Basic Improvements in Phosphate Soil Stabilization

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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 mecha-
nisms of solidification of soil with phosphatic materials.
Many of the treatments appear to be economically com-
petitive with the presently accepted techniques of soil solidi-
fication.

●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 ex-
tensive 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
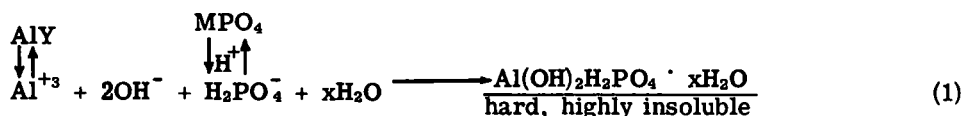the improvement of soil solidification by phosphate.

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 alu-
minum 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 indi-
cate 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:

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

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.

<div align="center">MATERIALS AND METHODS</div>

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:

<div align="center">TABLE 1</div>

<div align="center">PHYSICAL AND CHEMICAL PROPERTIES OF SOILS</div>

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) | | | | | |
| Elemental P,[a] Dry Soil Basis (%) | P (mm/100g) | H_2SO_4/100g Soil | | | HC 1/100g Soil | | |
		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 non-plastic 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		H_2SO_4 (meq/100g)	Ratio H:P	Residual pH	Strength (psi)
Elemental P, Dry Soil Basis (%)	P (mm/100g soil)				
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 $\frac{1}{2}$ 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
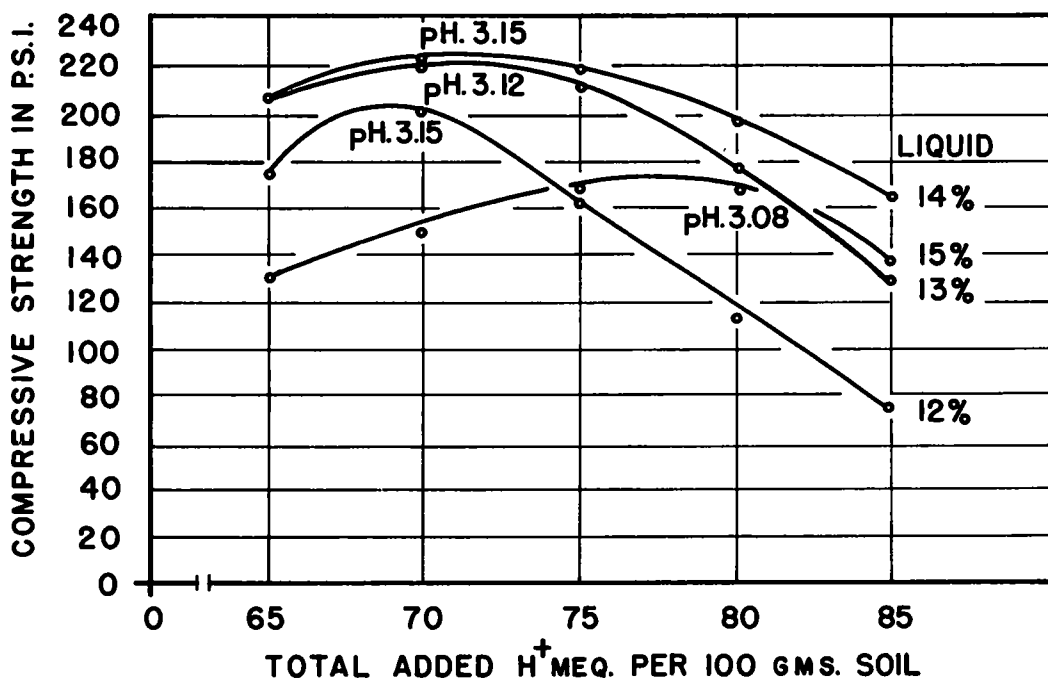
Figure 1. Plots of unconfined compressive strength of soil F-1, treated with 0.68 percent phosphorus as rock phosphate in conjunction with various rates of sulfuric acid vs total added hydrogen ion at various moisture contents.

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) |
| H₃PO₄ | | H₂SO₄ (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 con-
ducted 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 ob-
tained with the phosphoricsulfuric acid treatment. This corroborates the results ob-
tained 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-sulfu-
ric acid treatment. In addition, with equal meq of hydrogen ion the phosphoric-hydro-
chloric treatment results in a lower residual pH. It would be anticipated that the maxi-
mum 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) |
| H₃PO₄ | | 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 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

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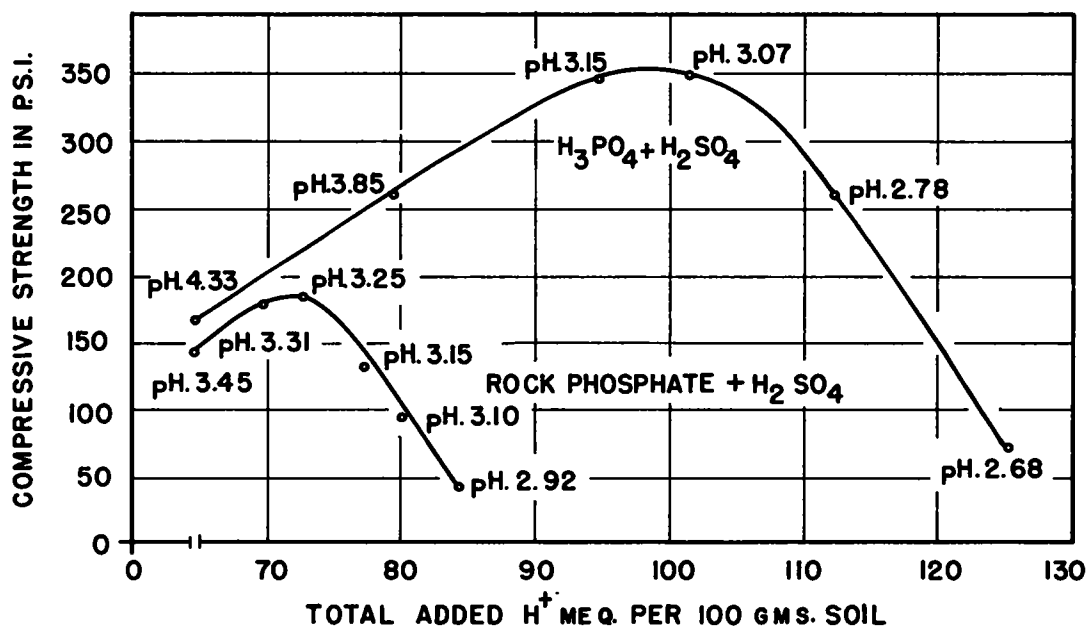

Figure 2. Plots of unconfined compressive strength of soil F-1, treated with 21.7 mmoles of phosphorus as both rock phosphate and phosphoric acid used in conjunction with various rates of sulfuric acid vs total added hydrogen ion.

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
$FeCl_2$	5.4	275
$FeCl_2$	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 (psi)
Salt	mm Salt/100 g Soil	
-	-	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 solidi-
fication 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 phos-
phoric acid-solidified soil. It is interesting that, from the results for the FeCl₂, 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 ap-
pears that the effects of these salts are not necessarily additive to the phosphate treat-
ment.

In conclusion, iron and aluminum salts are effective for increasing the strength im-
parted 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.

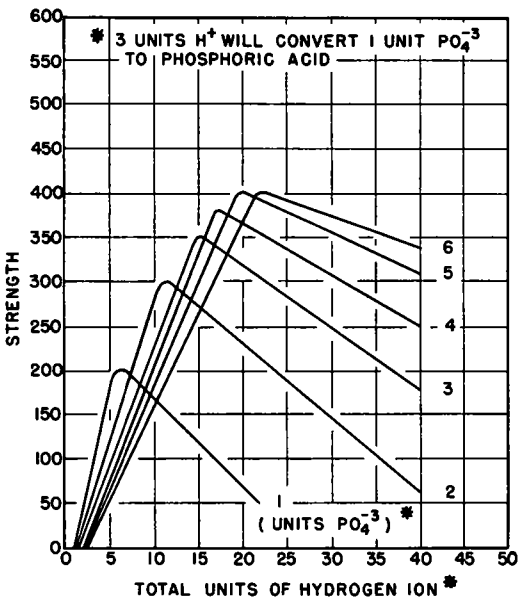If the strength needed in a particular situation corresponds to a strength value of

Figure 3.   Hypothetical plots of strength vs total acid content for various rates of phosphorus as rock phosphate.
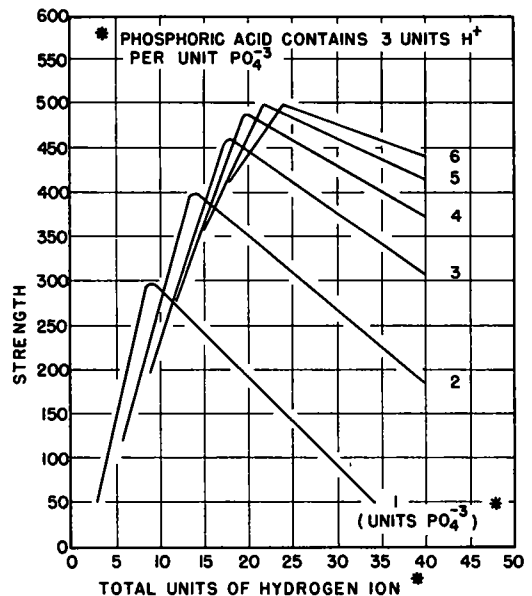
Figure 4.   Hypothetical plots of strength vs total acid content for various rates of phosphorus as phosphoric acid.

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.

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