

# ***Fine-Grained Soil Stabilization with Phosphoric Acid and Secondary Additives***

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The effectiveness of phosphoric acid as a stabilizer for two fine-grained soils (a clayey silt and a heavy clay) has been studied, with particular emphasis on the use of fluorine compounds as cure-accelerators and of amines as waterprooferers. The clayey silt (P.I. = 6.0) could be successfully stabilized with phosphoric acid alone, at concentrations of 2 percent acid on dry soil weight, and higher. With 2 percent acid, wet strength after 24-hr humid cure was 120 psi; this was increased to 220 psi by addition of 0.5 percent sodium fluosilicate. With 5 percent acid and 0.5 percent fluosilicate, wet strength of nearly 500 psi was achieved under similar conditions. Clayey silt treated with acid and fluosilicate disintegrates if immersed in water immediately after compaction; addition of only 0.05 percent (on soil) of octylamine, however, allows strength to develop under these conditions.

The heavy clay (P.I. = 32.2) could not be successfully stabilized with phosphoric acid alone. Incorporation of octylamine with phosphoric acid resulted in unusually effective stabilization of this soil; wet strength of 189 psi after 24-hr humid cure was obtained with 2 percent acid and 2 percent octylamine, and 268 psi with 5 percent acid and 1 percent amine. Fluorine compounds had no significant effect with this soil. With 2 percent acid and 2 percent amine, satisfactory strength (143 psi) development was observed even when the treated soil was immersed in water immediately after compaction.

These and earlier results indicate that phosphoric acid, with added fluorine compounds and/or amines, offers considerable promise for low-cost stabilization of fine-grained, carbonate-free soils under field conditions.

●RECENT WORK has shown that phosphoric acid, at 2 to 10 percent on dry soil weight, has a remarkable and unique ability to solidify a wide variety of soils (2,3,4). Furthermore, phosphoric acid seems to meet several of the requirements for an ideal soil stabilizer; it is effective at low concentrations, is easily mixed with soil, causes reasonably rapid cementation, and is of low cost.

It has been proposed (4) that the mechanism of stabilization involves

reaction of phosphoric acid with alumina and aluminosilicate in the soil to form acid soluble phosphates, followed by gelation and cementation as the unreacted acid is consumed. Sodium fluosilicate was found to accelerate cure rate (4), and amines were found to be promising waterprooferes (2,4). Because both rapid cure and water resistance are of great practical importance, an investigation has been carried out to study further stabilization of soil by phosphoric acid, with particular emphasis on secondary additives such as fluorine compounds and amines. The objective of this paper is to present and briefly discuss the most important practical results of this investigation.

## PROCEDURE

The two soils studied were Massachusetts clayey silt (MCS), a fine-grained illitic soil, and Vicksburg buckshot clay (VBC), a heavy clay containing about 25 percent of the expanding lattice montmorillonoid minerals. Liquids content at molding was maintained at 12.5 cc total liquids volume per 100 grams dry soil for the MCS, and 17.0 cc per 100 grams soil for the VBC; maximum compacted density was achieved under these conditions. Of considerable interest is the observation that strength of phosphoric acid-stabilized soil is generally less sensitive to molding water content and compacted density than untreated soil.

The preparation and testing of samples was similar to that used in previous studies (4). Briefly, soil at the proper water content was mixed uniformly with phosphoric acid. When other additives were used they were dissolved in the acid before mixing with the soil; additives included several fluorides and fluosilicates, and a number of primary aliphatic amines. It was assumed that the acid and amine react equimolarly to form the amine salt; acid in excess of that reacting with the amine was considered to be "free" acid.

After mixing, samples were compacted by two-end static compaction in a Harvard miniature mold under a load of 900 psi. At least six samples were prepared from each formulation, and two similar samples were tested for each curing condition. Curing conditions included immersion in water immediately after compaction for 24-hr cure in air at 100 percent relative humidity, and 24-hr water immersion after humid cure (wet strength). After curing, samples were tested to failure in unconfined compression. Deformation at failure was always less than 2 percent.

## RESULTS

### Fluorine Compounds as Cure Accelerators

Although sodium fluosilicate alone does not increase the unconfined compressive strength of soil, Figure 1 shows that small percentages greatly accelerate strength development in MCS stabilized with phosphoric acid. For a given acid concentration, the 24-hr humid cure strength increases approximately linearly with percent fluosilicate. The effect on the 5 percent acid treatment is remarkable, with 0.5 percent fluosilicate increasing 24-hr humid cure strength from 150 psi to 500 psi, accompanied by a similar increase in wet strength. Although the effect of fluosilicate is not as great with 2 percent acid as with 5 percent acid, a significant and consistent increase in cure rate is obtained with fluosilicate. Despite the accelerating effect, the fluosilicate has negligible effect on the 2-week humid cure strength, indicating that the effect of

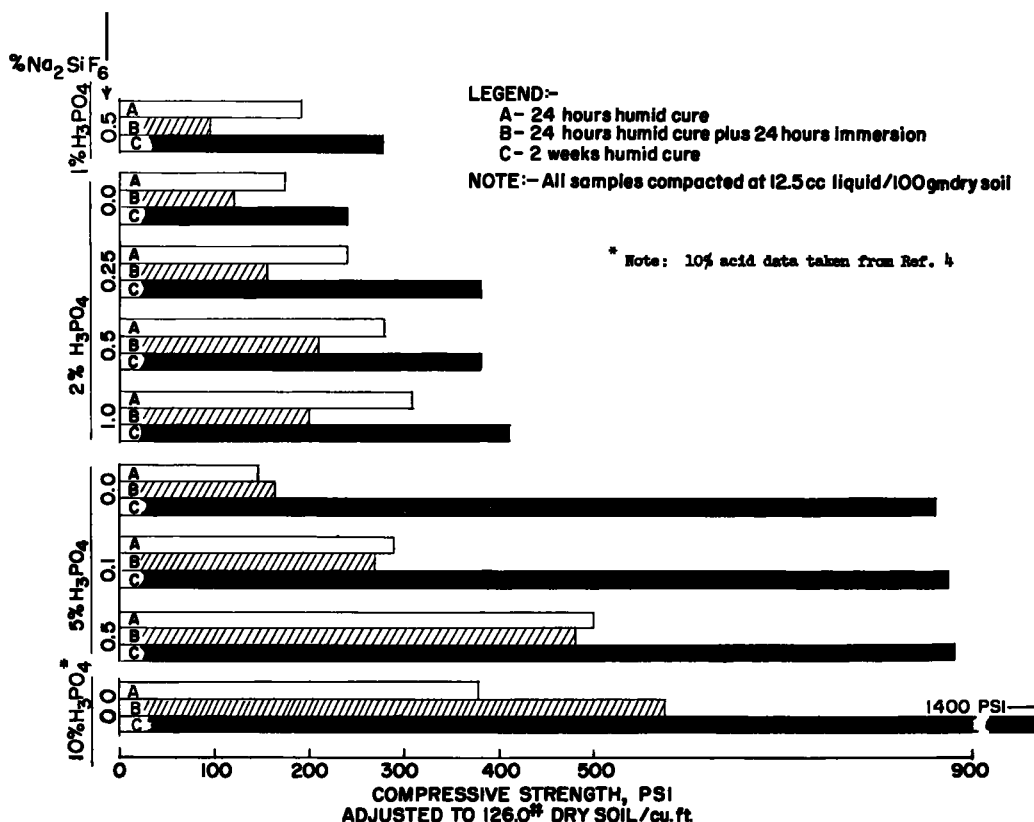


Figure 1. Effect of sodium fluosilicate concentration on strength development in MCS stabilized with phosphoric acid.

this salt is primarily one of catalysis and not of increasing the strength of the bonding phase. The increase in 2-week strength with 2 percent acid plus fluosilicate, compared with the 2 percent acid treatment alone, is believed to be due to incomplete reaction in the absence of accelerator, even after 2 weeks.

The results for 24-hr humid cure are surprising in that 5 percent acid without fluosilicate gives lower strength than 2 percent acid without fluosilicate. Addition of 0.5 percent sodium fluosilicate, however, results in much higher 24-hr cure strength with 5 percent acid than with 2 percent acid. These results not only emphasize the accelerating effect of the fluosilicate, but are also consistent with the proposed reaction mechanism for phosphoric acid stabilization of soil (4); that is, phosphoric acid reacting with alumina and aluminosilicates to form acid-soluble phosphates, followed by gelation as the acid is consumed. The low 24-hr strength with 5 percent acid is thus probably due to a large amount of unreacted acid solubilizing the aluminophosphate and preventing gelation.

Although the mechanism of the accelerating effect of sodium fluosilicate is not known for certain, the following mechanism is in complete agreement with the results and seems reasonable. It has been reported (5) that fluorides greatly accelerate the dissolution of aluminum metal in

phosphoric acid. Because the aluminum metal undoubtedly is coated with a film of hydrated alumina, which is similar to the surface presented by the soil, the effect of the fluorides appears to involve acceleration of the attack of alumina by acid. Specifically, it is believed that the fluorides aid in removing a passivating film of adsorbed phosphate which forms on the alumina and hinders further reaction. A number of fluorides and fluosilicates, including  $K_2SiF_6$ ,  $ZnSiF_6$ ,  $NaF$ , and  $AlF_3$ , have an accelerating effect similar to that of  $Na_2SiF_6$ . The effect of the fluosilicates, therefore, probably involves hydrolysis to the fluoride.

In contrast with their effect in the clayey silt (MCS), fluosilicates have no noticeable accelerating effect in the heavy clay (VBC) stabilized with up to 10 percent phosphoric acid. The reason for this ineffectiveness is believed to be that the acid-soil reaction is so rapid in the heavy clay even without accelerator, due either to high specific surface area of VBC or the presence of more readily acid soluble material, that the accelerating effect of fluosilicate is negligible.

### Amines as Waterproofers

The results in Figure 1 show that strength loss on immersion after 24-hr humid cure is not serious with the clayey silt, even without amines. Strength loss seems to depend on acid concentration, with a greater percent of 24-hr humid cure strength lost at lower acid concentrations. With 1 percent acid, wet strength is about 50 percent less than 24-hr humid cure strength; with 2 percent acid it is about 30 percent less; with 5 percent acid the strength is not changed by immersion; and with 10 percent acid, wet strength is considerably higher than 24-hr humid cure strength. Apparently, if the sample is only partially cured at the time of immersion, as with 5 percent or 10 percent acid, the strength increase due to 24-hr additional curing time, may exceed the strength loss due to immersion.

The need for a waterproofer with the clayey silt arises from the fact that uncured samples invariably disintegrate on immersion immediately after compaction. Because the soil has very little cohesive strength immediately after compaction, it might be expected that waterproofing, or even preventing disintegration on immersion, would be very difficult. In fact, however, Figure 2 shows that as little as 0.05 percent normal octylamine not only prevents disintegration of samples of clayey silt stabilized with 2 percent acid, but permits the development of about 70 psi after 24 hr. Although higher percentages of n-octylamine provide somewhat more effective waterproofing, additional amine is detrimental to humid cure strength, presumably because it reduces the free phosphoric acid content of the soil. Figure 2 also shows that normal octylamine is a much more effective waterproofer than 2-ethylhexylamine. This is probably due to the fact that n-octylamine is not branched, as the other eight-carbon amine is, and hence is more hydrophobic. The low amine requirement for waterproofing the clayey silt suggests that the mechanism of waterproofing involves reducing capillary pressure in the soil, probably by cation exchange; because 0.05 percent amine corresponds to only about 4 percent of the cation exchange capacity of MCS, however, it is unlikely that any other mechanism of waterproofing is involved.

Although the clayey silt is relatively easy to waterproof, Figure 3 shows that the heavy clay (VBC) is much more difficult. With VBC an amine is required even for wet strength after humid cure. As with the clayey silt, octylamine is a much more effective waterproofer than less hydro-

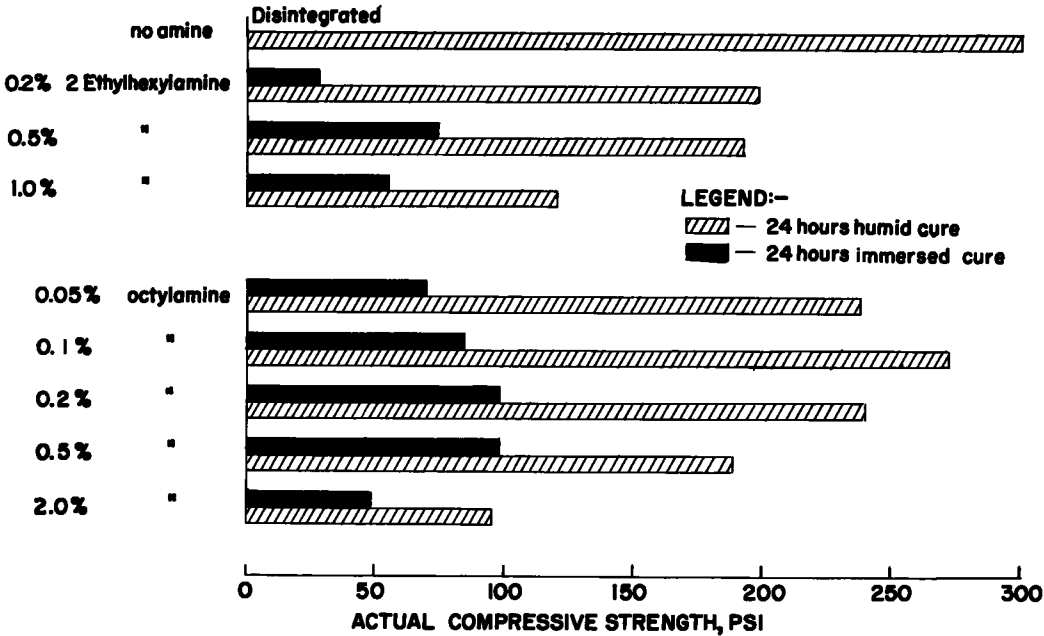
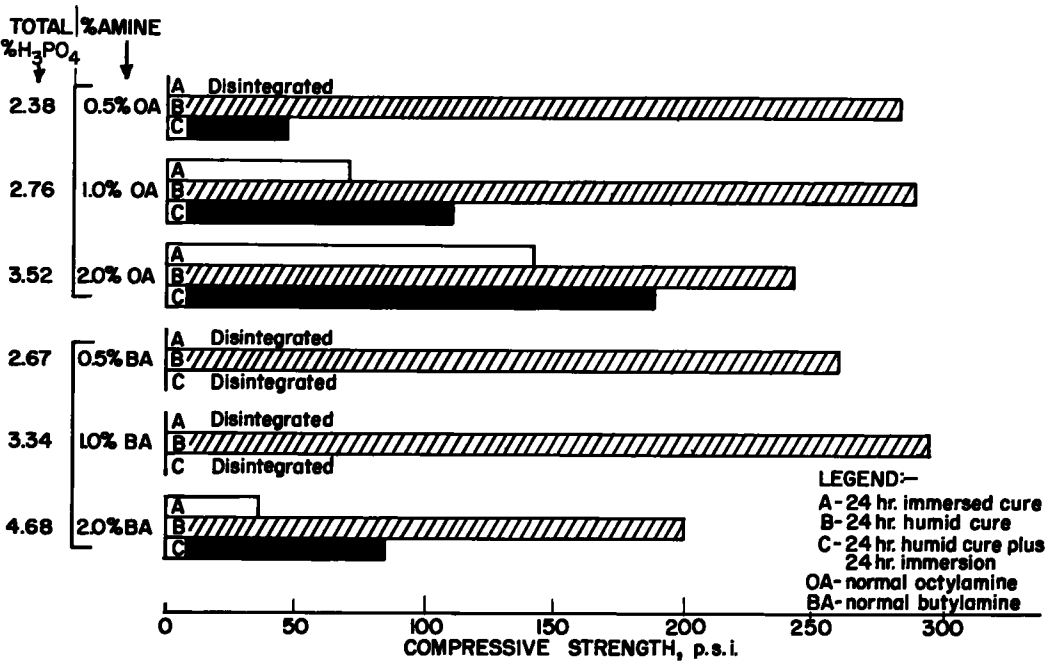


Figure 2. Effect of amine concentration on immediate immersion strength for Massachusetts clayey silt stabilized with 2 percent  $H_3PO_4$  + 0.5 percent  $Na_2SiF_6$ .



NOTE:- All samples VBC stabilized with 2% "free"  $H_3PO_4$  plus 0.5%  $Na_2SiF_6$  at approx. 15% volatile

Figure 3. Comparison of n-octylamine and n-butylamine as waterproofers for VBC stabilized with 2 percent "free"  $H_3PO_4$ .

phobic amines such as n-hexylamine or n-butylamine, both for immediate immersion of uncured samples and rewet strength. It should be noted that 2 percent "free" acid was used in all cases in Figure 3. The fact that 1-week humid cure strength does not increase with amine concentration (Table 1), even though total acid concentration increases greatly with higher amine concentration, indicates that only the "free" acid is effective in cementation. In fact, the decrease in humid cure strength with increasing amine concentration indicates that the amine salt may actually hinder cementation by blocking the soil surface to acid attack.

TABLE 1  
EFFECT OF PHOSPHORIC ACID AND OCTYLAMINE CONCENTRATIONS ON  
STABILIZATION OF VICKSBURG BUCKSHOT CLAY

% Free Acid on Soil	% OA Weight	Molding Liquids Content, cc/100 gm Soil	Compacted Density, lb Dry Solid/ pcf	No Cure 24-hr Immer- sion	Unconfined Compressive Strength, psi	
					24-hr Humid Cure	24-hr Humid Cure; 24-hr Immersion
2	0	17.0	113.5	D	290	D
2	0.5	17.0	113.3	D	283 <sup>+3</sup>	50 <sup>+25</sup>
2	1.0	17.0	113.5	71	290 <sub>-20</sub>	110 <sup>+40</sup>
2	2.0	17.0	112.5	143 <sup>+8</sup>	243 <sup>+22</sup>	189 <sup>+3</sup>
5	0	—	115.0	D	385	D
5	1	—	115.0	121 <sup>+0</sup>	303 <sup>+10</sup>	268 <sup>+4</sup>
5	2	—	115.0	103 <sup>+3</sup>	255 <sup>+15</sup>	254 <sup>+3</sup>

Water absorption data show that immediate immersion of uncured samples treated with 2 percent "free" acid and 2 percent octylamine results in 2.7 percent water pickup; with 1 percent amine, 8.6 percent water is absorbed; and with 0.5 percent amine the samples disintegrate on immediate immersion. Volume change on immersion corresponds to the amount of water absorbed. These results support the view that amines function in the heavy clay by replacing metallic cations, and thus reduce swelling of the montmorillonitic minerals. It is interesting to note that the 2 percent amine treatment corresponds to replacing about one-half of the exchangeable cations in VBC (assuming the amine salt exchanges completely), and that "immediate immersion strength" and "wet strength" are approximately linearly related to the percent amine. Although humid cure strength decreases rapidly with increasing water content, due to decreased compacted density, samples compacted at 20 percent water content require less amine for waterproofing than samples compacted at 15 percent water content.

Table 1 shows that the effect of amine concentration on the heavy clay stabilized with 5 percent acid is similar to that with 2 percent acid. Without amine, samples disintegrate on immersion, either before or after cure. On the other hand, 2 percent amine seems to be detrimental not only to humid cure strength, but even wet strength and immediate immersion strength, supporting the suggestion that the amine salt may interfere with cementation. Five percent acid plus 1 percent octylamine provide good stabilization; that is, 303 psi after 24-hr humid cure, 268 psi rewet

strength, and even 121 psi on immediate immersion after compaction.

Because octylamine is so much more effective than less hydrophobic amines, it might seem that even more hydrophobic amines would be better. In fact, however, longer chain amines have been found to be less effective because of insolubility of the amine salt, thus making uniform incorporation in the soil impossible.

#### Effect of Drying and Rewetting

A previously unanswered question concerned the effect of air-drying and reimmersion on the strength of phosphoric acid stabilized soil. Table 2 shows that with the clayey silt, relatively little deterioration occurs. For example, MCS stabilized with 2 percent acid, 0.5 percent sodium fluosilicate, and 0.5 percent 2-ethylhexylamine gives about 200 psi after 24-hr humid cure, and about 300 psi after 2-weeks humid cure. If the samples are air dried for 1 week after 24-hr humid cure, to about 1.6 percent water, strength increases to about 600 psi with negligible change in density. Subsequent water immersion for 1 week gives about 150 psi, or about one-half the humid cure strength. It is noteworthy that previous workers (4) found that samples air dried without humid cure underwent a density increase of about 4 percent; apparently the humid cure samples are rigid enough to resist shrinking.

TABLE 2

EFFECT OF DRYING AND REIMMERSION ON STRENGTH OF MCS STABILIZED WITH  
2 PERCENT  $H_3PO_4$ , 0.5 PERCENT  $NaSiF_6$ , AND 0.5 PERCENT  
2-ETHYLHEXYLAMINE

Cure Condition	Compressive Strength, psi	% Volatile at Test	Density at Test
24-hr humid cure	205 $\pm$ 11	11.5 $\pm$ 0	127.7 $\pm$ 0.8
24-hr humid cure plus 1 week ambient drying	635 $\pm$ 120	1.65 $\pm$ 0.05	127.2 $\pm$ 0.7
24-hr humid cure, 1 week ambient drying, 1 week water immersion	144 $\pm$ 15	11.2 $\pm$ 0.2	127.7 $\pm$ 0.3
2-wk humid cure	313 $\pm$ 20	0.4 $\pm$ 0.1	127.7 $\pm$ 0.3

The heavy clay, as might again be expected, is much more sensitive to drying and reimmersion than the clayey silt. Typical results, for VBC stabilized with various percentages of octylamine, are presented in Table 3. The only samples that effectively resisted drying and reimmersion were those containing 2 percent amine, although these did well. The large density change on drying and reimmersion, with resultant cracking of samples, is probably the primary cause of failure. The large increase in density on drying of stabilized VBC, compared with the negligible volume change on drying of the clayey silt, demonstrates the large shrinkage

TABLE 3

EFFECT OF OCTYLAMINE CONCENTRATION ON AIR DRY AND REWET STRENGTH OF VICKSBURG BUCKSHOT CLAY  
STABILIZED WITH 2 PERCENT FREE PHOSPHORIC ACID

Cure Cond.	Spec.	Oct. <sup>a</sup> H <sub>3</sub> PO <sub>4</sub> (%) <sup>a</sup>			Vol. <sup>b</sup> at Comp.	Comp. Str. (psi)	Density (pcf) <sup>c</sup>			Vol. (%) <sup>a,b</sup>			Water <sup>a,d</sup> Pickup (%)
		(%)	Tot.	Free			Air	Dry	At Test	Air	Dry	At Test	
As cast	1	0.5	2.38	2.0	14.2								
	2	1.0	2.76	2.0	14.7								
	3	2.0	3.52	2.0	14.7								
24-hr humid cure,	1					Dis. <sup>e</sup>							
24-hr air dry, plus	2					Dis. <sup>e</sup>	116.5	—	10.0	—			
24-hr immersion	3					185	117.0	115.0	9.1	14.0			
1-wk humid cure	1					457		114.5		14.2			
	2					557		114.5		14.7			
	3					513		113.0		14.7			
24-hr humid cure,	1					Dis. <sup>e</sup>							
6-day air dry,	2					Dis. <sup>e</sup>	117.0	—	4.0	—			
24-hr immersion	3					57	117.0	—	4.7	17.0			
7-day humid cure, 24-hr water immersion	1					20		—		24.7			10.2
	2					214		112.5		19.1			4.4
	3					250		113.0		17.5			2.8
7-day humid cure,	1					Dis. <sup>e</sup>							
24-hr air dry,	2					10	116.5	—	1.5	23.7			
24-hr immersion	3					93±7	115.0	112.5	9.4	17.4±0.6			

<sup>a</sup>Percentages by weight.

<sup>b</sup>Pounds volatile per 100 lb dry solids.

<sup>c</sup>In pounds of dry solids per cubic foot.

<sup>d</sup>Increase in percent volatile; that is, pounds of water pickup per 100 lb dry solids.

<sup>e</sup>Dis. = disintegrated.



pressures created on air-drying the heavy clay. The amine presumably reduces interlayer swelling in the heavy clay, and thus reduces shrinkage on air drying.

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

Based on the results of this and earlier investigations, it appears that phosphoric acid with secondary additives is a very attractive candidate for stabilizing fine-grained aluminosilicate soils. With silty clays such as MCS, the strength and water resistance obtained with as little as 2 percent acid appear adequate for highway subgrade and base applications; no conventional stabilizer has been found to yield comparable strength at this low a treatment level. Approximately 5 percent portland cement is required to achieve equivalent ultimate strength with MCS. For a highway base application, about 250 psi would be required; at the current price of about 7 cents per pound for phosphoric acid, and about 1.5 cents per pound for portland cement, the material cost for this stabilization would be \$3.78 per cu yd (2,700 lb soil) for the 2 percent acid treatment, and \$2.02 per cu yd for the cement. Economic considerations would thus favor use of portland cement for this soil unless rapid cure is essential, or if other factors such as low material requirements and ease of application should be important. The action of phosphoric acid in facilitating mixing and compaction of wet soils may prove to be particularly advantageous in this latter respect.

With heavy clays such as VBC, the stabilizing effectiveness of phosphoric acid (with octylamine) is extraordinary. No previously reported stabilizing system has even approached this combination at so low a treatment level. With 2 percent acid and 1 percent octylamine, the stability developed appears to be marginally satisfactory for road subgrade applications; almost 300 psi is developed after 24-hr humid cure, over 500 psi after 1-wk humid cure, and over 200 psi rewet strength is maintained after 1-wk humid cure (Table 1). Unfortunately, the amine requirements render this treatment virtually prohibitive in cost, because the amine is roughly five times as expensive as the acid. Thus, despite the unique effectiveness of the acid-amine treatment for heavy clays, its practical utility will probably be limited by economics to those field situations where circumstances demand that heavy clay be stabilized in place. Availability of a very inexpensive replacement for octylamine could, of course, make the economic picture much more favorable. The use of polyvalent metal ions, such as ferric, to reduce interlayer swelling offers much promise as far as strength retention after cure is concerned, although it appears that amines will be required for wet strength before cure.

Several questions concerning the use of phosphoric acid as a soil stabilizer still remain unanswered. Stabilization of soils containing carbonate minerals presents difficulties because of neutralization of phosphoric acid by these salts. It is possible that the acid-carbonate reaction may be hindered by formation of a passivating film similar to that postulated in the attack of clay by acid, or it may be possible to create such a film on the carbonate. Another unanswered question concerns the long-term durability of phosphoric acid stabilized soil under field conditions. Laboratory tests (that is, rewet strength, air-drying and reimmersion) indicate that resistance to weathering should be no worse than with conventional stabilizers; and field studies now in progress will hopefully clarify this issue within the next few years.

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