

STRUCTURE CHANGES OF LANTHANIDE (LN)-BENTONITES

KOVÁCS, E. M., KÓNYA, J. & M. NAGY, N.

Imre Lajos Isotope Laboratory, Department of Physical Chemistry, University of Debrecen, Debrecen, Hungary

E-mail: kovacs.eszter.maria@science.unideb.hu

In this work, the structure of lanthanide-bentonites was analyzed for nuclear waste treatment, and environmental protection purposed by several analytical methods. The main mineral of the bentonite is montmorillonite, which has a permanent negative charge. The negative charge is neutralized by cations attracted to the interlayer space where cation exchange takes place and sometimes modifies the properties of the bentonite. The natural interlayer cations may be exchanged by Lns. The importance of lanthanide ions is that they are model interactions between soil and transuranium ions, furthermore, lanthanide cations are produced during the fission of ^{235}U in nuclear power plants.

Ln-exchanged bentonites were prepared from Ca-bentonite by ion exchange procedure from Ln-perchlorate solution. To prove the successful modification, scanning electron microscopy, energy-dispersive X-ray analysis (SEM-EDX) was used showing distribution of Ln's and other components of bentonite. The natural bentonite and the lanthanide exchanged bentonites were characterized by X-ray diffraction (XRD), which revealed the same mineral composition, and the increase of the basal spacing of montmorillonite. The amount of Ca^{2+} , Fe^{3+} , and Ln^{3+} on the bentonite were determined by X-ray-fluorescence spectrometry (XRF). In most Ln-bentonites, the quantity of the exchanged Ln ions was about 80–90% of the cation exchange capacity (CEC) of the bentonite. For some lanthanide bentonite (Y^{3+} , La^{3+} , Ce^{3+} , and Gd^{3+}), the sorbed quantity of lanthanide ions was higher than the cation exchange capacity. Moreover, the iron(III) content of lanthanide bentonite was less than that of the original Ca-bentonite (KOVÁCS *et al.*, 2017).

The observation is that lanthanide ions can somehow supersede iron from the octahedral positions of crystal lattice. We assume that the departure of positively charged iron ions from the lattice increases the negative layer charge and the cation exchange capacity. This can motivate the enhance sorption of lanthanides.

To prove our previous statement, we examined how the pH and the concentration influences the bentonite structure without and with Lns. Ca-H, Ca-Y and Ca-La cation exchange were carried out. The results revealed that the pH had high influence during the Ca-H cation exchange procedure. The more acidic solution, the more calcium was exchanged. In this case, iron loss was not observed. In the case of Ca-Y, La cation exchange

procedure, the pH has low influence, meanwhile the concentration has higher influence to high amount of iron loss during divalent-trivalent cation exchange. Thus, the high amount of trivalent lanthanides cause the structural iron release (KOVÁCS *et al.*, 2019).

Furthermore, the concentration of lanthanide, calcium and iron ions undergoes a three-step change during the kinetic study of lanthanide ion sorption. We assumed that beside the bivalent-trivalent cation exchange, diffusion of the iron ion from the octahedral layer would be started from the first moment, due to the high concentration of the lanthanide ions. It also depends on the temperature, but the pH has only a slight influence on the three-step process.

A strong evidence detected by X-ray photoelectron spectroscopy (XPS) measurement that the bentonite is capable of such a big structural change in the presence of lanthanide ions. The increase of the negative layer charge of the Ln-bentonites can be confirmed by XPS since the positive or negative correlations between the Si 2s (2p), Al 2p and O 1s photoelectron binding energies refer to the silicate structure (SEYAMA & SOMA, 1984, 1985, 1988). The value of the photoelectron binding energies decreases with the increase in the negative layer charge of the silicate. Due to the over-sorption of the lanthanide ions and the decrease in iron content, the decrease of the binding energies is measured which is supported our statement.

References

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