

II. Secondary Additives, Acid Source, and Mechanism

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● THE SOILS and testing methods used were as described in Part I. In addition, the test soil was treated with phosphoric acid in the muller-and-plow mixer with about 15-16 percent water (optimum). The loose mixture was stored at room temperature and 100 percent relative humidity. Samples were taken periodically and treated as follows:

1. 24 g (20 g soil, 0.4 g H_3PO_4 , and 3.6 g H_2O) were whipped with 125 ml of boiled, distilled water for 30 sec in a kitchen blender. The slurry was washed into a beaker with 25 ml of boiled, distilled water and the pH was measured with a glass-calomel electrode pair.

2. The slurry was then washed into centrifuge bottles and spun for 15 min. The supernatant was decanted, diluted to 250 ml, and the pH was remeasured. The supernatant was analyzed for P_2O_5 and Al_2O_3 by standard wet chemical methods.

Chemicals used were as follows:

1. Phosphoric Acid (H_3PO_4)—reagent grade, commercial "wet process," and experimental "wet process";
2. Polyphosphoric acids ($\text{H}_2\text{O}/\text{P}_2\text{O}_5 = 2.46, 1.09$)—experimental chemicals made from reagent grade H_3PO_4 and P_2O_5 ;
3. Sodium tripolyphosphate—commercial;
4. Fluorapatite ($\text{Ca}_5\text{F}(\text{PO}_4)_3$)—commercial mineral (32 percent P_2O_5);
5. Hydroxylapatite ($\text{Ca}_5\text{OH}(\text{PO}_4)_3$)—commercial synthetic;
6. Sulfuric acid (H_2SO_4)—reagent grade;
7. Hydrofluoric acid (HF)—reagent grade;
8. Dodecylbenzene sulfonic acid—Monsanto Chemical Company;
9. Alkane Sulfonic acids—Indoil (Standard Oil of Indiana);
10. N-tetrapropenyl diethylene triamine—Monsanto Chemical Company;
11. Tridecanol-ethylene oxide condensate (10 EO)—Monsanto Chemical Company.

RESULTS

The study may be broken down into the following segments: (a) the effect of condensed phosphoric acids (or salts) alone or with orthophosphoric acid (Figs. 1-3); (b) changes in soil properties when different sources of orthophosphoric acid are used (Figs. 4-6); (c) effect of mixtures of hydrofluoric and orthophosphoric acids (Figs. 7-9); (d) effect of adding surface active agents (Figs. 10-11, Table 1); and (e) data pertaining to the reaction mechanism (Figs. 12-13).

Condensed Phosphoric Acids

In Figure 1, an inspection of the curves shows that a very noticeable decrease in compacted density occurs when condensed phosphoric acids are substituted for orthophosphoric acid. This loss in density undoubtedly accounts for the loss in immersed strength of the samples, inasmuch as the dependence of strength on density is well established. In Figure 2, various amounts of a long-chain phosphoric acid (approaching the meta composition) were added in different ways to the soil along with 2 percent orthophosphoric acid. In Figure 3, sodium tripolyphosphate was added to the 2 percent orthophosphoric acid-soil system. In no case did the immersed strength rise significantly above that obtained with the 2 percent orthophosphoric acid by itself, (see Fig. 1 for base-line data) and frequently losses in strength and density occurred. As postulated later, these results may actually indicate increased reaction of the clay with the acid in the presence of condensed phosphate acids or salts with the loss in strength directly related to this increase in rate of reaction.

Types of Orthophosphoric Acid

Because of the commercial availability of several types of orthophosphoric acid, the data in Figures 4 and 5 were obtained. In Figure 4, data are shown for three acids—"furnace" acid made by burning elemental phosphorus and absorbing the P_2O_5 in water, "wet acid" made via the reaction of sulfuric acid on phosphate rock, and an experimental "wet acid" made by the reaction of a spent sulfuric acid obtained from petroleum industry alkylators on phosphate rock. It is plain that the inorganic and organic impurities in the latter two types of phosphoric acid do not adversely effect the results as expressed by the immersed strengths of the soil samples. Indeed, there is some improvement in strength at the 5-day curing point that is less evident at 30 days. This latter point suggests that

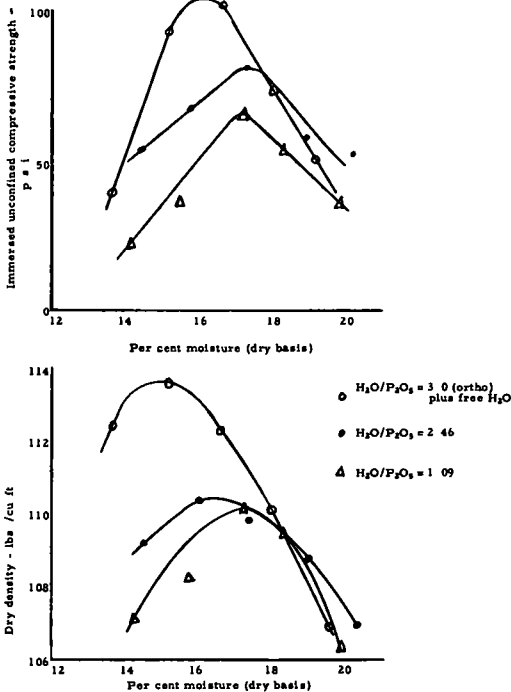


Figure 1. Effect of phosphoric acid chain length as shown by H_2O/P_2O_5 ratios—All equivalent in P_2O_5 to orthophosphoric acid; Keyport clay loam A-7-6(12); 2- by 4-in. cylinders, cured 5 days at 100 R.H., immersed in water 2 days.

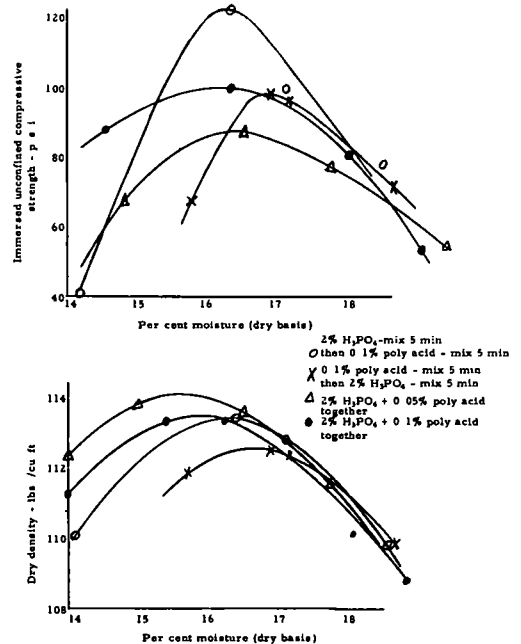


Figure 2. Effect of adding polyphosphoric acid ($H_2O/P_2O_5=1.09$) to orthophosphoric acid treatment—Keyport clay loam A-7-6(12); 2- by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed 12 days.

the impurities may not have long-range influence but act only as accelerators for the reaction.

Figure 6 presents the results of stabilization using phosphoric acid and calcium sulfate obtained from the reaction of sulfuric acid and phosphate rock either in situ in the soil or by addition of the premixed unseparated reaction mixture. This was done because of the anticipated cost savings by using the raw materials. Interesting differences were found between hydroxylapatite-sulfuric acid and fluorapatite-sulfuric acid in that good immersed strengths were found only with the former, yet good unsoaked strengths were found with both sources of rock. The densities are reduced with all the rock-acid treatments relative to straight phosphoric acid. This reduction in density is probably due to the flocculating power of the calcium in the system. It is

known that flocculation decreases density for a given compactive effort.

Hydrofluoric-Phosphoric Mixtures

Because of the evident influence of impurities in the "wet acids", a study was made wherein fluoride was introduced deliberately (fluoride is generated when fluorapatite is acidulated). Figures 7-9 show the effect of several levels of fluoride added as hydrofluoric acid. In Figure 7, the highest strength was obtained with 2 percent of an acid that was 30 percent in fluoride. It is noteworthy that 2 percent of the mixed acids was used, meaning that as the amount of hydrofluoric acid was increased the amount of phosphoric acid decreased. Nearly double the strength is obtained with the 30 percent fluoride mixture over the straight phosphoric acid run. This increase in strength was obtained despite a steady decrease in density. At levels of fluoride higher than 30 percent, strength decreases and density decreases even further. This indicates production of a soil that hardens so fast that densification is badly impaired.

To see whether the increased strengths in Figure 7 were real or merely an acceleration of initial reactions, the data of Figure 8 were taken. This graph shows that much higher strengths are obtained

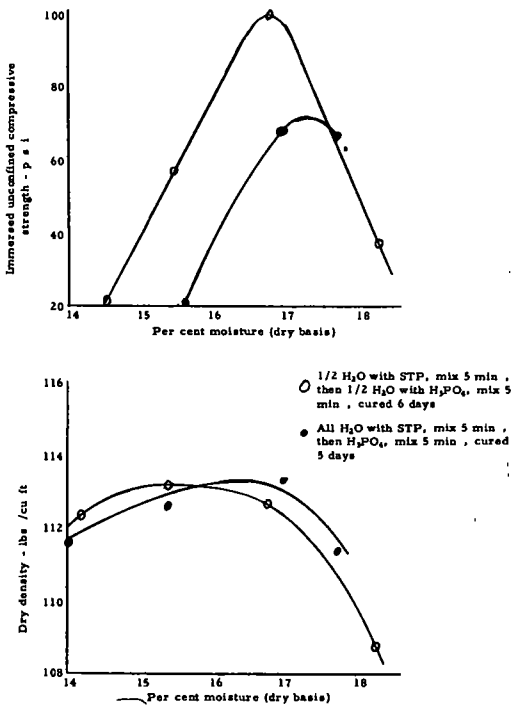


Figure 3. Effect of 0.3 percent sodium tripolyphosphate (STP) and 2 percent phosphoric acid added two ways to Keyport clay loam A-7-6(12)-2- by 4-in. cylinders, 8 blows per each of 4 layers, cured as shown, immersed 2 days.

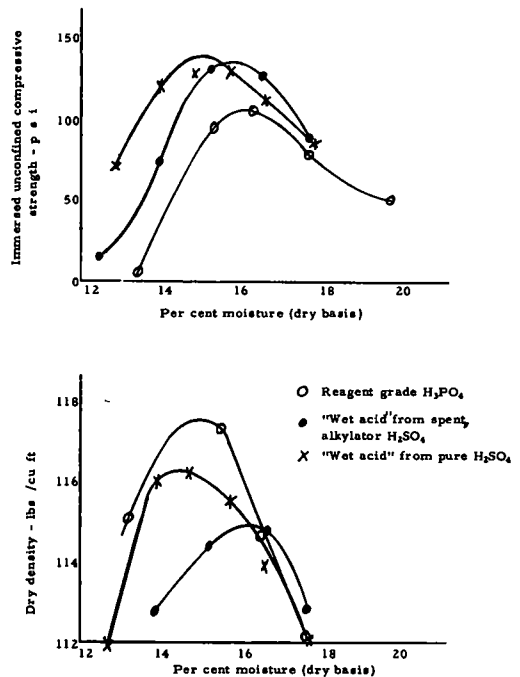


Figure 4. Comparison of three grades of phosphoric acid in Keyport clay loam A-7-6(12)-2- by 4-in. cylinders, 12 blows per each of 4 layers, cured 5 days, immersed 2 days.

with the mixed acid system (this run at 19.35 percent F in H₃PO₄) after about three months and that the increase over straight phosphoric acid is even more pronounced as curing progresses. For this silty soil, then, the improvement in strength is real at all curing times studied.

Figure 9 shows a much less impressive effect with Keyport clay loam and phosphoric-hydrofluoric mixed acid. This soil is much lower in silt and responds well to phosphoric

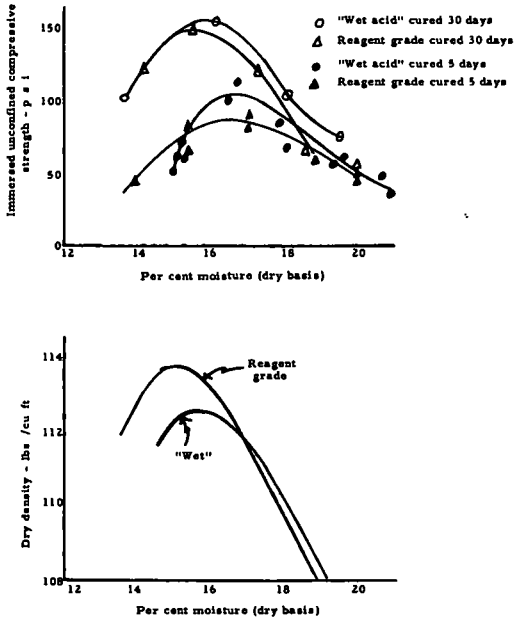


Figure 5. Comparison of two grades of phosphoric acid in Keyport clay loam A-7-6(12)-2 by 4-in. cylinders, 4 layers, 8 blows per layer, cured at 100 percent R.H., immersed for 2 days.

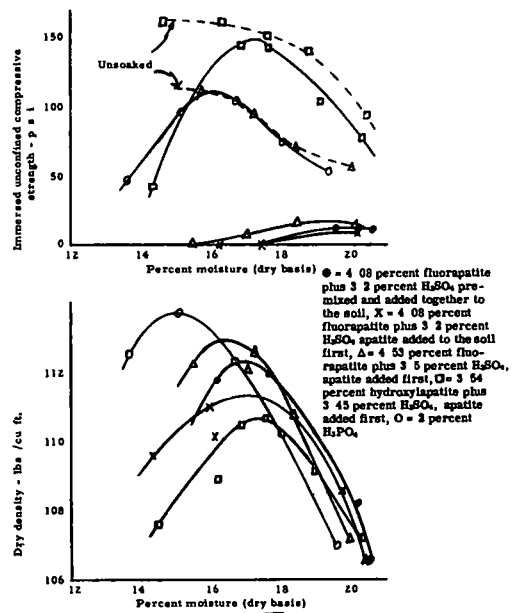


Figure 6. Phosphate rock plus sulfuric acid in Keyport clay loam A-7-6(12).

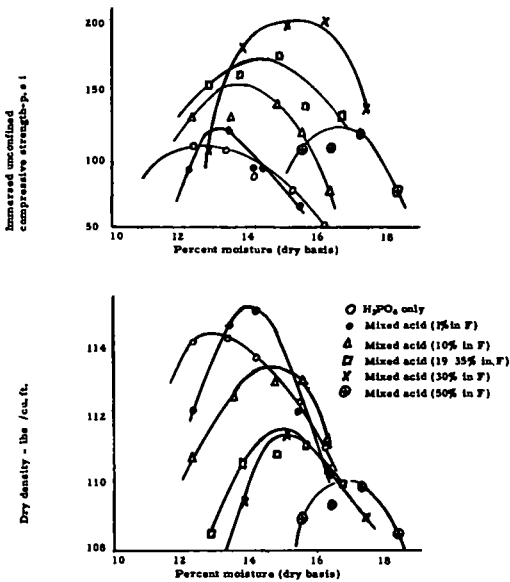


Figure 7. Addition of two percent (excluding free water) of mixtures containing phosphoric and hydrofluoric acids to Louisiana silty clay loam A-6(10)-2 by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed 2 days.

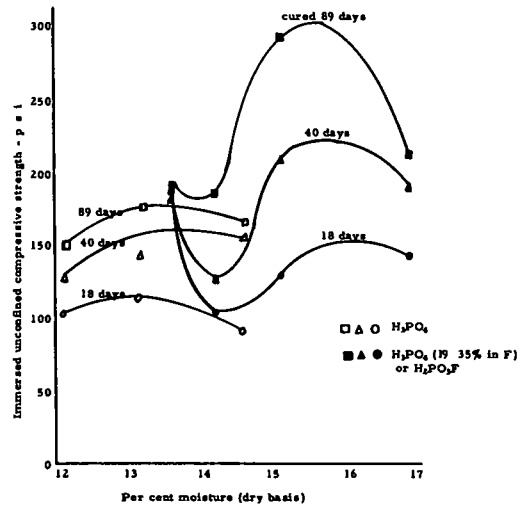


Figure 8. Orthophosphoric acid vs monofluorophosphoric acid cured varying times—Louisiana silty clay loam A-6(10), 2 by 4-in. cylinders, 8 blows per each of 4 layers.

acid alone. With the mixed acid there is a definite loss in strength and in density, both perhaps attributable to too rapid hardening of the soil before compaction. Evidently the effect of fluoride can be best used with clay soils having a high silt content.

Surface Active Agents

The curves in Figure 4 indicate that "wet process" acid made with a sulfuric acid containing alkyl sulfates or sulfonates (spent alkylation acid) was slightly better as a soil stabilizer than phosphoric acid made from pure sulfuric acid. Therefore, the effect of adding various organic surface active agents was studied. The results are given in Table 1. With 0.5 percent

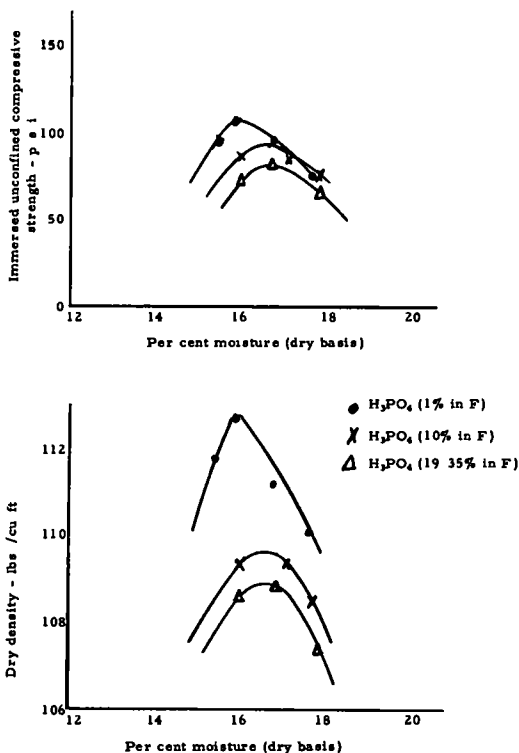


Figure 9. Effect of two percent of mixtures of phosphoric and hydrofluoric acids (free water in acids excluded) on Keyport clay loam A-7-6(12)-2- by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed 2 days.

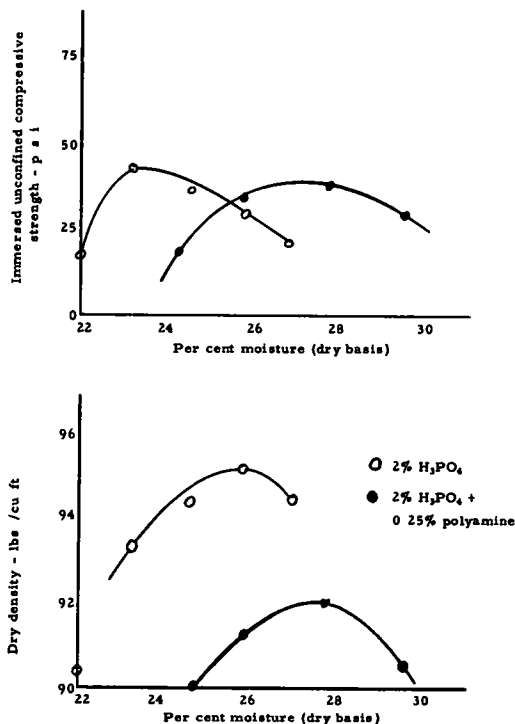


Figure 10. Effect of adding a substituted polyamine (N-tetrapropenyl diethylene triamine) with phosphoric acid to Putnam clay A-7-6(19)-2- by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed two days.

dodecylbenzene sulfonic acid, no change was observed, but with 0.2 percent of this material a significant improvement in strength occurred. Thus, too much surfactant can be harmful. With mixed alkane sulfonic acids such as might occur in spent alkylation acid, a similar strength improvement took place. A somewhat lesser change was found with the nonionic surfactant, but a change nonetheless. With the cationic, substituted polyamine, a drastic decrease in density occurred due to its potent flocculating properties. Strength loss was relatively minor compared to the density change, however. It is apparent that surfactants can play an important but not a dominating role in soil stabilization.

Figures 10 and 11 further develop the effect of adding the cationic agent, this time with the heavy Putnam clay. The loss of several pounds of density with the attendant

TABLE 1
EFFECT OF SURFACTANTS ON IMMERSSED STRENGTH OF KEYPORT CLAY
LOAM A-7-6(12) TREATED WITH 2 PERCENT $H_3PO_4^a$

| Additive | H ₂ O (%) | Dry Density (pcf) | Immersed Unconfined Compress. Str. (psi) |
|---|----------------------|-------------------|--|
| 2% A. R. H_3PO_4 only | 15.7 | 116.4 | 103 |
| 2% H_3PO_4 + 0.5% Dodecylbenzene sulfonic acid (DDBSA) | 15.6 | 114.2 | 101 |
| 2% H_3PO_4 + 0.2% DDBSA | 15.4 | 114.8 | 132 |
| 2% H_3PO_4 + 0.5% mixed alkane sulfonic acid (avg. C ₂) | 15.6 | 114.8 | 125 |
| 2% H_3PO_4 + 0.5% tridecanol-ethylene oxide condensate (10 E. O.) | 15.7 | 112.7 | 115 |
| 2% H_3PO_4 + 0.5% N-tetra-propenyl diethylene triamine (cationic) | 15.8 | 109.3 | 95 |

^aCured 5 days, soaked 2 days, 12 blows per each of 4 layers.

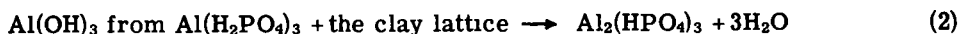
shift of optimum moisture content for strength and density to the higher moisture levels may be noted. There was only a small loss in maximum strength. This was accompanied by a broadening of the strength-moisture curves.

Reaction Mechanism

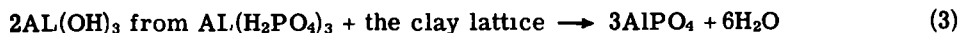
It is apparent that phosphoric acid effects changes in the properties of clay soils by reacting with the clay lattice itself. In addition to the evidence presented herein, the work of Demirel, Benn, and Davidson (1) is of interest. They recorded X-ray diffraction patterns of clay minerals before and after exposure to relatively large quantities of phosphoric acid. These patterns clearly show a breakdown of the clay crystals due to phosphoric acid treatment. Further refinement of this approach should lead to confirmation of the entire reaction mechanism. In this investigation, wet chemical data have been obtained indicating the nature of the mechanism.

Figure 12 shows the change in pH of the treated soil over several thousand hours. There is a distinct change in slope—for Keyport clay loam it occurs at about 120 hr, for the silty clay loam there are two changes, the times varying for the several acid combinations shown. As a check on the validity of this change in slope, the date of Figures 12a and 13 may be compared. The latter shows soluble aluminum and phosphorus for centrifuged samples from Figure 12a. The change in slope of the pH-time curve occurs simultaneously with a sharp drop in aluminum and phosphorus found in solution—all three changes occurring at 120 hr. A reaction takes place between the clay and the phosphoric acid in which initially aluminum dissolves from the clay and subsequently reprecipitates. As the acid is consumed the pH of the soil water rises. At the point represented by 120 hr, one may postulate that, for Keyport clay loam, at this point all the free phosphoric acid has been consumed. The acid pH is due to a soluble aluminum acid phosphate. As more time passes, this acid phosphate reacts further to precipitate a higher aluminum phosphate such as the one postulated by Michaels, Williams and Randolph (2).

The possible reactions are as follows:



OR



In Eqs. 1 and 2 taken together, two moles of water should be liberated per mole of acid consumed. In Eqs. 1 and 3, three moles of water should be produced per mole of acid. In Michaels work (2), only one mole of water per mole of acid was found to be evolved on drying soil treated in this same manner (presumably shortly after the acid-clay-water system was mixed). This mole of water is attributed by Michaels to a one-to-one molar reaction leading to a hydrated AlPO_4 structure at 110 C. The author's data indicate that the first reaction leads to the well-known water soluble monobasic salt, thereby generating one mole of volatile water per mole of acid. The data also clearly show the stepwise production of a less soluble material that is undoubtedly the cementing agent. From the solubility studies of Brosheer and his co-workers (3), it was found that $\text{Al}_2(\text{HPO}_4)_3$ does not exist in equilibrium with phosphoric acid. It is therefore postulated that the final product of the reaction is as represented in Eq. 3. The water

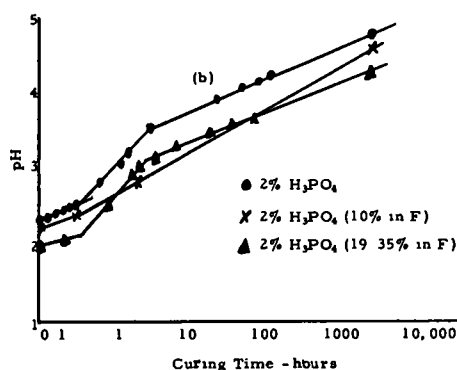
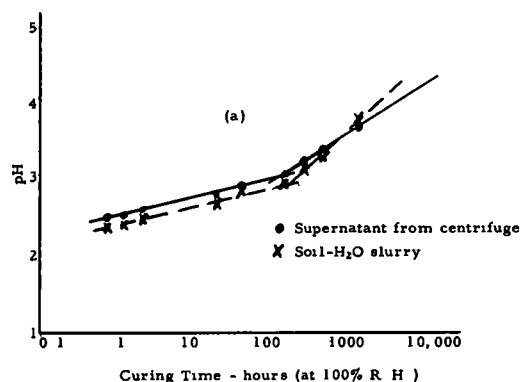
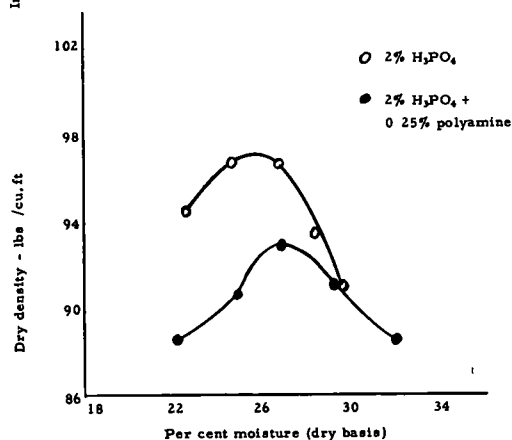
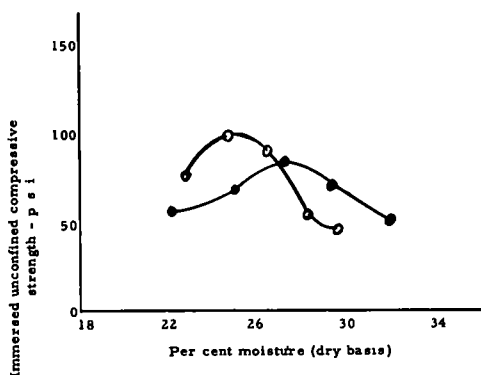


Figure 12. Change in pH of soil-water system with time of contact between soil and acid: (a) 2 percent phosphoric acid in Keyport clay loam A-7-6(12); (9b) 2 percent phosphoric or phosphoric-hydrofluoric acid in Louisiana silty clay loam A-6(10), pH measured in 50 percent solids soil-water slurry only; soil cured as slurry.

Figure 11. Effect of N-tetrapropenyl diethylene triamine on Cecil clay loam A-7-5(17) treated with 2 percent phosphoric acid—2 by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed 2 days.

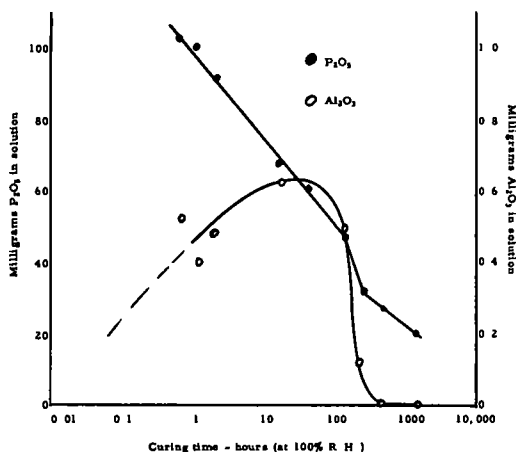
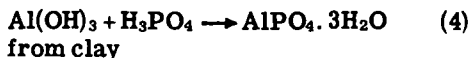


Figure 13. Change in soluble P_2O_5 and Al_2O_3 with time of contact between 2 percent phosphoric acid and Keyport clay loam A-7-6(12).

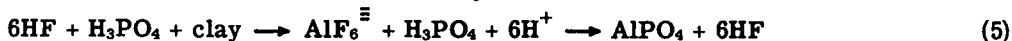
produced probably remains as the trihydrate, the existence of which has also been shown by Brosheer. Thus the over-all reaction at room temperature is:



In practice, the reaction does not go to completion for many months. Thus, the natural pH of Keyport clay loam is about 4.8, whereas after about 1,500 hr the treated soil pH is still less than 4. It may be predicted that more strength will be generated with time even after two months, because there is still some acidic material remaining to react with the clay.

With regard to the effect of hydrofluoric acid, no firm conclusions can be reached. Figure 12b shows that uniformly lower pH values are recorded for the mixed acid systems than for phosphoric acid alone. This should lead to a speeding up of the over-all reaction with the mixed acids. Possibly the hydrofluoric acid attacks the

silica portion of the clay lattice leaving exposed a hydrous alumina subject to reaction with the phosphoric acid. Alternatively, one might postulate the hydrofluoric acid first reacts with the aluminum of the clay but yields it to the phosphate in the pore liquor. The fluoride is then free to extract more aluminum from the clay. This latter mechanism is shown as follows:



This is an oversimplified view of what is undoubtedly a very complex reaction. To cite just two complications, (a) the mixed acids do not act independently, and (b) fluosilicate has also been shown to have an effect quite similar to that of the simple fluoride system. The 19.35 percent fluoride mixed acid, for example, has been shown, by nuclear magnetic resonance (4), to be monofluorophosphoric acid (H_2PO_3F) which is only partially dissociated in solution to its component acids. Whether this acid behaves as in Eq. 5 in contact with clay minerals or precipitates an aluminum fluorophosphate is not known. How the similar effect of fluosilicate reported by Michaels (2) fits with these postulates is also uncertain.

DISCUSSION

Nearly all the changes in immersed strengths compared to orthophosphoric acid reported above are accompanied by a change in density of the soil. This change in density reflects the tendency of the treated soil to agglomerate. Density is affected by the strength of these agglomerates during compaction. Agglomeration may be produced by simple electrochemical flocculants such as the calcium ions produced by the phosphate rock-sulfuric acid reaction, or by the polycationic amine. A decrease in density compared to orthophosphoric acid alone is found in both cases. Strength may be maintained despite the loss in density.

When polyphosphoric acids or mixtures of hydrofluoric and orthophosphoric acids were added to clay soil, a loss in density was observed compared to orthophosphoric acid alone. This decrease in density is attributed to an acceleration of the reaction with the clay resulting in chemical agglomeration. The partially reacted mass becomes firm enough to give noticeable resistance to compaction. This led to less dense, honey-combed samples. The hardening of the soil in some cases was apparent even to the touch. The high strengths obtained with some of these accelerated systems are even more significant in light of the lowered densities. Had the samples been compacted to

the density of plain soil or of the orthophosphoric acid-soil combination, very high strengths, indeed, would be expected. In field operations where somewhat higher than normal compactive efforts can often be applied, these phenomena should have practical significance and should not be overlooked.

The demonstration that phosphoric acid derived directly from phosphate rock by the action of sulfuric acid—so called "wet process" acid—performs as well as the pure variety of phosphoric acid has considerable economic significance, as will be shown in Part III. It is quite clear from the data presented here, that no disadvantage strength-wise will be met by using the "wet acids" of commerce. In fact, the presence of some amount of fluorides and surface active materials may prove to be of benefit. However, the direct use of phosphate rock and sulfuric acid (premixed on the site or applied to the soil separately) appears to be much inferior in the soils studied. These results are in conflict with those of Michaels (5), apparently due to the heavier textures of the soils used in the present study. Fairly good results were obtained with synthetic hydroxylapatite, but poor results were obtained with natural fluorapatite. The latter material represents most of the commercially available phosphate rock in this country. Fluorapatite is known to be less reactive than its hydroxyl counterpart. The high unsoaked strengths obtained with fluorapatite are interesting but are not felt to be of much importance as compared with the immersed- or exposed-strength data.

The effects noted with the synthetically contaminated orthophosphoric acids (added hydrofluoric acid, organic surface active agents, substituted polyamine, etc.) will be useful in some soil types. The hydrofluoric-phosphoric acid combination is applicable to the silty clay soils found, for example, in the delta regions of our great rivers. In fact, the hydrofluoric acid addition appears to be essential for satisfactory stabilization of silty clay from Louisiana. The effect of anionic or nonionic wetting agents appears to be that of improving the distribution of the phosphoric acid in the soil. As a result of more uniform distribution, wider utilization of the acid occurs yielding somewhat higher strengths. This effect should appear in nearly all clay soils. The more dramatic changes obtained with the cationic surfactant (polyamine) occur at higher concentrations (up to 0.5 percent) and are due to improved wetting coupled with some waterproofing and potent flocculation of the clay. The flocculation is equivalent to that obtained with larger amounts of multiply charged cations derived from simple salts; e.g. $\text{Al}_2(\text{SO}_4)_3$ and $\text{Ca}(\text{OH})_2$.

The use of the substituted polyamine is called for when the soil is decidedly wetter than optimum or when immediate strength is required. (Lyons (6) and Michaels (2) have shown that some immersed strength is obtained immediately when phosphoric acid and a few tenths of one percent of an amine are combined.) The effect of the polyamine on plasticity and workability will be discussed along with the economics of the system in Part III. It will suffice to say that wet soils are rendered more easily mixed with the amine-acid system and that during certain portions of the construction season use of the amine may be cheaper than waiting for natural drying of the soil.

The data presented strongly support the theory that phosphoric acid reacts with the clay crystals to produce an aluminum phosphate cement via well-known reactions. Of course, some of the acid may also react with free iron and aluminum oxides in the system as well as with other cations present. Future investigations of the reaction should include studies of highly purified clay minerals by the method described herein. In addition, more highly-refined X-ray diffraction and differential thermal analysis techniques will undoubtedly be developed that will permit detection of the reaction products when only a small percent of phosphoric acid is reacted with pure clays.

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III. Some Practical Aspects

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● ALL OF THE USUAL testing procedures and identification of most of the chemicals are included in Parts I and II and will not be repeated here. Other equipment and procedures were as follows:

1. The Brabender Plastograph. This instrument, made by the C. W. Brabender Instruments Company, South Hackensack, N. J., is a mixing chamber equipped to measure the torque on the mixing shaft as a function of time. The mixing chamber used in this particular test was a sigma-blade mixer with a 1-qt chamber. The soil was brought to the proper moisture content in an ordinary muller-and-plow mixer and placed in the plastograph. Then the chemicals were added and the change of mixing torque observed with time. This was done at approximately optimum moisture content.

2. The penetration tests made on the field-test patches were conducted with a Soiltest CN-419 Proctor penetrometer. The results were obtained using several of the needles and converted to equivalent pounds required for penetration of $\frac{1}{4}$ in. on the No. 252 needle (0.25-in. diameter). Conversions of readings taken with larger needles were done by use of a factor representing the approximate ratio of surface areas of the respective needles.

3. Corrosion inhibitors were obtained from several companies as well as from experimental lots prepared at Monsanto Chemical Company. Rodine 201 and 203 are made by AmChem Products, St. Joseph, Mo.; Riley 22 is made by Riley Chemical Company, Indianapolis, Ind. MOKI corrosion inhibitor is under development by Monsanto Chemical Company's Corrosion Laboratory, St. Louis, Mo.

4. Sixty-eight test cylinders (2 by 4 in.) were prepared representing some 17 different conditions of chemical treatment or mode of preparation. Each condition was represented in quadruplicate. The order of preparation of these samples was randomized to eliminate operator deviations. The samples were placed randomly in the ground and covered with closely packed earth from the site. Because of the randomization of the sample burial, factors such as drainage and temperature from the nearby building were eliminated. The samples were removed in pairs from the ground at two different times—one set in mid-winter, the other in spring—so that the results are averages of two strength tests per variable.

5. The soil used in the experiment described as the Creve Coeur parking lot test was sampled from another location, tested in the usual manner in the laboratory, and then trucked in and dumped on the construction site. The soil was spread and aerated by means of a garden rototiller until the desired moisture content was attained. Water and phosphoric acid were added to the soil from water cans and the mass mixed by the rototiller. Phosphoric acid was added as a 50 percent solution in water. Compaction was done with pneumatic hammers of the type commonly used in back-filling ditches and the like. The compacted soil was tested for density by means of the Soiltest Volume-measure CN-980, determinations of amount of phosphoric acid present in the compacted soil were done by the usual wet chemical methods and also by X-ray fluorescence. Moisture content was determined by drying in an oven at 105 C overnight. Pen-