STUDY OF THE CHANGE IN THE PROPERTIES OF Mn-BENTONITE BY AGEING

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Clay minerals play a very important role in nature, since they have ability of adsorption and ion exchange. The replacement of the octahedral Al^{3+} by Fe^{2+}, Mg^{2+}, and that of the tetrahedral Si(IV) by Al^{3+} results in negatively charged layers. It is neutralised by the intercalation of exchangeable hydrated cations. There are lots of papers dealing with the structure, properties and reactions of cation exchanged clay minerals. Though many works deal with the reaction of manganese and clays, as far as we know, no work dealt with the ageing of Mn(II)-montmorillonite. The change of the oxidation state of manganese compounds (that is the effect of ageing) was investigated by some workers, but clay minerals were not involved.

Some clays can adsorb different organic substances in the interlayer space, and can catalyse various organic syntheses. Therefore it is very important to study in what extent various cation exchanged montmorillonites can adsorb organic substances. The adsorption of valine on calcium-, copper-, zinc-montmorillonite and montmorillonite KSF was investigated by Nagy and Kónya (2004).

In this work the structure and properties of fresh manganese(II)-bentonite was compared with that of an old substance. It was concluded that the oxidation state of Mn changed during the years. This did not cause many changes in the scanning electron microscope (SEM) and in the X-ray diffraction (XRD) studies; caused minor changes in the Mn-concentration (determined by XRF), thermoanalytical and electron spectroscopy analysis (ESCA). The change in the oxidation state of manganese was highly indicated by the colours of the samples (fresh had a light colour, while the old one was dark brown), the difference in the surface sites, titration curves, redox potentials, adsorption and catalytic activity of the fresh and the old Mn-bentonite. Potentiometric titration data were evaluated by surface complexation model (Davis et al., 1978) using FITEQL3.2 program (Herbelin and Westall, 1996). Stability constants of edge charge reactions, the number of aluminol, silanol and edge sites (X^-) were calculated, and shown in the table below. Potentiometric titration data of commercial and freshly made MnO_2 were also evaluated; the calculated constants and site numbers were compared with that of found in literature. Catalytic and adsorption activity of the samples were also investigated. It was found that fresh Mn-bentonite does not adsorb valine, while the old one and MnO_2 does. Fresh Mn-bentonite does not catalyse the decomposition of H_2O_2, while the old one as well as MnO_2 does.

References

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Table 1:

	Fresh Mn-bentonite	Old Mn-bentonite	Commercial MnO_2	Fresh MnO_2
logK ($AlOH + H^+ \Leftrightarrow AlOH_2^+$)	7.365	8.092	–	–
logK ($AlOH - H^+ \Leftrightarrow AlO^-$)	–7.184	–8.165	–	–
logK ($SiOH - H^+ \Leftrightarrow SiO^-$)	–5.086	–7.065	–	–
logK ($MnOH + H^+ \Leftrightarrow MnOH_2^+$)	–	4.581	4.266	2.629
logK ($MnOH - H^+ \Leftrightarrow MnO^-$)	–	–7.447	–6.387	–3.331
[MnOH]$_{total}$ (mol/g)	–	$2.69E^{-3}$	$5.193E^{-4}$	$3.49E^{-3}$
[AlOH]$_{total}$ (mol/g)	$2.72E^{-4}$	$1.06E^{-4}$	–	–
[SiOH]$_{total}$ (mol/g)	$2.32E^{-3}$	$1.804E^{-4}$	–	–
[X^-]$_{total}$ (mol/g)	$1.04E^{-3}$	$2.643E^{-4}$	–	–