Effects of Iron Oxidation State and Organic Cations on Dioctahedral Smectite Hydration

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Abstract: Reduction of structural Fe in Na-exchanged dioctahedral smectites decreases swellability in water, but because clay interlayers also collapse in the process the concomitant effect on surface hydration energy is uncertain. This study examined the hydration behavior of oxidized and reduced dioctahedral smectite clays exchanged with polar (Na) and weakly-polar (organic) cations to determine the nature of the surface before and after Fe reduction, and to determine if clay surfaces are hydrophilic or hydrophobic. The H_2O content in various dioctahedral smectites decreased if Na was replaced by tetramethylammonium (TMA), trimethylphenylammonium (TMPA), or hexadecyltrimethylammonium (HDTMA). Among the organo-clays, H_2O adsorption decreased with increasing complexity of the cation. For oxidized smectites, those exchanged with TMPA retained less H_2O than those exchanged with Na at all pressures. The extent of this difference depended on the clay and decreased with increasing applied pressure. Reduction of Fe(III) to Fe(II) in the octahedral sheets decreased the swelling of Na-saturated smectites, apparently causing some previously swelling interlayers to collapse. If the Na interlayer cation was exchanged to alkylammonium after reduction, but prior to swelling-pressure measurements, the swelling increased or remained near constant, suggesting that the organo-cation disrupted the collapse process of the interlayers associated with the reduced smectite layers. Reduced TMPA-saturated smectite surfaces are more strongly hydrated if the octahedral sheet is reduced than if oxidized. Thus, reduction of structural Fe increases the hydration energy of smectite basal surfaces, but swellability could decrease or increase depending on the extent of interlayer collapse occurring with different exchangeable cations.

Key Words: Alkylammonium • Ferric Iron • Ferrous Iron • HDTMA • Hydrophilic Surface • Hydrophobic Surface • Interlayer Cation • Oxidation • Reduction • Surface Hydration • Swelling • TMA • TMPA

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