

## MINERALOGICAL AND CRYSTAL CHEMICAL ASPECTS OF METAL ION ADSORPTION ON MONTMORILLONITES

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The adsorption of copper, zinc, lead, cadmium, cobalt and nickel ions on four montmorillonites SWy-2, Istenmezeje (Hungary), Oraşu Nou and Valea Chioarului (Romania), with slightly different mineralogy, layer charge, cation exchange capacity, chemical composition and morphology was studied by X-ray diffraction (XRD) and analytical transmission electron microscopy (ATEM). The aim of this study was to reveal the effect of individual, intrinsic features of montmorillonites on the metal ion adsorption and their changes in metal ion adsorbed state.

The adsorption capacity of the studied montmorillonite samples is 0.35–0.4 mol/kg for copper, zinc, lead and cadmium and about the half for cobalt and nickel. Basically the metal ion adsorption of the four samples is determined by the layer charge and the cation exchange capacity of the montmorillonite. The amounts of absorbed cadmium, cobalt, lead, and zinc increase with these two crystal chemical parameters. The copper adsorption is independent from the layer charge; nickel adsorption has inverse relationship. When all these ions are present in the solution in 1000 mg/l concentration, the order of selectivity is the following: Cu > Co > Ni > Zn = Pb = Cd.

Based on ATEM studies montmorillonite crystallites contain 0.5–1.0 atomic percentage metal ions that exceeds slightly the interlayer sodium content of the starting montmorillonites. The decreasing sodium content of montmorillonites with increasing metal ion adsorption supports that the adsorption process basically is going on by ion exchange. Moreover other structural ions for example aluminium may be also removed during adsorption. ATEM measurements strengthened the fact that the role of other mineral impurities present in the montmorillonite samples in the adsorption processes—with some exception—have low importance. The amorphous SiO<sub>2</sub>—as a common phase associated with mont-

morillonites—does not take part in adsorption of heavy metals except nickel and cadmium.

If water vapour content is controlled, the basal spacing of metal montmorillonites is influenced by the species and concentration of the metal ion, and the pH. If all the adsorption sites are full with metal ions, the basal spacing of the copper and lead montmorillonites is 12.5 Å indicating one water layer in the interlayer space. In case of zinc, cadmium, cobalt, and nickel montmorillonites the basal spacing is 14–15 Å, i.e. two water layers in the interlayer space.

Based on XRD analysis the domain size of the adsorbed montmorillonite slightly decreased first, than increased remarkably till 20–40 layers with increasing metal ion concentration of the solution. It suggests that at small metal ion concentrations the crystallites disintegrate and at high metal ion concentration they are restructured. The electron diffraction patterns of the studied montmorillonites remain ring-like, therefore the increase in domain size is not followed by the increase of the three-dimensional structural order of the turbostratic structure.

Except cadmium, metal ions reduced the swelling capacity of the montmorillonites upon glycerol solvation especially the ones having low layer charge. Layer charge studies with alkylammonium method proved that metal ion adsorption reduced the layer charge. Some montmorillonite layers with low layer charge and heterogeneous layer charge distribution may loose all their layer charge due to the small sized metal ions entering the 2:1 silicate structure and causing the partial reduction of swelling capacity. Upon 250°C heat treatment copper and nickel enter the hexagonal cavities or the octahedral vacancies of the silicate lattice (Hofmann-Klemen effect). Cd<sup>2+</sup> ion does not cause reduction of the swelling capacity because it can not enter into the 2:1 silicate lattice due to its large size.