Miscellaneous Papers

PHOSPHATE FIXATION BY KAOLINITE AND OTHER CLAYS AS AFFECTED BY pH, PHOSPHATE CONCENTRATION, AND TIME OF CONTACT

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THE clay fraction of soils has long been known to be the most active portion so far as phosphate fixation is concerned. Until recently, the fixing power of the clay fraction was attributed to reactions of phosphate with iron and aluminum, present as exchangeable cations, as hydrous oxides, or in solution, and to reactions with calcium.

The work of Murphy (6) indicated that kaolinite is also very active in phosphate fixation under certain conditions. His data showed that the fixation is at a maximum in a strongly acid solution and rapidly decreases as the reaction is adjusted towards neutrality or alkalinity. Experiments of Stout (10) led to the conclusion that the fixation by kaolinite is a reversible anion exchange involving phosphate and the hydroxyl groups exposed on the surface of kaolinite lattice layers. The results of later investigations (1, 2) suggested that not all the phosphate fixation is confined to the replacement of hydroxyl groups on the surface of the clay particles, but that in addition some of the phosphate penetrates between the lattice layers and replaces hydroxyl groups inside the particles. While the original work showed this process to take place at pH 3, later experiments have shown the same type of results (but to a lesser degree) at pH 7.

The strong fixation by finely ground kaolinite at low pH values led Burd and Murphy (4) to believe that if dilute acids were used to extract phosphate from kaolinitic soils, considerable amounts of the dissolved phosphate would be “adsorbed” by the kaolinite and would not appear in the extract. Stelly’s pH-solubility curve for the native phosphate in kaolinite, however, showed that the solubility was at a minimum over the pH range of approximately 5 to 7. More phosphate was removed by solutions more acid or more alkaline than this pH range. The phosphate solubility curve for kaolinite to which a small amount of soluble phosphate had been added was similar to that for the native phosphate. These results indicate that the effect suggested by Burd and Murphy (4) is not always important. The data indicate further that the phosphate as well as the native phosphate is held by the replacement of clay hydroxyl ions in a particular sample of kaolinite used.

Thus, it appears that under some conditions, the fixation of phosphate by hydroxyl replacement may not take place to the extent indicated by the experiments of Murphy (6). Because of the apparently contradictory results obtained under different conditions, further work seemed desirable to obtain a more complete picture of the conditions under which phosphate reacts with kaolinite and of the importance of this fixation relative to that by other mechanisms. The experiments reported in this paper are intended to provide information on these points. The plan was to determine the influence of pH and phosphate concentration upon the phosphate fixation by various clays in equilibrium systems, to determine the amount of fixed phosphate held by the clays against water extraction, and to determine the ability to plants of phosphate added to the clay systems.

METHODS AND MATERIALS

The clays used in the experiments were prepared as follows: Kaolinite finer than 2μ effective diameter, from the stock sample by sedimentation, was treated to remove free iron oxides. This sample is designated as kaolinite No. 1. Finely ground kaolinite was prepared by grinding a portion of the stock sample in a ball mill for 10 days. The 2μ fraction of the Cecil clay soil was extracted, the organic matter was removed, and a portion was washed with 0.05 N HCl to remove free iron oxides. Exchangeable bases were removed from all samples. Details of the methods of preparation are previously published (1).

A second sample of kaolinite (kaolinite No. 2) was prepared by grinding a specimen of kaolinite to pass a 60-mesh sieve. A portion was left untreated, and the remainder was washed with 0.05 N HCl to remove exchangeable bases. Samples of hydrated halloysite (60-mesh) and 74