

NANO AND MICRO PARTICLES ON BENTONITE CLAY

NAGY, N. M., KÓNYA, J.

Isotope Laboratory, University of Debrecen [Izotóp Laboratórium, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary
E-mail: noemi@tigris.klte.hu

Clay minerals are important constituents of the natural environment. By their interfacial reactions they play an important role in several fields, for example in the nutrient cycle of soils, in the environmental protection, or even in the synthetic chemical industry. One of the interfacial reactions of clay minerals is the adsorption and cation exchange of metal ion.

Metal ions can be adsorbed in the interlayer space of some clay minerals (e.g. montmorillonite) and on the pH-dependent charges, silanol and aluminol sites, on the edges of clay minerals. The ratio of the two ways of cation adsorption depends on pH, but about 80–90% of the cation adsorption comes from the neutralisation of the layer charges, so this way of cation adsorption is determining.

The nature of the adsorption is different: in the interlayer space electrostatic forces are important; the ratio of charge and the cation size determine the adsorption ability. Cations in the interlayer space have their hydrate sphere. This process is the so-called outer-sphere complexation. On the edge charges the chemical properties of the metal ions are significant. The cations adsorb on the edge charges by oxygen–cation bonds, without hydrate sphere. This process is called inner-sphere complexation.

Both ways of cation adsorption primarily lead to the uniform distribution of metal ions on atomic scale. However, additional processes can be resulted in the formation of nano and micro particles in the interlayer space as well as on the outer surfaces. Nano and micro particles on clays have been produced by different chemical procedures, but they can be formed under environmental conditions. In this paper the formation of nano and micro particles on clay minerals under environmental conditions are discussed in metal ions—manganese, lead, zinc, and silver ions—and bentonite systems. A really natural micro particle on clay sediment is also shown.

Manganese(II) ions adsorbed in the interlayer space of montmorillonite by cation exchange reactions are spontaneously oxidised to manganese(IV) under atmospheric conditions. Consequently, the properties relating the oxidation state of manganese are different for the fresh and old manganese-bentonite samples. The concentration, distribution of manganese as well as the structure of bentonite, however, do not

change. The increase of the positive charge of manganese demands the neutralisation of the extra positive charge by oxide or hydroxide ions originated from the atmosphere, because the negative layer charge of the clay minerals is constant. The presence of a 2D layer of manganese in the interlayer space of montmorillonite is obvious because the montmorillonite has layered structure and manganese ions are introduced into the interlayer space by cation exchange. For this reason the distribution of manganese ions is uniform (as seen by scanning electron microscope, too) and it does not change under oxidation.

These results show that a two-dimensional nano layer is formed in the interlayer space where manganese ion is bonded to the clay layers by two positive charges and to oxides or hydroxides by the other two positive charges.

Lead ions are adsorbed on clays by two processes: by cation exchange in the interlayer space of montmorillonite and by adsorption on the edge sites. Cation exchange leads to the even distribution of the ions, while the adsorption on the edge sites can act as the initial of a heterogeneous nucleation on particle surface followed by a crystal growth. The nano and micro particles (lead enrichments) seen by SEM and AFM can likely be formed on these nuclei. The production of these particles is not expected from thermodynamic properties under conditions of the bulk solution. Similar micro particles are formed on clay sediments under environmental conditions.

Similar micro particles are observed in the case of zinc ion and silver ion. In case of silver-montmorillonite the reduction of silver(I) to metallic silver can also be observed.

As a conclusion we can say that beside the usual ion adsorption reactions, nano and micro particles can also be formed in the interlayer space as well as on the surface of clay minerals. These particles can be two- (2D) or three-dimensional (3D). Two-dimensional nano layer is formed in the interlayer space of montmorillonite by the spontaneous oxidation of manganese ions under atmospheric conditions. Three-dimensional particles are formed on the surfaces of clay minerals initiated by the metal ion (for example lead or zinc ions) adsorption on the deprotonated edge sites. The formation of micro particles on the surface can also be followed by the redox reaction of the metal ion (e.g. reduction of silver ion).