318

HIGHWAY RESEARCH BOARD

Bulletin 318

Soil Stabilization with Phosphorus Compounds and Additives

National Academy of Sciences—
National Research Council

publication 964

HIGHWAY RESEARCH BOARD

Officers and Members of the Executive Committee

1962

OFFICERS

R. R. BARTELSMEYER, *Chairman* C. D. CURTISS, *First Vice Chairman*
WILBUR S. SMITH, *Second Vice Chairman*
FRED BURGGRAF, *Director* WILLIAM N. CAREY, JR., *Assistant Director*

Executive Committee

REX M. WHITTON, *Federal Highway Administrator, Bureau of Public Roads* (ex officio)

A. E. JOHNSON, *Executive Secretary, American Association of State Highway Officials* (ex officio)

LOUIS JORDAN, *Executive Secretary, Division of Engineering and Industrial Research, National Research Council* (ex officio)

PYKE JOHNSON, *Retired* (ex officio, Past Chairman 1960)

W. A. BUGGE, *Director of Highways, Washington Department of Highways* (ex officio, Past Chairman 1961)

R. R. BARTELSMEYER, *Chief Highway Engineer, Illinois Division of Highways*

E. W. BAUMAN, *Director, National Slag Association, Washington, D. C.*

DONALD S. BERRY, *Professor of Civil Engineering, Northwestern University*

MASON A. BUTCHER, *County Manager, Montgomery County, Md.*

J. DOUGLAS CARROLL, JR., *Director, Chicago Area Transportation Study*

C. D. CURTISS, *Special Assistant to the Executive Vice President, American Road Builders' Association*

HARMER E. DAVIS, *Director, Institute of Transportation and Traffic Engineering, University of California*

DUKE W. DUNBAR, *Attorney General of Colorado*

MICHAEL FERENCE, JR., *Executive Director, Scientific Laboratory, Ford Motor Company*

D. C. GREER, *State Highway Engineer, Texas State Highway Department*

JOHN T. HOWARD, *Head, Department of City and Regional Planning, Massachusetts Institute of Technology*

BURTON W. MARSH, *Director, Traffic Engineering and Safety Department, American Automobile Association*

OSCAR T. MARZKE, *Vice President, Fundamental Research, U. S. Steel Corporation*

J. B. MCMORRAN, *Superintendent of Public Works, New York State Department of Public Works*

CLIFFORD F. RASSWEILER, *Vice President for Research and Development, Johns-Manville Corporation*

GLENN C. RICHARDS, *Commissioner, Detroit Department of Public Works*

C. H. SCHOLER, *Applied Mechanics Department, Kansas State University*

WILBUR S. SMITH, *Wilbur Smith and Associates, New Haven, Conn.*

K. B. WOODS, *Head, School of Civil Engineering, and Director, Joint Highway Research Project, Purdue University*

Editorial Staff

FRED BURGGRAF HERBERT P. ORLAND
2101 Constitution Avenue Washington 25, D. C.

The opinions and conclusions expressed in this publication are those of the authors
and not necessarily those of the Highway Research Board

NRC

HIGHWAY RESEARCH BOARD

Bulletin 318

Soil Stabilization with Phosphorus Compounds and Additives

Presented at the
40th ANNUAL MEETING
January 9-13, 1961

National Academy of Sciences—
National Research Council
Washington, D.C.
1962

$2 00

Department of Soils, Geology and Foundations

Miles S. Kersten, Chairman
Professor of Civil Engineering
University of Minnesota, Minneapolis

PHYSICO-CHEMICAL PHENOMENA IN SOILS

Hans F. Winterkorn, Chairman
Head, Soils Physics Laboratory
Princeton University, Princeton, New Jersey

G.C. Blomquist, Associate Professor of Civil Engineering, Michigan State University, East Lansing

Donald T. Davidson, Professor of Civil Engineering, Iowa State University, Ames

James H. Havens, Assistant Director of Research, Kentucky Department of Highways, Lexington

J.B. Hemwall, Agricultural Research, Dow Chemical Company, Seal Beach, California

Earl B. Kinter, Bureau of Public Roads, U.S. Department of Commerce, Washington, D.C.

Philip F. Low, Professor of Soil Chemistry, Agronomy Department, Purdue University, Lafayette, Indiana

R.C. Mainfort, Michigan State Highway Department, Olds Hall of Engineering, Michigan State University, East Lansing

Edward Penner, Division of Building Research, National Research Council of Canada, Ottawa

Ralph L. Rollins, Associate Professor of Civil Engineering, Brigham Young University, Provo, Utah

Elmer A. Rosauer, Engineering Experiment Station, Iowa State University, Ames

J.B. Sheeler, Associate Professor of Civil Engineering, Engineering Experiment Station, Iowa State University, Ames

F.L.D. Wooltorton, 399 Oxford Street, London W. 1, England

Contents

INTRODUCTORY REMARKS

Hans F. Winterkorn 1

PHOSPHORIC ACID IN SOIL STABILIZATION 4

I. Effect on Engineering Properties of Soils

J.W. Lyons and G.J. McEwan. 4

II. Secondary Additives, Acid Source, and Mechanism

J.W. Lyons, G.J. McEwan and C.D. Siebenthal 15

III. Some Practical Aspects

J.W. Lyons. 24

BASIC IMPROVEMENTS IN PHOSPHATE SOIL STABILIZATION

John B. Hemwall and Henry H. Scott 35

EVALUATION OF PHOSPHORIC ACID FOR STABILIZATION OF FINE-GRAINED PLASTIC SOILS

James A. Kelley and Earl B. Kinter 52

EFFECTS OF FLUORIDES, WATERPROOFING AGENTS, AND POLYPHOSPHORIC ACID ON SOIL STABILIZATION WITH ACIDIC PHOSPHORUS COMPOUNDS

Alan S. Michaels and F.W. Tausch, Jr. 57

REACTIONS OF PHOSPHORIC ACID WITH CLAY MINERALS

Turgut Demirel and Donald T. Davidson 64

FIELD STUDIES OF SOIL STABILIZATION WITH PHOSPHORIC ACID

J.W. Guinnee. 72

FROST STABILIZATION OF SEVERAL SOILS WITH SODIUM-TRIPOLYPHOSPHATE AND SODIUMPYROPHOSPHATE

K. Beltz and G. Müller-Schiedmayer 83

Introductory Remarks

HANS F. WINTERKORN, Director, Soil Science Laboratory, Princeton University

● SEVERAL REPORTS on the use of phosphoric acids and phosphates in soil stabilization were offered to the Department of Soils, Geology and Foundations after the deadline for acceptance of papers for the 1960 Annual Meeting of the Highway Research Board. Because it was too late for their inclusion in the already established program, and in view of the apparent renewal of interest in the use of such compounds in soil stabilization, it was decided that a symposium be organized on this topic for the 1961 meeting of the Board. J.W. Lyons, of the Monsanto Chemical Company, was asked to collect and organize papers for this symposium. This he did diligently and effectively, and it is deemed no more than fair that he take the chair during presentation of those papers due to his efforts.

This should not indicate a lack of interest in this area on the part of the committee chairman. On the contrary, in 1933 he was conducting field experiments for the Missouri State Highway Department on the soil stabilizing effect of soluble phosphates (1); subsequently, in the early 1940's, in work for the Civil Aeronautics Administration and the Air Force, and again in the later forties, in work for the Navy Department, he directed laboratory and field experiments on the soil stabilizing power of phosphoric acids and acid, neutral and basic phosphates, by themselves or in combination with organic amines, amine-aldehyde condensation products, partially neutralized resinous fatty and lignin acids, and other chemicals. A number of the soil systems thus treated could be considered as stabilized; however, the stringent requirements set up by the Government for that program, requiring that less than 2 percent of stabilizer had to provide effective stabilization under war construction conditions, and the vagaries encountered with phosphate stabilization, forced him to follow other more promising lines of research. Though much of this work was originally confidential, it has long since become declassified. In 1945, still under war-time restrictions, he wrote "So far, none of the soil treatments based on the formation of an insoluble silicate, phosphate, borate, or other inorganic salt in the soil has been successful in shallow soil stabilization, within an economical range of material employed. Winterkorn believes that no formation of an insoluble compound will result in satisfactory soil stabilization for road and airport bases, if such formation involves also the formation of a soluble salt, which may increase the water affinity of the soil system." (2) The obvious inference was that best results had been obtained by reaction between the phosphoric acids and aluminum and iron components of the solid soil minerals.

Such reactions, occurring at normal temperatures between soil constituents and phosphoric acids, as well as acid salts, had long been known and studied, mainly because of their undesirability in the manufacture of super- and double super-phosphate fertilizers (3) and in the fertilizing of soils possessing clay minerals of low silica-sesquioxide ratios. A good deal of research in agricultural chemistry has been and still is being devoted to the elucidation of this complex field. The complexity is, of course, one of the main reasons for the vagaries so often encountered in phosphate-soil stabilization.

With respect to the development of cementing power as a result of such reactions, a considerable body of knowledge was already available to the chemical art, by 1931. Proof of this can be found in practically every old-time chemical formulary or book of chemical recipes. A typical recipe (4) reads as follows:

<u>Dental Cement:</u>	Lithium phosphate	$\frac{1}{2}$ oz
	Phosphoric acid	5 oz
	Zinc phosphate	$\frac{1}{2}$ oz
	Aluminum phosphate	$\frac{1}{3}$ oz

The above is added to a ground porcelain of the following composition:

Alumina	30 - 50 oz
Feldspar	10 - 20 oz
Sand	25 - 40 oz
Zinc oxide	1 - 10 oz

The bearing of this recipe on phosphate soil stabilization is apparent from the composition of the ground solids to be cemented. It is also apparent that this "empirical" recipe is quite scientific insofar that the chemicals first mixed with phosphoric acid show the latter's molecules what type of reaction is expected from them.

An ever-present problem in producing either crystals of appreciable size, coherent coatings, or cementing substances by the interaction of two solutions is the formation of too many crystal nuclei deriving from too high a concentration or activity of the reagents. This often results in pulverulant, noncementing systems. Thus, Henin, in attempting to synthesize montmorillonite in an aqueous medium, obtained nothing but amorphous floccules when he added the soluble silicate even in very low concentrations. The desired synthesis occurred, however, by itself when the reagent-catalyst solution without the soluble silicate was stored for an extended period of time in a glass vessel. The rate of solution of silicate from the glass was slow enough to permit its orderly incorporation into a structure that proved to be montmorillonite.

Slow reactions of this kind are important in many types of soil stabilization. For quicker formation of cementing substances, one normally choses an aqueous phase of elevated viscosity. This viscosity is supposed to slow down the movement of the reacting ions or molecules to a sufficient extent to permit the development of a structure that possesses the desired cementing properties. This argument possesses validity as far as true viscosity is concerned. It breaks down, however, in the many cases of structural viscosity in which essentially the same molecular and ionic mobility may obtain, irrespective of whether the solvent is in the form of a free liquid or has become enmeshed within a gel structure. It may well be, though, that such gels or similar systems, which owe their high integral flow resistance to a secondary structure, induce the reactants to build themselves into this structure or at least to follow its pattern. Keeping in mind that silicates, phosphates, borates, and similar compounds are essentially oxygen structures, with positive ions built in whenever geometry and electric neutralization requirements call for it, and that the water molecule itself is volumetrically mostly oxygen, the importance of a reaction-directing gel or related structure should be apparent. Such a role is easily played by many hydrophilic organic substances such as carbohydrates and proteins, and their intimate interaction with phosphates both within and outside of living bodies is well known. The bearing of this on cementing action is also well illustrated by the following old recipe (4, 1:9).

Casein Glue, Water Resistant

Casein	39
Peanut meal	39
Hydrated lime	11
Trisodium phosphate	4
Sodium fluoride	7
Water	225-235

Add the solids slowly to the water while stirring with an efficient stirrer. Continue until smooth and free from lumps. Allow to stand 20-30 minutes and add a mixture of aldol ½, water 1, and 50 percent copper nitrate 2. Stir for 5 minutes then it is ready for use.

Before denouncing a formula of this type as "creeping empiricism", a second look had better be taken. This reveals an ingenious use of the following:

1. Interaction with water of the casein and peanut meal, on one hand, and of the inorganic ions, especially PO_4^{---}, on the other, with formation of specific hydration structures;
2. Interaction between PO_4^{---}, Ca^{++}, and F^-, influenced by their respective hydration structures and also by that of the organic components of the system;
3. Denaturation of the proteins by the excess of the inorganic ions over the amounts

required for apatite formation and sorptive binding of these excess ions by the organic matter.

4. Waterproofing treatment by reaction of the proteins with the aldol.
5. Utilization of the fungicidal and bactericidal properties of fluorine and copper ions.

With similar combinations, but employing aniline-furfural in small amounts, as more effective waterproofing and germicidal agents, beach sands have effectively been stabilized in the laboratory and in small field tests.

This composition may be viewed from another angle, namely, the stabilization of the very hydrophilic casein and peanut meal by means of a calcium phosphate compound. In stabilization of soils with phosphoric acid, calcium in the soil has been found quite detrimental. Are there not some valuable lessons to be learned from this formula for the potential phosphate stabilization of such soils and also from the fact that calcium-rich soils usually contain in their organic matter a goodly portion of proteins?

At the present time there are on the market several well-established cementing and waterproofing materials that are of lower cost than phosphoric acid with or without ancillary additives. To gain field experience for cementing phosphate stabilization, similar in extent and dependability to that accumulated in the past for bituminous, portland cement and line stabilization, for example, would require investments of a magnitude that no single chemical company could justify to its stockholders. Nor could any state highway department, singly or in combination with others, justify such expense or even in this time of shortage of highway engineering personnel justify assignment of the necessary trained men to such a development.

As far as cementing stabilization with the various phosphoric acids and phosphates is concerned, the limited available resources need to be directed to possible stabilization of such soils or soil conditions for which stabilization by presently available means and materials has definitely been proven ineffectual or uneconomical. Personnel from the chemical industry and from universities and research institutes that would follow this line, must add to their arsenal of so-called purer chemical and physical weapons those of colloid chemistry and even of alledgedly "crude" empiricism if they want to succeed. With growing familiarity with the intrinsic complexity and dynamism of natural and stabilized soil systems under actual service conditions, they will be better prepared to utilize the knowledge accumulated over the years by the many devoted and excellently qualified material and soils engineers in the highway departments.

Cementing stabilization, however, may hardly be considered as the most significant, potential contribution of phosphate and polyphosphate compounds to highway engineering. Rather, more important possibilities are presented by the effect of the respective anions on the structure of the water contained in soil pores and adsorbed on the surfaces of soil mineral and organic constituents. One consequence of such change in water structure is the repression of frost heave in normally susceptible soils. The last paper on the program treats of this subject.

Before concluding these introductory remarks, reference might be made to a case of naturally occurring phosphate-soil stabilization observed and excellently described by Tschebotarioff (5) under the title "An Unusual Case of Accidental Underwater Stabilization of a Natural Clay Deposit and Its Implications."

REFERENCES

1. Winterkorn, Hans F., "Job Experience with Exchange Phenomena Involving Inorganic and Organic Ions." ASTM Special Publication 142 (1952).
2. Winterkorn, Hans F., "Principles and Practice of Soil Stabilization." Colloid Chemistry, J. Alexander (Ed.), Reinhold, 6:490 (1945).
3. Ost, H., "Lehrbuch der Chemischen Technologie." 17th Ed., Leipzig, pp. 207-212 (1930).
4. Bennet, H., "Chemical Formulary." Van Nostrand, 3:15 (1936).
5. Tschebotarioff, G.P., "Soil Mechanics, Foundations and Earth Structures." pp. 325-327.

Phosphoric Acid in Soil Stabilization

This paper discusses the effect of phosphoric acid on several of the engineering properties of clay soils. Acid concentration, curing time, moisture-density relations, etc., are presented. This is followed by consideration of the different sources of acidic phosphate and a review of the effect of secondary additives. The mechanism of phosphoric acid stabilization is discussed from a wet-chemical viewpoint. The final part of the paper considers several variables that affect field application of the method; that is, extent of mixing, degree of compaction as percent of standard, etc. Two small test sections are described. The economics of phosphoric acid stabilization are reviewed.

1. *Effect on Engineering Properties of Soils*

J.W. LYONS and G.J. McEWAN, Inorganic Chemicals Division, Monsanto Chemical Company, St. Louis, Mo.

● IN RECENT YEARS much emphasis has been placed on the need for a chemical treatment to improve fine-grained soils for use in highway subgrade and base course construction (1, 2). Soils containing appreciable amounts of clay minerals generally require some form of stabilization because of the tendency to deteriorate structurally in the presence of excess water. Thus, many clay soils swell markedly in water and lose all, or nearly all, of their ability to support loads of the type encountered in highway or airport use. The alternative to stabilizing these clay soils is removing them and/or interposing a layer of select soil or aggregate beneath the surfacing. This layer of additional material is taken to be sufficiently thick so that the underlying clay soil is not considered at all or only slightly in the structural design. The cost of placing this select material is becoming prohibitive in many areas where sources are distant from the construction site. The need for an economical stabilizer for such clay soils has been growing more acute as construction activity increases. Furthermore, designs have become more stringent because of greater anticipated service requirements.

Phosphoric acid has been shown, in the laboratory, to be a suitable stabilizer for clay soils (3, 10). This series of papers presents laboratory data (some limited field experience is included, but large-scale field testing will be reported separately) showing the effect of several variables on the stability of soil treated with phosphoric acid. Among these variables are moisture content, degree of compaction, degree of mixing and curing, amount of stabilizer, type of soil, and type of exposure. In the second part of the series, the effect of secondary additives, type of phosphoric acid source, and mechanism of stabilization will be discussed. The third part will cover permanency, corrosion, and limited field test work, which led to construction of full-scale test roads. The economics of phosphoric acid treatments will also be reviewed in the third part.

EXPERIMENTAL FACTORS

Atterberg indices were determined by ASTM Procedures D423-39 and 424-39. Tests on stabilized soil were made after humid curing (usually for 5 days at room temperature and 100 percent R.N.), and pulverization with a rubber-covered pestle.

Standard or reference compaction curves were run according to AASHO T 99-49. Other compaction curves were prepared using a 2- by 4-in. specimen size in a device to be described.

Group index was calculated from the Atterberg indices and results of wet sieving on a No. 200 sieve using the relation shown in AASHO M 145-49

Unconfined compressive strength and volume change data were obtained from specimens prepared and treated in the following way:

1. Air-dry soil passing the No. 4 sieve was placed in a muller-and-plow mixer; water and chemicals were added to the running machine. Liquids were added with the water; solids were premixed with the air-dry soil unless otherwise noted. The mixer was run for exactly 5 min after chemical and water addition.
2. The mixture was cured under a wet cloth for exactly 15 min after mixing was stopped.
3. An amount of the mixture calculated to give a compacted specimen height of 4.0 ± 0.1 in. was compacted in a 2-in. diameter mold with a 4-lb hammer falling through a distance of 12 in. The number of blows per each of 4 layers of soil was correlated to compaction curves obtained by AASHO T 99-49 (varying from 6-12 blows per layer). After the first few blows were applied, a wedge was removed from beneath the mold and a lower piston thereby exerted pressure from below with every succeeding blow. (This so-called double-end compaction gave somewhat more uniform densities from top to bottom of each layer.)
4. The compacted specimens were measured, weighed, wrapped in a moisture barrier (Saranwrap), and stored in a humidity chamber at room temperature. The usual curing time was 5 days.
5. The samples were unwrapped, remeasured and reweighed, and immersed totally in water for 2 days. After immersion the samples were briefly drained, remeasured and reweighed, and tested for unconfined compressive strength in a Soiltest AP-170 machine modified to give a rate of strain of 0.25 in. per min. Volume change was computed from the before and after measurements; water absorption, by the weight change.

Test soils were generally air-dried and reduced to -¼-in. size by tamping or by cutting in a Fitzmill (with little or no pulverization of stony material or of sand permitted). The chemicals used were of a reagent grade. Distilled water was used throughout.

TABLE 1

CHARACTERISTICS OF THE TEST SOILS

Soil	Source	Liquid Limit	Plasticity Index	Opt Moist (%)	Max Dry Density (pcf)	Class
Keyport clay loam	Va	46	24	16.7	111.9	A-7-6(12)
Cecil clay loam	Ga [a]	56	25	25.6	95.5	A-7-5(17)
Clay loam	La	32	13	15.2	114.0	A-6(8)
Silty clay loam	La	36	19	15.0	114.0	A-6(10)
Putnam silty clay loam	Mo	40	19	18.1	108.2	A-6-(9)
Putnam clay	Mo	53	35	25.0	95.4	A-7-6(20)
Clay	Creve Coeur, Mo	43	23	17.0	109.7	(14)
Clay	Md	73	44	24.0	94.4	A-7-5(20)
Clay	Md	48	25	18.3	110.0	A-7-6(16)
Clay loam	Co	-	-	15.5	114.5	-

[a] Some 17 samples of Cecil clay soils have been received from Georgia and tested This is a typical material

RESULTS

Test Soil Properties

Table 1 gives the characteristics of the soils used in this work. Of these soils, a great deal of work has been done with the Keyport clay loam, and a considerable amount with the Georgia and Missouri soils. Only cursory studies have been made on the others. The soil from Colorado was a highly alkaline sample (pH 8-9), perhaps not typical of all soils west of the Mississippi, but indicative of many soils of that region. Two other samples from Colorado have been studied with results quite similar to those reported for this sample. Two other soils from Louisiana have been studied briefly, with results similar to those given for the A-6(8) clay loam from that state.

Group Index

Table 2 shows the effect of phosphoric acid on the group index of Putnam clay. A substantial lowering of this index means that the treated soil is much improved as a material of construction. The phosphoric acid treatment reduces the group index by more than half in this particularly plastic and heavy clay.

TABLE 2

EFFECT OF PHOSPHORIC ACID ON GROUP INDEX OF PUTNAM CLAY[a]

Treatment	% Passing No. 200 Sieve	Liquid Limit	Plasticity Index	Group Index
Untreated	85.3	75	55	20
1% H_3PO_4	79.7	51	24	16
2% H_3PO_4	68.4	47	19	11
3% H_3PO_4	60.4	45	17	8
4% H_3PO_4	60.3	47	18	9

[a] Compacted specimens humid-cured 5 days, immersed 2 days in water, air dried, and repulverized. Samples moistened with water and held overnight before testing to insure equilibration.

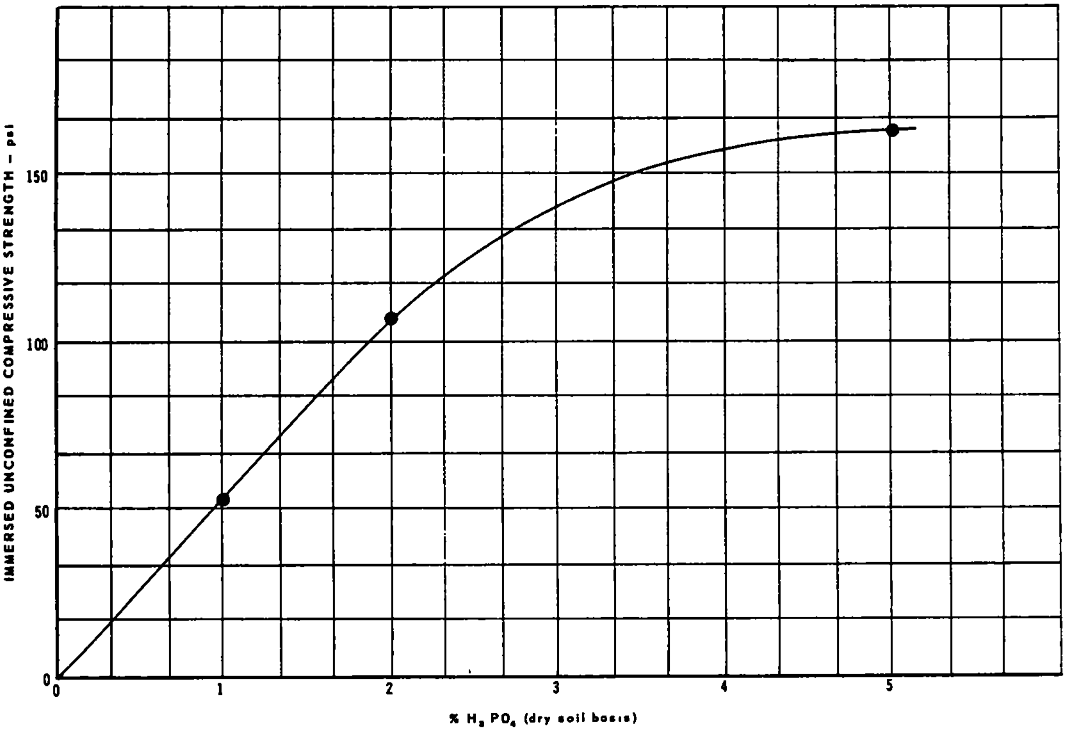


Figure 1. Strength vs phosphoric acid concentration—samples cured at 100 percent R. H. and room temperature 5 days, immersed in water 2 days; Keyport clay loam A-7-6 (12); 2- by 4-in. cylinders, 12 blows per each of 4 layers.

Acid Concentration and Curing Time Before Exposure

Addition of phosphoric acid to clay soil results in an almost linear increase in immersed strength up to about 2 percent H_3PO_4 (based on dry soil weight). Figure 1 shows the strength increases only slowly with greater amounts of acid when the samples are cured just 5 days before immersion. As acid concentration is increased, longer curing times are needed for the formation of the cementing substances (see mechanism discussion in Part II). Thus, Figure 2 shows linear strength increase up to nearly 5 percent H_3PO_4 when curing is extended to 30 days. (Difference in compactive effort in Figs. 1 and 2 is apparent.)

Figure 3 (compaction same as in Fig. 1, greater than in Fig. 2) shows the effect of curing time on immersed strength for a soil treated with 2 percent H_3PO_4. It is clear that the gain in strength is very rapid in the first week, somewhat slower during the next three weeks, and much slower thereafter.

Effect of Compaction

The effect of phosphoric acid on the moisture-density or compaction curve of a soil is of importance to the engineer in designing construction procedures and specifications. Figure 4 shows untreated and treated curves for 4 test soils where dry density is plotted against the moisture content obtained by drying a portion of the soil at 105-110 C. This is not the same as plotting density vs liquid volume, as shown in Figure 5 in which the data of Figure 4 (c) are replotted on a liquid volume basis. In both sets of curves it may be seen that (a) the addition of phosphoric acid shifts the point of maximum dry density from the untreated control and (b) the optimum moisture content is also shifted, considerably in some cases. Density may be lowered with a 2 percent acid treatment

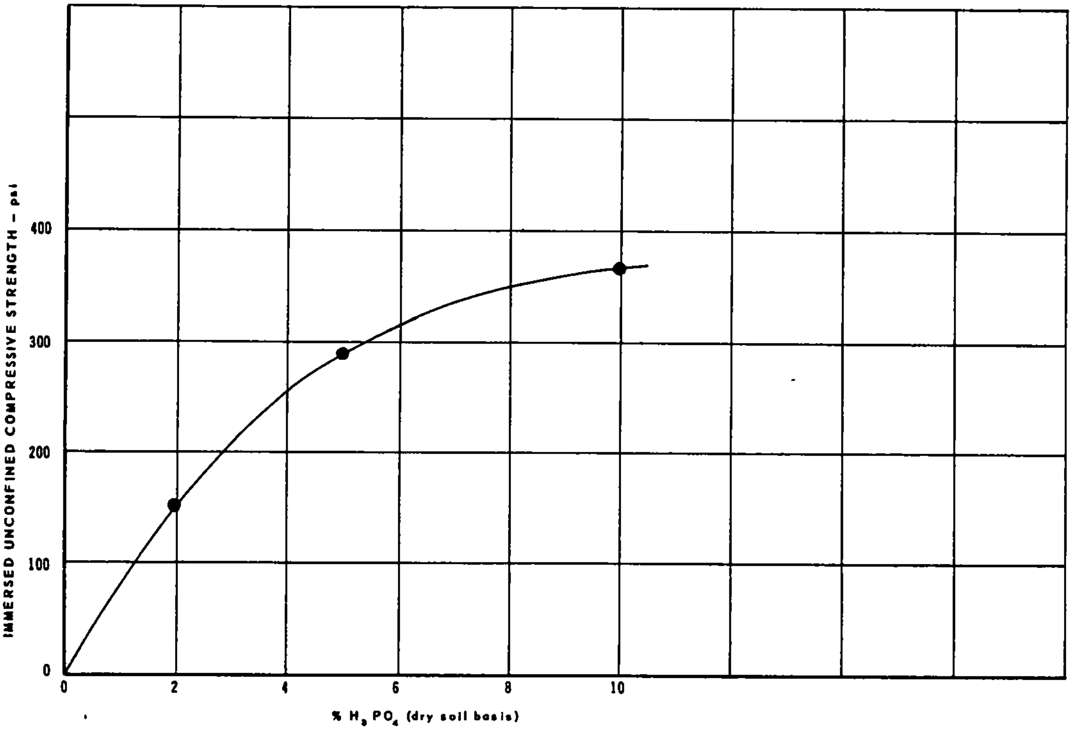


Figure 2. Strength vs phosphoric acid concentration—samples cured at 100 percent R. H. and room temperature 30 days, immersed in water 2 days; Keyport clay loam A-7-6 (12); 2- by 4-in. cylinders, 8 blows per each of 4 layers.

in soils in which the reaction is rapid. Because of the time lapse between mixing and compaction, rapid-harding samples will be more difficult to compact than the corresponding untreated soils. Table 3 compares optimum moisture and maximum dry density in several soils with and without acid treatment. It points up the variations in effect that are encountered.

The data in Table 3 also point to another important aspect; i. e., that the moisture content for maximum immersed strength may not be at optimum moisture for compaction. Figure 6 shows both strength and dry density plotted against molding moisture for the two Maryland soils. Samples prepared at optimum moisture content for density may exhibit somewhat less than maximum strength. A change in acid concentration shifts the moisture content for maximum strength noticeably. This fact has led to the preparation of samples over a range of moisture contents for every preliminary screening test run in this laboratory. This is to make certain that the true maximum stability is observed.

Effect of Soil Type

Table 3 presents a condensation of test results that gives the effect of soil type on strength and compaction with and without phosphoric acid. With two exceptions (Louisiana silty clay loam and Colorado clay loam), the soils studied were very well stabilized with phosphoric acid. Only two of the soils exhibited any appreciable resistance to water without treatment—Louisiana clay loam (44 psi with no acid) and Maryland clay (35 psi with no acid). Both of these clays benefited markedly from phosphoric acid treatment, thereby upgrading them from a position of questionable utility. It appears that soils high in silt and low in clay (Louisiana silty clay loam) will not be

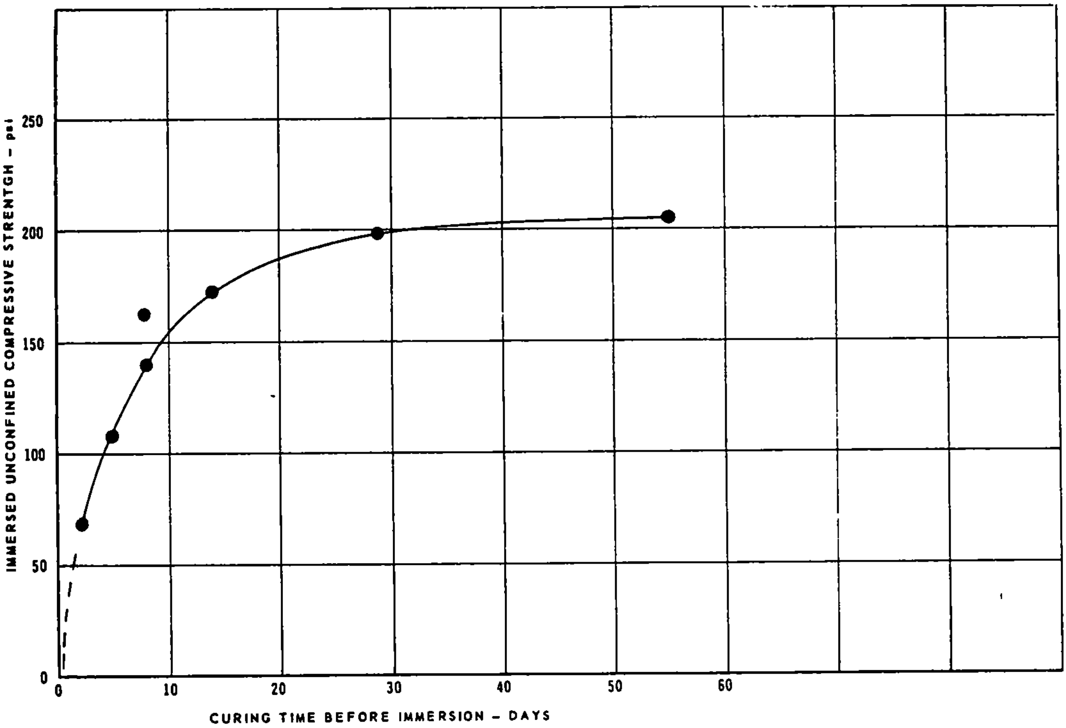


Figure 3. Immersed strength vs curing time—samples cured at 100 percent R. H. and room temperature, then immersed 2 days; Keyport clay loam A-7-6(12); 2 percent H_3PO_4, 2- by 4-in. cylinders, 12 blows per each of 4 layers.

well stabilized by phosphoric acid alone, although some improvement is noted. Highly alkaline soils, such as the Colorado sample, require excessive amounts of acid for relatively inferior stabilization.

Some idea of the anticipated performance within a variable series of related soils can be obtained from Figure 7. This plot shows results for 13 samples taken at 100-ft intervals from a Georgia roadside. Samples from stations 1, 2, 3, 12, and 13 were quite similar in all respects. The intervening samples contained some partially disintegrated shale of a granular nature. The effect on compaction as expressed by

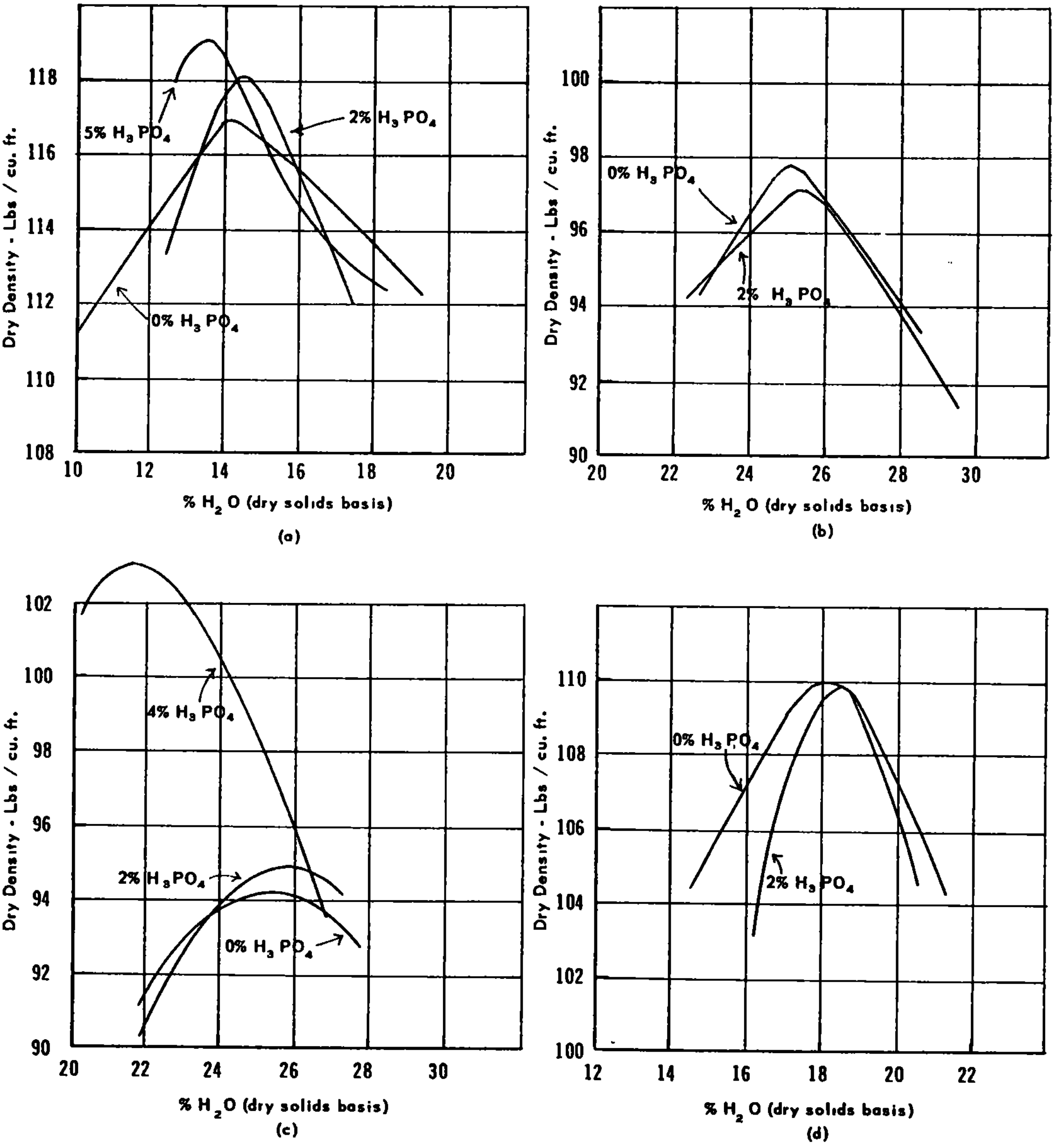


Figure 4. Dry density vs moisture content—2- by 4-in. cylinders compacted in 4 layers: (a) Keyport clay loam, A-7-6(12), 12 blows per layer; (b) Cecil clay loam, A-7-5(17), 8 blows per layer; (c) Putnam clay, A-7-6(20), 8 blows per layer; and (d) Clay, A-7-6(16), Maryland, 8 blows per layer.

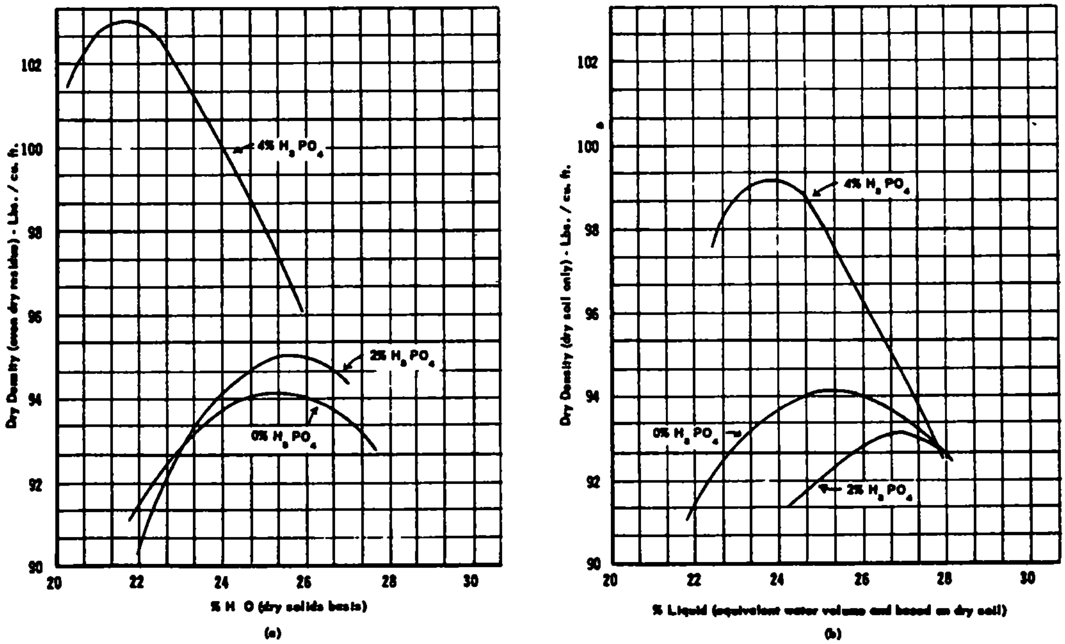


Figure 5. Compaction curves for Putnam clay A-7-6(20)—2- by 4-in. cylinders, 8 blows per each of 4 layers (a) as taken from volatile content in oven at 105-110 C and (b) subtracting the 100 percent H_3PO_4 from density and adding equivalent volume of water to liquid content (assuming 1 gr 100 percent H_3PO_4=0.537 cc H_2O).

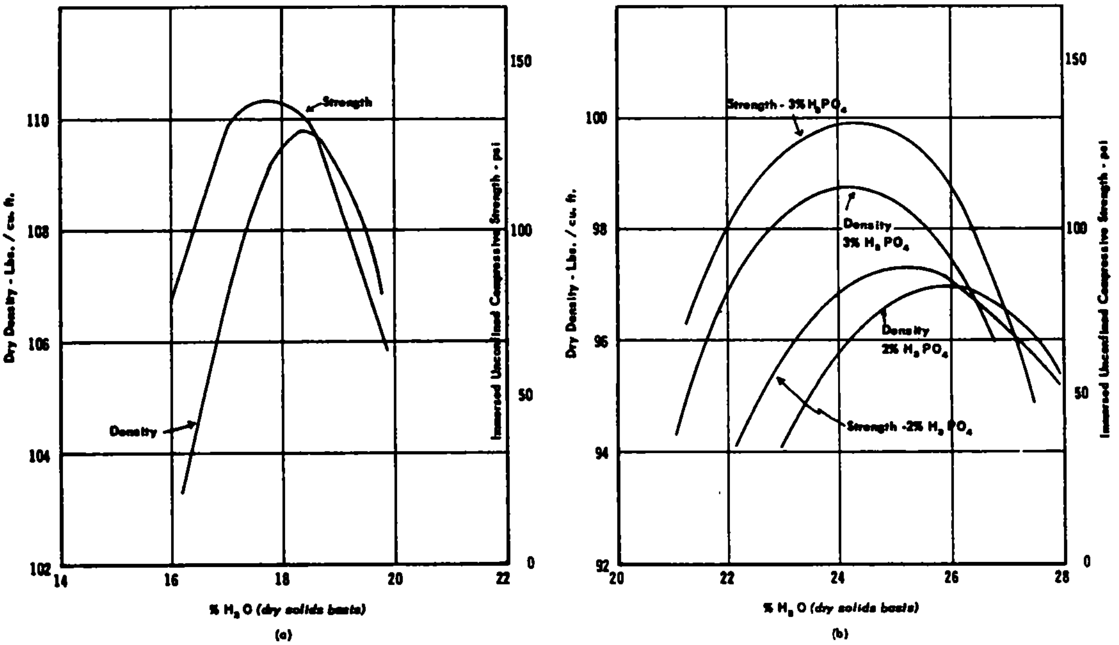


Figure 6. Immersed strength after 5 day humid cure and dry density vs molding moisture content for (a) clay from Maryland A-7-6(16) with 2 percent H_3PO_4 and (b) clay from Maryland A-7-6(20) (2- by 4-in. cylinders, 8 blows per each of 4 layers).

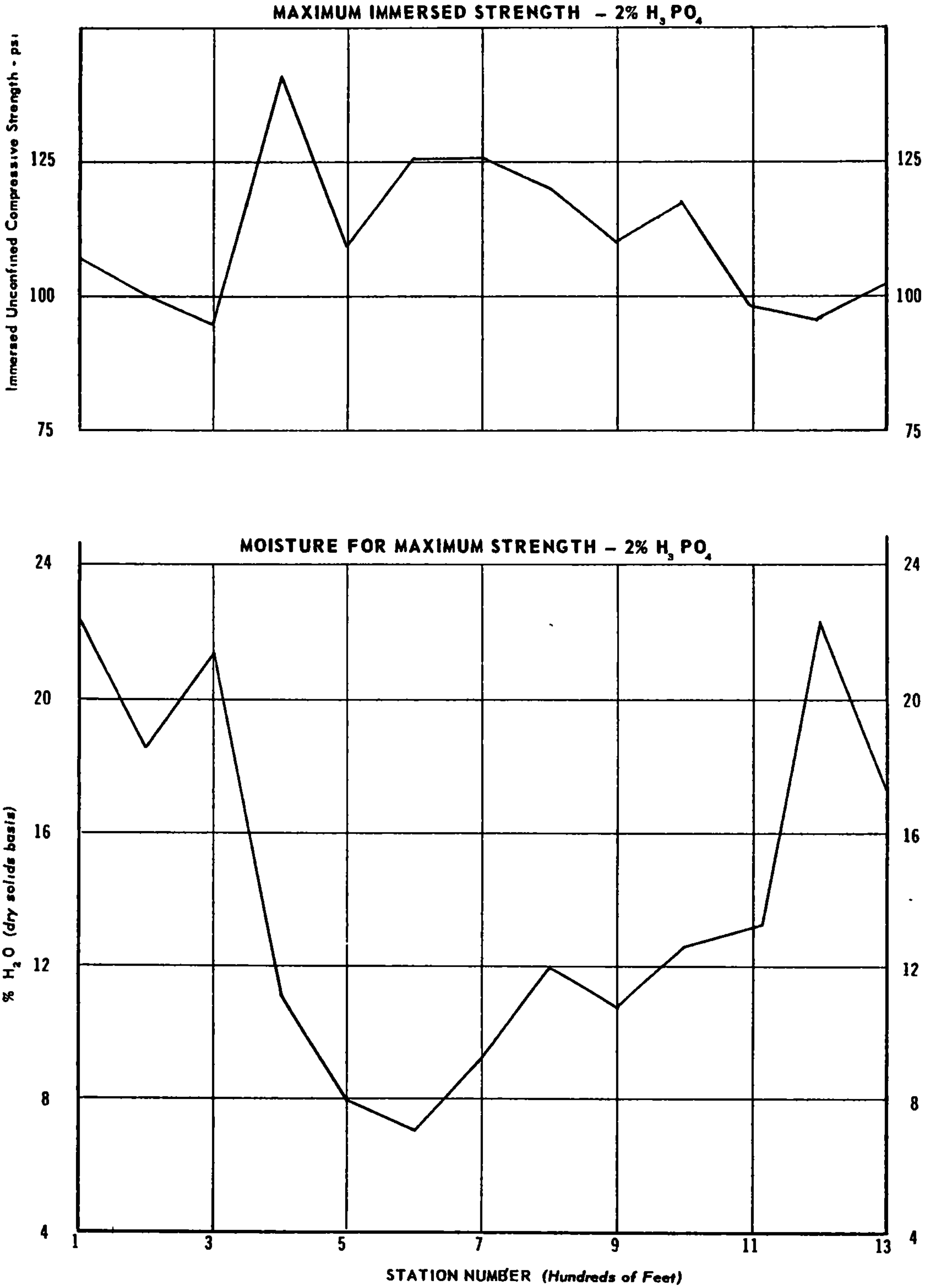


Figure 7. Maximum immersed strength after 5 day humid cure and moisture content for maximum strength vs location by station number (2 percent H_3PO_4, 2- by 4-in. cylinders, 7 blows per each of 4 layers).

TABLE 3

EFFECT OF PHOSPHORIC ACID ON PROPERTIES OF COMPACTED SOILS[a]

Soil	Degree of Compaction (blows/layer)	H_3PO_4 (%)	Opt H_2O (%)	Max. Dry Density (pcf)	Curing Time (days)	Maximum Immersed Strength (psi)	H_2O for Max. Str (%)	Vol Change[b] at Opt. H_2O for Strength (%)
Keyport clay loam, A-7-6(12), Va	12[c]	0	14.8	117	5	0	-	slaked
		1	14.9	117	5	53	16.4	0.0
		2	14.6	118	5	107	16.1	0.0
		5	13.6	119	5	162	14.7	0.5
	8[e]	0[d]	16.7	111.9	5	0	-	slaked
		2	15.0	113.7	5	107	15.8	0.12
Cecil clay loam, A-7-5(17), Ga.	12[c]	0	21.9	102.8	5	0	-	slaked
		2	21.8	103.6	5	103	22.5	0.12
	8[e]	0	25.2	97.7	6	0	-	slaked
		2	25.5	97.0	6	104	25.4	0.12
Clay loam, A-6-(8), La.	12[c]	0	14.0	118.6	5	44	15.8	0.25
		2	13.0	121.2	15	210	12.1	0.0
	24[c]	2	11.3	127.2	15	375	11.0	0.02
Silty clay loam, A-6-(10), La.	6¾[e]	0	16.5	113	5	12	18.8	8.0
		2	16.6	111.3	5	36	16.6	3.4
Clay, Creve Coeur, Mo	8[e]	0	16.8	110.9	5	0	-	slaked
		2	16.3	111.3	5	154	16.6	0.0
Putnam silty clay loam, A-6-(9), Mo.	8[e]	0	17.5	107.7	5	6	21.3	1.95
		2	17.8	106.9	5	117	17.6	0.0
Putnam clay, A-7-6(20), Mo.	8[e]	0	25.3	94.1	5	1	-	64.0
		2	25.8	95.1	5	68	23.4	0.02
		4	21.7	103.1	5	93	22.0	0.56
Clay, A-7-5(20), Md	8[e]	0	23.9	94.4	5	9	28.0	7.1
		2	26.0	97.0	5	89	25.1	0.12
		3	24.1	98.8	5	132	24.2	0.02
Clay, A-7-6(16), Md	8[e]	0	18.3	110.0	5	36	19.2	0.02
		2	18.4	109.8	5	130	17.6	0.0
Clay loam, Col.	8[e]	0	15.4	114.5	5	0	-	slaked
		2	15.5	112.7	5	7	17.6-19.1	20.5
		4	15.5	114.2	5	36	12.0[f]	1.95

[a] Data obtained from complete curves, such as shown in Figures 4 and 6.

[b] Obtained by cubing the percent change in height obtained on immersed specimens.

[c] Correlated to a density between standard and modified AASHO; modified AASHO density refering to compaction via a 10-lb hammer falling through 18 in. instead of the standard 5-lb hammer dropping 12 in. as in AASHO T99-49.

[d] 4- by 4.6-in. samples for untreated series; 2- by 4-in. for treated series.

[e] Standard AASHO.

[f] No maximum observed; strength rising with decreasing H_2O (max. probably slightly less than 12 percent).

optimum moisture contents is apparent. However, all samples contained considerable quantities of clay minerals. A fairly uniform degree of stabilization was achieved with 2 percent acid in all 13 samples. Proper moisture adjustment would be critical on this job site. Some degree of soil blending would seem to be required to achieve good compaction control. The data show that good stability will be reached provided this variability in moisture requirement for proper compaction is taken into account.

Volume Change

In the absence of chemical treatment, the soils studied exhibited appreciable volume change when immersed in water. Those having zero immersed strength (completely slaked in water) had an indeterminate but large volume change. Untreated samples that survived the soaking period nevertheless expanded considerably. The two exceptions—A-6(8) from Louisiana and A-7-6(16) from Maryland—exhibited considerable strength without stabilizer. Addition of phosphoric acid reduced the volume change to negligible proportions (less than 0.6 percent) in all cases where a high degree of stabilization was achieved. The Louisiana silt and the alkaline Colorado soil showed reductions in volume change but not to acceptable levels. These latter two soils were not stabilized to a satisfactory degree as previously pointed out, with regard to immersed strength data.

DISCUSSION

Phosphoric acid is an effective stabilizer for a broad range of clay-containing soils. Improvement in engineering properties is marked in nearly all cases.

The immersed strengths reported in Table 3, largely for 5-day curing intervals, are sufficient for subgrade construction and, in certain pavements, for base courses. It should be noted that immersed strengths represent the least strength expected from the treatment. Unsoaked strengths are usually considerably higher than immersed strengths. Some investigators have reported unsoaked (as-cured) strengths as a basis for determining stability. Early experience with as-cured strength data in this investigation disclosed that there was often no correlation with immersed strength. The most obvious case was for dried clay soils where strengths range as high as 2,000 psi and yet fall to zero in water. Instances were noted where samples cured at 100 percent R.H. gained considerably in strength over controls, but the immersed strength did not increase. Because the objective of the research was to confer resistance to exposure to water and other destructive effects, the collection of as-cured data was discontinued and none is reported in this paper.

The effective concentration range varies from 1 to 5 percent phosphoric acid, or perhaps even higher. A level of about 2 percent is generally sufficient for subgrade purposes. It is to be remembered that the listed strengths are for a short curing interval and that much more strength will be developed with the passage of time. Figure 3 indicates that a doubling of the 5-day strength may be expected after 30 days. Thus an immersed strength of 75 to 100 psi after 5 days is considered to be excellent stability. Figure 3 brings up an important point for laboratory investigators; i.e., the need for curing before testing. The reaction in the treated soil mass clearly requires at least a few days before a substantial amount of cementing takes place. It is essential that the investigator distinguish between treated and raw soil systems in this respect. As an example, the AASHO Standard Method of Test for Determination of Volume Change of Soils T 116-54 may be employed. This procedure calls for molding the sample, curing 15 min, adding water, and beginning the measurement. If this procedure is used with a sample treated with phosphoric acid, the result will be a measure of volume change of the unreacted mixture. In this case, the recommended procedure would be to compact the sample, place it in a humid curing chamber for, say, 5 days, and then resume the test procedure. The same holds for measurement of properties such as Atterberg limits, C.B.R. value, group index, or strength testing. This reasoning also holds true for most other methods of chemical stabilization. There is little value in testing a soil unless the stabilization reactions are allowed to go to at least partial completion.

Most acidic soils containing an appreciable amount of clay minerals will respond well to phosphoric acid treatment. Of the two soils in Table 3 that responded poorly to the treatment, one was highly alkaline and the other was largely silt. The alkalies neutralize the acid before attack at the clay surfaces can begin. Presumably a large quantity of acid would produce a satisfactory degree of stability, but the economics become unreasonable. Phosphoric acid will attack silica (silt) only very slowly at room temperature. Poor stabilization would be expected in samples predominantly made up of silica flour. The remaining soils in the table are neutral or acidic and contain large quantities of aluminosilicates. As discussed in Part II, it is the aluminosilicates that react with the phosphoric acid to produce the cementing substance. The clay soils in the table come from many different sources across the eastern half of the United States, indicating the broad usefulness of the method. Figure 7 further confirms the suitability of phosphoric acid in a range of soil types found on one site. The variation in compaction characteristics is broad, yet the response to the acid is uniform. One further point is brought out in the data shown in Table 3 and Figures 4 and 6—the necessity for preparing samples over a range of moisture contents. The recent literature on chemical soil stabilization contains descriptions of countless experiments in which samples are prepared at only one moisture content, often the optimum for compaction of the untreated soil. This is a potentially misleading practice that can lead to erroneous interpretation of results. To illustrate, suppose one is studying Putnam clay and uses a moisture content of 25.3 percent (optimum for compaction). Table 3 indicates that maximum strength with 2 percent H_3PO_4 was found at 23.4 percent moisture. Maximum with 4 percent H_3PO_4 was at 22.0 percent moisture. The investigator with information at 25.3 percent would report a strength appreciably less than maximum. The above is not to decry the effect of density on strength. Rather it is to point out the fact that the immersed strength does vary with density but that the maximum strength is not always coincident with maximum density. This undoubtedly has to do with internal pore water pressures during immersion (the point of best strength is frequently slightly wetter than optimum) and other factors peculiar to the exposure of the samples. In short, preparation of a series of five or six unreplicated samples over a broad moisture range may be much more valuable than a series of three replicates at one moisture content.

The use of phosphoric acid as a stabilizer for heavy clay soils has apparent merit. Because of the importance of this to engineers, more extensive work dealing with secondary additives, different sources of P_2O_5, and various practical aspects connected with field testing have been carried out and are reported in the subsequent parts.

ACKNOWLEDGMENTS

The authors are indebted to P.G. Arvan and M.J. Scott for their continued support and counsel. Most of the compressive strength procedure was developed under the guidance and counsel of the staff of the Soils Section, Physical Research Branch, Bureau of Public Roads, Washington, D.C., under the late Frank Olmstead.

REFERENCES

1. Ind. Eng. Chem., 47:2230 (1955).
2. Lambe, T.W., and Michaels, A.S., Chem. Eng. News, 32:488 (1954).
3. Demirel, T., Roegiers, J.V., and Davidson, D.T., "Use of Phosphates in Soil Stabilization." Proc., Iowa Acad. Sci., 65:311-316 (1958).
4. Demirel, T., Benn, C.H., and Davidson, D.T., "Use of Phosphoric Acid in Soil Stabilization." HRB Bull. 282, 38-58 (1961).
5. Lyons, J.W., "Stabilization of a Problem Soil—Cheaply." Eng. News-Record, 159:101-106 (Aug. 15, 1957).
6. Lyons, J.W., Construccion, 46:66 (1958).
7. Lyons, J.W., "Soil Stabilization." U.S. Patent 2,899,329 (1959).
8. Michaels, A.S., Williams, P.M., and Randolph, K.B., "Acidic Phosphorus Compounds as Soil Stabilizers." Ind. Eng. Chem., 50:889-894 (1958).
9. Michaels, A.S., and Tausch, F.W., Jr., "Fine-Grained Soil Stabilization with Phosphoric Acid and Secondary Additives." HRB Bull. 241, 109-118 (1960).
10. Michaels, A.S., and Tausch, F.W., Jr., "Phosphoric Acid Stabilization of Fine-Grained Soils: Improvements with Secondary Additives." HRB Bull. 282, 28-37 (1961).

II. Secondary Additives, Acid Source, and Mechanism

J.W. Lyons, G.J. McEwan, and C.D. Siebenthal, Inorganic Chemicals Division
Monsanto Chemical Company, St. Louis, Missouri

●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 ($H_2O/P_2O_5 = 2.46, 1.09$)—experimental chemicals made from reagent grade H_3PO_4 and P_2O_5;
3. Sodium tripolyphosphate—commercial;
4. Fluorapatite ($Ca_5F(PO_4)_3$)—commercial mineral (32 percent P_2O_5);
5. Hydroxylapatite ($Ca_5OH(PO_4)_3$)—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 the impurities may not have long-range influence but act only as accelerators for the reaction.

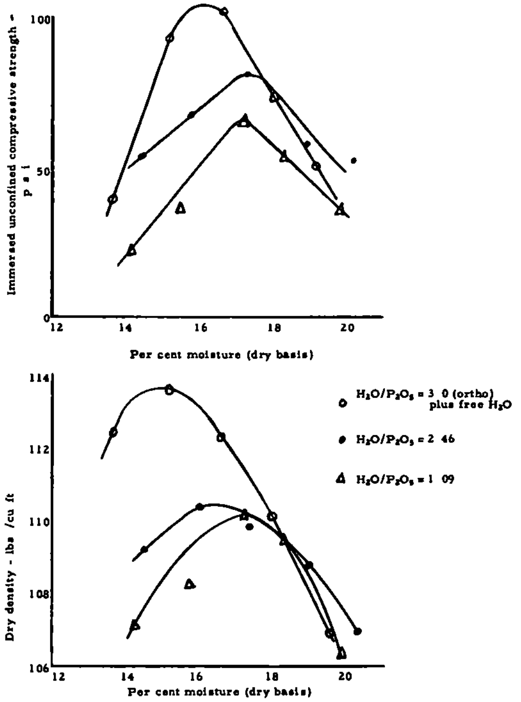


Figure 1. Effect of phosphoric acid chain length as shown by H_2O/P_2O_5 ratios—All equivalent in P_2O_5 to orthophosphoric acid; Keyport clay loam A-7-6(12); 2- by 4-in. cylinders, cured 5 days at 100 R.H., immersed in water 2 days.

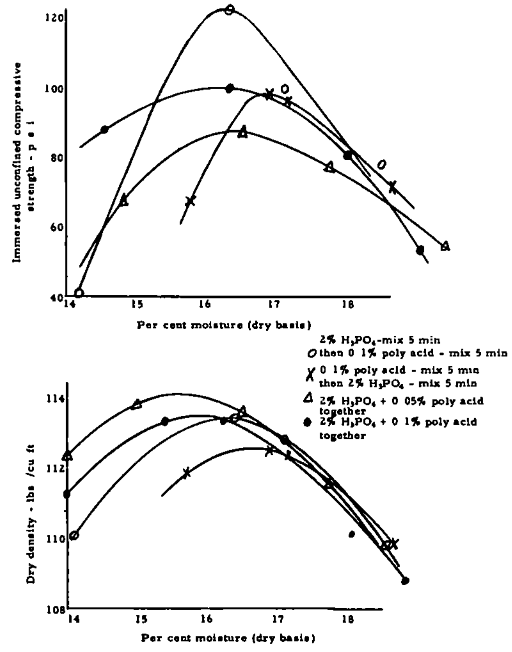


Figure 2. Effect of adding polyphosphoric acid (H_2O/P_2O_5=1.09) to orthophosphoric acid treatment—Keyport clay loam A-7-6 (12); 2- by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed 12 days.

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.

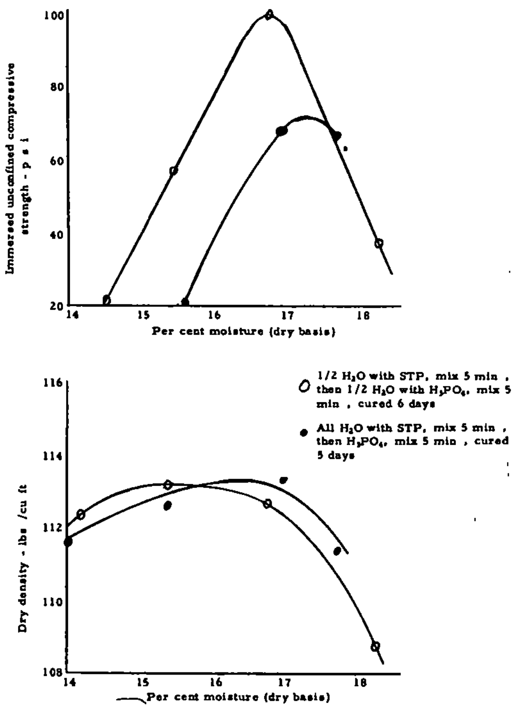


Figure 3. Effect of 0.3 percent sodium tripolyphosphate (STP) and 2 percent phosphoric acid added two ways to Keyport clay loam A-7-6(12)—2- by 4-in. cylinders, 8 blows per each of 4 layers, cured as shown, immersed 2 days.

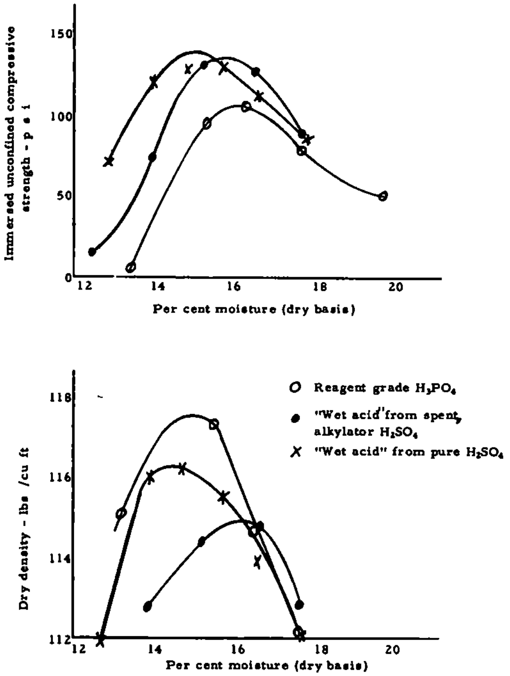


Figure 4. Comparison of three grades of phosphoric acid in Keyport clay loam A-7-6(12)—2- by 4-in. cylinders, 12 blows per each of 4 layers, cured 5 days, immersed 2 days.

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 with the mixed acid system (this run at 19.35 percent F in H_3PO_4) 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

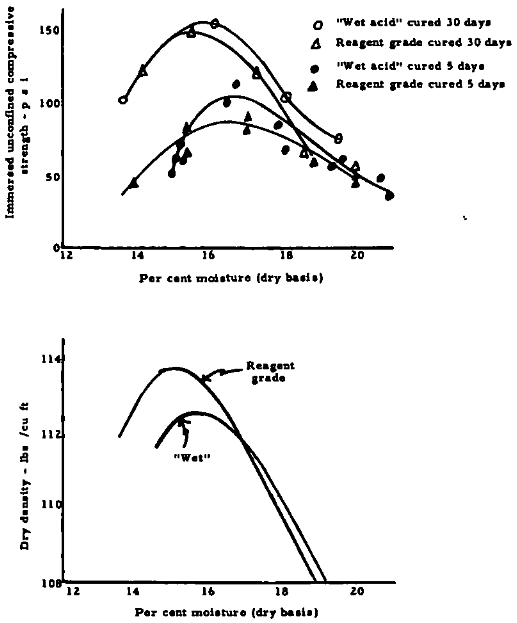


Figure 5. Comparison of two grades of phosphoric acid in Keyport clay loam A-7-6(12)—2- by 4-in. cylinders, 4 layers, 8 blows per layer, cured at 100 percent R.H., immersed for 2 days.

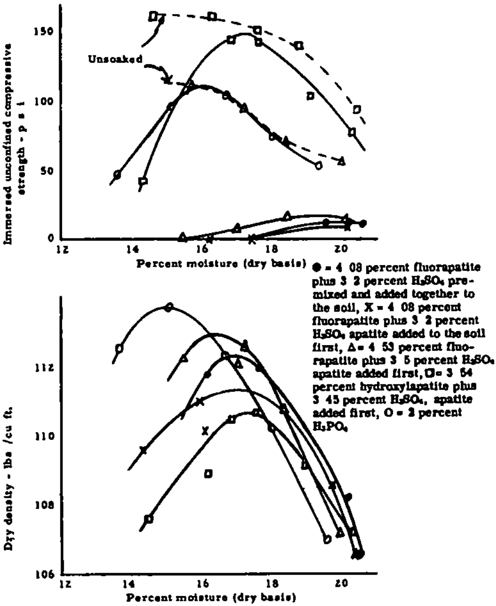


Figure 6. Phosphate rock plus sulfuric acid in Keyport clay loam A-7-6(12).

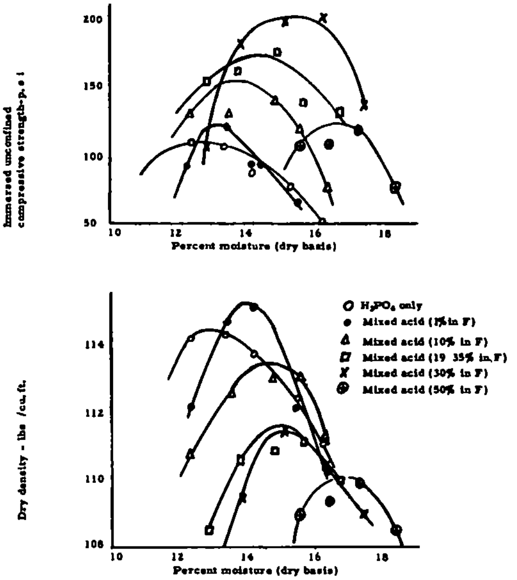


Figure 7. Addition of two percent (excluding free water) of mixtures containing phosphoric and hydrofluoric acids to Louisiana silty clay loam A-6(10)—2- by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed 2 days.

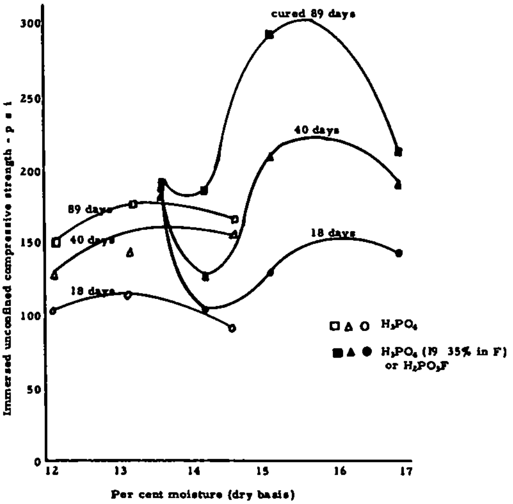


Figure 8. Orthophosphoric acid vs monofluorphosphoric acid cured varying times—Louisiana silty clay loam A-6(10), 2- by 4-in. cylinders, 8 blows per each of 4 layers.

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 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.

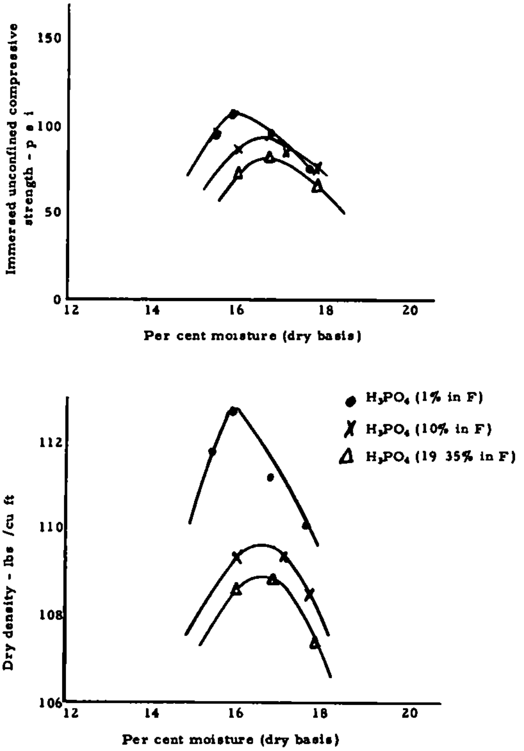


Figure 9. Effect of two percent of mixtures of phosphoric and hydrofluoric acids (free water in acids excluded) on Keyport clay loam A-7-6(12)—2- by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed 2 days.

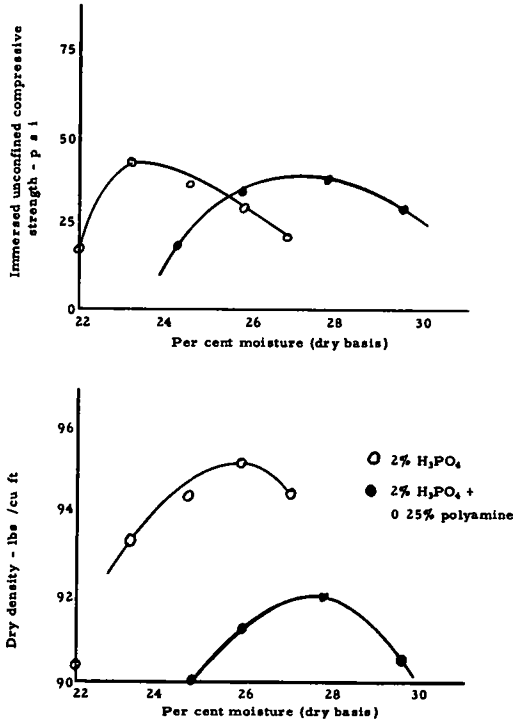


Figure 10. Effect of adding a substituted polyamine (N-tetrapropenyl diethylene triamine) with phosphoric acid to Putnam clay A-7-6(19)—2- by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed two days.

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 IMMERSED STRENGTH OF KEYPORT CLAY LOAM A-7-6(12) TREATED WITH 2 PERCENT H_3PO_4[a]

Additive	H_2O (%)	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-tetrapropenyl diethylene triamine (cationic)	15.8	109.3	95

[a] Cured 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 caly 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:

$$Al(OH)_3 \text{ from the clay lattice} + 3H_3PO_4 \longrightarrow Al(H_2PO_4)_3 + 3H_2O \qquad (1)$$

$$Al(OH)_3 \text{ from } Al(H_2PO_4)_3 + \text{the clay lattice} \longrightarrow Al_2(HPO_4)_3 + 3H_2O \qquad (2)$$

or

$$2AL(OH)_3 \text{ from } AL(H_2PO_4)_3 + \text{the clay lattice} \longrightarrow 3AlPO_4 + 6H_2O \qquad (3)$$

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 $Al_2(HPO_4)_3$ 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

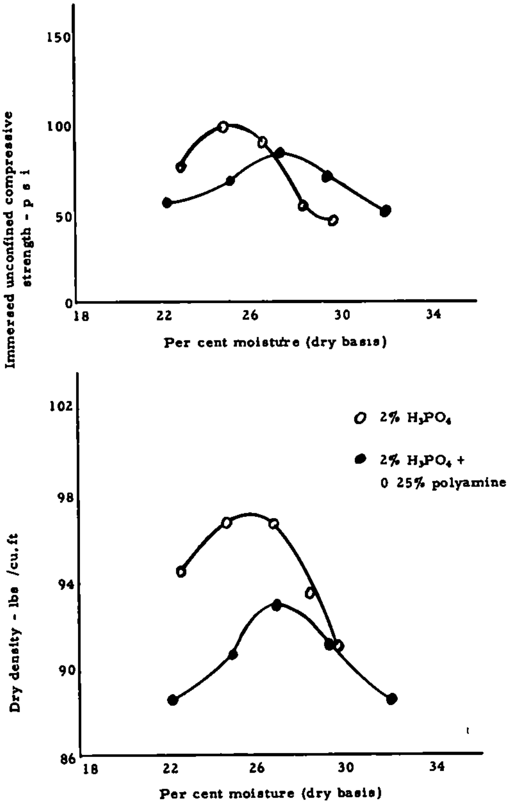


Figure 11. Effect of N-tetrapropenyl diethylene triamine on Cecil clay loam A-7-5(17) treated with 2 percent phosphoric acid—2- by 4-in. cylinders, 8 blows per each of 4 layers, cured 5 days, immersed 2 days.

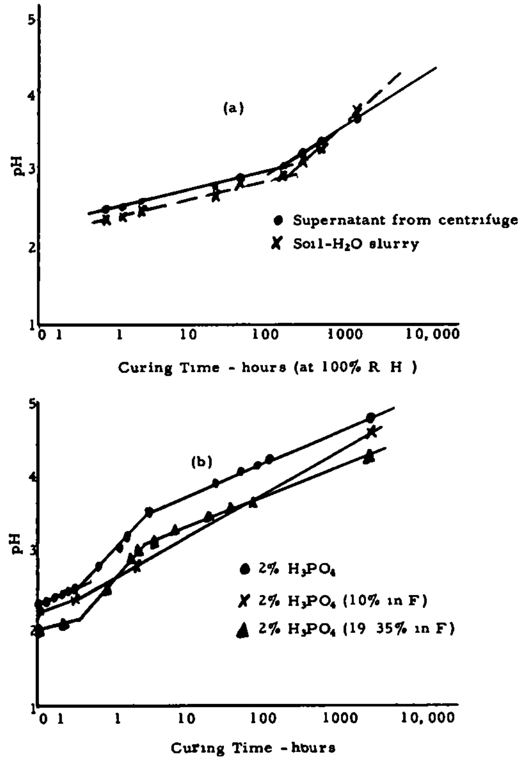


Figure 12. Change in pH of soil-water system with time of contact between soil and acid: (a) 2 percent phosphoric acid in Keyport clay loam A-7-6(12); (9b) 2 percent phosphoric or phosphoric-hydrofluoric acid in Louisiana silty clay loam A-6(10), pH measured in 50 percent solids soil-water slurry only;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

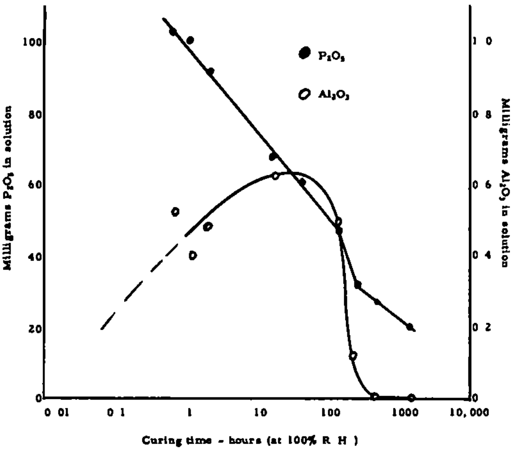


Figure 13. Change in soluble P_2O_5 and Al_2O_3 with time of contact between 2 percent phosphoric acid and Keyport clay loam A-7-6(12).

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:

$$\underset{\text{from clay}}{Al(OH)_3} + H_3PO_4 \longrightarrow AlPO_4 . 3H_2O \qquad (4)$$

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 than free to extract more aluminum from the clay. This latter mechanism is shown as follows:

$$6HF + H_3PO_4 + \text{clay} \longrightarrow AlF_6^{\equiv} + H_3PO_4 + 6H^+ \longrightarrow AlPO_4 + 6HF \qquad (5)$$

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 fluorphosphate 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, honeycombed 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 phonomena 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 strengthwise 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. $Al_2(SO_4)_3$ and $Ca(OH)_2$.

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.

REFERENCES

1. Demirel, T., Benn, C.H., and Davidson, D.T., "Use of Phosphoric Acid in Soil Stabilization." HRB Bull. 282, 38-58 (1961).
2. Michaels, A.S., Williams, P.M., and Randolph, K.B., "Acidic Phosphorus Compounds as Soil Stabilizers." Industrial and Engineering Chemistry, 50:889-94 (1958).

3. Brosheer, J.C., Lenfesty, F.A., and Anderson, J.F., Jr., J. Am. Chem. Soc., 76:5951 (1954).
4. Ames, D.P., Ohashi, Shigeru, Callis, C.F., and Van Wazer, J.R., J. Am. Chem. Soc., 81:6350 (1959).
5. Michaels, A.S. and Tausch, F.W., Jr., "Phosphoric Acid Stabilization of Fine-Grained Soils: Improvements with Secondary Additives." HRB Bull. 282, 28-37 (1961).

III. Some Practical Aspects

J.W. LYONS, Inorganic Chemicals Division, Monsanto Chemical Company,
St. Louis, Missouri

●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 ¼ 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 Volumeasure 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-

etration tests were made as previously described. The completed test patch (20 ft by 20 ft) was covered with road oil and then paved with hot-mix bituminous concrete.

RESULTS

Mixing Energy Requirements

The results of a brief study with the Brabender Plastograph are shown in Figure 1 for Keyport clay loam. In the figure, mixing torque is plotted vs time. In the upper plot, the mixing torque increased as the water was worked into the soil. Then 2 g or about 0. 5 percent of N-tetrapropenyldiethylene triamine (a polyamine) were added and a dramatic drop in mixing torque was observed. The validity of this effect was reinforced by visual observation of a drier appearance resulting from the addition of the amine. In the second plot, 2 percent of phosphoric acid was added to the moist soil in the mixer and an immediate decrease in torque was observed that slowly built up again. Subsequently, 0. 5 percent of the polyamine was added and again a dramatic drop in mixing torque was observed. In the lowest plot, the soil was mixed as in the upper plot for an extended period of time before addition of the phosphoric acid. Again, a decrease in torque was observed that returned to an intermediate level with further mixing. Torque decreased again by an addition of the polyamine. Therefore, Figure 1 seems to show that phosphoric acid by itself will decrease mixing torque (i. e., make field handling of the treated soil somewhat easier) and that a polyamine may be expected to improve dramatically the mixing qualities of clay soil.

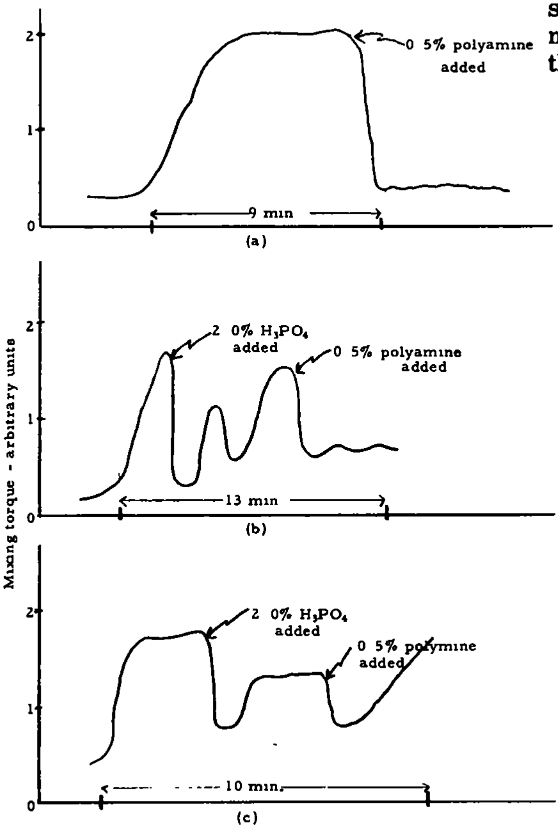


Figure 1. Mixing energy input for Keyport clay loam A-7-6 (12): (a) 392 g soil, 66 g H_2O; (b) 392 g soil 60.5 g H_2O; and (c) 392 g soil, 67.5 g H_2O.

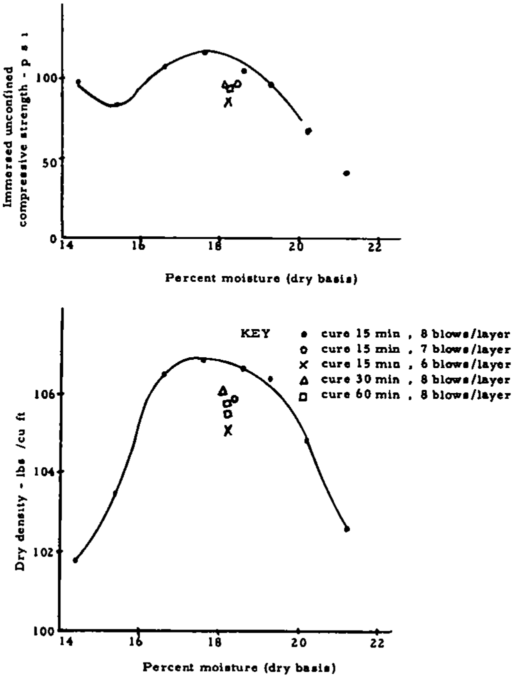


Figure 2. Effect of curing time before compaction and compactive effort on density and strength for 2 percent H_3PO_4 in Cecil clay loam.

The effect with phosphoric acid is probably due to a slight dispersion of the clay solids and has been noted qualitatively by Michaels, Williams, and Randolph (1). The effect of the polyamine has been discussed previously in Part II of this paper.

Effect of Some Variables on Compaction

In the usual laboratory tests described in Parts I and II the soil is mixed for the specified length of time (5 min) and then allowed to damp-cure for 15 min before compaction in a specified manner. For field work such rigid control will not be possible. Rather, a dry density is specified that the contractor must achieve irrespective of curing time and, to a lesser extent, irrespective of moisture content. Moisture contents are usually not specified closer than ± 1-2 percent of optimum. In Figures 2 and 3, the effect of changing curing time before compaction is shown for two clay soils. In Figure 2, the effect on a Cecil clay loam is shown. The loss in density under fixed curing conditions and less compaction is shown. With increased curing before compaction, a greater number of blows is required to duplicate the density obtained with the standard condition. The important fact, however, is that the strength and density can be duplicated by a moderate increase in compactive effort. In Figure 3, the effect on another Cecil clay is shown. The figure shows the loss in both density and strength by allowing 1 hr to elapse before compaction with 7 blows per layer. Again, the compensatory effect of increasing the number of blows per layer is demonstrated. Figure 2 shows that, although compaction will be somewhat more difficult as more curing time elapses, it will be possible to make up for the effect of the hardening of the soil by increasing the compactive effort. It is interesting that in Figure 3 on the wet side of optimum, even though density may be increased by extra compaction above the baseline condition, the strength of the soil evidently may not be increased appreciably as evidenced by the points falling approximately on the control line on the strength curve. Evidently, increased strength from

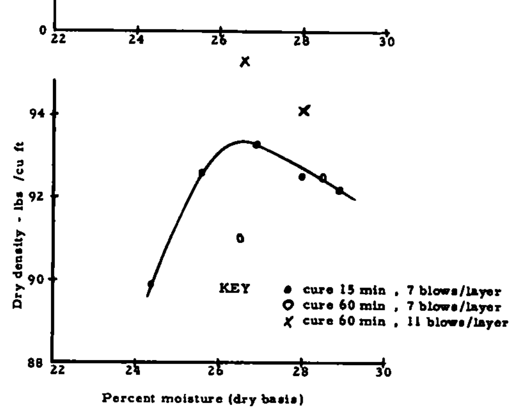


Figure 3. Effect of curing time before compaction and of compactive effort on density and strength for 2 percent H_3PO_4 in Cecil clay loam from Georgia.

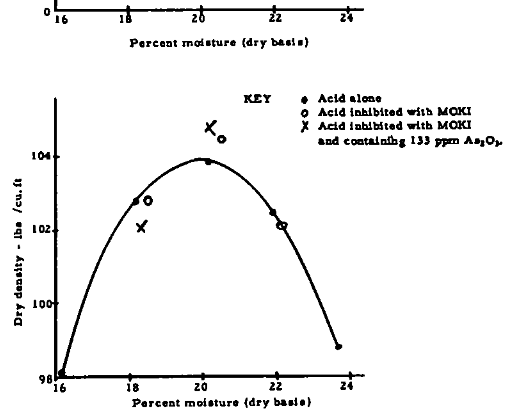


Figure 4. Effect of corrosion inhibitors on stabilization with 2 percent H_3PO_4 in Cecil clay loam A-7-5 (17).

extra compaction may be obtained at optimum moisture content or possibly at 1 or 2 percent less than optimum, but it will be very difficult to obtain increased strength on the wet side of optimum. The importance of maintaining close control on moisture as well as density is underscored.

Effect of Corrosion Inhibitors on Performance

Because phosphoric acid will normally be handled in mild-steel equipment by contractors, a corrosion inhibitor will often be added. These corrosion inhibitors are added in amounts of several tenths to 1 percent by weight of the acid. It was therefore required to know the effect of this amount of corrosion inhibitor on the performance of phosphoric acid as a soil stabilizer. Figures 4 and 5 show strength and density curves for phosphoric acid with several corrosion inhibitors. In Figure 4 the effect of adding Monsanto's MOKI inhibitor is shown to be negligible. Figure 4 also shows the effect of having 133 ppm As_2O_3 present in the acid. This represents one of the differences between food grade and non-food grade phosphoric acid. Again, it is seen that there is no significant change in either strength or density when either corrosion inhibitor or As_2O_3 is present in the acid. In Figure 5, results of a spot check are shown for three commercially available corrosion inhibitors. Little effect is found when Riley 22 or Rodine 201 is added. There seems to be some effect with Rodine 203 and this inhibitor should be tested in the soil and acid combination under study before use in the field. In general however, it is concluded that

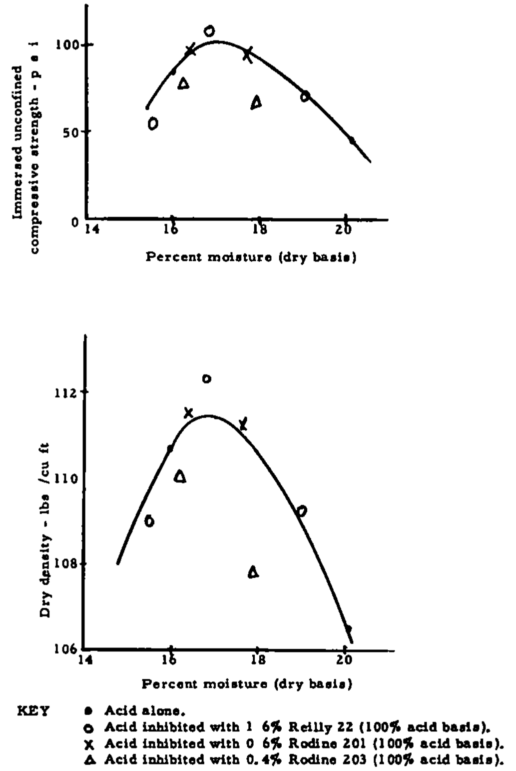


Figure 5. Effect of corrosion inhibitors on stabilization with 2 percent H_3PO_4 in Keyport clay loam A-7-6 (12).

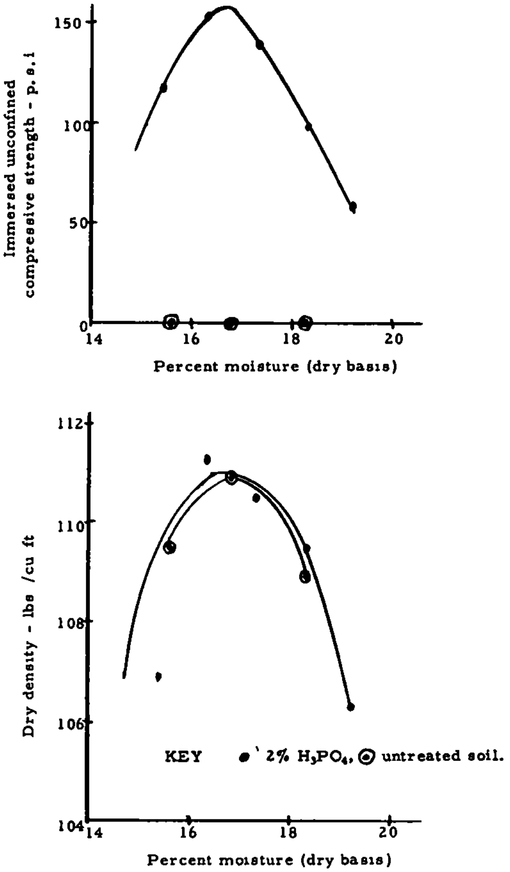


Figure 6. Stabilization with 2 percent H_3PO_4 in clay soil from Creve Coeur, Mo.

corrosion inhibitors have little effect on stabilized strength or dry density of clay soils.

Outdoor Exposure of Test Cyliners

Of the test cylinders prepared and buried in a statistical fashion in reasonably well-drained soil at Everett, Mass., in the fall of 1956, one-half of the samples were removed in February 1957 and broken in unconfined compression. The other half of the samples were removed and broken in May 1957. The results are shown in Table 1. The compactive effort was 12 blows per layer and 24 blows per layer. It is clear in the table that the plain soil samples essentially failed during this test; that is, 9 and 21 psi of unconfined compressive strength are not considered adequate for most modern subgrades. The results for the phosphoric acid treatment show that straight reagent-grade phosphoric acid is the least effective of the phosphoric acids tested, although it is satisfactory and gains strength with age, even under these exposure conditions. As described in Part II, the best sample was that prepared with a wet-process phosphoric acid containing organic sulfates and sulfonates. Using a high compactive effort, strength exceeded 200 psi after exposure and no loss was noted due to the longer exposure time. This same acid with the lesser compactive effort still had strengths approaching 200 psi, whether or not mixing time was normal or reduced by a factor of two (labeled "poor mixing").

The wet-process acid made from pure sulfuric acid (containing no organic matter from the sulfuric acid) performed less effectively than the acid made from spent sulfuric. However, an attempt to duplicate this acid by adding an organic sulfonate to

TABLE 1

OUTDOOR EXPOSURE OF 2- BY 4-IN. TEST CYLINDERS[a]

Treatment	Blows per Layer	Unconfined Compressive Strength (psi)	
		65 Days	155 Days
Untreated	12	9	21
	24	9	24
2% Reagent grade H_3PO_4	12	79	86
2% Wet acid from spent alkylator H_2SO_4	12	154	190
2% Wet acid from pure H_2SO_4	12	166	132
2% Wet acid from spent alkylator H_2SO_4 poor mixing	12	192	180
3% Wet acid from spent alkylator H_2SO_4	12	190	187
2% Wet acid from spent alkylator H_2SO_4	24	202	215
2% Reagent grade H_3PO_4 + 0.5% polyamine[b]	12	134	153
2% Reagent grade H_3PO_4 + 0.2% dodecylbenzene sulfonic acid	12	126	88
1% Polyamine alone	12	21	20

[a] Keyport Clay Loam A-7-6(12), buried Oct. 1956, tested Feb. or May 1957 at Everett, Mass.
[b] N-tetrapropenyldiethylene triamine.

reagent-grade phosphoric did not succeed. The effect of adding 0.5 percent polyamine also was not particularly notable. The effect of adding the amine by itself in larger quantities was a distinct failure. Three general conclusions are drawn:

1. Reagent-grade phosphoric acid is inferior to the wet-process acid in this particular test, but it can be improved considerably by addition of either organic sulfonates or polyamine.
2. Increasing the acid level in this test was not as effective as increasing the compactive effort.
3. A reduction in mixing time does not effect the strength adversely within the limits of this test.

Part II showed that the various acids produced changes of about 10 percent on strength. Because the present results are subject to many more errors due to the outdoor exposure, it is not necessarily true that such a wide difference in stabilizing power exists between types of phosphoric acids. The main conclusion to be drawn is that phosphoric acid-treated clay soil will withstand severe weathering and cycling of freezing and thawing as typified by the climate at Everett, Mass., during the winter of 1956-57. Thus, frost resistance, etc., is deemed to be sufficiently good to proceed with extensive field testing in frost zones as well as in the southern parts of the U.S.

Parking Lot Test Section

The construction of the 20- by 20-ft test patch at Creve Coeur, Mo. in 1958 was

Figure 7. Mixing and compacting treated soil at Creve Coeur, Mo., August 1958.

described in the experimental section of this paper. Figure 6 shows the density and strength curves obtained in the laboratory for untreated soil and soil treated with 2 percent phosphoric acid. Excellent stabilization resulted. The untreated soil had zero strength after immersion in water. Figure 7 shows some of the construction methods used in this small test patch. The soil was aerated until the moisture was reduced to about 13½ percent before beginning the work. Water was added to raise the moisture to the desired level at about 17 percent and phosphoric acid, as a 50 percent solution in water, was sprayed onto the site while mixing the soil with the rototiller. Screen size of the soil before the addition of acid was approximately 5 percent retained on a ⅜-in. screen and 38 percent retained on a No. 5 screen. Mixing was continued with the rototiller until uniformity was achieved by visual inspection. The patch was then compacted by hammering with pneumatic hammers until no futher densification could be achieved. Sampling in each of four locations by means of in-place density testing, revealed that at least 95 percent of standard density was achieved and moisture was controlled at 16.2 ± 0.5 percent. Phosphoric acid level was 2.3 ± 0.6 percent. Thus,

TABLE 2

PERFORMANCE DATA ON 20- BY 20- BY 0.5 FT TEST PATCH,[a] CREVE COEUR, MO.

Location	Date	Penetration Resistance (lb on No. 252 needle or equiv.)					
		0-1 in.	1-2 in.	2-3 in.	3 in. + Lower	H_2O (%)	H_3PO_4 (%)
N.W. Corner	Oct. 1958	74 ± 6	82 ± 4	92 ± 13	-	17.4	3.0
	May 1959	52 ± 6	44 ± 3	5 ± 0	0	20.8	1.23
Center	Oct. 1958	86 ± 13	84 ± 5	86 ± 12	-	17.9	2.26
	May 1959	35 ± 3	42 ± 2	41 ± 6	34 ± 3	19.4	1.73
S.E. Corner	Oct. 1958	71 ± 8	52 ± 8	37 ± 9	-	20.3	2.52
	May 1959	36 ± 6	44 ± 10	37 ± 4	32 ± 9	19.2	2.15

[a] Built Aug. 1958.

TABLE 3

PROFILE OF PENETRATION RESISTANCE AND ACID CONCENTRATION, 20- BY 20-FT TEST PATCH, CREVE COEUR, MO.[a]

Depth (in.)	Penetration Resistance (lb on No. 252 needle or equiv.)	H_3PO_4 (%)
0 - 1	37 ± 7	1.96
1 - 2	38 ± 6	1.87
2 - 3	34 ± 4	1.99
3 - 4	20 ± 5	1.95
4 - 5	7½ ± 2	1.43
5 - 6⅝	4 ± ½	0.61
6⅝ - 8	25 ± 7	0.43
8 - 9	5 ± ½	0.28
9 - 10	-	0.34
10 - 11	4 ± ¼	0.33
11 - 12	6 ± 1	0.40

[a] Data taken May 1959.

there was considerable variation in density, moisture, and acid level across the test section indicating some inadequacy on the part of the mixing equipment and the method of distributing the acid.

Each section was evaluated principally by obtaining data with a Proctor penetrometer. At the time of sampling with the penetrometer small portions of soil were removed for water and phosphoric acid analyses. Table 2 presents the data obtained in the fall of 1958 and again in the spring of 1959. The data were obtained in different holes through the pavement and therefore are not wholly comparable due to the variation in phosphoric acid level from spot to spot. The numbers in the table represent pounds of force necessary to force a needle 0.252 in. in diameter into the soil to a depth of ¼ in. The actual face area of the needle is .05 sq in., so that the numbers in Table 2 may be converted to psi by multiplying by 20. In short, even a relatively low number in the table represents a fairly high strength. In the table, the comparison between fall and spring readings in the top layer indicates reduction of 35 to 50 percent in strength, but a very strong layer is still retained. A similar result was obtained for the layer down

TABLE 4

COST DATA ON PHOSPHORIC ACID STABILIZATION[a]

Item	Cost ($)
Cost/ton 75% H_3PO_4	72[b]
Cost/lb 100% H_3PO_4	0.048
Cost/ft^3 soil at 100 pcf	0.096
Cost/yd^2 0.5 ft thick	0.432
Processing cost/yd^2	0.22
Total cost/yd^2	0.65
Competitive cost/ton for rolled stone in place	2.05

[a] 2% H_3PO_4, dry soil basis, fertilizer grade

[b] Approx. plus freight.

TABLE 5

ECONOMIC DATA FOR PHOSPHATE ROCK PLUS SULFURIC ACID

Item	Cost ($)
Phosphate Rock f.o.b. mine:	7-9
Grinding cost	2
Ave. freight	8
Total/ton	17-19
H_2SO_4/ton (inc. freight)	25
Raw material cost/ton of 100% H_3PO_4 produced	77[a]
Cost/yd^2 0.5 ft thick	0.35
Processing cost/yd^2 [b]	0.32
Total/yd^2	0.67[c]

[a] Cf. \$96 sale price for 100 percent acid.

[b] Includes extra \$0.10 for premixing or double in-place mixing.

[c] Cf. \$0.65/yd^2 for acid per se.

TABLE 6

RAW MATERIAL COSTS FOR ADDING AMINES TO STABILIZER

Concentration (%)	Amine (Cost/yd^2 0.5 ft thick)	
	at \$0.20/lb	at \$0.50/lb
0.1[a]	0.009	0.22
0.5	0.45	1.10

[a] Dry soil basis.

1 to 2 in. from the top. In the third layer from 2 to 3 in. down, the same conclusions hold except for the hole in the northwest section where apparently no acid was present in this 2- to 3-in. layer as evidenced by essentially no strength. Also, the water content had increased in the northwest and center sections from a starting point of around 16 percent when the job was built to 17.4 to 17.9 percent in the fall, and up to about 19.4 to 20.8 percent by spring. Conversely, in the southeast corner, which was wet by accidental conditions during the construction, a decrease in moisture was found during the winter season. Phosphoric acid analyses for these same holes show considerable variation.

Due to the rapid decrease in strength in the northwest sample hole in the spring of 1959 when descending from about the 2-in. level to about the 3-in. level, one large hole was opened up and sample readings carefully taken at 1-in. intervals down to a depth of 1 ft. These data are presented in Table 3. Penetration resistance is shown to be at a fairly high level down to the 4-in. mark and phosphoric acid content also at a reasonably high level down to the 4- to 5-in. mark. Below this point the acid level dropped sharply as did the penetration readings. The base-line phosphate reading in this soil is about 0.2 to 0.3 percent and it is concluded that no migration downward of the phosphoric acid occurred. This is a measure of the permanence of the treatment. The penetration resistance should fall off about 1 in. sooner than the acid level due to the nature of the test; i.e., there must be some support from beneath in order to get a good reading. The test at the 4- to 5-in. level is really a test of strength of the material somewhat below 5 in. which had very little phosphoric acid in it. Table 3 shows that the phosphoric acid level was about as expected down to 3 to 4 in. and began to fall off rather sharply thereafter. When the phosphoric acid was applied to the top surface of the soil, the rototiller did not fully distribute the liquid down to the full depth of mixing. The rototiller was actually combing the soil rather than thoroughly homogenizing it. Subsequent observations on the operations of large-scale pulvimixers of a similar design show that true homogenizing does occur with the latter mixers because of the much more violent action obtained.

TABLE 7

COST OF HYDROFLUORIC-PHOSPHORIC ACID MIXTURE AT EQUAL PERFORMANCE LEVELS IN SILTY CLAY[a,b]

Acid Concentration	Raw Material (Cost/yd^2 0.5 ft thick)
2% H_3PO_4	0.43
1% Mixed acid (30% in F)	0.36
1.2% Mixed acid (19.35% in F)	0.38
1.33% Mixed acid (10% in F)	0.36
1.7% Mixed acid (1% in F)	0.41

[a] See Part II, Figure 7, for performance curves.
[b] 70 Percent HF at $0.134/lb.

The 20- by 20-ft test patch has performed very satisfactorily, is now 2 years old, and is judged to be in better condition than the adjacent surfaces, which are paved over a thin 3-in. layer of crushed stone.

ECONOMIC ASPECTS

Table 4 presents some cost figures for phosphoric acid stabilization. The table assumes the use of fertilizer-grade acid, a soil that compacts to a dry density of about 100 pcf, and the use of modern soil stabilization equipment. The cost table is developed for treatment with 2 percent of 100 percent H_3PO_4 based on dry soil weight. The raw material cost to treat 1 sq yd of road surface to a compacted depth of 6 in. is seen to be $0.432 and the total cost assuming a processing charge of $0.22 per sq yd is then $0.65. The $0.22 figure for processing includes the cost of distributing the acid from a pressurized tank wagon, mixing with a high-speed rototiller or a pug-mill device, and shaping and compacting to grade. The figure does not include costs necessary to bring the road surface to a rough grade, nor does it include sealing with asphaltic material and ultimate surfacing. The figure used is a typical one given by a state highway organization. It is lower than the figures normally given for soil-cement or soil-lime stabilization in light of the advantages to be obtained by use of a water-soluble, liquid soil stabilizer. The assumption has been made in the table that the phosphoric acid can be satisfactorily handled in normal mild-steel equipment provided that a corrosion inhibitor is added to the acid. The figure of $0.65 per sq yd compares favorably with other methods of soil stabilization even in sandy-type, less intractable soils. Note that this method of stabilization will compete with a rolled stone base at $2.05 per ton compacted in place at the same thickness. $2.00 per ton is a commonly encountered figure that is often exceeded in those states that are experiencing shortages of aggregates. There will be other states where stone is available at a price considerably less than this figure. In this latter case, the approach of building a road foundation with stabilized soil might not be considered in any case.

Table 5 shows the economics for treating soil with a mixture of phosphate rock and sulfuric acid to produce, in situ, phosphoric acid. The figures are typical for costs of phosphate rock in this country, either in Florida or in Tennessee (for the eastern markets). An additional $0.10 to $0.15 per sq yd processing cost is added because of the difficulty of premixing phosphate rock and sulfuric acid in equipment made of materials other than rubber-lined or stainless steel or because of the additional processing step necessary in a two-step in-situ mixing operation. The over-all economics then become very similar to those for straight phosphoric acid soil stabilization and it would probably be easier in most cases, to use phosphoric acid itself rather than its components.

Table 6 shows cost figures for addition of amines to phosphoric acid at two price levels and two concentration levels and indicates that addition of amines will be prohibitively expensive. The table also gives costs for mixtures of phosphoric and hydrofluoric acids at equal performance levels in silty clay soils (Part II, see Fig. 7). From 1 to 10 percent HF based on phosphoric acid present will reduce the economics somewhat as compared to straight phosphoric acid in silty soils. Conversely, somewhat more than the amounts of acid shown may be used in silty soils at a cost equivalent to that for 2 percent phosphoric acid. The latter case will usually prevail because 2 percent phosphoric acid alone is not adequate in many silty soils. In some cases it may be necessary to go as high as 2 percent of the 30 percent mixture and the raw material cost will rise to over $0.70 per sq yd; the total cost will approach $1.00 per sq yd.

The commercially available Rodine corrosion inhibitors will add approximately $3.00 per ton to the cost of 75 percent phosphoric acid or about $0.002 per lb of acid used. Some of the experimental inhibitors now under study at Monsanto Chemical Company will add about $1.20 per ton, or less than $0.001 per lb of acid.

In sum, the method of stabilization described in this paper is an economical procedure that can be used in those states where aggregate shortages exist. The costs compare quite favorably with other soil stabilization methods now used in this country.

POTENTIALS

The technical feasibility of stabilizing clay soils with phosphoric acid has been demonstrated conclusively by these investigations and by those of many others now working in this field. The preliminary field-test work described herein indicates that there are no insurmountable problems pertaining to the field application of the method. Durability of the stabilized soil appears to be good. The attractive features of a liquid, water-soluble stabilizer that is economically priced and widely available have interested many organizations. Many laboratory investigations are now underway in laboratories of state highway organizations, and more than one field test installation has been installed. This method shows promise of becoming widely accepted as a means of stabilizing fine-grained, problem soils.

REFERENCE

1. Michaels, A.S., Williams, P.M., and Randolph, K.B., "Industrial and Engineering Chemistry." 50:889 (1958).

Basic Improvements in Phosphate Soil Stabilization

JOHN B. HEMWALL and HENRY H. SCOTT, The Dow Chemical Company,
Agricultural Chemical Research Laboratory, Seal Beach, Calif.

This paper describes an investigation concerning the use of phosphate to solidify soil, thus rendering the soil more suitable for certain engineering uses. The treatments reported involve the use of rock phosphate, sulfuric acid, phosphoric acid, and salts of iron and aluminum to achieve the desired results. The results, given in terms of the unconfined compressive strength of immersed treated soil samples, reveal the importance of materials balance to achieving optimum solidification with these treatments. Further, the results lend additional insight into the mechanisms of solidification of soil with phosphatic materials. Many of the treatments appear to be economically competitive with the presently accepted techniques of soil solidification.

● IN RECENT YEARS an increasing amount of research has been devoted to finding chemical treatments capable of stabilizing soil so as to render it a more suitable engineering material. Of particular interest has been the chemical solidification of soil to increase its load-bearing capacity. One of the more promising new chemical treatments for soil solidification is phosphoric acid, which was first reported by Lyons (1) and Michaels et al (2). This treatment has been notably successful in solidifying fine-grained or high clay soils, which are classically regarded as problem soils and as very difficult to stabilize.

Considering the interesting results presented by Lyons and Michaels et al, together with the information available on the chemistry of phosphate reactions in soil, one is led to several interesting hypotheses on possible modifications of this basic treatment which might yield improved treatments and, most important, more economically feasible treatments. This paper contains the results of investigations designed to explore these hypotheses.

LITERATURE REVIEW

The reactions of phosphates in soil have been the subjects of numerous investigations for over 100 years because of the agronomic importance of soil phosphate. The extensive literature resulting from these investigations has been reviewed in recent years by Wild (3), Dean (4), and Hemwall (5). The reader is referred to these reviews for a comprehensive discussion of the existing knowledge and theories regarding the soil-phosphate reaction. There are several reported investigations, however, that are pertinent to the formulation of a reasonable basis from which to advance hypotheses for the improvement of soil solidification by phosphate.

The fact has been accepted for many years that the addition of phosphate, either as the acid or as one of its many salts, to soils results in the formation of iron and aluminum phosphates in the soil. In recent years, several workers have attempted by various techniques to identify or characterize these compounds which are formed. Most noteworthy have been the results obtained by Swenson et al (6), Haseman et al (7, 8), Cole and Jackson (9, 10), and Kittrick and Jackson (11, 12, 13, 14), which indicate that the compounds formed approximate Fe or $Al(OH)_2H_2PO_4 \cdot xH_2O$. The exact composition of these compounds is a function of the pH and other cations and anions present in solution at the time the compounds are formed as shown by Haseman et al. Generally these compounds are quite hard and highly insoluble.

For many years it has also been accepted that the source of the iron and aluminum in the soil is the various hydrated and unhydrated iron and aluminum oxides. More recent evidence presented by Haseman et al (7), Low and Black (15), Kittrick and Jackson (11, 13, 14, 16), and Hemwall (17), using a rather wide variety of experimental techniques reveals that soil clay minerals that are highly insoluble alumina silicates also react with phosphate to form similar compounds.

In most soils, therefore, and notably in fine-grained soils, phosphate can be expected to react with a significant portion of the soil to form the aforementioned compounds. Due to the preponderance of aluminum as compared to iron in most soils, the aluminum phosphates are the compounds of greater significance. Thus, Michaels et al (2) in their discussion of the solidification of soil by phosphoric acid proposed that the cementing compound formed was dihydroxy aluminum dihydrogen phosphate.

This discussion can be generalized by the following simplified equation:

$$\begin{array}{c} AlY \\ \downarrow\uparrow \\ Al^{+3} \end{array} + 2OH^- + \begin{array}{c} MPO_4 \\ \downarrow H^+ \uparrow \\ H_2PO_4^- \end{array} + xH_2O \longrightarrow \underset{\text{hard, highly insoluble}}{\underline{Al(OH)_2H_2PO_4 \cdot xH_2O}} \qquad (1)$$

in which AlY represents the soil or aluminum source, and MPO_4 represents the orthophosphate source, which may be phosphoric acid or some salt. This equation predicts that any phosphate source (MPO_4) added to a soil (AlY) will react to form the aluminum phosphate product until the concentrations of Al^{+3} and $H_2PO_4^-$ in equilibrium with their respective sources is equal to their concentration in equilibrium with the aluminum phosphate product. Generally this reaction will proceed far to the right because of the much lower concentrations of aluminum and phosphate supported by the aluminum phosphate as compared to the AlY or MPO_4 components under almost all conditions. It is of utmost importance, however, to bear in mind that the rate at which the product will be formed is a function almost solely of the concentrations of the aluminum and phosphate ions in solution rather than of the concentrations of the respective sources in the solid phase. Thus, the solubility and rate of dissolution of the aluminum and phosphate sources are of paramount importance in determining the rate of formation of the aluminum phosphate and hence, within reasonable time limits, the amount of aluminum phosphate formed. These factors can be related by the use of the following generalized rate equation:

$$\Delta P_{AlPO_4} = k_r C_{Al} C_{PO_4} \Delta t \qquad (2)$$

in which ΔP_{AlPO_4} is the amount of aluminum phosphate product formed, k_r is a reaction rate constant, C_{Al} is the aluminum concentration in solution, C_{PO_4} is the phosphate concentration in solution, and Δt is the time interval during which the reaction has been occurring. (Though Eq. 2 is probably not the exact rate equation for this reaction, it is applicable in principle.) Thus, treating a normal soil, which would have a very low C_{Al}, with a fairly insoluble source of phosphate such as rock phosphate would not result in solidification within any time less than many months if not several years. Eventually, however, solidification would occur.

Basically, the soils engineer is interested in having this reaction occur in a relatively short period of time. This has been accomplished very satisfactorily through use of phosphoric acid. Phosphoric acid provides a very soluble source of phosphate which, of course, increases the rate of aluminum phosphate formation. Further, it provides hydrogen ion which is known to dissolve the various aluminum sources in soil to provide a greatly enhanced aluminum concentration. This too increases the rate of aluminum phosphate formation with the net result that effective solidification is accomplished within days after treatment.

Based on the above observations and facts hypotheses can be put forth on several other phosphate treatments that might result in effective soil solidification, some of which could be accomplished more economically than by phosphoric acid. A first possibility is the use of a cheaper source of phosphate, and the cheapest form of phosphate would be crude rock phosphate. If this material were mixed with soil and sufficient mineral acid, such as sulfuric or hydrochloric acids, were added to convert all or part of the rock phosphate to phosphoric acid, reactions similar to those resulting from phosphoric acid should occur.

Referring to Eqs. 1 and 2, it is possible to hypothesize that the addition of a more soluble source of aluminum than the sources normally found in soil would result in an increased rate of aluminum phosphate formation. Because iron also forms compounds similar to aluminum phosphate, more soluble forms of iron also might be beneficial. These more soluble forms of iron and aluminum would probably be most advantageously used with the most soluble form of phosphate; i.e., phosphoric acid or rock phosphate used in conjunction with a mineral acid.

Another possible improvement becomes evident when the very weakly acidic properties of phosphoric acid are considered. Because increasing acidity results in marked increases in soluble aluminum from the various soil aluminum sources, there is a possibility that the use of stronger acids in conjunction with the phosphoric acid will result in greater participation of the soil aluminum in the reaction and consequently more cementing aluminum phosphate.

The results to be presented were obtained from investigations of these three possible improvements in phosphate soil solidification.

MATERIALS AND METHODS

Soils

The soils used in this investigation are given in Table 1 together with several of their physical and chemical properties. These soils will be referred to throughout this paper by their reference numbers in Table 1. All soils were air-dried, pulverized, and screened through a 20-mesh sieve before use.

Chemicals

The following chemicals were used:

TABLE 1

PHYSICAL AND CHEMICAL PROPERTIES OF SOILS

Ref. No.	Mechanical Analysis			pH	$CaCO_3$ (%)	Organic Matter (%)	Opt. Moist. (%)	Plastic Index
	Clay	Silt	Sand					
F	37	38	25	6.6	0	1.8	13-15	11.0
F-4	37	43	20	7.1	0	1.4	13-15	12.7
F-1	18	56	26	7.0	0	1.3	13-15	14.7
B-1	22	52	26	5.3	0	10.7	24-26	11.1
N-1	32	24	44	7.3	0	1.0	15-17	21.4
F-2	52	46	2	6.3	0	1.9	17-19	15.3
M-1	23[a]	39	38	5.7	0	1.7	22-24	8.4
E-1	22	62	16	7.7	4.5	1.4	15-17	13.8
G-1	16	31	53	7.5	0	0.1	11-13	0.0
H-1	6	14	80	5.5	0	0	8-10	0.0
D-1	12	46	42	6.0	0	1.0	10-12	0.0
Q-1	23	38	39	5.7	0	32.2	40-42	-
M-2	42	36	22	6.3	0	1.2	26-28	-

[a] Clay fraction made up predominately of iron oxides rather than alumino-silicates.

1. Rock phosphate supplied by the Westvaco Mining Products Company, Pocatello, Idaho, and containing 12.5 percent phosphorus. It was air-dried, pulverized, and screened through a 100-mesh sieve before use.
2. Acids were C.P. Reagent grade acids.

Preparation of Soil Plugs

All chemicals except the acids were added to 200 g of dry soil and intimately mixed. The predetermined amount of acid was mixed with enough water to bring the soil sample up to optimum moisture content and was then sprayed onto the soil sample with continuous mixing. Immediately after mixing, two approximately 90-g aliquots and one approximately 20-g aliquot of the treated soil were placed in cylindrical molds 3 cm in diameter and statically compacted from both ends. A Carver laboratory press was used to compact the aliquots with a load of 750 lb. After compaction the resultant soil plugs were ejected from the molds. The two larger soil plugs were 3.0 cm in diameter and about 6 cm in height and were eventually tested for unconfined compressive strength. The smaller plug was eventually tested for pH.

Next, the large plugs were placed in a 100 percent relative humidity curing cabinet and cured for 6 days at room temperature. After curing the plugs were immersed in water for 24 hr prior to being stressed in the unconfined compression test. Thus, all results are for immersed samples.

Determination of Unconfined Compressive Strength

The unconfined compressive strength was determined using the unconfined compression test apparatus manufactured by Soiltest, Inc. (Model U-160, motor driven). The rate of strain produced by the apparatus was 0.07 in. per min, and the unconfined compressive strength was calculated from the maximum load at failure. The results are the averages for two specimens.

In those cases where it was desirable to make more than two plugs for each treatment the above procedure was followed except that a larger soil sample was used.

pH Determination

The pH of each treatment was determined twice. The first determination was made immediately after treatment but before compaction of the soil. The second determintion was made on the small plug specimens after the specimen had cured for 6 days in the 100 percent relative humidity cabinet. It was necessary to pulverize these cured specimens before the pH could be determined.

TABLE 2

UNCONFINED COMPRESSIVE STRENGTHS OF SOIL F TREATED WITH VARIOUS RATES OF ROCK PHOSPHATE USED IN CONJUNCTION WITH VARIOUS RATES OF SULFURIC AND HYDROCHLORIC ACID

Rate of Rock Phosphate		Strength (psi)					
		H_2SO_4/100g Soil			HC 1/100g Soil		
Elemental P,[a] Dry Soil Basis (%)	P (mm/100g)	30 Meg[b]	60 Meg	120 Meg	30 Meg	60 Meg	120 Meg
0.4	12.9	54	91	61	34	61	42
0.8	25.8	41	135	95	24	69	75
1.6	51.6	34	115	237	0	74	88

[a] 0.4 percent elemental P equivalent to about 1.5 percent reagent grade phosphoric acid (85 percent H_3PO_4) and to 3.2 percent rock phosphate.

[b] 3 meg acid necessary to convert 1 mmole of P to H_3PO_4; thus, 38.7 meg acid convert 12.9 mmoles P to H_3PO_4.

The pH was determined by adding distilled water to the treated soil until a nonplastic slurry resulted. The pH value of the slurry was then measured using a Beckman H-2 meter with a glass electrode assembly.

RESULTS AND CONCLUSIONS

Rock Phosphate-Mineral Acid Soil Solidification

The first experiment was designed to determine if soil could be successfully solidified by treatment with rock phosphate in conjunction with sulfuric or hydrochloric acid. The rock phosphate and two acids used have previously been described. The soil used was soil F (Table 1).

The soil was treated with three rates of rock phosphate and each rate of rock phosphate with three rates each of sulfuric and hydrochloric acid, as given in Table 2. The soils were treated and the plugs prepared as previously described. The unconfined compressive strengths are shown in Table 2.

Table 2 reveals a number of interesting points. First, the data show clearly that soil can be solidified by the use of rock phosphate and mineral acid. It is apparent, however, that the acid to phosphate ratio is very significant to the effectivity of the treatment.

The results in Table 2 for the lowest rate of both acids reveal that as the amount of phosphate is increased, the strength decreases. The results for the highest rate of acid, however, reveal that as the amount of phosphate is increased, the strength increases. The difference between these two situations is that at the low rate of acid the amount of aluminum solubilized from the soil is the limiting factor in how much cementitious aluminum phosphate is formed. Because additional basic rock phosphate merely neutralizes more acid before it can react with the soil, the net effect is less solubilized aluminum and consequently less aluminum phosphate. At the high rate of acid, however, it is the amount of solubilized phosphate that is the limiting factor. Then, additional rock phosphate, in spite of the fact that it might reduce the aluminum

TABLE 3

UNCONFINED COMPRESSIVE STRENGTH AND RESIDUAL pH OF SOIL F-4
TREATED WITH VARIOUS RATES OF ROCK PHOSPHATE USED
IN CONJUNCTION WITH VARIOUS RATES OF SULFURIC ACID

Rate of Rock Phosphate					
Elemental P, Dry Soil Basis (%)	P (mm/100g soil)	H_2SO_4 (meq/100g)	Ratio H:P	Residual pH	Strength (psi)
0.45	14.5	21.8	1.50	3.72	20
		43.6	3.00	3.45	102
		54.3	3.75	3.32	123
		65.3	4.50	3.15	117
		87.0	6.00	2.80	91
0.90	29.1	43.6	1.50	3.75	100
		87.0	3.00	3.48	246
		109.0	3.75	2.90	95
		131.0	4.50	2.78	45
1.35	43.6	43.6	1.00	3.88	41
		87.0	2.00	3.85	213
		131.0	3.00	3.15	213
		163.5	3.75	2.70	88
		196.0	4.50	2.52	46

concentration somewhat, results in much more solubilized phosphate and consequently more aluminum phosphate.

Table 2 also shows that at the high rate of phosphate and increase in acid results in an increase in strength. At the low rate of phosphate, however, an increase in acid results first in an increase in strength followed by a decrease in strength. The first observation is easily explained inasmuch as increase in acid will increase the solubility of both the phosphate and aluminum and hence will result in the formation of more cementitious aluminum phosphate. The latter observation, however, indicates that excessive amounts of acid in comparison to the amount of phosphate exerts a deleterious effect. This point was investigated further and the results are presented later.

Table 2 also reveals that the sulfuric acid generally gives better strength to the solidified soil than does the hydrochloric acid. Results presented later also show this same phenomenon; therefore, discussion will be deferred until their presentation.

The purpose of the next experiment was to determine if the observed decrease in strength with high acid contents could be attributed to an excessive residual acidity that might be dissolving the aluminum phosphate cement. Soil F-4 was treated with rock phosphate at three rates of phosphorus and with several rates of sulfuric acid.

The results, shown in Table 3, reveal that, for all three rates of rock phosphate, increasing acid content is accompanied first by an increase in soil strength followed by a decrease in soil strength. The occurrence of the maximum strength for each phosphate treatment rate appears to be more closely correlated with the residual pH of the treated soil than with either the total amount of acid used or the acid to phosphate ratio. This "optimum residual pH" in all cases appears to be in the range of 3.1 to 3.5. Residual acidities in excess of this range apparently are deleterious to the strength obtained from the treatment. This reduction in strength is not a result of less aluminum phosphate cement being produced, because, as pointed out earlier, an increase in acid content should increase the soluble aluminum and phosphate concentrations and consequently increase the amount of aluminum phosphate produced. One might argue that the aluminum phosphate itself becomes very soluble at these acidities and consequently does not precipitate. Referring to the results presented by Kittrick and Jackson (11) and Hemwall (17) for the solubility of aluminum phosphate, one can calculate that the acidity must approach a pH of 1 before as much as 10 percent of the aluminum phosphate would become soluble. At a pH of 3 the aluminum phosphate would support a soluble phosphorus concentration on the order of 1/10,000 lb per 100 lb of soil as compared to ½ lb or more of total phosphorus present. Thus, the decreases in strength found cannot be attributed to the aluminum phosphate becoming soluble. One tenable explanation for this apparently anomolous result is that the degree of polymerization of the aluminum phosphate cement decreases as the residual acidity increases. The decrease in polymerization would result in the aluminum phosphate cement being weaker and, in spite of the increased amount of this material, would result in the treated soil having less strength.

In a further effort to establish the broad nature of these observations, experiments similar to the above were performed on several other soils. The soils selected were each treated with one rate of rock phosphate and several rates of sulfuric acid.

The results, shown in Table 4, reveal that for all three soils there is an optimum residual pH. Soil F-1 appears to have an optimum residual pH between 3.2 and 3.4, soil B-1 between 2.8 and 3.1, and soil N-1 above 3.0. Although these data are not conclusive, it appears that the optimum residual pH is in the general range of 2.9 to 3.3.

To obtain maximum strength, the amount of acid to be used with any given amount of rock phosphate in any soil is therefore limited by the "acid consuming" capacity of the soil-rock phosphate mixture. Another factor that determines the maximum strength for almost all soil treatments is the moisture content at compaction. The maximum strength, of course, is obtained at the optimum moisture content. Because moisture content is very likely to affect the residual acidity, an experiment was conducted to elucidate the relationship between moisture and residual pH. Soil F-1 was mixed with 0.68 percent phosphorus as rock phosphate and was then treated with various amounts of sulfuric acid and water (Fig. 1).

TABLE 4

UNCONFINED COMPRESSIVE STRENGTH AND RESIDUAL pH OF SOILS TREATED WITH ROCK PHOSPHATE USED IN CONJUNCTION WITH VARIOUS RATES OF SULFURIC ACID

Soil	Rate of Rock Phosphate		H_2SO_4 (meq/100g soil)	Ratio H:P	Residual pH	Strength (psi)
	Elemental P, Dry Soil Basis (%)	P (mm/100g soil)				
F-1	0.68	21.7	65.0	3.00	3.45	133
			70.2	3.24	3.31	162
			75.3	3.47	3.20	158
			80.4	3.71	3.10	90
			85.5	3.94	2.92	41
B-1	1.35	43.3	130.0	3.00	3.10	164
			140.4	3.24	2.91	191
			150.6	3.47	2.82	172
			160.8	3.71	2.72	157
			171.0	3.94	2.65	144
N-1	1.35	43.3	130.0	3.00	3.05	345
			140.4	3.24	2.82	296
			150.6	3.47	2.60	102
			160.8	3.71	2.45	49
			171.0	3.94	2.38	34

It is evident from Figure 1 that there is a different amount of acid used for maximum strength at each moisture content. However, the pH data indicate that the maximum strength at each moisture content occurs at a common optimum residual pH value of 3.1 to 3.2. Also, as the moisture content increases, the amount of acid that yields the optimum residual pH value increases. Once again, it is apparent that maximum strength occurs at the optimum residual pH, and that the amount of acid that results in the optimum pH increases as the water content of the soil increases.

Of more practical importance, however, the data also reveal that there is a single optimum moisture content for maximum strength for all rates of acid. Consequently, optimum moisture must be determined first, and then the optimum amount of acid can be determined. In this manner the maximum strength for any given rate of phosphorus can be obtained.

In conclusion, the rock phosphatesulfuric acid treatment is an effective treatment for the solidification of soil. There is an optimum amount of acid to be used with any given rate of rock phosphate to result in maximum strength. This optimum rate of acid is reflected by an optimum residual pH in the treated soil that appears in the general range of 2.9 to 3.3, though the value does vary somewhat between soils and between different rates os phosphate.

Sulfuric acid is a more effective acid for use with phosphate than is hydrochloric. Additional data leading to this conclusion will be presented.

The moisture content of the treated soil has an effect on the optimum total acidity, and consequently optimum moisture and optimum acid content are dependent. Inasmuch as all acid contents have a common optimum moisture, it is prudent to determine first the optimum moisture content at some arbitrary acid content and then the optimum acid content at the optimum moisture content.

Phosphoric Acid-Mineral Acid Soil Solidification

Earlier in this paper it was hypothesized that the relatively weakly acidic nature of phosphoric acid might preclude the maximum participation of the soil aluminum in the formation of the cementitious aluminum phosphate. Certainly this situation would

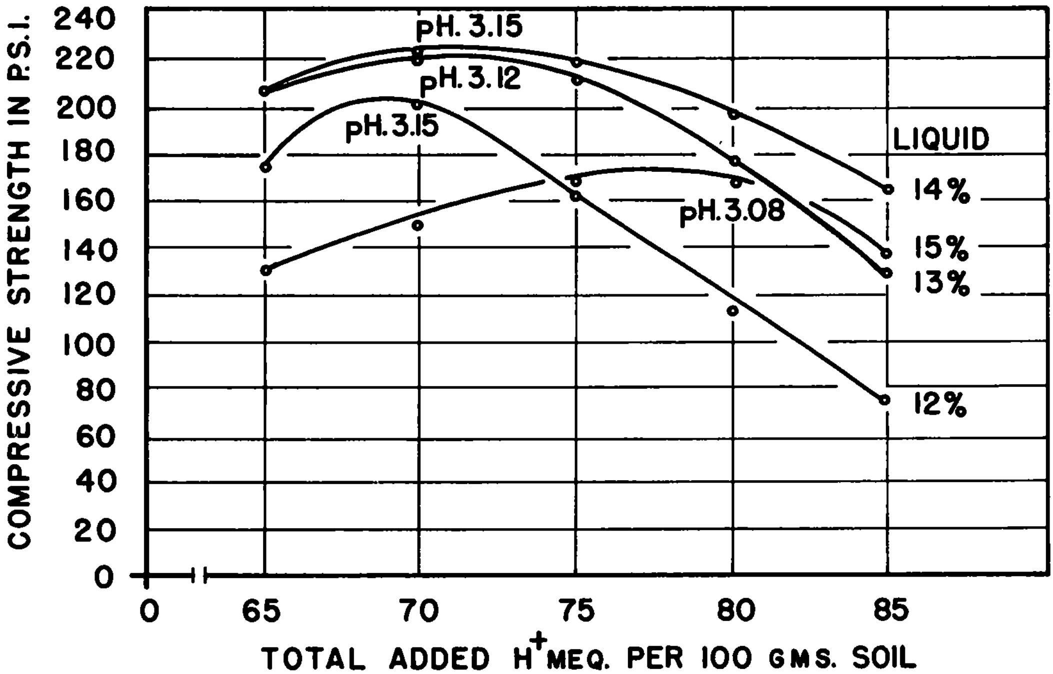


Figure 1. Plots of unconfined compressive strength of soil F-1, treated with 0.68 percent phosphorus as rock phosphate in conjunction with various rates of sulfuric acid vs total added hydrogen ion at various moisture contents.

result in soil strengths inferior to those that might be obtained from the phosphate used. The results presented in the previous section revealed that the amount of sulfuric acid necessary to obtain maximum strength with rock phosphate was usually in excess of the amount necessary to convert the rock phosphate to phosphoric acid; i.e., more than 3 meq of acid per mole of phosphorus were needed. These results certainly lend credence to the hypothesis that additional acid will increase the effectivity of the phosphoric acid. An experiment was therefore designed to test the validity of this hypothesis.

Soil F-1 was treated with phosphoric and sulfuric acids at various ratios and concentrations. The results given in Table 5 certainly corroborate the hypothesis that additions of relatively strong acids with phosphoric acid to soil result in superior solidification. Further, the results correlate with those presented in the previous section in that there is a point where further additions of acid cause a decrease rather than an increase in strength. Once again the most tenable explanation for this decrease in strength is that the relatively high residual acidity interferes with the polymerization of the aluminum phosphate, thus reducing the strength imparted to the soil.

The results for the straight phosphoric acid treatments also should be noted. Phosphoric acid is a relatively weak acid and, as the data indicate, does not result in the high initial acidity that can be accomplished by the sulfuric acid. With additional amounts of phosphoric acid only small increases in initial acidity are noted, and probably these small changes increase the concentration of solubilized aluminum only slightly. However, as would be expected from Eq. 2, when the amount of soluble phosphorus is increased, there is an increase in the amount of cementitious aluminum phosphate formed and consequently in the resulting strength.

At this point the question might well be asked if the increases in strength obtained with the sulfuric-phosphoric combination might be the result of the formation of aluminum sulfate in the soil. Results reported by Michaels et al (2) and unpublished results obtained by the authors indicate that sulfuric acid itself imparts very little strength to soil. Consequently, the increases in strength obtained with the addition of sulfuric acid

TABLE 5

UNCONFINED COMPRESSIVE STRENGTH AND RESIDUAL pH OF SOIL F-1 TREATED WITH PHOSPHORIC ACID USED IN CONJUNCTION WITH VARIOUS RATES OF SULFURIC ACID

Rate of Treat./100g Soil			Ratio Total H:P	Initial pH	Residual pH	Strength (psi)
H_3PO_4		H_2SO_4 (meq H)				
mm P[a]	meq H					
21.7	65.0	-	3.0	1.60	4.65	254
		21.7	4.0	0.70	3.93	397
		43.5	5.0	<.70	3.05	445
		65.0	6.0	<.70	2.68	262
29.0	86.5	-	3.0	1.45	4.60	352
35.0	108.5	-	3.0	1.30	4.55	400
43.5	130.0	-	3.0	1.15	4.53	445

[a] 21.7 mmoles of phosphorus as phosphoric acid corresponds to 2.5 percent of 85 percent H_3PO_4.

to the phosphoric acid treatment cannot be attributed to the aluminum sulfate that might be formed.

In the preceeding section, data were presented indicating that hydrochloric acid used in conjunction with rock phosphate gave inferior results as compared to sulfuric acid. Therefore, an experiment was conducted to see if this same result would be obtained using phosphoric acid as the phosphate source. This experiment was conducted using soil F-1 and the treatments indicated in Table 6. The results from this experiment are also shown in this table.

The results in Tables 5 and 6 reveal that the maximum strength obtained with the phosphoric-hydrochloric acid treatment is much lower than the maximum strength obtained with the phosphoricsulfuric acid treatment. This corroborates the results obtained with these two acids when used with rock phosphate. Also, Tables 5 and 6 show that the maximum strength for the phosphoric-hydrochloric acid treatment is reached at a much lower hydrogen to phosphorus ratio than in the case of the phosphoric-sulfuric acid treatment. In addition, with equal meq of hydrogen ion the phosphoric-hydrochloric treatment results in a lower residual pH. It would be anticipated that the maximum strength is obtained with less hydrochloric acid, and that the residual pH values

TABLE 6

UNCONFINED COMPRESSIVE STRENGTH AND RESIDUAL pH OF SOIL F-1 TREATED WITH PHOSPHORIC ACID USED IN CONJUNCTION WITH VARIOUS RATES OF HYDROCHLORIC ACID

Rate of Treat./100 g Soil			Ratio Total H:P	Initial pH	Residual pH	Strength (psi)
H_3PO_4		HCl (meq H)				
mm P[a]	meq H					
21.7	65	-	3.00	1.60	4.65	254
		5.5	3.28	<.70	4.40	264
		11.0	3.54	<.70	4.05	284
		17.0	3.81	<.70	3.85	259
		21.7	4.00	<.70	3.25	267
		43.5	5.00	<.70	2.52	138
		65.0	6.00	<.70	2.28	99

[a] 21.7 mmoles of phosphorus as phosphoric acid corresponds to 2.5 percent of 85 percent H_3PO_4.

are lower for comparable amounts of acid, inasmuch as the hydrochloric acid is a stronger acid than sulfuric. However, these differences in acid strength do not explain why the resulting maximum strengths with the phosphoric-hydrochloric acid treatments were not higher. It can be seen that the initial pH values are low, and, therefore, the aluminum should be readily solubilized forming normal amounts of product. Also, the residual pH values are sufficiently high that acidity should not be interferring with the polymerization of the aluminum phosphate. Thus it appears that the chloride ion in some manner is adversely affecting the strength of these treatments.

An experiment was conducted using two other soils to compare further the effectivity of hydrochloric acid vs sulfuric acid. The experiment was conducted using the treatments indicated in Table 7. The results (Table 7) reveal once again that the sulfuric acid is more effective, although substantial gains can sometimes be realized from the use of hydrochloric acid.

In the course of performing the experiments reported in Tables 6 and 7, it was observed that the specimens treated with hydrochloric acid would exude water during their curing process in the humidity cabinet. With the vast differences in the solubility of the sulfates and chlorides formed in the treated soil, the ionic strength of the soil solution would be extremely high for the hydrochloric-phosphoric treatment as compared to the sulfuricphosphoric treatment. This high ionic strength could account for the hydrochloric-phosphoric treated soils imbibing water from the high humidity atmosphere. The effect of increasing the water content in the soils after compaction would cause swelling, and this expanding or rearranging of the soil particles could rupture some of the cementitious bonds in the soil. Such a phenomenon could be at least partially responsible for the inferior strengths obtained. Another very tenable hypothesis is that the high ionic strength of the hydrochloric acid treatment is interfering with the polymerization of the aluminum phosphate and thus reducing strength.

The data thus far have indicated that increasing acidity of the phosphoric acid soil treatment also increases the strength of the soil until the point is reached where the residual acidity becomes sufficient to interfere with the polymerization of the cementitious aluminum phosphate, at which point strength begins to decrease. A series of experiments was designed to substantiate this point further on a variety of soil types. The soils were not necessarily selected to represent typical problem soils, but rather to represent a wide variety of soil types. The various treatments and rates used in these experiments are given in Table 8.

Although the results in Table 8 corroborate the previously presented results, there are several points of interest elucidated by considering each soil individually. First, the calcareous soil E-1 appears very difficult to stabilize with straight phosphoric acid.

TABLE 7

UNCONFINED COMPRESSIVE STRENGTH OF SOILS TREATED WITH PHOSPHORIC ACID USED IN CONJUNCTION WITH EITHER HYDROCHLORIC OR SULFURIC ACID

Soil	Rate of Treatment per 100 g Soil				Ratio Total H:P	Strength (psi)
	H_3PO_4		Secondary Acid			
	mm P	meq H	Acid	meq H		
F-2	21.7	65.0	-	-	3.0	97
	21.7	65.0	HCl	21.7	4.0	174
	21.7	65.0	H_2SO_4	21.7	4.0	193
	29.0	86.7	-	-	3.0	195
M-1	21.7	65.0	-	-	3.0	93
	21.7	65.0	HCl	21.7	4.0	115
	21.7	65.0	H_2SO_4	21.7	4.0	200
	29.0	86.7	-	-	3.0	122

This is undoubtedly due to the neutralization of the acid by the carbonate minerals which precludes the acid solubilizing any appreciable quantities of aluminum. The data do reveal, however, that the addition of substantial quantities of sulfuric acid does result in reasonable strengths. The optimum residual pH for this soil unfortunately is not well defined by the data available, although it appears to be around a pH of 3.

TABLE 8

UNCONFINED COMPRESSIVE STRENGTH AND RESIDUAL pH OF VARIOUS SOILS TREATED WITH PHOSPHORIC ACID USED IN CONJUNCTION WITH VARIOUS RATES OF SULFURIC ACID

			mmoles P per 100g Soil			
			21.7		43.3	
Soil[a]	Distinguishing Features	Ratio Total H:P	Residual pH	Strength (psi)	Residual pH	Strength (psi)
E-1	Calcareous	3.00[b]	5.80	failed	5.18	1
		3.75			4.62	137
		4.50			4.20	229
		6.00			2.62	209
		10.00			0.83	failed
G-1	Alkaline, non-calcareous, low clay, high sand	3.00[b]	2.88	30	2.80	69
		3.75	2.63	61		
		4.50	2.23	64		
		6.00	1.80	13		
		10.00	1.20	failed		
H-1	Acid, very low clay content	3.00[b]	2.93	50	2.48	15
		3.75	2.18	24		
		4.50	1.73	19		
		6.00	1.20	14		
		10.00	0.60	failed		
D-1	Acid, low clay content	3.00[b]	2.95	46	2.60	100
		3.75	2.30	92		
		4.50	1.62	80		
		6.00	1.33	45		
		10.00	0.80	failed		
B-1	Acid, moderate clay content, high organic matter	3.00[b]	4.30	71	3.80	163
		3.75	3.73	79	3.22	244
		4.50	3.28	96	2.63	284
		6.00	2.68	141	2.20	156
		10.00	2.15	101	1.45	49
Q-1	Acid, moderate clay content, very high organic matter	3.00[b]	5.03	40	4.90	75
		3.75	4.28	38	3.95	109
		4.50	4.08	52	3.35	135
		6.00	3.65	69	2.45	197
		10.00	2.35	110	1.55	96
M-2	Clay content predominantly iron oxides	3.00[b]	4.02	105	3.35	196
		3.75	3.08	135	2.60	104
		4.50	2.92	110	2.53	89
		6.00	2.72	62	2.35	76
		10.00	2.58	49	2.00	failed

[a] Physical and chemical properties given in Table 1.

[b] Straight phosphoric acid.

Soil G-1, which is an alkaline, non-calcareous soil with a very low clay content, once again reveals the optimum residual pH principle. In this soil, the optimum residual pH appears to be between 2.2 and 2.6. It should be noted that when the rate of phosphoric acid is doubled for soil G-1, the residual pH comes very close to the optimum value. It is dubious, therefore, if much of an improvement in strength could be realized by the further addition of either phosphoric or sulfuric acid to this soil.

Soil H-1, which is an acid soil with a very low clay content, also reveals the optimum residual pH principle. In this case, however, the low rate of phosphoric acid is already at or near the optimum residual pH value. Thus, further additions of either phosphoric or sulfuric acid resulted in decreased strength. The optimum residual pH for this soil appears to be in the range of 2.5 to 2.9.

Soil D-1 is another example of an acid soil with a relatively low clay content, though it contains more clay than does soil H-1. Once again the optimum residual pH principle is demonstrated. For this soil, the optimum pH appears to be about 2.3 or somewhat higher. With this soil, as with G-1, when the rate of phosphoric acid is doubled, the residual pH comes very close to the optimum value, and consequently it is doubtful if much strength improvement could be realized from further additions of either acid.

Soils B-1 and Q-1 are both acid soils containing large amounts of organic matter and reasonable amounts of clay. Both soils at both rates of phosphoric acid again reveal the optimum residual pH principle. It is interesting to note that the organic matter content of both soils lends a great deal of "buffering capacity" to the soils. Consequently, large amounts of acid are needed to approach the optimum residual acidity. The optimum residual pH for both these soils appears to be in the range of 2.3 to 3.0.

Soil M-2, a soil in which the clay consists of iron oxides instead of alumino-silicates as in the other soils, also exhibits the optimum residual pH principle. Apparently the ferric phosphate behaves similarly to the aluminum phosphate cement.

In conclusion, the phosphoric-sulfuric acid treatment is a very effective treatment for the solidification of soil. Further, this treatment is more effective and more economical than is the straight phosphoric acid treatment. Once again sulfuric acid is superior to hydrochloric acid, although hydrochloric acid is effective.

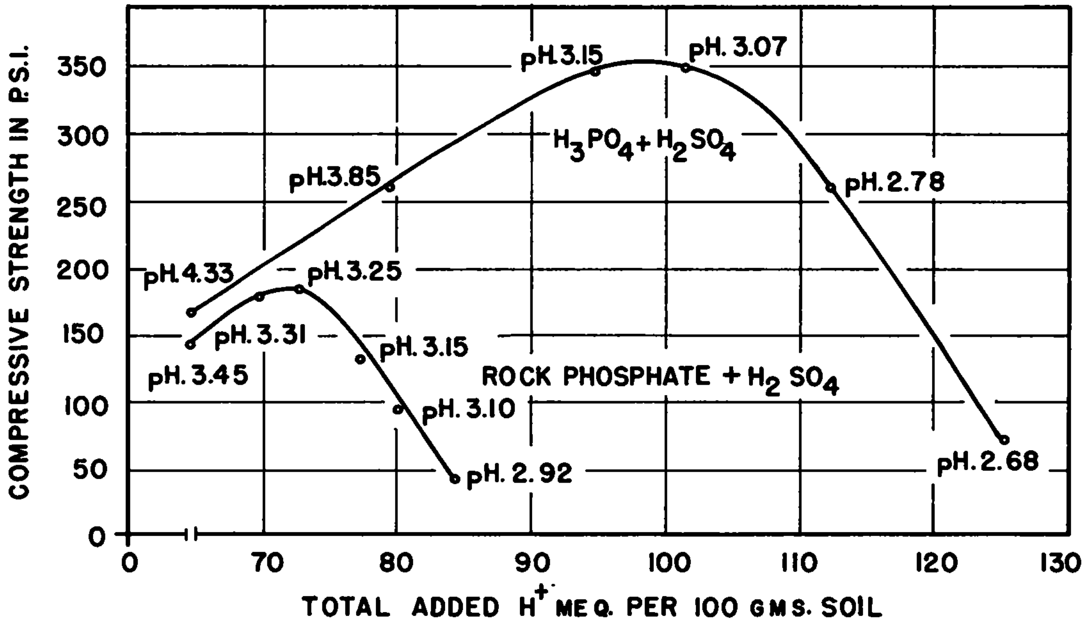


Figure 2. Plots of unconfined compressive strength of soil F-1, treated with 21.7 mmoles of phosphorus as both rock phosphate and phosphoric acid used in conjunction with various rates of sulfuric acid vs total added hydrogen ion.

There is an optimum amount of acid to be used with any given rate of phosphoric acid to result in maximum strength. This optimum rate of acid is reflected by an optimum residual pH in the treated soil that appears to be in the general range of 2.3 to 2.9, though the value varies somewhat between soils and between different rates of phosphate.

Obtaining Maximum Strength Per Unit of Phosphorus

Thus far the results and conclusions presented have revealed that for any given amount of phosphorus added to a soil, either as rock phosphate or phosphoric acid, there is an optimum amount of acid necessary to result in maximum strength. The data also have indicated that for any given amount of phosphorus the maximum strength obtainable with the phosphoric-sulfuric acid treatment is superior to that obtainable with the rock phosphate-sulfuric acid treatment. An experiment was conducted to further elucidate and demonstrate this point.

Soil F-1 was treated with both rock phosphate and phosphoric acid at the rate of 21.7 mmoles of phosphorus per 100 g of soil and with various rates of sulfuric acid. The results, shown in Figure 2, corroborate the previous observations; i.e., greater maximum strengths per unit of phosphorus can be obtained with the phosphoric-sulfuric treatment than can be obtained with the rock phosphate-sulfuric acid treatment.

The pH results (Fig. 2) reveal two reasons for this difference in maximum strength. First, the rock phosphate-sulfuric acid treatments have a higher residual acidity than do the phosphoric-sulfuric acid treatments at comparable rates of total added hydrogen ion. Thus, the rock phosphate-sulfuric acid treatment attains the optimum residual pH level at a lower total added hydrogen ion content. It should be realized that at the point of maximum strength for the rock phosphate-sulfuric acid treatment, the strength of the phosphoric-sulfuric acid treatment at a comparable total added hydrogen ion content may be superior, equal, or inferior to the rock phosphate-sulfuric acid treatment. The main point however, is that the phosphoric-sulfuric acid treatment can tolerate additional acid and consequently continue to produce more cementitious aluminum phosphate before the strength-imparting ability of the aluminum phosphate is impaired.

The second reason for the superiority of the phosphoric-sulfuric acid treatment is that it has a higher optimum residual acidity (lower pH). This factor also means that the rock phosphate-sulfuric acid treatment attains its optimum residual pH level at a lower total added hydrogen ion content. Once again, this means that the rock phosphate-sulfuric acid treatment cannot tolerate as much acid and consequently cannot produce as much cementitious aluminum phosphate before the strength-imparting ability of this aluminum phosphate is impaired. The net result of these two factors is the marked

TABLE 9

UNCONFINED COMPRESSIVE STRENGTH OF SOIL F-1 TREATED WITH PHOSPHORIC ACID USED IN CONJUNCTION WITH VARIOUS RATES OF VARIOUS IRON AND ALUMINUM SALTS

Treatment[a]		Strength (psi)
Salt	mm Salt/100 g Soil	
-	-	130
$FeCl_3$	5.4	275
$FeCl_3$	10.8	180
$FeNH_4(SO_4)_2$	5.4	210
$FeNH_4(SO_4)_2$	10.8	225
$Al_2(SO_4)_3 . 18H_2O$	5.4	210
$Al_2(SO_4)_3 . 18H_2O$	10.8	230

[a] Includes 21.7 mmoles phosphoric acid per 100 g soil.

FIGURE 10

UNCONFINED COMPRESSIVE STRENGTH OF SOIL F-1 TREATED WITH OPTIMAL PHOSPHORIC-SULFURIC ACID USED IN CONJUNCTION WITH AN IRON AND AN ALUMINUM SALT

Treatment[a]		Strength
Salt	mm Salt/100 g Soil	(psi)
-	-	405
$Al_2(SO_4)_3 . 18H_2O$	5.4	271
$FeSO_4 . 7H_2O$	5.4	336

[a] Includes 21.7 mmoles phosphoric acid and 79 meq sulfuric acid.

difference in maximum strength seen in Figure 2. However, depending on the soil and on the actual rate of phosphorus used, these differences in maximum strength may be lesser or greater than those shown in Figure 2.

The reason for the lower optimum residual acidity of the rock phosphate-sulfuric acid treatment is somewhat obscure. It would appear, however, that the extraneous calcium and other materials present in the rock phosphate do increase the sensitivity of the aluminum phosphate to hydrogen ion; i. e., lower concentrations of hydrogen ion interfere with the strength-imparting properties of the aluminum phosphate.

In conclusion, the rock phosphate-sulfuric acid treatment cannot tolerate as much total hydrogen ion or acid as can the phosphoric-sulfuric acid treatment. Consequently, the phosphoric-sulfuric acid treatment has a higher optimum acid treatment level and will impart greater maximum strength to the treated soil than will the rock phosphate-sulfuric acid treatment as comparable phosphorus treatment levels.

Iron and Aluminum Salts as Additives for Phosphoric Acid-Stabilized Soil

Earlier it was hypothesized that salts of iron or aluminum would improve the solidification of soil by phosphoric acid by virtue of the greater solubility of these salts. A few preliminary experiments were conducted in an effort to verify this hypothesis.

In the first experiment iron and aluminum salts were used at the two rates given in Table 9 in conjunction with 21.7 mmoles of phosphoric acid. The results (Table 9) reveal that, as hypothesized, iron and aluminum salts do improve the strength of phosphoric acid-solidified soil. It is interesting that, from the results for the $FeCl_2$, as the rate is increased the strength begins to decrease. This corroborates the previous results where the presence of chloride is deleterious to the phosphate treatment.

Another experiment analogous to the last one was conducted using soil F-1, except that in this experiment a phosphoric-sulfuric acid treatment was used with the amount of acid optimum for maximum strength. The treatments are given in Table 10.

The results in Table 10 reveal that the addition of the soluble metal salts gave no improvement in the treatments. In fact, the presence of the salts apparently caused a loss of strength. The reasons for this are not readily apparent. However, it appears that the effects of these salts are not necessarily additive to the phosphate treatment.

In conclusion, iron and aluminum salts are effective for increasing the strength imparted to soil by phosphoric acid. However, when a phosphoric-sulfuric acid treatment is applied at the optimum total acid level, no benefit is derived from these salts.

DISCUSSION

The results have been based on comparing the strengths obtainable with various treatments. Such an approach is very useful when trying to study the effects of various factors on the performance of a basic treatment. The soil engineer, however, is usually interested in the level of any treatment that will result in a particular standard strength. Thus, the soil engineer is not interested in the fact that adding sulfuric acid to the phosphoric acid treatment will result in greater soil strengths but rather that a given strength can be achieved more economically by using a mixture of phosphoric and sulfuric acids. The following discussion, therefore, will be based on the previously presented results but will be translated into the normal frame of reference of the engineer.

The first problem before the engineer is to decide what degree of solidification he desires to have in his soil. Once he has done this he must determine the methods he has available to accomplish this solidification. In the event that he has a choice of more than one method he obviously chooses the one that accomplishes the job most economically. If the engineer wishes to consider the rock phosphate-sulfuric acid treatment or the phosphoric-sulfuric acid treatment, the question arises as to how he should determine the most economical treatment rates and combinations.

The proper rate can be determined most directly by treating the soil in question with several rates of either rock phosphate of phosphoric acid used in conjunction with several rates of sulfuric acid. Then, by using suitable evaluation procedures, such as unconfined compressive strength, each treatment should be quantitatively assessed. The results for each rate of phosphorus should then be plotted so that the maximum strength for each rate can be observed and, hence, the optimum acid level. Next, it is only necessary to select the treatment combination that has a maximum strength corresponding to the desired strength. This resulting treatment will be the most economical combination for achieving the desired strength with either the rock phosphate-sulfuric acid treatment or the phosphoric-sulfuric acid treatment. Figures 3 and 4 are hypothetical, idealized examples of how such plots look. These plots, though hypothetical, are consistent with the previously presented experimental results. The figures at the right end of each line in both figures represent the amount of phosphate present in the treatment. The figures along the abscissa represent the amount of total hydrogen ion present in the treatment and are scaled such that one unit of phosphate as phosphoric acid will supply three units of hydrogen ion. The figures along the ordinate are in arbitrary strength units.

If the strength needed in a particular situation corresponds to a strength value of

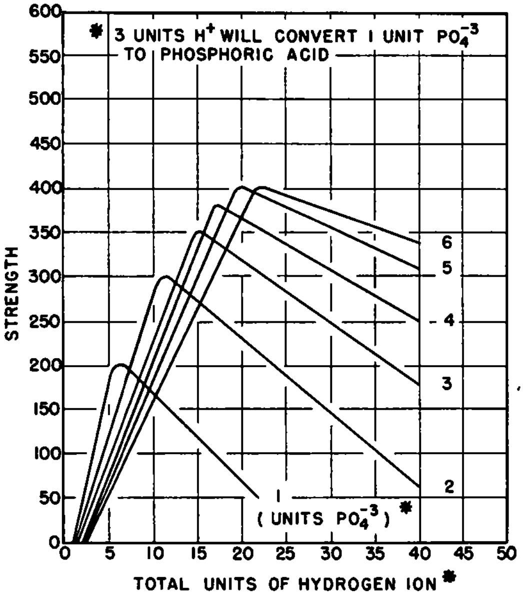


Figure 3. Hypothetical plots of strength vs total acid content for various rates of phosphorus as rock phosphate.

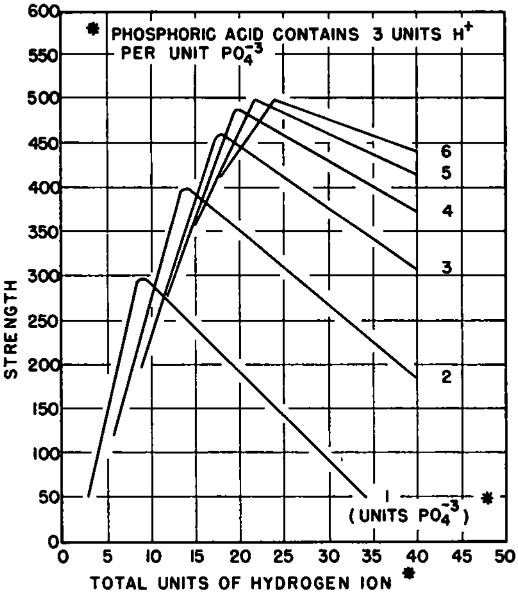


Figure 4. Hypothetical plots of strength vs total acid content for various rates of phosphorus as phosphoric acid.

300, it can be seen from Figure 3 that the rock phosphate-sulfuric acid treatment requires 2 units of phosphate and 12 units of total acid. The phosphoric-sulfuric acid treatment (Fig. 4) requires 1 unit of phosphate and 9 units of total acid. Inasmuch as 3 units of acid come with the 1 unit of phosphoric acid, only 6 additional units are needed.

Some cost comparisons between these two alternative treatments can be provided by the following figures based on recent price quotations of rock phosphate, phosphoric acid, and sulfuric acid. Assuming 1 unit of phosphate as rock phosphate costs 10.0¢, 1 unit of hydrogen ion as sulfuric acid will cost 4.6¢, and 1 unit of phosphate as phosphoric acid will cost 68.6¢ (with this unit of phosphate comes 13.8¢ worth of hydrogen ion so that the phosphate actually costs only 54.8¢). Thus the rock phosphate-sulfuric acid treatment would cost 75.2¢ and the phosphoric-sulfuric acid treatment would cost 96.2¢. In this case, the rock phosphate-sulfuric acid treatment is more economical.

Another example can be given by assuming that the strength value needed is 400. In this event, it can be seen (Fig. 3) that the rock phosphate-sulfuric acid treatment will require 5 units of phosphate and 20 units of hydrogen ion for a net cost of 142.0¢. The phosphoric-sulfuric acid treatment will require 2 units of phosphate and 14 units of total hydrogen ion for a net cost of 174.0¢. Once again, the rock phosphate-sulfuric acid treatment is the more economical treatment in spite of the far greater efficiency of the phosphoric-sulfuric acid treatment. This economy is a result of the far greater cost of phosphate as phosphoric acid as compared to rock phosphate.

Although the examples shown do not reveal it, there are instances where the phosphoric-sulfuric acid treatment will turn out to be more economical. It also is possible that some economies can be realized by the phosphoric-sulfuric acid treatment because it can be applied in a single application with whatever water is needed rather than as two applications, one of which is a solid to be intimately mixed with the soil. These, however, are points of consideration for the engineer.

SUMMARY

This investigation concerns the use of phosphate to solidify soil, thus rendering the soil more suitable for certain engineering uses. More specifically, the investigation was designed to determine if basic modifications in the phosphoric acid treatment might not yield both improved and more economical treatments.

The results presented reveal that sulfuric acid used in conjunction with either rock phosphate or phosphoric acid does result in improved treatments. The results further reveal that sulfuric acid is superior to hydrochloric acid for this use.

The amounts of sulfuric acid that can be used with either the rock phosphate or the phosphoric acid are limited by the fact that excess residual acidity impairs the strength of the cementitious aluminum phosphate formed by this treatment. Thus, for all soils there is an optimum amount of acid to be used in conjunction with the phosphate source to result in maximum strength. The phosphoric-sulfuric acid treatment has a higher optimum acid content than does the rock phosphate-sulfuric acid treatment and consequently results in higher maximum strengths per unit of phosphorus. This greater efficiency of the phosphoric acid over the rock phosphate is largely compensated, however, by the much higher costs per unit of phosphorus in the phosphoric acid.

Salts of iron and aluminum were found to be beneficial to the phosphoric acid treatment. These salts, however, were not beneficial to the phosphoric-sulfuric acid treatment under conditions of optimum acidity.

REFERENCES

1. Lyons, J.W., "Stabilizing a Problem Soil—Cheaply." Eng. News-Record, 159:No. 7, 101-106 (1957).
2. Michaels, A.S., Williams, P.M., and Randolph, K.B., "Acidic Phosphorus Compounds as Soil Stabilizers." Ind. Eng. Chem., 50:889-894 (1958).
3. Wild, A., "The Fixation of Phosphorus by Soils: A Critical Review." J. Soil Sci., 4:72-85 (1949).
4. Dean, L.A., "The Fixation of Soil Phosphorus." Advan. in Agron., 1:391-411 (1949).

5. Hemwall, J. B., "The Fixation of Phosphorus by Soils." Advan. in Agron, 9:95-112 (1957).
6. Swenson, R.M., Cole, C.V., and Sieling, D.H., "Fixation of Phosphate by Iron and Aluminum and Replacement by Organic and Inorganic Ions." Soil Sci., 67:3-22 (1949).
7. Haseman, J.F., Brown, E.H., and Whitt, C.D., "Some Reactions of Phosphate and Clays and Hydrous Oxides of Iron and Aluminum." Soil Sci., 70:257-271 (1950).
8. Haseman, J.F., Lehr, J.R., and Smith, J.P., "Mineralogical Character of Some Iron and Aluminum Phosphates Containing Potassium and Ammonium." Soil Sci. Soc. Amer. Proc., 15:76-84 (1950).
9. Cole, C.V., and Jackson, M.L., "Colloidal Dihydroxy Dihydrogen Phosphates of Aluminum and Iron with Crystalline Character Established by Electron and X-ray Diffraction." J. Phys. Chem., 54:128-142 (1950).
10. Cole, C.V., and Jackson, M.L., "Solubility Equilibrium Constant of Dihydroxy Aluminum Dihydrogen Phosphate Relating to a Mechanism of Phosphate Fixation in Soils." Soil Sci. Soc. Amer. Proc., 15:84-89 (1950).
11. Kittrick, J.A., and Jackson, M.L., "Application of Solubility Product Principles to the Variscite-Kaolinite System." Soil Sci. Soc. Amer. Proc., 19:455-457 (1955).
12. Kittrick, J.A., and Jackson, M.L., "Common Ion Effect on Phosphate Solubility." Soil Sci., 79:415-421 (1955).
13. Kittrick, J.A., and Jackson, M.L., "Rate of Phosphate Reaction with Soil Minerals and Electron Microscope Observations on the Reaction Mechanism." Soil Sci. Soc. Amer. Proc., 19:292-295 (1955).
14. Kittrick, J.A., and Jackson, M.L., "Electron-Microscope Observations of the Reaction of Phosphate with Minerals Leading to a Unified Theory of Phosphate Fixation in Soils." J. Soil Sci., 7:81-89 (1956).
15. Low, P.F., and Black, C.A., "Phosphate Induced Decomposition of Kaolinite." Soil Sci. Soc. Amer. Proc., 12:180-184 (1947).
16. Kittrick, J.A., and Jackson, M.L., "Electron Microscope Observations of the Formation of Aluminum Phosphate Crystals with Kaolinite as the Source of Aluminum." Nature, 120:508-509 (1954).
17. Hemwall, J.B., "The Role of Soil Clay Minerals in Phosphorus Fixation." Soil Sci., 83:101-108 (1957).

Evaluation of Phosphoric Acid for Stabilization Of Fine-Grained Plastic Soils

JAMES A. KELLEY and EARL B. KINTER, Highway Research Engineers,
Division of Physical Research, U.S. Bureau of Public Roads

A laboratory study was made on the effectiveness of phosphoric acid in improving the engineering properties of six fine-grained plastic soils. The properties studied include plasticity, moisture and density relations, volume change, and unconfined compressive strength. The acid was applied at rates up to 4 percent of the weight of dry soil. Tests were also made using 0.5 percent of an amine compound as a supplement to the acid. In general, plastic properties were moderately affected, and there was little change in moisture-density relationships. Pronounced increases in unconfined compressive strength of soaked specimens were obtained for most of the soils when treated with acid alone, and slight additional increases resulted when the amine was also used. Volume change, as measured for five of the soils, was reduced to a level considered satisfactory. Using 2 percent of the acid and 0.5 percent of the amine, a compressive strength of 184 psi was obtained for the Penn soil, which had no strength before treatment. Although strength gains for two of the remaining soils were not of practical magnitude, gains for the other three were quite sufficient to indicate that phosphoric acid offers considerable promise as a stabilizer for a wide variety of fine-grained plastic soils.

● IN 1954, the Bureau of Public Roads, in an effort to stimulate interest in the development of chemical products for use in the stabilization of soils, invited chemical manufacturers to aid in the search for suitable chemicals. Agreements were made with a number of companies under which chemicals would be subjected to preliminary laboratory testing by the manufacturer and, if found promising, submitted to the Bureau for further laboratory testing and possible subsequent recommendation to State highway departments for full-scale trials in the field. As a result of this program, phosphoric acid was proposed by the Monsanto Chemical Company and tested for use in the stabilization of fine-grained plastic soils.

This paper presents some of the results of the laboratory evaluation of phosphoric acid conducted by the Bureau of Public Roads between 1955 and the present time.

The successful use of phosphoric acid with one fine-grained plastic soil was first reported by Lyons (1), who obtained for compacted soil specimens containing about 2 percent of the acid, unconfined compressive strengths ranging from 110 to 200 psi, depending on the length of the curing period. Lyons also found that the addition of 0.5 percent or less of a compound identified as Amine ODT facilitated mixing, practically eliminated the critical dependence of the strength of the soil on the water content at the time of compaction, and rendered the soil water-resistant early in the curing period. Michaels, Williams, and Randolph (2), working with five soils of varying texture, also obtained substantial increases in unconfined compressive strengths as a result of treatment with phosphoric acid or its equivalent of phosphoric anhydride, and with a number of other acidic phosphoric compounds. The latter authors also found that a small amount of a primary aliphatic amine would accelerate curing and improve strength retention on water immersion, although ultimate strengths were somewhat reduced. Michaels and Tausch (3) in studying supplementary additives for improving or reducing the cost of the stabilizing soils with phosphoric acid, found orthorhombic phosphorous pentoxide and phosphate rock plus sulfuric acid to be effective. They also found that, supplemental to phosphoric acid treatment, ferric chloride and octylamine were effective in waterproofing soils. Demirel, Benn, and Davidson (4) found phosphoric acid to increase the unconfined compressive strengths of a number of soils, and showed that calcium carbonate in soils reduced or eliminated strength gains because of the consumption of the acid by the carbonate.

EXPERIMENTAL WORK

The experimental work by the Bureau of Public Roads was conducted with two grades of liquid phosphoric acid, which were supplied by Monsanto Chemical Company: reagent grade furnace acid containing 85 percent H_3PO_4; and "wet process" acid containing 40 to 45 percent H_3PO_4. In preliminary tests, wet process acid was found to produce higher values of unconfined compressive strength in soil-acid mixtures than the reagent grade and was therefore used exclusively in subsequent testing. An organic compound identified as SA-4 amine, used as a supplementary additive, was also supplied by Monsanto Chemical Company.

The characteristics of the experimental soils are given in Table 1. Table 2 lists the tests applied to the raw soils and, except for the mechanical analysis test, also to the soil-acid mixtures. Test values selected as criteria to evaluate whether a given soil had been satisfactorily improved by the stabilizing treatment are also listed in Table 2.

Mixtures of soil, water, and the chemicals were prepared with a mechanical mixer. Air-dry soil was placed in the mixer bowl and the calculated amount of chemical in water solution was slowly added while the mixer was in operation. The mixing time was 5 min. Atterberg limit tests were performed on a portion of the mixture cured in a high humidity chamber at room temperature for 8 days. Volume change specimens were made and tested in accordance with AASHO T 116. Triplicate cylindrical test specimens 2 in. in diameter and 4 in. in length were compacted at maximum dry density and optimum liquid content. Moisture absorption

TABLE 1

CHARACTERISTICS OF EXPERIMENTAL SOILS

Soil[1]	Clay Mineral	pH	$CaCO_3$ (%)	Passing Sieve No 10 (%)	Passing Sieve No. 40 (%)	Passing Sieve No. 200 (%)	Silt 0.05-0.005 mm (%)	Clay <0.005 mm (%)	Liquid Limit	Plasticity Index	Max Dry Density[2] (pcf)	Opt Moist[2] (%)	AASHO Class
Penn	Illite and chlorite	5.0	0	100	81	62	28	45	48	22	110	18	A-7-6(11)
Jordan	Montmorillonite	7.6	10	100	99	91	44	36	34	10	100	21	A-4(8)
Keyport	Montmorillonite	4.6	0	100	93	62	21	36	46	24	111	17	A-7-6(12)
Pierre	Montmorillonite	7.0	0	100	99	98	34	61	79	46	92	26	A-7-5(20)
Hagerstown	Kaolinite and illite	5.4	0	100	99	98	25	72	78	48	91	27	A-7-5(20)
Sassafras	Kaolinite and vermiculite	5.7	0	100	94	75	23	49	48	23	108	19	A-7-6(15)

[1] Penn soil from C horizon, others from B horizon.
[2] AASHO T99-57, Method A.

TABLE 2

TESTS AND CRITERIA FOR EVALUATING NEW SOILS AND SOIL-ACID MIXTURES

Test	AASHO Designation	ASTM Designation	Test Value for Satisfac. Matl.
Mechanical analysis	T 88	D 422	-
Liquid limit	T 89	D 423	Not over 30
Plastic limit	T 90	D 424	-
Plasticity index	T 91	D 424	Not over 6
Compaction	T 99-57	D 698-58	-
Volume change	T 116	-	Not over 2½ percent
Moisture absorption	-[1]	-[1]	Not over 2 percent
Unconfined compressive strength	-[2]	-[2]	100 psi or greater

[1] See text.
[2] Rate of loading in testing machine = 0.05 in. per min.

and unconfined compressive strength were measured for each of these specimens after the specimen was cured for 5 days at room temperature and high humidity and immersed in water for 2 days. If an immersed specimen showed no evidence of slaking, it was surface-dried and weighed to determine the moisture absorption. If complete disintegration of the specimen occurred, measurements of both moisture absorption and compressive strength were naturally obviated, and if there was more than a trace of slaking, the moisture absorption could not be accurately measured. After soaking and weighing, the specimens were tested for unconfined compressive strength.

The 2- by 4-in. cylindrical specimens were prepared by an impact compaction device similar to that developed by the U.S. Waterways Experiment Station (5). This device employs a 4-lb hammer with a 12-in. drop. Depending on the type of soil used, from 8 to 14 blows were required to produce specimens having the same maximum density as obtained in the AASHO T 99 standard method.

RESULTS AND DISCUSSION

Data in Table 3 show the effects of three rates—1, 2, and 3 percent—of phosphoric acid, with and without 0.5 percent of SA-4 amine, on the unconfined compressive strength

TABLE 3

EFFECT OF CONCENTRATION OF PHOSPHORIC ACID ALONE, AND WITH SA-4/ AMINE ADDITIVE, ON THE UNCONFINED COMPRESSIVE STRENGTH OF THREE SOILS

Treatment[1]		Unconfined Compressive Strength of Soil		
Acid (%)	Amine (%)	Keyport (psi)	Jordan (psi)	Penn (psi)
0	0	0	0	0
1	0	75	13	-[2]
2	0	113	15	170
3	0	156	14	202
1	0.5	78	-[2]	-[2]
2	0.5	118	34	184
3	0.5	165	-[2]	226

[1] Based on dry weight of soil (110 C).
[2] Not determined; insufficient material for test.

TABLE 4

EFFECT OF PHOSPHORIC ACID AND SA-4 AMINE ON THE PROPERTIES OF SIX SOILS

Soil	Acid (H_3PO_4) (%)	Amine (%)	Unconf. Compress. Str. (psi)	Vol. Change (%)	Moist. Absorp. (%)	Opt. Moist. (%)	Max. Dens. (pcf)	Liquid Limit	Plastic Limit	Plasticity Index
Penn	0	0	0	9.7	-[2]	18	111	48	26	22
	2	0	170	-[1]	1.0	17	114	-[1]	-[1]	-[1]
	2	0.5	184	-[1]	0.1	18	111	-[1]	-[1]	-[1]
Jordan	0	0	0	9.0	-[2]	20	104	34	24	10
	2	0	15	1.1	2.4	23	101	40	24	16
	2	0.5	34	1.5	2.9	23	99	36	25	11
Keyport	0	0	0	9.2	-[2]	17	111	46	22	24
	2	0	113	1.5	1.0	15	114	43	22	21
	2	0.5	118	0.3	1.2	18	110	40	24	16
Pierre	0	0	0	21.7	-[2]	26	92	79	33	46
	2	0	2	0.7	-[2]	24	91	68	34	34
	2	0.5	8	1.2	-[2]	25	91	56	36	20
	4	0	28	-[1]	7.0	24	92	56	35	21
	4	0.5	77	-[1]	6.0	25	91	50	36	14
Hagerstown	0	0	5	3.9	4.2	27	91	78	30	48
	2	0	37	-[1]	0.7	26	88	52	30	22
	2	0.5	38	-[1]	3.9	26	86	51	33	18
Sassafras	0	0	31	1.0	1.0	19	108	48	25	23
	2	0	74	0	0.2	20	107	33	22	11
	2	0.5	85	0	1.1	20	103	35	25	10

[1] Insufficient material for test.

[2] Specimen completely or partially disintegrated when immersed.

of soaked specimens of three soils. There was considerable strength development with Keyport and Penn soils, the effect increasing with increasing rates of acid. In contrast, very little strength was developed with the Jordan soil. This may be largely attributed to the calcium carbonate content of this soil, which is more than sufficient to prevent the desired soil-acid reaction and, therefore, the strength development (4). The strengths developed in Keyport and Penn soils with 2 percent of the acid more than meet the 100 psi criterion selected for this property. Small additional increases resulted from the addition of amine.

Inasmuch as satisfactory strengths were provided by 2 percent of the acid, this rate was used for most of the subsequent work. Data showing the effects of 2 percent of the acid on the properties of several soils are given in Table 4. In the case of the Pierre soil, a 4 percent rate of acid was also used and, for all of the soils tested, data were also obtained for treatment with 2 percent of acid plus 0.5 percent of amine.

The effectiveness of the acid is seen to vary considerably, depending on the soil and the specific property under consideration. Values of compressive strength obtained with the Penn and Keyport soils were well over the selected criterion of 100 psi, but were slightly less (74 psi) for the Sassafras soil, considerably less for the Jordan and Hagerstown soils, and very low (for the 2 percent rate) with the Pierre soil. Volume change and moisture absorption values were in most cases brought to satisfactory levels. Maximum density, optimum moisture, and the plastic limit were not greatly affected for any soil tested. Marked reductions in the liquid limit were obtained for the Pierre, Hagerstown, and Sassafras soils, but there was very little effect with the Keyport soil and the liquid limit of Jordan soil was actually raised slightly. Inasmuch as addition of the acid had little effect on the plastic limit, the changes in plasticity index corresponded closely to the changes in liquid limit. The reduction in the liquid limit values of the Pierre soil at the low rate of acid application was accompanied by a large decrease in volume change, but there was little effect on other properties. The higher rate of acid further decreased the liquid limit and greatly increased compressive strength. These pronounced effects on the properties of the Pierre soil are particularly notable because it contains 61 percent of a high volume change clay (particles smaller than 0.005 mm).

The 0.5 percent amine supplement to the acid appreciably reduced the liquid limit of the Pierre soil, but there was little change in the plasticity values of any of the other soils. It also increased the compressive strength of all of the soils, but the effect was pronounced only with the Pierre soil. There was little effect of the amine on any of the other properties studied.

An additional experiment was performed with the Keyport soil to determine the importance of the time interval between the preparation of the soil-acid mixture and the molding of specimens. Compressive strengths obtained for ¼-, 6-, and 24-hr intervals were 104, 80, and 70 psi, respectively, indicating that for the development of maximum compressive strength, there should be very little delay between the mixing and compaction operations.

CONCLUSIONS

Phosphoric acid produced marked increases in the unconfined compressive strength of two fine-grained plastic soils, 2 percent of the acid bringing the strength to a level considered satisfactory for practical stabilization. With four other fine-grained plastic soils treated with 2 percent of the acid, strength development was unsatisfactory.

When calcium carbonate was present, the effectiveness of the acid was sharply reduced.

Values of volume change and moisture absorption were generally brought to satisfactory levels, but changes in moisture-density relations were slight.

For some soils, the liquid limit was greatly lowered, but for others, there was little effect. Plastic limits were practically unchanged. Consequently, changes in the plasticity index corresponded closely to changes in the liquid limit.

For most of the experimental soils, the addition of an amine compound moderately increased the compressive strength and produced moderate decreases in the liquid limit. With the highly plastic Pierre soil the amine caused a pronounced decrease in the liquid limit.

It was shown for one soil that the effectiveness of the acid in increasing compressive strength was appreciably reduced by too long an interval between the mixing and compaction operations.

REFERENCES

1. Lyons, J.W., "Stabilizing a Problem Soil—Cheaply." Eng. News-Record, 159:101-6 (August 15, 1957).
2. Michaels, A.S., Williams, P.M., and Randolph, K.B., "Acidic Phosphorous Compounds as Soil Stabilizers." Ind. and Eng. Chem., 50:889-894 (June 1958).
3. Michaels, A.S., and Tausch, F.W., Jr., "Phosphoric Acid Stabilization of Fine-Grained Soils: Improvements with Secondary Additives." HRB Bull. 282, 28-37 (1961).
4. Demirel, T., Benn, C.H., and Davidson, D.T., "Use of Phosphoric Acid in Soil Stabilization." HRB Bull. 282, 38-58 (1961).
5. "Resinous Water Repellents for Soils." U.S. Waterways Experiment Station, Vicksburg, Miss., Tech. Memo. 217-1 (May 1946).

Effects of Fluorides, Waterproofing Agents, and Polyphosphoric Acid on Soil Stabilization with Acidic Phosphorus Compounds

ALAN S. MICHAELS and F.W. TAUSCH, JR., Soil Stabilization Laboratory, and Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge

The influence of trace-quantity additions of fluosilicate, amines, ferric chloride, and orthorhombic P_2O_5 on the strength development of fine-grained soils stabilized with phosphoric acid has been further studied. In a low plasticity (PI = 8) clayey silt, incorporation of only 0.05 percent by weight o-P_2O_5 with phosphoric acid significantly increases compacted density, and produces a large (80 percent) increase in soaked strength. Although addition of fluosilicate greatly accelerates cure, this compound negates the beneficial effect of o-P_2O_5 on density. An explanation for this phenomenon is offered.

A heavy, montomorillonoid soil (PI = 38), at variance with earlier reported results, has been found to exhibit major improvement in soaked strength by incorporation of relatively high (0.5 to 2.0 percent by weight) concentrations of sodium fluosilicate in conjunction with phosphoric acid. A stabilizing system comprising 3 percent orthophosphoric acid, fluosilicate, and either octylamine or ferric chloride, has yielded soaked compressive strengths (after 1 day's cure) of as high as 140 psi. A special (non-catalytic) role of fluosilicate in montmorillonoid soils is suggested by these results.

●THE NOW well-confirmed effectiveness of phosphoric acid and other acidic phosphorus compounds as fine-grained soil stabilizers (1-8) has been receiving increased attention by highway and construction engineers, and field application of this stabilization method promises soon to become a reality. The ultimate practicability of the technique will be determined by the balance of such factors as cost of stabilization, serviceability, and ease of incorporation of stabilizer. As has been true with many other soil stabilization techniques, phosphoric stabilization appears to be amenable to substantial improvement and cost-reduction by proper utilization of selected secondary additives (3-8). This paper summarizes some recent observations of the effects of a few secondary additives on the properties of two phosphoric acid-stabilized, aluminosilicate soils.

MATERIALS AND PROCEDURE

The two soils studied were Massachusetts clayey silt (MCS), a moderately fine-grained illitic soil (PI=6), and Vicksburg buckshot clay (VBC), a heavy clay containing about 25 percent of the expanding-lattice montmorillonoid minerals (PI = 35). The physical properties and mineralogical compositions of these soils are given in Table 1.

Chemicals used in this work were as follows:

Phosphoric acid (86.1 percent H_3PO_4), reagent grade;

Orthorhombic phosphoric anhydride (P_2O_5), Victor Chemical Works;
Sulfuric acid (98 percent H_2SO_4), reagent grade;
Sodium fluosilicate (Na_2SiF_6), reagent grade;
Ferric chloride ($FeCl_3 \cdot 6H_2O$), reagent grade;
Octylamine ($C_8H_{17}NH_2$), Sharples Chemical Co.;
Pulverized Florida Phosphate Rock, supplied by International Minerals and Chemicals Co., analyzing 29.6 percent CaO, 32.27 percent P_2O_5, and 2.72-4.08 percent F; 93 percent finer than 60 mesh, 63 percent finer than 200 mesh.

The preparation and testing of samples were similar to those described in earlier papers (6, 7). Liquids content at molding was usually maintained at 12.5 cc total liquids volume per 100 g dry soil for MCS, and 17.0 cc per 100 g soil for VBC; maximum compacted density was achieved under these conditions. Additives were incorporated with wet soil in a finger-prong mixer and blended for several minutes. Phosphate rock, when used, was preblended with sulfuric acid before addition to the soil. Orthorhombic P_2O_5 was predissolved in warm water immediately before addition to the soil. Other additives were preblended with the primary stabilizer before incorporation with the soil. Compression test samples were then prepared by two-end static compaction in a Harvard miniature mold. Compaction pressure was always approximately 1,000 psi. Samples were cured at about 70 F and 100 percent relative humidity for various periods

TABLE 1

PROPERTIES OF SOILS INVESTIGATED

Property	Mass. Clayey Silt	Vicksburg Buckshot Clay
Textural composition[1] (% by wt):		
Sand, 0.06 mm to 2 mm	47	0
Silt, 0.002 mm to 0.06 mm	41	65
Clay, <0.002 mm	12	35
Physical properties:		
Liquid limit (%)	20	63-67
Plastic limit (%)	14	27-28
Plasticity index (%)	6	35-40
Specific gravity 20C/20C	2.7	2.67
Max. dry density[2] (pcf)	122.0	105.0
Opt. water content (%)	13.3	22.0
Chemical properties:		
Organic matter (% by wt)	-	1.1
pH	-	4.6
Total soluble salts (meq NaCl/100g)	-	0.3
Soluble sulfates (meq NaCl/100g)	-	-
Carbonates (% by wt)	-	-
Mineralogical compositions[3]		
Clay composition (%)	30	50
Illite: montmorillonoid: clay-chlorite	1:0:1	1:1:0
Chlorite, nonclay (%)	-	-
Calcite (%)	-	-
Free iron oxide (% Fe_2O_3)	2.9	1.9
Gypsum (%)	-	-
Source	Mass.	Miss.

[1] M.I.T. Classification System.
[2] Harvard Miniature Compaction, 40 lb tamper, 3 layers, 25 blows per layer.
[3] For -0.074-mm fraction.

of time, and in some cases subsequently subjected to 24 hr water immersion, then tested to failure in unconfined compression and dried at 110 C for 24 hr. They were weighed and measured after molding, testing, and drying.

RESULTS AND DISCUSSION

Effects of Orthorhombic P_2O_5, Fluosilicate, and Octylamine on Stabilization of MCS with 2 Percent Phosphoric Acid

With lean clay soils such as MCS, previous work (5-8) has shown that (a) sodium fluosilicate functions as a cure accelerator for phosphoric acid, greatly increasing strength at short (e.g., 1 day) cure times; (b) octylamine functions as a waterproofing agent, reducing water absorption on immersion of the soil and thereby reducing strength loss on immersion; and (c) orthorhombic P_2O_5 functions as a soil-deflocculant, allowing significant densification of the soil on compaction and thereby increasing cured-strength. The object of this study was therefore to determine whether suitable combinations of these three secondary additives might function collaboratively to yield still further stabilization improvement.

Results are summarized in Table 2 and Figure 1. Addition of 0.05 percent by weight of orthorhombic P_2O_5 increases by about 50 percent the soaked strength after 1 and 7 days' humid cure, relative to that obtained with 2 percent H_3PO_4 alone. This improvement is traceable primarily to an increase of roughly 1.5 pcf in as-cured dry density of the stabilized soil, resulting from the deflocculating action of the anhydride. Addition of anhydride, however, does not prevent disintegration of the soil on immersion immediately after compaction. Addition of 0.5 percent Na_2SiF_6 in lieu of anhydride produces comparable increases in soaked strength after cure, but with an accompanying density decrease. This observation, coupled with the fact that soil containing fluosilicate exhibits substantial strength on immersion immediately after compaction, confirms the accelerating action of fluosilicate on the alumina-phosphoric acid cementation process.

Unfortunately, addition of both 0.5 percent fluosilicate and 0.05 percent anhydride does not produce the strength improvement that might be expected from their individual actions. Because the compacted densities of samples prepared with both additives are about equal to those obtained with fluosilicate alone, it appears that fluosilicate interferes with the deflocculation action of the anhydride. Attempts to minimize this interference by reducing the concentration of fluosilicate from 0.5 to 0.1 percent (see Table 2) were successful insofar as increasing compacted density was concerned, but strengths were still inferior to those obtained with 0.05 percent P_2O_5 alone. These results point

TABLE 2

EFFECT OF SECONDARY ADDITIVES ON MCS STABILIZATION[1]

Additive on Dry Soil (%)			1-Day Humid Cure			Compress. Strength[2] (psi)		
Na_2SiF_6	C_8Amine	o-P_2O_5	Volatiles on Dry Solids (%)	Density of Dry Solids (pcf)	Compress. Str. (psi)	0-Day Cure	1-Day Cure	7-Day Cure
0	0	0	10.1	132.1	325 ± 15	0.0	200 ± 15	275 ± 15
0.5	0	0	9.8	131.8	540	190	325 ± 20	440 ± 5
0	0	0.05	9.9	133.6	410 ± 10	-	340 ± 30	420 ± 5
0.5	0	0.05	9.6	131.0	540 ± 5	-	365 ± 50	400 ± 20
0	0.05	0.05	9.1	134.5	375 ± 5	155 ± 5	425 ± 5	430
0.1	0	0.05	9.8	133.2	370	-	285 ± 5	430 ± 10
0.5[3]	0	0.05	10.2	131.5	330	-	205 ± 5	365 ± 25
0.5	0.05	0	9.1	128.5	510	165 ± 5	280 ± 10	290
0.5	0.05	0.05	9.6	131.4	450 ± 20	175 ± 5	295 ± 5	-
0.5	0.05	0.10	9.3	130.0	400 ± 20	140 ± 5	275 ± 5	-
0.5	0.05	0.25	9.2	125.9	385 ± 15	120 ± 20	190 ± 5	-

[1] Phosphoric acid content = 2 percent on dry soil.

[2] One-day immersion following humid cure for period shown.

[3] AlF_3.

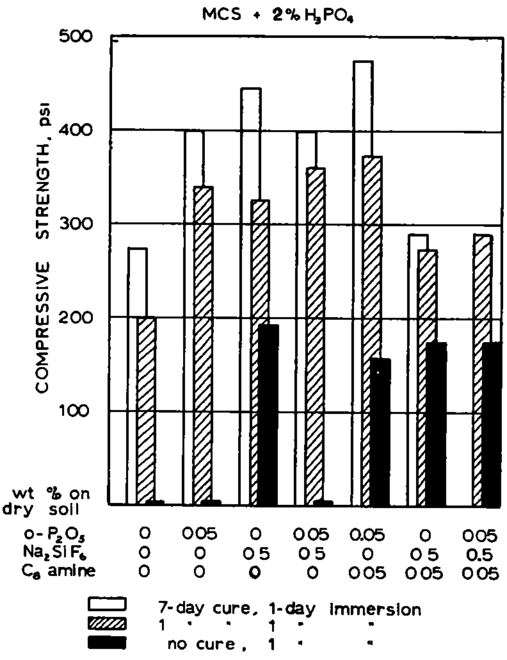


Figure 1.

to some specific role of the anhydride in the anhydride in the aluminophosphate cementation process, apart from its dispersive action; the mechanism of this action is not clarified by these data. It is also interesting that aluminum fluoride, as well as sodium fluosilicate, interferes with the dispersive action of the anhydride; this implicates the fluoride ion as the key interfering constituent and suggests that preferential sorption of fluoride by the clay mineral prevents sorption of polyphosphoric acid. The similarity to the action of fluoride ion in preventing clay deflocculation by alkali polyphosphates is striking.

Addition of as little as 0.05 percent octylamine to MCS treated with 2 percent H_3PO_4 tends to reduce the water affinity of the stabilized soil, and thereby reduces both water uptake and strength loss on immersion. However, the amine has a significant flocculating effect on the clay minerals in the soil, causing a rather large decrease in compacted density (from about 131 to 128 pcf). Thus, although amine addition allows freshly compacted soil to withstand immersion in water, strength development on cure is often substantially less than that observed with phosphoric acid alone. It was anticipated that, if orthorhombic P_2O_5 could exert its dispersive action in the presence of the amine, a combination of these two additives would have a decided beneficial effect on stabilization. It is apparent from Figure 1 and Table 2 that the anhydride is active in the presence of amine, increasing compacted density nearly 6 pcf and substantially increasing soaked strength before and after humid cure. It appears that, for a suitable balance of high-soaked strength after cure and resistance to deterioration on soaking before cure, a stabilizer formulation comprising 2 percent H_3PO_4, 0.05 percent amine, and 0.05 percent orthorhombic anhydride is the most satisfactory system of those studied here.

Addition of sodium fluosilicate to systems containing both amine and anhydride is found to be detrimental to both strength development and density (Table 2). Increasing the anhydride content from 0.05 to 0.25 percent does not offset the detrimental effects of the fluosilicate; on the contrary, properties worsen as anhydride content increases. This observation is consistent with the earlier reported observation (7) that the anhydride itself causes flocculation of the soil when used in too high concentrations.

Also, 0.05 percent anhydride increases compacted density when both amine and fluosilicate are present, but nowhere near the degree it does in the absence of fluosil-

TABLE 3

STABILIZATION OF MCS WITH PHOSPHORIC ACID[1]

	1-Day Humid Cure						7-Day Humid Cure					
	0-Day Immersion			1-Day Immersion			0-Day Immersion			1-Day Immersion		
H_3PO_4 (%)	Actual Compress Str (psi)	Volatiles (%)	Dry Density (pcf)	Actual Compress Str (psi)	Volatiles (%)	Dry Density (pcf)	Actual Compress Str (psi)	Volatiles (%)	Dry Density (pcf)	Actual Compress Str (psi)	Volatiles (%)	Dry Density (pcf)
0 5	250	9 2	129 2	85±5	10 3	129 0	370	8 5	129 5	90	11 0	128 7
1 0	290	10 3	128 5	-	-	-	395±5	9 6	127 8	175±15	10 6	129 0
1 5	355±5	9 9	129 5	170	11 2	128 9	470	9 7	128 3	240±10	11 0	128 9
2 0	540	9 8	131 8	325±20	10 7	131 1	780	9 6	-	440±5	10 4	131 0
3 0	770	-	-	630±20	10 4	130 8	1020±50	9 1	130 1	610±30	10 4	131 8

[1] Samples contain 0 5 percent Na_2SiF_6; percentages of additives based on dry soil

icate. From this, it is inferred that, while fluorides prevent sorption of polyphosphoric acid by clays, polyphosphoric acid prevents sorption of amine. It seems not unlikely that the amine will react preferentially with the polyphosphoric acid to form the corresponding insoluble amine polyphosphate salt; slow hydrolysis of the polyphosphate will then gradually release amine for sorption on the soil, but this will take place only after considerable cementation has occurred. The use of orthorhombic P_2O_5 or polyphosphoric acid, as a means of temporarily inactivating amines and other organic cationic chemicals and thereby facilitating compaction of soil, appears to warrant further study as a technique for improving stabilization effectiveness.

Effect of Phosphoric Acid Concentration on MCS Stabilization

Table 3 shows the effect of varying the concentration of phosphoric acid (between 0.5 and 3.0 percent on the dry soil weight) on the compressive strength of MCS; 0.5 percent sodium fluosilicate was present in all cases. Both as-cured and soaked strengths increase monotonically with acid concentration; the rate of strength increase with acid concentration is highest in the range 1.5 to 2.0 percent. It will be noted that the fractional strength loss on immersion (for both 1- and 7-day humid cure) decreases from about 75 percent of the cured strength at 0.5 percent acid to about 40 percent of the cured strength at 3.0 percent acid. This illustrates that interparticle cementation sufficient to produce rather high compressive strength after cure is often not great enough to resist soil breakdown from the high positive porepressures generated on water immersion. Compressive strength after soaking is thus a very severe test of stabilization effectiveness, and it is evident that phosphoric acid-fluosilicate admixtures are quite adequate stabilizers for MCS at acid concentrations above about 1.5 percent acid by weight.

Stabilization of VBC

In earlier investigations (6-8) it was found that high-plasticity VBC could not be adequately stabilized with phosphoric acid unless significant amounts of octylamine or ferric chloride were added. These secondary additives were concluded to function by undergoing interchange with the interlaminar cations (mainly sodium and calcium) present in the montmorillonoid of the soil, thereby greatly reducing interlaminar swelling on immersion. In the present study, objectives were to establish (a) whether addition of fluosilicate has any beneficial effect on the acidamine or acid-ferric chloride system, (b) whether partial replacement of phosphoric acid by low-cost sulfuric acid can be made without loss in stabilization, and (c) whether orthorhombic P_2O_5 can be successfully used as a substitute for phosphoric acid in this soil.

Results are summarized in Table 4. Treatment of VBC with 2.76 percent H_3PO_4

TABLE 4

STABILIZATION OF VICKSBURG BUCKSHOT CLAY

Additives on Dry Soil (%)					At Molding					
Acid		Na_2SiF_6 (%)	Waterproofer		Volatiles on Dry Solids (%)	Density of Dry Solids (pcf)	1-Day Humid Cure Str (psi)	Compressive Strength (psi)		
Type	%		Type	%				1-Day Cure	7-Day Cure	14-Day Cure
H_3PO_4	2.76	0	C_8amine	1	21.6	104.3	215±15	45±5	-	-
H_3PO_4	2.76	0.5	C_8amine	1	23.3	104.0	205±5	45±5	50	-
H_3PO_4	2.76	2.0	C_8amine	1	23.9	101.7	215±5	135±25	140±10	-
H_3PO_4	4.0	1.0	-	-	21.0	107.2	330±20	55±5	105±5	-
H_3PO_4	4.0	1.0	$FeCl_3$	1.6	21.1	107.6	240±5	75±10	215±10	235±5
H_3PO_4 H_2SO_4	2.0 2.0	1.0	$FeCl_3$	1.6	22.0	106.0	345±5	55±5	135±10	-
P_2O_5	1.75	-	C_8amine	1	22.1	104.6	-	25	65±10	55±10
P_2O_5	3.6	-	C_8amine	1	22.0	105.0	-	70±10	155	180±20
P_2O_5	3.1	-	$FeCl_3$	1.6	20.6	107.5	190±30	30±5	160±5	230±10
P_2O_5	3.12	0.5	$FeCl_3$	1.6	21.4	106.6	290±10	135±5	280±20	290
P_2O_5	3.1	2.0	$FeCl_3$	1.6	21.1	107.3	350±10	105±5	420±20	415±10

[1] One-day immersion following humid cure for period shown.

(of which 0.76 percent is used to neutralize the amine, leaving 2 percent "free" acid) and 1 percent octylamine produces only marginal stabilization (45-psi soaked strength after 1-day cure), and addition of 0.5 percent fluosilicate has no significant beneficial effect. However, increasing the fluosilicate content to 2 percent causes nearly a threefold soaked strength increase. This improvement does not appear to be caused by mere acceleration of the acid-soil reaction (as with MCS), inasmuch as there is no comparable increase in humid cure strength when fluosilicate is present. Some direct participation of the fluosilicate anion in the cementation process is thus suggested, but the nature of the reaction remains unclear.

The importance of a waterproofing additive in VBC is made particularly evident with the behavior of a sample stabilized with 4 percent phosphoric acid and 1 percent fluosilicate; this composition, despite its far higher as-cured strength relative to those containing half as much acid with amine, exhibits much lower soaked strength. Addition of 1.6 percent ferric chloride produces a nearly twofold increase in soaked strength, by reducing interlaminar clay swelling; the rather marked decrease in humid cure strength produced by the introduction of the iron salt is probably caused by the formation of ferric phosphate, which reduces the amount of phosphoric acid available for reaction with the soil alumina. This suggests that only a fraction of the total ferric ion provided by the ferric chloride is actually utilized in ion exchange with the montmorillonoid. Because this soil has a rather high acid-binding capacity, the pH of a mixture containing even as much as 4 percent phosphoric acid is likely to be high enough to favor considerable hydrolysis of the ferric chloride to ferric hydroxide. Because ferric hydroxide would not be expected to provide ferric ions for cation exchange with the clay, inefficient utilization of the iron for this purpose is perhaps to be expected.

Use of an equal-weight mixture of 2 percent phosphoric and 2 percent sulfuric acids in conjunction with fluosilicate and ferric chloride yields stabilized soil whose soaked strengths are lower by about 30 percent than those of the similar formulation containing 4 percent phosphoric acid. Inasmuch as soaked compressive strength tends to vary almost linearly with phosphoric acid concentration, it is deduced that the sulfuric acid contributes in some degree to the stabilization, but is not equivalent to the corresponding amount of phosphoric acid. Sulfuric acid may aid stabilization by (a) solubilizing alumina from the soil, and thereby making alumina more rapidly available for reaction with the phosphoric acid, and/or (b) reacting preferentially with free ferric iron from the ferric chloride, and thereby releasing more phosphoric acid for alumino-phosphate formation. Either or both of these effects is suggested by the observation that the as-cured strength of the samples stabilized with the acid mixture is higher than that observed with samples containing 4 percent phosphoric acid.

Replacement of 2 percent phosphoric acid with a stoichiometrically equivalent amount of orthorhombic phosphoric anhydride (Table 4), using 1 percent amine as the waterproofer, effects essentially the same degree of stabilization as does the acid; hence, the anhydride proves to be an acceptable alternative in VBC, as has previously been found with MCS (7, 8). With 3.6 percent anhydride (equivalent to 5 percent "free" acid) and 1 percent amine, rather high soaked strengths are obtained, but the composition cures rather slowly. With 3.1 percent anhydride (equivalent to 5 percent total acid) and 1.6 percent ferric chloride, ultimate soaked strengths are higher still, but cure rate is lower than with amine. Addition of as little as 0.5 percent fluosilicate, however, greatly accelerates curing and increases ultimate soaked strength, whereas 2 percent fluosilicate nearly doubles the ultimate soaked strength again, although with some decrease in cure rate. Soaked strengths in excess of 400 psi obtained with this latter formulation are higher than any previously recorded in this laboratory with VBC for any stabilization system.

The influence of fluosilicate upon stabilization with orthorhombic P_2O_5 appears to be different in no important respects from that suggested earlier for phosphoric acid-fluosilicate combinations. There is evidence of an accelerating effect of the fluosilicate on cure (the 1-day humid cure strengths increase with fluosilicate content), but direct participation of the fluosilicate in the cementation process is strongly suspected.

CONCLUSIONS

Phosphoric acid-stabilized clayey silt (MCS) can be materially improved in wet strength by incorporation of trace amounts of orthorhombic P_2O_5 and octylamine. Sodium fluosilicate accelerates strength development and is recommended where high early-strength is desired; however, fluosilicate cannot be used in conjunction with orthorhombic P_2O_5 because it eliminates the beneficial effect of the latter compound on soil-compacted density. A formulation comprising 2 percent phosphoric acid, 0.05 percent o-P_2O_5, and 0.05 percent octylamine will develop with MCS a soaked compressive strength of nearly 500 psi after one week's humid cure.

Strength development of phosphoric acid stabilized MCS is a nearly linear function of acid concentration.

Relatively high concentrations (1 to 2 percent) of sodium fluosilicate, in conjunction with phosphoric acid and either octylamine or ferric chloride, have a definitely beneficial effect on strength development in VBC. Participation of the fluosilicate in the cementation reaction is suspected. Orthorhombic phosphoric anhydride is a satisfactory substitute for phosphoric acid in VBC, and is recommended under conditions where a granular solid stabilizer can be more conveniently utilized than liquid phosphoric acid.

ACKNOWLEDGMENTS

This investigation is part of a general program of soil stabilization research, supported by the U.S. Army, Corps of Engineers, Waterways Experiment Station, Vicksburg, Miss., and by grant-in-aid contributions from industrial sponsors of the Soil Stabilization Laboratory. Thanks are due to W.G. Shockley and R. Kozan of W.E.S. for their critical evaluation of the manuscript, and to C. Sonino, who performed much of the experimental work.

REFERENCES

1. Demirel, T., Benn, C.H., and Davidson, D.T., "Use of Phosphoric Acid in Soil Stabilization." HRB Bull. 282, 38-58 (1961).
2. Lyons, J.W., "Stabilization of a Problem Soil—Cheaply." Eng. News-Record, 159:101-106 (1957).
3. Lyons, J.W., "Soil Stabilization." U.S. Patent 2,899,329 (Aug. 11, 1959).
4. Lyons, J.W., "Soil Stabilization." U.S. Patent 2,899,330 (Aug. 11, 1959).
5. Michaels, A.S., Williams, P.M., and Randolph, K.B., "Acidic Phosphorus Compounds as Soil Stabilizers." Ind. Eng. Chem., 50:889-894 (1958).
6. Michaels, A.S., and Tausch, F.W., Jr., "Fine-Grained Soil Stabilization with Phosphoric Acid and Secondary Additives." HRB Bull. 241:109-118 (1960).
7. Michaels, A.S., and Tausch, F.W., Jr., "Phosphoric Acid Stabilization of Fine-Grained Soils: Improvements with Secondary Additives." HRB Bull. 282, 28-37 (1961).
8. Michaels, A.S., and Tausch, F.W., Jr., Ind. Eng. Chem., 52:857 (1960).

Reactions of Phosphoric Acid with Clay Minerals

TURGUT DEMIREL and DONALD T. DAVIDSON, respectively, Research Associate and Professor of Civil Engineering, Iowa Engineering Experiment Station, Iowa State University, Ames

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 44μ 55% finer than 1μ	71.6
Volclay (Bentonite SVP)	American Colloid Co., Skokie, Ill	Montmorillonite	92-95	Feldspar	96% finer than 74μ 86% finer than 0.5μ	524.6
Concentrated vermiculite ore	Zonolite Co., Chicago, Ill	Vermiculite	-	-	Wet ground and sieved through 325-mesh (44μ) screen	70.4
Prochlorite	Wards Natural Science Establishment, Inc., Rochester, N Y	Chlorite	-	-	Wet ground and sieved through 325-mesh (44μ) screen	32.7
Grundite	Illinois Clay Products Co., Chicago, Ill.	Illite	-	-	100% finer than 420μ 75% finer than 5μ	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, $AlCl_3 . 6H_2O$.

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

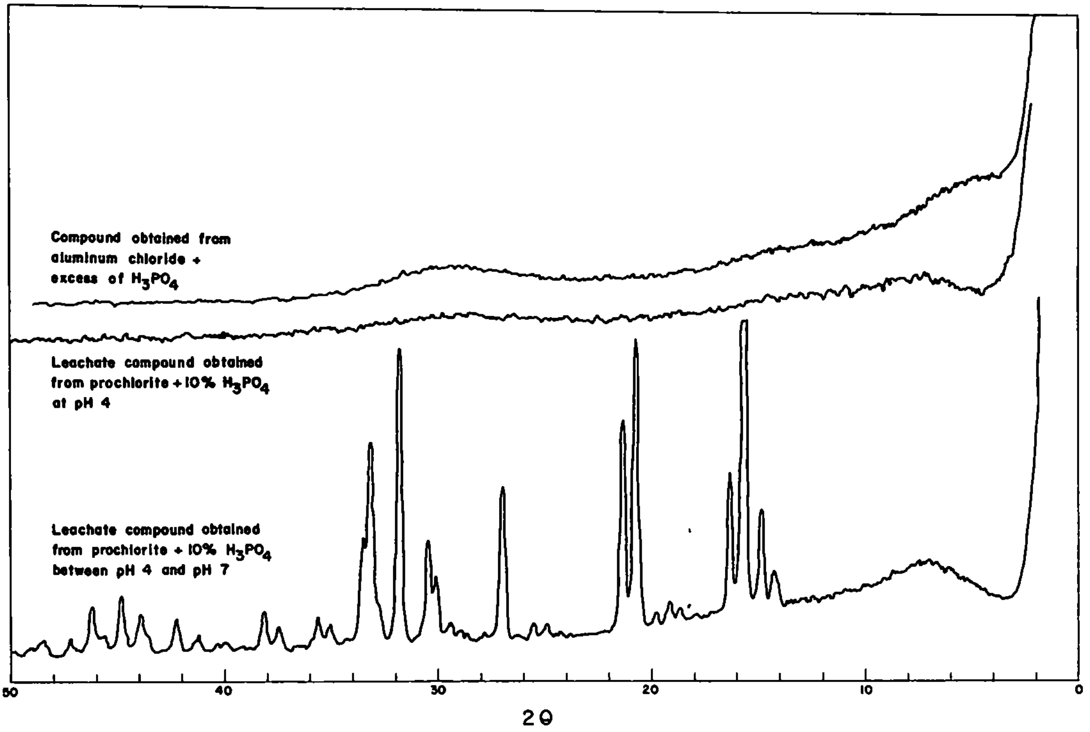


Figure 1. X-ray diffractometer charts of the precipitates.

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-

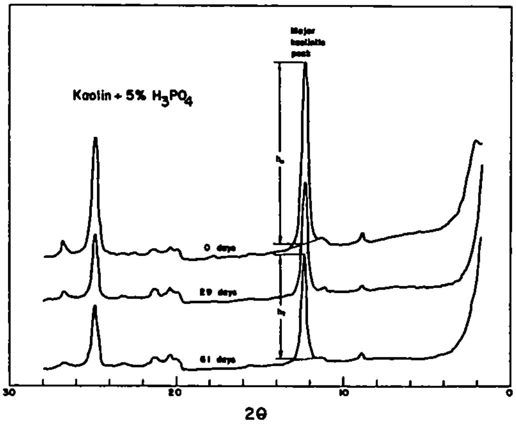


Figure 2. X-ray diffractometer chart showing changes in peak intensities of kaolin + 5 percent phosphoric acid mixture with time.

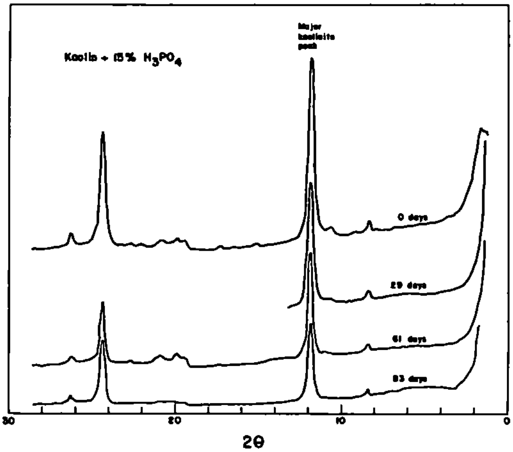


Figure 3. X-ray diffractometer chart showing changes in peak intensities of kaolin + 15 percent phosphoric acid mixture with time.

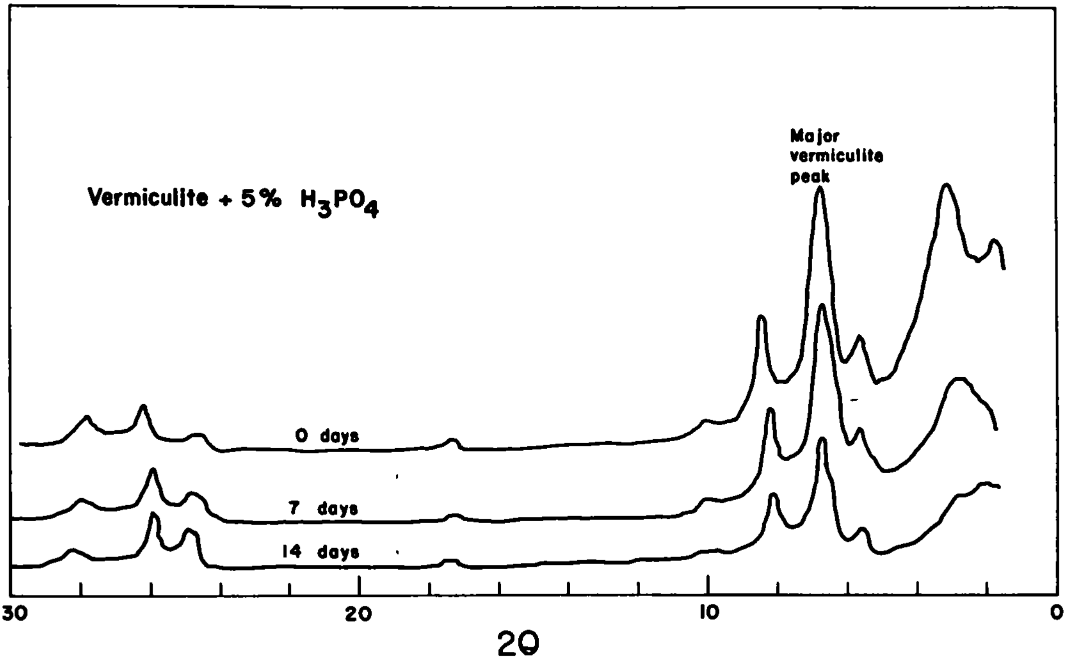


Figure 4. X-ray diffractometer chart showing changes in peak intensities of vermiculite + 5 percent phosphoric acid mixture with time.

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 ± 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.

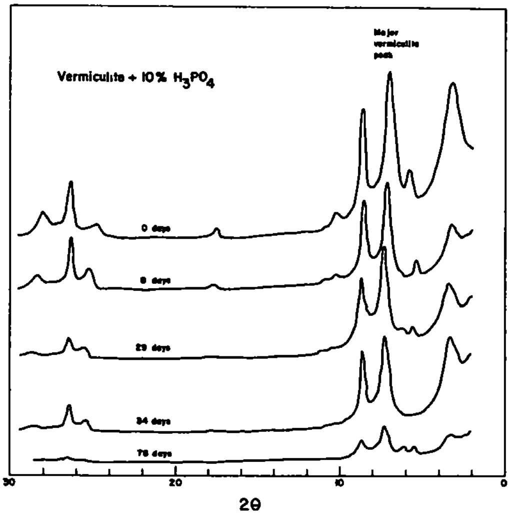


Figure 5. X-ray diffractometer chart showing changes in peak intensities of vermiculite + 10 percent phosphoric acid mixture with time.

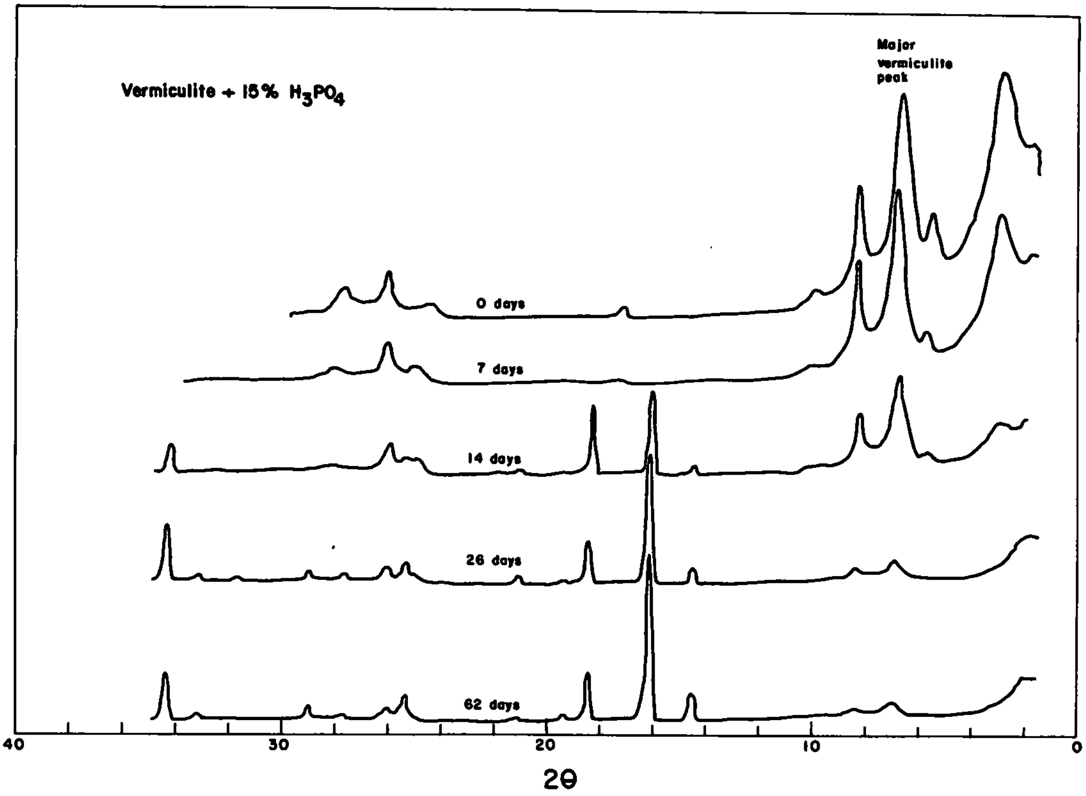


Figure 6. X-ray diffractometer chart showing changes in peak intensities of vermiculite + 15 percent phosphoric acid mixture with time.

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-

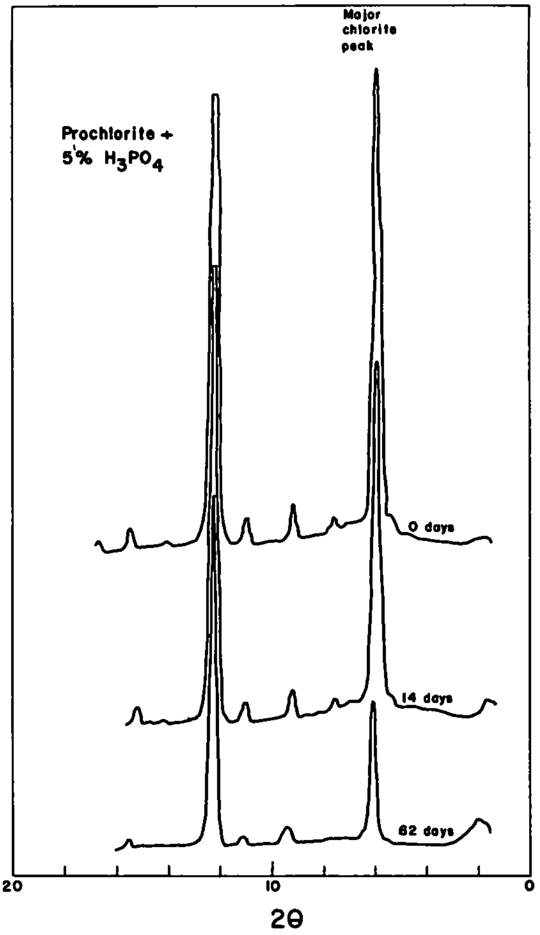


Figure 7. X-ray diffractometer chart showing changes in peak intensities of prochlorite + 5 percent phosphoric acid mixture with time.

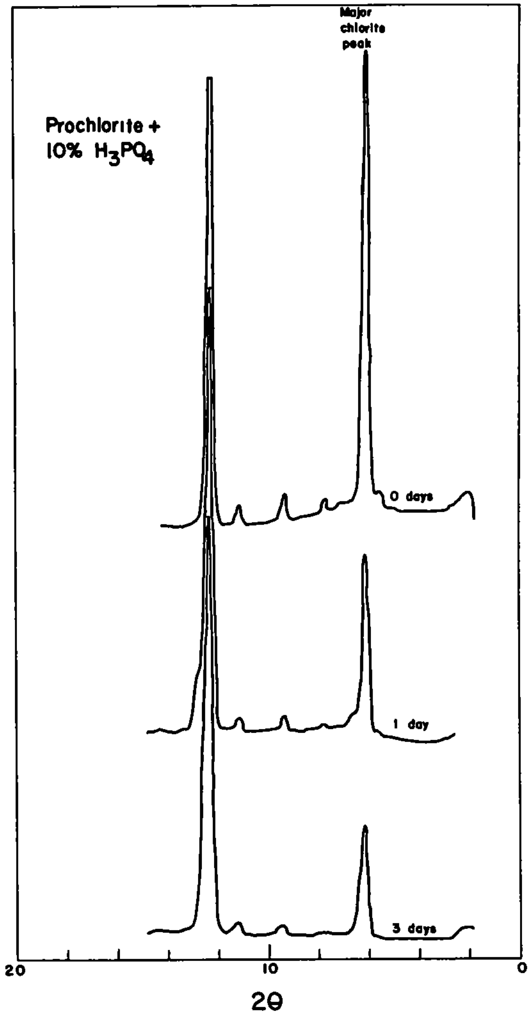


Figure 8. X-ray diffractometer chart showing changes in peak intensities of prochlorite + 10 percent phosphoric acid mixture with time.

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 phorphoric 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 idication 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.

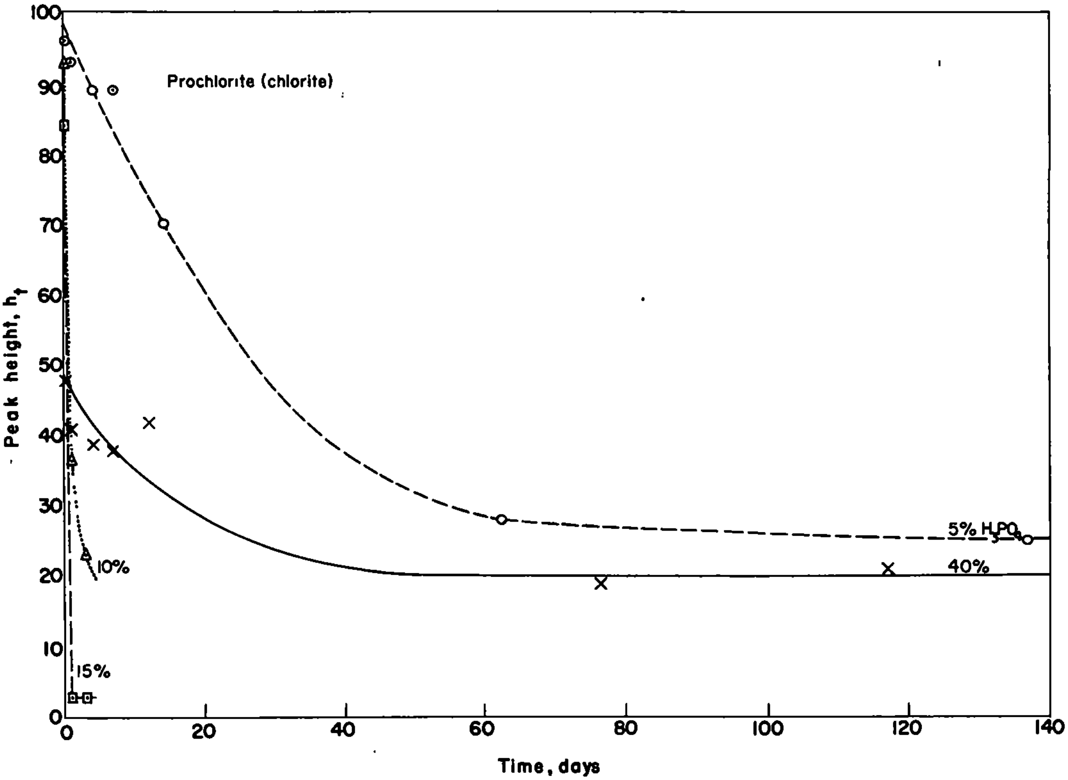


Figure 9. Major peak heights vs time for prochlorite treated with 5, 10, 15, and 40 percent phosphoric acid.

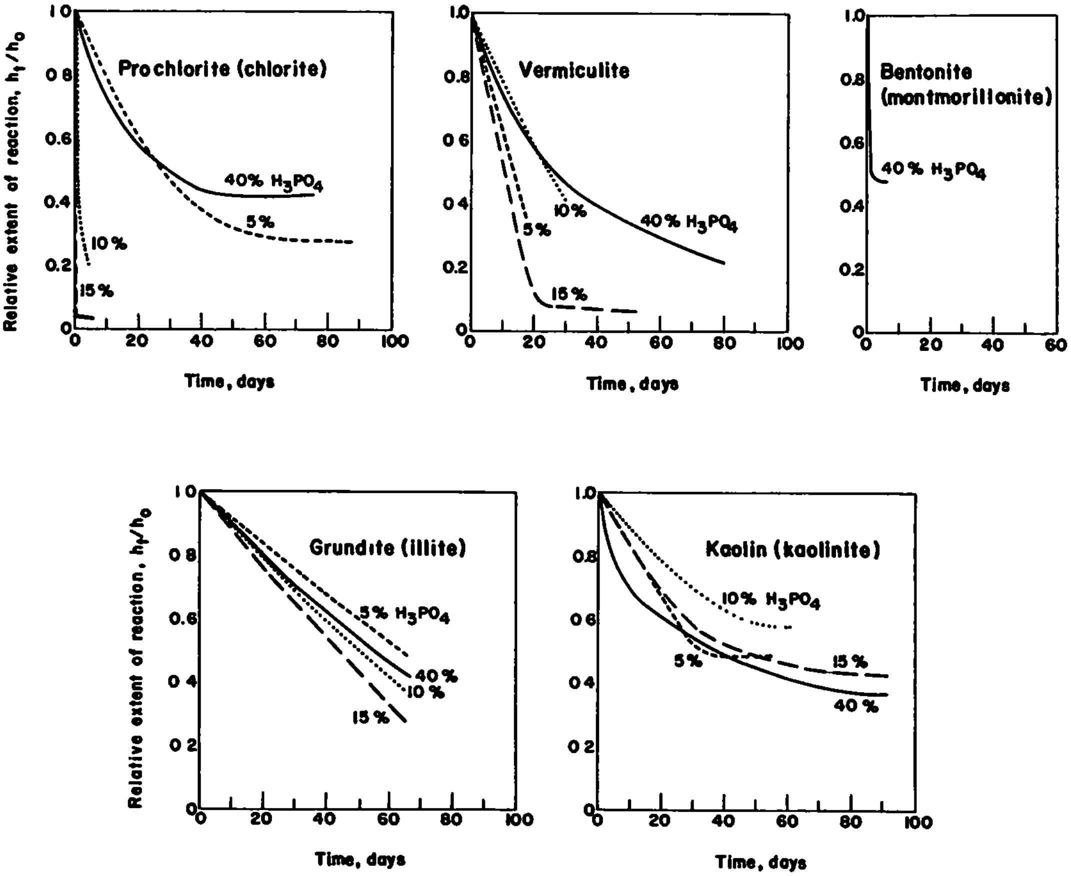


Figure 10. Relative extent of the reaction vs time for all clays and phosphoric acid percentages studied.

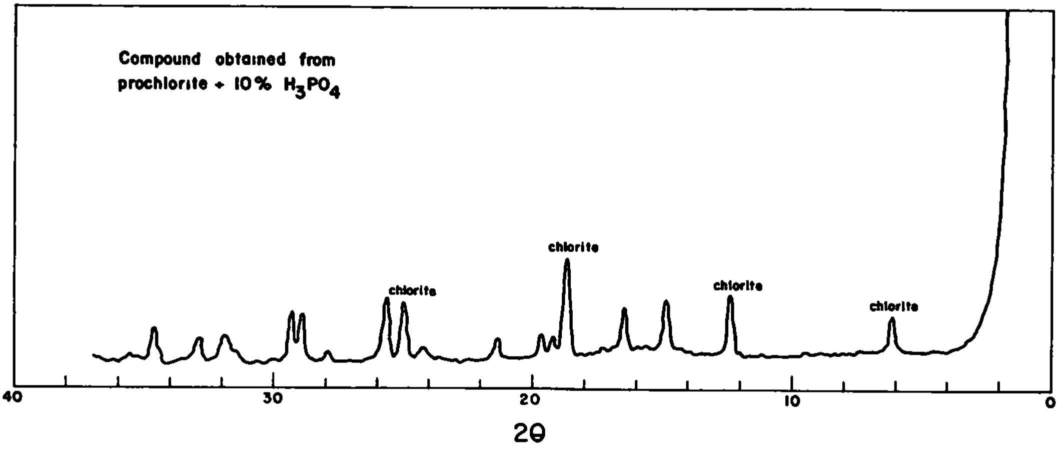


Figure 11. X-ray diffractometer chart of crust formed on surface of prochlorite + 10 percent phosphoric acid.

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.

ACKNOWLEDGMENT

The subject matter of this report was obtained as part of the research under Project 283-S of the Engineering Experiment Station of Iowa State University. This project, "The Loess and Glacial Till Materials of Iowa; an Investigation of Their Physical and Chemical Properties and Techniques for Processing Them to Increase Their All-Weather Stability for Road Construction," is under contract with the Iowa Highway Research Board as Project HR-1 and is supported by funds supplied by the Iowa State Highway Commission.

Thanks are given to Mr. L. Gotter for assisting in the preparation and analysis of samples and Dr. E.A. Rosauer for reading the manuscript and offering helpful advice.

REFERENCES

1. Demirel, T., Benn, C.H., and Davidson, D.T., "Use of Phosphoric Acid in Soil Stabilization." HRB Bull. 282, 38-58 (1961).
2. Lyons, J.M., McEwan, F.J., and Siehenthal, C.D., "Phosphoric Acid in Soil Stabilization: II. Secondary Additives, Acid Source, and Mechanism." HRB Bull. 318, 15-24 (1962).

Field Studies of Soil Stabilization With Phosphoric Acid

J.W. GUINNEE, Soils Research Engineer, Missouri State Highway Department

Two clay soils (Putnam) typical of certain areas of Missouri were tested in the laboratory for response to phosphoric acid as a stabilizer. The effect of the stabilizer on group index, moisture-density relations, and immersed unconfined compressive strength is shown. Promising results from these tests indicated the desirability of a pilot field installation. A location on Route J, Calloway County, Mo., was selected for this test and test results on soil samples are given. The construction of the test section by state maintenance personnel in early October 1958 is discussed. Evaluation is continuing. Further laboratory work on samples from a projected field site of a more extensive test section is described.

● THE MISSOURI STATE Highway Department first became interested in the use of phosphoric acid as a soil stabilizer when approached by representatives of Monsanto Chemical Company in October 1957. Monsanto had started studies of possible chemical soil stabilizers at the request of the Bureau of Public Roads.

The first consideration among Missouri highway personnel was that if it could stabilize Putnam silt loam, it probably could stabilize anything. Therefore, laboratory trials were set up to study the effects on Putnam silt loam. The apparent advantage to Missouri was in the realm of stabilizing high group index soils (heavy clays, of which Missouri has sufficient) in areas where the cost of good aggregates is prohibitive. It was suggested that it be considered at first a method for substituting a portion of the aggregate base as required by the flexible design chart. If further tests proved it suitable, it might then be considered as a complete substitution.

The preliminary tests with phosphoric acid were run on a "C" horizon Putnam silt loam. Because Monsanto had already made numerous tests using a 2- by 4-in. mold and because Missouri does not use that size, it was decided to use Monsanto's molding

TABLE 1

EFFECTS OF PHOSPHORIC ACID ON THE CHARACTERISTICS OF "C" HORIZON PUTNAM SILT LOAM

Additive ($\% H_3PO_4$)	Liquid Limit	Plastic Limit	Plasticity Index	Passing No. 200 (%)	Group Index	Standard		Strength (psi)		Modified		Strength (psi)	
						Max Dens	Opt Moist	Cured	Soaked	Max Dens	Opt Moist	Cured[1]	Soaked[2]
0	53.0	17.6	35.4	84.0	19.0	96.0	25.0	-	0	106.0	-	196	0
1	43.7	22.9	20.8	75.0	13.0	96.3	24.8	-	9	-	-	-	-
2	42.1	22.9	17.5	50.5	5.7	98.0	23.6	-	51.0	110.0	-	274	123
3	38.3	23.3	15.0	37.0	1.5	98.5	21.4	-	41.0	-	-	-	-
4	34.6	26.4	8.2	35.0	-	101.0	21.3	-	59.0	-	-	-	-
2+0.5% Amine	37.4	27.2	10.1	30.5	-	92.6	25.2	-	53.0	-	-	-	-

[1] Cured 7 days

[2] Cured 5 days, soaked 2 days

equipment to forestall having to correlate different sample sizes. The results are shown in Table 1 and the moisture-density relations are shown in Figure 1.

The increase in soaked unconfined compressive strength from 0 to 51 and the re-

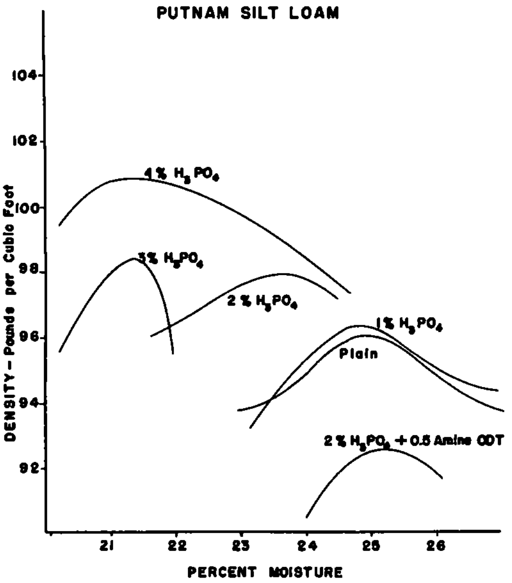


Figure 1. Effect of phosphoric acid on moisture-density relations (Missouri Laboratory).

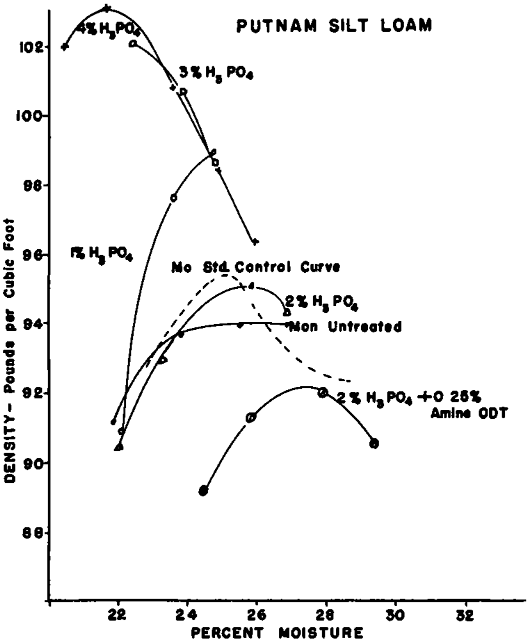


Figure 2. Effect of phosphoric acid on moisture-density relations (Monsanto Laboratory).

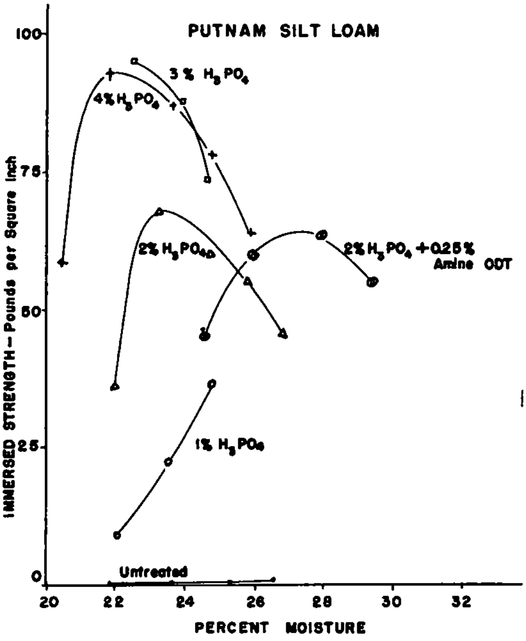


Figure 3. Effect of phosphoric acid on immersed strength-moisture relations (Monsanto Laboratory).

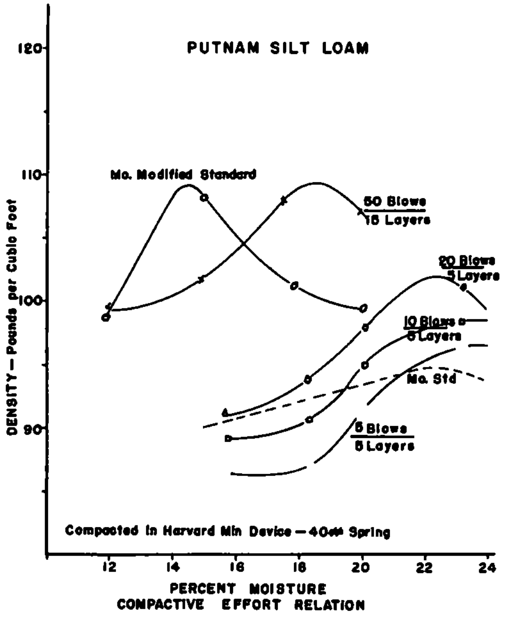


Figure 4. Effect of compactive effort on moisture-density relations.

duction in group index from 19 to 6 made these first tests appear very promising. Other tests, as performed in the Monsanto Laboratory at St. Louis (1), on a companion soil sample produced the results shown in Figures 2 and 3. Further testing in the Highway Department determined the difference for the correlation to the standard compaction curves. Monsanto used a drop hammer and sleeve and Missouri used an automatic with wedge foot. With these factors corrected, the two laboratories agreed on produced results with the consensus that the Putnam was changed by the addition of 2 percent acid to give an average increase in soaked unconfined compressive strength from 0 to 60 with the subsequent decrease in group index from 20 to 6.

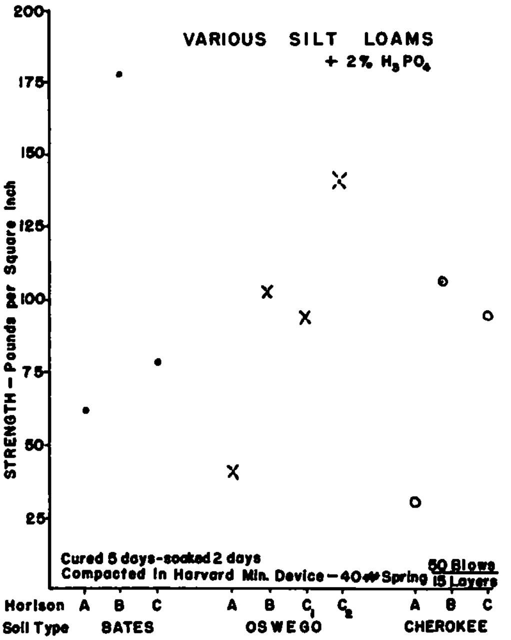


Figure 5. Strength of various silt loams with 2 percent H_3PO_4.

Further testing was done in the Missouri laboratory using the Harvard Min. apparatus. First, a series of tests was run on the "C" horizon Putnam silt loam to determine what combination of spring, blows, and layers would produce a moisture-density relationship similar to that obtained by the modified AASHO compaction. The curves are shown in Figure 4. Fifty blows with the 40-lb spring on each of 15 layers was chosen as coming the closest, although the moisture content did not match.

Tests on several soils were run at this compactive effort giving the results shown in Figure 5. Table 2 shows the characteristics of the soils studied.

Although these laboratory results seem promising, it would be more indicative of the practical limitations of this material, to construct a pilot field test section. The advantages of a pilot field test to discover the problems of construction and also to determine the performance, as only a field

TABLE 2

SOIL CHARACTERISTICS

Soil Horizon	Liquid Limit	Plastic Index	Clay (%)	Opt. Moist.	Max. Dens.	Classification
Bates:						
A	19.1	0.6	15.2	12.8	115.0	A-4-(8)
B	21.6	7.4	20.0	12.2	124.3	A-4-(8)
C	20.7	0.4	13.8	12.7	119.0	A-2-4-(0)
Oswego:						
A	29.3	3.2	18.5	17.2	104.5	A-4-(8)
B	33.1	10.8	26.5	17.4	107.9	A-6-(9)
C_1	56.1	35.1	37.8	22.6	99.6	A-7-6-(19)
C_2	33.2	17.4	34.5	14.5	112.0	A-6-(11)
Cherokee:						
A	23.6	2.7	17.5	14.6	110.0	A-4-(8)
B	58.7	26.2	45.0	29.7	87.7	A-7-5-(18)
C	34.8	16.2	33.5	18.6	107.4	A-6-(11)

TABLE 3

BORROW SOIL CHARACTERISTICS

Station	Passing No (%) 10	40	60	200	Silt (%)	Clay (%)	Colloids (%)	Opt Moist	Max Density	Liquid Limit	Plastic Limit	Plastic Index	Texture	Group Index	Field Moist
III	100 0	98 0	96 8	94 6	55 5	28 0	20 0	18 7	104 0	33 7	19 9	13 8	Silty Clay Loam	A-6-(9)	20 3
IV	100 0	98 0	97 0	96 0	59 0	24 0	16 0	19 4	102 6	32 2	22 6	9 6	Silty Clay Loam	A-4-(8)	21 0
V	100 0	98 0	96 0	94 0	59 0	27 0	22 0	19 2	101 6	33 9	21 8	12 1	Silty Clay Loam	A-6-(9)	15 9

test can, outweigh the lack of complete laboratory testing in every phase prior to the field test. That is, the field test may determine the lines of study for future laboratory work or show that certain laboratory testing is unrealistic.

With these thoughts in mind, a search was made for a project suitable for the construction of a test section. From practical necessity, it could not be on location where it would seriously interfere with a large traffic volume if there were a failure. Many of the locations investigated were either of the temporary detour type, where detour traffic might be so great as to destroy the project before any sound comparisons could be made, or of the county road type where only patch work was necessary. A location of the latter type was finally found where construction of a 100-ft test section was possible. Although it was realized that a section of such a limited length would not be an accurate or fair test of the acid stabilization, the information gained would be of value for future planning and evaluation.

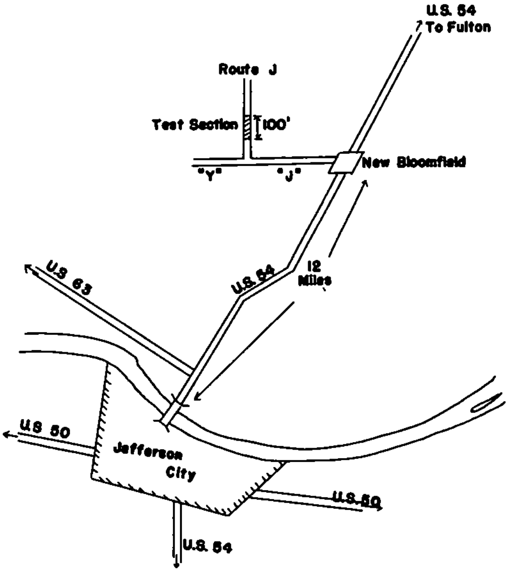
The site (Fig. 6) chosen for the study section is located on Route "J", Callaway County, approximately ¼ mi west of New Bloomfield and approximately 100 yd north of the junction with Callaway County Route "Y". The road is 20 ft wide and of a "built-up" construction with an armor coat surface of MC-3 and stone chips. The section chosen had previously failed, and continued to be in bad condition, due to heavy hauling by quarry trucks for a resurfacing job on Route 54, close by. The failed section was over 300 ft long, but the test section was chosen as the 100 ft starting approximately 30 ft from the north end of the poor section. The treated section was to be 6 in. thick, 20 ft wide and 100 ft long.

Samples from the roadway indicated there was enough stone to contribute to mechanical stabilization, which would have overshadowed the effects of the acid. Because the existing grade was to be retained, it then became necessary to undercut the proposed section and replace with "borrow" soil. This was done to obtain uniform soil conditions on which to measure the effects of the proposed stabilization.

The soil was borrowed from the adjacent backslope on the west. This was identified as the rolling phase of the Putnam silt loam. Table 3 presents the data from samples taken from this borrow area.

Preliminary strength and density tests to determine the amount of acid needed were performed in the Monsanto Laboratory, where the molding equipment had been returned. The results, as reported by Monsanto (Figs. 7 and 8) indicated that 2 percent acid by dry weight of soil would provide satisfactory stabilization.

September 29 and 30, 1958, were spent in preparation, checking equipment to be



TEST SECTION LOCATION

Figure 6. Test section location, Callaway County, Mo.

used on the project. Moisture samples of the borrow soil (Table 4) were obtained to determine what action should be taken to bring the soil close to optimum moisture for compaction. It was found that, due to rain the previous day, moisture would have to be reduced approximately 6 percent. October 1 was spent in moving the required amount of soil to the undercut section and in thoroughly aerating it so that the moisture content would be reduced to the optimum moisture (18 percent). October 2 was spent in actual construction of the project. The east half (10 ft) of the 100-ft section was constructed first, with the following procedure:

1. Thorough mixing of the soil to a depth sufficient to give 6 in. compacted on the road.
2. Acid applied as 75 percent acid but in an amount to give a total of 2 percent (by weight of dry soil) of 100 percent acid on the road; amount applied in complete passes with the distributor (8 trips with 5-ft spray bar).
3. Following each complete pass (2 trips) with the distributor, the soil and acid mixed by means of the Seaman tiller; after full amount of acid added, the soil again thoroughly mixed.

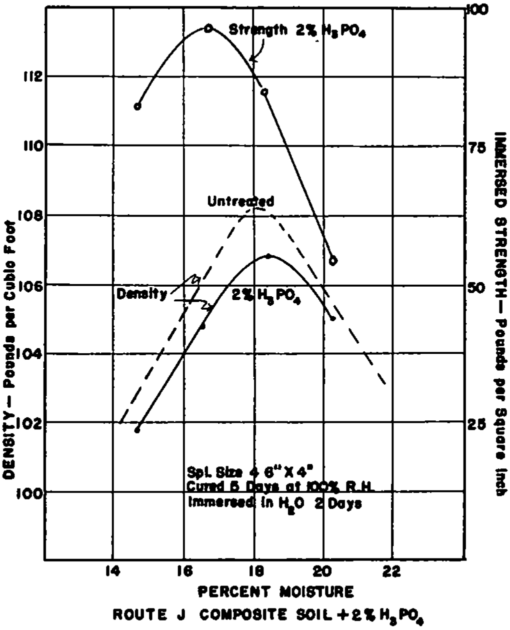


Figure 7. Moisture density, immersed strength moisture, relations for Route "J" composite soil.

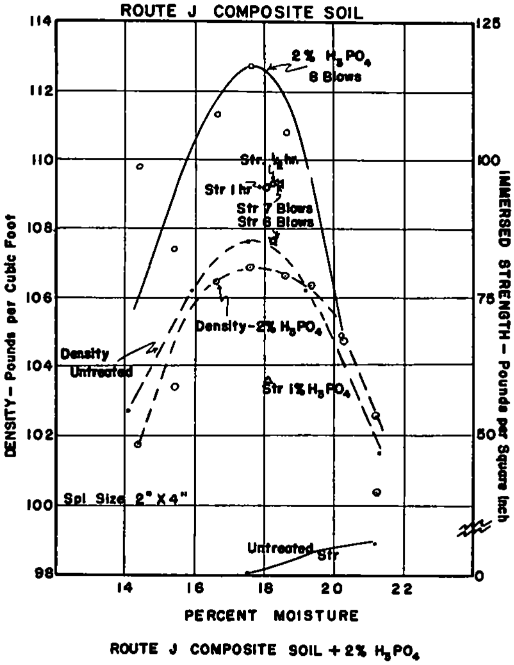


Figure 8. Moisture density, immersed strength moisture, relations for Route "J" composite soil also showing the effects of compactive effort.

TABLE 4

BORROW SOIL NATURAL DENSITY

	Sta. III + 50		Sta. IV + 50	
	Depth 1½ to 7½ In.	Depth 7½ to 13½ In.	Depth 1½ to 7½ In.	Depth 7½ to 13½ In.
Natural density	93.2	93.5	92.5	90.7
Natural moisture	25.9	22.9	24.9	25.4

4. The section shaped and smoothed with a motor patrol grader.
5. The section compacted with a sheepsfoot roller until it "walked out". (On this section, the roller "walked out" more quickly than desired because of the compacted tracks of the grader.)
6. The section shaped with the grader.
7. The section rolled with a smooth steel roller.
8. The section sealed with a tack coat of MC-3 cut back with 20 percent kerosene.
9. The section chipped with limestone chips.

This half-section was started at 12:53 p.m. and completed by 2:12 p.m.

It was felt that there had been too much lag between time of adding acid and start of compaction and that some of the soil acid system may have taken an initial set. Consequently, the second half of the section was constructed by the following procedure:

1. Thorough mixing of the soil.
2. Acid applied in 4 complete passes (8 trips) with the distributor.
3. Following two complete passes (4 trips), the soil and acid mixed with the Seaman tiller, thorough mixing following the final addition of the acid.
4. Compaction with sheepsfoot roller until the section "walked out".
5. The section shaped and smoothed with grader.
6 The section rolled with smooth steel roller.
7. The section sealed with tack coat of MC-3 cut back with 20 percent kerosene.
8. The section chipped.

This half-section was started at 3:12 p.m. and completed at 4:30 p.m.

Traffic was permitted on each section immediately after the chipping operation.

A list of the equipment and its use in this operation is as follows:

1. Motor Patrol Grader. Scarified and undergraded roadbed, stripped vegetation from borrow soil, transferred borrow soil to roadbed, and smoothed and shaped entire section.
2. Seaman Tiller. Aerated soil on roadbed to reduce moisture and mixed acid into soil.
3 Sheepsfoot Roller. Compacted the mixed soil and acid.
4. Smooth Steel Roller. Compacted and smoothed surface of section.
5. Flat bed truck with acid tank, spray bar, and acid supply. Distributed acid to soil.
6. Pressure Distributor. Distributed tack coat to stabilized surface.
7. Dump truck. Distributed chips to surface.

TABLE 5

PERCENT PHOSPHORIC ACID

	West Half Road	East Half Road
	2.64	2.99
	2.81	3.56
	2.19	3.54
	1.75	3.51
Average	2.35	3.40

Generally, the condition of the west (second) half of the road seemed to be better than that of the east. In the east half, the time between the start of the distribution of acid and the start of compaction was 49 min. Thus the west half seemed to have been compacted in the more nearly optimum time of 30 min and compaction seemed to have been more uniform in depth.

Both sides were found to contain appreciable quantities of limestone aggregate. The east side contained much more than the west and this served to kill the effects of the acid to some degree, for there was an immediate reaction. The inclusion of limestone was not anticipated. It apparently was picked up by the tiller from the subgrade. Possibly some stone was also picked up as the borrow soil was graded across the ditch and onto the road. On noting this reaction, a small amount of acid was added to the east section in the subsequent passes of the distributor in an effort to overcome this deficiency. The reaction of the acid with the limestone continued to be evidenced by the bubbling of the gas through the oiled surface. This reaction continued for approximately 24 hr.

Chemical tests of samples taken from each half of the road gave the phosphoric acid contents shown in Table 5. The tests are based on the amount of phosphorus in the total sample, but they do not truly indicate the amount of acid available for stabilization, for much of the H_3PO_4 had been neutralized by the limestone.

At the time of construction (October 2, 1958) Proctor needle penetration tests

TABLE 6

PROCTOR NEEDLE PENETRATION DATA [1]

		Proctor Needle Penetration			
		West Side		East Side	
Date Taken	Sample	2 Ft From Edge	2 Ft From Ctr. Line	2 Ft From Edge	2 Ft From Ctr. Line
Oct. 2, 1958[2]	1	20[3]	40[3]	32[3]	28[3]
	2	22	40	51	44
	3	16	35	43	42
	4	21	40	32	37
	5	25	30	54	31
	6	20	21	55	33
	7	12[4]	34[4]	30[4]	30[4]
	8	32	22	50	55
	9	12	20	64	78
	10	16	38	32[5]	38[5]
	12	20[5]	16[5]		
Avg.		19	30	44	42
Nov. 26, 1958	1	77[3]	-	-	115[3]
	2	94[4]	-	-	91[4]
	3	119	-	-	105
	4	110[5]	-	-	85[5]
Avg.		100	-	-	99
Feb. 9, 1959[6]	1	63[3]	-	-	53[3]
	2	68	-	-	-
	3	30[5]	-	-	-
Apr. 22, 1959	1	83[3]	-	-	54[3]
	2	80	-	-	46
	3	114[4]	-	-	56[4]
	4	103[5]	-	-	46[5]
Avg.		95	-	-	51
Oct. 14, 1960	1	118[3]	-	-	49[3]
	2	72[4]	-	-	43[4]
	3	85	-	-	42
	4	122[5]	-	-	91[5]
Avg.		99	-	-	66

[1] 0.1 sq in. end area.
[2] Before seal coat.
[3] Northend.
[4] 100 ft.
[5] Southend.
[6] Skinned spots.

(0.1-sq in. end area) were performed on the stabilized soil immediately after compaction and just before the application of the seal coat. These results are shown in Table 6. Another set of penetration readings was taken on November 26, 1958, after approximately two months of curing and service.

Spot checks on the project where the surface had been skinned off by a snow plow were taken on February 9, 1959. Tests were performed again on April 22, 1959, and October 14, 1960.

During February 1959 a snow plow in its normal operation removed some sections of the surfacing of the stabilized section, as well as the snow. This happened at many spots along Route J and was not confined to this section. For research purposes the skinned places on the test section were left exposed to the weather and traffic. The spots on the other portion of the roadway were sealed shortly thereafter, for some of them would have grown to rather large, deep holes if left unattended. The skinned places on the test section surprisingly did not develop in area and only rutted to a depth of approximately 1 in. These were resealed in the latter part of March after it became apparent that their progressive deterioration would be neither rapid nor severe.

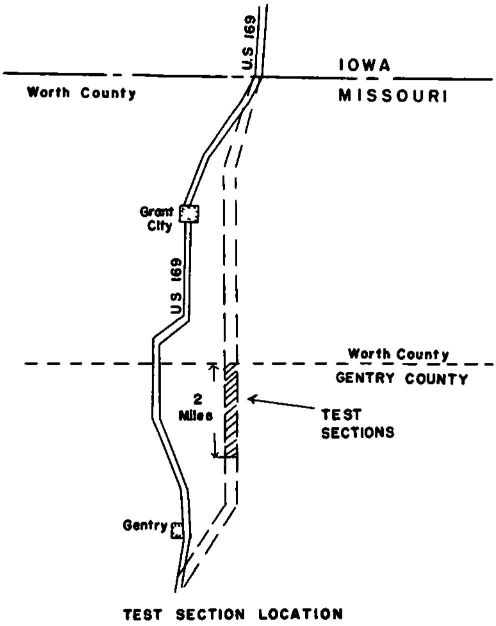


Figure 9. Proposed test section location Gentry County, Mo.

Although these penetration tests are not definite indications of bearing or stability, they are used here to show comparative changes in the apparent strength of the stabi-

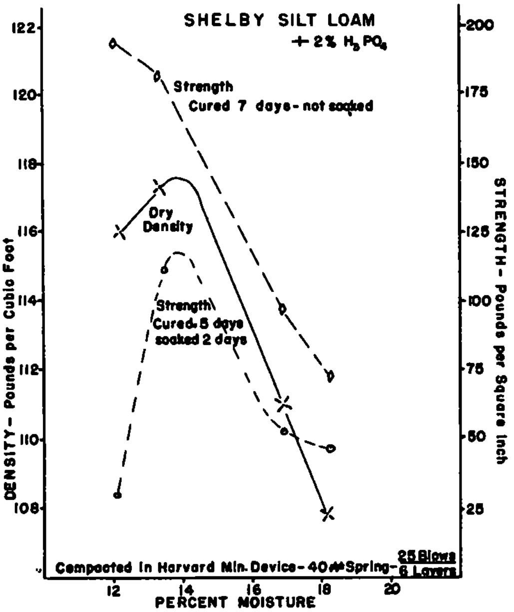


Figure 10. Effect of 2 percent H_3PO_4 on Shelby silt loam.

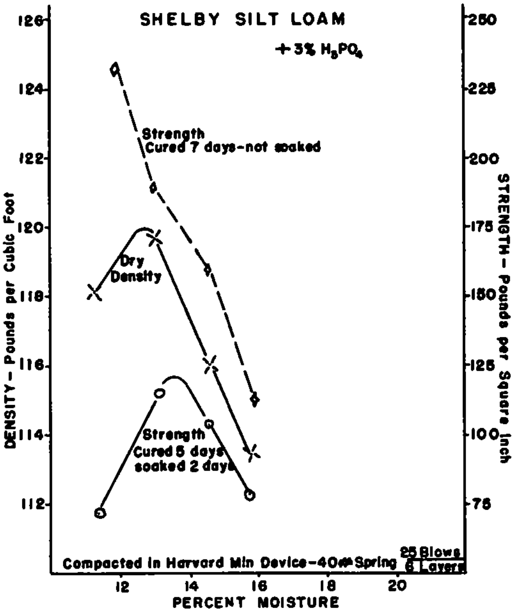


Figure 11. Effect of 3 percent H_3PO_4 on Shelby silt loam.

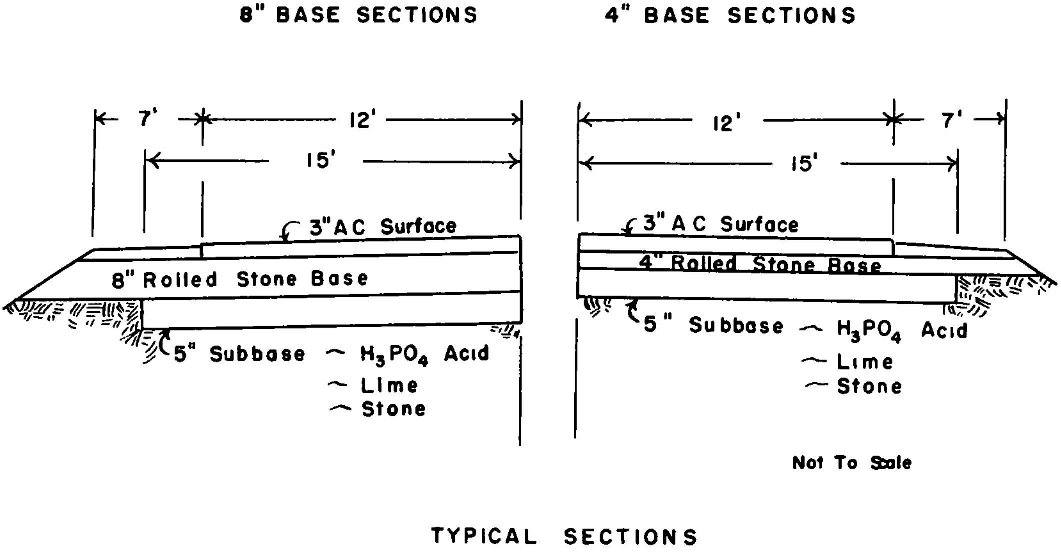


Figure 12. Typical cross-section for the proposed test in Gentry County, Mo.

lized section. The indication is that the west side had approximately the same strength in October 1960 as it did in November 1958 (1-month curing). The east side apparently has lost strength, though there is no visual difference in the performance of the sides.

Visual observation of the project indicates that the project has stood up as well as, if not better than, the adjacent roadway that was reconstructed and repaired at about the same time. At the time of construction, a soft spot in the subgrade on the east side of the stabilized section started to "show through". Concurrently, a soft spot in the subgrade of the reconstructed roadway just to the south of the project "showed through" also. In the time between October 1958 and April 1959, the soft spot to the south was repaired by the addition of stone and cold mix patching materials at least 6 times and the soft spot on the phosphoric acid-stabilized project had its first cold mix applied in April 1959. Although it is fully realized that any number of other factors besides the difference in treatment could be the decisive influence, it is still rather apparent that progressive deterioration was not active in the stabilized section but was so active in the adjacent section that it now includes practically the whole roadway width.

An unconfined compression sample was cut from each side of the road in September 1960. These undisturbed samples were approximately 10 in. square and 6 in. thick but, due to the large number of stones within, only one unconfined specimen (approximately 2 by 2 by 6 in. could be cut from each sample. The irregularity of each specimen makes the results approximate. The specimen representing the west side gave an unconfined strength of 150 psi and the specimen from the east side gave 90 psi.

A search was again instituted to find a location where a more complete study could be made. In this type of a study, one cannot just go out and pick the best location, but rather try to locate a place where a road that will suit this purpose (soil, traffic, etc.) might be built in the near future. Then one goes out (after the line is set) and takes samples to see if it really does suit, but still the problem is

TABLE 7

FACTORIAL BLOCK

Thickness of Base		8 In.	4 In.
Means of Subbase Stabilization	Lime	XX	XX
	Phosphoric Acid	XX	XX
	Rolled Stone	XX	XX
	No Subbase	XX	XX

TABLE 8

TEST SECTION LOCATIONS

Location No.	Station - Station		Base	Subbase
1	0 + 00	6 + 60	8 in. rolled stone	5 in. lime
2	6 + 60	13 + 20	"	5 in. H_3PO_4 acid
3	13 + 20	19 + 80	"	5 in. lime
4	19 + 80	26 + 40	"	5 in. rolled stone
5	26 + 40	33 + 00	"	None
6	33 + 00	39 + 60	"	5 in. H_3PO_4 acid
7	39 + 60	46 + 20	"	None
8	46 + 20	52 + 80	"	5 in. rolled stone
9	52 + 80	59 + 40	4 in. rolled stone	5 in. lime
10	59 + 40	66 + 00	"	5 in. rolled stone
11	66 + 00	72 + 60	"	5 in. lime
12	72 + 60	79 + 20	"	None
13	79 + 20	85 + 80	"	None
14	85 + 80	92 + 40	"	5 in. H_3PO_4 acid
15	92 + 40	99 + 00	"	5 in. H_3PO_4 acid
16	99 + 00	105 + 60	"	5 in. rolled stone

not so simple. It is undesirable to sample and test all possible locations of projects without having some idea that the project can be constructed, so it really becomes a matter of looking for a project in the area where the soil might be suitable.

At any rate, the only project coming up in the near future that seemed to bear promise for utilization as a test road was one located in District 1, Route 169, shown in Figure 9.

A few laboratory tests were run on a sample of soil from the general vicinity of the proposed line. Figures 10 and 11 show the density and strength relations for the addition of 2 and 3 percent H_3PO_4. These tests indicated that a satisfactory stabilization could probably be obtained, so it was proposed that a test section be included as part of the project.

The project was planned to be built on Route 169 in Gentry County, Project F-524(2). Group index of typical Shelby soil is 16 and the estimated 20-year commercial traffic is 135 per day. The project design calls for 3-in. asphaltic concrete surface on 8 in. rolled stone base on 5-in. lime-stabilized soil subbase.

It was proposed that test sections be constructed to obtain an evaluation of the efficiency of phosphoric acid as a soil stabilizer. In this case, it was intended that the acid-stabilized soil be used as a replacement for the lime-stabilized soil. It was also considered desirable to construct sections using rolled stone as the entire base course to establish a comparison with the standard design chart and also to construct sections with no subbase to assess the effects of the base alone. Sections of lesser total thickness were recommended to provide further data for assessment of strength equivalents.

It was thus proposed that two factors of design be studied: (a) the thickness of base, to contain two levels (8 in. of rolled stone base and 4 in. of rolled stone base), and (b) the means of stabilization of the subbase, to contain four levels (5 in. of lime-stabilized soil, 5 in. of phosphoric acid-stabilized soil, 5 in. of rolled stone base material, and no subbase). Typical design cross-sections are shown in Figure 12.

This suggestion would provide the factorial block shown in Table 7 with the X's indicating the replicated factorial sections.

It is further suggested that all sections be 660 ft long. This will provide ½ mi of each level of subbase treatment. This factorial block should allow an assessment of comparative values with reasonable means of evaluating the construction error. This proposal was accepted and the test sections were designated to begin at the Worth County line and extend south into Gentry County for 2 mi.

For practical construction procedure, all of the 8-in. rolled stone base sections were to be in the first 8 sections, and all of the 4-in. rolled stone base sections were to be in the last 8 sections. Otherwise the sections, listed in Table 8, were located by random selection.

Tentative letting date for this project is in the early part of 1961 so that construction of the test sections should be in late 1961 or early 1962. Plans are being made for as complete a coverage of field testing and control as feasible and in this regard any suggestions as to nondestructive performance testing of the finished product will be welcome. Use of the Benkelman beam, rut depth gauge, roughometer is planned to supplement the visual condition surveys.

CONCLUSION

The preliminary tests of the use of phosphoric acid as a stabilizing agent for heavy clay soils show promise of obtaining an adequate stabilizing effect if basic soils or inclusions of lime are avoided.

ACKNOWLEDGMENTS

The author wishes to acknowledge the continued assistance of Charles E. Thomas in performing much of the testing, and of John W. Lyons for his cooperation and many valuable suggestions. To F.B. Reagel, W.C. Davis, and the many others who contributed suggestions and guidance, much thanks is also due.

REFERENCE

1. Lyons, J.W., "Soil Stabilization Data Summary, Missouri Putnam Silt Loam." Monsanto Chemical Company.

Frost Stabilization of Several Soils with Sodiumtripolyphosphate and Sodiumpyrophosphate*

K. BELTZ and G. MÜLLER-SCHIEDMAYER, Research Laboratory of Knapsack-Griesheim A.G. Western Germany

The behavior of three German soils of different origin and composition without and with addition of polyphosphates was investigated in the freezing cabinet. Determination was made of the frost heave and water intake during a freezing period of 4 days. Two of the soils, considered as strongly frost sensitive in accordance with the criterion of A. Casagrande, also showed large frost heave and water intake in the freezing cabinet. Addition of small amounts of polyphosphates sufficiently surpressed the frost heave and water intake during the freezing period so that the water content after the freezing period did not exceed the optimum moisture content at the standard proctor density. The frost stability remained after the polyphosphates had been washed out of the soil.

The dispersing effect of the polyphosphates increased the degree of soil densification achieved, the dry densities obtained being a function of the concentration of the polyphosphates. The connection between frost stabilization and densification is pointed out.

● WITHIN RECENT years, increasingly important new methods based on soil stabilization with chemicals have appeared in road construction. The purpose of such chemical treatment is to render the natural soil in place serviceable for road construction purposes through improvement of its mechanical properties and decrease of its frost sensitivity by means of small amounts of chemical admixtures. Although a considerable amount of research work has already been performed in the United States on chemical soil stabilization, the German effort along this line has been relatively limited. In practice, the desired soil improvement is usually obtained by improving the granulometry of the soil in place or by replacing the unsuitable soil with a layer of gravel, crushed stone, or blast furnace slag. This replacement, though expensive and time-consuming, is still the best practical method of protecting roads against frost action if they are built over frost-sensitive soils. Especially stimulated, by the extensive American investigations and experience which have been reported in a number of publications, German scientists have a growing interest in chemical soil stabilization with the hope that more economical and less time-consuming methods may be developed by such means, particularly in view of the increasing activity in road construction.

The investigations, which started at the beginning of 1959, are mainly concerned with the prevention of frost damage by means of chemical admixtures to frost-susceptible soil materials. Publications by Lambe (1, 2) indicated the effectiveness against frost action of chemicals, especially polyphosphates, that have a dispersing effect on soils. The polyphosphates fulfill a number of requirements that are important for a large-scale use in road construction. These include (a) low cost, which is a precondition for widespread economical application; (b) effectiveness at small concentrations; (c) long-lasting protection against frost action; (d) effectiveness over a wide range of soil composition; and (e) easy and quick incorporation into the soil to be treated.

There exists, on the other hand, a great variability among different soils as to the degree of frost protection imparted by treatment with polyphosphates. As yet this can-

---

*Translated by Hans F. Winterkorn, Princeton University.

not be predicted by simple means. Hence, extensive investigations on many different soils must be made before large-scale use of polyphosphates for frost protection can become a reality.

EXPERIMENTATION

Materials

Soils. —The three soils tested are from different parts of western Germany: a loamy soil from Bavaria (I), a silty sand from Franconia (II), and a sandy soil from the vicinity of Cologne (III). The respective soil characteristics are given in Table 1 and the size compositions in Figure 1. All soils were used in their natural state, but due to the admixture of the chemicals they could not be tested in the undisturbed condition. The Casagrande criterion indicated a great frost sensitivity for soils I and II, inasmuch as they were of nonuniform character with a < 0.02 mm content over 3 percent. For the nearly uniformly sized sand III with its very small content in < 0.02 mm material, no marked frost susceptibility was to be expected. The test results confirmed these expectations, with soils I and II showing great susceptibility to frost heave. These soils contained only a few free calcium ions; hence, no interference with the effectiveness of the phosphates was to be expected on their account.

Admixtures. —Sodiumtripolyphosphate and sodiumpyrophosphate of 98 percent purity (remainder being other condensed phosphates) based on thermic phosphoric acid were used. These products correspond to C.P. quality. The finely pulverized chemicals were spread on the soil samples and mixed in by hand. In some cases when water addition was necessary, as in the determination of the maximum Proctor density, the polyphosphates were first dissolved in the mixing water. No difference was observed in the tests made on samples produced by either method. The natural soil moisture combined with the saturation period in the frost cabinet appeared to be sufficient to ensure solution and distribution throughout the specimens of the phosphates added in powder form. The concentration of the admixtures is given as a percentage of the moist weight of the soils.

Freezing Cabinet Test

Frost heave can occur only if three conditions are fulfilled:

TABLE 1

PROPERTIES OF THE INVESTIGATED SOILS[1]

Properties	Soils		
	Loam I	Silty Sand II	Sand III
Size composition (% by wt):			
Gravel > 2 mm	-	8.0	14.0
Sand 2 mm - 0.06 mm	41.0	23.0	79.0
Silt 0.06 - 0.002 mm	54.0	9.0	6.0
Clay < 0.002 mm	5.0	-	1.0
Nonuniformity	10	7	5
Physical properties:			
Simple Proctor density (tons/m^3)	1.82	1.85	1.93
Optimum moisture (%)	18.9	9.6	10.5
Specific gravity	2.64	2.503	2.54
Chemical properties:			
Organic matter (%)	0.8	0.1	0.1
Natural water content (%)	12.2	5.5	6.2
pH	7.1	6.7	6.7

[1] Compaction work=60,000 kgm/M^3 (3 layers).

1. A frost susceptible soil whose capillary spaces do not oppose too much resistance to the upward movement of water;
2. The presence of a reservoir from which water can be supplied for upward movement; and
3. Frost penetration from the surface down and sufficient duration of freezing conditions; it must be kept in mind that the freezing temperature in soils, especially in the case of admixtures, may be below 0C.

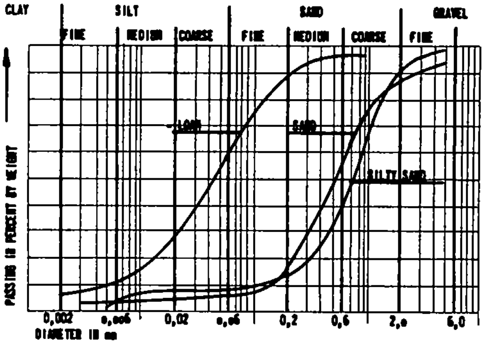


Figure 1. Drain size distribution.

Already because of the normal expansion of water on freezing, by about 10 percent of its volume, moist soils may show a small volume increase on through-freezing without heaving. This volume increase was not observable in the case of these experiments (in which the samples could also freely expand in the lateral direction) and, therefore, did not affect the results of the tests. The particular mechanism of frost heave is, of course, the formation of ice lenses. These result from the solidification at the freezing front of water that is conducted there by capillary action from the water supply below. Because all water that is conducted to the freezing front freezes, the soil can by ice lens formation take in much more water than corresponds to its maximum saturation capacity. The volume increase connected with ice lens formation is much larger than that which would occur if only the normal saturation water would be frozen. When thawing takes place from the surface down, then the melt water cannot drain away through the underlying, still frozen soil and the thawed soil loses its mechanical stability because of its excessive water content.

Because the formation of ice lenses depends on the rate of upward water movement, the rate of penetration of the frost zone plays an important role. Slow penetration results in the formation of thick ice lenses and bands. If the rate of frost penetration exceeds that of water supply, then no ice lenses are formed and no frost heave is noticed even in highly frost susceptible soils.

In comparative investigations of frost heave produced in frost cabinets, the rate of frost penetration should be kept constant. Taking account of the temperature gradient in the specimen and its thermometric conductivity, the surface temperature was regulated so that the rate of frost penetration per day was about 6.5 cm. This value was approximately kept in the case of all comparative investigations. At the completion of each test, the frost penetration into the sample was determined. This eliminated the possibility that frost stabilization could be ascribed solely to a depression of the freezing point of the pore water by the admixtures. All samples investigated had been frozen to a constant depth. No great difference was found in the penetration of the freezing front for the different soils and different treatments.

The required freezing conditions were created in a frost cabinet described by A. Bley (3) as suitable for the direct determination of the frost sensitivity of soils. Similar types of freezing tests and apparatus have also been developed by the Arctic Construction and Frost Effects Laboratory (ACFEL) (4, 5, 6, 7). A description of the experimental procedure is restricted to the following statements. To eliminate as much as possible disturbing influences that may be due to structural variations, relatively large samples (diameter = 8 cm; height = 30 cm) were used. As one of the factors that influence the soil condition, the compaction work required in the molding of the cylindrical test specimens was standardized. To permit comparison with the later determined Proctor curves, the compaction work was standardized at 60,000 mkg per cu m, which corresponds to that employed in the standard Proctor compaction. Before the start of the refrigeration, the densified soil cylinders were saturated for 20 hr by lifting a connected water supply vessel to be level with the top of the cylinders. Excess water thus supplied drained off after lowering of the supply vessel. Each freezing test was conducted for a period of 4 days. Determinations were made of the amount of saturation water, water intake during freezing, and frost heave.

RESULTS

Freezing Experiments Without Admixtures

The tests with natural untreated soils gave the absolute values for frost heave and water intake during the freezing period and indicated the accuracy and the comparative value of this type of test. Table 2 gives the average data obtained in series of 4 tests each. Figure 2 shows the heave of the samples and their water intake as a function of time. The frost heave as well as the water intake are approximately linear functions of time. Small variations that were not caused by temperature variations may be considered as due to small differences in sample composition and structure.

TABLE 2

FROST EFFECT ON THE UNTREATED NATURAL SOILS

Changes During Freezing	Soils		
	Loam I	Silty Sand II	Sand III
Av. daily frost heave during 4-day period (mm)	11, 11, 12, 10	5, 10, 11, 10	2, 3, 2
Total heave (mm)	44	36	7
Saturation water, 20-hr intake (ml)	170	200	100
Av. daily water intake during freezing period (ml)	70, 85, 85, 62	60, 80, 65, 70	40, 15, 15, 10
Tot. water intake (ml)	302	275	80
Soil moisture after thawing (%)	26.2	19.1	11.6
Water content of natural soils (%)	12.2	5.5	6.0

As expected, soils I and II were found to be strongly frost susceptible. The water content after thawing was considerably above the optimum moistur content. Soil III with its good granulometry behaved quite differently and showed very little frost effect. As Table 2 and Figure 2 show, the standardization and uniformity of all test variables resulted in good reproductibility of the results. The experimental errors were within the following limits: absolute amount of frost heave ± 5 percent; saturation water ± 3 percent; freezing water ± 10 percent; and frost penetration ± 5 percent. These results show that the method employed is suitable for a comparative investigation of the frost susceptibility of natural soils without and with protective admixtures. The frost-protective effects of admixtures were found to lie far outside the determined limits of error.

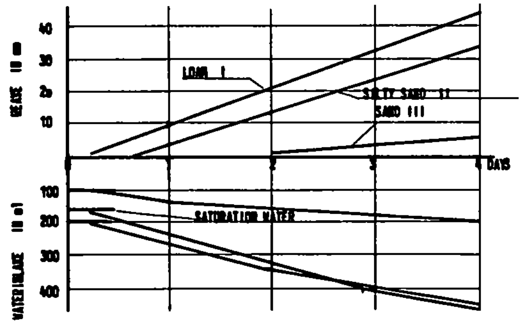


Figure 2. Relation between heave and water intake.

Frost Stabilization by Polyphosphates

The soil samples treated with the polyphosphates were tested in the same manner as described. Although the samples with the admixed polyphosphates were not given a special aging period, one might consider

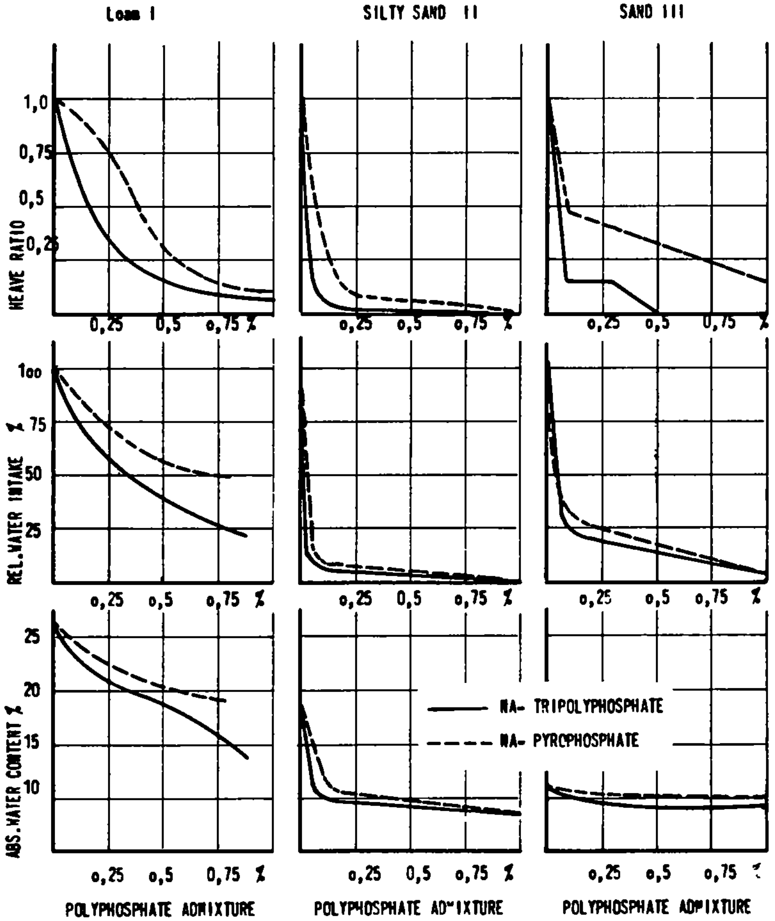


Figure 3. Frost heave water intake and final soil moisture as functions of phosphate additions.

the 20-hr saturation period as such. The ratio of the frost heaves observed in the treated and untreated samples, respectively,

$$HV = \frac{\text{Frost heave with admixture}}{\text{Frost heave without admixture}},$$

as well as the relative water intake during the freezing period as compared to that of the untreated soil were considered as criteria of the frost-stabilizing effectiveness of sodiumtripolyphosphate and sodiumpyrophosphate. The sum of the original water content, saturation water, and water intake during freezing gives the total soil-water after thawing. The amounts of frost heave and water intake vary as functions of the added amounts of polyphosphates. Figure 3 shows the relative frost heave and water intake as functions of the weight percentages of polyphosphate. The resulting total soil moisture after thawing contains the saturation water, which also is reduced due to the effect of the admixtures. Inasmuch as the relative values are of primary interest, the absolute data have not been shown. The latter, however, may be easily calculated from the data in Table 2. The experimental data bring out the following facts:

1. Despite the great difference in origin and size composition of the three soils tested, addition of polyphosphates resulted in stabilization against frost action in all three cases. The effectiveness of sodiumtripolyphosphate is somewhat greater than

that of sodiumpyrophosphate, especially for the very frost-susceptible fine-grained soil I.

2. Frost heave can be prevented almost completely by addition of polyphosphates. The curves for the relative frost heaves in case of soil III are somewhat deceptive because of the very small absolute values involved. Despite the high HV-values, the absolute heaves in this case are very small and almost within the limits of error. A polyphosphate admixture of less than 0.5 percent by weight, which is within economic limits, reduces frost heave by at least 85 percent. Admixtures above 0.5 percent do not give proportionate increases in effectiveness.

The water intake during the freezing period shows the same dependence on phosphate admixture as does the relative frost heave. This is in accordance with the indicated mechanism of frost heave as a result of ice lens formation. The relative water intake can be reduced by more than 75 percent. In this connection, it is of interest that the water permeability of soils is greatly reduced by phosphate admixtures. This effect persists even after washing out of the polyphosphate.

3. The total water content after thawing of frost-stabilized soils does not exceed the value of the optimum moisture content at standard Proctor density. The observed increase in moisture content is due mainly to the sorbed saturation water. The test specimens had been molded at the natural water contents of the soils. Greater densification would have required a higher water content. This, however, would not have changed the total water content after thawing.

If one considers the use of chemicals in road construction, one wants to know first of all how fast these will be washed out of the soil and to what extent the effect of frost stabilization is thereby lost. Because of the normal water movements in soils, such washing out must be considered in the case of all chemicals. In an investigation that has not yet been completed, but deserves mentioning at this place, the frost-stabilizing effect has been found to persist in the tested soils despite washing out of the polyphosphate under extreme conditions. This effect, which probably is due to the dispersing action of the polyphosphates, permits a permanent frost stabilization with their use.

Soil Densification with the Help of Polyphosphates

The chemical-physical phenomena in soils are so complicated that until today there has been no complete and generally accepted clarification of the water transport to the location of ice lens formation and its modification by means of added chemicals. Such soil properties as grain size distribution, pore volumes, water permeability and soil-water interfacial characteristics play important roles.

Polyphosphates have a dispersing effect on soil particles which permits the achievement of a higher degree of order in particle arrangement with resulting decrease in pore volume; i.e. greater density at equal moisture content and compactive effort. The reduction in pore size is one of the determinant factors with respect to capillary water transport in soils. Thus, a connection exists between densification and frost stabilization.

The effect of polyphosphate addition on densification was investigated by means of Proctor compaction curves. The results of the frost stabilization and densification experiments are directly comparable, because the same amount of densification work in kgm per cu m were employed in the molding of the samples. Figure 4 shows the standard Proctor densities of the silty sand II and the uniform sand III as functions of water content at different polyphosphate contents. Because of insufficient supply of soil I, no tests on these relationships could as yet be run. The Proctor curves are easily reproduced if fresh material is used for each tamping; otherwise, marked deviations occur despite efforts toward loosening of the soil. The standardized amount of compaction work was 60,000 kgm per cu m and the soil was compacted in three layers. The frost-susceptible soil II showed a change in maximum dry density from 1.852 to 1.90 tons per cu m at a polyphosphate admixture of 1 percent by weight. This corresponds to an improvement by about 2.5 percent of the maximum Proctor density. As was to be expected from its grain size, composition, and small frost susceptibility, soil III did not show any increase in maximum Proctor density on polyphosphate addition;

sodiumtripolyphosphate and sodiumpyrophosphate are equally effective, aside from small differences. With the increase in dry density, go changes in optimum moisture content. The increase in optimum moisture content in the case of larger amounts of the polyphosphates probably is the result of an additional water-binding influence of the polyphosphates which, however, is noticeable only at higher polyphosphate concentrations. Because the investigated soils possessed only a small optimum moisture content for maximum Proctor density, the decrease in optimum moisture on addition of the polyphosphates was small.

In connection with frost stabilization, densification at natural moisture contents at which the specimens for the freezing experiment were molded was of particular interest. The respective curves show that at water contents from 5.5 to 6 percent phosphate addition resulted in increased densities. Although the increases in dry density in these cases are small in comparison with the maximum values, they appear to be sufficient for frost stabilization. In the case of frost-sensitive soils, it cannot be predicted to what extent the pore space must be changed so that the absorbed water hulls of the soil

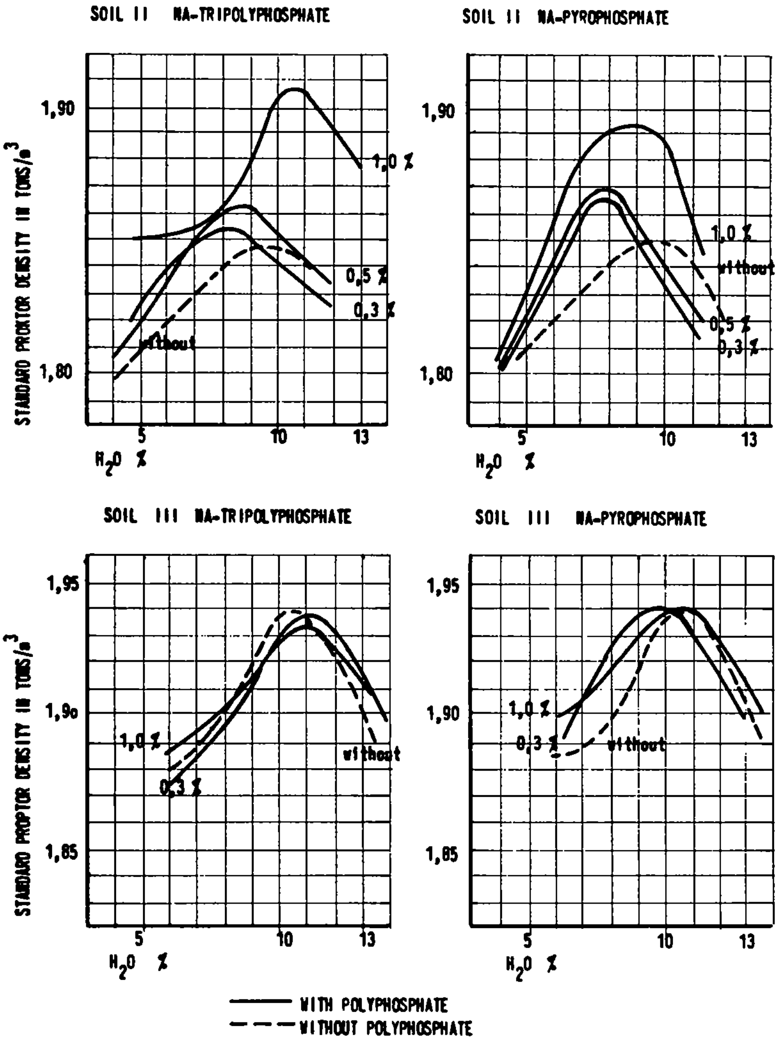


Figure 4. Proctor curves as influenced by admixtures of NA-tripolyphosphate and NA-pyrophosphate.

particles may impede the capillary upward transport of free water. Another problem concerns to what extent the surfaces of the soil particles themselves are changed by admixtures that possess dispersive action.

SUMMARY

Several soils were tested in the laboratory for frost sensitivity in a freezing cabinet and the possibility of their stabilization against frost action by means of polyphosphates was investigated. Polyphosphate admixtures in amounts that can be justified economically resulted in good stabilization; i.e. prevention of frost heave and reduction of water intake during the freezing period. Connected with stabilization against frost action is an increase in dry density. Although it can be expected that the polyphosphates are similarly effective for all frost-susceptible soils, the investigations must be extended over a larger number of soils because of the wide range in composition and properties of soils found in nature. It is felt that the safest way to extensive field tests on frost susceptibility and stabilization is one that starts with a thorough laboratory study of representative samples.

REFERENCES

1. Lambe, T.W., "Modification of Frost-Heaving of Soils with Additives." HRB Bull. 135, 1-23 (1956).
2. Lambe, T.W., "Inprovement of Soil Properties with Dispersants." J. Boston Soc. Civil. Engrs., 41:No. 2, 184-207 (1954).
3. Bley, A., Strasse und Undergrund II, 37:21 (1958).
4. Arctic Construction and Frost Effects Laboratory (ACFEL), "Interim Report of Cold-Room Studies (1949-50)." New England Division, US Army Corps of Engineers, Boston (July 1950).
5. ACFEL, "Cold-Room Studies, Second Interim Report of Investigations (FY 1950-51)." 2 Vols., New England Division, US Army Corps of Engineers, Boston (June 1951).
6. ACFEL, "Cold-Room Studies, Third Interim Report (FY 1952-53)." 2 Vols., New England Division, US Army Corps of Engineers, Boston (1953).
7. Haley, J.F., "Cold-Room Studies of Frost Action in Soils, A Progress Report." HRB Bull. 71, 1-18 (1953).

HRB:OR-502

THE NATIONAL ACADEMY OF SCIENCES—NATIONAL RESEARCH COUNCIL is a private, nonprofit organization of scientists, dedicated to the furtherance of science and to its use for the general welfare. The ACADEMY itself was established in 1863 under a congressional charter signed by President Lincoln. Empowered to provide for all activities appropriate to academies of science, it was also required by its charter to act as an adviser to the federal government in scientific matters. This provision accounts for the close ties that have always existed between the ACADEMY and the government, although the ACADEMY is not a governmental agency.

The NATIONAL RESEARCH COUNCIL was established by the ACADEMY in 1916, at the request of President Wilson, to enable scientists generally to associate their efforts with those of the limited membership of the ACADEMY in service to the nation, to society, and to science at home and abroad. Members of the NATIONAL RESEARCH COUNCIL receive their appointments from the president of the ACADEMY. They include representatives nominated by the major scientific and technical societies, representatives of the federal government, and a number of members at large. In addition, several thousand scientists and engineers take part in the activities of the research council through membership on its various boards and committees.

Receiving funds from both public and private sources, by contribution, grant, or contract, the ACADEMY and its RESEARCH COUNCIL thus work to stimulate research and its applications, to survey the broad possibilities of science, to promote effective utilization of the scientific and technical resources of the country, to serve the government, and to further the general interests of science.

The HIGHWAY RESEARCH BOARD was organized November 11, 1920, as an agency of the Division of Engineering and Industrial Research, one of the eight functional divisions of the NATIONAL RESEARCH COUNCIL. The BOARD is a cooperative organization of the highway technologists of America operating under the auspices of the ACADEMY–COUNCIL and with the support of the several highway departments, the Bureau of Public Roads, and many other organizations interested in the development of highway transportation. The purposes of the BOARD are to encourage research and to provide a national clearinghouse and correlation service for research activities and information on highway administration and technology.