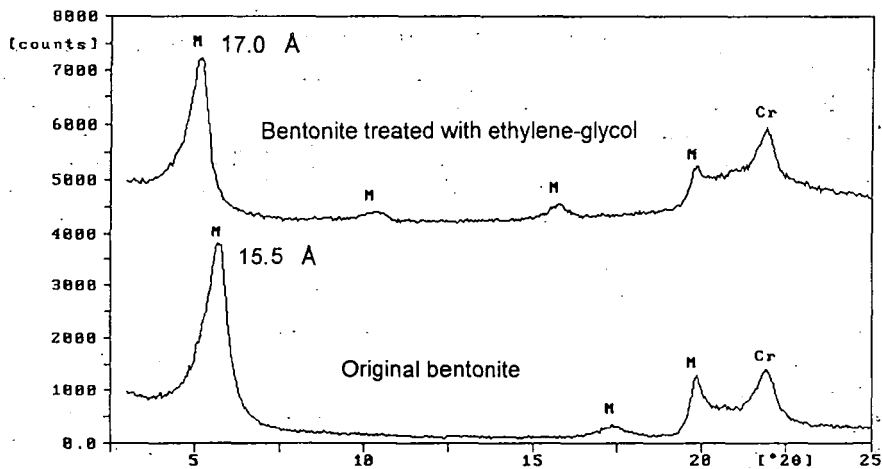


Fig. 1. Diffractograms of bentonite from Istenmezeje (NE Hungary), original and glycolated (M=montmorillonite, Cr=cristobalite)

SAMPLE PREPARATION. The $<2\mu\text{m}$ fraction has to be used for preparation of monoionic minerals. Thus, bentonite sample was ground in grinding mill (Pulverisette-2) for 5 minutes. Grinding should not have been continued because mechanochemical activating shatters the structure and examination of the original structure is required (TÓTH, 1980). The $<2\mu\text{m}$ fraction was prepared using settling tubes filled with distilled water.

Mineral composition of the $<2\mu\text{m}$ fraction:

montmorillonite 92%
cristobalite 8%

Mineral composition of original material and of the $<2\mu\text{m}$ fraction is practically the same.

The $<2\mu\text{m}$ fraction of bentonite was washed with 1N NaCl at 25°C to prepare a Na-monoionic form. Then solution was removed and washing was repeated 3 times with 1N NaCl again (FARRAH and PICKERING, 1976, TOKARZ and SHABTAI, 1985).

NH₄-monoionic form was prepared in similar way with 1N NH₄Cl (TOKARZ et al., 1985).

After ion exchange Cl⁻ ions were washed out with deionized water, centrifugated and washed out with deionized water again. This process was repeated until we could find no more Cl⁻ ions in the in the solution. The samples were dried at 40°C for 24–36 hours.

X-RAY DIFFRACTION (XRD). For qualitative and quantitative analysis, domain-size and deformation calculations of materials X-ray diffraction has been used. Measurements were performed with a Philips PW-1710 diffractometer. (Table 1.)

Instrumental conditions and measurement procedure

Equipment	Diffractometer PW-1710
Radiation	Cu K α , 35 mA, 45 kV
Slits	divergence slit 1°, detector slit 0.2 mm, graphite monochromator
Counter	Proportional counter
Goniometer	routine measurement: 3–70 °2 θ 0.05° increment 1 sec. basal reflection (001) (for calculation of domain size, lattice strain): 3–10 or 4–9°2 θ 0.01° increment 1 sec.
Computer	IBM 486 DX
Software	APD PW-1877 3.5B version
K α_2	not stripped
SmC (Smectite Crystallinity)	measured from the unresolved 12–15 Å complex
Domain size	calculated with variance- and Voigt-analysis
Lattice strain	calculated with variance- and Voigt-analysis

ADSORPTION ISOTHERMS. The monoionic montmorillonite-forms were equilibrated with 20 different concentrations of CuSO₄-solution from 0 to 1400 ppm. Starting pH was 4.5. Three parallel series were made for controlling adsorption data. Samples were stored at 25°C for 48 hours (shaked twice). We assumed that our system nearly reaches equilibrium within this period and further uptake can be neglected. We got this conclusion by previous studies (GARCIA-MIRAGAYA et al., 1986, PULS and BOHN, 1988). The solid material was filtered and dried at 25°C.

The simple way to examine the total amount of adsorbed metals is the analysis of adsorption isotherms [plotted adsorbed amounts (mol/kg) vs. equilibrium metal concentration of solution (mol/dm³)]. (Equilibrium concentrations of the solutions were measured with atomic absorption spectrophotometer Varian 10 AAS). This method cannot distinguish between different forms of adsorbed metal but gives special parameters related to the binding process itself applying relevant mathematical equations. We have chosen Langmuir-equation in spite of the fact that it is basically contributed to systems in which the binding sites of the surface are homogenic and the enthalpy remains the same during the sorbent uptake because statistical analysis of the experimental data based on it give average values of adsorption maximum (b) and binding energy (log K).

CHEMICAL ANALYSIS. Chemical composition of the original sample and of those treated with different concentrations of CuSO₄-solutions was analyzed by atomic adsorption spectroscopy (PERKIN ELMER 5000 AAS).

CALCULATION OF DOMAIN SIZE AND DEFORMATION. Montmorillonite (smectite) crystallinity index (SmC) is the calibrated width measured at half-height of the X-ray diffraction (001) basal reflection of smectite.

Connection between the degree of Cu-intercalation and SmC in different monoionic montmorillonite forms was examined. Value of SmC depends on a combination of different factors: instrumental effects, crystallite size (mean/effective size of the domains that scatter X-rays coherently, or effective thickness in case of layer silicates) and the

various kinds of lattice imperfections, e.g. lattice strain or lattice distortion (Klug and Alexander, 1974).

There are several methods for calculating the effects of crystallite size and lattice strain by analyzing XRD line profiles. The following examinations were accomplished with variance analysis (Wilson, 1963, Árkai and Tóth, 1983, 1985, Tóth, 1980) and Voigt method (Langford, 1987, Árkai et al. 1996).

FORMER INVESTIGATIONS. Original Ca-montmorillonite of bentonite (from Istenmezeje) treated with Cu was investigated from the point of changes in line profiles of basal reflection (001).

Original Ca-montmorillonite treated with four different concentrations of CuSO_4 -solution show that adsorption of copper causes collapse in the structure of Ca-montmorillonite and line-broadening. Collapse means a decrease in basal spacing, from 14.71 to 12.75 Å. (Fig. 2.)

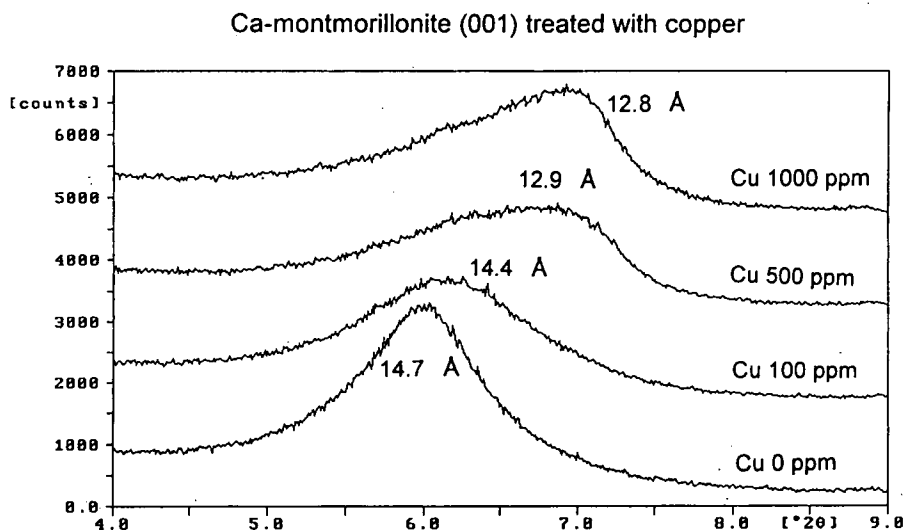


Fig. 2. XRD basal reflections (001) of original bentonite from Istenmezeje treated with 0, 100, 500, 1000 ppm CuSO_4 -solution

RESULTS AND DISCUSSION

The two different montmorillonite-forms (Na- and NH_4 -forms) have different character during and after adsorption of copper. The reason is that a pre-treatment was applied on the original montmorillonite so as to create Na- and NH_4 -forms thus adsorption of Na and NH_4 may have intervened in the structure in advance. This difference appears in adsorptional and structural characteristics.

The adsorptional processes can be well described by adsorption isotherms. Using the Langmuir adsorption isotherm (it was followed by the experimental data in both cases) we evaluated $\log K$ (indicating the affinity of binding sites for metal cations) and b (the maxima of adsorption) values of the processes. These parameters cannot be regarded as absolute values but are sufficient to establish comparison between adsorption processes.

pH was also measured in equilibrium solutions. After adding bentonite to solutions of pH=4.5 and different Cu-concentrations the value of equilibrium pH was in a range of 7.5–4.5. Because of the competition between Cu^{2+} - and H^+ -ions the higher is the Cu-uptake the lower is the measured pH in solution.

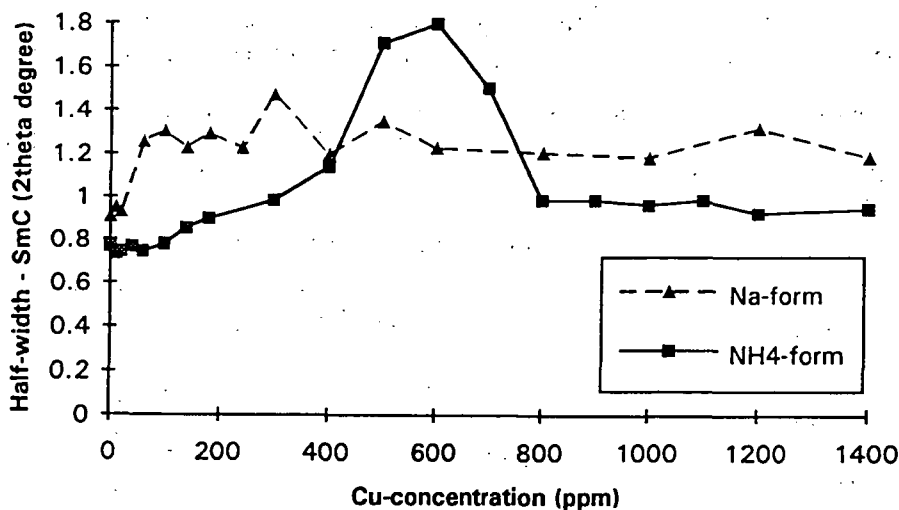


Fig. 3. Changes in half-width of basal reflection (001) of Na- and NH_4 -montmorillonites treated with 0–1400 ppm CuSO_4 -solution

Changes of half-width of basal reflection (001) can be observed in case of both montmorillonite-forms. (Fig. 3.) But as it is only one (and not the most significant) indicator for changes of structure more significant variables should be found for representing these changes. Size of domains coherently scatter X-rays and deformation (lattice strain) tends to be suitable for characterizing structural changes.

First a comparison follows between the Na- and NH_4 -forms from the point of adsorption and structural changes (half-width, domain size and lattice strain), then we try to correspond results obtained from different methods.

TABLE 2

Wyoming-type montmorillonite (MACEWAN and WILSON, 1980)

Interlayer cation	32% rel. humidity	52% rel. humidity	79% rel. humidity
Na^+	12.5 Å	12.5 Å	14.8 Å (broad)
NH_4^+	11.7 Å	11.7 Å (broad)	11.9 Å
Ca_2^+	15.2 Å	15.1 Å	15.5 Å

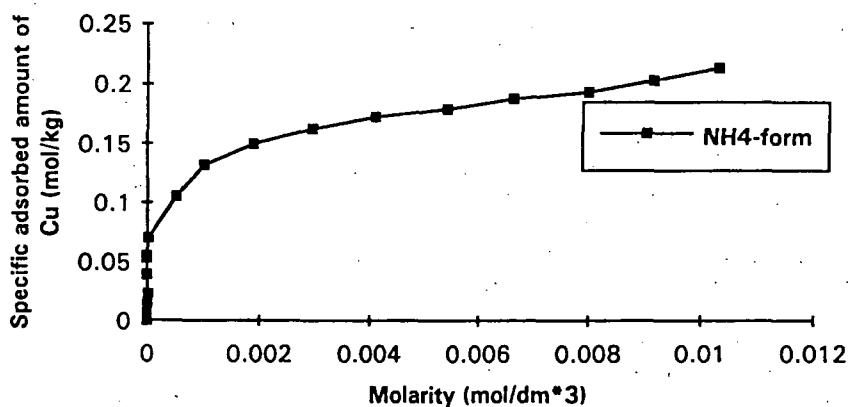
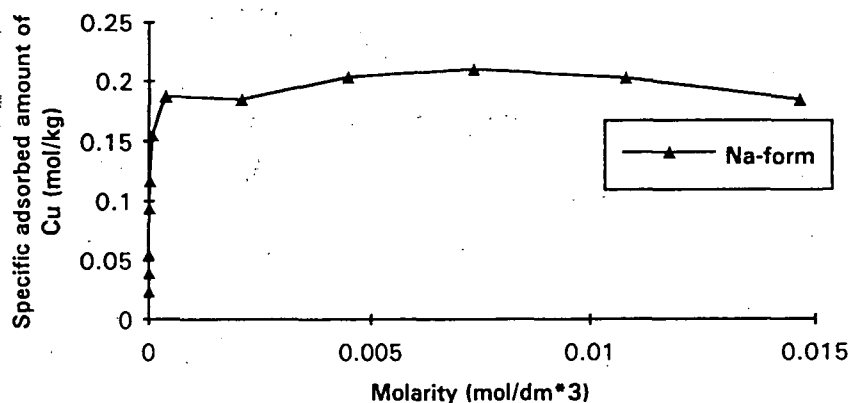


Fig. 4. Cu-adsorption isotherms for Na- and NH₄-form montmorillonites

NA-FORM MONTMORILLONITE

The adsorption isotherm of Na-montmorillonite shows a sudden saturation. At low initial concentrations of Cu nearly the whole amount of sorbent was taken up. Then the very steep slope of the curve changes rather sharply and becomes nearly linear and horizontal. It means that increasing of equilibrium concentrations the amount of sorbed Cu remains the same. The calculated value of $\log K$ was 4.54 which shows quite a strong binding. The adsorption capacity ($b=0.195$ mol/kg) is very close to the experimental value of maximum adsorption (0.21 mol/kg) so the system can be considered to be saturated. (Fig. 4.)

In general, the binding sites of Na-montmorillonite had a great affinity for Cu²⁺ cations and the maximum adsorption was reached very fast (at 500 ppm).

Na-montmorillonite (001) treated with copper

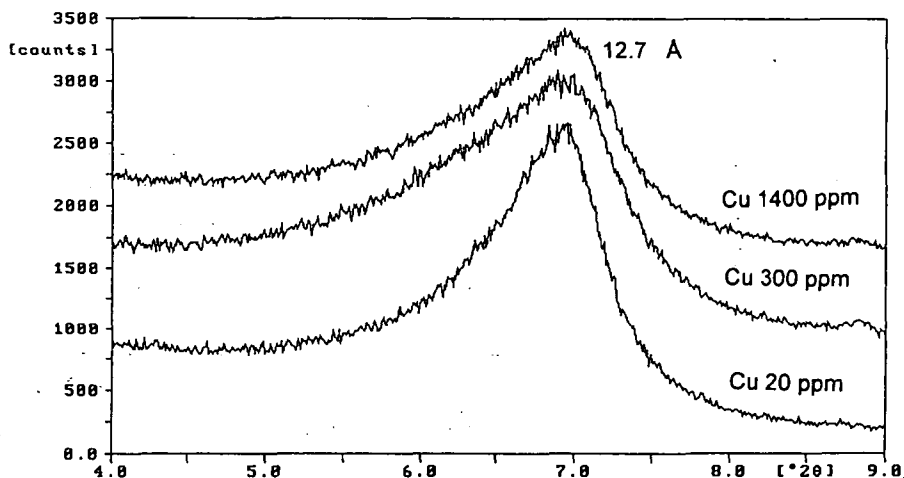


Fig. 5. XRD basal reflections 001 of Na-montmorillonite treated with 20, 300 and 1400 ppm CuSO₄-solution

Basal reflections (001) of XRD-patterns of Na-montmorillonite treated with CuSO₄-solutions of 3 different concentrations show that adsorption of copper on Na-montmorillonite does not cause significant changes in basal spacing, it remains around 12.7 Å. The basal spacing of Cu-form montmorillonite is almost equal to that of the Na-form (Table 2), thus adsorptional process cannot be followed by this parameter but a line-broadening can be observed during adsorption. Half-width indicates some changes in structure but on the basis of half-width only a small transformation of structure could be suspected. (Fig. 5.)

In case of Na-montmorillonite a quite fast decrease then a slower increase in domain size can be observed as Cu-concentration increases (Table 3). Deformation has an opposite change of direction deformation increases first, then it decreases. Changes are variable, and stabilization cannot be observed even at higher concentrations. The smallest domain size and the strongest deformation is at 300 ppm. (Fig. 7.)

Results obtained by chemical analysis show that Cu-uptake is fast at the beginning (Cu-amount is 0.76% at 180 ppm of CuSO₄, 1.65% at 400 ppm and 2.08 % at 1400 ppm), and adsorption does not continue so fast after that. Na-leaving is most significant also between 180 and 400 ppm (Na₂O-concentration is 2.16% at 60 ppm, 1.7% at 180 ppm, 0.77% at 400 ppm, and 0.47% at 1400 ppm of CuSO₄-solution).

A kind of correlation can be observed between changes of domain size and deformation and results of adsorption isotherms. When Cu starts to enter the structure of Na-montmorillonite, particles begin to separate easily at low concentrations, Cu can be gradually bound to the binding sites of the mineral and Na releases first from the edges of particles then from the space between layers. When domain size is large and deformation is weak, copper ions are bound mostly to the edges of particles. When domain size is the smallest and deformation is the strongest Cu-ions begin to enter the layer-space of montmorillonite.

Rebuilding (domain size increase) starts at 300 ppm, earlier than mineral reaches saturation on copper. After decay (when domains have the smallest size) montmorillonite

can uptake a little more copper but at 500 ppm Cu-concentration practically reaches saturation. The reason may be that copper-uptake causes a disordering among domains (domains become smaller) thus strong connection of layers does not prevent further Cu-uptake to binding sites of interlayer space. After that, layers can rebuild (order) again, but Cu continues to be adsorbed on the more and more ordered layers until saturation. The ordering process is slow and no stabilization can be seen in domain size and deformation even at the highest concentration of our work.

The process points to change from a disordered structure beginning at low concentration to a quasi ordered one.

NH₄-FORM MONTMORILLONITE

On the surface of NH₄-montmorillonite saturation occurs more gradually. The first part of the adsorption isotherm is also very steep but then the slope of the curve changes slowly. The log K (3.38) is significantly lower than in case of Na-form, b is very similar (0.212 mol/kg). The last part of the isotherm seems to have linear character with a rate higher than zero. This could happen because of loss of other Cu²⁺-ions from the solution. (Fig. 4.)

In comparison with Na-form NH₄-montmorillonite saturated more gradually at higher equilibrium concentration of Cu and the connection between copper and binding sites was not so strong.

NH₄-montmorillonite (001) treated with copper

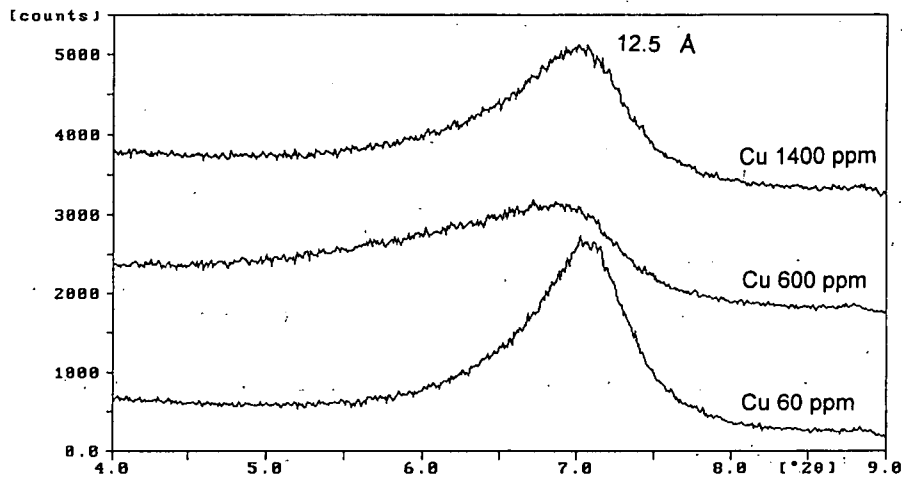


Fig. 6. XRD basal reflections (001) of NH₄-montmorillonite treated with 60, 600 and 1400 ppm CuSO₄-solution

Adsorption of copper on NH₄-montmorillonite does not cause a change in basal spacing practically. It can be seen from basal reflection (001) of XRD-pattern. In case of NH₄-form and Cu-form montmorillonites basal spacing is almost equal (Table 2), but line-broadening shows an intensive transformation in the structure of montmorillonite. Changes

in half widths of basal reflections (001) are quite significant in case of NH_4 -montmorillonite. (Fig. 6.)

Domain-size and deformation show considerable effects (Table 3). Decreasing of domain size is quite slow and starts at concentration of 400 ppm. Deformation shows similar but opposite effect, starting to increase quite slowly. The smallest domain size and strongest deformation is at the concentration-range between 400 and 600 ppm. NH_4 -montmorillonite shows a faster ordering after saturation than Na-form. Above 1000 ppm domain size and deformation practically remain the same. (Fig 7.)

Results obtained by chemical analysis show that at 1400 ppm CuSO_4 concentration 0.24% NH_4 -ions remained in the structure and that Cu-uptake is quite fast below 400 ppm (amount was 0.25% at 40 ppm of CuSO_4 , 0.58% at 140 ppm, 1.28% at 400 ppm and 1.77% at 1400 ppm). Copper concentration does not increase too much at higher concentrations and saturation cannot be observed even at 1400 ppm.

We tried to find some reasons for the considerable effects of changes in domain-size and deformation of NH_4 -montmorillonite. At the beginning of treatment copper tries to replace ammonium-ions. As montmorillonite has a great affinity for ammonium-ions (FARRAH and PICKERING, 1976) Cu cannot build in the structure easily, a competition begins between the two ions. When copper concentration is high enough copper starts to build in montmorillonite and domain size starts to decrease. Montmorillonite consisting of smaller particles has a larger specific surface thus more and more copper can be adsorbed on the mineral surface with domain size decrease. In the intermediate state when domains are the smallest and deformation is the strongest copper ions are not tied regularly yet and certain amount of NH_4 remains in the structure. That is why domains cannot be connected to each other. At 600 ppm domain size increase begins (rebuilding starts). Cu-adsorption continues until saturation (that cannot be observed at these concentrations). Disordering and rebuilding are well shown by the change of domain-size and deformation.

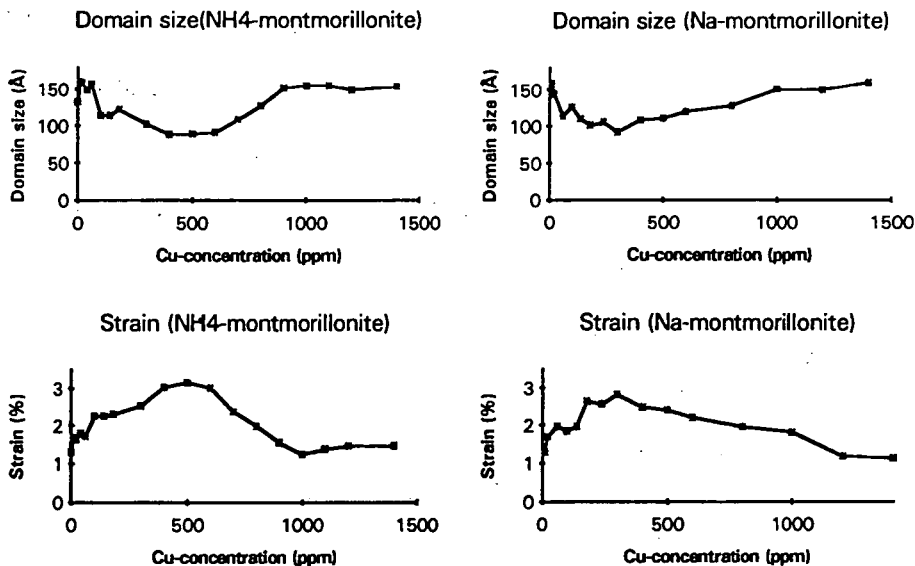


Fig. 7. Changes in domain size and deformation /in the direction of Na- and NH_4 -montmorillonites treated with CuSO_4 -solution

CONCLUSION

SmC indices of monoionic montmorillonites treated by CuSO₄-solution are good indicators describe the intercalation process (during adsorption). Correlation between formation of a quasi ordered structure form a disordered (amorphous) structure and half-width changes (increase and decrease) can be well detected particularly in case of NH₄-montmorillonite. Tendency is similar in case of Na-montmorillonite, but changes are not so considerable. The determination of the two parameters (domain size and lattice strain) influencing half-width gives further opportunity to specify results. When SmC indices do not change significantly, the values of domain sizes and strain show considerable differences. Therefore, the knowledge of these parameters may promote the interpretation of sorptional processes.

TABLE 3

Domain sizes and deformation of Na- and NH₄-montmorillonites

NH ₄ -form				Na-form			
Cu-conc. (ppm)	Half-width (degree)	Domain size (Å)	Strain (%)	Cu-conc. (ppm)	Half-width (degree)	Domain size (Å)	Strain (%)
0	0.7665	132	1.31	0	0.9089	131	2.06
10	0.7337	160	1.68	10	0.9527	159	1.29
20	0.7446	159	1.63	20	0.9308	145	1.69
40	0.7665	149	1.79				
60	0.7446	157	1.72	60	1.2593	114	1.96
100	0.7775	114	2.25	100	1.3031	126	1.84
140	0.8541	114	2.25	140	1.2264	110	1.96
180	0.8979	122	2.29	180	1.2921	101	2.63
				240	1.2264	105	2.56
300	0.9855	102	2.53	300	1.4717	92	2.82
400	1.1388	88	3.02	400	1.1957	108	2.48
500	1.7082	89	3.16	500	1.3469	111	2.39
600	1.7958	91	3.01	600	1.2264	120	2.19
700	1.5002	108	2.37				
800	0.9855	127	1.98	800	1.2045	128	1.95
900	0.9855	152	1.55				
1000	0.9636	155	1.25	1000	1.1826	151	1.81
1100	0.9855	155	1.38				
1200	0.9198	149	1.47	1200	1.314	150	1.18
1400	0.9417	154	1.48	1400	1.1826	160	1.13

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REFERENCES

- ÁRKAI, P. and TÓTH, M. N. (1983): Illite crystallinity: combined effects of domain size and lattice distortion; *Acta Geol. Hung.* **26**, 341–358.
- ÁRKAI, P. and TÓTH, M. N. (1985): The Variance Method Investigation of Illite Crystallinity; 5th Meeting of the European Clay Groups, Prague, p. 91–98, Charles University, Prague.
- ÁRKAI, P.–MERRIMAN, R. J.–ROBERTS, B.–PEACOR, D. R.–TÓTH, M. (1996): *Eur. J. Miner.*, **8**. (in press)
- FARRAH H. and PICKERING W. F. (1976): The Sorption of Copper Species by Clays. II. Illite and Montmorillonite; *Aust. J. Chem.*, **29**, 1177–84.
- GARCIA-MIRAGAYA, J.–CARDENAS, R.–PAGE, A. L. (1986): Surface loading effect on Cd and Zn sorption by kaolinite and montmorillonite from low concentration solutions; *Clays and Clay Minerals* Vol 34, No. 2, 181–187.
- KLUG, H. P. and ALEXANDER, L. E. (1974): *X-ray Diffraction Procedures (For Polycrystalline and Amorphous Materials)*; John Wiley & Sons, Inc.
- KOPPELMAN, M. H. and DILLARD, J. G. (1977): A study of the adsorption of Ni(II) and Cu(II) by clay minerals; *Clays and Clay Minerals* **25**, 457–462.
- LANGFORD, J. I. (1978): A rapid method for analysing the breadths of diffraction and spectral lines using the Voigt function; *J. Appl. Cryst.* **11**, 10–14.
- MACEWAN, D. M. C. and WILSON, M. J. (1980): Interlayer and Intercalation Complexes of Clay Minerals: in *Crystal Structures of Clay Minerals and their X-ray Identification*; in G. W. BRIDLEY–G. BROWN eds. *Crystal Structures of Clay Minerals and their X-ray Identification*; Monograph No. 5, Mineralogical Society, London 202–211.
- POSNER, A. M. and QUIRK, J. P. (1964): Changes in basal spacing of montmorillonite in electrolyte solutions; *Journal of Colloid Science* **19**, 782–812.
- PULS, R. W. and BOHN, H. L. (1988): Sorption of Cd, Ni and Zn by kaolinite and montmorillonite suspensions; *Soil. Sci. Soc. Am. J.* **52**, 1289–1292.
- SPOSITO, G. (1984): *The Surface Chemistry of Soils*; Oxford University Press, Oxford.
- STADLER, M. and SCHINDLER, P. W. (1993): Modeling of H⁺ and Cu²⁺ adsorption on Calcium-montmorillonite; *Clays and Clay Minerals*, Vol. 41, No. 3, 288–296.
- TOKARZ, M. and SHABTAI, J. (1985): Cross-linked smectites. IV. Preparation and properties of hydroxylaluminium-pillared Ce- and La-montmorillonites and fluorinated NH₄⁺-montmorillonite; *Clays and Clay Minerals*, Vol. 33, No. 2, 89–98.
- TÓTH, M. N. (1980): X-ray variance method to determine the domain size and lattice distortion of ground kaolinite samples. – *Acta Miner. Petrogr. Szeged*, **24**: 115–119.
- WILSON, A. J. C. (1963): *Mathematical theory of X-ray powder diffractometry*. – Eindhoven, Philips technical Library.

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