Effectiveness of Certain Derivatives of Furfural as Admixtures in Bituminous Soil Stabilization

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The effectiveness of furfural derivatives, especially those obtained by reaction with plain and substituted aniline and other aromatic and aliphatic amines, as soil stabilizers by themselves and as additives in bituminous stabilization, has been known since the early 1930's. To obtain maximum benefit from such use, it is necessary with some soil materials to employ catalysts and reaction modifiers that are compatible or even synactive with the furfural derivative in proportions that are fitted to the particular soil-stabilizer combination. This may require more experience and judgment on the part of the user than he is able to muster or afford. It is desirable, therefore, to develop combinations that are effective with all soils likely to be encountered within a certain region, especially with those soils in it that would require special attention if the most economical combination (that is, aniline-furfural, were used). Following this reasoning, laboratory experiments were made in which either or both special catalytic and synactive substances were added to the aniline-furfural combinations or chlorinated anilines were employed in the mixtures. The results of these experiments are discussed.

•THE EFFECTIVENESS of furfural derivatives, especially those obtained by reaction with aromatic amines, as cementing and waterproofing agents for soils has been known since the early 1930's (1, 2). Their stabilization potential for both cohesive and granular soils, by themselves and also as additives in bituminous stabilization, was thoroughly investigated during the 1940's, and the general principles underlying their effectiveness were established during that time (3, 4, 5, 6). Within recent years, some of the knowledge of the 1940's has been rediscovered, indicating that a good deal of this knowledge has been forgotten or had never reached those for whom the publications had been intended. It is the purpose of the present paper to add to the available information on this subject and to clarify certain extant questions.

The basic problem in the stabilization of cohesive soils is to maintain part of the water-induced cohesion, but to control excessive water intake (7). Systems of this kind possess sufficient cohesion for all practical purposes and they also have the ability to breathe; that is, to prevent water accumulation, which is likely to occur beneath water-impervious layers. The water affinity of a soil is a function of the extent and character of the internal surface and of the type and number of the exchangeable ions. Treatment with organic amines aims to control the water affinity of soils by replacing some of the water-attractive ions by the amines that possess the amino group as cationically active head and a water-repellent body represented by the remainder of the organic molecule. If such cation exchange takes place on the basal planes of the clay minerals, then the lumpy organic molecule will interfere greatly with the parallel force fields on such planes and will thus reduce the amount of osmotic swelling possible in such soils. The relationship between electric structure on the basal plains and osmotic swelling has been discussed elsewhere (8).

TABLE 1

SIZE COMPOSITION OF N.J. HAGERSTOWN SOIL

Separate	Size (mm)	Bouyoucos Method (%)	ASTM Method (%)
Sand	1 - 0.05	10.5	12.2
Silt	0.05 - 0.005	51.5	74.3
Clay	<0.005	38.0	13.6
Colloids	<0.002	20.0	6.7

To effect a replacement of the natural cations present in the soil for cations derived from the organic amines, enough moisture must be present to induce these cations to get out of their places in the mineral surfaces and into the water phase. In addition, it is necessary that the system be acid either throughout or locally, by having close combinations or associations of the amines with inorganic or organic acids or acid-salt complexes. It is also advantageous if the released exchange ions form insoluble salts with the respective acids. In the case of calcium carbonate particles (such as coral beach sands) coatings of calcium salts, with either inorganic or organic anions, possessing very low solubility must be produced in the stabilizing process.

Osmotic swelling increases with decreasing charge of inorganic exchange ions. Also, in the monoionic soils, except for the hydrogen exchange ions, the pH increases with decreasing charge of the exchange ions. Hydrogen soils tend to become iron and aluminum soils when stored long because of the interaction of the hydrogen with the skeleton of the clay mineral. With respect to mechanical resistance of soils, it is, of course, well known that such resistance increases with increasing densification of the soil. However, if increased dry density is purchased at the price of too low a moisture content (that is, one that is insufficient to bring about the desired exchange of the natural ions on the soil for the amine ions), then compaction to higher densities may actually result in lesser stabilization effectiveness, especially with respect to weathering resistance.

The following presentation is divided into three parts:

1. The preparation of the monoionic modifications of N.J. Hagerstown soil and their response to stabilizing treatment with two percentages of the two aniline -1 furfural reaction product, on specimens prepared at two different densities and different moisture contents.
2. The effect of aniline-furfural admixtures to bitumen (MC-2) on the stabilization of natural N.J. Hagerstown soil in comparison with that of other admixtures and stabilizing agents.
3. The effect of A-F admixtures on bituminous stabilization of local Princeton red clay and is also concerned with questions of general importance, such as overcompaction, water requirements, and physical significance of testing procedures.

Characterization of Soil Materials Employed

The soil employed was a Hagerstown clay (B-horizon of the profile) obtained in the vicinity of Peapack, N.J., on a location designated as typical by the Soils Department of Rutgers University, New Brunswick, N.J. The latter institution has been using material from the same location for its own investigations. This allowed a certain mutual checking of the experimentally determined soil characteristics.

Hydrometer analyses were made according to the Bouyoucos and the ASTM methods. The results are given in Table 1. As observed on other occasions, the ASTM method often fails to disperse and register the finer soil fractions properly. The natural soil sample had the following chemical characteristics; for a cation exchange capacity of 9.6 meq per 100 g of soil, the exchangeable cations per 100 g of soil are H, 0.0 meq; Ca, 5.83 meq; Mg, 4.27 meq; and K, 0.007 meq.

The value for the cation exchange capacity given is that obtained by electrometric titration; this value is identical with the one obtained by Rutgers College in their investigations; a slightly smaller value was obtained using the ammonium acetate method. The value of 9.6 was employed in the making of the homoionic soil modifications.

PREPARATION OF HOMOIONIC MODIFICATIONS

The H-, Na-, K-, Mg-, Ca-, Al-, and Fe- soils were prepared and employed in this investigation. They were made in batches of 60 lb of soil (obtained by quartering of the total soil sample) dispersed in about 50 l of distilled water. As reaction vessels, paraffined galvanized iron cans were employed, the paraffine preventing reaction of the soil and of the chemicals with the metal.

The H- soil was prepared by adding hydrochloric acid in sufficient amount to reduce the pH of the soil suspension to about 4, and washing off the chlorides formed in the process.

The Na-, K-, Mg-, and Ca-soils were made by adding the calculated amounts of hydroxides to the previously prepared H-system. It is of interest that approximately 7,000 gal of distilled water were required to wash the chlorine ions out of the H- soil batches.

The Fe- and Al- soils were prepared from the natural soil by adding an excess of the respective chlorides, and by washing the ionic reaction products and the excess Fe- and Al- salts by means of distilled water until only a faint trace of chlorine ion was found in the soil-water system.

The seven homoionic modifications and the natural soil were dried at a temperature of about 150 F, pulverized to pass a No. 10 sieve, and stored in galvanized cans.

The physical and chemical properties of the different soil modifications are given in Table 2. Though the data speak for themselves, attention is called to the following points:

1. The liquid limits and consequently the plasticity indexes of the Na- and K-modifications appear to be rather low. This may possibly be due to a sampling error. In the preparation of the K- and Na- modifications, the clay material separated from the remainder of the soil and formed very hard crusts in drying. Although this material was ground with the remainder of the soil and well mixed with the latter, it is possible that, in getting the -40 sieve fraction for the consistency tests, a disproportionate amount of these hard aggregations remained on the sieve.

TABLE 2

PHYSICAL AND CHEMICAL PROPERTIES OF THE NEW JERSEY HAGERSTOWN HOMOIONIC SOILS

Soil	pH	Liquid Limit (%)	Plastic Limit (%)	Plastic Index	Specific Gravity (H_2O)	Specific Gravity (xylene)	Homoionic Ion Saturation[a] (meq/100 g)	Shrinkage Limit (%)	Moisture-Density Relationship: Proctor H_2O (%)	Moisture-Density Relationship: Proctor Max Dry Dens. (pcf)	Moisture-Density Relationship: Mod. AASHO H_2O (%)	Moisture-Density Relationship: Mod. AASHO Max Dry Dens. (pcf)
Nat	7.72	29.5	21.8	7.7	2.68	2.71	7.1	20.5	18.8	103.0	16.5	113.0
Na	9.00	22.5	18.7	3.8	2.68	2.71	5.5	22.5	17.7	105.6	16.4	110.4
K	8.62	24.5	21.3	3.2	2.68	2.70	6.0	23.3	20.7	102.0	17.8	110.2
H	5.62	32.2	28.6	3.6	2.68	2.72	0.5	26.2	19.5	102.3	17.8	108.9
Al	4.92	30.3	25.3	5.0	2.68	2.71	0.5	27.9	20.2	103.2	18.3	108.2
Fe	5.80	33.3	26.0	7.3	2.68	2.71	0.0	28.4	20.8	100.3	19.4	108.9
Mg	7.01	29.3	20.0	9.3	2.68	2.71	7.6	22.8	17.7	104.9	16.0	112.3
Ca	7.70	29.0	21.0	8.0	2.67	2.70	9.5	24.2	18.3	105.0	16.7	112.8

[a] NH_4Ac extractable ions.

TABLE 3

BATCH COMPOSITION OF SPECIMENS MADE AT PROCTOR DENSITY

Property	Soil							
	Nat	Na	K	Ca	Mg	H	Fe	Al
Hygroscopic moisture (%)	3.4	2.9	7.3	4.4	2.0	7.8	6.9	4.2
Specimen weight (g)	209.0	211.5	210.0	212.0	210.5	209.0	207.0	212.0
Air-dry soil (g)	1,945	1,975	2,000	1,995	1,950	2,015	1,965	1,965
H_2O added (cc)	289	284	249	266	300	219	255	302
1 percent[a] (cc):								
Aniline	12.4	12.5	12.1	12.5	12.5	12.1	12.0	12.4
Furfural	5.4	5.5	5.4	5.5	5.5	5.4	5.3	5.4
2 percent[a] (cc):								
Aniline	24.8	25.0	24.2	25.0	25.0	24.2	24.0	24.8
Furfural	10.8	11.0	10.7	11.0	11.0	10.7	10.3	10.8

[a] Amount of water employed in these specimens was reduced equivalent to volume of liquid stabilizers added.

2. The pH of the H- soil changed after the wet preparation from about 4 to 5.6, the soil having been dried and redispersed. The Hagerstown soil is a reddish soil and as such contains surface-adsorbed iron and aluminum hydroxides. Because these hydroxides were not entirely removed, they had a chance to react with the exchange positions, probably resulting in at least partial Fe- and Al- modifications.
3. The specific gravities in xylene were somewhat larger than those in water. This also seems to be related to the coating of the soil particles with iron and aluminum hydroxides.
4. The low values for ionic saturation of the H-, Al-, and Fe- soils are due to the fact that the trivalent Fe- and Al- ions cannot be replaced by ammonium; therefore, these values do not indicate actual ionic saturation.

Preparation and Testing of Specimens

The stabilizers employed were 1 and 2 percent based on the dry weight of the soil of a combination of 2 parts of aniline and 1 part of furfural in liquid form. To replace every exchangeable ion in the soil with the cation produced by the reaction of 2 mols of aniline and 1 mol of furfural would have required 2.68 percent of the 2A-1F combination. Cylindrical test specimens (2 in. by 2 in.) were prepared using the floating ring compaction method. The dry compacted densities corresponded to those previously determined for the different ionic modifications by both the Proctor and the modified AASHO methods, as did the quantities of moisture employed. Ten specimens were made in each batch and cured for 7 days without loss of moisture in a moist room (90 to 100 percent relative humidity). Duplicate specimens were submitted to the following exposures before being tested for compressive strength:

1. One day of capillary absorption followed by 7 days water immersion.
2. One cycle of wetting and drying.
3. Four cycles of wetting and drying.
4. One cycle of freezing and thawing.
5. Four cycles of freezing and thawing.

One cycle of wetting and drying consisted of 24 hr of complete immersion in water followed by 24 hr of drying in an oven at 60 C (140 F). All specimens undergoing the wetting and drying test were immersed in water for 24 hr after the last drying cycle before they were tested for compressive strength.

One cycle of freezing and thawing consisted of 24 hr of freezing at -10 F followed by 24 hr of immersion in water. All specimens undergoing freezing and thawing cycles were immersed in water 24 hr before the first freezing cycle.

TABLE 4

BATCH COMPOSITION OF SPECIMENS MADE AT MODIFIED AASHO DENSITY

Property	Soil							
	Nat	Na	K	Ca	Mg	H	Fe	Al
Hygroscopic moisture (%)	3.4	3.5	7.3	4.4	2.0	7.8	6.9	4.2
Specimen weight (g)	225.0	220.0	221.0	224.5	222.5	219.0	222.5	219.0
Air-dry soil (g)	2,121	2,065	2,150	2,106	2,080	2,135	2,120	2,060
H_2O added (cc)	269	260	210	252	286	218	233	261
1 percent (cc):								
Aniline	13.3	13.1	13.1	13.3	13.3	12.9	12.9	12.9
Furfural	5.9	5.8	5.8	5.9	5.7	5.7	5.7	5.7
2 percent (cc):								
Aniline	26.6	26.2	26.2	26.6	26.6	25.8	25.8	25.8
Furfural	11.8	11.6	11.6	11.8	11.8	11.4	11.4	11.4

Tables 3 and 4 give the batch compositions for the specimens and densities employed. Table 5 gives the compressive strength of the corresponding, compacted unstabilized monoionic and natural soils after curing for 7 days without loss in moisture content.

Test Results

The test results are given in Table 6 and Figure 1. The discussion of the test data is based mainly on the compressive strength values, because of the close relationship between moisture content and compressive strength of the specimens, and the obviously primary importance of the latter for engineering purposes.

It is of interest to present first a few general relationships on the following items—(a) the beneficial or deteriorating effect of the different weathering exposures, (b) the effect of density on the initial compressive strength and on the resistance of the specimens to deterioration, and (c) the average compressive strength of the untreated and unweathered specimens as compared with that of the treated but weathered specimens:

1. The average compressive strength was 50 and 128 psi, respectively, for untreated, unweathered specimens compacted at the Proctor and modified Proctor densities. The modified Proctor specimens were therefore two and one-half times as strong as the standard Proctor specimens.
2. The average compressive strength over all ionic soil modifications, all stabilizing treatments, and all weathering exposures was 64 psi for the standard Proctor and 136 psi for the modified Proctor density. The treated modified Proctor specimens were, therefore, more than twice as good as the treated standard Proctor specimens.

TABLE 5

COMPRESSIVE STRENGTH OF UNSTABILIZED HOMOIONIC N. J. HAGERSTOWN SOIL

Soil Modification	Compressive Strength (psi)	
	Proctor Density	Modified Proctor Density
Nat	50	140
H	75	175
Na	50	140
K	50	145
Mg	50	110
Ca	50	125
Al	50	95
Fe	25	95
Avg.	50	128

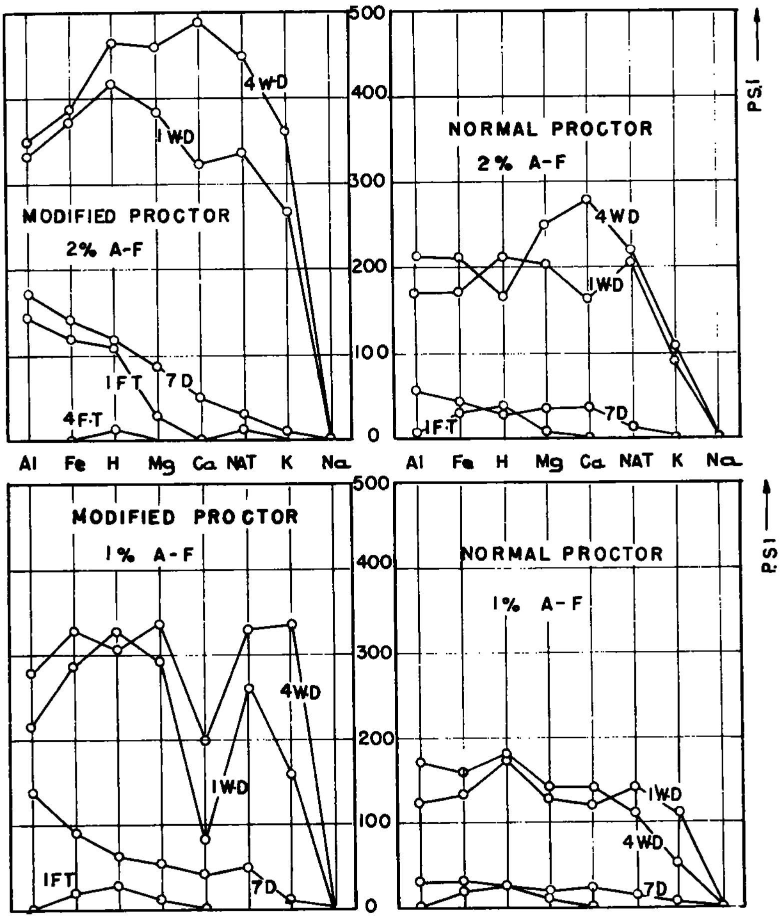

Figure 1. Compressive strength of treated soil specimens.

3. The average compressive strength over all ionic modifications, all stabilizing treatments, and all weathering exposures was 128 and 106 percent, respectively, of that of the average value of the non-treated and non-weathered specimens at the Proctor and modified Proctor densities.

4. The beneficial or detrimental effect of the different weathering exposures is shown by the average compressive strength values given in Table 7 for the Proctor and modified Proctor densities.

The relative susceptibility to aniline-furfural stabilization of the different ionic soil modifications is indicated by the strength values averaged for each ion over the two percentages of admixture, the two densities, and all pretest treatments (Table 8).

INFLUENCE OF RESIN ADMIXTURE ON STABILIZING EFFECTIVENESS OF MC-2 CUTBACK

In the investigation presented in the preceding part, the specimens were permitted to cure for 7 days without loss of water before being submitted to the different exposures. In previous tests, partial drying was allowed during the curing period. It is still an open question which curing procedure is preferable; that is, which corresponds most closely to field conditions. As a contribution to the eventual settlement of this question, and also for the purpose of a direct comparison between resinous and bituminous soil stabilization, a second set of experiments was run, employing the natural Hagerstown

TABLE 6

COMPRESSIVE STRENGTH OF TREATED SOIL SPECIMENS AFTER DIFFERENT WEATHERING EXPOSURES

A-F	Compacting Density	Treatment	Exchange Ion							
			Al	Fe	H	Mg	Ca	Nat	K	Na
A_o 1%	Mod Proctor	7-day immers.	138	96	63	54	42	50	21	0
		1 W-D	217	284	326	292	80	268	163	0
		4 W-D	276	326	305	334	200	330	234	0
		1 F-T	84	63	67	21	0	15	0	0
		4 F-T	0	0	8	0	0	0	0	0
	Normal Proctor	7-day immers.	29	29	25	21	21	13	6	0
		1 W-D	122	134	173	130	121	142	117	0
		4 W-D	171	166	180	142	142	117	52	0
		1 F-T	0	21	27	13	0	0	0	0
		4 F-T	0	0	4	0	0	0	0	0
B_o 2%	Mod. Proctor	7-day immers.	173	142	129	89	49	31	11	0
		1 W-D	333	372	422	382	324	333	266	0
		4 W-D	350	386	466	460	488	475	364	0
		1 F-T	146	120	111	31	0	13	0	0
		4 F-T	0	0	13	0	0	0	0	0
	Normal Proctor	7-day immers.	58	44	32	36	35	13	0	0
		1 W-D	173	173	213	204	164	208	93	0
		4 W-D	213	213	168	248	275	222	107	0
		1 F-T	7	31	36	9	0	0	0	0
		4 F-T	0	0	7	0	0	0	0	0

TABLE 7

AVERAGE COMPRESSIVE STRENGTH FOR PROCTOR AND MODIFIED PROCTOR DENSITIES

Type of Weathering	Average Compressive Strength (psi)		
	Proctor	Modified Proctor	Avg.
(1) 7 days immersion	22.5	65	44
(2) 1 wetting-drying	135.5	254	195
(3) 4 W-D	151	313	232
(4) 1 F-T	8	42	25
(5) 4 F-T	4	0.7	2.3
(0) none	50	128	89

TABLE 8

Property	Ionic Modification							
	H	Fe	Al	Mg	Nat	Ca	K	Na
Avg. compres. str. (psi)	139	130	125	123	112	97	72	0
pH of soil mod.	5.6	5.8	4.9	7.0	7.7	7.7	8.6	9.0

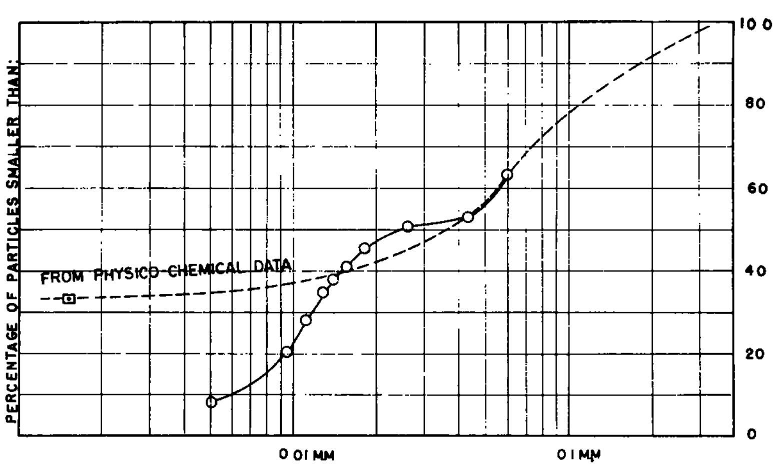

Figure 2. Grain-size cumulative curve.

TABLE 9

Identification	Stabilizing Admixture[a]
I	10% MC-2
II	10% MC-2 + 2.5% $Ca(OH)_2$
III	10% MC-2 + 10% $Ca(OH)_2$
IV	8% MC-2 + 0.06% aniline-furfural
V	8% MC-2 + 0.12% aniline-furfural
VI	8% MC-2 + 0.24% aniline-furfural
VII	1% Tall oil (25% neutralized with NaOH)
VIII	10% MC-2 + 0.24% aniline-furfural
IX	10% MC-2 + 0.24% high resin tall oil 1/4 neutralized
X	10% MC-2 + 0.24% normal tall oil 1/4 neutralized

[a] Percentages based on dry soil weight.

soil, moist and dry curing, modified Proctor compaction, and stabilizing admixtures as given in Table 9.

Tests Performed and Results

Two curing methods—wet and dry curing for a period of 7 days—were employed. Thereupon, duplicate specimens for each type of curing were submitted to the same exposure conditions as described in the preceding part and tested for compressive strength. The test data are given in Table 10. The over-all average performance of the stabilized specimens as a percentage of the average compressive strength of the non-treated, non-weathered compacted specimens was 134 percent for the dry cure and 118 percent for the moist cure.

This difference was due mainly to the poor performance of the moist-cured specimens in the freeze-thaw cycles. If the freeze-thaw data are omitted in the averaging, then one obtains 187 percent for the dry cure average and 174 percent for the moist cure average.

Because the freeze-thaw test may be too severe for many actual construction conditions, the effectiveness of the different stabilizers has been evaluated in two ways: (a) employing all test data including those obtained in the freeze-thaw tests; and (b) employing all but the freeze-thaw data. This evaluation is given in Table 11. The respective

TABLE 10

AVERAGE COMPRESSIVE STRENGTH AFTER DIFFERENT EXPOSURES

Cure	Stabilizer	Average Compressive Strength (psi)						
		7-Day Immersion	1 Wet-Dry	4 Wet-Dry	1 Freeze-Thaw	4 Freeze-Thaw	Avg.	Perf.[a]
Dry	I	34	182	394	28	19	131	93
	II	204	358	439	250	161	282	201
	III	350	546	483	353	283	403	287
	IV	32	191	358	24	14	124	89
	V	50	293	454	32	18	169	121
	VI	91	296	461	54	21	185	132
	VII	38	42	41	27	0	39	27
	VIII	127	342	532	115	25	228	163
	IX	49	205	430	32	19	147	105
	X	83	218	431	48	21	160	114
	Avg.	106	277	402	96	58	188	134
	Perf.	76	197	287	68	41	134	
Wet	I	32	135	322	24	0	103	74
	II	251	318	455	204	94	264	188
	III	309	474	600	325	188	379	270
	IV	35	169	402	17	0	125	89
	V	54	185	400	10	0	130	93
	VI	72	233	496	8	0	162	116
	VII	73	43	35	26	0	35	25
	VIII	107	264	546	29	0	189	135
	IX	90	126	361	16	0	119	85
	X	104	178	425	19	0	145	103
	Avg.	113	213	404	68	28	165	118
	Perf.	80	152	289	48	20	118	

[a] Average compressive strength as a percentage of compressive strength of untreated and unweathered compacted specimens, which was 140 psi.

data speak for themselves. Of course, their engineering evaluation must take into account such factors as materials costs, effect of admixtures on the ease and hence economics of mixing and compaction, cost of transportation, etc.

STABILIZATION STUDIES ON LOCAL RED CLAY SOIL FROM PRINCETON, N.J.

The local red clay soil from Princeton, N.J., possesses certain features that are of significance in bituminous soil stabilization, but which are likely to be overlooked by the average practitioner. The soil is derived from a triassic red shale which itself was a well-leached clay soil previous to geologic consolidation. The grain-size composition obtained by the ASTM method and the moisture density relationships under compaction by the 2,000-psi static load method were determined by Tschebotarioff whose plots of these properties are shown in Figures 2 and 3 (9).

The ASTM grain-size analysis method gave less than 10 percent -2-μ material and there was a definite break in the cumulative size curve at 0.03 mm. On request by Tschebotarioff, a physico-chemical study of this soil had been undertaken by the senior author (10). This study included the following:

1. Separation of the -2-μ fraction from the whole soil and determination of its mineralogical character by means of the DTA method.

2. Determination of the base exchange capacity of the -2-μ fraction and of the whole soil by potentiometric titration.
3. Determination of water adsorption isotherms for the whole soil and the separated -2-μ fraction, and calculation of the base exchange capacity and clay content of the whole soil from known relationships between these properties and water vapor absorption under specified conditions.

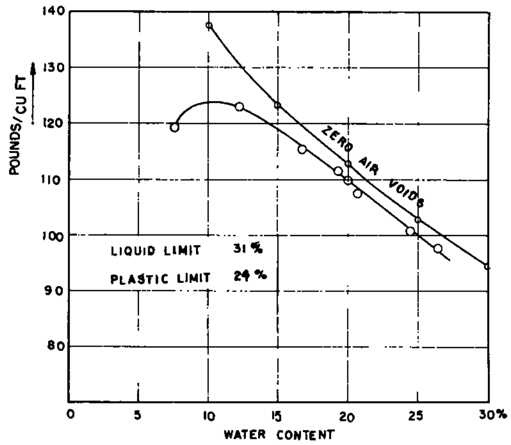

Figure 3.

The extracted clay fraction consisted almost entirely of kaolinite with an effective particle size smaller than 0.1-μ. Because of this small particle size, the experimentally determined base exchange capacity of the -2-μ fraction had the relatively high value of 30.4 meq per 100 g of clay. The base exchange capacity of the whole soil was about 9.6 meq per 100 g of soil. This gives a calculated clay content for the whole soil of about 32 percent, whereas clay contents calculated from the isothermal absorption data ranged from 28.4 to 32 percent.

According to the physico-chemical evidence, the red soil contained about 32 percent of -0.1-μ clay. In its geological history, this clay had been aggregated with sufficient force that even after weathering to the present soil, this clay content did not become apparent in the ASTM analysis nor in the moisture-density data obtained by compaction tests. On the other hand, intensive mechanical working of the soil changed its plastic and liquid limits in a similar manner as known and reported for certain lateritic soils (11) showing that the clay could be activated by mechanical working in the presence of water and probably also in a new chemical environment; for instance, such as created by chemically active soil stabilization agents.

Using the 2,000-psi static compression method, Tschebotarioff had obtained a maximum density of about 123 pcf at an optimum moisture content of about 12 percent.

TABLE 11

RATING OF TREATMENTS[a]

Treatment		Rating	
		Incl. F-T Data	Excl. F-T Data
III	10% MC-2 + 10% $Ca(OH)_2$	270	330
II	10% MC-2 + 2.5% $Ca(OH)_2$	188	244
VIII	10% MC-2 + 0.24% A-F	135	218
VI	8% MC-2 + 0.24% A-F	116	191
X	10% MC-2 + 0.24% Tall oil, normal	103	174
V	8% MC-2 + 0.12% A-F	93	152
IV	8% MC-2 + 0.06% A-F	89	144
IX	10% MC-2 + 0.24% Tall oil, high rosin	85	137
I	10% MC-2	74	116
VII	1% Tall oil, 25% neutralized with NaOH	25	36

[a] Moist curing, modified Proctor compaction. Percentages of all admixtures based on dry weight of soil. For complete base exchange with A-F combination, 2.68 percent of latter would have been required. Hence, maximum A-F admixture of 0.24 percent represents 9 percent of base exchange capacity of soil involved.

Approximately the same values were obtained in the laboratories of the Soil Stabilization Development Corporation with the Dictert compactor (20 blows), whereas the standard Proctor hammer method gave about 105 pcf at an optimum moisture content of 20 percent. The liquid limits and plastic limits, found by Tschebotarioff to be 31 and 25 percent, respectively, were duplicated by the SSDC in normal procedure, but both values became smaller with increased working of the moist soil. The same happened in the case of the shrinkage limit which was found to range between a high of 25 percent and a low of 17 percent.

TABLE 12

COMPOSITION OF ADDITIVES

Designation	Component	Weight Proportion
A	3,4 bichloraniline	3
	furfural	1
B-1	Aniline	2
	Furfural	1
	Het acid	4 17
B-2	Aniline	2
	Furfural	1
	Het acid	2 1
C-1	Aniline	2
	Furfural	1
	Isophthalic acid	1 78
C-2	Aniline	2
	Furfural	1
	Isophthalic acid	0 89

Stabilization Experiments

Despite the warning signs that could be read in the results of the physico-chemical and consistency tests, the SSDC desired to utilize the advantage that seemed to lie in the great density obtained by both the static and the Dictert compaction method. Accordingly, soil-bitumen-water mixtures were designed to give dry soil densities of 2-in. cylindrical test specimens by the use of the Dictert method in the order of 120 pcf. Various contents of MC-2 cutbacks were used in the mixtures, whereby the lubricating effectiveness of the volume of cutback employed was considered as one-half that of the

TABLE 13

COMPRESSIVE STRENGTH OF SPECIMENS MADE WITH 8 PERCENT MC-2 CUTBACK ASPHALT CONTAINING 0.5 TO 2 PERCENT ADDITIVES[a]

Additive		Compressive Strength (psi)					Water Intake (% of air dry wt.)			
No.	%	0 Days	1 Day	7 Days	14 Days	28 Days	1 Day	7 Days	14 Days	28 Days
A	0.5	403	243	103	50	38	4.5	8.5	13.7	18.3
	1.0	390	253	108	65	28	2.3	7.4	12.3	17.2
	1.5	350	238	123	65	48	2.6	6.6	11.8	16.1
	2.0	365	222	157	60	53	3.0	7.0	13.3	15.8
B-1	0.5	333	212	57	32	30	3.3	11.0	18.0	20.3
	1.0	325	225	77	40	43	3.1	9.6	15.2	17.8
	1.5	370	233	87	50	50	2.8	9.3	14.8	18.4
	2.0	375	220	67	45	35	3.5	10.7	15.5	18.6
B-2	0.5	318	213	72	35	30	3.4	11.3	16.3	19.2
	1.0	350	233	90	50	37	2.5	9.0	15.5	18.0
	1.5	325	225	80	47	43	2.8	8.7	15.0	18.3
	2.0	343	260	95	55	50	3.0	9.2	15.2	17.8
C-1	0.5	280	180	37	25	22	3.0	17.9	18.3	20.3
	1.0	293	211	76	43	42	2.7	10.1	15.9	16.5
	1.5	318	206	65	36	45	2.2	10.3	15.3	16.0
	2.0	330	243	110	65	67	1.8	8.3	17.0	14.8
C-2	0.5	325	187	41	25	18	2.9	14.5	12.8	17.3
	1.0	317	209	75	53	42	2.0	9.6	15.1	16.0
	1.5	305	213	78	30	44	2.3	10.0	14.8	16.5
	2.0	308	236	93	50	53	1.8	8.6	13.8	15.7

[a] Based on weight of cutback in air-dry condition and after 1, 7, 14, and 28 days of immersion.

TABLE 14

COMPRESSIVE STRENGTH OF SPECIMENS AS FUNCTION OF ADDITIVE COMPOSITION[a]

Additive	Compressive Strength (psi)					Avg. Water Intake (% of air-dry wt.)			
	0 Days	1 Day	7 Days	14 Days	28 Days	1 Day	7 Days	14 Days	28 Days
A	377	241	123	60	42	3.1	7.4	12.8	16.8
B-1	351	222	72	42	40	3.2	10.2	15.9	18.8
B-2	334	233	84	47	40	2.9	9.5	15.5	18.3
C-1	305	210	72	42	44	2.4	11.6	16.6	16.9
C-2	314	201	72	40	40	2.3	10.7	14.1	16.4

[a] Averaged over four different percentages of additive employed.

same volume of water. This means that the total compaction water requirements were reduced by one-half the volume of the cutback employed. The amount of MC-2 employed ranged from 6 to 10 percent of the weight of the dry soil. The cutback was used by itself as well as with various additives. The bitumen-treated specimens were cured in the laboratory air to constant weight and then submerged in water at room temperature.

All these high-density specimens, irrespective of bitumen and additive percentage and composition, cracked sooner or later after immersion in water, showing expansion failure typical for overcompacted specimens. It was then decided to design test specimens at the Proctor dry density of 105 pcf and an optimum liquid content of 20 percent by weight of the dry soil. The latter was to be supplied by 12 percent of water, which corresponded to the lubricating needs for the maximum density in the 2,000-psi static and in the Dictert compaction, and 8 percent of the MC-2 cutback. With this mix design and speciman density, stabilization of the red clay soil could be achieved with the help of certain additives to the bitumen.

Effectiveness of Certain Furfural-Derived Additives

In the course of stabilization studies with this soil, it was decided to check the possibility of obtaining better results than using the plain aniline-furfural compound by employing dichlor aniline instead of the aniline or by using the chlorinated Het acid instead of isophthalic acid which in previous work had proven itself, similarly to pentachlorophenol, as a most effective catalytic and synactive agent of the 2A-F additive (12). Accordingly, specimens were fabricated with the previously stated mix design and density, but in which the MC-2 cutback contained 0.5, 1, 1.5, and 2 percent, respectively, of the additives designated as A, B-1, B-2, C-1, and C-2 whose compositions are given in Table 12.

The weight of the compacted 2- by 2-in. cylindrical specimens averaged 208 g as fabricated. They were permitted to dry in air to constant weight which was in the vicinity of 187 g. Ten specimens were made of each composition, two of which were weighed and tested for compressive strength after air curing, and two after air curing plus 1, 7, 14, and 28 days, respectively, of immersion in water. The results of these tests are given in Table 13. Table 14 gives the compressive strength and water intake values as a function of the additive composition, obtained by averaging over all four different percentages of the additive used, whereas Table 15 gives compressive strength and water intake data of the most effective compositions as judged by the test results after 28 days of immersion.

In accordance with the test results, the additive compositions can be rated in the following order of decreasing effectiveness: C - 1 > A = C - 2 > B - 1 = B - 2. If the ionically effective mass is calculated per unit weight of additive,

A > C - 2 > C - 1 > B - 2 > B - 1
0.78 0.77 0.63 0.59 0.42

TABLE 15

COMPOSITIONS GIVING BEST DATA AFTER 28 DAYS OF IMMERSION FOR EACH TYPE OF ADDITIVE

Additive		Compressive Strength (psi)					Water Intake (% of air-dry wt.)			
No.	%	0 Days	1 Day	7 Days	14 Days	28 Days	1 Day	7 Days	14 Days	28 Days
A		365	222	157	60	53	3.0	7.0	13.3	15.8
B-1	1.5	370	233	87	50	50	2.8	9.3	14.8	18.4
B-2	2.0	343	260	95	55	50	3.0	9.2	15.2	17.8
C-1	2.0	330	243	110	65	67	1.8	8.3	--	14.8
C-2	2.0	308	236	93	50	53	1.8	8.6	13.8	15.7

If the additive compositions are ranked in accordance with the relative proportions of cation equivalents per unit mass of admixture,

$$\begin{array}{ccccc} C-2 & > C-1 & > A & > B-2 & > B-1 \\ 1.00 & 0.81 & 0.78 & 0.76 & 0.55 \end{array}$$

The C-2 composition contains about 5.5 mmole of amine per gram of additive; that is, about 0.9 mmole per 100 g of soil if the additive is 2 percent of the weight of the MC-2 employed. Because the soil had a base exchange capacity of 9.6 meq per 100 g, the maximum amount of additive employed represented less than one-tenth of the amine requirements for complete base exchange. The highest ranking in stabilizing effectiveness was achieved by the C-1 composition which had third rank in effective ionic mass and second ranking in cationic equivalents. This indicates a special synactive benefit produced by the isophthalic acid component.

Duration of Water Exposure

In analogy with the short-cut testing on soil-cement specimens, it has become customary in many places to judge the quality of stabilized soil systems by compressive strength tests after 7 days of water immersion of 2-in. diameter cylindrical test specimens. Such a procedure is justified only after previous establishment of the actual relationship between the compressive strength after 7 days of immersion and that obtained after immersion of a duration, following which no further decrease in strength is obtained. The latter cannot be predicted a priori, but is a function of such factors as water affinity of the specimen, initial and final permeability and others. Thus, in the reported test series, judgment from the compressive strength obtained after 7 days of immersion would have given first rank to the A-composition which is much more expensive and considerably less effective than the C-1 composition.

The confusion that exists in many places concerning the proper time of water immersion for specimens of a certain size, water affinity and permeability is paralleled by one concerning the change in exposure time required by change in size of test specimens. Although it is always best to determine such time requirements by direct test, the problem is illustrated by the following calculations made for cylindrical test specimens under the assumption that all water movement is normal to the cylindrical peripheral surface and that the hydrostatic head is negligible as compared with the physico-chemical water suction forces. These calculations have been made by J. Riera, undergraduate research assistant at the Soil Physics Laboratory of Princeton University.

Referring to the cross-sectional cylindrical slice of unit thickness shown in Figure 4, the driving force is $D = f(R - x)\, 2\pi . 1$ where f is a constant that depends on the nature of both the liquid and the specimen. Consequently, the gradient

$$i = \frac{2\pi f(R - x)}{x}$$

and

$$\frac{dx}{dt} = k\frac{2\pi f(R - x)}{x}$$

If

$$2\pi fk = A, \text{ then}$$

$$\frac{dx}{dt} = A\frac{R - x}{x}$$

$$\frac{dxx}{R - x} = A\ dt$$

and

$$A\int_{0}^{T} dt = \int_{0}^{W} \frac{x}{R - x}\ dx$$

Performing this integration yields

$$T = \frac{1}{A}\left[R \ln \frac{R}{R - u} - u\right]$$

in which u is the distance from the specimen perimeter to the saturation line; that is, $u = x$.

Theoretically, the saturation time is infinite. Hence, u-values must be chosen that are physically significant but fall short of reaching R.

1. Assuming a u-value equal to 0.95 R,

$$T_S = \frac{R}{A}\left[\ln \frac{1}{1 - 0.95} - 0.95\right]$$

$$= \frac{R}{A}\left[3.00 - 0.95\right] = \frac{2.05}{A} R$$

Accordingly, the time necessary for saturation of the specimen would be proportional to its radius.

2. It is assumed that physically significant saturation is reached when a core of predetermined radius r is not yet saturated. The size of r should be a function of material and pore characteristics of the specimen. In this case,

$$T_S = \frac{1}{A}\left[R \ln \frac{R}{r} - (R - r)\right]$$

r, of course, is assumed to be constant for all specimens of a certain soil composition even if the specimens vary in size. Considering two specimens, one of radius R, the other of radius 2R, their respective saturation times will be

$$T_{S1} = \frac{1}{A}\left[R \ln \frac{R}{r} - (R - r)\right]$$

and

$$T_{S2} = \frac{1}{A}\left[2R \ln \frac{2R}{r} - (2R - r)\right]$$

Therefore,

$$\frac{T_{S1}}{T_{S2}} = \frac{\ln \frac{2R}{r} - \left(1 - \frac{r}{2R}\right)}{\ln \frac{R}{r} - \left(1 - \frac{r}{R}\right)}$$

$$= 2\,\frac{\ln\frac{R}{r} + \ln 2 - 1 + \frac{r}{R} - \frac{r}{2R}}{\ln\frac{R}{r} - 1 + \frac{r}{R}}$$

$$= 2\left(\frac{\ln\frac{R}{r} - 1 + \frac{r}{R}}{\ln\frac{R}{r} - 1 + \frac{r}{R}} + \frac{\ln 2 - \frac{r}{R}}{\ln\frac{R}{r} - 1 + \frac{r}{R}}\right)$$

$$= 2 + 2\,\frac{\ln 2 - \frac{r}{R}}{\ln\frac{R}{r} - 1 + \frac{r}{R}}$$

If $r = 0.1R$, then $\frac{T_{S2}}{T_{S1}} = 2 + 2\,\frac{\ln 2 - 0.05}{\ln 10 - 1 + 0.1} = 2 + 2\left(\frac{0.69 - 0.05}{2.30 - 0.9}\right) = 2 + 2\left(\frac{0.64}{1.4}\right)$ or $T_{S2} \cong 3\,T_{S1}$. For $r \to 0$, $T_{S2} = T_{S1}$.

These calculations show that times of immersion can not be chosen arbitrarily for specimens of different sizes, if they are to yield significant and comparable information.

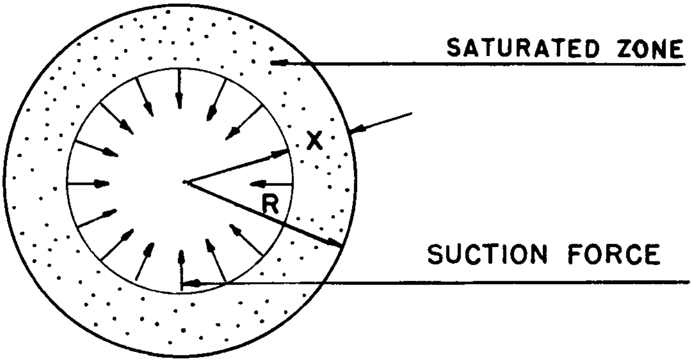

Figure 4.

SUMMARY AND CONCLUSIONS

Tests have been described and results presented on the use of cationically active condensation products of furfural with aniline and dichlor aniline with and without other admixtures by themselves and as additives to asphaltic bitumen in the waterproofing stabilization of clay soils.

1. One of these clay soils was used in the natural condition as well as in several monoionic modifications. The influence of the exchange ions on the stabilization susceptibility of the soil went parallel with that on the pH value. This is logical because the amines require association with H^+ ions to become cationically effective.

2. Increase in density of test specimens resulted in an increase in strength and weathering resistance as long as such density increase was not purchased at the price of using an amount of water insufficient to satisfy the affinity requirements of the soil, or in the case of soils that are susceptible to overcompaction because of strong aggregation of their clay mineral components in the natural state.

3. In the case of cationically active organic admixtures, it is important that (a) they contain as many potential cation equivalents per unit mass as possible and (b) that there

be enough H- ions in the system to change them into the ionically active ammonium ion derivative. If the natural soil is lacking in H- ions (that is, if its exchange complexes are largely saturated by other cations), H- ions must be introduced into the system by means of acid admixtures, preferably of types that their anions form insoluble salts with the exchange cations present in the natural soil.

4. Test methods employed for the evaluation of the effectiveness of stabilizing materials and procedures must be carefully analyzed with respect to the pertinent physical and physico-chemical phenomena involved if they are to give significant information.

By proper consideration of the known facts pertinent to bituminous soil stabilization and to the action of chemical additives, there is no greater uncertainty in the design of stabilized soil mixtures than there is in the design of hydraulic mortars and concretes in which air-entraining and dispersion agents are employed.

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