Surface Area of Montmorillonite from the Dynamic Sorption of Nitrogen and Carbon Dioxide

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Abstract: Surface area determinations were made on a montmorillonite with various cations emplaced on the exchangeable sites, utilizing nitrogen and carbon dioxide as adsorbates at 77 ° K and 195 ° K, respectively, in a dynamic system. From the fraction of a Mississippi montmorillonite less than about 1 μ in size, samples were prepared by replacing the original exchangeable cations with Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{++}, Ca^{++}, Ba^{++}, and NH_4^+, forming a series of homoionic montmorillonite species.

Surface areas from 3-point B.E.T. plots (half-hour adsorption points), with nitrogen as the adsorbate, ranged from 61 $m^{2/}$/g for Li-montmorillonite to 138 m^2/g for Cs-montmorillonite, thus reflecting a certain degree of nitrogen penetration between layers. Complete penetration should theoretically result in a surface area of over 300 m^2/g for this clay with a nitrogen monolayer between each pair of platelets. The experimental data indicate that the extent of penetration is time-dependent and is also a function of the interlayer forces as governed by the size and charge of the replaceable cation. This finding negates the generally accepted concept that nitrogen at 77 ° K does not penetrate the layers and provides a measure only of the external surface of expandable clay minerals.

A further measure of the variation of interlayer forces is provided by the adsorption of carbon dioxide at 195 ° K. Surface area values ranged from 99 m^2/g for Li-montmorillonite to 315 m^2/g for Cs-montmorillonite. Although the carbon dioxide molecule is larger than the nitrogen molecule, its greater penetration apparently is a result of its being kinetically more energetic (with a larger diffusion coefficient) at its higher adsorption temperature. Similar differences have been found with both adsorbates in the study of microporous substances, such as coal, where activated diffusion is of considerable significance.

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