

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

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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, montmorillonoid 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 20 C/20 C	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.

¹M.I.T. Classification System.

²Harvard Miniature Compaction, 40 lb tamper, 3 layers, 25 blows per layer.

³For -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 STABILIZATION¹

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	-

¹Phosphoric acid content = 2 percent on dry soil.

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

³AlF₃.

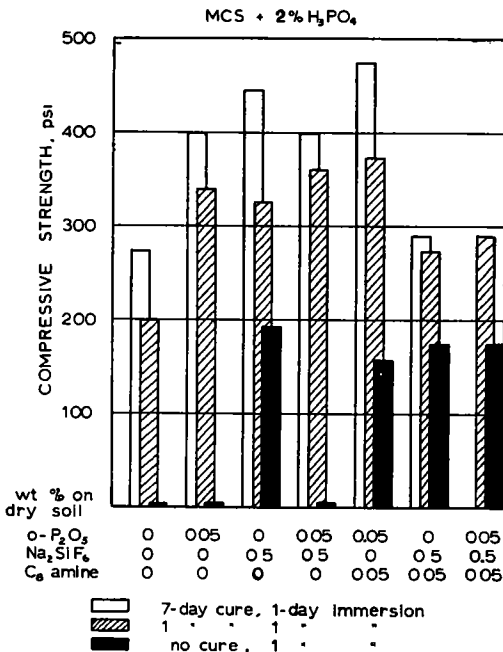


Figure 1.

less than that observed with phosphoric acid alone. It was anticipated that, if orthorhombic P₂O₅ 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 H₃PO₄, 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 ACID¹

H ₃ PO ₄ (%)	1-Day Humid Cure						7-Day Humid Cure					
	0-Day Immersion			1-Day Immersion			0-Day Immersion			1-Day Immersion		
	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}	10.8	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

¹Samples contain 0.5 percent Na₂SiF₆; percentages of additives based on dry soil.

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 H₃PO₄ 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

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			Compressive Strength (psi)		
Acid	Na_2SiF_6	Waterproofer		Volatiles on Dry Solids	Density of Dry Solids	1-Day Humid Cure Str	1-Day Cure	7-Day Cure	14-Day Cure
Type	%	Type	%	(%)	(pcf)	(psi)			
H_3PO_4	2.76	0	C ₈ amine	1	21.6	104.3	215 [±] 15	45 [±] 5	-
H_3PO_4	2.76	0.5	C ₈ amine	1	23.3	104.0	205 [±] 5	45 [±] 5	50
H_3PO_4	2.76	2.0	C ₈ amine	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
H_3PO_4	2.0	1.0	FeCl ₃	1.6	22.0	106.0	345 [±] 5	55 [±] 5	135 [±] 10
H_2SO_4	2.0								
P_2O_5	1.75	-	C ₈ amine	1	22.1	104.6	-	25	65 [±] 10
P_2O_5	3.6	-	C ₈ amine	1	22.0	105.0	-	70 [±] 10	155
P_2O_5	3.1	-	FeCl ₃	1.6	20.6	107.5	190 [±] 30	30 [±] 5	180 [±] 5
P_2O_5	3.12	0.5	FeCl ₃	1.6	21.4	106.6	290 [±] 10	135 [±] 5	280 [±] 20
P_2O_5	3.1	2.0	FeCl ₃	1.6	21.1	107.3	350 [±] 10	105 [±] 5	420 [±] 20
									55 [±] 10
									180 [±] 20
									230 [±] 10
									290
									415 [±] 10

¹One-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 three-fold 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 aluminophosphate 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 water-proofer, 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.

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