

# Reactions of Phosphoric Acid with Clay Minerals

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Commercial clays comprised of montmorillonite, vermiculite, illite, chlorite, or kaolinite were treated with various amounts of phosphoric acid in the presence of water. Progress of the reactions was checked by X-ray diffraction and chemical analyses performed at certain intervals. Lowering of treated clay mineral X-ray diffraction peak intensities was used for estimating the extent of the reaction, the early reaction products showing a characteristic amorphous halo. Chemical analyses were used for further characterization of the reactions.

● WHEN SOILS containing different clay minerals are stabilized with phosphoric acid, different strength characteristics are developed (1). Differences in strength characteristics were attributed to different responses of each class of clay mineral toward phosphoric acid. It was hypothesized that these responses were due to the differences in rapidity and extent of the chemical reactions that took place between clay minerals and phosphoric acid. Analysis of strength data utilizing this hypothesis leads to the conclusions that the reaction between chlorite and phosphoric acid was rapid and complete, the reaction between montmorillonite and phosphoric acid was rapid but incomplete, and the reaction between kaolinite and phosphoric acid and that between vermiculite and phosphoric acid were slow but continuous. These conclusions may leave the way open to some doubts inasmuch as they were not directly deduced and some of the soils contained more than one clay mineral in addition to the predominant clay mineral.

TABLE 1  
DESCRIPTION OF COMMERCIAL CLAY SAMPLES

Sample	Producer	Clay Mineral		Other Constituents	Fineness	Liquid Limit (%)
		Type	%			
Florida clay (Kaolin)	Edgar Plastic Kaolin Co , Edgar, Fla	Kaolinite	84	14% loss on ignition	100% finer than 44 $\mu$ 55% finer than 1 $\mu$	71.6
Volclay (Bentonite SVP)	American Colloid Co , Skokie, Ill	Montmorillonite	92-95	Feldspar	96% finer than 74 $\mu$ 86% finer than 0 5 $\mu$	524.6
Concentrated vermiculite ore	Zonolite Co , Chicago, Ill	Vermiculite	-	-	Wet ground and sieved through 325-mesh (44 $\mu$ ) screen	70 4
Prochlorite	Wards Natural Science Establishment, Inc , Rochester, N Y	Chlorite	-	-	Wet ground and sieved through 325-mesh (44 $\mu$ ) screen	32.7
Grundite	Illinois Clay Products Co , Chicago, Ill.	Illite	-	-	100% finer than 420 $\mu$ 75% finer than 5 $\mu$	55

The present study was undertaken to compare further the reactivities of various clay minerals with phosphoric acid. Commercially available monomineralic clays were treated with distilled water and phosphoric acid and the mixtures were analyzed at various intervals by X-ray diffraction. Changes in the height of major diffraction peaks of the clay mineral were used as an index of reactivity with phosphoric acid. At this point it must be emphasized that this technique cannot be used to predict the chemical mechanism of the complex heterogeneous clay mineral-phosphoric acid reaction or its extent in a thermodynamic sense. However, the results obtained can be compared with each other, and thus relative measures of reactivities with regard to the rapidity and the extent of reactions may be established, and they can also be compared with the previous conclusions obtained from the analysis of strength data.

### MATERIALS

The commercially available clays used are listed in Table 1. The phosphoric acid used was reagent grade, 86 percent orthophosphoric acid,  $H_3PO_4$ . All additives are expressed as percentages of pure (100 percent) phosphoric acid, based on the oven-dry weight of the soil. Distilled water was used to bring the clays up to liquid limit consistencies. The hydrochloric acid used to extract the reaction products was 2 Normal and was prepared from 36 percent reagent grade hydrochloric acid. The ammonium hydroxide used for precipitation was diluted reagent grade concentrated ammonia solution. Aluminum chloride used to obtain reference precipitates was reagent grade,  $AlCl_3 \cdot 6H_2O$ .

### METHODS OF PREPARING SAMPLES AND TESTING

Distilled water was mixed with clay samples to bring them to liquid limit consistencies. After addition of each increment of water and thorough mixing, consistencies

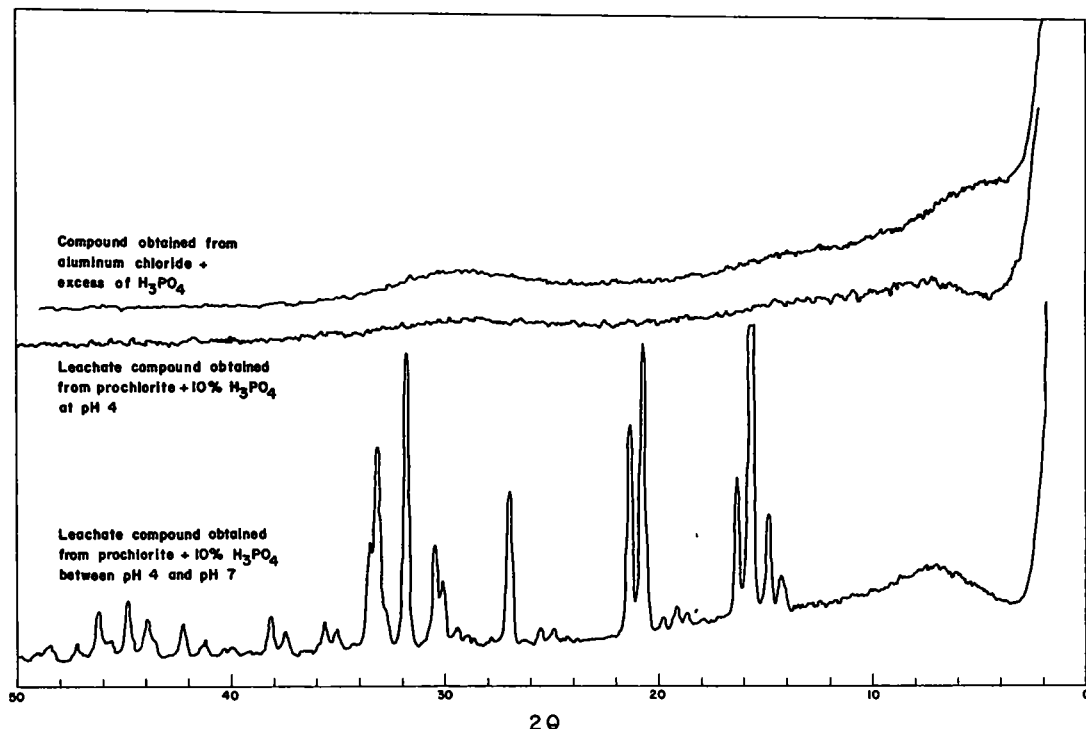


Figure 1. X-ray diffractometer charts of the precipitates.

of the mixtures were checked by a liquid limit device. When the liquid limits were reached, the mixtures were placed in polyethylene containers and tightly covered. Then from each clay-water mixture, samples corresponding to 10 g of oven-dry clay were taken and mixed with enough phosphoric acid to give the desired acid percentage. Mixing was done using a spatula for 20 min in a small polyethylene container. Imme-

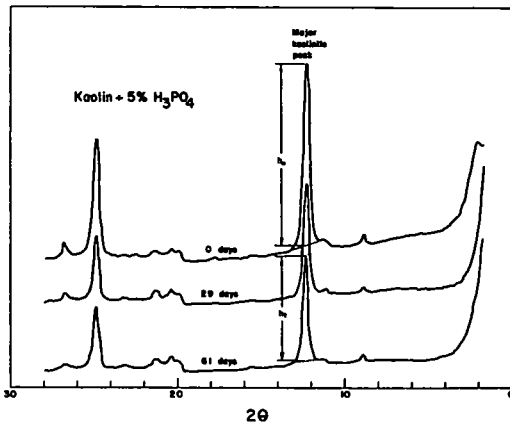


Figure 2. X-ray diffractometer chart showing changes in peak intensities of kaolin + 5 percent phosphoric acid mixture with time.

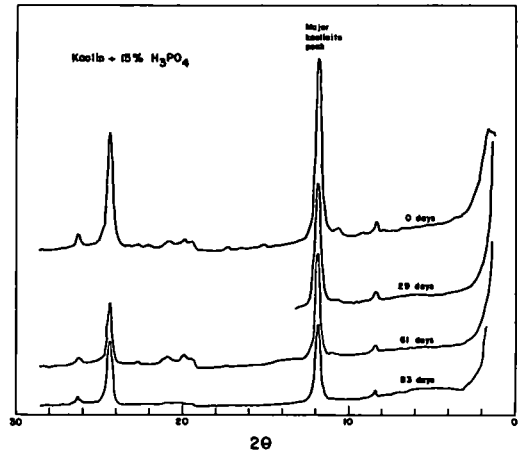


Figure 3. X-ray diffractometer chart showing changes in peak intensities of kaolin + 15 percent phosphoric acid mixture with time.

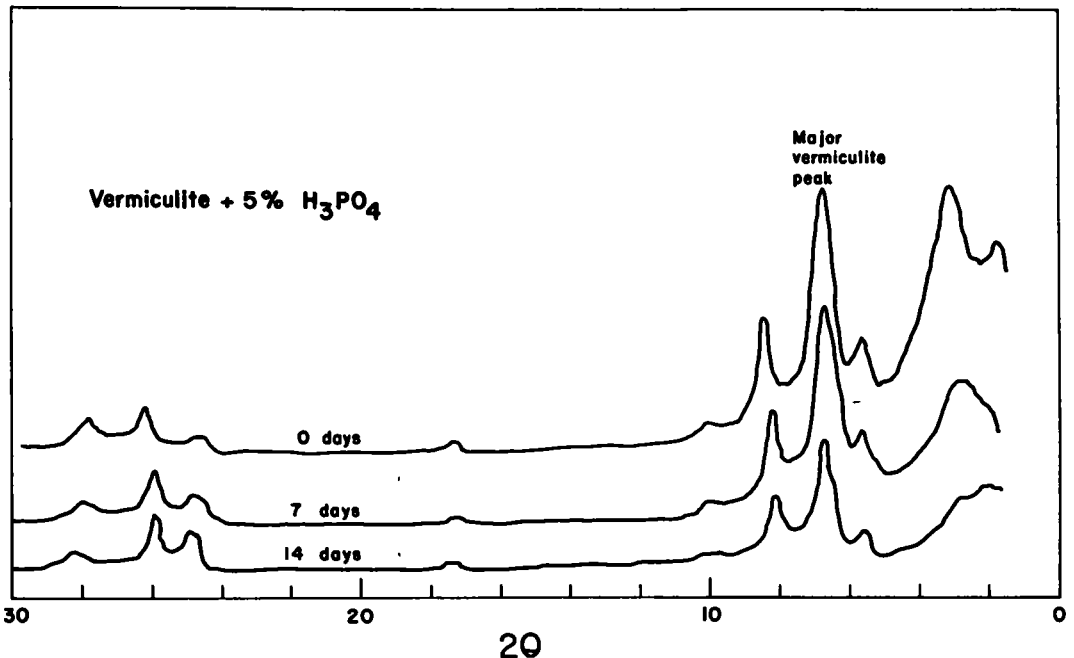


Figure 4. X-ray diffractometer chart showing changes in peak intensities of vermiculite + 5 percent phosphoric acid mixture with time.

diately after mixing, a slide was prepared from each mixture and analyzed by X-ray diffraction, using nickel-filtered copper radiation. Then the slide and the container with the clay-water-phosphoric acid mixture were placed in a chamber maintained at an average temperature of  $73 \pm 3$  F and 100 percent relative humidity. At intervals, X-ray diffraction analyses were repeated on the slides stored or on freshly prepared slides from clay-water-phosphoric acid mixtures stored. Some of the mixtures after a period of storage were extracted with 2N HCl and the extracts were titrated with dilute ammonium hydroxide to various pH values; the precipitates obtained were filtered and washed with distilled water. X-ray analysis was made on these precipitates along with the reference precipitate obtained from the titration of a mixture of aluminum chloride solution and an excess of phosphoric acid with dilute ammonium hydroxide.

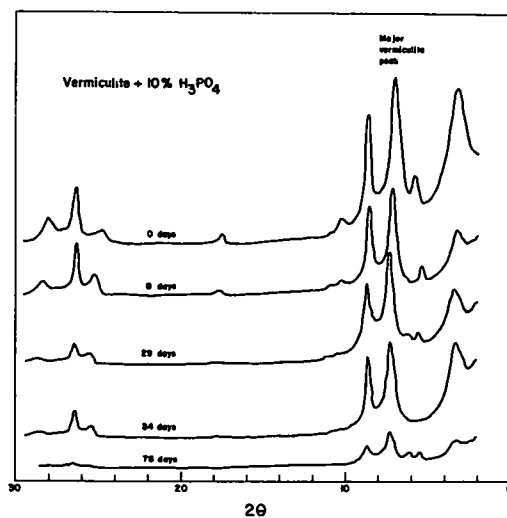


Figure 5. X-ray diffractometer chart showing changes in peak intensities of vermiculite + 10 percent phosphoric acid mixture with time.

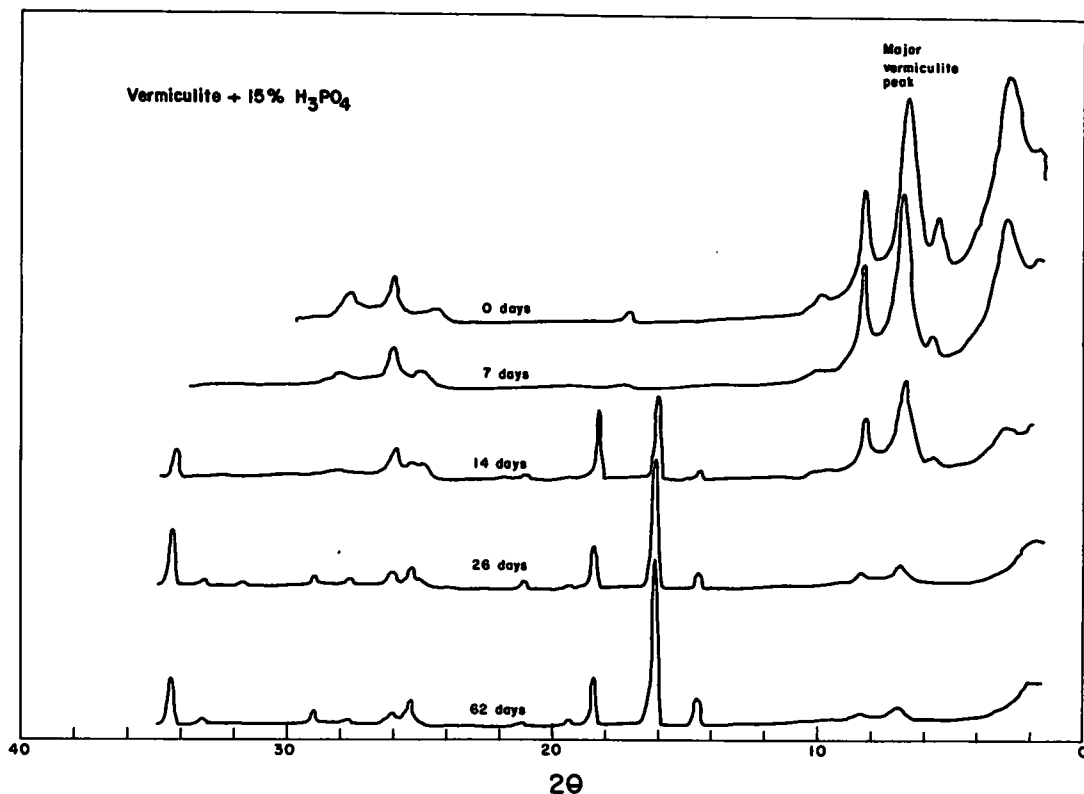


Figure 6. X-ray diffractometer chart showing changes in peak intensities of vermiculite + 15 percent phosphoric acid mixture with time.

## RESULTS

X-ray diffractometer charts of the precipitates for prochlorite treated with 10 percent phosphoric acid are given in Figure 1. The precipitate obtained from the HCl extract at pH 4 was amorphous and gave an X-ray diffraction chart similar to the one obtained by the reference precipitate. However, the precipitate obtained between pH 4 and 7 from the HCl extract of the prochlorite sample was crystalline (Fig. 1). The crystalline compound or compounds have not yet been identified. It is believed that these precipitates form in phosphoric acid-stabilized soils as the Ph rises upon curing. Lyons et al (2) showed that the pH of phosphoric acid-treated soils increases with age.

Amounts of phosphoric acid used were 5, 10, 15, and 40 percent with all clay samples except bentonite. Only 40 percent phosphoric acid was used with bentonite due to difficulties in mixing lower amounts at liquid limit consistency. Treated samples were analyzed by X-ray diffraction two to four times during the first week of their preparation; thereafter at periods of two weeks, one month, and four months after they had been prepared. A series of X-ray diffrac-

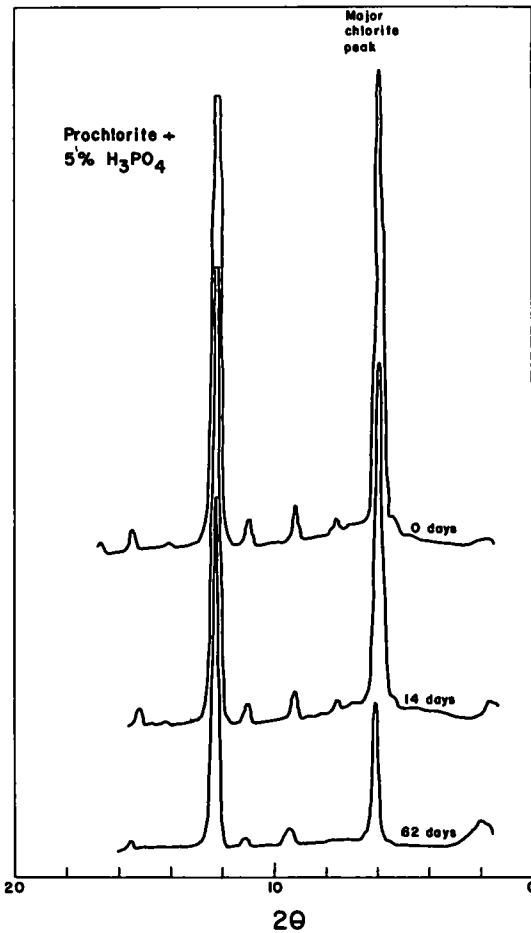


Figure 7. X-ray diffractometer chart showing changes in peak intensities of prochlorite + 5 percent phosphoric acid mixture with time.

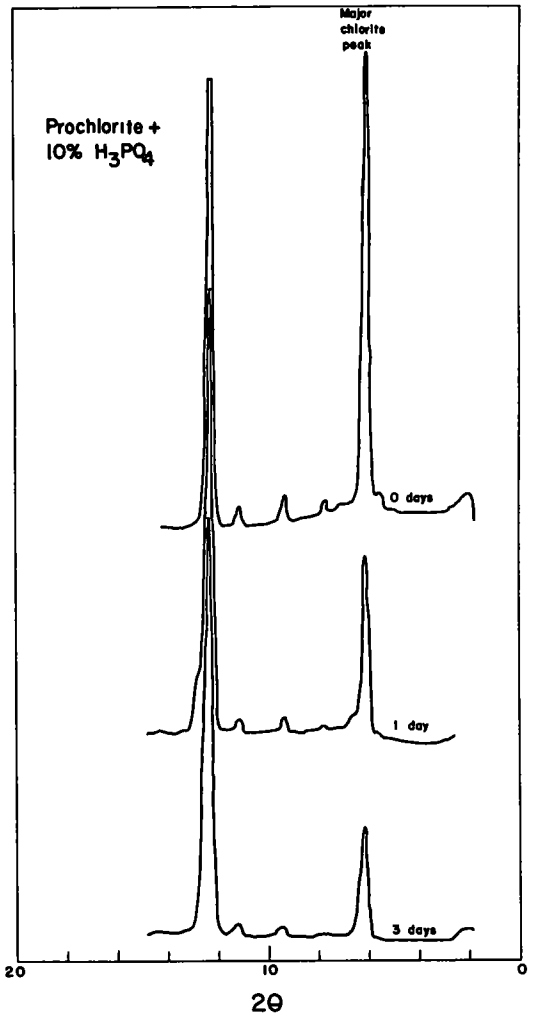


Figure 8. X-ray diffractometer chart showing changes in peak intensities of prochlorite + 10 percent phosphoric acid mixture with time.

tometer charts obtained are given in Figures 2 through 8. All of the diffraction peak intensities corresponding to various "d" spacings were lowered by the treatment. The major diffraction peaks of the clay minerals used for tracing the reactions are indicated in these figures. After each analysis, heights of the major peaks were measured as sketched in Figure 2 and plotted against time, as shown in Figure 9. From the curves of Figure 9, diffraction peak heights at certain intervals of time were read and each was divided by the original height also obtained from Figure 9 at zero time. This ratio is termed the "relative extent of reaction." Figure 10 is a plot of relative extent of the reactions against time. Rapid and extensive reactions are shown by chlorite and vermiculite clays. The reaction with kaolinite was rather slow and incomplete. Montmorillonite clay gave a rapid but incomplete reaction. Illite clay appeared to react slowly and continuously. Except for the conclusion reached for kaolinite and vermiculite, these results closely agree with the conclusions reached by the authors on analyzing the strength characteristics of phosphoric acid-stabilized soils. The disagreement concerning kaolinite and vermiculite is believed due to the presence of both of these minerals in the same soil investigated in the strength study (1). It is believed that their response toward phosphoric acid is masked by interference.

The stored slides were carefully and frequently examined for surface irregularities due to chemical reactions. Surface irregularities occurred more frequently with prochlorite and vermiculite than with other clay samples, this being another indication of their reactivities. When surface irregularities were observed, fresh slides were prepared from the stored samples. With some of these new slides, peak heights of the original slide were not reproducible. Therefore, use of X-ray diffractometer charts in preparing "relative extent of reaction" vs time curves (Fig. 10) was discontinued.

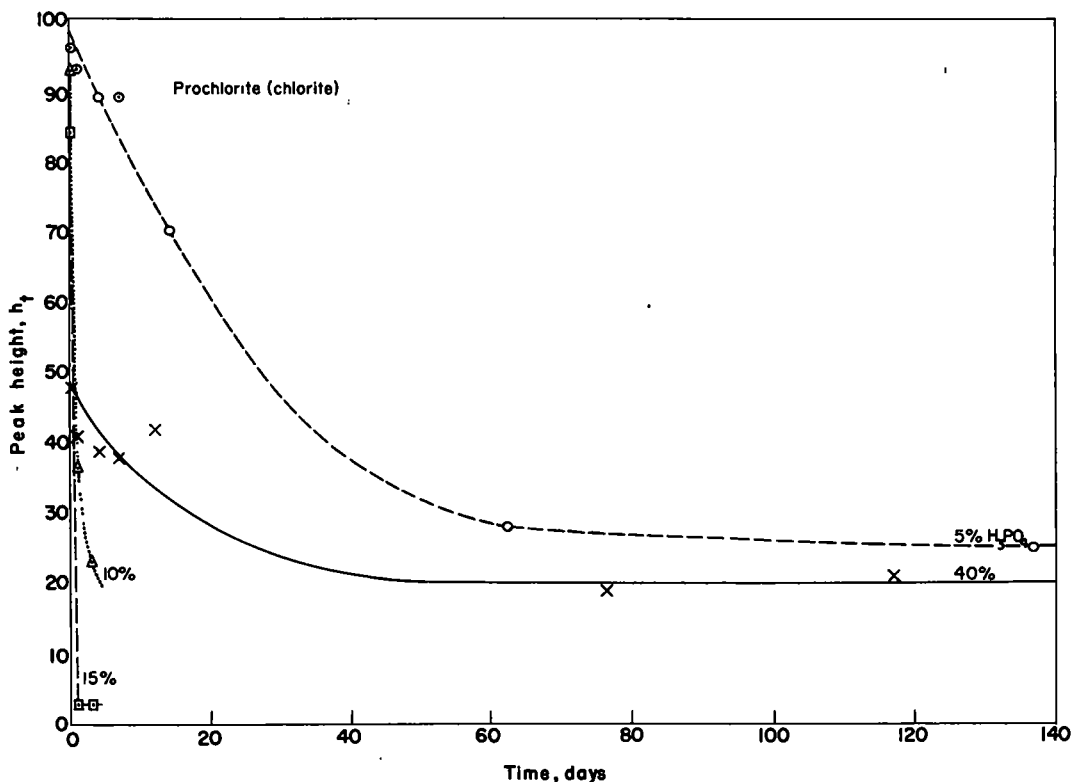


Figure 9. Major peak heights vs time for prochlorite treated with 5, 10, 15, and 40 percent phosphoric acid.

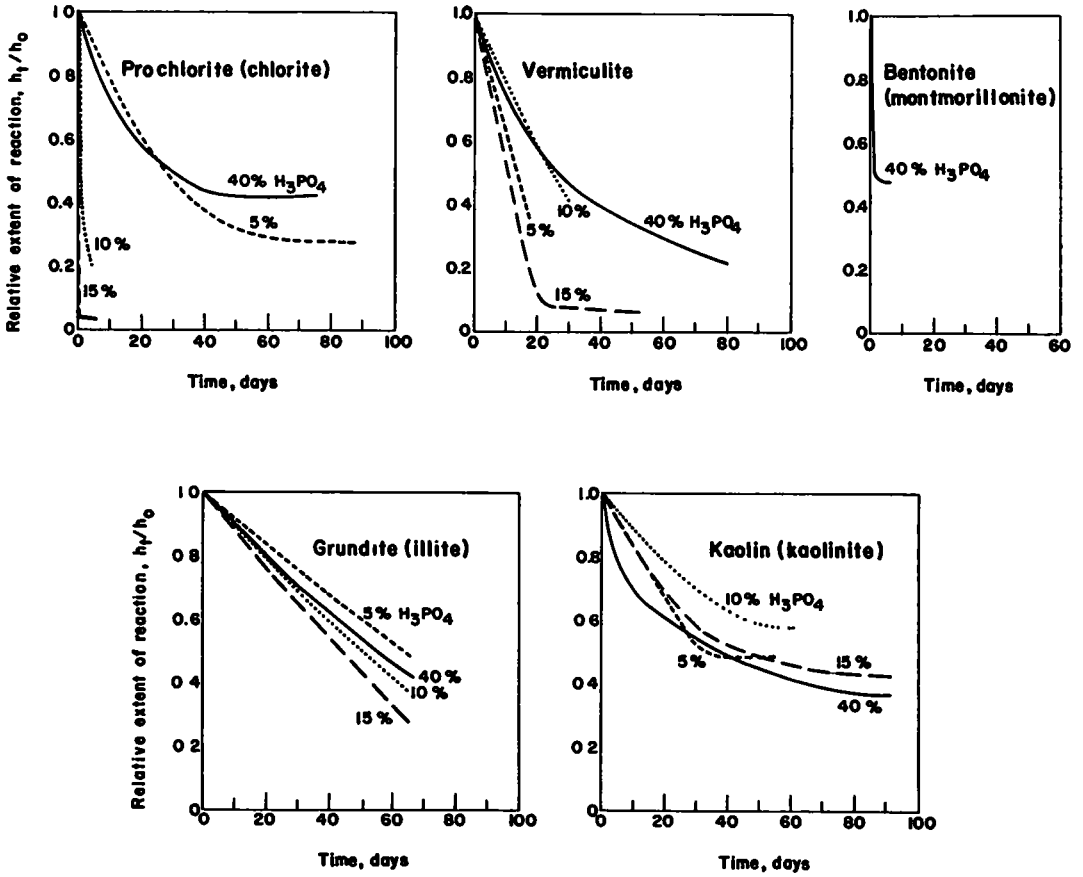


Figure 10. Relative extent of the reaction vs time for all clays and phosphoric acid percentages studied.

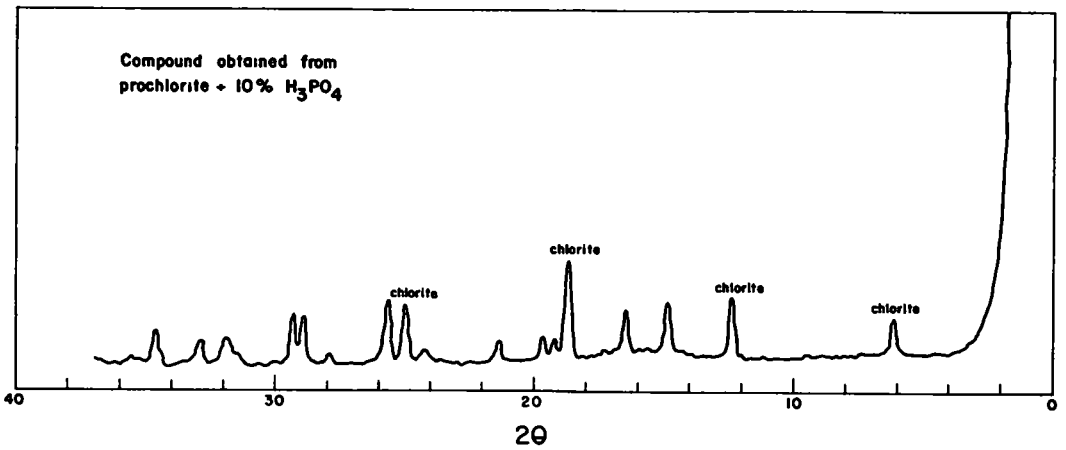


Figure 11. X-ray diffractometer chart of crust formed on surface of prochlorite + 10 percent phosphoric acid.

A water-insoluble crust was formed on the surface of prochlorite samples. This crust was most pronounced with 10 percent phosphoric acid treatment; however, there was no crust on the prochlorite sample treated with 40 percent phosphoric acid. X-ray analysis of the crust isolated from the 10 percent phosphoric acid sample 132 days after preparation showed new peaks in addition to weak chlorite peaks, indicating that a crystalline compound or compounds had formed (Fig. 11). Identification of newly formed compounds is presently being undertaken.

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