

# Phosphoric Acid Stabilization of Fine-Grained Soils: Improvements with Secondary Additives

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Several techniques for improving, or reducing the cost, of phosphoric acid stabilization of a clayey silt and a heavy clay have been examined.

With the clayey silt, treatment with mixtures of calcium phosphate, or pulverized Florida phosphate rock, and sulfuric acid yields humid cure strengths greater than with the equivalent amount of phosphoric acid, but lower immersed strengths. Using phosphate rock, however, the reduction in cost of stabilization is so great that higher concentrations of this mixture can be used to produce satisfactory stabilization at a cost competitive with conventional stabilizers.

Granular, orthorhombic phosphorus pentoxide can be used to stabilize clayey silt as effectively as phosphoric acid or ordinary  $P_2O_5$ , and with potentially greater field-convenience. Trace amounts (0.1 percent on soil) of this compound function as an excellent soil-dispersant, and when used in conjunction with phosphoric acid or phosphate rock-sulfuric mixtures, greatly increase compacted density and strength.

Ferric chloride, at 1.6 percent on soil, is as effective a water-proofer for phosphoric-acid-stabilized heavy clay as 0.5 percent octylamine. Although this substitution brings about a substantial reduction in stabilization cost, the materials costs for very heavy clay stabilization are still too high to be attractive for all but emergency situations. Development of an inexpensive, highly effective waterproofer may broaden the usefulness of phosphoric acid in such soils.

● **USE OF PHOSPHORIC acid** for stabilization of fine-grained soils has become a subject of growing interest in recent years; this interest stems from the experimental observations that (a) phosphoric acid exhibits impressive stabilizing ability in a wide variety of aluminosilicate soils, (b) acid requirements for effective stabilization are low, and (c) strength development in phosphoric acid-treated soils occurs rapidly under humid conditions (1, 3, 4). These characteristics of phosphoric acid make it potentially competitive with conventional soil stabilizers, such as portland cement, asphalt, and lime.

Despite its effectiveness and breadth of utility as a stabilizer, phosphoric acid suffers several limitations which have deterred its field evaluation. The most important of these are:

1. The cost of phosphoric acid stabilization of moderately fine-grained soils is considerably higher than that of conventional stabilization methods. Although the acid is uniquely effective in heavy clays (relative to conventional stabilizers), the cost of amine waterproofer required for this purpose is far too high to make the method attractive except in special situations.

2. Phosphoric acid stabilization (as is true with most other stabilization methods) is quite sensitive to initial soil moisture content, and to the degree of soil compaction prior to cure.

3. Phosphoric acid, in concentrated form, presents problems in the field regarding transportation and handling with conventional soil-processing equipment. A safe, granular solid product would be more attractive from this standpoint.

The object of this investigation has been to explore a number of possible solutions to the aforementioned problems. These include studies of (a) the use of calcium phosphate-sulfuric acid mixtures as alternatives to phosphoric acid, (b) the use of granular orthorhombic phosphoric anhydride as an acid substitute, and (c) the use of polyvalent metal salts as substitutes for amines for the waterproofing of acid-stabilized heavy clay

## 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 ( $PI=32$ ). The physical properties and mineralogical compositions of these soils have been previously published (3).

Chemicals used in this work were as follows:

Phosphoric acid (86.1%  $H_3PO_4$ ) — Reagent grade

Orthorhombic phosphoric anhydride ( $P_2O_5$ ) — Victor Chemical Works

Sulfuric acid (98%  $H_2SO_4$ ) — Reagent grade

Tricalcium phosphate ( $Ca_3(PO_4)_2$ ) — Reagent grade

Calcium monohydrogen phosphate ( $CaHPO_4$ ) — Reagent grade

Calcium dihydrogen phosphate ( $Ca(H_2PO_4)_2$ ) — Reagent grade

Sodium fluosilicate ( $Na_2SiF_6$ ) — Reagent grade

Ferric chloride ( $FeCl_3 \cdot 6H_2O$ ) — Reagent grade

Aluminum chloride ( $AlCl_3 \cdot 6H_2O$ ) — Reagent grade

Magnesium chloride ( $MgCl_2 \cdot 6H_2O$ ) — Reagent grade

Chromic chloride ( $CrCl_3 \cdot 6H_2O$ ) — Reagent grade

Pulverized Florida phosphate rock — supplied by International Minerals and Chemicals Co., analyzing 29.6%  $CaO$ , 32.27%  $P_2O_5$ , and 2.72 - 4.08%  $F$ ; 93% finer than 60 mesh, 63% finer than 200 mesh (5).

The preparation and testing of samples were similar to those used in previous studies (3, 4). Liquids content at molding was usually maintained at 12.5 cc total liquids volume per 100 gm dry soil for MCS, and 17.0 cc per 100 gm soil for VBC; maximum compacted density was achieved under these conditions. Methods of additive incorporation depended on the type of additive, and in some cases variations in procedure were studied; therefore the method of addition will be specified in the discussion. In general, chemicals were added to the soil and blended for several minutes in a finger prong mixer. 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 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

### Stabilization of Massachusetts Clayey Silt with Phosphate-Sulfuric Acid Admixtures

**Calcium Phosphate-Sulfuric Acid Stabilization.** — Because calcium phosphates react with aqueous sulfuric acid (in sufficiently high concentration) to form phosphoric acid and hydrated calcium sulfate, it was believed that if this reaction would proceed in the presence of soils, successful stabilization would result. To explore this possibility, moist Massachusetts clayey silt was blended with the various calcium phosphates, then mixed with a stoichiometric quantity of concentrated sulfuric acid, compacted, and cured.

Table 1 gives the compressive strengths obtained with MCS treated with each of the

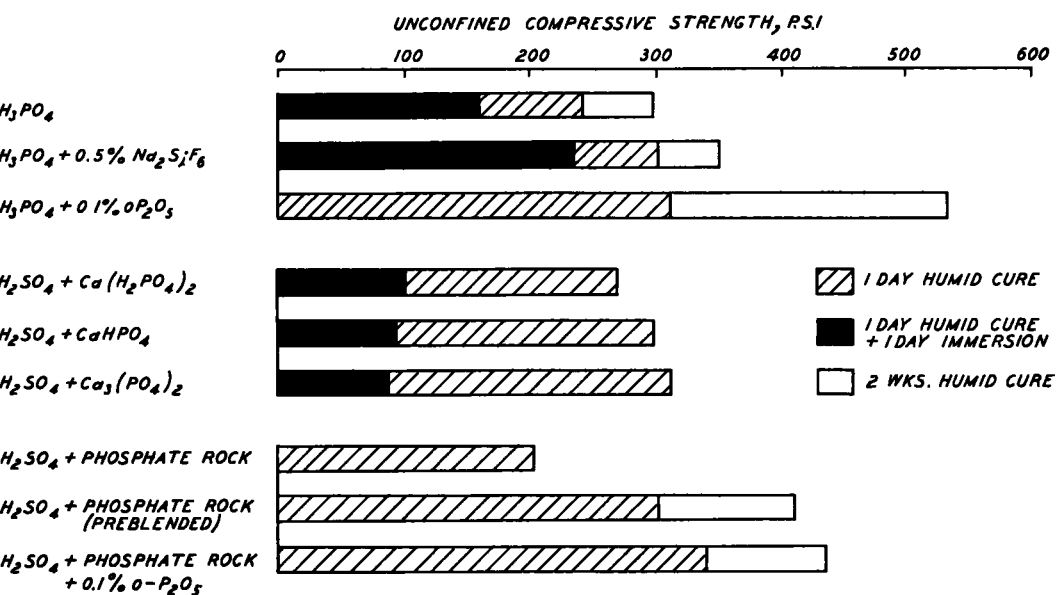


Figure 1. Comparison of various phosphorus-based stabilizing systems (equivalent to 2 percent by weight  $H_3PO_4$ ) on properties of Massachusetts clayey silt.

three calcium phosphates and sulfuric acid at various volatiles contents after 1- and 7-day humid cure, and after 1-day humid cure followed by 1-day immersion. For comparison, results with phosphoric acid are also included.

At equal densities, the samples prepared with calcium phosphates have considerably higher 7-day humid cure strengths than samples with  $H_3PO_4$ , but immersed strengths after 1-day humid cure are significantly lower. There is a significant downward trend in compressive strength as the ratio of calcium to phosphate in the salts is increased, even though the phosphate content was held constant.

Because the sulfuric acid will, in part at least, be consumed by reaction with alumina in the soil, the observed trends are perhaps to be expected: the more basic calcium phosphates are less soluble and more refractory to acid attack, and therefore are more slowly converted to phosphoric acid. Considering the competition between soil

TABLE 1  
STABILIZATION OF MCS WITH MIXTURES OF CALCIUM PHOSPHATES AND SULFURIC ACID  
EQUIVALENT TO 2 %  $H_3PO_4$

%	Phosphate	100 % $H_2SO_4$ %	Humid Cure				24-Hr Humid Cure & 24-Hr Immersion		
			Compressive Strength (psi)		Dry Solids Density at Test (pcf)	% Volatiles at Test	Comp. Strength (psi)	Dry Solids Density at Test (pcf)	% Volatiles at Test
			24 Hr	7 Days					
2	$H_3PO_4$	—	242 ± 9	300	131.0	11.0	160 ± 8	131.0	11.4
2	$H_3PO_4$	—	184 ± 9	271 ± 15	128.4	11.3	—	—	—
2.07	$Ca(H_2PO_4)_2$	0.85	270 ± 20	410 ± 110	131.3 ± 0.6	10.1 ± 0.1	100 ± 0	129.5 ± 0.7	11.1 ± 0.1
2.07	$Ca(H_2PO_4)_2$	0.85	263 ± 22	—	131.3 ± 0.2	10.0 ± 0.1	77 ± 13	129.5 ± 0.1	11.9 ± 0.2
2.36	$CaHPO_4$	1.70	300 ± 10	375 ± 45	129.5 ± 0.3	10.6 ± 0.1	95 ± 10	127.2 ± 0.7	12.6 ± 0.1
2.72	$Ca_3(PO_4)_2$	2.58	248 ± 28	—	124.3 ± 0.4	8.9 ± 0.2	—	—	—
2.72	$Ca_3(PO_4)_2$	2.58	235 ± 15	333 ± 47	125.8 ± 1.2	9.7 ± 0.2	—	—	—
2.72	$Ca_3(PO_4)_2$	2.58	313 ± 3	—	127.3 ± 0.3	10.5 ± 0.1	87 ± 8	124.9 ± 0.1	12.8 ± 0.0
2.72	$Ca_3(PO_4)_2$	2.58	257 ± 23	—	126.9 ± 0.7	10.7 ± 0.3	—	—	—
2.72	$Ca_3(PO_4)_2$	2.58	287 ± 8	—	128.1 ± 0.1	11.5 ± 0.2	—	—	—

Note: All percentages are based on dry soil weight.

and phosphate for sulfuric acid, it is remarkable that these mixtures exhibit such pronounced stabilizing action. The observation that the immersed strengths of samples treated with phosphate-sulfuric acid mixtures are considerably lower than those obtained with phosphoric acid appears to support the belief that less than the stoichiometric quantity of acid is generated in the process.

Another factor which is undoubtedly of importance is precipitation in the soil of the slightly soluble calcium sulfate formed in the reactions. The small amounts of precipitate formed in the dihydrogen phosphate appear to increase solids density and humid cure strength. Larger quantities of sulfate, such as with tri-calcium phosphate, appear to reduce density and strength. In any case, the increase in density would not be expected to improve inter-particle cementation and, indeed, the sulfate may tend to hinder cementation; this factor may contribute to the lower immersed strength obtained with the phosphates.

The data in Table 1 also show the effect of variations in molding water content on strength and density. Strength and density increase with water content up to about 10.5 percent, beyond which both decrease. This behavior is similar to results with pure phosphoric acid, and suggests that optimum water content for phosphate-sulfuric acid stabilization is about the same as for pure phosphoric acid.

**Phosphate Rock-Sulfuric Acid Stabilization.** — In light of the established stabilizing action (on MCS) of calcium phosphate-sulfuric acid mixtures, a series of experiments was conducted using finely ground Florida phosphate rock (consisting predominantly of fluorapatite —  $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ ) and sulfuric acid to treat this soil. Inasmuch as fluorapatite is considerably more refractory to acid attack than the fluorine-free calcium phosphates, it was expected that less phosphoric acid would be generated in situ in the soil with this mineral. To clarify this point, samples were prepared (a) by mixing rock and soil and then adding sulfuric acid, and (b) by preblending rock and acid and then mixing the blend with soil. Results are given in Table 2.

Consistent with predictions, soils stabilized by mixing with rock followed by acid addition are substantially weaker than those stabilized with equivalent concentrations of phosphoric acid, or of pure phosphate-sulfuric acid mixtures. However, soil treated with rock-sulfuric preblends exhibited cured strengths substantially higher than those stabilized with phosphoric acid or pure phosphate-sulfuric acid mixtures. The explanation for the latter result lies, it is believed, in the previously established catalytic activity of fluoride ion in the phosphoric acid-alumina reaction (4). Included in Table 2 are data determined earlier for phosphoric acid-stabilized MCS containing a small amount of sodium fluosilicate; compressive strengths for these formulations are equal

TABLE 2  
STABILIZATION OF MCS WITH PHOSPHATE ROCK AND SULFURIC ACID

Formulation and Manner of Addition to Soil	1-Day Humid Cure			7-Day Humid Cure			14-Day Humid Cure		
	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)
(Concentration Equivalent to 2% $\text{H}_3\text{PO}_4$ )									
$\text{H}_3\text{PO}_4$	184 $\pm$ 4	11.4	128.3	—	—	—	271 $\pm$ 15	11.3	128.5
$\text{H}_3\text{PO}_4$	242 $\pm$ 9	11.0	131.0	—	—	—	300	11.0	131.0
$\text{H}_3\text{PO}_4 + 0.5\% \text{Na}_2\text{SiF}_6$	305 $\pm$ 17	11.3	129.3	—	—	—	357	11.3	129.0
Phosphate rock-sulfuric acid, dry mixed	158 $\pm$ 8	9.8 $\pm$ 0.2	128.3 $\pm$ 0.3	191 $\pm$ 10	9.9 $\pm$ 0.1	127.5 $\pm$ 0.7	204	9.9	128.1
Phosphate rock-sulfuric acid, dry mixed	222 $\pm$ 12	10.3 $\pm$ 0	128.0 $\pm$ 0	171 $\pm$ 14	10.7 $\pm$ 0.1	128.3 $\pm$ 0.8	145 $\pm$ 35	11.3 $\pm$ 0.6	128.1 $\pm$ 0.1
Phosphate rock-sulfuric acid, dry mixed	282 $\pm$ 6	11.4 $\pm$ 0.2	131.8 $\pm$ 0.2	378 $\pm$ 6	11.5 $\pm$ 0.1	131.4 $\pm$ 0.1	—	—	—
Phosphate rock-sulfuric acid, preblended	305 $\pm$ 25	9.8 $\pm$ 0.5	129.8 $\pm$ 0.3	387 $\pm$ 45	8.9 $\pm$ 0.1	130.3 $\pm$ 0.6	415 $\pm$ 27	8.7 $\pm$ 0.1	130.0 $\pm$ 1.5
(Concentration Equivalent to 5% $\text{H}_3\text{PO}_4$ )									
$\text{H}_3\text{PO}_4$	225 $\pm$ 10	10.7	132.5	—	—	—	843	10.8	132.5
$\text{H}_3\text{PO}_4 + 0.5\% \text{Na}_2\text{SiF}_6$	495 $\pm$ 20	11.0	131.0	—	—	—	1,015	11.0	131.0
Phosphate rock-sulfuric acid, dry mixed	242 $\pm$ 23	10.1 $\pm$ 0	128.3 $\pm$ 0.2	—	—	—	307 $\pm$ 4	11.6 $\pm$ 0.1	127.4 $\pm$ 0.2
Phosphate rock-sulfuric acid, preblended	464 $\pm$ 8	10.0 $\pm$ 0.1	127.8 $\pm$ 0.3	620 $\pm$ 25	9.6 $\pm$ 0.2	128.4 $\pm$ 0.2	9.0 $\pm$ 5	10.0	128.7
Phosphate rock-sulfuric acid, preblended	529 $\pm$ 34	9.4 $\pm$ 0.1	127.0 $\pm$ 0.2	740 $\pm$ 75	9.4 $\pm$ 0.1	126.5 $\pm$ 0.7	870 $\pm$ 55	9.2 $\pm$ 0.2	—

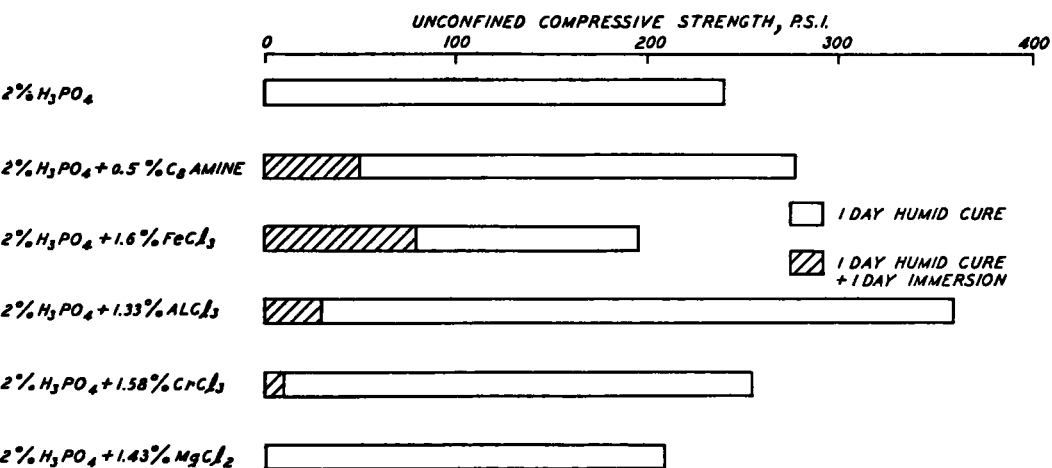


Figure 2. Comparison of various waterproofing additives on phosphoric acid-stabilized Vicksburg buckshot clay.

to or higher than those for rock-sulfuric acid treated specimens. It is thus apparent that a phosphate rock-sulfuric acid premix is quite suitable as a stabilizer for MCS; although all the phosphoric acid potentially available from such a mixture is evidently not used, the presence of fluoride more than compensates as regards rate of strength development.

Another cause of poor strength development in soils blended initially with rock arises from small amounts of calcium carbonate in the rock; this salt evolves carbon dioxide in contact with acid, building up pressure within the soil and breaking down the structure. Thus, another advantage of preblending rock and acid is elimination of gaseous reaction products prior to incorporation with the soil.

**Accelerating Effect of Sodium Fluosilicate.** — To determine whether the strength development of soil stabilized with pure calcium phosphate-sulfuric acid systems could be accelerated by means of fluoride, a series of tests was run with the various phosphates, at both 2 percent and 5 percent equivalent  $H_3PO_4$ , and both with and without 0.5 percent sodium fluosilicate. These results are presented and compared with other fluoride-containing systems in Table 3.

Table 3 shows that, at the equivalent of 2 percent  $H_3PO_4$ , fluosilicate results in only about 50 percent increase in 1-day strength with either pure phosphoric acid or pure calcium phosphate. This relatively slight accelerating effect, in addition to the even smaller increase in ultimate (7-day) strength, are in agreement with previous results. At the equivalent of 5 percent  $H_3PO_4$ , however, the accelerating effect of sodium fluosilicate is much more apparent, although ultimate strength is again only slightly increased. There is a significant and consistent decrease in the effectiveness of fluosilicate as the acidity of the phosphate decreases; that is, the accelerating effect is 150 percent with  $H_3PO_4$ , 135 percent with  $Ca(H_2PO_4)_2$ , and 95 percent with  $Ca_3(PO_4)_2$ . The fact that fluosilicate results in only 18 percent increase in 1-day strength with phosphate rock is undoubtedly due to the already high fluorine content of this material, making additional fluosilicate relatively ineffective.

#### Waterproofing of VBC with Polyvalent Metal Ions

Previous work (4) has indicated that the mechanism of waterproofing VBC by amines involves reducing swelling of the montmorillonoid minerals by replacing interlayer metallic cations with amine molecules. Because some polyvalent metallic cations, such as ferric ion, are known to have a similar effect in reducing lattice swelling, an investigation was carried out to evaluate a number of soluble salts of metallic ions as waterproofers for VBC stabilized with phosphoric acid. Salts studied included  $FeCl_3$ ,

TABLE 3  
COMPARISON OF THE EFFECT OF  $\text{Na}_2\text{SiF}_6$  ON THE STRENGTH OF  
MCS STABILIZED WITH VARIOUS ACIDIC PHOSPHORUS SYSTEMS

Phosphate	% Equivalent $\text{H}_3\text{PO}_4$	Compressive Strength (psi)					
		1-Day Humid Cure			7-Day Humid Cure		
		% $\text{Na}_2\text{SiF}_6$		% Increase Caused by $\text{Na}_2\text{SiF}_6$	% $\text{Na}_2\text{SiF}_6$		% Increase Caused by $\text{Na}_2\text{SiF}_6$
		0	0.5		0	0.5	
$\text{H}_3\text{PO}_4$	2	210	305	45	285	345	21
$\text{Ca}_3(\text{PO}_4)_2$ (dry mixed)	2	235	350	50	333	414	25
$\text{H}_3\text{PO}_4$	5	165	420	150	840	1,100	35
$\text{Ca}(\text{H}_2\text{PO}_4)_2$ (dry mixed)	5	269	655	135	890	1,155	30
$\text{Ca}_3(\text{PO}_4)_2$ (dry mixed)	5	252	487	95	418	510	22
Rock (preblended)	5	464	529	18	620	740	19

$\text{AlCl}_3$ ,  $\text{CrCl}_3$ , and  $\text{MgCl}_2$ . Ferric chloride and two percent phosphoric acid were used in most cases and salt concentration was usually maintained at 30 milliequivalents per 100 g of soil, which is the cation exchange capacity of VBC.

Although none of the samples waterproofed with polyvalent metal ions resisted immediate immersion, Table 4 shows that the addition of salts noticeably improved the water resistance of the soil after 24-hr humid cure. Here strengths of up to 80 psi were obtained, and 1.62 percent  $\text{FeCl}_3$  seems to be as effective as 0.5 percent octylamine.

Table 4 also indicates that none of the salts have any appreciable effect on 24-hr humid cure strength, if used at a concentration equivalent to the cation exchange capacity of the soil. When double this amount of  $\text{FeCl}_3$  was used, however, humid cure strength was decreased. In these samples a reddish exudation was observed; because

TABLE 4  
INVESTIGATION OF POLYVALENT METALLIC SALTS AS WATERPROOFERS FOR VBC STABILIZED WITH  $\text{H}_3\text{PO}_4$

$\text{H}_3\text{PO}_4$ (%)	$\text{FeCl}_3$ (%)	Pre- treat- ment (hr)	24-Hr Immersion Comp. Str. (psi)	24-Hr Humid Cure			24-Hr Humid Cure and 24-Hr Immersion		
				Comp. Strength (psi)	Dry Density (pcf)	Volatiles (%)	Comp. Strength (psi)	Dry Density (pcf)	Volatiles (%)
2	—	—	0	240 $\pm$ 5	112.0 $\pm$ 0.2	16.9 $\pm$ 0.4	0	—	—
2	0.81	48	0	242 $\pm$ 20	113.7 $\pm$ 0.1	15.4 $\pm$ 0	TWTT <sup>b</sup>	—	—
2	0.81	— <sup>a</sup>	0	333 $\pm$ 15	115.2 $\pm$ 0.4	15.25 $\pm$ 0.1	70 $\pm$ 5	108.5 $\pm$ 0.6	21.1 $\pm$ 0.1
2	1.62	0	0	220 $\pm$ 11	112.4 $\pm$ 0.4	15.7 $\pm$ 0.1	TWTT <sup>b</sup>	—	—
2	1.62	2	0	174 $\pm$ 7	112.5 $\pm$ 0.3	15.75 $\pm$ 0.1	TWTT <sup>b</sup>	—	—
2	1.62	2	TWTT <sup>b</sup>	280 $\pm$ 35	112.9 $\pm$ 0.2	17.9 $\pm$ 0.2	60 $\pm$ 5	106.3 $\pm$ 0.5	22.5 $\pm$ 0.4
2	1.62	2	TWTT <sup>b</sup>	196 $\pm$ 5	110.9 $\pm$ 0.2	19.0 $\pm$ 0.1	80 $\pm$ 15	105.4 $\pm$ 0.8	21.7 $\pm$ 0.3
2	3.24	24	0	162 $\pm$ 16	115.2 $\pm$ 0.2	15.1 $\pm$ 0.1	TWTT <sup>b</sup>	—	—
3	1.62	0	0	380 $\pm$ 20	115.1 $\pm$ 0.1	15.2 $\pm$ 0.2	48 $\pm$ 7	108.0	20.5
5	1.62	0	0	255 $\pm$ 15	115.1 $\pm$ 0.1	16.0 $\pm$ 0.1	79 $\pm$ 4	108.3 $\pm$ 0.2	20.6 $\pm$ 0.1
<b>Other Salts</b>									
2	1.33%	0	TWTT <sup>b</sup>	360 $\pm$ 10	114.0 $\pm$ 0.4	17.4 $\pm$ 0.2	32 $\pm$ 1	—	—
	$\text{AlCl}_3$								
2	1.58%	0	0	258 $\pm$ 8	113.9 $\pm$ 0.4	17.3 $\pm$ 0.2	7 $\pm$ 2	—	—
	$\text{CrCl}_3$								
2	1.43%	0	0	210 $\pm$ 25	114.4 $\pm$ 0.7	17.1 $\pm$ 0.3	TWTT <sup>b</sup>	—	—
	$\text{MgCl}_2$								

<sup>a</sup>For these samples, the soil was pretreated for 48 hr with  $\text{FeCl}_3$ , then dried at 110 deg for 24 hr, and finally re-equilibrated with water for 24 hr.

<sup>b</sup>TWTT means that the samples retained their shape but were too weak to test.

TABLE 5  
STABILIZATION OF MCS WITH 1.25 PERCENT ORTHORHOMBIC  $P_2O_5$   
(Equivalent to 2 Percent Phosphoric Acid)

Formulation and Manner of Addition to Soil	1-Day Humid Cure			7-Day Humid Cure			14-Day Humid Cure		
	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)
2% $H_3PO_4$	184 $\pm$ 4	11.4	128.3	—	—	—	271 $\pm$ 15	11.3	128.5
2% $H_3PO_4$	242 $\pm$ 9	11.0	131.0	—	—	—	300	11.0	131.0
1.25% $P_2O_5$ dry mixed with soil	215 $\pm$ 4	11.1 $\pm$ 0.1	133.1 $\pm$ 0.1	364	9.6	133.4	—	—	—
1.25% $P_2O_5$ dry mixed with soil	230 $\pm$ 5	9.2 $\pm$ 0.1	129.4 $\pm$ 0.1	—	—	—	300 $\pm$ 87	8.7 $\pm$ 0.3	127.8 $\pm$ 0.6
1.25% $P_2O_5$ solution, prepared by letting $P_2O_5$ stand undisturbed in water overnight	268 $\pm$ 8	10.2 $\pm$ 0.2	134.8 $\pm$ 0.2	386 $\pm$ 22	10.6 $\pm$ 0.1	136.1 $\pm$ 0.1	490 $\pm$ 5	9.2 $\pm$ 0.1	136.5 $\pm$ 1.1
1.25% $P_2O_5$ solution, prepared by heating the $P_2O_5$ - $H_2O$ mixture until clear solution was obtained ( $\frac{1}{2}$ hr)	246 $\pm$ 4	10.6 $\pm$ 0.1	133.3 $\pm$ 0.4	571 $\pm$ 69	9.6 $\pm$ 0.4	133.1 $\pm$ 0.4	680	8.1	132.7
3.75% $P_2O_5$ solution, prepared by heating the $P_2O_5$ - $H_2O$ mixture until clear solution was obtained ( $\frac{1}{2}$ hr)	231 $\pm$ 29	10.6 $\pm$ 0	131.0 $\pm$ 0	527 $\pm$ 18	10.3	132.0	585 $\pm$ 10	10.2 $\pm$ 0.1	131.1 $\pm$ 0.3

Note: All percentages based on dry soil weight.

this effect is not produced at lower concentrations it is concluded that a certain amount of salt combines with the soil, presumably in a cation exchange reaction. The excess  $FeCl_3$  apparently is detrimental to humid cure strength. It is also likely that reaction of excess ferric ion with phosphoric acid to produce insoluble ferric phosphate reduces the quantity of acid available for cementation of the clay.

It was believed that pretreatment of the soil with the ferric chloride before adding the phosphoric acid might allow the salt to diffuse into and adsorb on the clay. The effect of the pretreatment in practice (Table 4) is not entirely clear, but it does not seem to increase even the resistance of the soil to immediate immersion, the condition under which it would be expected to be most noticeable.

In one case, however, soil was pretreated with  $FeCl_3$ , allowed to equilibrate, dried at 110 C for 24 hr, then re-equilibrated with water for 24 hr and stabilized with  $H_3PO_4$ . In this case the soil proved to be much more water resistant than other  $FeCl_3$ -treated samples. This supports the postulate that ferric ion exchanges with univalent ions in

TABLE 6  
EFFECT OF TRACE QUANTITIES OF  $\alpha$ - $P_2O_5$  ON MCS STABILIZED WITH THE EQUIVALENT OF 2%  $H_3PO_4$

Formulation and Manner of Addition to Soil	1-Day Humid Cure			7-Day Humid Cure			14-Day Humid Cure		
	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)	Comp. Str. (psi)	% Volatile at Test	Dry Solids Density at Test (pcf)
2% $H_3PO_4$ alone	242 $\pm$ 9	11.0	131.0	—	—	—	300	11.0	131.0
2% $H_3PO_4$ + 0.1% $P_2O_5$ added to acid	315 $\pm$ 3	9.8 $\pm$ 0.1	135.2 $\pm$ 0.3	333 $\pm$ 54	9.6 $\pm$ 0	134.7 $\pm$ 0.2	538 $\pm$ 2	9.0 $\pm$ 0	135.1 $\pm$ 0.2
Phosphate rock-sulfuric acid mixture + 0.1% $P_2O_5$ added to soil dry (phosphate rock dry mixed)	188 $\pm$ 15	9.5 $\pm$ 0	126.3 $\pm$ 0.3	200 $\pm$ 28	8.8 $\pm$ 0.4	127.0 $\pm$ 1.0	—	—	—
Phosphate rock-sulfuric acid mixture alone (phosphate rock dry mixed)	265 $\pm$ 35	10.5 $\pm$ 0.1	128.7 $\pm$ 0.7	315 $\pm$ 65	10.5 $\pm$ 0.1	128.7 $\pm$ 0.7	—	—	—
Phosphate rock-sulfuric acid mixture + 0.1% $P_2O_5$ added to acid (phosphate rock dry mixed)	341 $\pm$ 23	9.8 $\pm$ 0.1	134.6 $\pm$ 0.6	422 $\pm$ 19	9.8 $\pm$ 0.1	134.1 $\pm$ 0.2	437 $\pm$ 27	10.9 $\pm$ 0.2	134.3 $\pm$ 0.1

the montmorillonoid lattice. The lattice shrinkage occurring on drying would then be irreversible due to the binding effect of the ferric ions. In fact, soil treated in this way behaves more like a clayey silt than a heavy clay.

Of the other polyvalent metal salts tested, only  $\text{AlCl}_3$  gave results comparable to those obtained with  $\text{FeCl}_3$  (Table 4).  $\text{CrCl}_3$  and  $\text{MgCl}_2$  appear to be much less effective as waterproofers.

### Soil Stabilization with Orthorhombic Phosphoric Anhydride

**Characteristics of Orthorhombic Phosphoric Anhydride ( $\text{o-P}_2\text{O}_5$ ).—** Previous work (2) showed that  $\text{P}_2\text{O}_5$  was effective as a soil stabilizer and possessed several important advantages over phosphoric acid, including lower material requirements and higher permissible soil water content. The irritating properties of the powdered anhydride, however, and its violent reactivity with water, make its use in the field both troublesome and hazardous.

Recently a new crystalline form of phosphoric anhydride (orthorhombic  $\text{P}_2\text{O}_5$ ) has become available which, because of its lower reactivity, seemed promising as a soil stabilizer. It is the anhydride of metaphosphoric acid, rather than orthophosphoric acid, and differs from normal  $\text{P}_2\text{O}_5$  in that it is only slowly soluble in cold water, yielding a solution of the following composition (6):

Orthophosphoric acid	6.3 %
Pyrophosphoric acid	0.6 %
Tetraphosphoric acid	0.4 %
Tri-metaphosphoric acid	8.6 %
Tetra-metaphosphoric acid	9.1 %
Penta-metaphosphoric acid	6.4 %
Higher ( $\text{P}_6$ - $\text{P}_9$ ) metaphosphoric acids	12.0 %
Poly ( $\text{P}_{10}$ and up) metaphosphoric acid	56.8 %

Although the reaction with water is quite exothermic, the slow rate of hydration prevents extreme local heat generation. At room temperature, solution of an amount sufficient to produce the equivalent of 50 percent  $\text{H}_3\text{PO}_4$  solution occurs only after about 24 hr. By keeping the mixture near its boiling point, however, the process can be speeded and a clear solution obtained in 30 min. It is presumed that in the soil these various condensed phosphoric acids are converted progressively into orthophosphoric acid, the stable form in aqueous medium, which reacts with the soil alumina in the usual manner.

**Stabilization of MCS with  $\text{o-P}_2\text{O}_5$  (Tables 5 and 6).—** Initial tests were made by hand mixing the soil at approximately 8 percent volatiles with dry  $\text{o-P}_2\text{O}_5$  and then adding the rest of the required water during the mechanical mixing process (dry mixing). Strengths comparable to those obtained with  $\text{H}_3\text{PO}_4$  were developed in this manner (Table 5).

To clarify the effect of the slow dissolution rate of the anhydride on strength development, soil samples were prepared using the poly-acid solution produced by dissolving the anhydride in water. Results (Table 5) show that, although the 1-day humid cure strength is not significantly improved by this technique, the 7- and 14-day strengths are markedly increased, greatly surpassing even those obtained with orthophosphoric acid. From these observations, it is concluded that (a) polyphosphoric acid is superior to orthophosphoric acid as a soil stabilizer (at least for moderately fine-grained soils), and (b) orthorhombic  $\text{P}_2\text{O}_5$  is less effective as a stabilizer than its hydration products. The latter result probably is explained by the fact that admixture of granular anhydride with the soil leads to non-uniformity of acid distribution, and hence non-uniform cementation on cure.

The excellent stabilizing action of polyphosphoric acids appears primarily to result from the pronounced dispersive action of these acids on MCS, allowing increases in compacted density of as much as 4 pcf. Because very small quantities of orthorhombic  $\text{P}_2\text{O}_5$  (or its hydration products) were found to exert this dispersing effect, the influence of trace quantities (0.1 percent by weight of soil) of the anhydride on strength of other acidic-phosphorus-compound stabilized soils was studied. Results are given in Table 6.



TABLE 7  
COST COMPARISONS FOR EQUIVALENT STABILIZATION OF MCS

Method	Cost	
	¢/lb	\$/cu yd, soil
Orthophosphoric acid		
H <sub>3</sub> PO <sub>4</sub> : 54 lb/cu yd	6.65	3.59
Na <sub>2</sub> SiF <sub>6</sub> : 13 lb/cu yd	6.50	0.85
Total		4.44
Phosphate rock-sulfuric acid (pre-blended)		
Phosphate rock: 105 lb/cu yd	0.30	0.32
Sulfuric acid: 70 lb/cu yd	1.05	0.74
Total		1.06
Phosphate rock-sulfuric acid (no pre-blending)		
Phosphate rock: 105 lb/cu yd	0.30	0.32
Sulfuric acid: 70 lb/cu yd	1.05	0.74
Orthorhombic P <sub>2</sub> O <sub>5</sub> : 3 lb/cu yd	30.0 <sup>a</sup>	0.90
Total		1.96
Orthophosphoric acid-o-P <sub>2</sub> O <sub>5</sub>		
H <sub>3</sub> PO <sub>4</sub> : 30 lb/cu yd (est.)	6.65	2.00
0-P <sub>2</sub> O <sub>5</sub> : 3 lb/cu yd	30.0 <sup>a</sup>	0.90
Total		2.90

<sup>a</sup>Experimental product; estimated tonnage price.

When added to orthophosphoric acid, traces of o-P<sub>2</sub>O<sub>5</sub> very greatly improve humid-cure strength, measured values closely matching those obtained using polyphosphoric acids alone, as do compacted densities. This essentially confirms the hypothesis that the dispersive action of polyphosphoric acid is responsible for its superior stabilizing ability. Of even greater practical interest (Table 6) is the fact that addition of a trace of o-P<sub>2</sub>O<sub>5</sub> to sulfuric acid, followed by mixing with soil blended with phosphate rock (that is, without preblending rock and acid), yields humid-cure strength values significantly higher than obtained with orthophosphoric acid alone. Because the incremental cost of 0.1 percent o-P<sub>2</sub>O<sub>5</sub> is rather small, this modified formulation appears to offer excellent promise, on both economic and technical grounds, as a very low cost soil stabilizer. Whether such a stabilizing system will be operative in heavy clay soils (where phosphoric acid-amine mixtures appear to be uniquely effective) remains to be established; studies with this objective in mind are currently under way.

#### PRACTICAL AND ECONOMIC ASPECTS OF PHOSPHORIC SOIL STABILIZATION

The results of this study indicate that "marginal" soils, such as MCS, can be successfully stabilized not only with phosphoric acid, but also with (a) phosphate rock-sulfuric acid mixtures, provided rock and acid are preblended before compaction in soil; (b) phosphate rock-sulfuric acid mixtures without preblending if 0.1 percent orthorhombic P<sub>2</sub>O<sub>5</sub> is added; and (c) orthophosphoric acid-o-P<sub>2</sub>O<sub>5</sub> mixtures. Comparative costs of these four systems are given in Table 7. It is evident from these calculations that rock-sulfuric mixtures are substantially lower in cost than treatments based on orthophosphoric acid alone, or with additives. Indeed, the cost of treatment with a rock-sulfuric preblend is lower than that of a conventional stabilization with lime, cement, or asphalt which would produce the equivalent mechanical strength. From the stand-

point of convenience in the field, use of a plant-mixed preblend of rock and acid would appear to be preferable to the two-step operation of mixing first rock, and then acid with the soil. Should the two-stage treatment for any reason prove to be desirable, however, this could be carried out successfully, but at an increment of cost (for orthorhombic  $P_2O_5$ ) of about 90 cents per cubic yard of soil.

For stabilization of heavy clay soils, such as VBC, where significant amounts of waterproofing additives are required in addition to phosphoric acid, materials costs are substantially higher than for "marginal" soils such as MCS. The discovery that ferric chloride can be used as a replacement for octylamine as a waterproofer in VBC, however, results in a significant cost reduction: treatment with 2 percent phosphoric acid and 0.5 percent octylamine (at 30 cents per lb) costs about \$7.60/cu yd, while 2 percent phosphoric acid and 1.6 percent ferric chloride (at 5 cents per lb) costs only \$5.74/cu yd. Despite this improvement, the expense of stabilization of heavy clays remains much higher than that of soils of moderate plasticity. Continuation of the search for a low-cost stabilizing system for heavy clays thus remains a major research objective.

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