Proceedings of the Iowa Academy of Science

Volume 69 | Annual Issue Article 59

1962

Use of Phosphoric Acid and Furfuryl Alcohol for Soil Stabilization

G. L. Roderick
Iowa State University

T. Demirel
Iowa State University

D. T. Davidson
Iowa State University

Use of Phosphoric Acid and Furfuryl Alcohol for Soil Stabilization

G. L. RODERICK[1], T. DEMIREL[2], and D. T. DAVIDSON[3]

Abstract. This paper presents results of an investigation of the effects of phosphoric acid and furfuryl alcohol on the resistance and strengths of a clayey soil and of a sandy soil. Results indicate that greater water resistance and higher strengths can be obtained with both soils by using the admixtures. For the sandy soil, a certain optimum amount of phosphoric acid gives the maximum strengths for all furfuryl alcohol contents. The stabilization mechanism for the clayey soil is thought to be a combination of the formation of phosphoric gels and of a resin product of a furfuryl alcohol polymerization reaction. The mechanism for the sandy soil is the formation of the polymerization resin product.

Introduction. The use of phosphoric acid for stabilization of clayey soil is a relatively new method first introduced in 1957 by Lyons (7), who found that compacted clayey soils treated with as little as 2% phosphoric acid have greatly improved resistance to water and weathering. Further studies have been conducted by the Iowa Engineering Experiment Station, M.I.T., the Dow Chemical Company, and the Missouri State Highway Department on the mechanism of the stabilization reaction and on the applicability of this method of soil stabilization to a variety of soils (2, 3, 4, 5, 6, 9, 10). These investigations have shown that non-calcareous clayey soils can generally be stabilized with phosphoric acid.

The use of furfuryl alcohol and sulfuric acid for soil stabilization was studied by Mainfort (8) in 1945. He reported fair results for sandy soils and very little improvement for other types of soils.

This paper presents the results of a preliminary investigation of stabilization of soils with phosphoric acid and furfuryl alcohol. The purposes of the study were to determine if the use of both phosphoric acid and furfuryl alcohol with a clayey soil would give better strength and water resistance properties than those obtained with phosphoric acid alone, and to determine the effect of the resin formed by the reaction of furfuryl alcohol and phosphoric acid on the strength and water resistance properties of a cohesionless sandy soil.

LABORATORY INVESTIGATION

Soils and Admixtures

Two different soils were used. The first was a silty clay, C-horizon Wisconsin loess, and the second was a dune sand (Table 1). The phosphoric acid (85%) was C. P. grade, the furfuryl alcohol was technical grade for laboratory use. Distilled water (pH=6 to 7) was used in all tests.

[1] Graduate Assistant, Iowa Engineering Experiment Station, Iowa State University, Ames, Iowa.
[2] Research Associate, Iowa Engineering Experiment Station, Iowa State University, Ames, Iowa.
[3] Professor of Civil Engineering, Iowa Engineering Experiment Station, Iowa State University, Ames, Iowa.

Table 1. Description and Properties of Soils

	Silty clay, C-horizon Wisconsin loess (Lab No. AR-7)	Dune sand (Lab No. S-6-2)
Textural composition, %		
Gravel (> 2.0 mm)	0	0
Sand (2.0 – 0.074 mm)	0.2	94
Silt (0.074 – 0.005 mm)	60.8	4
Clay (> 0.005 mm)	39.0	2
Predominate clay mineral	Montmorillonite	Montmorillonite
Physical properties		
Liquid limit, °	52.1	..
Plastic limit, %	20.0	..
Plasticity index	32.1	Non-plastic
Chemical properties		
Cat. ex. cap., m.e./gm	23.5	..
Carbonates, %	1.5	Non-calcareous
pH	5.6	..
Organic matter, %	0.2	..
Classification		
Textural	Silty clay	Fine sand
Engineering (AASHO)	A-7-6(18)	A-3(O)

Apparatus Used

Two methods of molding and testing the test specimens were used in this study.

The first method, used in the study with clayey soil, utilizes 2 inch diameter by 2 inch high specimens molded by a dynamic compaction device developed by Davidson and Chu (1) at the Iowa Engineering Experiment Station. Unconfined compression strength tests were made with a proving ring type testing machine.

The second method, used in the study with sand soil, utilizes ½ inch diameter by 1 inch high miniature specimens. These are molded and tested with new devices under development at the Iowa Engineering Experiment Station. Compaction is accomplished by applying static pressure to soil in a mold. The unconfined compressive strength machine utilizes a spring with a specific load-deformation constant, and plots stress versus strain on a chart. This machine for testing miniature specimens was modeled after a larger one developed and used at the Road Research Laboratory, Great Britain (12).

Method of Investigation (Silty Clay Soil)

Specimen preparation. Twelve mix designs were studied. These consisted of 3, 4, and 5% phosphoric acid, each with 0, 2, 4, and 6% furfuryl alcohol (amounts expressed as per cent of the oven dry weight of the soil). Each mix design was prepared with five different moisture contents so density-moisture and strength-moisture relationships could be determined.

The soil (passing #10 sieve) and a portion of the distilled water was machine mixed for one minute, hand mixed ½ minute; the phosphoric acid added, machine mixed for one minute, hand mixed ½ minute; distilled water added to bring the mixture to the desired moisture content, machine mixed one minute, and hand mixed for ½ minute. Immediately after mixing, eight 2 inch diameter by 2 inch high specimens were molded. Moisture samples were taken from the mixture before molding the first specimen and immediately after molding the sixth specimen so the average molding moisture content could be determined. The specimens were measured, weighed, and the first seven wrapped in waxed paper.

Curing. The specimens wrapped in waxed paper were cured for seven days in a humidity room at a temperature of 70 ± 3°F and a relative humidity of not less than 90%. The eighth specimen was air dried at room temperature for seven days.

Testing. At the end of the curing period, three of the specimens cured in the humidity room were tested for unconfined compressive strength (unimmersed strength), and three were completely immersed in distilled water for 24 hours and then tested for unconfined compressive strength (immersed strength). The seventh specimen from the humidity room was allowed to air dry for seven days at room temperature, then was immersed in distilled water for 24 hours and tested for unconfined compressive strength. The eighth specimen (seven day air dry core) was immersed in distilled water for 24 hours and then tested for unconfined and compressive strength.

The average dry density for each mixture was determined from the weight and volume of the first six specimens, and the average molding moisture content.

Method of Investigation (Sandy Soil)

Specimen preparation. Twelve mix designs were studied. These consisted of ½, 1, 2, and 3% phosphoric acid, each with 2, 4, and 6% furfuryl alcohol (amounts expressed as per cent of the oven dry weight of soil).

The soil (passing #40 sieve) was hand mixed with the phosphoric acid, furfuryl alcohol, and enough distilled water to bring the moisture content to the optimum for compaction. The correct weight of mixture to produce a specimen ½ inch in diameter by 1 inch in height with a predetermined dry density was placed in a mold and compacted with static pressure. Twelve such specimens were molded from each mix design.

Curing. Six of the specimens from each mixture were cured for seven days in the humidity room and six were cured by air drying at room temperature for seven days.

Testing. At the end of the curing period, one-half of the specimens from each curing procedure were tested for unconfined compressive strength (unimmersed strength) and the other half were completely immersed in distilled water for 24 hours and then tested for unconfined compressive strength (immersed strength).

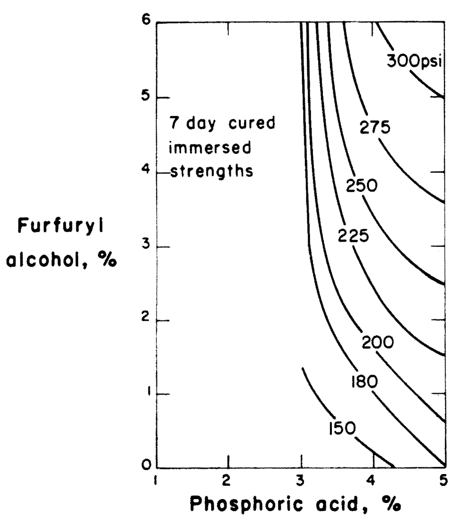
Discussion of Results

Silty Clay Soil

Using average values obtained for the first six specimens given the seven day humidity room cure, curves for dry density, unimmersed strength, and immersed strength versus molding moisture content were plotted. Maximum values and their corresponding molding moistures are presented in Table 2. The mixture composition-maximum immersed strength relationship is shown in Figure 1, and the mixture composition-maximum unimmersed strength relationship is shown in Figure 2.

Figures 1 and 2 show that further investigation with higher and lower phosphoric acid contents and with higher furfuryl alcohol contents would be necessary to fully establish any trends in the mixture composition-strength relationships.

For the mix designs investigated, Figures 1 and 2 show that increasing the furfuryl alcohol content for a fixed phosphoric acid content results in increasing strength. Also, increasing phosphoric acid content for a fixed furfuryl alcohol content results in increasing strengths. Further investigation may establish optimum admixture contents above which no increases in



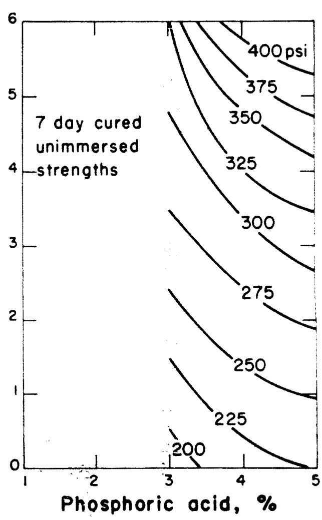


Figure 1. Mixture composition—immersed strength relationship for the clay soil.
Figure 2. Mixture composition—unimmersed strength relationship for the clay soil.

Table 2. Effect of Phosphoric Acid and Furfuryl Alcohol on Maximum Density and Maximum Strength of the clay soil

		Density		7 Day Humidity Room Cure			
				Immersed Strength		Unimmersed Strength	
Phosphoric Acid content, %	Furfuryl Alcohol content, %	Max. density pcf	Molding moisture %	Max. strength psi	Molding moisture %	Max. strength psi	Molding moisture %
	0	108.1	19.2	117	18.8	185	18.2
	2	108.8	18.0	162	16.6	248	16.2
3	4	111.2	16.4	174	16.8	270	16.0
	6	112.1	15.2	180	13.2	319	12.5
	0	110.6	18.1	138	17.2	216	16.9
	2	111.0	17.1	215	17.1	276	16.5
4	4	111.6	15.7	255	15.1	307	15.1
	6	113.4	14.6	298	13.8	418	12.2
	0	110.3	17.5	180	16.8	223	16.6
	2	105.6	18.9	238	17.8	292	13.4
5	4	103.2	16.6	223	16.4	333	12.6
	6	109.8	16.4	312	15.4	445	11.2

strength are obtained. For example, Figure 1 indicates that for constant phosphoric acid contents the maximum immersed strengths may occur with a furfuryl alcohol content of a little more than 6%.

For the seventh and eighth specimens of each mixture, which were given air dry cures as described above, those containing no furfuryl alcohol slaked completely when immersed in distilled water. Those containing furfuryl alcohol were benefited, but specimens swelled and cracked during immersion so that meaningful strength values could not be obtained. For the mix designs investigated, increasing furfuryl alcohol contents brought increasing benefits.

Dune Sand

The test specimens cured for seven days in the humidity room gave no meaningful strength values for either the unimmersed or immersed state. However, the specimens immersed in distilled water did not slake.

The specimens which were cured for seven days by air drying at room temperature could be tested for unconfined compressive strength. The values (average of 3 specimens) obtained are presented in Table 3. The mixture composition-immersed strength relationship is shown in Figure 4.

Table 3. Effect of Phosphoric Acid and Furfuryl Alcohol on Immersed and Unimmersed Strengths of the Sandy Soil

Phosphoric Acid Per cent	Furfuryl Alcohol Per cent	7 Day Air Dry Cure Immersed strength psi	7 Day Air Dry Cure Unimmersed strength psi
	2	0	25
0.5	4	0	46
	6	0	0
	2	17	78
1	4	28	144
	6	55	287
	2	34	87
2	4	153	269
	6	255	398
	2	26	66
3	4	125	250
	6	289	420

For the soil and mix designs investigated, examination of Figure 3 shows that the highest immersed strengths for any furfuryl alcohol content always occurs when the phosphoric acid content is near 2.3%. This relationship is also shown, to a lesser degree, for unimmersed strengths in Figure 4. The 2.3% phosphoric acid content is represented by the vertical dashed lines in Figures 3 and 4.

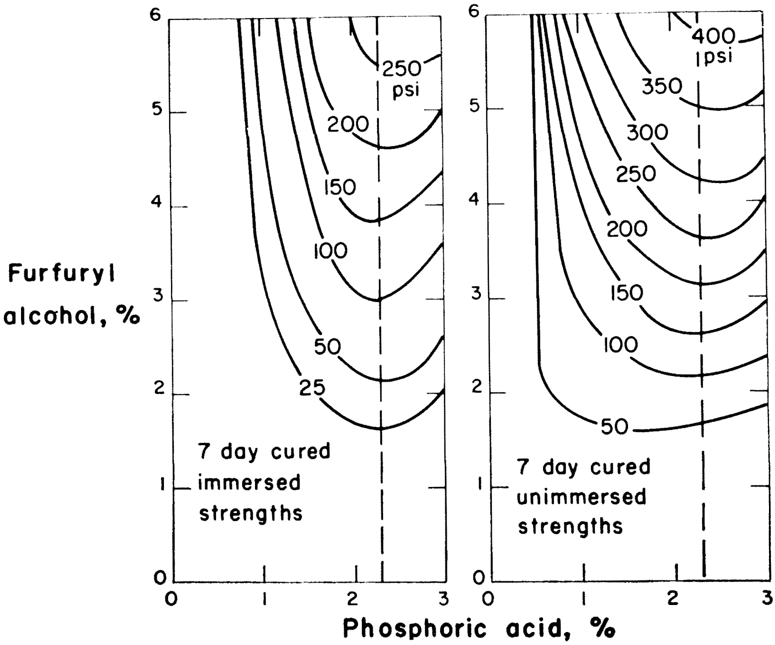


Figure 3. Mixture composition–immersed strength relationship for the sandy soil.
Figure 4. Mixture composition–unimmersed strength relationship for the sandy soil.

The near constant amount of phosphoric acid required to obtain maximum strengths indicates that it serves as a catalyst for a furfuryl alcohol polymerization reaction, a certain amount of phosphoric acid being required to cause the polymerization reaction to begin. The small deviations from 2.3% phosphoric acid content for maximum strengths as shown in Figures 3 and 4 may have been caused by its reaction with small amounts of clay minerals present in the soil.

If the trend described above exists for all sandy soils, the method of investigation can be simplified. For investigation of another sandy soil, three or four specimens with a specific furfuryl alcohol content and phosphoric acid contents which bracket the 2.3% value (say from 2 to 3%) may be prepared, cured and tested. The phosphoric acid content which results in maximum strength may thus be determined. This percentage may then be used with different amounts of furfuryl alcohol to determine the maximum strengths obtainable with those amounts. In an ivestigation, other specimens with phosphoric acid contents on either side of the assumed optimum would also be prepared and tested to establish whether or not it really is the optimum, and to determine if the stress contour lines so formed will be shifted in a horizontal and/or vertical direction from those illustrated in Figures 3 and 4.

If further investigation shows that the relationships illustrated in Figures 3 and 4 are typical for sandy soils in general, a simple design method is suggested. By proceeding vertically along the 2.3% phosphoric acid line until the desired strength value is reached and then proceeding horizontally to the furfuryl alcohol % axis, the amount of furfuryl alcohol which will give the desired strength may be determined. If further investigation shows that sandy soils in general display a certain optimum phosphoric acid content for maximum strengths, but that the stress contours may be displaced horizontally and/or vertically from those in Figures 3 and 4, the above design method could be used with a minimum amount of testing. Three or four specimens with a specific furfuryl alcohol content and with phosphoric acid contents bracketing the probable optimum could be prepared and tested to determine that optimum. Using this optimum phosphoric acid content with a few other amounts of furfuryl alcohol would establish the location of maximum stress values. The design could then be made as described above.

Possible Mechanism

The stabilization achieved by the used of phosphoric acid and furfuryl alcohol with a clayey soil is probably a combination of the reaction of phosphoric acid with clay minerals to form phosphate gels (2, 3), and the formation of resin product of a furfuryl alcohol polymerization reaction catalyzed by the phosphoric acid. The stabilization achieved by use of the admixtures with a sandy soil results from the latter polymerization reaction, very little clay minerals being available for formation of gels.

The resin formed in the polymerization reaction (11) is thought to be higher molecular weight condensation products in which furan rings are linked together by methylene bridges in a linear chain. A network of cross linkages may be formed by addition polymerization involving the nuclear double bonds to complete the resinification. Experimental evidence (11) shows that other secondary reactions further contribute to cross linkage.

The polymerization product apparently adheres to the soil particle surfaces and so binds them together. The tendency for adhering to particle surfaces has been observed when drying moisture samples containing phosphoric acid and furfuryl alcohol. Untreated soil samples in the drying oven become coated with a dark substance apparently adsorbed from vapor phase in the oven.

Conclusions

The following conclusions are made on the basis of the experimental findings:

1. The use of phosphoric acid and furfuryl alcohol with a clayey soil results in higher immersed and unimmersed strengths than those obtained by the use of phosphoric acid alone. More investigation would be required to establish any trends in the strength development.

2. The use of phosphoric acid and furfuryl alcohol with a clay soil gives more water resistance after air drying than does the use of phosphoric acid alone.

3. The use of phosphoric acid and furfuryl alcohol with a sandy soil, when cured by air drying, provides cohesion which results in attainment of immersed and unimmersed unconfined compressive strengths.

4. For the sandy soil used, a certain optimum phosphoric acid content gives the maximum inmmersed and unimmersed strengths for all amounts of furfuryl alcohol.

Acknowledgments

The subject matter of this report was obtained as part of the research being done under Project 450-S of the Engineering Experiment Station of the Iowa State University. This project entitled "Research on Soil Stabilization using Chemicals." is being carried on under contract with the Iowa Highway Research Board and is supported by funds supplied by the Iowa State Highway Commission.

Bibliography

1. Davidson, D. T. and Chu, T. Y. 1955. Some laboratory tests for the evaluation of stabilized soils. Paper presented at the 58th annual meeting of the American Society for Testing Materials, Atlantic City, N. J. Ames, Iowa. Eng. Exp. Sta. Iowa State University. Authors. (Mimeographed report.)
2. Damirel, T., Ben, C. H., and Davidson, D. T. 1961. Use of phosphoric acid in soil stabilization. Highway Research Board Bull. 282:38-58.
3. Demirel, T. and Davidson, D. T. 1961. Reaction of phosphoric acid with clay minerals. Presented at the 40th annual meeting of the Highway Research Board, Washington, D. C.
4. Demirel, T., Roegiers, J. V., and Davidson, D. T. 1958. Use of phosphates in soil stabilization. Iowa Academy of Science, Proceedings, 65:311-316.
5. Guinee, G. W. 1961. Field studies of soil stabilization with phosphoric acid. Presented at the 40th annual meeting of the Highway Research Board, Washington, D. C.
6. Hemwall, J. B. and Scott, H. H. 1961. Basic improvements in phosphate soil stabilization. Presented at the 40th annual meeting of the Highway Research Board, Washington, D. C.
7. Lyons, J. W. 1957. Stabilizing a problem soil-cheaply. Engineering News-Record. 159(7):101-106.
8. Mainfort, R. C. 1951. A summary report on soil stabilization by the use of chemical admixture. Civil Aeronautics Administration Technical Development Report 136.
9. Michaels, A. S. and Tausch, F. W., Jr. 1961. Effects of fluorides, waterproofing agents, and polyphosphoric acid on soil stabilization with acidic phosphorus compounds. Presented at the 40th annual meeting of the Highway Research Board, Washington, D. C.

10. Michaels, A. S. and Tausch, F. W., Jr. 1961. Phosphoric acid stabilization of fine grained soils: improvements with secondary additives. Highway Research Board Bull. 282:28-37.
11. Quaker Oats Company. 1953. Furfuryl alcohol. Quaker Oats Co. Bull. 205:8-10.
12. Road Research Laboratory. 1952. Soil mechanics for road engineers. Her Majesty's Stationery Office, London.

Destructive Distillation Products of Certain Iowa Carbonaceous Shales

LIONEL K. ARNOLD[1]

Abstract. Modified Fischer retort assays resulted in up to 23.2 gallons of oil per ton of shale from carbonaceous shales from southern Iowa coal fields. Destructive distillation was also carried out in two different laboratory retorts. Yields of an oily liquid up to 39.9 gallons per ton were secured. Analyses showed one sample consisting of 89.4 per cent pentene-1 and 9.2 per cent 2-methyl butane with minor amounts of other compounds. Some combustible gas and a solid residue of possible value for road use were also obtained.

INTRODUCTION

In the southern half of Iowa the Pennsylvania sediments are made up largely of clays and shales. Many of the shales are associated with coal seams and contain bituminous material. They may form an overburden on the coal seams of a few inches to as 35 feet or even more. The carbonaceous content of these shales varies considerably, as is obvious from the variation in color through shades of gray to black and from analytical data. The shales constitute a considerable part of the familiar "gob" piles at mine sites.

Because of the scarcity of good road building materials in southern Iowa there has been considerable interest in modifying these shales by heat treatment to use in place of limestone or gravel. As a result a research project sponsored by the Iowa State Highway Commission* has been carried out by the chemical engineering group in the Iowa Engineering Experiment Station at Iowa State University of Science and Technology, Ames, Iowa. Most of the work was concerned with burning the carbonaceous portion of the shale to produce heat enough to convert the inorganic portion of the shale into a product with sufficient strength and abrasion resistance to serve as road material. In addition work was carried out on the destructive distillation of the

[1] Iowa Engineering Experiment Station, Iowa State University of Science and Technology, Ames, Iowa.
* Iowa Highway Research Board Project HR-32.