

COMMUNICATIONS TO THE EDITOR

A COMPARISON OF SORPTION CHARACTERISTICS OF SOME MINERALS HAVING A LAYER STRUCTURE

Sir:

The report by Young and Healey¹ showing that unactivated chrysotile adsorbed approximately twice as much water as nitrogen, expressed in units of surface area, is of interest to the science and technology of some minerals possessing a layer structure. It has recently been reported² that the mineral tobermorite ($4\text{CaO} \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$) the probable binder of autoclaved concrete block, also adsorbed approximately twice as much water as nitrogen. Because tobermorite has a layer structure the large adsorption of water compared to that of nitrogen became of interest regarding the drying shrinkage of concrete. Theoretical considerations indicate that the shrinkage is not a capillary phenomenon. Bernal³ suggested that tobermorite may undergo the swelling-shrinkage changes similarly as do some clays which also have a layer structure. Such volume changes in clays are easily demonstrated by X-ray results on clays before and after drying. A similar hypothesis on concrete shrinkage was studied in these laboratories but it could not be demonstrated² that the water involved in volume change was inter-layer water. X-Ray results obtained subsequently⁴ show that phases closely related to tobermorite may undergo significant structural changes during in-vacuum drying and subsequent re-saturation, but it has not yet been shown how such structural changes may be due to the movement of water or what effect they produce on the properties of concrete.

The present comments are being presented because similar sorption results on minerals having the layer structure have been interpreted differently by the writer, and Young and Healey. The sorption behavior of tobermorite (and antigorite as mentioned by these authors) shows that a portion of the water is accommodated differently than is nitrogen. Because these minerals generally occur as flat plate-like crystals explanations based on capillary phenomenon do not apply.

Young and Healey pointed out that chrysotile occurs in the form of capillaries having a bore of approximately 150 Å. and a diameter of about 350 Å. They postulate formation of water plugs at the ends of the capillaries which are permeable to polar substances, water and ammonia, but not to non-polar adsorbents as nitrogen. The water

required to fill the pores would account for the much larger sorption of water than nitrogen.

Results on properties of chrysotile and antigorite components of serpentine, now being prepared for publication, included density measurements on several kinds of chrysotile in form of relatively large "bundles" of fiber and also in highly micro-nized form; the samples were tested as received. Water and carbon tetrachloride were used as immersion media. The density results were the same within limit of experimental error for both media and regardless of the degree of subdivision of the fiber. The spread in values amounted to about 2% but generally the differences were less than 1%. If the ends of the capillaries were plugged with water, the density results obtained with carbon tetrachloride, a non-polar medium, would be approximately 15 to 20% lower than in water. These results, and others on the crystal habits of antigorite and chrysotile which will be submitted for publication, suggest that water plugs probably do not form in the tube-shaped crystals of chrysotile.

Antigorite and chrysotile are either the same in compositions and atomic structure or very closely related. It would seem, therefore, that the sorption characteristic should be the same for both. The mechanism of adsorption-desorption of these two minerals may be the same as that for tobermorite, presumably that of movement of structural water. As mentioned, however, this hypothesis remains to be resolved experimentally. It would appear that careful studies on sorption characteristics and surface energy changes such as those being conducted at the Surface Chemistry Laboratories at Lehigh University, should provide an unequivocal proof on the manner in which the excess water is adsorbed by the layer structure minerals. Such basic information will be of great help to concrete technology, to mention only one field of application.

OWENS-ILLINOIS COMPANY
1700 NORTH WESTWOOD
TOLEDO, OHIO

G. L. KALOUSEK

RECEIVED JANUARY 27, 1955

FORMATION OF DIBORANE DURING THE SLOW OXIDATION OF PENTABORANE

Sir:

When dry air was admitted slowly to a gas absorption cell containing pure pentaborane at 25° and a pressure of 50 mm., partial oxidation took place and diborane, hydrogen and a white solid were formed. The reaction was conducted in a cell 10 cm. in length, with a volume of 150 ml. Absorption measurements were made with a Perkin-Elmer Model 21 double-beam infrared recording spectrometer. The progressive disappearance of pentaborane and the simultaneous accumulation of diborane were followed by infra-

(1) G. J. Young and F. H. Healey, *THIS JOURNAL*, **58**, 881-884 (1954).

(2) G. L. Kalousek, *J. Amer. Concr. Institute*, **26**, 233-248 (1953).

(3) J. D. Bernal, "Structures of Cement Hydration Compounds," *Proc. 3rd International Symp. on Chemistry of Cements*, p. 216-236 (1952).

(4) G. L. Kalousek, "Tobermorite and Related Phases in the System $\text{CaO-SiO}_2\text{-H}_2\text{O}$," *J. Amer. Concr. Institute*, accepted for publication.