

Use of Phosphoric Acid in Soil Stabilization

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The purpose of this investigation was to determine the effect of phosphoric acid treatments on the stability of compacted calcareous and non-calcareous clay soils. Unimmersed and immersed strengths and freeze-thaw resistance of phosphoric acid-treated soil specimens were used as criteria for stability.

The unimmersed and immersed strengths of phosphoric acid-treated soils were studied relative to the curing conditions, carbonate contents of soils, and use of secondary additives. Moist curing was found beneficial to strength. Soils containing CaCO_3 required more phosphoric acid than CaCO_3 free soils because CaCO_3 reacted with the acid available for stabilization. No worthwhile benefit was found from the use of secondary additives.

X-ray diffraction analysis and quantitative chemical analyses were used to trace the chemical reactions after treatment. These analyses lead to the conclusion that phosphoric acid and clay minerals react to produce an amorphous aluminum phosphate gel which serves as a cementing agent.

● PHOSPHORIC acid stabilization of clay soils is a relatively new method, first introduced in 1957 by Lyons (5) who found that compacted specimens of clayey soils treated with as little as 2 percent phosphoric acid withstood exposure to water and to wintering.

An evaluation study by the Soil Research Laboratory, Iowa Engineering Experiment Station, Iowa State University, showed that the water resistance of a non-calcareous plastic loess was improved by treatments with phosphoric acid, or phosphoric acid and salts of calcium, magnesium or aluminum (3). It was hypothesized that the immersed strength of the compacted, moist-cured mixtures was due to the formation of amorphous phosphates in a gel form, and that the metallic cations needed for the insoluble gel formation could be provided by the soil or by adding salts of the desired cations.

Previous work indicated that phosphoric acid, used in amounts between 1 and 10 percent of the dry soil weight, was a promising stabilizer for fine-grained soils (6). Strengths were dependent on moisture content and density, highest strengths were developed when specimens were cured under humid conditions, and certain additives accelerated the curing process and improved the strength retention after immersion. On the basis of more recent studies it was concluded that phosphoric acid with added fluorine compounds and/or amines promised low-cost stabilization of fine-grained, carbonate-free soils under field conditions (7).

The present investigation was undertaken to evaluate further the use of phosphoric acid for stabilizing clay soils. The principal objectives of the investigation were:

1. Determine the effect of phosphoric acid treatments on the strength of compacted clay soils.
2. Determine the resistance of phosphoric acid stabilized clay soil to alternate cycles of freeze and thaw.
3. Determine the factors and soil compositional variables, if any, which may limit the use of phosphoric acid stabilization.

To accomplish these objectives it was first necessary to determine:

1. The relationship between the molding moisture content for maximum dry density and the molding moisture content for maximum immersed strength for the phosphoric acid-treated soils.
2. The best method of curing phosphoric acid-treated soil specimens.

A preliminary study was made to determine whether combination treatments of a clay soil with phosphoric acid and other chemicals would give better immersed strength than obtainable from phosphoric acid treatment alone.

MATERIALS USED

Soils

Descriptions and properties of the seven soils used in the investigation are given in Table 1. The first five soils were used in the strength studies; the leached and unleached Kansan till samples were used in supplementary studies.

The five main study soils were chosen so that the effects of different clay minerals and of varying calcium carbonate content could be evaluated. Three of these soils had montmorillonite as the dominant clay mineral: the non-calcareous plastic loess, the non-calcareous Kansan gumbotil and the calcareous alluvial clay. The dominant clay minerals in the calcareous Detroit clay were illite and chlorite; kaolinite (halloysite) and vermiculite were the dominant clay minerals in the non-calcareous Virginia clay.

Phosphoric Acid

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.

Other Chemicals

The following chemicals were used with phosphoric acid. Additives of these chemicals are expressed as percentages of the oven-dry weight of the soil, with no correction made for crystal water or solvents.

Aluminum Sulfate. — Reagent grade aluminum sulfate with 18 moles of crystal water, $Al_2(SO_4)_3 \cdot 18H_2O$, was dissolved in distilled water before adding to the soil.

Arquad 2HT. — Suspensions of Arquad 2HT in distilled water were prepared from chemical supplied by Armour and Company, Chicago, Ill. This chemical contained 75 percent active Arquad 2HT.

Sodium Fluoride. — Reagent grade sodium fluoride, NaF, was added to the soil in powdered form.

Aluminum Hydroxide. — Reagent grade aluminum hydroxide, $Al_2O_3 \cdot 3H_2O$, was used in powdered form.

Calcium Chloride. — Reagent grade anhydrous calcium chloride, $CaCl_2$, was dissolved in distilled water before being added to the soil.

Sodium Metasilicate. — Reagent grade sodium metasilicate with 9 moles of crystal water, $Na_2SiO_3 \cdot 9H_2O$, was dissolved in distilled water before being added to the soil.

Calcium Carbonate. — Reagent grade calcium carbonate, $CaCO_3$, was added to the soil in powdered form.

METHODS OF PREPARING AND TESTING SPECIMENS

Preparation of Mixtures

Air dried soil passing the No. 10 sieve was weighed and placed in an aluminum mixing bowl. Distilled water for the specified moisture content was added slowly to the soil while it was being mixed with a Hobart Model C-100 mixer. (Allowance was made for the water in the 86 percent phosphoric acid and the hygroscopic water of the soil in calculating the mix water needed for a specified moisture content.) After adding the water, phosphoric acid in the required amount was added slowly as mixing continued

TABLE 1
DESCRIPTION AND PROPERTIES OF SOIL SAMPLES

Sample	Plastic Loess (Lab. No. 528-4)	Kansan Gumbotl (Lab. No. 528-8)	Alluvial Clay (Lab. No. 827-1)	Detroit Clay (Lab. No. AR-4)	Virginia Clay (Lab. No. AR-5)	Leached Kansan Till (Lab. No. 418-4)	Unleached Kansan Till (Lab. No. 409-12C)
Geological description	Wisconsin-age loess, non-calcareous	Kansan-age gumbotl, highly weathered, non-calcareous	Missouri River floodplain alluvium, calcareous	Probably Wisconsin-age glacial till, calcareous	Residual soil over diorite, non-calcareous	Kansan-age till, non-calcareous	Kansan-age glacial till, calcareous
Location	Keokuk Co., Ia.	Keokuk Co., Ia.	Harrison Co., Iowa	Monroe Co., Mich.	Virginia	Warren Co., Iowa	Ringgold Co., Iowa
Soil Series	Mahaska	Mahaska	None	Unknown	Davidson	Shelby	Shelby (Burchard)
Horizon	C	Fossil B [†]	None	C	B	C	C
Sampling depth, ft	3 to 6 1/2	7 1/2 to 8 1/2	0 to 4	Unknown	Unknown	7 to 9	4 1/2 to 10 1/2
Textural composition, %							
Gravel (>2 mm)	0	0	0.0	0.0	0	1.3	0
Sand (2-0.074 mm)	0.2	16.0	0.5	7.0	21.0	32.6	31.5
Silt (74-5 μ)	60.8	13.5	27.5	36.0	37.0	29.1	30.0
Clay (<5 μ)	39.0	70.5	72.0	57.0	42.0	37.0	38.5
Colloids (<1 μ)	31.0	66.0	50.0	43.0	29.0	27.0	31.0
Predominant clay mineral [‡]	Montmorillonite	Montmorillonite	Montmorillonite	Illite-Chlorite	Kaolinite (Halloysite) - Vermiculite	Montmorillonite	Montmorillonite
Chemical properties:							
Cat. ex. cap, m. e./gm ^b	23.5	41.0	36.4	14.5	12.4	14.8	29.5
Carbonates, %	0.0	0.8	5.1	7.2	0.7	0.0	4.9
pH ^c	5.6	6.5	6.5	8.4	5.9	7.4	6.3
Organic matter, %	0.2	0.2	1.3	0.6	2.6	0.75	0.2
Physical properties:							
Liquid limit, %	52.1	75.6	65.8	44.0	43.5	38.2	42.4
Plastic limit, %	20.0	25.8	26.4	21.1	27.0	15.1	20.5
Plasticity index, %	32.1	50.0	39.4	22.9	16.5	23.1	21.9
Classification							
Textural [‡]	Silty clay	Clay	Clay	Clay	Clay	Clay	Clay
Engineering (AASHTO)	A-7-6(18)	A-7-6(20)	A-7-6(20)	A-7-6(14)	A-7-6(12)	A-6(11)	A-7-6(12)

^aBy x-ray diffraction analysis.

^bFor fraction passing No. 10 sieve.

^cBy versenate method, includes all acid extractable calcium as calcium carbonate.

^dFor fraction passing No. 10 sieve.

^eFrom triangular chart developed by U.S. Bureau of Public Roads, but 0.074 mm was used as the lower limit of the sand fraction.

[†]Underlies C horizon loess of Mahaska series.

This mixing of water and phosphoric acid took about 1 min. The mixture was then machine mixed for an additional 1 min; hand mixed for 30 sec to insure that no unmixed soil adhered to the bottom of the bowl, machine mixed for another minute, and finally hand mixed for approximately 30 sec.

Chemicals used in the dry form were dry mixed with the soil for 1 min prior to the addition of water. The other chemicals were added to the soil in the mix water before adding the phosphoric acid.

A 2-min period of machine mixing following the addition of phosphoric acid was chosen because longer mixing produced a hard and lumpy mix. A shorter period of machine mixing did not properly mix all the ingredients with the soil.

Molding

From each mix, six 2-in. diameter by 2 ± 0.05 -in. high test specimens were prepared by use of the molding apparatus shown in Figure 1. The 5-lb hammer was dropped a distance of 12 in. The specimen was compacted by five blows of the hammer on each end of the specimen for a total of ten blows. This gave a compactive effort approximately equal to the standard ASTM (Proctor) compactive effort (ASTM Method D 558-57) when the molding is done on a wooden table (9). Immediately before molding the first specimen and immediately after molding the last specimen, a sample was taken from the mix for moisture content determination, and the two moisture contents were averaged. A moisture content of ± 1 percent of the specified moisture content was maintained. All specimens were weighed to the nearest 0.1 gram and measured for height to the nearest 0.001 in.

Mixtures of plastic loess and varying percentages of phosphoric acid were used to determine the optimum molding moisture content for maximum immersed strength. Specimens of each mixture were molded at different moisture contents to determine the dry density versus moisture content relationship. After the specimens had been weighed and measured for density calculations, they were moist cured for 7 days and then were immersed for 24 hr in distilled water before being tested for unconfined compressive

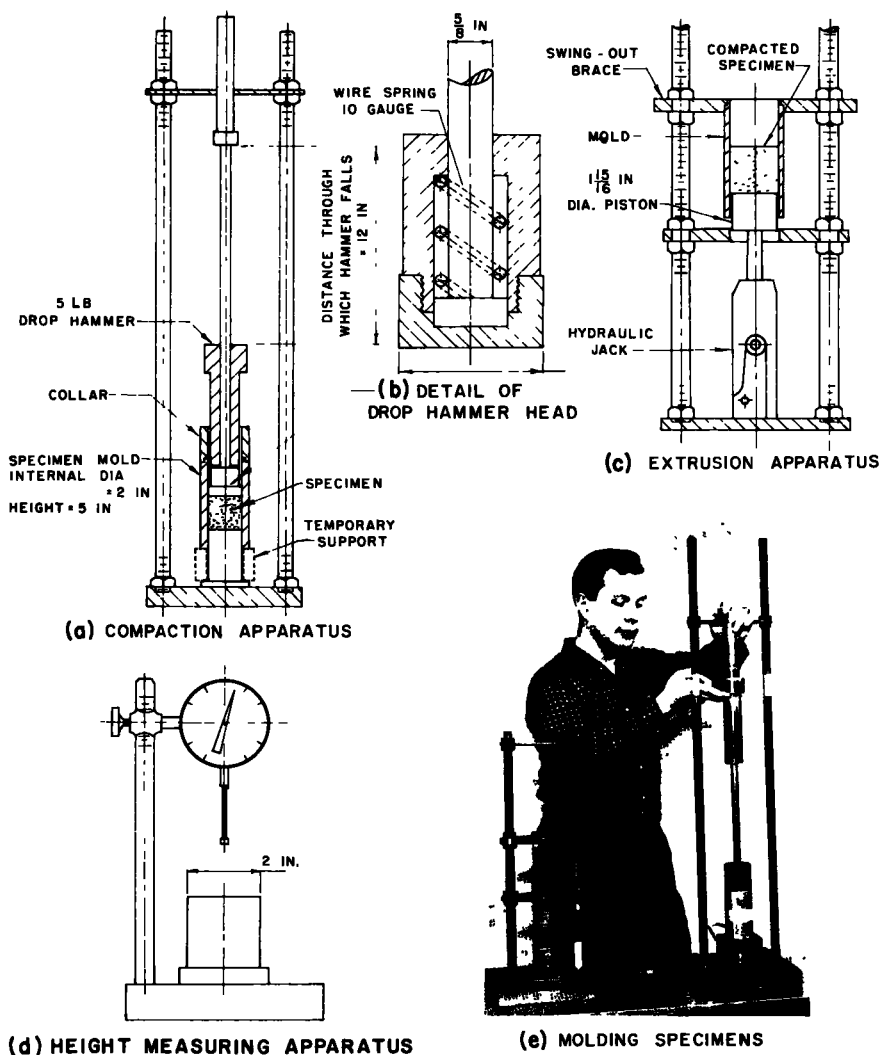


Figure 1. Apparatus for molding 2-in. diameter by 2-in. high test specimens.

strength. Optimum moisture contents for maximum dry density and for maximum immersed strength of each mixture were interpolated from graphs of density versus molding moisture content, and of immersed strength versus molding moisture content. These optimum moisture contents were then plotted against phosphoric acid content as shown in Figure 2. It is evident that the two optimum moisture contents are nearly identical. Hence, optimum molding moisture contents for mixtures of phosphoric acid and each of the other soils used in the main study were interpolated from dry density versus moisture content curves and specimens for strength studies were molded at these optimum moistures. The effect of phosphoric acid content on the optimum molding moisture contents so selected are shown in Figure 3 for each of the five soils. The data indicate that there is an inverse relationship between optimum moisture content and phosphoric acid content, with optimum moisture decreasing about 3 to 5 percent, based on the dry soil weight, as the phosphoric acid content is increased to 10 percent. The untreated soil generally had a slightly lower optimum moisture content than after treatment with 1 to 2 percent acid.

Curing

Two methods of curing phosphoric acid-treated soil were compared before selecting a curing method for the main study. The test specimens for the comparative study were prepared from a mixture of plastic loess and 7.5 percent phosphoric acid. In both curing

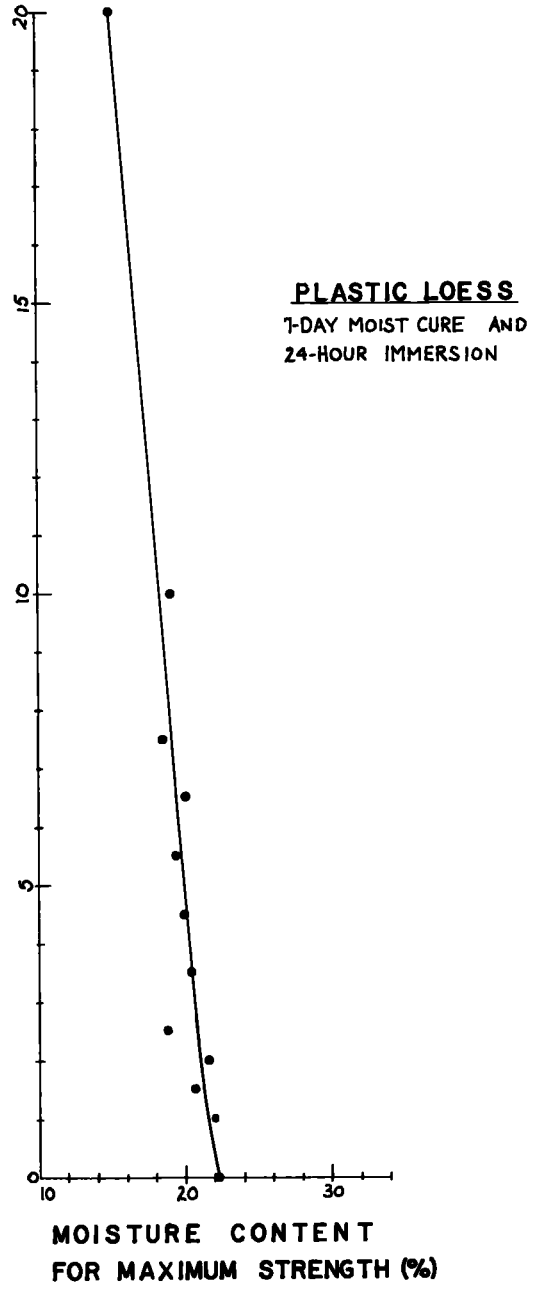
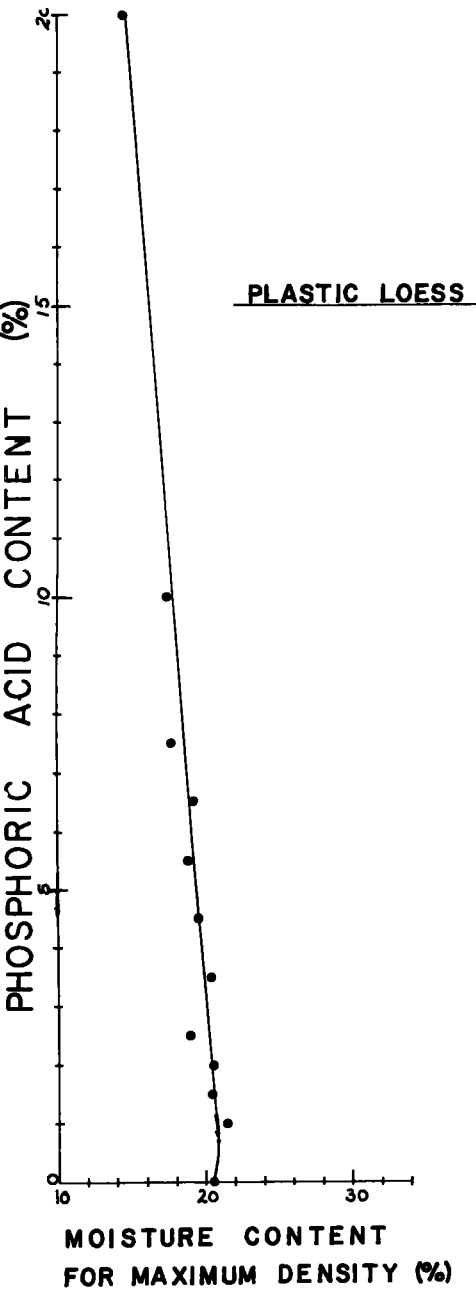


Figure 2. Effect of phosphoric acid content of mixtures with plastic loess on the optimum moisture contents for maximum standard Proctor density and for maximum immersed strength.

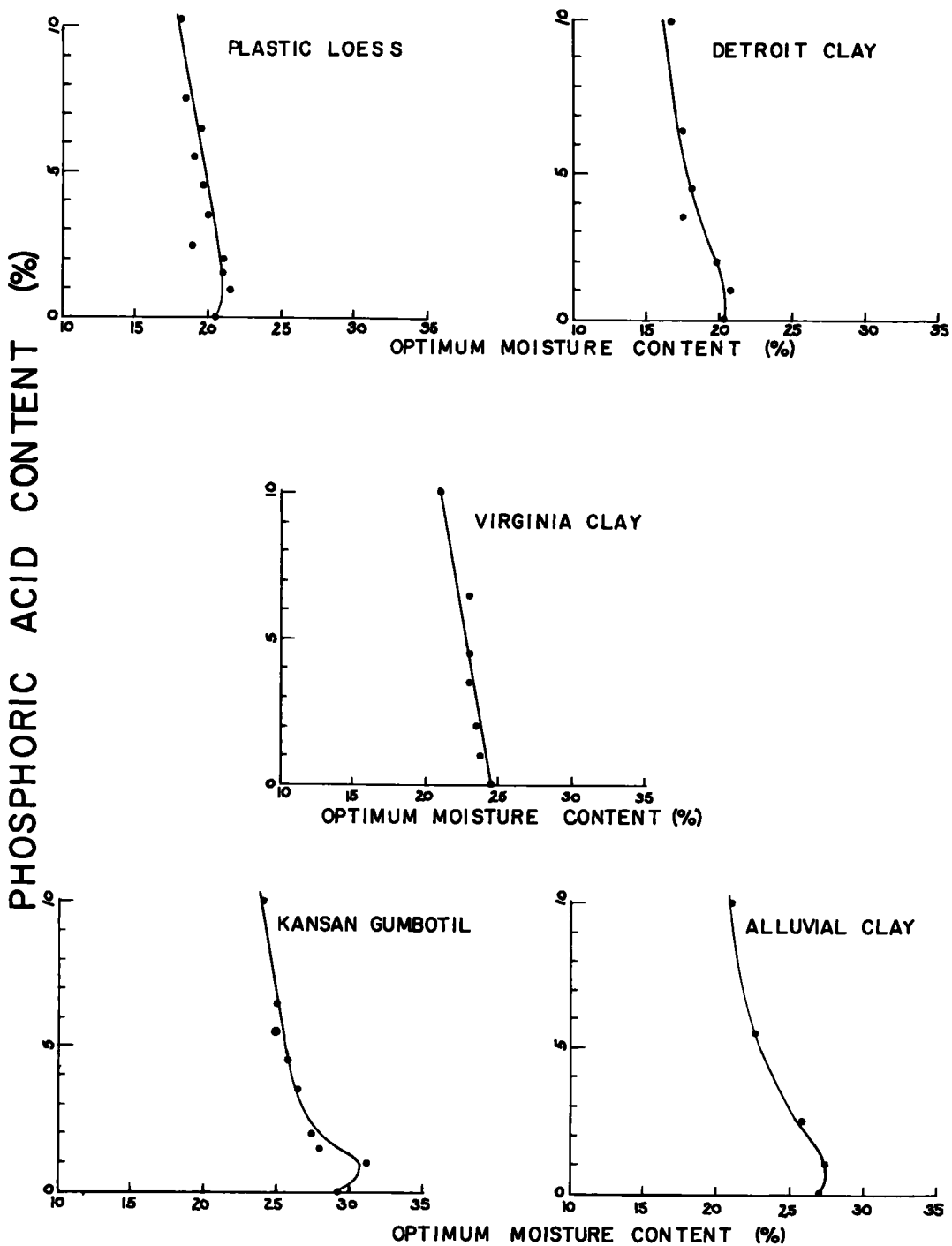


Figure 3. Effect of phosphoric acid content of mixtures with plastic loess, Detroit clay, Virginia clay, Kansan gumbotil and alluvial clay on optimum moisture content for maximum standard Proctor density.

methods the molded specimens, wrapped in wax paper and sealed with cellophane tape, were first placed in a curing room at 70 ± 4 F and 95 ± 5 percent relative humidity for 7, 14 or 28 days. In one method the specimens were unwrapped after each moist curing period and immersed in distilled water for 24 hr before testing for strength. In the other method, after moist curing 7, 14 or 28 days, the specimens were unwrapped and placed in open air for 7 days and then immersed for 24 hr in distilled water before testing for strength.

The specimens cured by the first method were molded at optimum moisture for maximum dry density because maximum density gives near maximum immersed strength as previously discussed. In the second curing method the specimens were molded at various moisture contents for 7 days moist curing and 7 days air curing; all specimens cured in this manner slaked on immersion. The last specimens to slake were those molded at optimum moisture for maximum dry density. For this reason all the specimens prepared for 14 or 28 days moist curing and 7 days air curing were molded at optimum moisture content; however, these specimens also slaked on immersion.

On the basis of these results it was decided, for the major portion of the investigation, to cure all specimens in the humid room and immediately after each curing period to either test them for unimmersed strength or immerse them in distilled water for 24 hr before testing for unconfined compressive strength. Immersion in water before testing was to simulate the detrimental effect of water on inadequately stabilized soil in the field, although complete immersion for 24 hr is a more severe treatment than usually encountered in roads.

Unconfined Compressive Strength Testing

The specimens were tested for unconfined compressive strength by a testing machine having a load travel rate of 0.1 in. per minute. The compressive strength was taken as the maximum test load in pounds per square inch sustained by a specimen. Unless otherwise indicated, strengths reported in this paper are averages for three specimens. In only a few did the difference between the individual values and the average value exceed 10 percent of the average value.

Freeze-Thaw Testing

The resistance of phosphoric acid stabilized soil to alternate cycles of freeze and

ADDITIVES

0.6% H_3PO_4

0.6% $H_3PO_4 + 3\% Al_2(SO_4)_3 \cdot 18H_2O$

2% H_3PO_4

2% $H_3PO_4 + 3\% Al_2(SO_4)_3 \cdot 18H_2O$

2% $H_3PO_4 + 10\% Al_2(SO_4)_3 \cdot 18H_2O$

4% H_3PO_4

4% $H_3PO_4 + 1\% Al_2(SO_4)_3 \cdot 18H_2O$

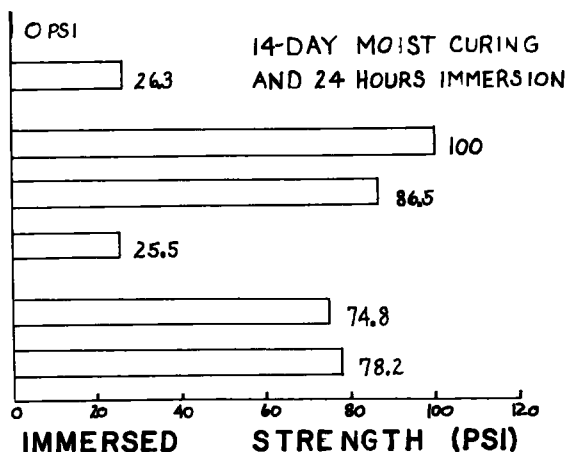


Figure 4. Immersed strengths of 14-day cured specimens of non-calcareous Kansan till treated with phosphoric acid and with phosphoric acid plus aluminum sulfate.

thaw was evaluated by the modified British standard freeze-thaw test (2). Only one soil, the plastic loess, treated with 2, 4.5 and 7.5 percent phosphoric acid was used in this study. For each curing period, two identical 2-in. diameter by 2 ± 0.05 -in. high specimens were molded from each mixture at optimum moisture content; the curing periods were 7 and 14 days. One specimen was designated the control specimen and the other the freeze-thaw specimen (1, 2, 4). After moist curing, the top flat surface of both specimens was spray painted with a resin-base paint to a thickness of approximately 1 mm. The control specimen was immersed for 15 days in distilled water at a temperature of 77 ± 4 F and then tested for unconfined compressive strength. The freeze-thaw specimen was immersed in distilled water at a temperature of 77 ± 4 F for 24 hr, then was exposed alternately to temperatures of 23 ± 2 F and 77 ± 4 F for 14 cycles, each cycle lasting 24 hr, and finally tested for unconfined compressive strength. (A vacuum flask specimen container was used to cause freezing to occur from the top down and to supply unfrozen water to the bottom of the specimen throughout the test.)

PRELIMINARY STUDY

Previous work had indicated the possibility that metallic salts or amines with phosphoric acid might give better results than phosphoric acid alone. A preliminary study was made to check this. The soil used was the leached (non-calcareous) kansan till (Table 1).

Figure 4 shows the 14-day cured immersed strengths produced by soil-phosphoric acid mixtures with and without aluminum sulfate. At 0.6 percent phosphoric acid, 3 percent aluminum sulfate increased immersed strength; at 2 percent phosphoric acid, 3 percent aluminum sulfate decreased immersed strength, and 10 percent caused a further decrease; at 4 percent phosphoric acid, 1 percent aluminum sulfate only slightly increased immersed strength.

ADDITIVES

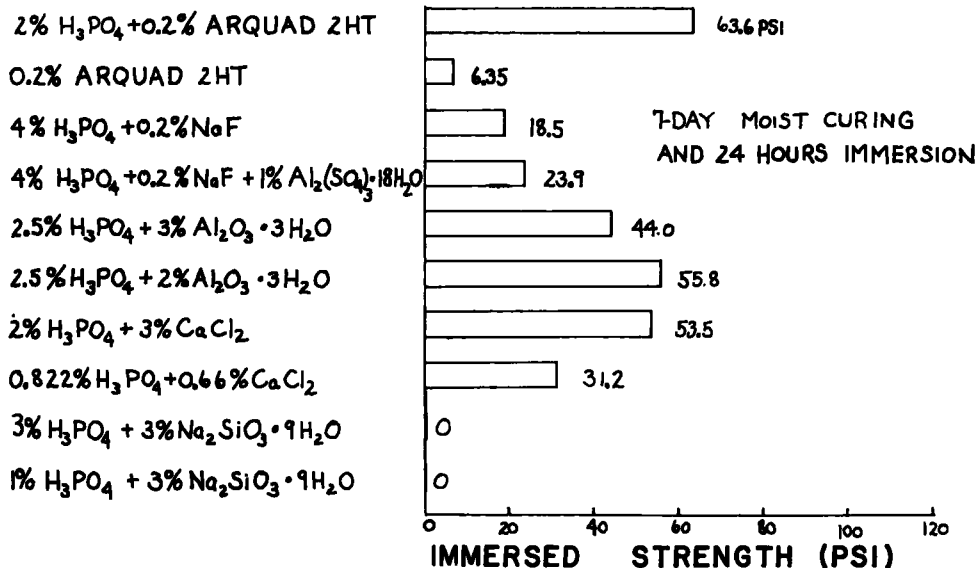


Figure 5. Immersed strengths of 7-day cured specimens of non-calcareous Kansan till treated with phosphoric acid plus various other chemicals.

The 7-day cured immersed strength results obtained with treatments of the other chemicals show that the highest immersed strength was obtained with 2 percent phosphoric acid and 0.2 percent Arquad 2HT, but it is probably only slightly better than obtainable with 2 percent phosphoric acid alone (Fig. 5). The other additives also did not produce promising results.

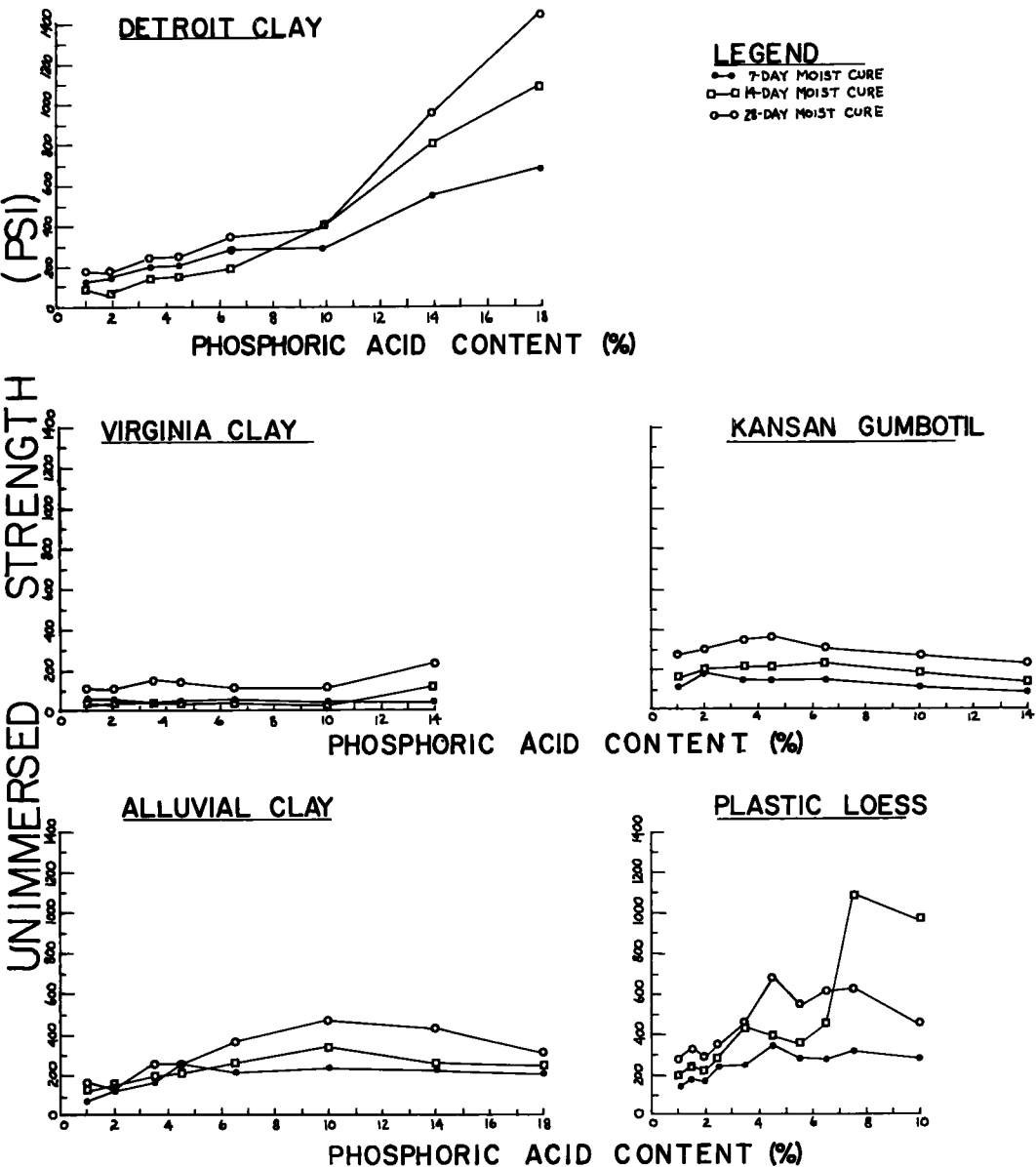


Figure 6. Effect of phosphoric acid content of clay soils on unimmersed strengths of 7-, 14- and 28-day cured test specimens.

STRENGTH STUDIES

Unimmersed Strength

The effects of amount of phosphoric acid treatment on the unimmersed specimen strengths of the five soils after 7, 14 and 28 days moist curing are shown in Figure 6. The montmorillonitic clay soils (Kansan gumbotil, alluvial clay, and plastic loess) generally reached a maximum strength with from 2 to 10 percent phosphoric acid. More chemical generally caused a decrease in strength.

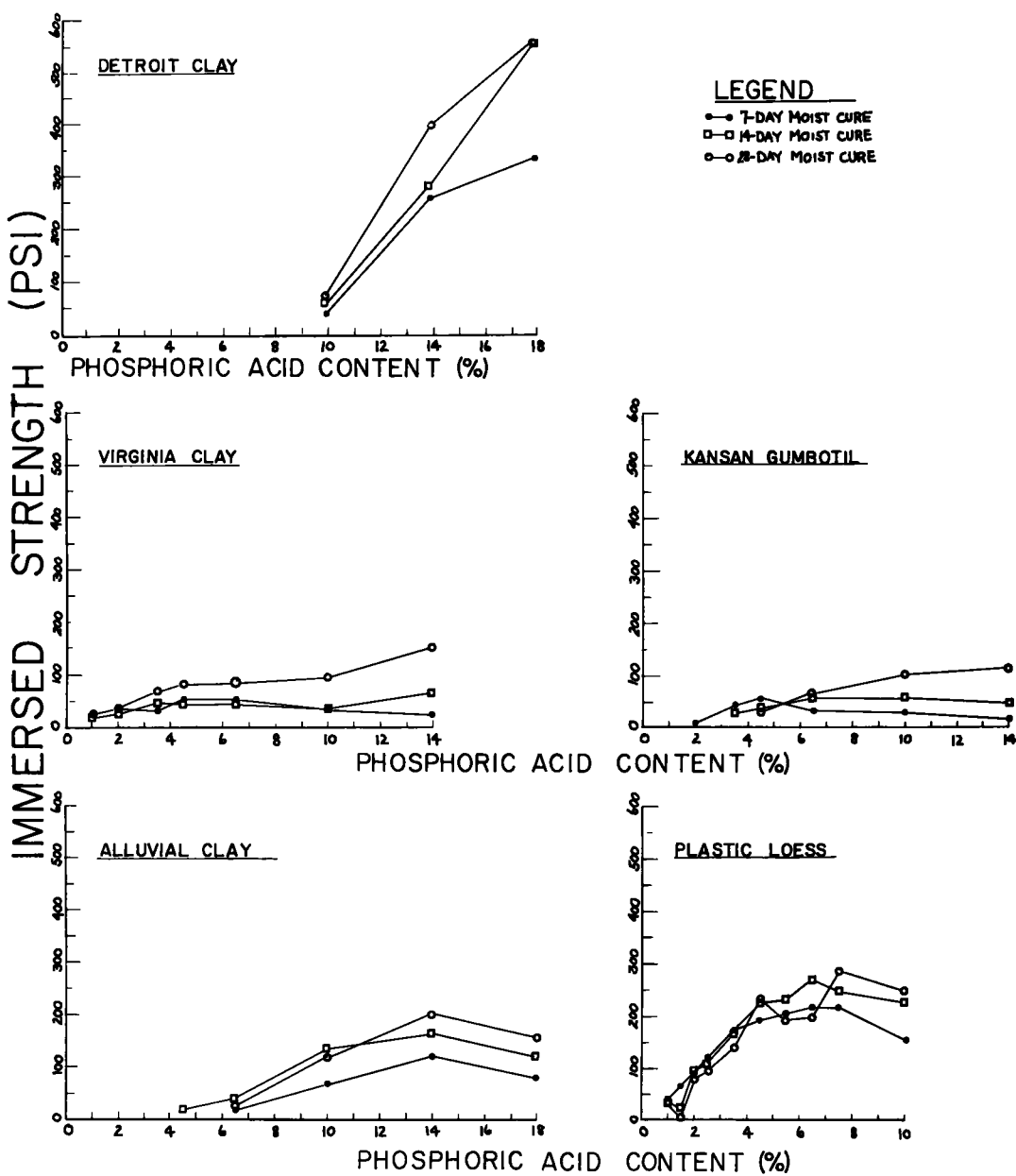


Figure 7. Effect of phosphoric acid content of clay soils on immersed strengths of 7-, 14- and 28-day cured test specimens.

No optimum phosphoric acid content was observed with the illitic-chloritic clay soil (Detroit clay). Up to 10 percent phosphoric acid, strength increased slowly at a uniform rate with increased acid content; but at 10 percent or above, the rate of strength gain increased sharply, and at all curing times it continued at the increased rate up to 18 percent acid, the largest amount used. This change in the rate of strength increase, discussed later, was due to the calcium carbonate content of the soil.

The strengths of the phosphoric acid-treated kaolinite-vermiculite clay soil (Virginia clay) specimens were low, and did not reach a maximum with from 1 to 14 percent acid. At 14 percent phosphoric acid, the 14- and 28-day strengths were still increasing, indicating that use of more acid might further increase strength.

Because the unimmersed strength of a stabilized soil is an indicator of cementing action derived from the stabilizer, phosphoric acid treatment of soil can be said to produce a cementing agent.

Immersed Strength

The effect of the phosphoric acid treatments on the immersed strength of the five soils after 7, 14 and 28 days moist curing are shown in Figure 7. The montmorillonitic clay soils (Kansan gumbotil, alluvial clay, and plastic loess) tended to reach a maximum or near maximum immersed strength at each curing time with from 4 to 14 percent phosphoric acid. More than the optimum amount of acid generally caused a decrease in strength.

Specimens of the illitic-chloritic clay soil (Detroit clay) containing less than 10 percent phosphoric acid failed during immersion. However strength gain was rapid as acid content was increased above 10 percent, and at 18 percent the strength probably had not reached a maximum.

The 14- and 28-day strengths of the kaolinite-vermiculite clay soil (Virginia clay) specimens generally showed gradual increase with from 1 to 10 percent phosphoric acid without reaching to a maximum, and above 10 percent the rate of strength gain was somewhat greater. The 7-day strength reached a maximum at 4 to 5 percent acid, and strength slowly decreased with use of more acid.

The immersed strengths obtained in these tests indicate that the cementing product produced by the interaction of phosphoric acid and soil is water insoluble.

It will be noted in Figure 7 that the use of small percentages of phosphoric acid with

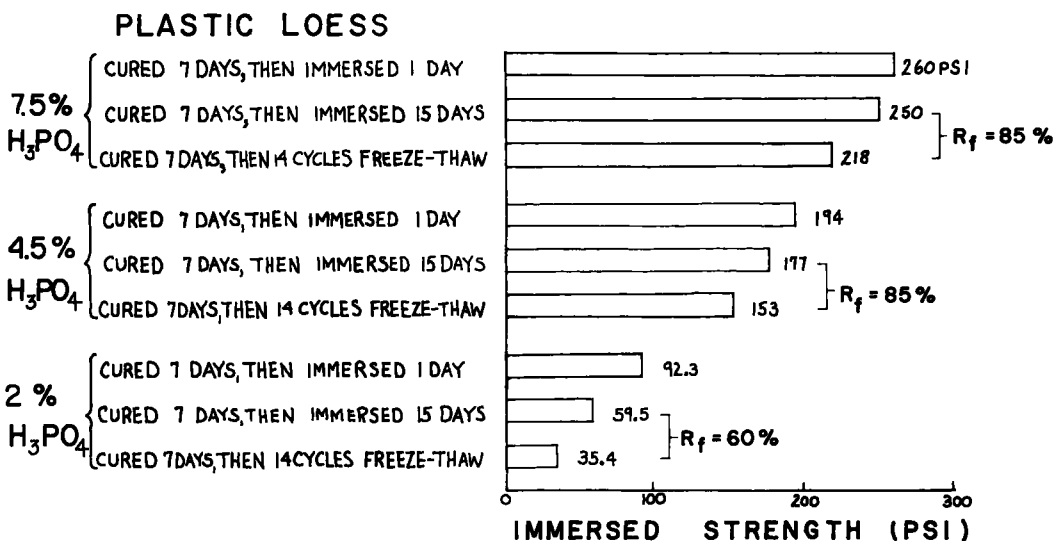


Figure 8. Results of modified British freeze-thaw tests of 7-day cured specimens of phosphoric acid-treated plastic loess.

Detroit clay and alluvial clay did not produce immersed strength. This is due to the calcium carbonate content of these soils, as explained later. Here it is enough to say that phosphoric acid reacts with calcium carbonate and this increases the amount of phosphoric acid necessary to obtain immersed strength.

Analysis of the Strength Data

The different responses of different soils to phosphoric acid treatments (Figs. 6 and 7) may be hypothesized as being due to differences in the rapidity and the extent of the chemical reactions which furnish the reaction products that cement soil grains together and thus increase strength. Any remaining unreacted phosphoric acid lubricates the soil particles and tends to decrease the strength. Therefore, when the ratio of unreacted phosphoric acid to the reaction product is excessive, a net decrease in specimen strength occurs. The relative amounts of unreacted phosphoric acid and the reaction product depend on how far the reaction has progressed towards equilibrium, which for any given time depends on the rapidity of the reaction.

Generally both a maximum unimmersed and immersed strength were obtained with montmorillonitic clay soils; but with the range of treatment, maxima were not reached with the illite-chlorite and the kaolinite-vermiculite rich clay soils. The highest strengths were obtained with the illite-chlorite rich soil and the lowest strengths with the kaolinite-vermiculite rich soil. The three montmorillonitic soils gave mid-range strengths.

The rapid attainment of high strengths with the illitic-chloritic clay soil (Detroit clay) (Figs. 6 and 7) may be due to the rapid and complete reaction of phosphoric acid with the chlorite in the soil. As discussed later, x-ray diffraction analysis (Fig. 11) showed that chlorite is much more highly reactive with phosphoric acid than the other clay minerals; therefore it is believed that the chlorite in the Detroit clay reacted completely with phosphoric acid, which was largely responsible for the high strengths obtained.

Phosphoric acid-treated montmorillonitic clay soils attained moderate strengths rapidly (Figs. 6 and 7). This indicates that the rate of reaction may be as rapid in the montmorillonitic clay soils as it is in the illitic-chloritic clay soil, but that the extent of the reaction is not as great in the montmorillonitic clay soils. Consequently with the montmorillonitic clay soils an appreciable amount of unreacted phosphoric acid

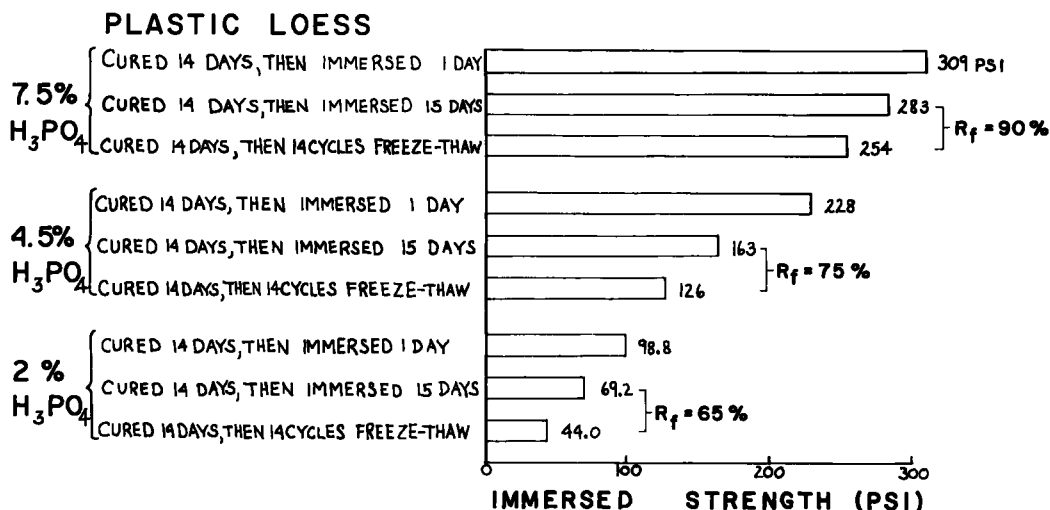


Figure 9. Results of modified British freeze-thaw tests of 14-day cured specimens of phosphoric acid-treated plastic loess.

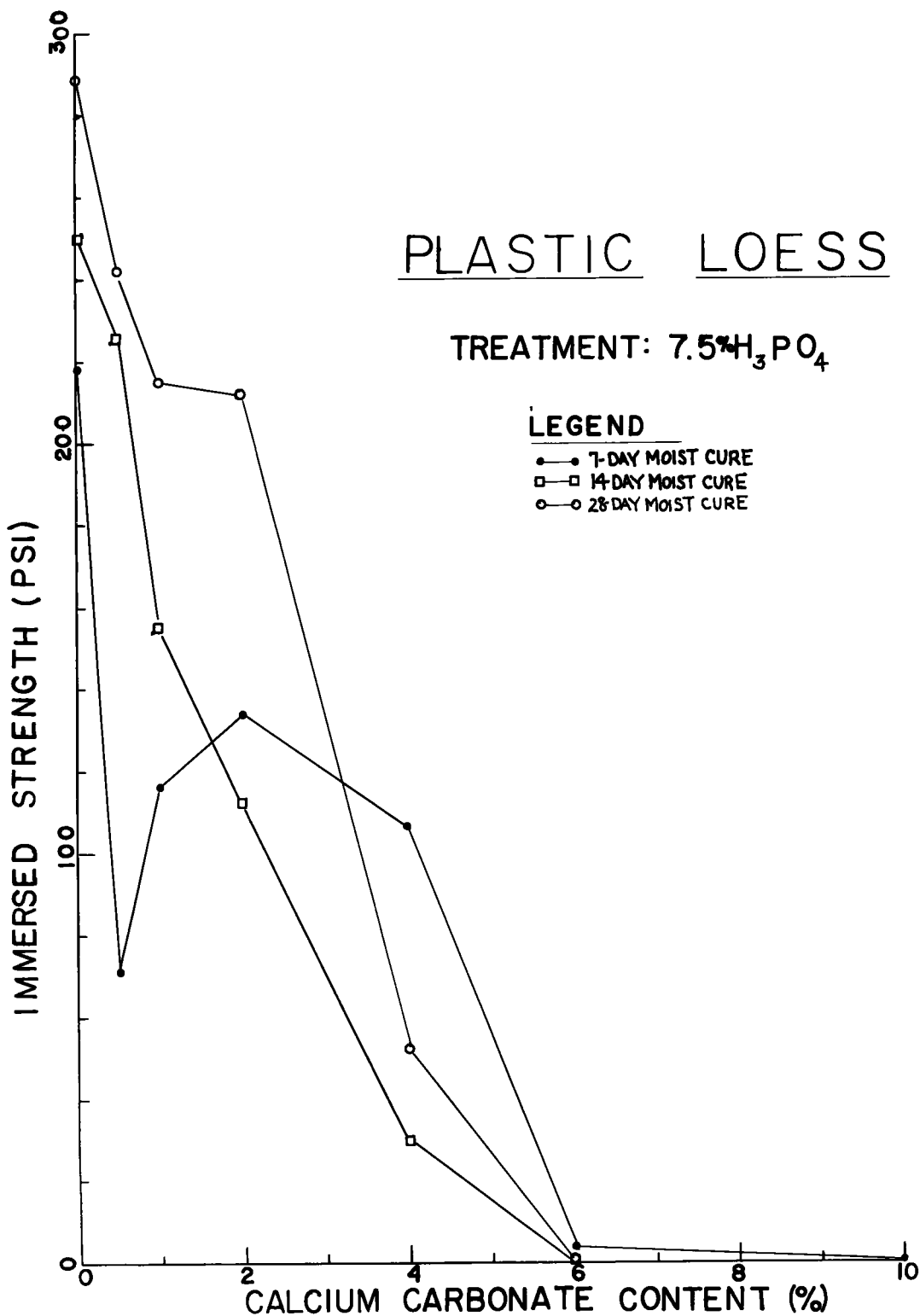


Figure 10. Effect of calcium carbonate additives to plastic loess on the immersed strengths of 7-, 14- and 28-day cured specimens containing 7.5 percent phosphoric acid, based on the dry weight of the loess- $CaCO_3$ mixture.

was always present when equilibrium was reached and its lubricating action tended to detract from the cementation effects of the reaction product. When the amount of unreacted phosphoric acid at higher levels of treatment became excessive, a net decrease in strength resulted, giving rise to the occurrence of the strength maxima in Figures 6 and 7. It also appears that both the amount of the optimum phosphoric acid treatment

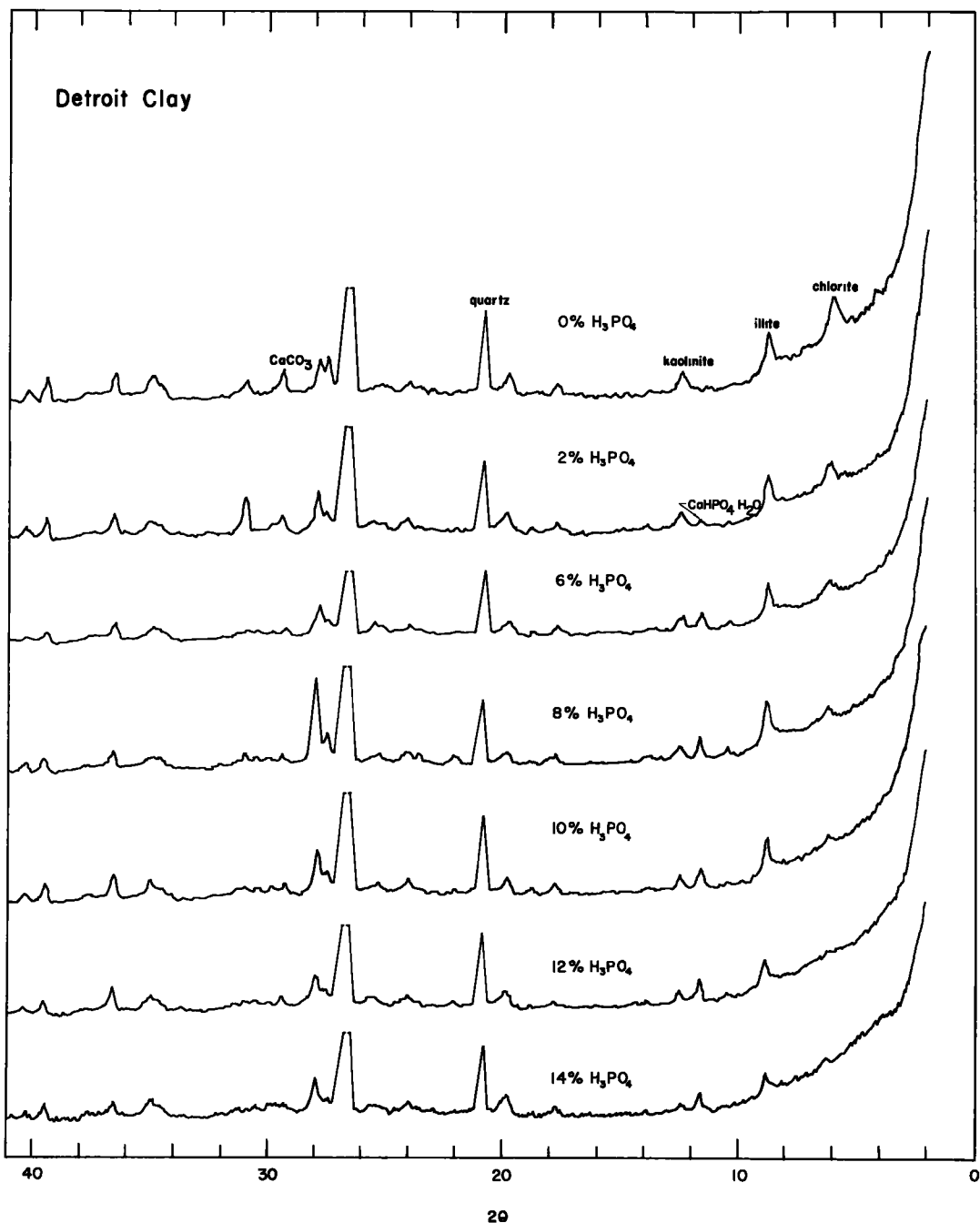


Figure 11. X-ray diffractometer chart showing the effect of various percentages of phosphoric acid on the clay minerals of the Detroit clay. (Filtered copper K α radiation was used.)

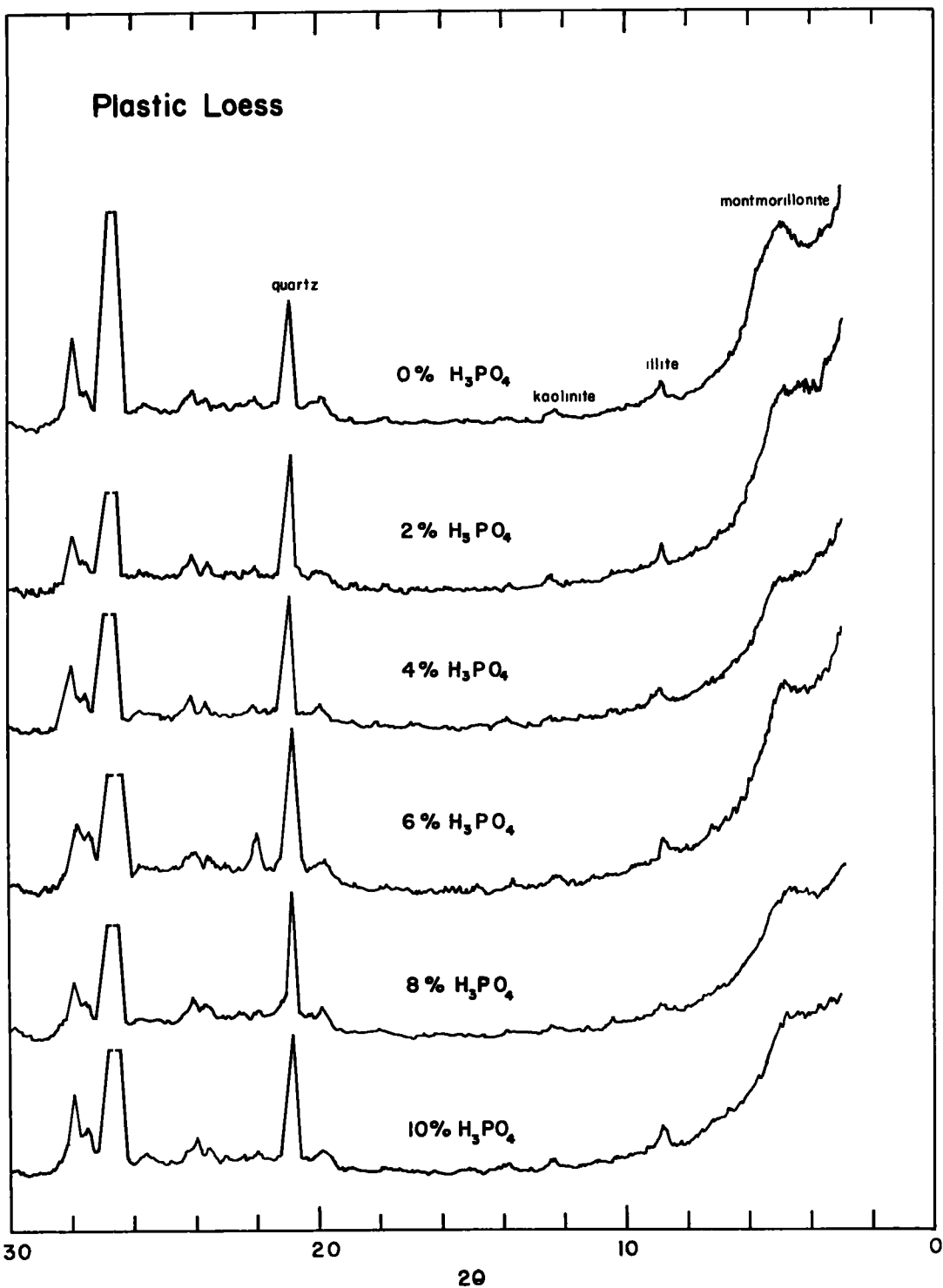


Figure 12. X-ray diffractometer chart showing the effect of various percentages of phosphoric acid on the clay minerals of the plastic loess. (Filtered copper K α radiation was used.)

and the magnitude of the maximum strength depend on the amount of clay-size material present in the montmorillonitic clay soils. Generally, the higher the clay content the more phosphoric acid was required for optimum results and the lower the maximum strength value. Reduction of the maximum strength with increasing clay content may be due to the resulting decrease in coarser grained fractions which contribute to internal friction in the stabilized soil and oppose the lubricating action of untreated phosphoric acid.

Phosphoric acid-treated kaolinite-vermiculite clay soil (Virginia clay) specimens generally showed a gradual increase in strength with longer curing time and with increased phosphoric acid contents. This may be attributed to a slow rate of reaction and the equilibrium conditions in favor of the products. The continued progress of the reaction more than compensates for the lubricating effect of the unreacted phosphoric acid as well as reducing the amount of unreacted material. Thus the slow but continuous strength gain results.

It is believed that the reaction product which furnishes cementation is essentially the same for all clay minerals and is a complex amorphous aluminum phosphate in the form of a gel—a conclusion also reached more or less by others (3, 6, 7). This point is further discussed in the mechanism section of this paper.

Summarizing the results of the foregoing discussion, chlorite clay minerals seem to be the most reactive of clay mineral groups investigated in this study. Montmorillonitic minerals react rapidly with phosphoric acid but the reaction does not proceed very far. Kaolinite and vermiculite react slowly with phosphoric acid, and the reaction may proceed to an appreciable extent. An accelerator or a catalyst may aid the stabilization of kaolinite or vermiculite rich soils by speeding the reaction but can hardly benefit montmorillonite rich soils, inasmuch as the reaction is already rapid. This conclusion is substantiated by the results reported by Michaels and Tausch (7), which show that fluorides and fluosilicates do not affect the phosphoric acid-clay reaction in montmorillonitic soils; however, they do accelerate the reaction in illitic soils. Thus, in all probability, illite reacts similarly to kaolinite or vermiculite. The general behavior of the illite group minerals cannot be predicted from the data of the present study, because the reaction was obscured by the presence of chlorite.

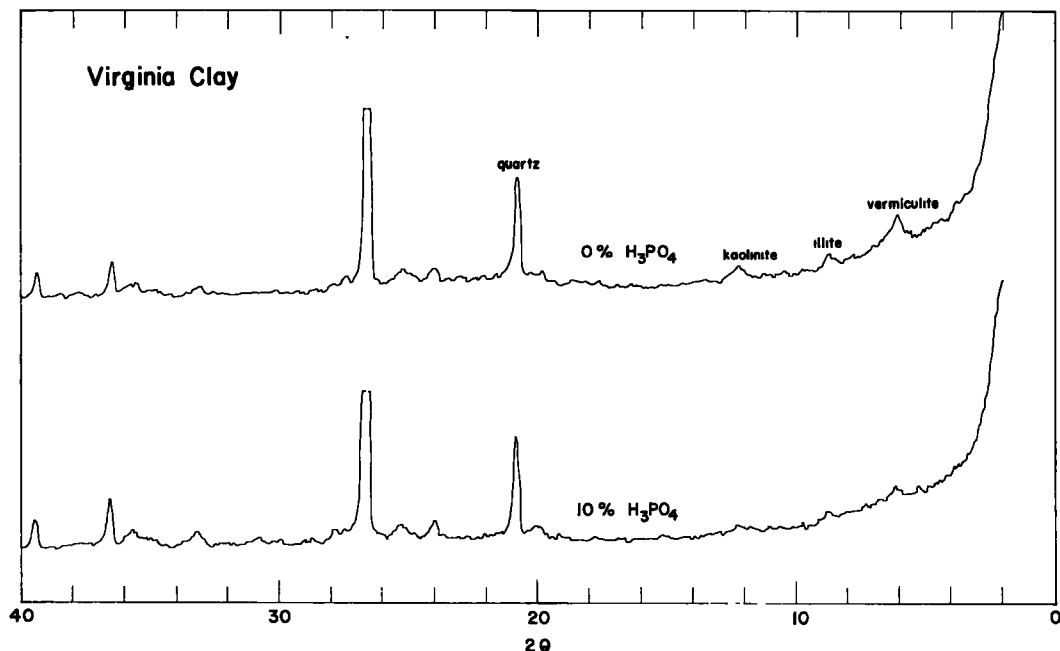


Figure 13. X-ray diffractometer chart showing the effect of 10 percent phosphoric acid on the clay minerals of the Virginia clay. (Filtered copper K α radiation was used.)

FREEZE-THAW STUDY

The modified British freeze-thaw test (2) was used to evaluate the durability of 7- and 14-day cured specimens of selected mixtures of plastic loess and phosphoric acid. Bar graphs in Figures 8 and 9 show unconfined compressive strengths after curing and 1-day immersion; after curing and 15 days immersion (control specimen, p_c); and after curing, 1-day immersion, and 14 cycles of freeze-thaw (freeze-thaw specimen, p_f).

Criteria of Durability

Two criteria have been used for the evaluation of the freeze-thaw test results (2). The first criterion is the value of the index of resistance to the effect of freezing (R_f), defined by the following equation and expressed as a percentage of the nearest 5 percent:

$$R_f = \frac{100 p_f}{p_c}$$

The minimum R_f value considered indicative of satisfactory field performance of stabilized soils in road base courses in Great Britain is 75 percent. (Private communication, 1958, from D. J. Maclean, Harmondsworth, Middlesex, England — information on the British Standard Test No. 1924.) This same minimum value was adopted for the present study.

The second criterion requires a minimum value for the unconfined compressive strengths of the control specimen (p_c) and the freeze-thaw specimen (p_f). The tentative minimum requirement for both p_c and p_f , for stabilized base course mix design in Iowa, is 250 psi, the value used in the present study. The selection of this value is discussed by Davidson and Bruns (2).

Discussion of Results

Specimens Cured 7 Days. — Resistance to the damaging effects of immersion and of freezing and thawing showed marked increases with increased phosphoric acid content in the treatment range 2 percent to 7.5 percent (Fig. 8), but judged on the basis of 7

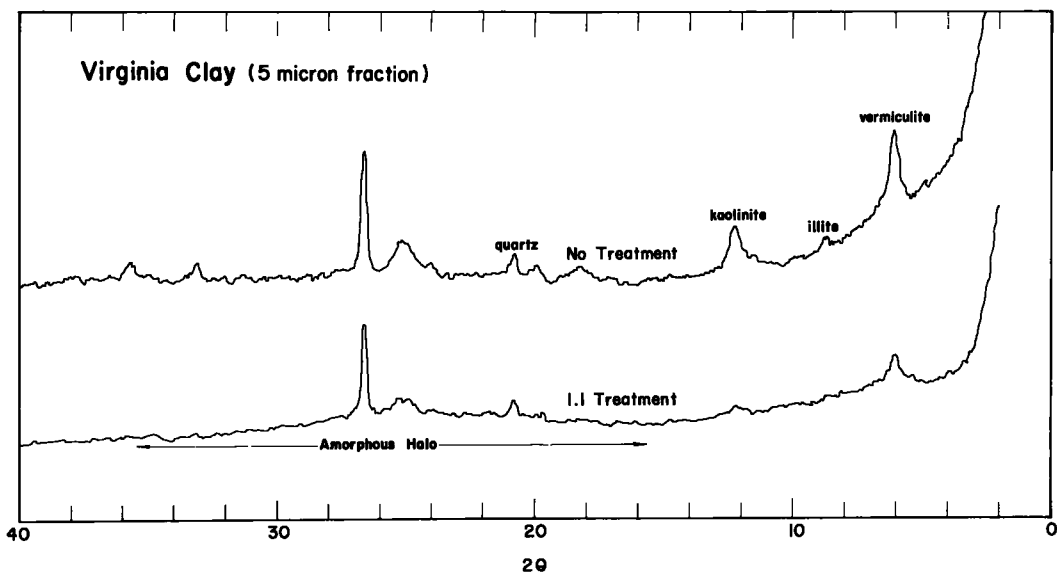


Figure 14. X-ray diffractometer chart showing the effect of phosphoric acid on the clay minerals of the minus 5 micron fraction of the Virginia clay. (Filtered K α radiation was used.)

days curing, none of the mixtures would be considered adequate for road bases in Iowa. However, the mixture with 7.5 percent phosphoric acid came close to being satisfactory in that $R_f = 85$ percent, $p_c = 250$ psi and $p_f = 218$ psi, the latter value being the only one that did not meet the minimum requirements for durability.

Specimens Cured 14 Days. — If mix design was based on 14-day curing of test specimens, Figure 9 indicates that 7.5 percent phosphoric acid would satisfactorily stabilize plastic loess for road bases in Iowa. Lesser amounts of phosphoric acid probably would not provide adequate durability.

Time of Immersion. — A comparison of the strengths of the specimens immersed for one day with those of similar specimens immersed for 15 days (Figs. 8 and 9) shows that as phosphoric acid content was increased the amount of strength reduction due to the longer time of immersion was generally reduced.

LIMITATION STUDY

The presence of calcium carbonate in many soils can be one limitation to the use of phosphoric acid stabilization. The cost of phosphoric acid stabilization can be another.

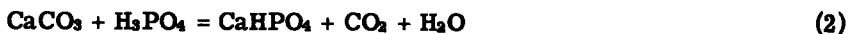
Calcium Carbonate

In a preliminary study of phosphoric acid stabilization using the calcareous (unleached) Kansan till (Table 1) no immersed strengths were obtained, that is, the specimens failed by slaking. Because of this it was decided to study the effect of calcium carbonate content on the immersed strength of phosphoric acid stabilized soil. Two experimental approaches were used. In one, natural soils that contained known amounts of calcium carbonate were used to evaluate the effect of calcium carbonate on immersed strength. The five soils used contained amounts of calcium carbonate varying from 0 to 7.2 percent (Table 1). The second approach was to use the non-calcareous plastic loess and add specific amounts of calcium carbonate and study the effect on immersed strength.

Natural Soils. — The effect of calcium carbonate content on immersed strength is shown by the curves for the five soils in Figure 7. Non-calcareous plastic loess showed an immediate increase of immersed strength with the addition of 1 percent phosphoric acid. Alluvial clay with 5.1 percent CaCO_3 did not develop immersed strength until about 6.5 percent phosphoric acid was used. Detroit clay which contained 7.2 percent CaCO_3 did not develop immersed strength until the phosphoric acid content was at least 10 percent. Therefore it seems that the amount of phosphoric acid necessary to obtain immersed strength is increased as the calcium carbonate content is increased.

Plastic Loess Plus CaCO_3 Additives. — The effects on 7-, 14- and 28-day cured immersed strengths of adding different amounts of calcium carbonate to plastic loess are shown in Figure 10. (The phosphoric acid treatment was held constant at 7.5 percent based on the dry weight of the soil- CaCO_3 mixtures.) Increasing the amount of calcium carbonate decreased the immersed strengths, until at about 6 percent CaCO_3 the strengths were zero or close to it.

Phosphoric acid (H_3PO_4) gives three principal calcium salts: tricalcium diphosphate, $\text{Ca}_3(\text{PO}_4)_2$; calcium hydrogen phosphate, CaHPO_4 ; monocalcium tetra hydrogen diphosphate, $\text{CaH}_4(\text{PO}_4)_2$. Formation of these salts from CaCO_3 and H_3PO_4 may be represented stoichiometrically, by the following equations:



The actual occurrence of these reactions is governed by the acid and base strengths of the reactants and the products. Because $\text{Ca}_3(\text{PO}_4)_2$ is a much stronger base than CaCO_3 , the first reaction can hardly take place. However, if the pH of the medium in which CaCO_3 and H_3PO_4 are reacting is controlled, any of these reactions may be made possible. Constituents of a soil may furnish such a control and make any one of these reactions possible.

An indirect approach was used to decide which one of these reactions predominantly takes place when a calcareous soil is treated with phosphoric acid. The ratio of the weight of phosphoric acid to calcium carbonate based on the aforementioned three stoichiometric equations is, respectively, 0.987, 1.98 and 2.96. The ratio of phosphoric acid to calcium carbonate at which immersed strengths were obtained with the calcareous soils studied was as follows: alluvial clay, 1.18; Detroit clay, 1.25. For the plastic loess with different amounts of calcium carbonate added the ratio of phosphoric acid to calcium carbonate content at the point where the immersed strength was zero was 1.25. These three ratios are very close to one another and to the ratio of phosphoric acid to calcium carbonate, 0.987, in Eq. 1. The slight difference between the first three values and the latter may be because phosphoric acid reacts with the calcium carbonate to a small extent according to the second reaction in Eq. 2, and also because small amounts of phosphoric acid may react with other soil constituents.

The presence of calcium carbonate in soil increases the amount of phosphoric acid necessary to stabilize the soil. This appears to be due to the phosphoric acid acting to neutralize the calcium carbonate before reacting with the other soil constituents. The amount of phosphoric acid necessary to neutralize the calcium carbonate in the soils studied was about 1.25 times the amount of the calcium carbonate present. The neutralization of the calcium carbonate in a soil apparently contributes nothing to strength but would of course add to the cost of the stabilization.

Cost. — Cost is another factor that may limit the use of phosphoric acid for soil stabilization. Phosphoric acid currently costs about 7.5 cents a pound (8). For comparison, portland cement costs about 1 cent a pound, and is used in soil stabilization of fine-grained soils in amounts of from 12 to 20 percent. To compete cost-wise with cement, the amount of phosphoric acid that can be used must be in the range 1.6 to 2.7 percent. This estimate is based only on the cost of the additive, and does not take into account methods of construction. Phosphoric acid could be added in the water for compaction, which might be an advantage over cement. Also phosphoric acid might be cheaper to handle than portland cement, due to the smaller amount of additive involved. These are matters to be investigated, and experience in the field is necessary for a final decision on them.

MECHANISM

The mechanism of phosphoric acid stabilization is embodied in chemical changes taking place on treating soils. In the present study X-ray diffraction analysis and quantitative chemical analysis were used for tracing the chemical changes. Figures 11, 12 and 13 show the X-ray diffraction charts for the three soils — Detroit clay, plastic loess, and Virginia clay — all treated with various percentages of phosphoric acid and cured 7 days in a humid atmosphere. Figure 14 shows the X-ray diffractometer charts for the minus 5 micron fraction of the kaolinite-vermiculite rich soil (Virginia clay) before and after treatment with an equal amount of phosphoric acid by weight, diluted approximately to liquid limit consistency with water, and cured in a humid atmosphere for 7 days. The purpose of this 1:1 treatment was to augment the changes taking place on phosphoric acid treatment.

Examination of the X-ray charts indicates an amorphous halo and no newly formed crystalline substances resulting from phosphoric acid treatment, except that the chart for calcareous Detroit clay gives calcium phosphate peaks resulting from the reaction between calcium carbonate and phosphoric acid. All three treated soils showed a decrease in the intensities of clay mineral peaks depending on the level of the treatment, suggesting that phosphoric acid had reacted with clay minerals. The amorphous halo is attributed to the reaction products.

Quantitative chemical analyses made on Detroit clay treated with phosphoric acid showed an appreciable increase in HCl-soluble aluminum compounds depending on the level of the phosphoric acid treatment (Table 2). The cation exchange capacity of Detroit clay and plastic loess treated with various percentages of phosphoric acid increased, depending on the level of the treatment (Table 2).

Based on these data it is hypothesized that phosphoric acid releases aluminum ions

TABLE 2

EFFECT OF PHOSPHORIC ACID ON THE CATION EXCHANGE CAPACITIES OF DETROIT CLAY AND PLASTIC LOESS, AND ON THE AMOUNTS OF HYDROCHLORIC ACID EXTRACTABLE ALUMINUM COMPOUNDS OF THE DETROIT CLAY

Soil	H ₃ PO ₄ ^a (%)	Cation Exchange Capacity ^b (me/100 g)		N. HCl Extractable Aluminum ^b (%)	
		On the Basis of the Total Weight of the Mixture	On the Basis of the Soil Fraction of the Mixture	On the Basis of the Total Weight of the Mixture	On the Basis of the Soil Fraction of the Mixture
Detroit Clay	0	14.5	14.5	1.1	1.1
	2	18.9	19.3		
	4	21.6	22.5		
	6	27.9	29.7		
	8	28.8	31.3	1.7	1.9
	10	29.4	32.7		
	12	38.0	43.2		
	14	45.9	53.4		
Plastic Loess	0	23.5	23.5		
	1	40.4	40.8		
	2	43.4	44.3		
	4	45.0	46.9		
	6	52.5	55.9		
	8	52.3	56.8		
	10	50.3	55.9		

^aExpressed as percentage of pure (100 percent) phosphoric acid based on the oven-dry weight of the soil.

^bDetermined after moist curing for 7 days, and expressed as a percentage of the oven-dry weight of the sample.

from clay mineral lattices by destroying the clay mineral structure. Aluminum ions released combine with the phosphate anions to form a irreversible gel having a high cation exchange capacity. This gel acts as a cementing agent by bonding to the surfaces of other mineral constituents of the soil.

CONCLUSIONS

1. Phosphoric acid treatment improves the strength and durability characteristics of compacted, moist cured, clayey soils. The degree of the improvement depends on the amount of phosphoric acid used and on the types and amounts of clay minerals in the soil. Chlorite appears to be much more reactive with phosphoric acid than montmorillonite-, illite-, kaolinite-, or vermiculite-type clay minerals.

2. There is an optimum amount of phosphoric acid which produces the highest unimmersed and immersed strengths in stabilized soils.

3. Moist curing phosphoric acid stabilized soils gives higher immersed strengths than curing in open air.

4. The molding moisture content for maximum dry density of soil-phosphoric acid mixtures correlates closely with molding moisture content for maximum immersed strength.

5. For each combination of phosphoric acid and soil there appears to be a curing time beyond which there will be no further increase in immersed strength. This time is a function of the amount and the type of clay minerals reacting, and the amount of phosphoric acid available for the reactions.

6. The resistance of phosphoric acid stabilized soil to alternate cycles of freeze

and thaw increases with increasing percentages of phosphoric acid.

7. Phosphoric acid acts to neutralize the calcium carbonate in a soil before reacting with the other soil constituents; this increases the amount of phosphoric acid necessary to stabilize the soil. Each percentage of calcium carbonate consumes about 1.25 percent phosphoric acid.

8. Based on the (1959) relative costs of portland cement and phosphoric acid, the maximum percentage of phosphoric acid that can be used economically in soil stabilization is about 3 percent, based on the dry soil weight. Soils containing more than 2.5 percent calcium carbonate may consume more than 3 percent phosphoric acid in the neutralization of calcium carbonate without gaining in stability. Therefore in regions like Iowa, where calcareous soils are abundant, phosphoric acid stabilization may not be an economical method of stabilizing soils for roads. A reduction in the price of phosphoric acid, however, could make it economical to use for stabilizing calcareous clayey soils.

9. In reacting with clay minerals phosphoric acid produces a water insoluble cementing compound. Based on chemical and X-ray diffraction analyses it is believed that this cementing compound is an irreversible gel composed of amorphous aluminum phosphates.

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