
Properties of Reduced Charge Montmorillonites: Hydrated Cu(II) Ions as a Spectroscopic Probe*

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Abstract: A series of Cu(II) reduced charge montmorillonites (RCM) of varying charge reduction has been prepared by exchange of the parent Li(I)-Na(I) mineral with CuCl_2 in 95 per cent ethanol solution. The Cu(II) exchange capacity, as determined by Na(I) exchange in 1:1 (v/v) ethanol-water, is a linear function of the fraction of Li(I) initially present on the exchange sites, F . Selective Cu(II)-saturation on internal and external sites was achieved at maximum charge reduction ($F = 1 \cdot 0$). Water sorption isotherms and (001) basal spacings are interpreted in terms of an increasing tendency toward interlayer collapse with increasing charge reduction. Because of the higher hydration energy of the Cu(II) ion, however, the fraction of non-expandible interlayers at a given F value is lower than those present in the corresponding Li(I)-Na(I) RCM. Electron spin resonance spectra of oriented samples show that under air-dried conditions (*ca.* 40 per cent r.h.) the predominant Cu(II) species present, whether on internal or external sites, is the planar $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ion. The symmetry axis of the ion is oriented perpendicular to the a - b plane of the silicate sheets. In the presence of a full partial pressure of water, the Cu(II) ions on the external sites and those which are in expandible interlayers become totally hydrated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and tumble rapidly. The $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ions in non-expandible layers retain their restricted orientation on the silicate surface. Some general conclusions have been drawn regarding the nature of charge distribution in the mineral.

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