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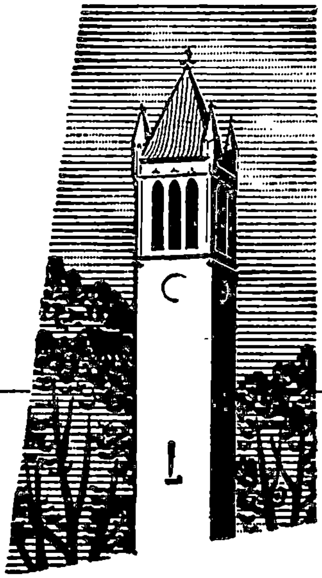
SOIL STABILIZATION WITH CHEMICALS

by
Donald T. Davidson
and
Associates

IOWA ENGINEERING EXPERIMENT STATION



Iowa State University
Ames, Iowa

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The Iowa Engineering Experiment Station, first of its kind in the country, was organized in 1904 for the purpose of providing organized research of the character needed to foster and develop the industries of the State.

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Soil Stabilization With Chemicals

by

D. T. Davidson, Professor, Civil Engineering
and Associates

(Twenty related manuscripts)

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CONTENTS

PREFACE

This bulletin is the second in a series of compilations of reports on completed research done for the Iowa Highway Research Board Project HR-1, "The Loess and Glacial Till Materials of Iowa; an Investigation of Their Physical and Chemical Properties and Techniques for Processing Them to Increase Their All-Weather Stability for Road Construction." The research, started in 1950, was done by the Iowa Engineering Experiment Station under its project 283-S. The project was supported by funds from the Iowa Highway Research Board of the Iowa State Highway Commission.

In Iowa the abundance and wide distribution of loess and glacial till materials makes them the logical ones with which to start working.

The principal objectives of the project may be summed up as follows:

1. To determine by means of both field and laboratory studies the areal and stratigraphic variation in the physical and chemical properties of the loess and glacial till materials of Iowa.
2. To develop new equipment and methods for evaluating physical and chemical properties of soil where needed.
3. To correlate fundamental soil properties with the performance of soils in the highway structure.
4. To develop a scientific approach to the problem of soil stabilization based on the relationships between the properties of the soils and those of the admixtures.
5. To determine the manner in which the loess and glacial till materials of Iowa can be processed for optimum performance as highway embankments, sub-grades, base courses, and surface courses.

Many of the papers in this bulletin were prepared originally as graduate theses required by the Department of Civil Engineering for master or doctoral degrees at Iowa State University. Each was then rewritten with the assistance of other project workers and was submitted to the Iowa Highway Research Board as a report on a phase of the research. This explains the several authors for each paper. The research work was all done under Dr. D. T. Davidson as project leader in charge.

Practically all the papers herein have been published previously. The title page for each manuscript identifies all authors and gives the place and date of first publication. No attempt has been made to revise, update, and change the data; hence some contradictions are evident. The facts and conclusions presented are those of the authors at the time the manuscript was submitted. Much of the repetition of material has been eliminated, and the papers have been arranged by subject matter.

The list of **REFERENCES** at the end of each manuscript gives only the first, or original printing, though the paper referred to may have appeared later in various forms in several publications, and some are included herein. Those shown as theses in the Iowa State University Library are so indicated because only in the thesis are all the data shown.

EXPLORATORY EVALUATIONS OF SOME ORGANIC CATIONS AS SOIL STABILIZING AGENTS

by

D. T. Davidson, Professor, Civil Engineering

(Highway Research Board Proceedings 29: 531-537. 1949.)

ABSTRACT

In the search for new soil stabilizing agents the effects of six organic cations on plastic limit, liquid limit, shrinkage limit, air-dry strength and rate of slaking of a highly plastic clay subsoil were studied. In all cases the plasticity index and shrinkage were reduced by the treatments. The air-dry strength was lowered in varying degree, which was the only undesirable effect noted. With one exception resistance to slaking was improved. It is concluded that large organic cations show promise as possible stabilizing agents for highly plastic fine-grained soils.

INTRODUCTION

Ever since soil has been used as a material for building roads, engineers have searched for methods or materials to make it stable under traffic in all kinds of weather. The goal of this search has been well expressed:[7]

> The alchemists of ancient times sought the philosopher's stone, which was believed to have the power to transmute the baser metals into gold. The philosopher's stone that intrigues the imagination of the highway engineer is the thing or method that will have the power to transmute cheaply any kind of soil into a material that will resist abrasion and displacement under traffic in all kinds of weather, and that will retain these properties indefinitely.

Numerous reports on the ionic-exchange method of altering the engineering properties of cohesive fine grained soils have been made in the literature[6, 9]. Most investigators, however, have been primarily concerned with the inorganic ca-

TABLE I. ENGINEERING PROPERTIES OF EDINA SUBSOIL

Liquid limit, percent of oven-dry wt. of soil	78.0
Plastic limit, percent of oven-dry wt. of soil	26.3
Plasticity index, percent of oven-dry wt. of soil	51.7
Shrinkage, limit, percent of oven-dry wt. of soil	6.0
Shrinkage ratio	2.02
Hygroscopic moisture[*], percent of oven-dry wt. of soil	7.02
Centrifuge moisture equivalent, percent of oven-dry wt. of soil	29.7
Specific gravity	2.74
Organic content, percent of oven-dry wt. of soil	0.72
pH value	4.90
Base exchange capacity[†], m.e. per 100 g.	40.0
Max. Statndard Proctor dry density, p.c.f.	88.2
Optimum moisture, percent of oven-dry wt. of soil	29.9
Max. Modified A. A. S. H. O. dry density, p.c.f.	104.4
Optimum moisture, percent oven-dry wt. of soil	18.6
Textural classification	Clay
Revised (1945) Public Roads classification	A-7-6 (20)

[*] After being exposed to air at room temperature (80° F. + 5°) for fourteen days.

[†] Determined by the Soils Subsection, Iowa Agricultural Experiment Station, Iowa State College, Ames, Iowa.

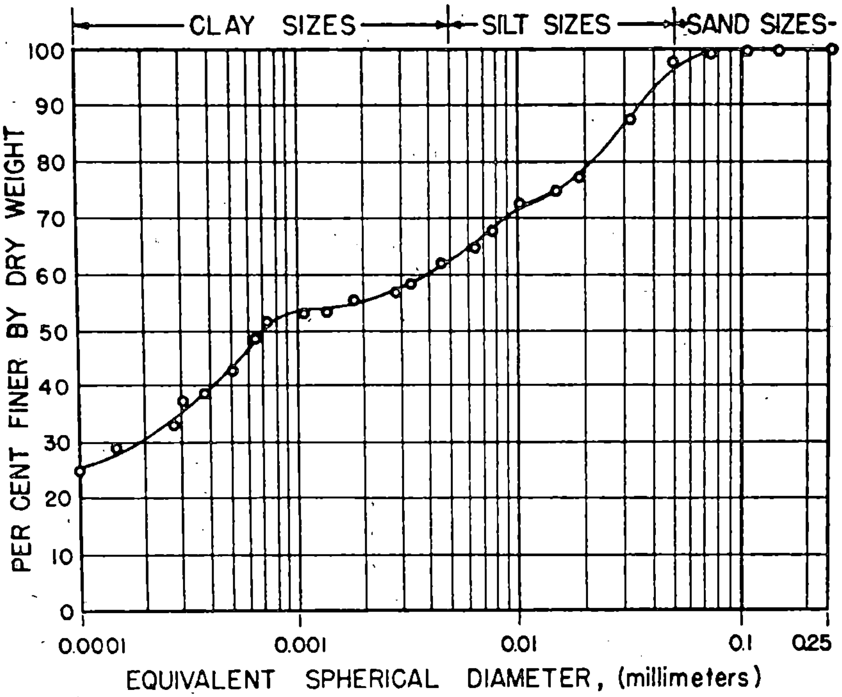


Fig. 1. Grain size distribution of Edina subsoil.

tions. Very little work has been reported on the use of organic cations. This paper presents the results of an exploratory investigation to evaluate as soil stabilizing agents six cationic compounds that furnish large organic cations when dissolved in water.

Materials

The six water soluble organic compounds used are available commercially under the trade names Armac T, Armac 18D, Armac 12D, Rosin Amine-D Acetate, Amine 220, and Ammonyx T. They are all cationic in character, dissociating in water to furnish, with the exception of Amine 220, large monovalent cations. Amine 220 furnishes divalent cations. The composition and constants of each compound are given by the manufacturer[2, 3, 5, 8].

The soil treated with the cationic compounds was Edina subsoil, a dull gray, highly plastic clay from Wayne County, Iowa. Figure 1 shows its grain-size distribution curve. A differential-thermal analysis of the minus one micron (0.001 mm.) portion indicated that montmorillonite type clay minerals were predominant. Additional engineering properties of Edina subsoil are presented in table I.

EXPERIMENTAL PROCEDURE

Organic cations in amounts less than equivalent to the base exchange capacity of the soil are rather completely adsorbed in base exchange reactions; and amounts in excess of the base exchange capacity tend to be adsorbed by a different reaction, probably dependent on the action of the van der Waals' forces[4]. In the present investigation, organic cations were added in amounts less than equivalent to the base exchange capacity of Edina subsoil.

Prior to cationic treatment, the air-dry soil was ground by means of a mortar and pestle to pass the No. 40 sieve and then divided into 1000-g. (oven-dry weight) samples. Initially each compound was added to three soil samples in amounts sufficient to satisfy their base exchange capacities to the extent of 1, 10, and 75 percent of saturation. Later the investigation was extended to include samples having their base exchange capacities 25 and 50 percent saturated with Armac T and Armac 18D, and 5 percent saturated with Rosin Armine D Acetate. Table II gives the relationship between percent saturation of base exchange capacity, and percent by oven-dry weight of soil for each admixture.

The weights of each cationic material required to satisfy the base exchange capacities of the soil samples to the various percentages of saturation were calculated by means of the equivalent weight of the chemical and the base exchange capacity of the soil. A sample calculation for Armac T will illustrate the procedure.

Example—Calculate the weight of Armac T needed to saturate to 75 percent the base exchange capacity of 1000 grams of Edina subsoil.

Given: Molecular weight of monovalent Armac T = 322 and the base exchange capacity of Edina subsoil = 40 milliequivalents per 100 g.

Solution:

Gram-molecular wt. of Armac T = 322 g.
Equivalent wt. of Armac T = $322 \div 1 = 322$ g.
1 milliequivalent of Armac T = 322 mg.

Therefore, 75 percent saturation of 1000 g. of soil will require $40 \times 10 \times 0.75 \times 322 = 96600$ mg. = 96.6 g. of Armac T.

Before being added to the soil, each amount of chemical was dissolved in 1000 ml. of distilled water. The solutions were immediately added to the soil samples in large, shallow pans and the mixtures were stirred thoroughly for 10 min. with

TABLE II. RELATIONSHIP BETWEEN PERCENT SATURATION OF BASE EXCHANGE CAPACITY AND PERCENT BY OVEN DRY WEIGHT OF SOIL

Chemical admixture, saturation b.e.c. %	Chemical admixture, percent of oven-dry weight of soil					
	Armac T	Armac 18D	Armac 12D	Rosin Amine-D Acetate	Amine 220	Ammonyx T
0	0.00	0.00	0.00	0.00	0.00	0.00
1	0.13	0.13	0.10	0.22	0.07	0.17
5	...	...	...	1.07	...	...
10	1.29	1.30	0.98	2.15	0.70	1.74
25	3.22	3.26	...	...	...	...
50	6.44	6.52	...	...	...	...
75	9.66	9.78	7.32	16.11	5.25	13.08

a stiff-bladed spatula. Drying was at room temperature over a period of several days. When air-dry, the treated samples were ground with a mortar and pestle to pass the No. 40 sieve.

The tests used to determine the effect of the cationic treatments were: 1. plastic limit; 2. liquid limit; 3. plasticity index; 4. shrinkage limit; 5. ratio of shrinkage limit to liquid limit; 6. air-dry strength; 7. rate of slaking. Since most of these tests were performed in accordance with standard procedures of the American Society for Testing Materials[1], only the non-standard test procedures will be described. However, the significance of all tests will be briefly covered.

The plastic limit (A.S.T.M. Designation: D424-39) represents the moisture content, expressed as percentage of the oven-dry soil weight, of change from the friable to the plastic consistency. According to the film theory of plasticity, orientation of particles and their subsequent sliding over each other takes place at this point; since sufficient water has been added to provide a film around each particle.

The liquid limit (A.S.T.M. Designation: D 423-39) signifies the moisture content at which the water films become so thick that cohesion is decreased and the soil flows under an applied force.

The plasticity index is the numerical difference between the liquid limit and the plastic limit. Essentially it is the amount of water necessary to thicken the films from the moisture content at which plasticity develops to that at which flow occurs under an applied force. As its name implies, the plasticity index is a qualitative measure of soil plasticity. The higher its value, the more plastic the soil.

The shrinkage limit (A.S.T.M. Designation: D427-39) is the moisture content, expressed as a percent of the oven-dry soil weight, below which further loss of moisture by evaporation does not result in a reduction of volume.

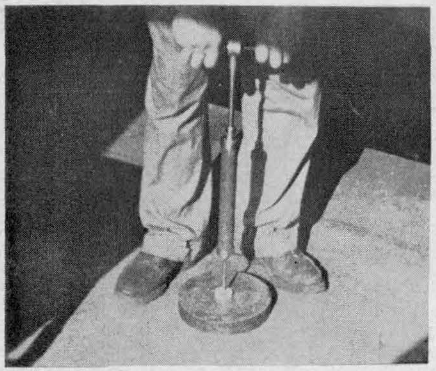
The ratio of shrinkage limit to liquid limit, expressed as a percentage, is indictative of the shrinkage properties of a soil[10]. The larger this ration, the smaller will be the tendency of a soil to shrink.

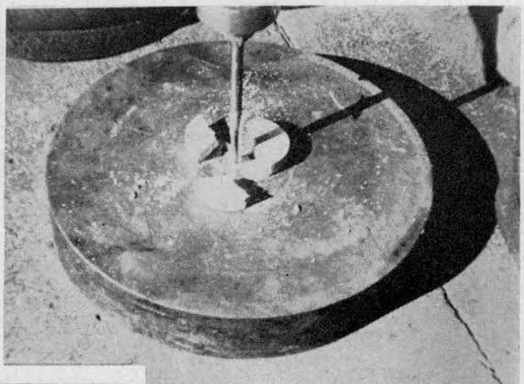
The air-dry strength of chemically treated soil specimens may be considered as a measure of the effect of the admixtures on the cohesive properties of the soil. The specimens used in this investigation were air-dried shrinkage pats prepared in circular porcelain milk dishes having a flat bottom and being about 1¾-in. in diameter and about ½-in. high. The pats were molded in accordance with A.S.T.M. Designation: D427-39 and then air-dried to constant weight at room temperature.

The relative strengths of the air-dried pats were determined by loading them to failure with a soil penetrometer of the type used for measuring penetration resistance in the standard Proctor density test (A.S.T.M. Designation: D698-42T). The needle tip having 1/20-sq. in. bearing area was found to be most suitable for Edina subsoil. The testing procedure consisted of placing a pat on a smooth steel surface and manually loading it with the penetrometer at a slow and uniform rate until either the maximum measurable load was applied or the pat ruptured (figure 2). A sliding ring on the calibrated portion of the penetrometer gave the failure load in pounds. Usually the first break of a full size specimen divided it into two or more pieces (figure 3) each of which was large enough to be used for further testing. The average failure load of several tests on two pats made from the same material, divided by the area of the needle tip, was recorded as the air-dry strength in pounds per square inch. Since 110 lb. was the maximum load that could be measured with the penetrometer, pats that were not ruptured by this load had their strengths recorded as 2200 + lbs. per sq. in.

The slaking test is essentially a determination of the rate at which a soil specimen disintegrates when immersed in water. The rate of slaking depends upon such factors as the affinity of the soil for water, the amount of expansion of the soil when wetted, the speed with which the water penetrates the soil, and the character of the cracking produced by unequal expansion of the sample. This test may be used to determine the effectiveness of different admixtures as water-proofing agents for a given soil.

The slaking specimens used were air-dried shrinkage pats similar to those used for measuring air-dry strength. Prior to immersion, the pats were placed on copper wire rings whose diameters were ⅛ of an inch smaller than the bottom diameters of the soil pats supported on them (figure 4). The testing procedure consisted of immersing the pats in distilled water and observing the time in





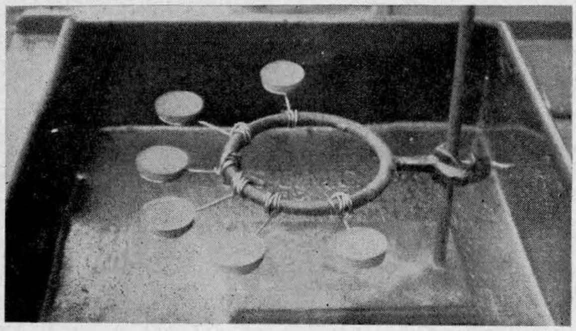


Fig. 2. Soil penetrometer used to load and rupture air dried shrinkage pat.

Fig. 3. First break of an air dried shrinkage pat.

Fig. 4. Slating pats ready for immersion.

minutes for each pat to drop through its supporting ring. The recorded slaking time was the average of two tests. Pats that did not disintegrate sufficiently to drop through their rings were kept immersed for 7 days. The slaking time of these pats was recorded as "didn't fail". The water was at room temperature throughout the tests, and the depth over the pats was maintained at 1-in.

RESULTS

The curves in figure 5 indicate the manner in which admixtures of the six cationic compounds increased the plastic limit. Figure 6 shows the effect of the same admixtures in decreasing the liquid limit. The numerical difference be-

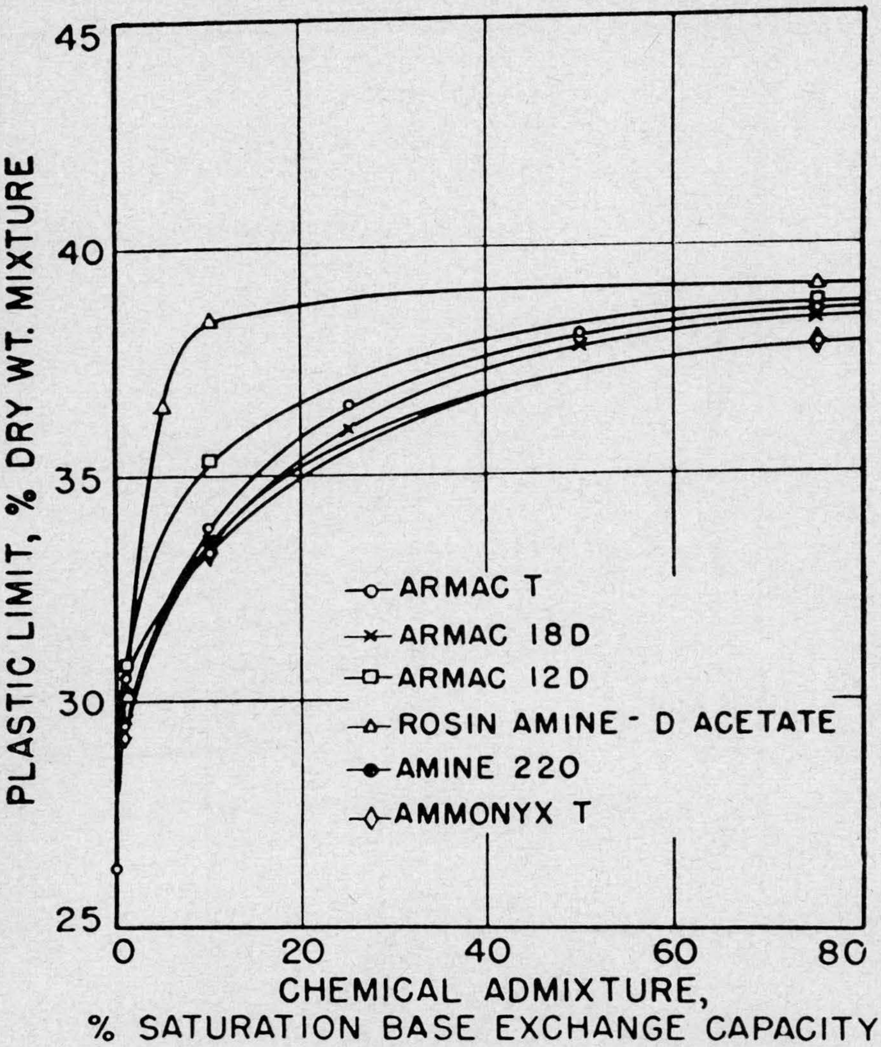


Fig. 5. Effect of cationic compounds on plastic limit.

tween the two limits is the plasticity index, and figure 7 illustrates how it was decreased.

The relative effectiveness of the cationic materials in raising the shrinkage limit is shown in figure 8. Figure 9 illustrates the manner in which the ratio of shrinkage limit to liquid limit was increased.

Table III shows how air-dry strength was reduced by the cationic admixtures. Table IV indicates the effect of the admixtures on slaking time.

Discussion

The plasticity index of Edina subsoil was lowered by all cationic treatments. Since the plasticity index is a qualitative measure of soil plasticity, it may be

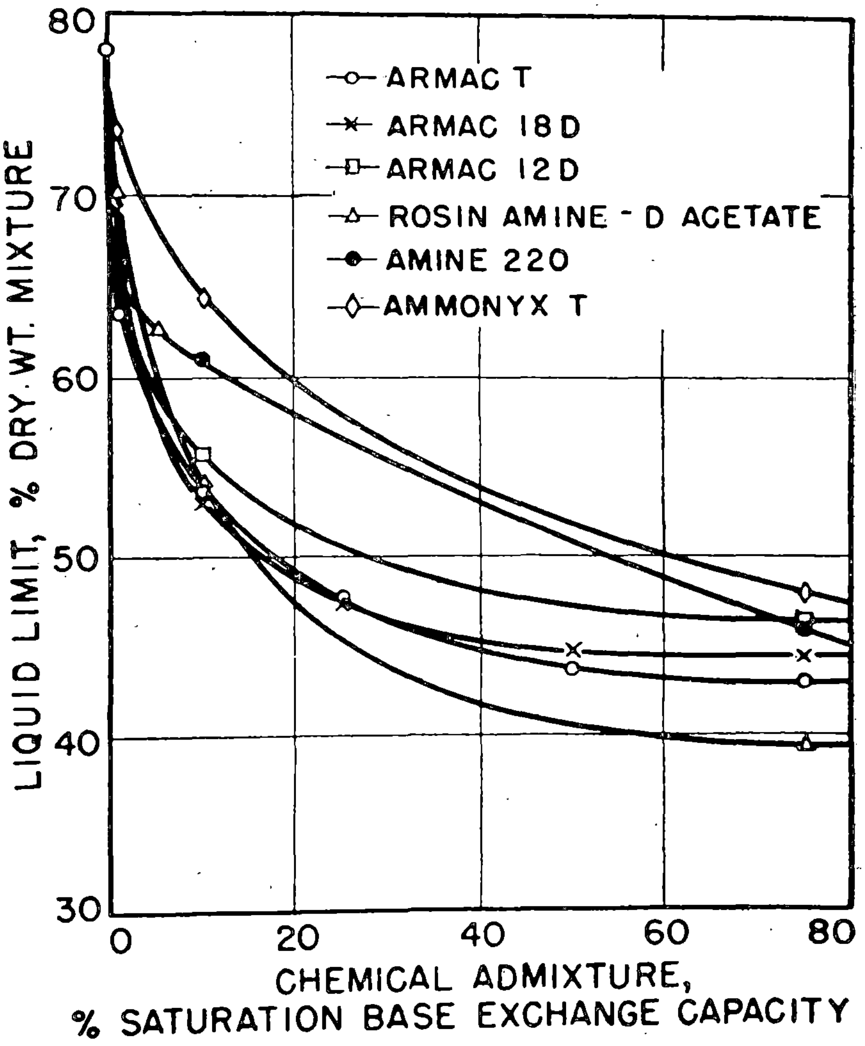


Fig. 6. Effect of cationic compounds on liquid limit.

concluded that all admixtures were effective in reducing this property. Likewise all treatments reduced shrinkage, as indicated by an increase of both the shrinkage limit and the ratio of shrinkage limit to liquid limit. The rate of reduction of plasticity and shrinkage varied with the type of cationic compound and the percent saturation of the soil's base exchange capacity; but, in the case of each compound, the sharpest reduction was caused by the initial 10 percent saturation. Rosin Amine-D acetate was especially effective in lowering both properties.

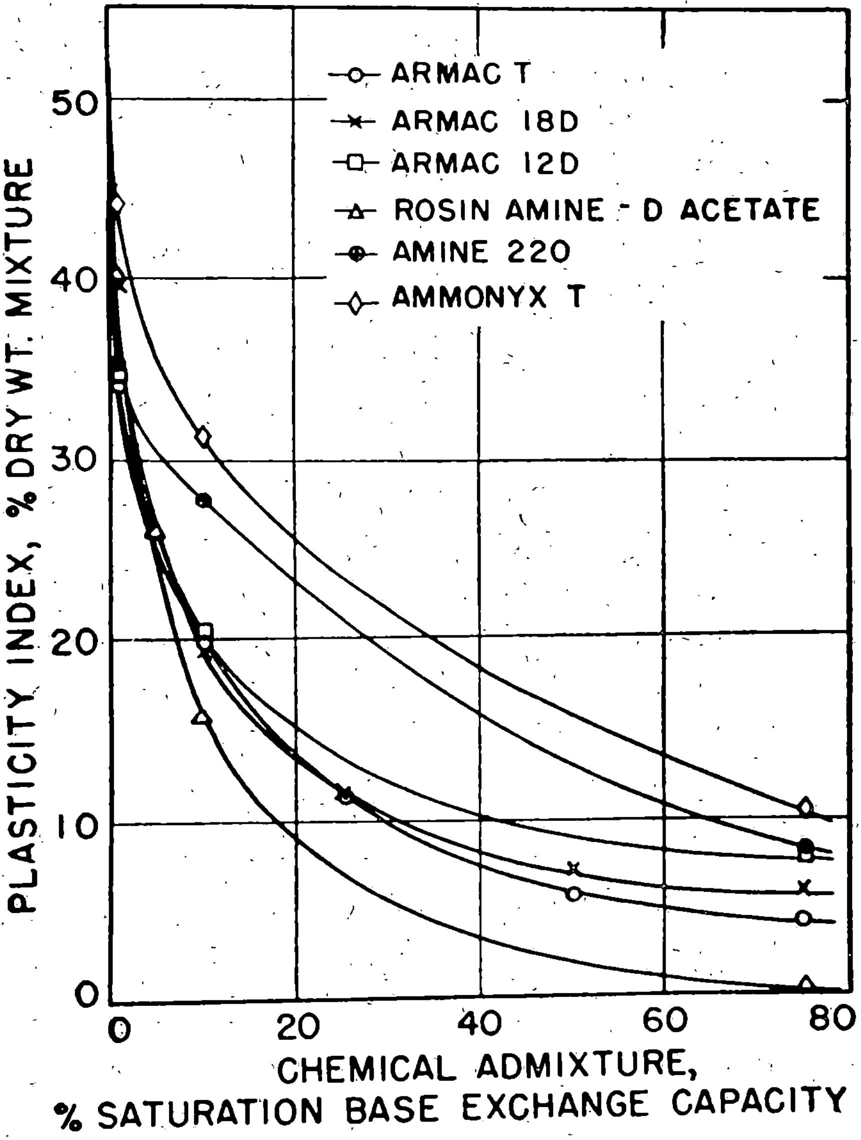


Fig. 7. Effect of cationic compounds on plasticity index.

Admixtures of all compounds caused a reduction of Edina subsoil's air-dry strength by decreasing its cohesive properties. With the exception of Rosin Amine-D Acetate, the loss was not great for admixtures up to 10 percent saturation of the base exchange capacity. Rosin Amine-D Acetate in dosages larger than 5 percent caused very great loss of strength. For Armac T and Armac 18D, the loss was only gradual up to 25 percent saturation. All 75 percent treatments greatly reduced air-dry strength. Armac T admixtures caused the least loss of strength. For example, 10 percent Rosin Amine-D Acetate caused almost as great a reduction as 75 percent Armac T.

Ten percent saturation of Edina subsoil's base exchange capacity with all compounds except Ammonyx T greatly improved its resistance to disintegration during the slaking test. Ammonyx T had practically no beneficial effect on the

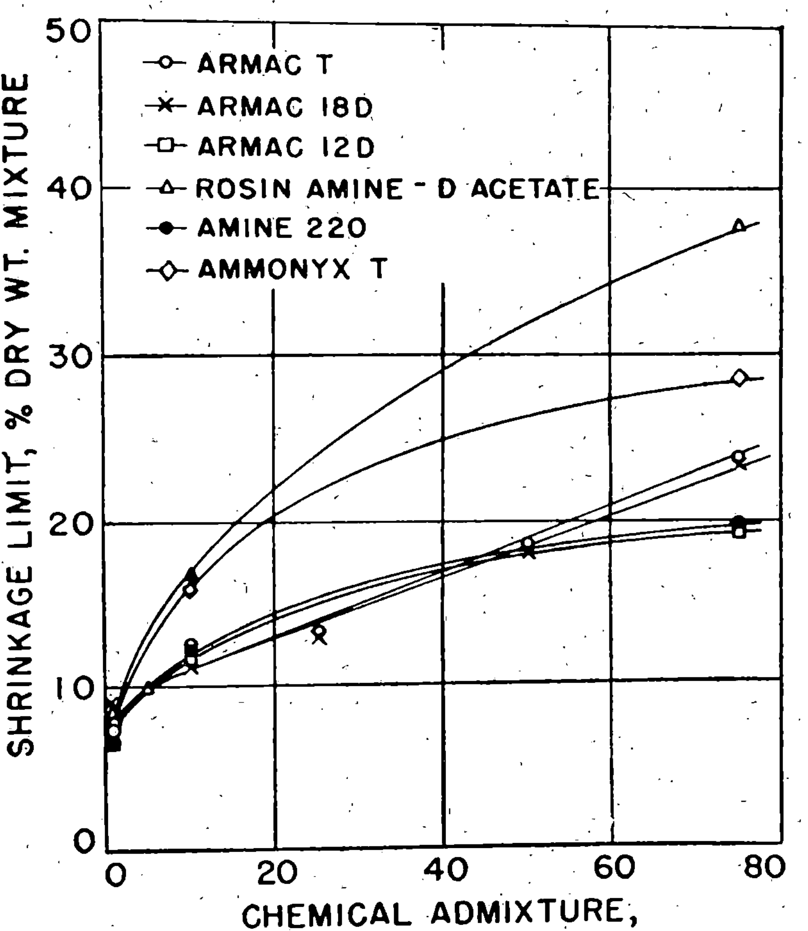


Fig. 8. Effect of cationic compounds on shrinkage limit.

rate of disintegration. Five percent Rosin Amine-D Acetate was very beneficial. In general, admixtures larger than 10 percent did not appreciably increase slaking resistance. With the exception of Armac T, the 75 percent treatments did not prevent pats from dropping through their supporting rings; and in some cases the slaking time was less than for the untreated pats. This was probably due to the very low air-dry strength of the 75 percent saturated pats that failed. Observation of these pats during disintegration revealed that the individual pieces that broke off were not wetted by the water.

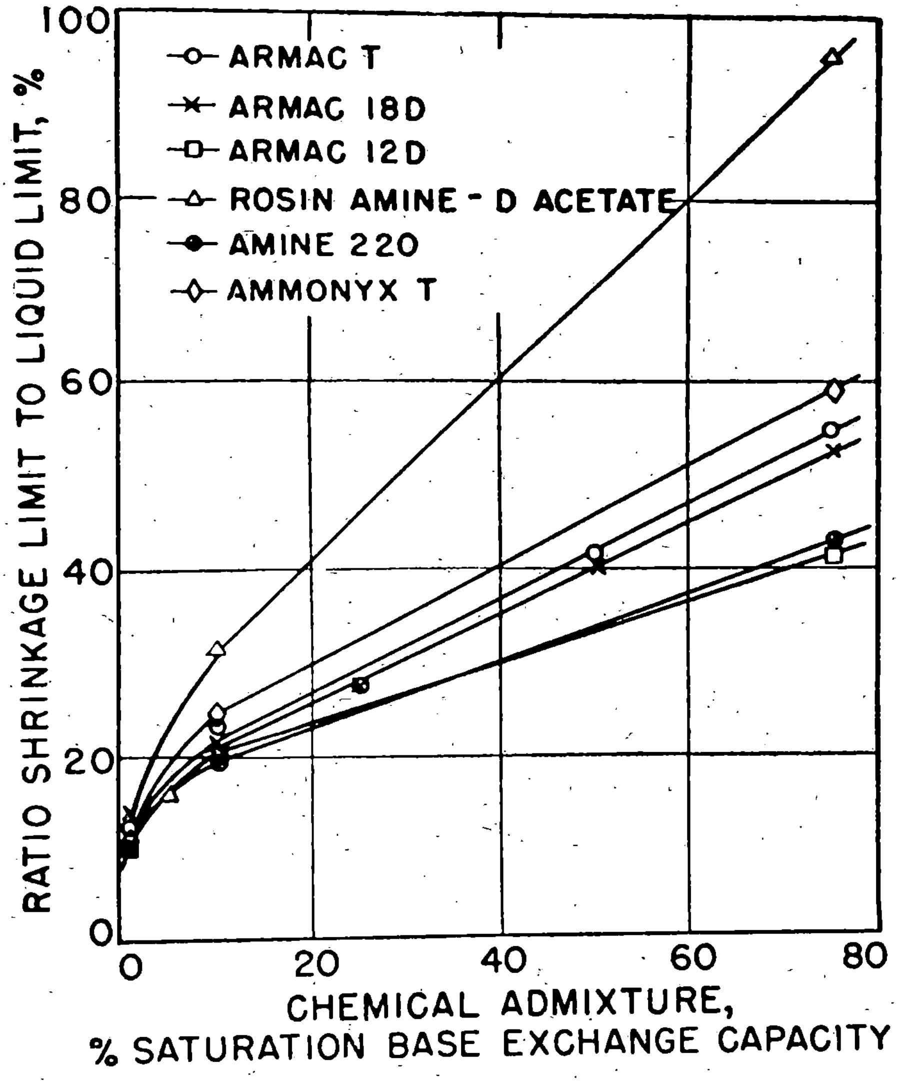


Fig. 9. Effect of cationic compounds on ratio of shrinkage limit to liquid limit.

CONCLUSION

This investigation, while only of an exploratory nature, indicates that large organic cations have considerable promise as stabilizing agents for highly plastic fine-grained soils. Reduction of air-dry strength was the only undesirable property change caused by the cations studied. All other modifications were decidedly beneficial from the standpoint of all-weather stability.

Of the six cationic compounds investigated, Armac T and Rosin Amine-D Acetate showed the most promise. Both should receive further study.

Table III. Effect of Cationic Compounds on Air Dry Strength

Chemical admixture, saturation b.e.c. %	Air-dry Strength, psi Armac T	Armac 18D	Armac 12D	Rosin Amine-D Acetate	Amine 220	Ammonyx T
0	2200+	2200+	2200+	2200+	2200+	2200+
1	2200+	2200+	2200+	2200+	2200+	2200+
5	. .	.	. . .	2200+	.	.
10	2200+	2040	2120	420	2200+	2040
25	2120	1960	. . . .	. . . .	. . . .	. . . .
50	1000	720	.	.		.
75	400	40	350	10	160	120

Table IV. Effect of Cationic Compounds on Slaking Time

Chemical admixture, saturation b.e.c. %	Slaking time, minutes Armac T	Armac 18D	Armac12D	Rosin Amine-D Acetate	Amine 220	Ammonyx T
0	4.5	4.5	4.5	4.5	4.5	4.5
1	7.0	6.5	11.0	369.0	6.5	5.7
5	.		. .	Didn't fail	. .	. .
10	Didn't fail	Didn't fail	Didn't fail	Didn't fail	Didn't fail	3.5
25	Didn't fail	Didn't fail	. .	. .	.	. .
50	Didn't fail	Didn't fail	. .	.	. .	. .
75	Didn't fail	32.0	14.5	1.5	2.5	13.0

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AN ORGANIC COMPOUND
AS A STABILIZING AGENT
FOR TWO SOIL AGGREGATE MIXTURES

by

D. T. Davidson, Professor, Civil Engineering
J. E. Glab, Captain, Corps of Engineers, U. S. Army

(Highway Research Board Proceedings 29: 537-543. 1949.)

ABSTRACT

Laboratory investigations at Iowa State University have indicated that certain organic compounds which furnish large organic cations when dissolved in water have considerable promise as admixtures to increase the all-weather stability of soils. An investigation is described in this paper wherein one promising compound was evaluated as a stabilizing agent for two soil-aggregate mixtures having plasticity indices higher than considered desirable for highway subgrade material.

The test results indicate that water solutions of the chemical admixtures had the same qualitative effect on the two soil-aggregate samples. The following properties were decreased: plasticity, shrinkage, maximum modified AASHO density and optimum moisture content, and unsoaked California Bearing Ratio. The soaked CBR of both samples was increased and swelling was reduced.

The need for more research is indicated before any definite rcommendations can be made regarding the use of water soluble organic compounds for soil stabilization purposes. However, the results of this investigation show that admixtures of the compound evaluated had a beneficial effect on some engineering properties related to the all-weather stability of the soil-aggregate mixtures.

INTRODUCTION

During the last three decades a large number of organic compounds have been developed which promote or effect lubrication, wetting, detergency, foaming, emulsification, water repellancy, and other effects associated with the term *surface activity*. Many of these surface active agents have a molecular structure which is essentially oblate, that is, considerably longer than it is wide. Usually they are dipolar, one end of the oblate structure comprising a hydrocarbon radical of hydrophobic (water-hating) nature, and the other end is of a hydrophilic (water-loving) nature. The cation active or cationic surface active agents are characterized by the fact that the hydrophobic group forms part of a cation when the compound is dissolved in water. A typical example of this class is octadecyl ammonium chloride which dissociates in water according to the equation

$$C_{18}H_{37}NH_3Cl \rightarrow (C_{18}H_{37}NH_3)^+ + Cl)^-$$

Research being carried on at Iowa State University, while only in the exploratory stage, has indicated that organic cations have considerable promise as stabilizing agents for fine-grained soils. The investigation reported herein covers only one phase of this research. Its purpose was to determine by laboratory tests the value of a promising cationic surface active agent as an admixture for two soil-aggregate mixtures having high plasticity indices to bring them within the limits recommended by the Bureau of Public Roads for highway subgrade material.

Materials

The two soil aggregate samples will be referred to hereafter as soils A and B. Soil A was rust red in color and came from a small pit in Prince George's County, Maryland, about five and one-half miles south of the District of Columbia line just off the road to Indian Head, Maryland. Soil B had a brownish color and was taken from a pit located on U. S. Coast Guard property near the Hybla Valley Experimental Area in Fairfax County, Virginia.

Both soils met the Iowa State Highway Commission's gradation requirements for stabilized base course material (figure 1). Table I gives additional properties of soils A and B as determined by test procedures of the American Association of State Highway Officials. The modified AASHO density and California Bearing Ratio tests were performed in accordance with test procedures of the Corps of Engineers[11]. The plasticity index of both soils was considerably higher than the upper limit of 3 recommended by the Bureau of Public Roads for subgrade material. It will be noted that the revised Public Roads classification was A-2-6(0) in the case of each soil.

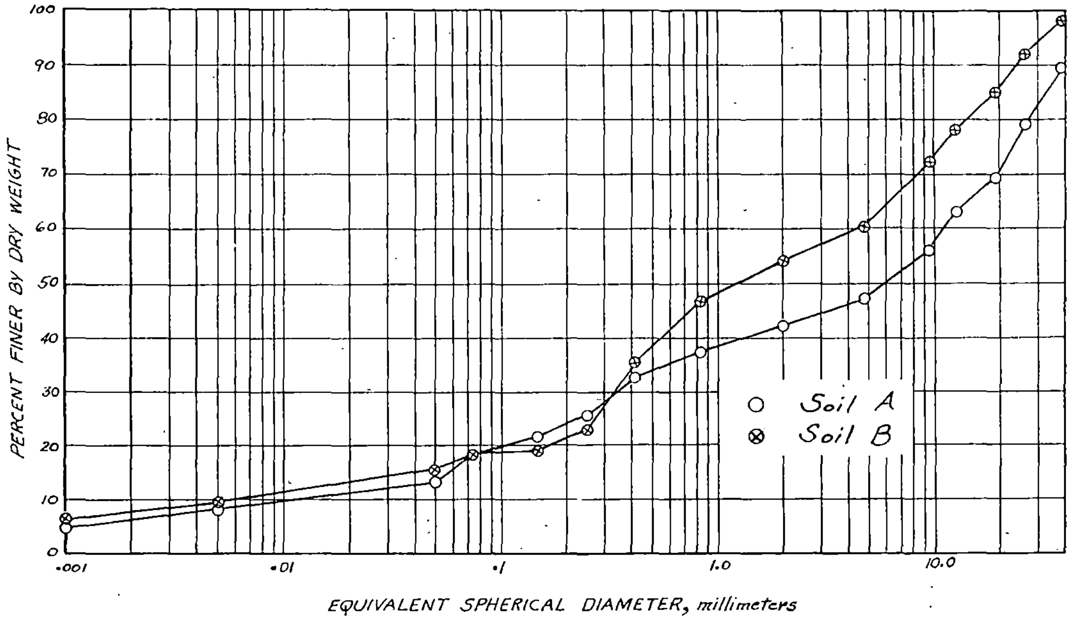

Fig. 1. Grain-size distribution curves for soils A and B.

Figure 2 shows the differential-thermal analysis curves for the colloid portions (minus 0.001 mm.) of soils A and B. Numerous reports on this method of determining the mineralogical constitution of clay samples have been made in the literature[8]. In comparing the curves in figure 2 with the characteristic curves for the pure clay minerals[5, 9], it was concluded that the colloid portion of both soils contained predominantly kaolinite type clay minerals.

The cationic surface active agent selected for evaluation as an admixture was

TABLE I. PROPERTIES OF SOILS A AND B

Properties	Soil A	Soil B
Liquid limit, percent dry wt. soil	32.6	29.4
Plastic limit, percent dry wt. soil	19.9	17.6
Plasticity index, percent dry wt. soil	12.7	11.8
Shrinkage limit, percent dry wt. soil	14.9	16.6
Shrinkage ratio	1.77	1.84
Hygroscopic moisture*, percent dry wt. soil	1.06	1.01
Specific gravity (minus No. 40 sieve soil)	2.68	2.68
pH value	5.3	5.1
Modified AASHO dry density, pcf	139.5	141.3
Optimum moisture content, percent dry wt. soil	8.8	7.0
California Bearing Ratio, percent std. crushed rock:		
Unsoaked	95†	144‡
Soaked	57†	60‡
Revised (1945) Public Roads classification	A-2-6(0)	A-2-6(0)

* After having been stored in cloth bags for over one month and then exposed to air at room temperature for 10 days.

† At 0.1 inch penetration (1).

‡ At 0.2 inch penetration (1).

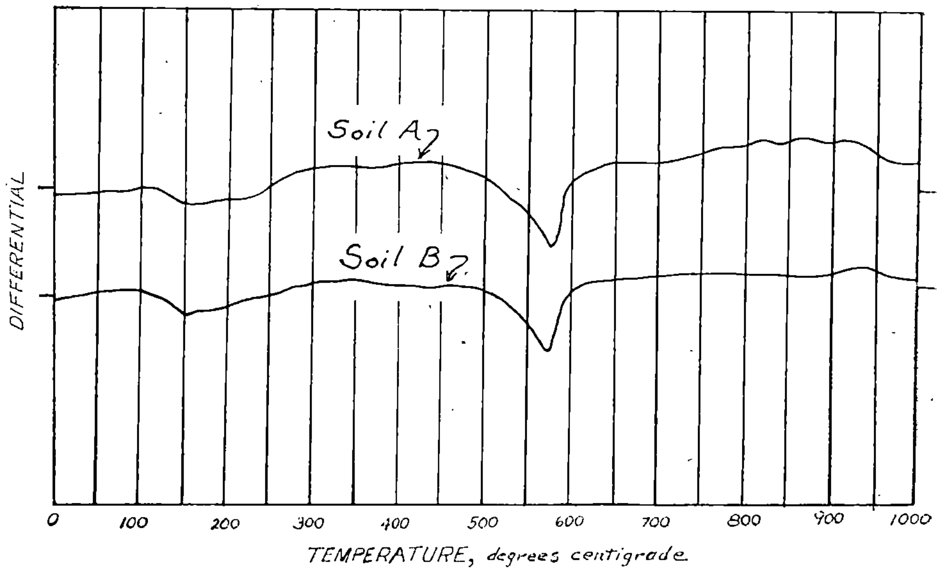

Fig. 2. Differential-thermal analysis curves for colloid portion of soils A and B.

a fatty acid amine acetate made from the fatty acids derived from beef tallow. Of the six cationic compounds investigated in 1948, this material appeared to be one of the most promising for use in soil stabilization work. The chemical structure may be written as RNH_3Ac, where the R grouping represents the long carbon chain grouping found in the original fatty acid. When dissolved in water it dissociates according to the equation

$$RNH_3Ac \rightarrow (RNH_3)^+ + (Ac)^-$$

to furnish large fatty amine cations. These cations are used in industry for the purpose of causing certain types of water-loving surfaces to become water-repelling and oil-loving. The compound has been found to be very effective as a germicide, fungicide, and algacide.

The compound discussed is currently available in carload quantities on from one to three weeks' notice. According to the price list of October 21, 1949, this chemical is listed at 32 cents per pound in carload lots, f.o.b. Chicago, Illinois. The manufacturer has indicated that a new plant for the manufacture of chemicals will soon be opened and that prices will be lowered considerably as soon as increased production makes such action possible. As and if demand increases, undoubtedly the output will be increased; since the compound is a by-product of the packing industry, the potential for its manufacture is in good supply. Also others in the packing industry can make a similar chemical; and without doubt they will do so if there is a demand.

EXPERIMENTAL PROCEDURE

The investigation was carried out in three parts. The first part consisted of determining the effect of ½, 1, and 3 percent admixtures of the chemical by dry weight of the minus No. 40 sieve soil on the Atterburg plasticity and shrinkage values of soil A. The plasticity index (PI) data was then used to find the percentage of chemical needed to reduce the PI to 3. The objective of the second part of the investigation was to determine the effect of this single admixture on the modified AASHO density, optimum moisture content, and California Bearing Ratio of soil A. In the third and last part, the same series of tests were performed on soil B containing only the percentage of the chemical needed to reduce the PI of soil A to 3.

In preparing samples for the plasticity and shrinkage tests, the cationic admixtures were made to the minus No. 40 sieve soil. In the case of the density and CBR tests, the minus ¾-in. sieve samples were treated with the compound by percentage of the dry weight of the minus No. 40 sieve fraction.

Before adding to the air-dry soil, each admixture dissolved in an amount of distilled water equal in weight to the sample to be treated. The solutions were immediately added to the soil samples and the mixtures stirred thoroughly in large shallow pans with a stiff-bladed spatula. Drying was carried out at room temperature over a period of several days. When air-dry the treated samples were ground with mortar and pestle to pass through either the No. 40 or ¾-in. sieve, depending on the tests to be performed with the samples.

RESULTS

The curve in figure 3a indicates the manner in which the cationic admixtures increased the plastic limit of soil A. Figure 3b shows the effect of the same admixtures in decreasing the liquid limit. The numerical difference between the two limits is the plasticity index, and figure 3c illustrates how it was decreased. The general trend of the data on the three graphs agrees with the

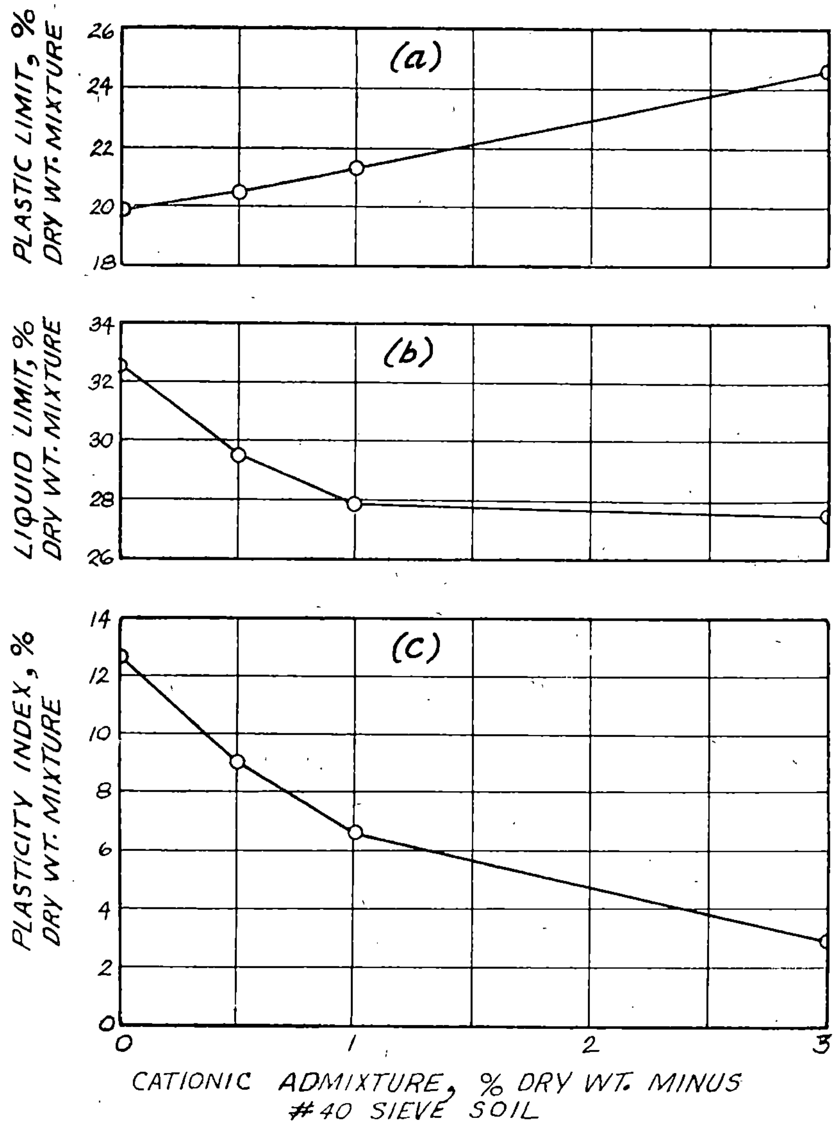

Fig. 3. Effect of cationic admixtures on plastic limit, liquid limit, and plasticity index of soil A.

results obtained previously (figure 3)[1]. From figure 3c it is apparent that the plasticity index reduction for Soil A between 0 and 1 percent admixture was almost twice as great as between 1 and 3 percent. However, approximately 3 percent admixture was needed to reduce the PI value to 3.

Table II compares the effect of 3 percent cationic admixtures on the plasticity values of soils A and B. It will be noted that this percentage of the chemical also reduced the PI of soil B to slightly less than 3. In terms of the revised Public Roads classification system, treatment with 3 percent admixture reduced the plasticity of both soils sufficiently to change their classification from A-2-6(0) to A-1-b. Soils classifying in this latter group are considered desirable for subgrade use[10].

The reduction of plasticity by the cationic material can perhaps be explained on the basis of the effect of large organic cations on the adsorptive capacity of the clay surface for water. When cations of the type used in this investigation are adsorbed by the clay in base exchange reaction with the basic nitrogen atom of the molecule closely held to the mineral surface and with the hydrophobic part of the molecule arrayed on the surface or directed outward from the surface, considerable areas are formed on the mineral that are not wetted by water[4]. Since the plasticity index may be considered the amount of water necessary to thicken the surface films from plastic limit consistency to liquid limit consistency, it would necessarily be decreased by the exclusion of water from large large areas of the surface concerned.

The effect of the admixtures in decreasing the shrinkage of soil A is illustrated by the shrinkage limit and shrinkage ratio curves in figure 4. The data indicate that admixtures up to 1 percent increased the shrinkage limit and decreased the shrinkage ratio at a much greater rate than those above 1 percent. Table III compares the shrinkage values of soils A and B after treatment with 3 percent chemical. Apparently 3 percent had a slightly greater effect upon soil A than upon soil B.

The decrease in shrinkage due to adsorption of large organic cations on the clay surface of the soil can probably be ascribed to disrupted water films. As water evaporates from a soil, capillary tension acts like a taut skin on the surface of the soil mass and gradually draws the particles closer together until the shrinkage limit is reached. At this moisture content the resistance of the soil to further compression supposedly equals the force exerted by evaporating

TABLE II. EFFECT OF CATIONIC ADMIXTURES ON PLASTICITY VALUES OF SOILS A AND B

Cationic Admixture, percent dry wt. minus No. 40 sieve soil	Liquid Limit, percent dry wt. mixture		Plastic Limit, percent dry wt. mixture		Plasticity Index, percent dry wt. mixture	
	Soil A	Soil B	Soil A	Soil B	Soil A	Soil B
0	32.6	29.4	19.9	17.6	12.7	11.8
½	29.5		20.5		9.0	
1	27.9		21.3		6.6	
3	27.5	25.7	24.6	23.1	2.9	2.6

moisture. The creation of water repellant areas on the clay surface and the destruction of the structure of the hexagonal network of water molecules on the remainder of the surface[7], would tend to weaken the force of evaporating moisture. These surface changes would result in less shrinkage of the soil.

Figure 5 illustrates the effect of 3 percent admixture on the maximum dry density and optimum moisture content of soils A and B as determined by the modified AASHO method. The slightly reduced values of these properties agree with previous findings[12]. A possible explanation may be that the creation of

TABLE III. EFFECT OF CATIONIC ADMIXTURES ON SHRINKAGE VALUES OF SOILS A AND B

Cationic Admixture, percent dry wt. minus No. 40 sieve soil	Shrinkage Limit, percent dry wt. mixture		Shrinkage Ratio	
	Soil A	Soil B	Soil A	Soil B
0	14.9	16.6	1.77	1.84
½	20.5		1.63	
1	23.5		1.55	
3	25.1	24.9	1.46	1.61

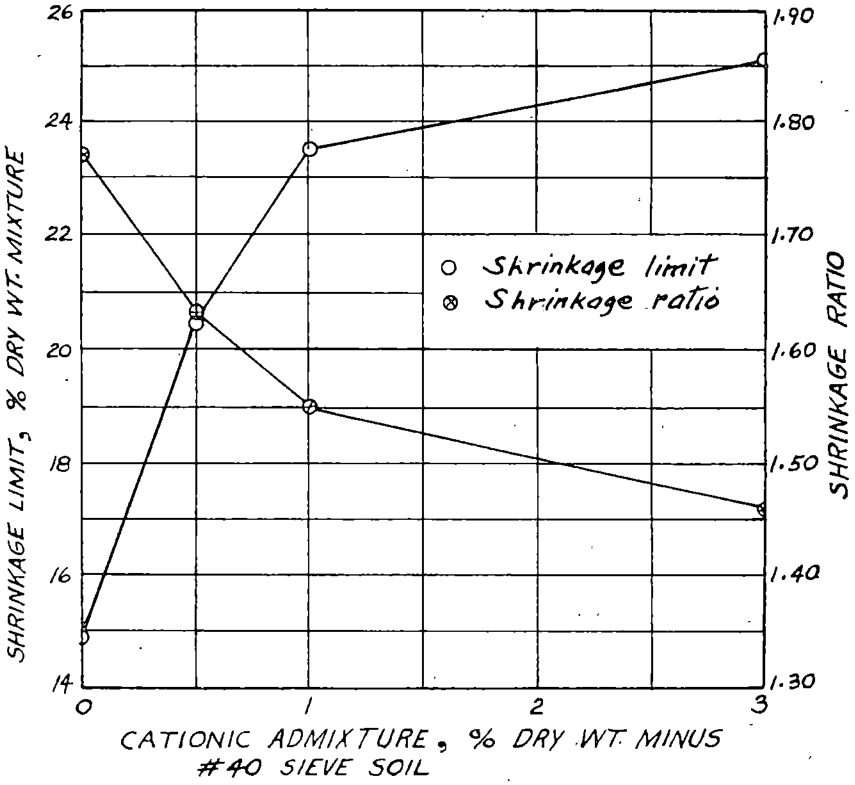

Fig. 4. Effect of cationic admixtures on shrinkage limit and shrinkage ratio of soil A.

water repellant areas on the clay surface by the adsorbed cations reduced the efficiency of the clay particles as lubricating agents.

Figures 6 and 7 show the results of California Bearing Ratio tests on natural and treated specimens of soils A and B, respectively. It will be noted that CBR values are compared at 0.1-in. penetration for soil A specimens and at 0.2-in. penetration for soil B specimens. This conforms with instructions of the Corps of Engineers which state that the CBR value at 0.2-in. penetration will be used for design purposes when it is lower than the value at 0.1-in. penetration[11].

The data of figures 6 and 7 indicate that the unsoaked California Bearing Ratios of soils A and B were decreased by treatment with 3 percent admixture. The soaked CBR value of both soils, however, was increased by the cationic treatment. Since the soaked CBR is customarily used in pavement design, it may be concluded the 3 percent treatments had a favorable effect on the stability of soils A and B. The soaked CBR of 73 percent for treated soil A shows it to be a good to excellent base material, while a corresponding value of 91 percent for treated soil B indicates it to be excellent for use as a highway base course.

The effect of the cationic admixture in reducing the swelling characteristics of the two soils is indicated by the fact that the amount of swell for specimens soaked four days under a ten pound surcharge was reduced from 4.51 to 0.83 percent in soil A and from 4.32 to 0.80 percent in soil B.

The reduction of the California Bearing Ratios of the unsoaked specimens by

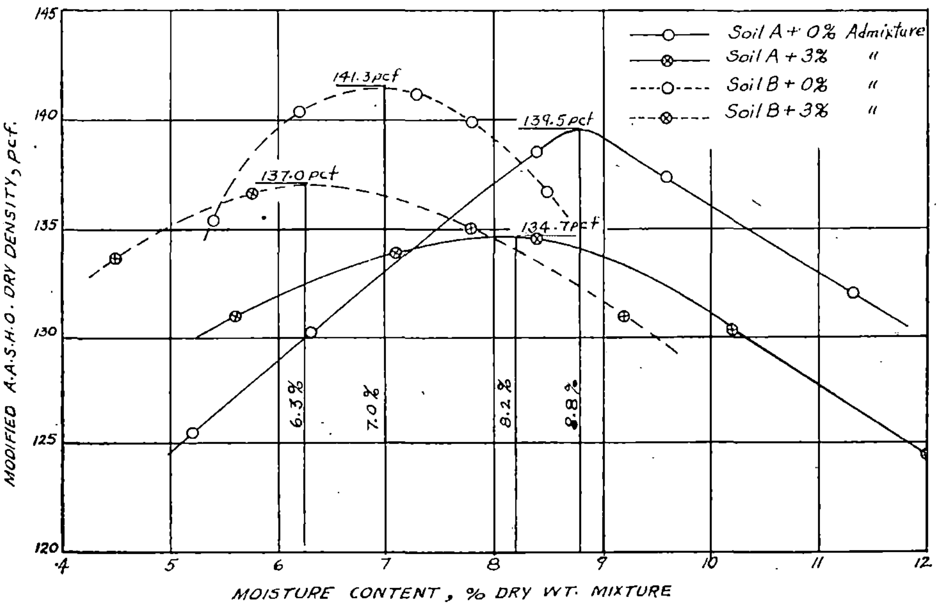

Fig. 5. Modified A.A.S.H.O. dry density-moisture content curves for soils A and B containing 0% and 3% admixtures of cationic material.

treatment with 3 percent admixture can perhaps be explained on the basis of the work of Grim and Cuthbert[6], who found that the development of cohesion in clay bodies is contingent upon the formation of continuous films of water on the surfaces of the individual clay particles. Such films would not be continuous upon the surfaces of clay particles containing adsorbed organic cations of the type furnished by the cationic compound. The higher CBR values of

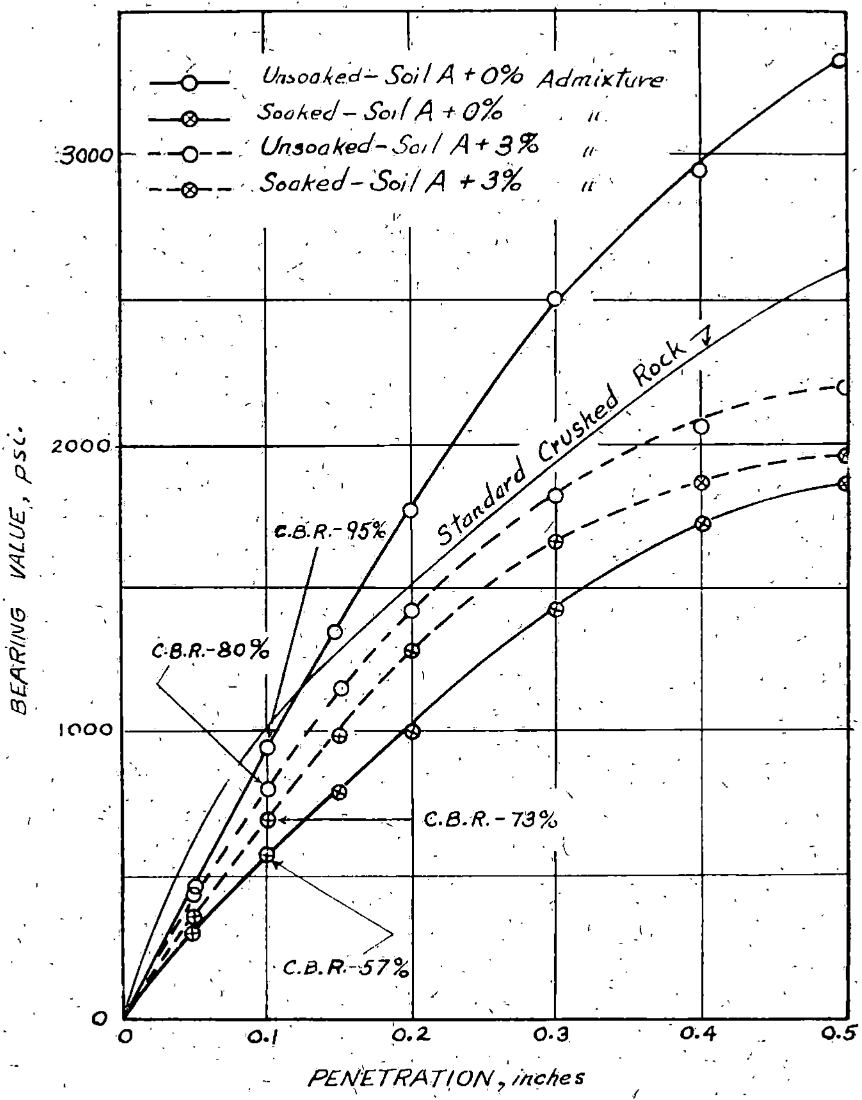

Fig. 6. C.B.R. test curves for soil A treated with 0% and 3% cationic material.

the soaked specimens containing the compound are attributed to the waterproofing ability of the cations[1].

No tests were performed in this investigation to determine the permanency of the substituted organic cations. A previous laboratory experiment[1] with the fatty acid amine acetate had indicated that repeated washing of treated soil with distilled water had little, if any, effect on engineering properties.

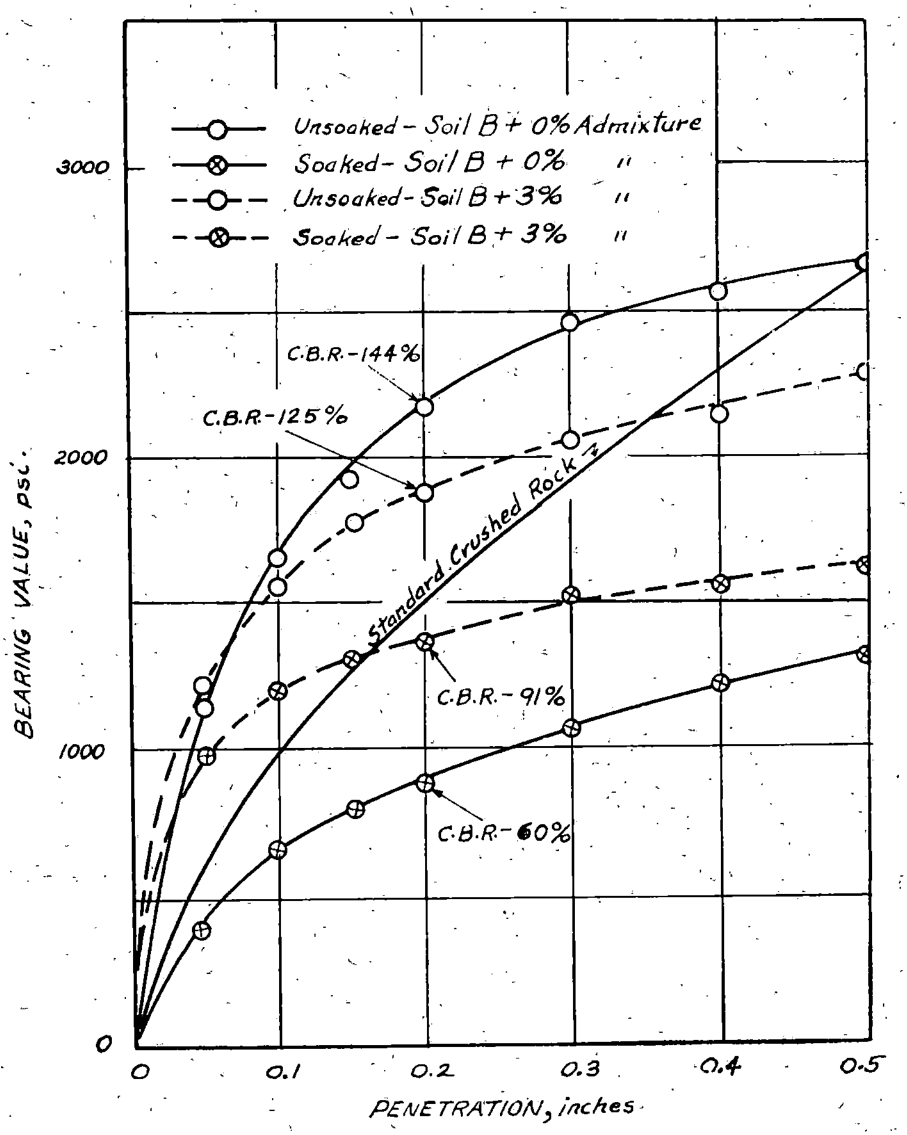

Fig. 7. C.B.R. test curves for soil B treated with 0% and 3% cationic material.

Another indication of the permanency of this type of soil treatment is that large substituted ammonium cations of the NH_3R^+, $NH_2R_2^+$, and NR_4^+ types were very strongly adsorbed on the surfaces of montmorillonite type clay minerals[3]. These cations could be replaced by other organic cations of approximately the same size, but they were not exchanged by hydrogen (H^+) which is very effective in replacing small inorganic cations.

CONCLUSIONS

In evaluating the results of this investigation only one method of adding the fatty acid amine acetate to the soils was used. Accordingly, all experimental findings and conclusions drawn therefrom apply only for this mixing procedure. Further study of this phase of the subject is needed.

The following are some of the conclusions drawn from the experimental data:

1. Cationic admixtures reduced the plasticity index of soil A by lowering its liquid limit and raising its plastic limit.
2. The admixtures reduced the shrinkage of soil A, as indicated by an increase in its shrinkage limit and a decrease in its shrinkage ratio.
3. While all percentages of the chemical reduced plasticity and shrinkage, the rate of reduction decreased as the percent admixture was increased.
4. The qualitative effect of 3 percent admixture on the Atterburg plasticity and shrinkage values of soils A and B was similar.
5. Treatment of soils A and B with 3 percent admixture reduced their plasticity indices to slightly less than 3 and changed the revised Public Roads classification of both from A-2-6(0) to A-1-b.
6. The maximum dry density and optimum moisture content of both soils as determined by the modified AASHO method were slightly lowered by 3 percent admixture.
7. The unsoaked California Bearing Ratios of soils A and B were decreased by treatment with 3 percent of the chemical.
8. The soaked California Bearing Ratio of both soils was increased by the 3 percent treatment.
9. Treatment with 3 percent admixture reduced the swell of soils A and B.

Much more research is necessary before any concrete recommendations can be made regarding the use of the fatty acid amine actate as a stabilizing agent for highway subgrade and base course materials. However, the work done so far indicates that it has considerable promise as an admixture to improve the all-weather stability of soil-aggregate mixtures such as those used in this investigation.

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MECHANISM OF STABILIZATION OF COHESIVE SOILS BY TREATMENT WITH ORGANIC CATIONS

by

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(Proceedings, Ninth National Clay Conference. 1960.)

ABSTRACT

The amount of moisture in a soil and its orientation to individual soil particles may be influenced by small additions of organic cationic compounds. Clay particles adsorb these cations, and because of their hydrophobic nature, a waterproofing effect occurs. Thermodynamic considerations are presented to explain the strength retention of treated soils.

INTRODUCTION

The mechanical properties of a soil vary substantially as a function of the water content. Addition of chemicals to a soil markedly inflluence the amount of water and the manner in which it is associated with soil particles. Organic compounds, for example, can decrease the water permeability of a soil used for lining a reservoir or an irrigation canal. Some success has been obtained in improving soil structure by the addition of certain organic chemicals. Such additives also reduce the plasticity of a soil, partly by increasing the size of the soil aggregates.

From an engineering standpoint the most important influence large organic compounds have on soils is that of strength retention. A soil which is compacted has a certain amount of strength, or resistance to a load or force. If the compacted soil is immersed in water, the strength is greatly reduced and may become zero. However, if a soil is first treated with small additions of an organic cationic compound, then compacted and immersed in water, the strength is not reduced as drastically. It becomes obvious then that the organic compound influences the water absorption of a soil.

Two other phenomena occur when organic cationic chemicals are added to soil. As the amount of chemical added to the soil is increased, the strength of the specimen after immersion in water is increased, but above a certain optimum amount of the chemical, the strength is rapidly reduced. And secondly, the strength of an air dried treated soil is lower than that of an air dried untreated soil, that is, if specimens are not immersed in water prior to testing.

So it appears that organic cationic compounds have a two-fold influence on soil moisture: the amount of water absorbed by a treated soil from its environment and the manner in which water is associated with or oriented to soil particles.

CHARACTERISTICS OF LARGE ORGANIC CATIONIC CHEMICALS

These chemicals fall under the general heading of amines, and have large hydrocarbon radicals with 8 to 22 carbon atoms. As might be expected, not all of them are soluble in water. Frequently, the organic complex is so treated as to produce a soluble salt such as an organic chloride. These salts are distinguished by having a positively charged cationic end and a negatively charged anionic end. The resultant cations formed have both a hydrophilic nature due to the net positive charge of the amine group and a hydrophobic nature due to the large hydrocarbon radical.

Experiments have indicated that a very intimate mixing of chemical and soil provide for maximum effect. Therefore, the amount of organic chemical added depends on cost, solubility, ease of mixing, and needed and obtained effectiveness. If the additive can be added in a water solution or dispersion, effectiveness is increased, and usually less than 1% by weight of the dry soil is required.

In laboratory experiments a concentrated stock solution or dispersion of the chemical is prepared and then added to the soil to give the desired ratio of chemical to dry soil. Sufficient water is then added to provide optimum moisture for compaction of the particular soil.

If field conditions are such that the soil is very wet, the organic chemical may be added in the most concentrated form which will still enable field machinery, such as spray bars, to function properly. The procedure then is to allow the soil, chemical, and water mixture to dry back to optimum moisture prior to compaction.

Regardless of field or laboratory conditions or the type of machinery available the salient fact is that moisture serves the double purpose of acting as a carrier for the organic cations and of providing the optimum moisture for maximum compaction. The latter is by nature inter-dependent on the soil type and mineralogy. The amount of compaction in turn depends on the engineering requirements of the soil.

Generally—and this by no means describes the limits—soils treated with organic cationic compounds are used for lower pavement components where stability requirements cannot be met by untreated soils. It was stated that soils treated with organic compounds exhibit lower dry strengths than those which are untreated. This strength is, however, still above the minimum desirable. It is under adverse but normal environmental conditions that the treated soil shows more strength retention than the untreated soil.

The stability of a soil may be considered as a happy marriage of strength and durability, both measured in terms of resistance to a decrease when subjected to adverse conditions. It is important, therefore, that a minimum stability be maintained by such additives.

THE INFLUENCE OF ORGANIC CATIONS ON SOIL MOISTURE

Orientation of Water Dipoles

Dry soils are generally hard because the moisture still present is oriented as a thin dipolar film linking soil particles. If water is added to the soil, the film thickens, dipoles are disorganized, and the hardness or strength disappears.

When organic cations are added to a soil, the negative surface charge of clay particles is balanced by the cationic end of the chemical, the clay tends to flocculate and has less ability to take up water.

In addition, the particle surfaces are partially coated with a thin film of a dilute solution of the organic cationic compound which exposes its hydrophobic end. Thus, the soil particles are essentially waterproofed. Excessive additions of organic cations (i.e., above the optimum percentage for the soil) will more completely coat soil particles and destroy the bonding action of the water. This in part explains why strength is reduced if organic cations are added above the optimum amount.

The importance of orientation of soil moisture to soil particles is clearly indicated in the following experiment: A set of treated soil specimens was compacted and then allowed to air dry. An identical set of treated specimens was compacted and then allowed to age or cure in a moist atmosphere. Both sets of specimens were immersed in water before testing. The moist cured specimens had less strength than the air dried specimens. Drying, therefore, is instrumental in obtaining a better arrangement of water films on soil particles. And since immersed strengths of chemically treated soils are higher than those of untreated soils, it may be possible that the organic cationic chemical so influences the arrangement of water films as to stabilize the bonding action of these films.

Because of the strong field associated with inorganic cations, water dipoles are oriented with respect to the cation and the clay particle. The affinity for water in this system is relatively great: therefore, additional water can enter and cause disorganization of the oriented dipoles. Organic cations, however, set up a weaker electric field, thus inducing less orientation of water dipoles; the affinity for water is weak, and additional water is not pulled into the system. Therefore, organic cations stabilize the bonding action of the weakly oriented water dipoles already present.

Preliminary X-ray analyses of soils treated with organic cations indicate that the above conclusion is valid. A sample of a Wyoming bentonite (sodium bentonite) was treated with a dilute dispersion of an organic cation, Arquad 2HT. An untreated sample wetted with distilled water served as a control. The data are presented in table I.

TABLE I. THE EFFECT OF ARQUAD 2HT ON THE BASAL SPACINGS OF A WYOMING BENTONITE

Moisture condition	Basal spacings in Angstroms			
	Treated		Untreated	
Air dried	11.9		11.0	
Moisture chamber for 24 hrs.	15.5	59	15.5	59
” re-wetted	20	63	20	v. weak 68
Moisture chamber for 5 days	18.0		18.8	
” re-wetted	19.6		19.6	v. weak 88

In manual re-wetting of the specimens it was observed that the untreated sample re-wetted readily, but the treated specimen strongly resisted the addition of water *until* sufficient mechanical energy was applied to form a paste. The effect of aging or curing in a moist atmosphere on the basal spacing is seen in the slight increase from about 11 Å to about 18 Å. X-ray analysis of the re-wetted specimens after 5 days of moist curing shows that the treated sample has expanded to a basal spacing of 19.6 Å. But the untreated sample shows two basal spacings: a very weak spacing at 19.6Å, indicative of limited water adsorption, and a very strong spacing at about 88 Å, indicative of free water adsorption. This indicates that after 5 days of moist curing the organic cation strongly inhibits the swelling properties of this clay. A moist-cure period of 24 hours is not sufficient to inhibit expansion of the treated clay. Therefore, the length of curing is important in obtaining maximum effectiveness of the organic cation by supplying the necessary moisture for effective orientation of water dipoles.

It is significant that after 5 days the untreated specimen shows a very weak spacing at 19.6 Å which is similar to the stable spacing of the treated sample. This shows that water will expand the clay lattice, but that this lattice spacing is an unstable one inasmuch as addition of water will cause a shift to a higher spacing. This effectively demonstrates the ability of the organic cation to stabilize the bonding action of weakly oriented water dipoles.

Surface Tension

Organic cations also reduce the surface tension in a soil water mix. This reduction has two pronounced effects on the soil: the cohesion is reduced and the surface free energy is reduced. The lowered cohesion results in the observed decrease in dry strength of treated soils, as well as in lowered plasticity. From the observed slight increase in internal friction and the decrease in cohesion, it follows that the shearing strength decreases.

In any reaction there is a change in the free energy of the system. In the system under consideration this is influenced by the chemical potential and the surface energy; the latter in turn is influenced by the surface area. The free energy strives for a minimum. In the following considerations the influence of any change in the surface area is neglected.

Since clay particles adsorb organic cations, an equilibrium takes place between the clay surface and its liquid film (Donnan membrane equilibrium). Since the surface tension of this film is reduced by the presence of these cations, the clay micelles have a lower surface energy than in the presence of pure water.

Leaching tests performed on treated soils indicate that organic cations are strongly held by the clay surface; therefore, it may be concluded that the ion exchange is in favor of the clay surface, and that the bulk of the micelle liquid contains very low concentrations of the organic cation.

Changes in concentration of the chemical in the low range have a more pronounced effect on the surface tension of water than changes in concentration in the high range (figure 1). Therefore, when clay micelles expose a surface which essentially is a dilute solution of the chemical, and if water is absorbed from the environment, the surface free energy of the system increases, again assuming the surface area to be constant.

Since organic chemicals have both polar hydrophilic groups and non-polar hydrophilic groups, their solvation energy is low, and the chemical potential at a certain activity (which is a function of concentration) may be considered low. If the negative of the free energy change is small compared with the increase in surface free energy, the system would defeat absorption of excess water, since this would cause an increase in the total free energy.

In applying these considerations to a soil specimen which has been treated with an organic cation the following conditions are indicated. As the specimen is cured or air dried, water leaves the system. The concentration of the cation increases, the concentration of water decreases, and the surface tension increases (figure 1). However, since the surface energy strives for a minimum, the increase in energy is slight and equilibrium is maintained. This is true only in the very low concentration range. If the concentration of chemical is greatly increased (by oven drying, for example) the change in surface tension upon addition of water is practically zero. If placed in a humid atmosphere, the

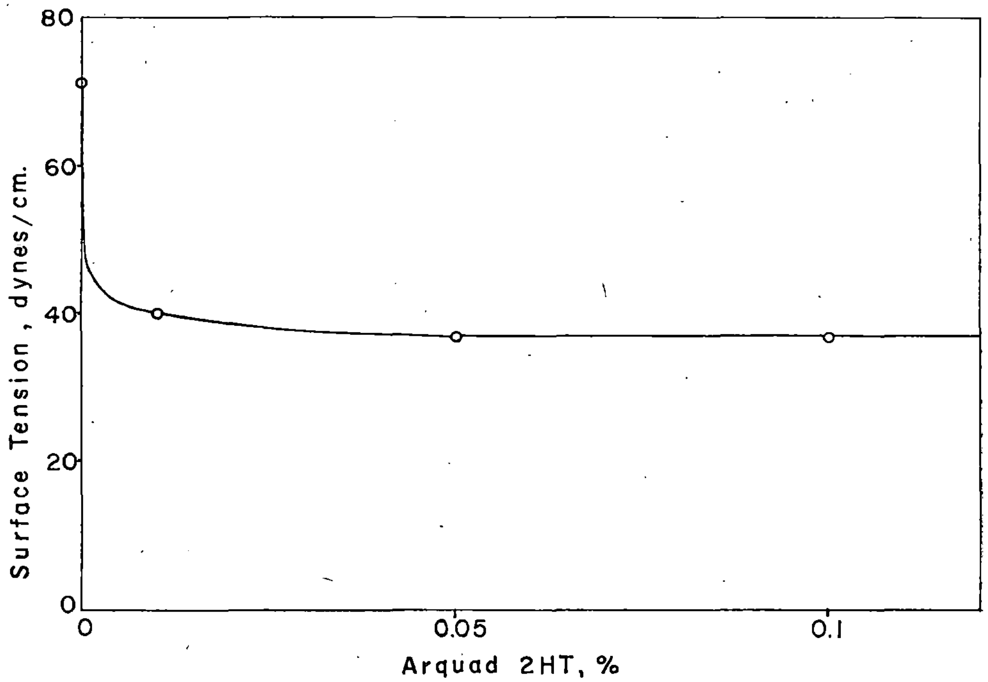

Fig. 1. Data by courtesy of the Armour Industrial Chemical Company. Arquad 2HT is a typical organic cationic chemical, specifically a quaternary ammonium chloride.

system can readily take up moisture due to the chemical potential and the absence of a great surface energy change.

Excessively dried, treated soils should, therefore, readily take up moisture from the environment, but air dried specimens should adsorb only a limited amount. Experimental evidence substantiates this.

CONCLUSIONS

Organic cationic chemicals influence the amount of water adsorbed by a treated soil as well as the bonding action of water dipoles. X-ray diffraction analysis shows that this bonding action is stabilized by the presence of organic cations after proper curing. These chemicals also reduce the surface tension in a soil, water mix, resulting in a waterproofing condition. These two concepts explain why immersed strengths of treated soils are higher than those of untreated soils, and why treated soils require a period of curing before definite strength properties are exhibited.

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PRELIMINARY EVALUATION OF SOME ORGANIC CATIONIC CHEMICALS AS STABILIZING AGENTS FOR IOWA LOESS

by

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(Highway Research Board Bulletin 129: 22-25. 1956)

ABSTRACT

A number of organic cationic chemicals were used as stabilizing agents for Iowa loess, which ranges texturally from silty loam to silty clay. An unconfined compression test is used for rating the chemicals. In this test, the principal criteria of stability are compressive strength, moisture absorption, and swelling after 24 hours immersion in water. The effects of the chemicals on air dry strength and shrinkage during air drying are also considered in evaluating the benefits to stability.

Though of a preliminary nature, the investigation demonstrates the superiority of several of the nineteen cationic chemicals used. Chemicals designated by the trade names Arquad 2HT, Arquad 2S, Armeen Residue, Armac T, Crude Amine, and Armeen Residue Arquad are considered particularly worthy of further study. These chemicals in amounts ranging from 0.08 to less than 1.0 percent by dry weight of the soil substantially improve the stability of loess. Used in such amounts, the cost of the chemicals per square yard of base course six inches thick ranges from about $0.14 to $1.13, which is economically feasible for highway construction.

Conventional highway construction equipment and procedures could be used for the processing of soil with organic cationic chemicals. The most practical method of applying the chemicals to the soil is as solutions or dispersions in water; a solution or dispersion would be added to the soil in the amount necessary for compaction to near standard Proctor density. In the concentrations used, the viscosity of the solution or dispersion is low enough to permit spraying. Field experimentation will be necessary to evaluate more fully the effectiveness of the chemicals.

INTRODUCTION

Soil stabilization research in progress in the Iowa Engineering Experiment Station since 1950 is directed towards finding economical ways of stabilizing the more common soil materials of Iowa for road construction purposes. Studies to 1956 have been primarily concerned with loess, which is the surficial deposit over approximately two-thirds of the state. Organic cationic chemicals are among the many compounds that have been screened as possible stabilizing agents for Iowa loess.

The term *organic cationic chemical* denotes a chemical, organic in nature, which dissociates in water to produce organic cations which may have exceedingly complex structures. Compared with the inorganic cations such as calcium, magnesium, hydrogen, or sodium, the organic cations are large, hence *large organic cations*. A characteristic of organic cations is that one or more organic radicals of hydrophobic (water hating) nature are part of the cation. When incorporated in the soil in amounts less than the cation exchange capacity, the organic cations are adsorbed rather completely to the clay surfaces of the soil in cation exchange reactions, replacing smaller, inorganic cations that are present. The adsorbed organic cations may be visualized as being oriented in such a way that the hydrophobic part of the cation is arrayed on the clay surface or directed outward from the surface. Considerable areas are thus formed on the involved clay surfaces that are not wetted by water. The more completely the clay surfaces are covered by adsorbed organic cations, the more hydrophobic the clay becomes.

Iowa Engineering Exeperiment Station studies of large organic cations as soil stabilizing agents date back to 1947. Results with fine grained soils and with soil aggregate mixtures which have been reported[7, 8, 9, 17, 24] indicate that large organic cations have considerable promise as soil stabilizing agents. Small amounts of organic cations, sufficient only to saturate partially the cation exchange capacities of the soils, were very effective in decreasing the soil's water absorption, swelling, plasticity, and shrinkage properties. Reduction of air dry strength was the only undesirable property change noted, but this was more than compensated for by the increase in immersed strength.

Among the organic cationic chemicals investigated in the earlier Iowa studies, a long chain fatty amine acetate known as *Armac T* was considered most promising. The quantitative effect of Armac T on soil properties related to all-weather stability was found to be a function of at least three variables: amount of clay, types of clay minerals, and kinds of exchangeable inorganic cations. An amount of Armac T equivalent to 10 to 25 percent of the soil's cation exchange capacity was judged to give near optimum results when both dry and immersed strength were used as criteria for stability. Treatment of two soil-aggregate mixtures with an amount of Armac T equal to 3 percent of the dry soil weight reduced the plasticity indices from 12.7 and 11.8 to less than 3 and changed the engineering classification of both soils from A-2-6(0) to A-1-b; the four day soaked CBR values were increased from 60 percent and 57 percent to 91 percent and 73 percent.

After the Iowa work started Armac T was used as the control chemical in a comparison of several organic compounds as stabilizing agents for a Pennsylvania clay loam[23]. Armac T gave the best strength preserving qualities of the chemicals tested; with a 2 percent admixture based on the soil weight, over 60 percent of the natural compacted soil strength was retained after a four-day soaking period.

The number of organic cationic chemicals that can be produced is large, and it seemed probable that Armac T, while promising, did not represent the best possible organic cationic chemical for soil stabilization purposes. Therefore in the loess stabilization research a number of additional chemicals were selected, primarily on the basis of recommendations by the manufacturer, for a preliminary-type evaluation. The most promising chemicals of previous studies, including Armac T, were included for comparison. The principal objectives of the investigation were: (1) to rate the chemicals according to their promise as soil stabilizing agents, and (2) to determine if one or more of them would warrant further and more detailed study.

Soils

Loess of Wisconsin geological age is one of the most abundant and widely distributed soil materials in Iowa. The Iowa Engineering Experiment Station has been engaged in engineering and geological property studies of Iowa loess since 1950, and several reports on this work have been presented[10, 11, 12, 13, 16, 20, 22]. The loess ranges texturally from silty loam to silty clay.

Two samples of C-horizon loess were used in the evaluation of the organic cationic chemicals; soil A was chosen to represent the friable, calcareous loess, soil B to represent the plastic, leached loess (table I). X-ray analysis of the minus 2 micron clay material of the two soils indicate: for soil A, montmorillonite is abundant, with about one-third as much illite, possibly a trace of kaolinite, and about 10 percent quartz; and for soil B, montmorillonite is predominant, with very little illite, no kaolinite, and about 10 percent quartz. Attention is directed to the difference in cation exchange capacity of the two soils; soil B has almost twice the exchange capacity of soil A. The predominant cations associated with the clay in both soils are calcium (Ca^{++}).

Chemicals

The amines and quaternary ammonium salts constitute the largest groups of

TABLE I. PROPERTIES OF WHOLE WISCONSIN LOESS SAMPLES

Properties		Soil A	Soil B
Physical properties	Liquid limit, %	30.8	51.9
	Plastic limit, %	24.6	18.5
	Plasticity index, %	6.2	33.4
	Shrinkage limit, %	22.3	19.1
	Specific gravity, 25°C/4°C	2.71	2.72
	Standard Proctor density test:		
	Max. dry density, lbs/ft^3	108.4	104.3
	Opt. Moist. content, %	18.0	19.1
Chemical properties	Organic matter, %	0.17	0.37
	Carbonates, %$CaCO_3$	10.2	0.5
	Oxidation	oxidized	oxidized
	pH	8.7	6.7
	Cation exchange capacity, m.e./100g.	13.4	24.4
	Exchangeable cations, m.e./100g.		
	Na	1.5	1.3
	K	1.6	1.3
	Ca	10.3	21.8
Textural composition*	Sand, %	1.4	0.4
	Silt, %	78.8	60.2
	Clay: Finer than 5μ, %	19.8	39.4
	Finer than 2μ, %	16.0	33.0
Engineering classification (AASHO)		A–4(8)	A–7–6(18)

* Sand — 2.0 to 0.074 mm, silt — 0.074 to 0.005 mm, clay — finer than 0.005 mm

organic cationic chemicals, and most of the chemicals studied are of these groups (table II). The chemicals are listed by their trade names as a matter of convenience, since more descriptive designations are space consuming, and for the average civil engineer difficult to understand. Available information on the chemistry of the chemicals is given in Appendix A. Vinsol NVX and Pulverized Vinsol are not considered to be cationic; they were included for comparison with the cationic materials and because they have been investigated as soil stabilizers by other investigators[21]. The major criteria for the selection of the chemicals were present or future availability and cost, and probable effectiveness as soil stabilizing agents. The chemicals designated as available in pilot plant or experimental quantities could, according to the manufacturers, be produced in commercial quantities if a demand existed.

Preparation of chemicals. It was determined by experimentation and correspondence with the manufacturers that the most practical way of adding the chemicals to soil was either as a solution or dispersion in distilled water, or as a powder, depending on the chemical nature of the material used. The chemicals are grouped in table II according to the procedure followed in preparing them, in the physical state indicated, for addition to the soil. Details of the procedure for each group are given in Appendix B. The concentrations of chemical in water solution or dispersion prepared for the first two chemicals tested were ½, 1, 3, 5, 7, and 9 percent by weight. The completion of these tests indicated

TABLE II. CHEMICALS EVALUATED, GROUPED ACCORDING TO PROCEDURE FOR PREPARING THEM FOR ADDITION TO SOIL

Group	Chemical	Physical state of chemical for mixing with soil	Availability from manufacturer	1954-55 price, dollars per lb. in car load quantities
A	Armac T	Solution in water	Commercial	0.30
	Arquad 2HT	Dispersion in water	Commercial	0.36
	Arquad 2S	Dispersion in water	Commercial	0.43
	Armeen Residue Arquad	Dispersion in water	Experimental	0.23 (estimated)
	Rosin Amine D Citrate in Pine Oil and Emulsifier	Emulsion in water	Experimental	. . .
	N (3-aminopropyl) Rosin Amine D Diacetate	Solution in water	Experimental	. . .
	Vinsol NVX	Solution in water	Commercial	0.0615
B	Duomeen T	Solution in water	Commercial	0.37
	Ethomeen T/12	Solution in water	Pilot Plant	0.49
	Ethomeen T/15	Solution in water	Commercial	0.47
	Ethoduomeen T/13	Solution in water	Commercial	0.45
	Crude Amine	Solution in water	Commercial	0.18
	Armine Residue	Solution in water	Commercial	0.09
C	Rosin Amine D Acetate	Solution in water	Commercial	0.18
	Monoethanol Rosin Amine D Acetate	Solution in water	Commercial	0.25
	Polyrad 0200 Acetate	Solution in water	Experimental	. . .
	Polyrad 0500 Acetate	Solution in water	Experimental	. . .
	Polyrad 1100 Acetate	Solution in water	Experimental	. . .
	Polyrad 2000	Solution in water	Commercial	0.36
D	Rosin Amine D Citrate	Powder	Experimental	. . .
	Pulverized Vinsol	Powder	Commercial	0.04

that optimum results might be expected from ½ to 3 percent concentrations; thereafter, concentrations of ½, 1, 3, and 7 percent were prepared of the other chemicals. Since the specific gravities of the chemicals were very close to that of water, solutions were prepared on a weight basis without adjustments for variations in specific gravity.

PRELIMINARY EVALUATION

An unconfined compression test of 2 in. diameter by 2 in. high cylindrical specimens molded to near standard Proctor density was used for rating the chemical treatments. In this test the principal criteria of stability of specimens are compressive strength, moisture absorption, and swelling after 24 hours complete immersion in water. The effect of the chemical treatment on air dry strength and shrinkage during air drying may also be considered in evaluating the benefits to stability.

This method of evaluation was selected because the nature of the investigation called for a simple and quick, yet sufficiently severe, method of comparing a large number of chemical treatments. Other tests will be used for further evaluation of the chemicals considered most promising as soil stabilizing agents.

Mixing

Mixing was done in a Model K4-B Kitchen Aid mixer. Twelve hundred grams of air dry soil passing the No. 10 sieve, enough for preparing six specimens, was placed in the mixing bowl, and, for a given concentration of chemical in water solution or dispersion, an amount necessary for compaction to standard Proctor density was added; the exact amount added depended on the optimum and hygroscopic moisture contents of the soil, and on allowances for evaporation but was the same amount for the concentrations of each chemical used. Mixing was done at No. 2 speed for about two minutes.

The two chemicals used in powder form were added to the air dry soil in amounts equivalent to the additives of chemical in water solution or dispersion, and then were dry mixed with the soil; next, enough distilled water was added to bring the mixture to optimum standard Proctor moisture content plus 0.5 percent for evaporation; mixing was then continued as in the preceding paragraph.

The amount of chemical mixed with the soil may be expressed in three ways: percent concentration of chemical in the water added for compaction to standard Proctor density; second, percent of oven-dry weight of soil; and third, percent saturation of the cation exchange capacity of the whole soil. In the relationships between these different ways of expressing the amount of chemical additive, given in tables III, IV, V, and VI, it will be noted that none of the treatments in the latter two tables was equivalent to 50 percent saturation of the cation exchange capacity of either soil, and the percent saturation with most treatments was much less than 50 percent. An example of the calculation of the percent saturation of cation exchange capacity has been given[7, 8].

Molding

Six 2 in. diameter by 2 in. high specimens were molded with a drop-hammer type molding apparatus for each combination of soil and chemical evaluated[6]. Approximately 200 grams of soil-chemical mixture was placed in the cylindrical mold in one layer and compacted to near standard Proctor density by ten blows of the 5 pound hammer dropping from a height of 12 inches. Immediately after molding, each specimen was weighed and the height measured. After the third of the six specimens was molded, a representative sample of the mixture was taken from the mixing bowl for a moisture content determination; it was found to be unnecessary to correct the moisture determination for the amount of chemical present in the sample.

TABLE III. RELATIONSHIP BETWEEN CHEMICAL CONCENTRATION IN WATER AND PERCENT DRY WEIGHT OF SOIL FOR A AND B AND GROUP I CHEMICALS

Chemical admixture	Soil A						Soil B					
	Amount of chemical* added to soil for water concentrations† shown below.											
	½%	1%	3%	5%	7%	9%	½%	1%	3%	5%	7%	9%
Armac T	0.08	0.16	0.49	0.82	1.14	1.47	0.08	0.15	0.45	0.76	1.06	1.36
Duomeen T	0.08	0.16	0.49	0.82	1.14	1.47	0.08	0.15	0.45	0.76	1.06	1.36
Ethomeen T/12	0.08	0.16	0.49	‡	1.14	. . .	0.08	0.15	0.45	. . .	1.06	. . .
Ethomeen T/15	0.08	0.15	0.46	. . .	1.08	. . .	0.08	0.15	0.45	. . .	1.06	. . .
Ethoduomeen T/13	0.08	0.15	0.46	. . .	1.08	. . .	0.08	0.15	0.45	. . .	1.06	. . .
Arquad 2HT	0.08	0.16	0.49		1.14	. . .	0.08	0.15	0.45		1.06	. . .
Arquad 2S	0.08	0.16	0.49	0.82		. . .	0.08	0.15	0.45	0.76	. . .	. . .
Crude Amine	0.08	0.15	0.46	. . .	1.08	. . .	0.08	0.15	0.45	. . .	1.06	. . .
Armeen Residue	0.08	0.15	0.47	. . .	1.08	. . .	0.08	0.15	0.45	. . .	1.06	. . .
Armeen Residue Arquad	0.08	0.16	0.48	0.95§	. . .	. . .	0.08	0.15	0.45	0.90§	. . .	. . .

* Percent dry weight of soil.
† Percent by weight of total solution.
‡ Dashes indicate that specimens were not molded.
§ 6% chemical concentration in water.

TABLE IV. RELATIONSHIP BETWEEN CHEMICAL CONCENTRATION IN WATER AND PERCENT DRY WEIGHT OF SOIL FOR SOILS A AND B AND GROUP II CHEMICALS

Chemical admixture	Soil A				Soil B			
	Amount of chemical* added to soil for water concentrations† shown below							
	½%	1%	3%	7%	½%	1%	3%	7%
RADA	0.08	0.16	0.49	1.14	0.08	0.15	0.45	1.06
Monoethanol RADA	0.08	0.16	0.49	1.14	0.08	0.15	0.45	1.06
P 0200 A	0.08	0.16	0.46	1.08	0.09	0.17	0.51	1.19
P 0500 A	0.08	0.16	0.46	1.08	0.09	0.17	0.51	1.19
P 1100 A	0.08	0.16	0.46	1.08	0.09	0.17	0.51	1.19
P 2000	0.08	0.16	0.46	1.08	0.09	0.17	0.51	1.19
RAD Citrate	0.07	0.15	0.45	1.04	0.08	0.17	0.50	1.16
RAD Cit. Solution in Pine Oil and Emulsifier	0.07	0.15	0.45	1.04	0.08	0.17	0.50	1.16
N (3-aminopropyl) RAD Diacetate	0.07	0.15	0.45	1.04	0.08	0.15	0.45	1.05
Vinsol NVX	0.07	0.15	0.45	1.04	0.08	0.17	0.50	1.16
Pulverized Vinsol	0.07	0.15	0.45	1.04	0.08	0.17	0.50	1.16

* Percent dry weight of soil.
† Percent by weight of total solution.

Curing

The effectiveness of organic cationic chemicals as soil stabilizers was found to be related to the curing procedure used[19]. The highest degree of stability as determined by the immersion compression test was obtained by air drying the compacted 2 in. diameter by 2 in. high specimens to constant weight prior to testing; seven days at room temperature proved sufficient to accomplish this. Specimens tested without drying back to a low moisture content had a lower degree of stability; oven drying at elevated temperatures was not beneficial.

It was decided to use the most favorable curing procedure in the preliminary evaluation of the chemicals. Accordingly, all molded specimens were air dried for seven days, then they were weighed and the decrease in height was measured.

TABLE V. RELATIONSHIP BETWEEN CHEMICAL CONCENTRATION IN WATER AND PERCENT SATURATION OF CATION EXCHANGE CAPACITY FOR SOILS A AND B AND GROUP I CHEMICALS

Chemical admixture	Soil A						Soil B					
	Percent saturation of cation exchange capacity for chemical concentration in water* shown below											
	½%	1%	3%	5%	7%	9%	½%	1%	3%	5%	7%	9%
Armac T	1.9	3.8	11.3	18.9	26.4	34.0	1.0	1.9	5.7	9.6	13.4	17.3
Duomeen T	2.4	4.7	14.1	23.5	32.9	42.2	1.2	2.4	7.2	12.0	16.7	21.6
Ethomeen T/12	1.5	3.0	9.0	. . †	20.9	. . .	0.8	1.5	4.6	. . .	10.6	. . .
Ethomeen T/15	1.1	2.1	6.4	. . .	14.9	. . .	0.6	1.2	3.4	. . .	8.0	. . .
Ethoduomeen T/13	1.0	2.1	6.2	. . .	14.4	. . .	0.6	1.1	3.3	. . .	7.8	. . .
Arquad 2HT	0.8	1.6	4.7	. .	10.9	. . .	0.4	0.8	2.4	. .	5.6	. . .
Arquad 2S	1.0	2.0	6.1	14.3	. . .	. . .	0.5	1.0	3.1	5.2		. . .
Crude Amine	1.7	3.3	10.0	. . .	23.4	. . .	0.9	1.8	5.4	. . .	12.6	. . .
Armeen Residue	1.2	2.3	7.0	. . .	16.2	. . .	0.6	1.2	3.7	. . .	8.7	. . .
Armeen Residue Arquad	0.7	1.5	4.4	8.8‡	. . .	. . .	0.4	0.8	2.3	4.6‡	. . .	. . .

* Percent by weight of total solution.

† Dashes indicate that specimens were not molded.

‡ 6% chemical concentration in water.

TABLE VI. RELATIONSHIP BETWEEN CHEMICAL CONCENTRATION IN WATER AND PERCENT SATURATION OF CATION EXCHANGE CAPACITY FOR SOILS A AND B AND GROUP II CHEMICALS

Chemical admixture	Soil A				Soil B			
	Percent saturation of cation exchange capacity for chemical concentration in water* shown below.							
	½%	1%	3%	7%	½%	1%	3%	7%
RADA	1.1	2.3	6.8	15.8	0.6	1.2	3.5	8.1
Monoethanol RADA	1.1	2.1	6.3	14.6	0.5	1.2	3.2	7.4
P 0200 A	1.3	2.6	7.9	18.4	0.8	1.6	4.8	11.1
P 0500 A	1.0	2.1	6.2	14.4	0.6	1.2	3.7	8.7
P 1100 A	0.6	1.3	3.8	9.8	0.4	0.8	2.3	5.4
P 2000	0.4	0.9	2.7	6.2	0.3	0.5	1.6	3.8
RAD Citrate	1.2	2.4	7.2	16.7	0.7	1.4	4.4	10.2
RAD Cit. Solution in Pine Oil and Emulsifier	1.2	2.4	7.2	16.7	0.7	1.4	4.4	10.2
N (3-aminopropyl) RAD Diacetate	1.0	2.0	6.1	14.2	0.6	1.1	3.4	7.8

* Percent by weight of total solution.

Testing

Specimens were tested for compressive strength by the unconfined compression test. The maximum load in pounds causing failure of the specimen was taken as the compressive strength. The test load was applied at a rate of deformation of 0.05 inch per minute per inch of height of the specimen. Three specimens of each set were tested in the air dry condition, and the other three were tested after 24 hours complete immersion in distilled water; the heights of the immersed specimens were measured prior to testing. Moisture determinations were made after testing on the second specimen of each group; the whole soaked specimen, and a sample obtained from the central portion of the air dry specimen were used as moisture samples.

Results

The relative effectivenss of the different chemicals and amounts of chemicals as stabilizing agents for the two loess materials was compared by using the previously given method of evaluation. Since the test method used has not been correlated with the field performance of stabilized soils, the test results give only an indication of relative stability. Criteria for judging relative stability of the test specimens are the change in height and the amount of moisture absorbed during 24 hours immersion, and the air dry and immersed compressive strengths. Low volume change and moisture absorption and improvement in immersed strength are the principal indications of benefits to stability by chemical treatment.

Complete immersion of air dry test specimens in an unconfined condition is a very severe treatment, particularly when the stabilizer is not of the bonding or cementation type as was true in this investigation. Chemically untreated soil specimens completely disintegrate after only a few minutes immersion.

The data have been divided into two groups, groups I and II, on the basis of the source of the chemicals (Appendix A). For easier understanding, the amount of chemical admixture is usually presented as percent of oven dry weight of soil, but conversions to the other ways may be made (tables III to VI). Test results are the average of data obtained from at least three test specimens.

Unconfined Compressive Strength

Unconfined compressive strength results were obtained with mixtures of soils A and B and varying amounts of the different chemicals (figures 1, 2, 3, and 4).

Air dry strength. All chemicals caused a reduction of air dry strength, but some caused less than others. In general, the trend of the data shows a rather sharp reduction in air dry strength from 0 to 0.17 percent admixture, based on the oven dry weight of the soil, and then a gradual leveling off with the larger amounts of additive. The air dry strengths of soil A specimens varied from a maximum of 2850 lb for the chemically untreated soil to a minimum of about 300 lb for the largest amount of additive; with soil B specimens, this range was 3220 lb to about 550 lb. The irregularities to be noted in some of the curves were checked by testing additional samples, but no appreciable change from the original data was found. It is of interest to note that the two non-cationic resinous materials, Pulverized Vinsol, and Vinsol NVX, had the least effect on air dry strength.

The effect of the chemicals on soil density, in the amounts added to the soils, was found to be slight; and the moisture contents of the air dry test specimens were found to decrease with increasing amounts of a chemical. On the basis of these findings and what is known about the nature of the chemicals, the reduction of air dry compressive strength by the chemical treatments is attributed to the partial destruction of the natural cohesion in the soil furnished by thin continuous films of water on clay surfaces. Such films cannot be continuous on clay surfaces partially shielded by adsorbed large organic cations of a hydrophobic

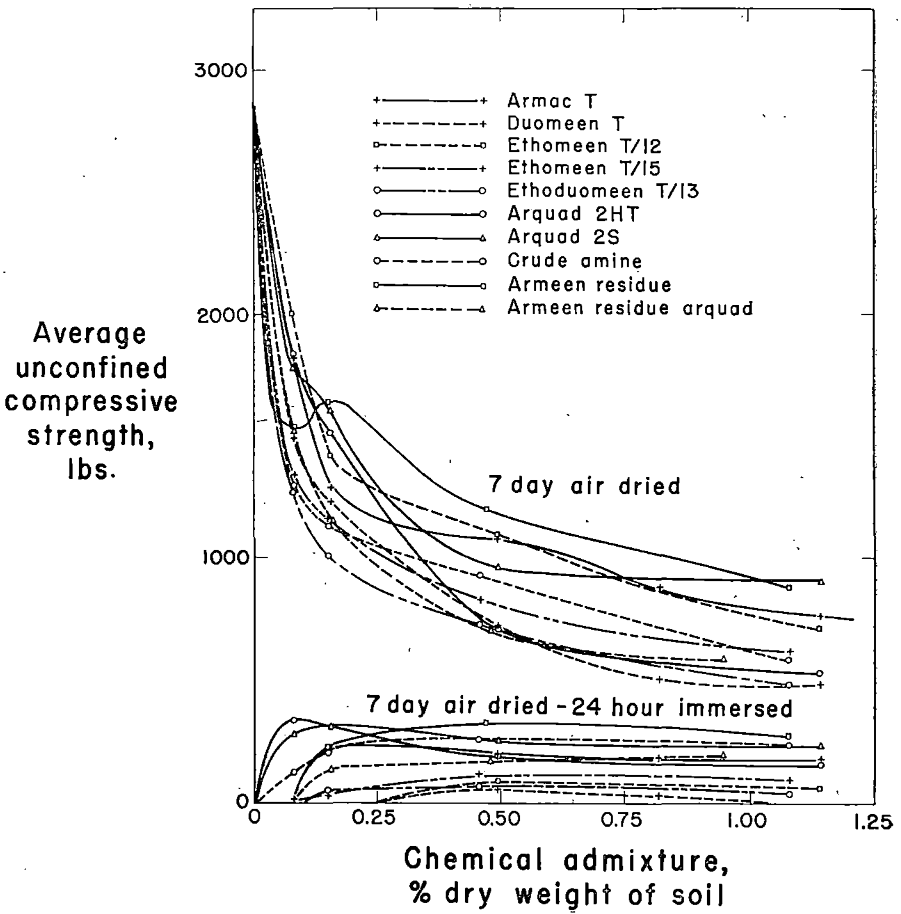

Fig. 1. Effect of amount of chemical admixture on average unconfined compressive strength of soil A with group I chemicals.

nature. The two non-cationic resinous materials would appear to have a similar but lesser effect on cohesion.

Immersed strength. The immersed strength data (figures 1, 2, 3, and 4) demonstrate the superiority of some of the chemicals as waterproofing agents. Taken as a whole, group I chemicals showed up better than group II chemicals; untreated specimens, as expected, failed within minutes after immersion.

The trend of the data on specimens that did not fail shows an increase in immersed strength from zero to a maximum and then either no further gain or a decrease in strength with increasing amounts of chemical. The only data showing a significant variance from this trend are those of Armeen Residue Arquad — soil B mixtures (figure 2). Due to the small amount of this chemical available for experimental purposes, it was impossible to carry the curve further.

In general, the chemicals were less effective with the plastic loess, soil B,

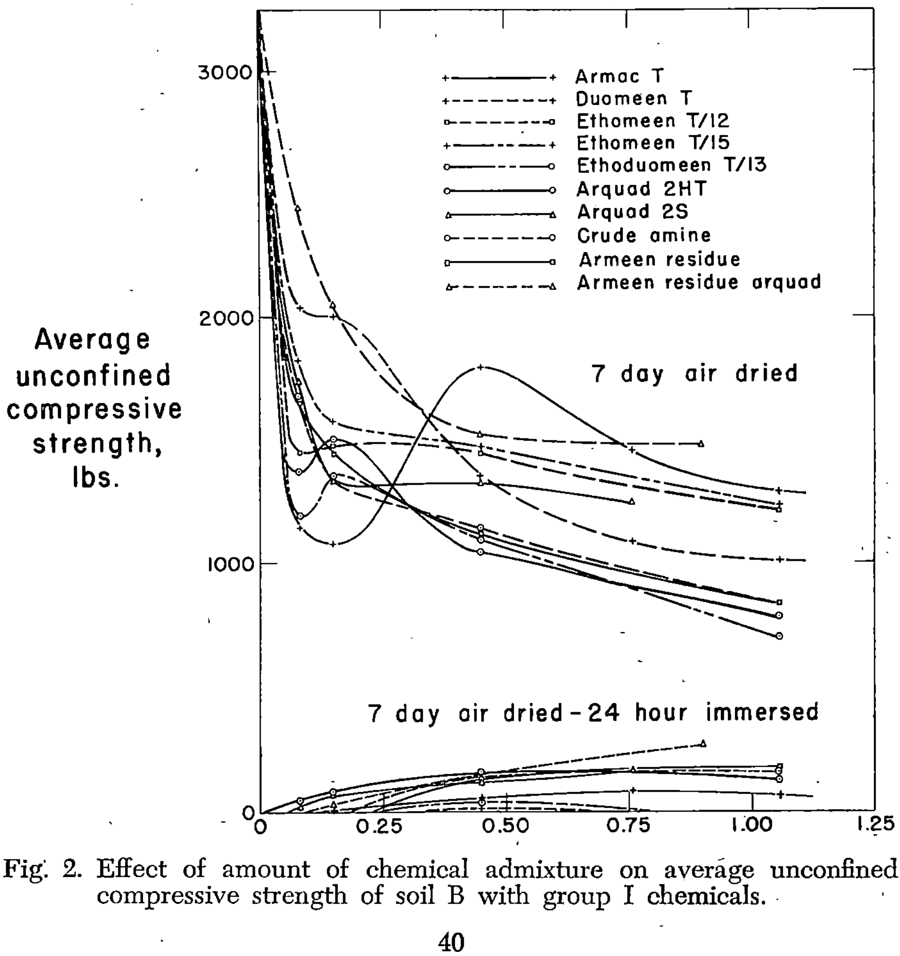

Fig. 2. Effect of amount of chemical admixture on average unconfined compressive strength of soil B with group I chemicals.

than with the friable loess, soil A. Except for one chemical, the maximum immersed strengths obtainable with soil A were greater than those of soil B; Vinsol NVX gave both soils approximately the same maximum immersed strength. Also, the amount of chemicals needed to obtain maximum immersed strength with soil B was greater than with soil A.

Moisture Absorption and Swelling

As a general rule the trends of the moisture absorption and volume change data agreed with the immersed strength data and showed that chemical treatments giving highest immersed strength also gave lowest moisture absorption and swelling. The moisture increase and swelling that did occur during the 24 hour immersion apparently introduced stresses and strains and increased the

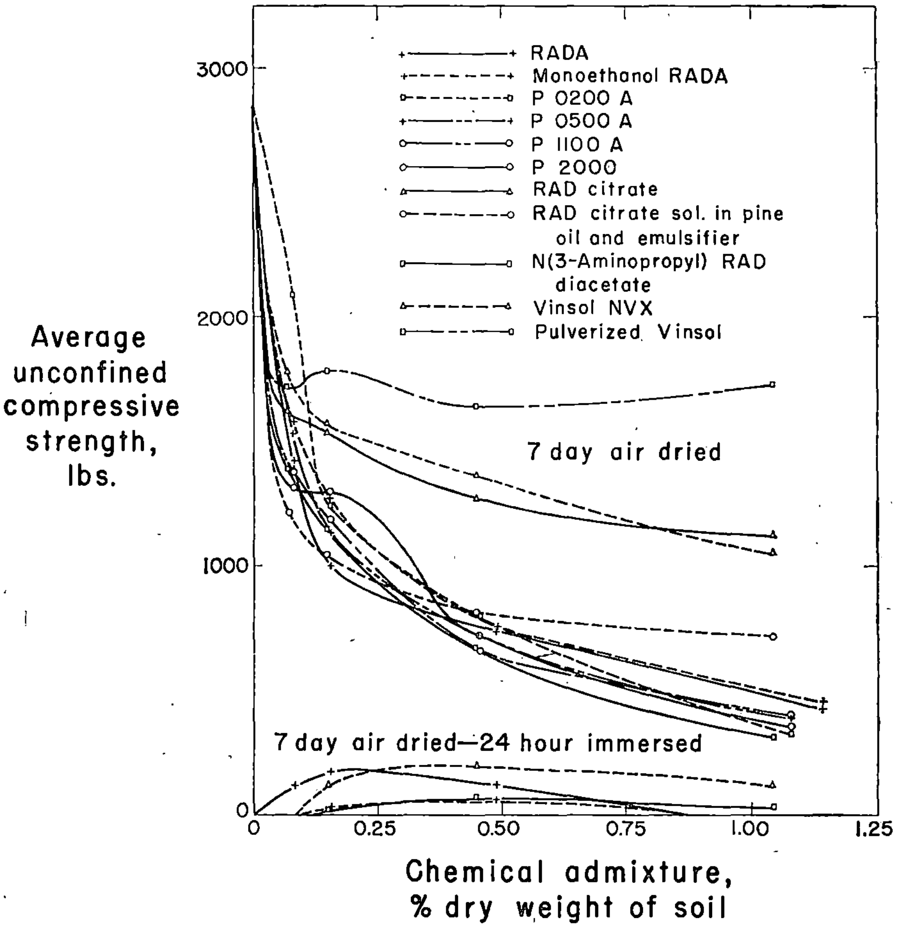

Fig. 3. Effect of amount of chemical admixture on average unconfined compressive strength of soil A with group II chemicals.

thickness of water films on clay surfaces to the extent that unconfirmed compressive strength was decreased below that of the air dry specimens.

Most Promising Cationic Chemicals

Though of a preliminary nature, the investigation demonstrated the superiority of several of the cationic chemicals evaluated. Arquad 2HT, Arquad 2S, Armeen Residue, Armac T, Crude Amine, and Amine Residue Arquad are considered particularly worthy of further study. Test results obtained with near optimum amounts of these chemicals for soil A and for soil B are summarized

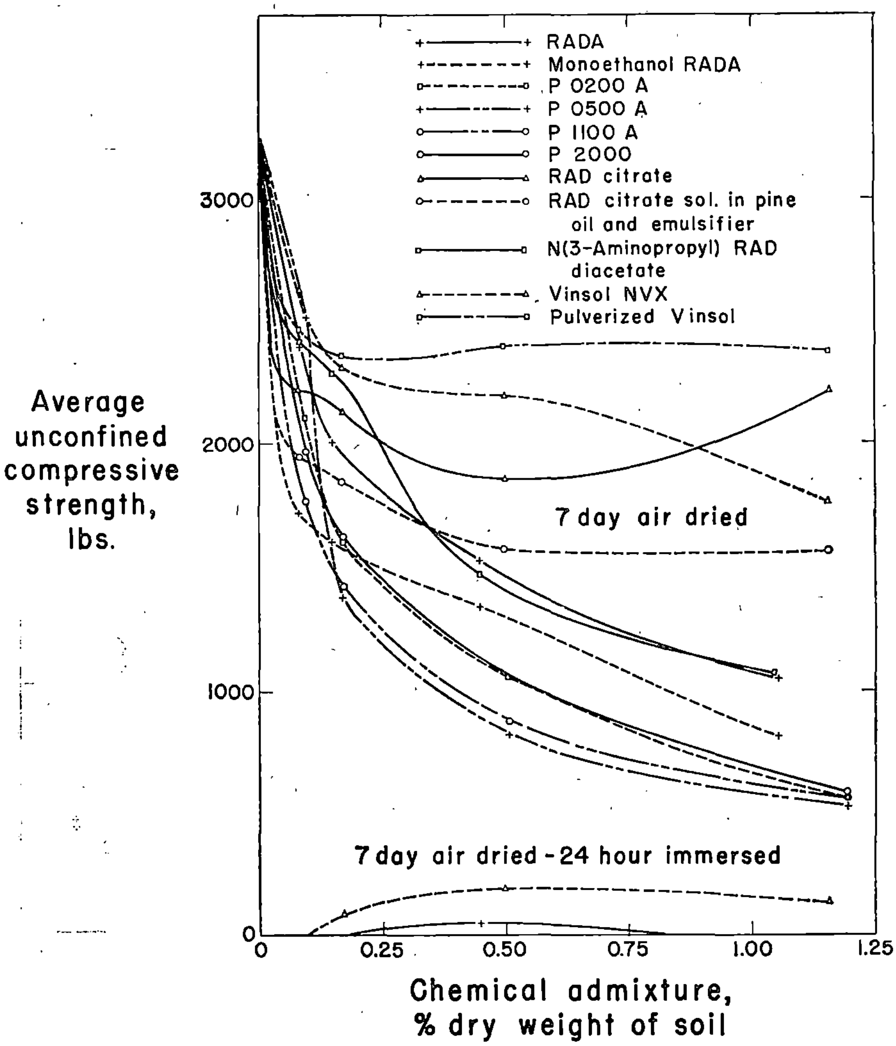

Fig. 4. Effect of amount of chemical admixture on average unconfined compressive strength of soil B with group II chemicals.

(tables VII, VIII), for soil B. Amounts of the chemicals ranging from 0.08 to less than 1.0 percent by oven dry weight of the soil are capable of substantially improving the stability of Iowa loess. Used in such small amounts, the cost of the

TABLE VII. SUMMARY OF RESULTS WITH CHEMICALS SHOWING THE BEST STABILIZING EFFECTS WITH SOIL A

	Raw Soil	Arquad 2HT	Arquad 2S	Armeen Residue	Armac T	Crude Amine	Armeen Residue Arquad
Amount of chemical, % dry wt. of soil	....	0.08	0.16	0.38	0.24	0.30	0.50
Amount of chemical, % saturation of C.E.C.	....	0.8	2.0	6.0[*]	5.5[*]	6.6[*]	3.7[*]
Av. unconfined comp. strength after 7 days air drying, lbs.	2847	1830	1660	1300	1200	1010	770
Av. unconfined comp. strength after 7 days air drying and 24 hr. immersion, lbs.	....	330	310	330	215	260	170
Av. decrease in height after 7 day air drying, in.	0.012	0.0074	0.0102	0.0085[*]	0.0066[*]	0.0067[*]	0.0106[*]
Av. increase in height after 24 hr. immersion, in.	....	0.0203	0.0173	0.0110[*]	0.0155[*]	0.0110[*]	0.0110[*]
Moist. cont. at time of molding, % oven-dry wt. of treated soil	18.7	18.8	19.2	18.8[*]	16.7[*]	18.7[*]	17.5[*]
Moist. cont. after 7 day air drying, % oven-dry wt. of treated soil	1.7	3.1	2.3	1.8[*]	2.9[*]	2.5[*]	2.2[*]
Moist. cont. after 24 hr. immersion, % oven-dry wt. of treated soil	....	9.0	7.7	7.7[*]	9.5[*]	8.0[*]	8.3[*]
Av. dry density, lbs/ft.^{3}[†]	105.0	99.9	103.4	102.0[*]	100.1[*]	101.6[*]	100.5[*]
Cost of chemical/yd.^{2} of surf. area, 6 in. thick, \$[‡]	....	0.14	0.34	0.17	0.36	0.27	0.57

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[*] Interpolated from tables and graphs.

[†] Near standard Proctor density.

[‡] This is the cost of the chemical for a compacted volume one yard square and six inches thick, with a density of 110 lbs/ft.^{3}

chemicals per square yard of base course six inches thick would range from about $0.14 to $0.13, which is economically feasible for highway construction. It is of interest to note here that Armac T, the most promising cationic chemical discovered

Table VIII. Summary of results with chemicals showing the best stabilizing effects with soil B

	Raw Soil	Arquad 2HT	Arquad 2S	Armeen Residue	Armac T	Crude Amine	Armeen Residue Arquad
Amount of chemical, % dry wt. of soil	....	0.45	0.45	0.60	0.76	0.60	0.45
Amount of chemical, % saturation of C.E.C.	....	2.4	3.1	5.4*	9.6	8.0*	2.3
Av. unconfined comp. strength after 7 days air drying lbs.	3220	1040	1330	1050	1460	1060	1520
Av. unconfined comp. strength after 7 days air drying and 24 hr. immersion, lbs.	....	160	120	150	90	160	150
Av. decrease in height after 7 day air drying, in.	0.051	0.0120	0.0253	0.0135*	0.0274	0.0130*	0.0248
Av. increase in height after 24 hr. immersion, in.	...	0.0517	0.0503	0.0220*	0.0610	0.0200	0.0536
Moist. cont. at time of molding, % oven-dry wt. of treated soil	19.5	18.2	18.4	17.7*	17.2	17.7*	18.6
Moist. cont. after 7 day air drying, % oven-dry wt. of treated soil	3.7	5.1	4.5	2.6*	3.3	2.6*	4.3
Moist. cont. after 24 hr. immersion, % oven-dry wt. of treated soil	....	13.9	13.6	10.6*	16.3	9.8*	13.2
Av. dry density, lbs/ft^3†	103.5	97.4	97.8	92.7*	97.4	99.2*	100.6
Cost of chemical/yd^2 of surf. area, 6 in. thick, $‡	....	0.80	0.96	0.27	1.13	0.54	0.51

---

* Interpolated from tables and graphs.

† Near standard Proctor density.

‡ This is the cost of the chemical for a compacted volume one yard square and six inches thick, with a density of 110 lbs/ft^3.

in the earlier studies of the Iowa Engineering Experiment Station, was not found to be best in this investigation.

From a comparison of the data on soils A and B the organic cationic chemicals selected as showing the most promise would be usable and beneficial to both friable and plastic loess; but the amounts of the chemicals needed with the plastic loess would be greater, and the degree of stability obtained would be lower. The difference in results obtained with the two soils is mainly due to difference in amount and kind of clay minerals. Soil B has approximately twice the clay content and cation exchange capacity of soil A, and has a higher proportion of montmorillonite type clay minerals.

Comparison With Other Kinds of Stabilizing Agents

The 24 hour immersed unconfined compressive strengths of 2 in. diameter by 2 in. high specimens of soil A, stabilized with four of the more promising organic cationic chemicals and those stabilized with other inorganic and organic additives are compared (table IX). Of the stabilizing agents compared, Portland cement, hydrated lime, and cutback asphalt have been quite widely used in highway construction with varying degrees of success; and lime, fly ash, and aniline furfural have shown considerable promise as stabilizing agents. The immersed strength obtained with Arquad 2HT, Arquad 2S, Armeen Residue, and Crude Amine, as compared with that obtainable with the better known stabilizers, further demonstrates the potentialities of organic cationic chemicals for the improvement of the stability of Iowa loess.

The cost per pound of the organic cationic chemicals may be much higher than

TABLE IX. AVERAGE UNCONFINED COMPRESSIVE STRENGTH OF SOIL A TREATED WITH VARIOUS ADDITIVES

Additive		Method of curing	Compressive strength, lb. (after 24 hr. immersion)	Cost[*] of stabilizing material per sq. yd. of surf. area, 6 in. thick, dollars
Type	Amount, % dry wt. of soil			
Portland cement, Type I	15	7 days in moist cabinet at approximately 70°F.	1780	0.70
Hydrated lime	6	Same as above	250	0.32
Lime-fly ash (1:2)	18	Same as above	485	0.42
Aniline-furfural (2:1)	5	7 days air drying	1100	4.71
Cutback asphalt RC-1	10	Same as above	220	1.17
Arquad 2HT	0.08	Same as above	330	0.14
Arquad 2S	0.16	Same as above	310	0.34
Armeen Residue	0.38	Same as above	330	0.17
Crude Amine	0.30	Same as above	260	0.27
Raw soil with no additive	. . .	Same as above	Failed during immersion	. . .

[*] This is the cost of the stabilizing material for a compacted volume one yard square and six inches thick, with a density of 110 lbs/ft^3.

that of such stabilizing agents as Portland cement, lime, and bituminous materials. But, since smaller amounts of the cationic materials are needed, stabilization may be cheaper with their use than with some of the more common stabilizing agents (table II).

Use in Highway Construction

It is believed that conventional highway construction equipment and procedures can be used for the processing of loess with organic cationic chemicals. The most practical method of applying the chemicals to the soil would be as solutions or dispersions in water; a solution or dispersion would be added to the soil in the amount necessary for compaction to near standard Proctor or other density. In the concentrations used, the viscosity of the solution or dispersion is low enough to permit spraying. Good mixing with the soil is important to obtain adequate exposure of clay surfaces to the large organic cations. The presence of large organic cations in the mix water tends to benefit workability of plastic soils, since the consistency properties are much improved by the cation exchange reactions.

Field experimentation with organic cationic chemicals will be necessary to develop a recommended method of construction, but more laboratory study is needed. Many things, such as use with different kinds of soil, curing requirements, and resistance to freezing and thawing, wetting and drying, and soil organisms need further investigation. The question also naturally arises of whether a better organic cationic chemical for soil stabilization purposes can be produced. The chemical industry might be able to answer this question if more fundamental knowledge about the requirements and mechanism of soil stabilization with large organic cations were made available.

ACKNOWLEDGMENTS

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J. N. Borglin, Naval Stores Department, Hercules Powder Co., Inc., Wilmington, Delaware.

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APPENDIX A

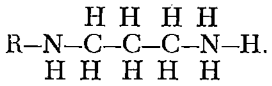
CHEMICALS USED

Information on each of the chemicals used in this study is summarized in the following paragraphs. Where they are available, the trade names of each are used to assist the reader.

Chemicals

Armac T[1] is a water soluble primary amine acetate made from fatty acids. It may be written as $[RNH_3]^+ [Ac]^-$, similar to ammonium acetate except that a fatty group replaces one of the hydrogens. It has a molecular weight of 310.

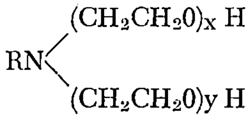
Duomeen T[2, 3] is a fatty di-amine of the general formula:



$$\begin{array}{ccccccccccccc} & & & & H & & H & & H & & H & & \\ R & - & N & - & C & - & C & - & C & - & N & - & H. \\ & & H & & H & & H & & H & & H & & \end{array}$$

The *R* represents an alkyl group derived from a tallow fatty acid. Being only slightly dispersible in water, the Duomeen T was treated with 30.0 parts of glacial acetic acid per 100.0 parts of 80 percent active Duomeen T by weight to form the water soluble di-acetate salt. Duomeen T has a molecular weight of 320.

Ethomeens[3, 4]. The Ethomeens are tertiary amines of the general formula:



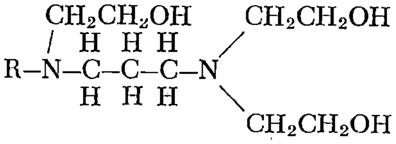
$$RN\begin{array}{l} \diagup (CH_2CH_20)_x H \\ \diagdown (CH_2CH_20)y H \end{array}$$

The *R* represents a fatty alkyl group derived from various fatty sources having from 12 to 18 carbon atoms. Attached to the nitrogen are two polyoxethylene groups. Although the Ethomeens are normally mildly cationic, these properties are more pronounced in the water soluble salts found by neutralizing the Ethomeens with acids. However, these salts are not stable to strong alkali.

Ethomeen T/12 has one fatty alkyl group derived from tallow amine. In the previous general formula for the Ethomeens, the T/12 has two mols. of ethylene oxide (x + y). It has an average molecular weight of 365 and was made water soluble by neutralizing with 16.4 parts glacial acetate acid per 100 parts of T/12, by weight.

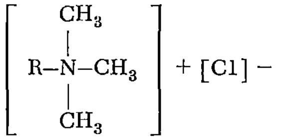
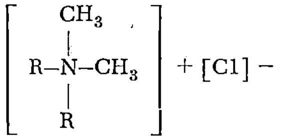
Ethomeen T/15 has one fatty alkyl group derived from tallow amine but has five mols. of ethylene oxide (x + y) in the two polyoxyethylene groups shown in the previous general formula for the Ethomeens. It has an average molecular weight of 497 with a water soluble salt being formed by neutralizing 100 parts of T/15 with 12.1 parts by weight of glacial acetic acid.

Ethoduomeen T/13 has the following general structural formula:



The di-acetate salt of the T/13 was prepared by adding 21.6 parts of glacial acetic acid to every 100 parts by weight of the chemical. The molecular weight of Ethoduomeen T/13 is 558.

Arquads[3, 4]. The Arquads are quaternary ammonium chlorides that retain their surface activity at either high or low pH and are not precipitated by calcium or magnesium hardness in water. They are described by the manufacturer as follows:

> A quaternary ammonium salt may be thought of as the organic counterpart of an ammonium salt. For example, if ammonium chloride (NH_4Cl) has all its hydrogen atoms replaced by organic groups, it becomes a quaternary ammonium salt. Arquads are quaternary ammonium salts of this type. They fall into two general groups: fatty alkyl trimethylammonium chlorides.
>
> 
>
> $$\left[\begin{array}{c} CH_3 \\ | \\ R\text{–}N\text{–}CH_3 \\ | \\ CH_3 \end{array}\right] + [Cl]^-$$
>
> and di-fatty alkyl, dimethylammonium chlorides.
>
> 
>
> $$\left[\begin{array}{c} CH_3 \\ | \\ R\text{–}N\text{–}CH_3 \\ | \\ R \end{array}\right] + [Cl]^-$$

Arquad 2HT is a di-hydrogenated tallow di-methylammonium chloride which is easily dispersible in water for dispersions up to about 8 percent by weight. It is supplied as 75 percent active in isopropanol and has an average molecular weight of about 585.

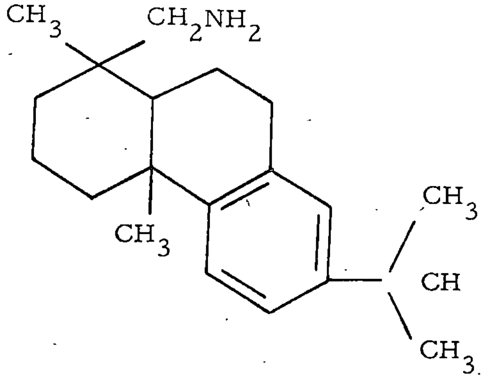
Arquad 2S is a di-methyl dialkyl quaternary ammonium salt derived from soybean oil. It is currently supplied as 75 percent active in isopropanol and is dispersible in water at 1 to 2 percent concentrations forming flowable gels as high as 12½ percent. It has an average molecular weight of about 595.

Armeen Residue is a crude material resulting from the process of amine distillation with a molecular weight of 497. It is a mixture of 30 to 40 percent primary amine, approximately 30 percent secondary amine, and a remainder of crude material including some polymerized material. Due to variations in the composition of the Armeen Residue from lot to lot, it was necessary to determine the amount of glacial acetic acid needed to form the water soluble acetate. By plotting a titration curve for Armeen Residue with varying amounts of the acid, it was determined that 6.3 parts glacial acetic acid per 100 parts Armeen Residue, by weight, were needed.

Armeen Residue Arquad is a quaternary made by treating Armeen Residue with methyl chloride. It is made up as a 50 percent solution in isopropanol, the active portion having a molecular weight of 804. The structural formula is a mixture of $RN(CH_3)_3 + Cl -$ and $R_2N(CH_3)_2 + Cl -$ where the *R* is primarily tallow.

Crude Amine is a 50-50 combination of Armeen Residue and Armeen T. It has a primary amine content of approximately 60 percent, the remainder being made up of secondary and tertiary amine. Due to the variation in percentages of amines with each lot manufactured, a titration curve for crude Amine with varying amounts of glacial acetic acid were plotted to determine the amount of acid needed for the water soluble acetate formation. Thus it was found that 15.6 parts acid per 100 parts crude Amine, by weight, were needed. It should be noted that there was incomplete acetate formation for both the crude Amine and the Armeen residue following treatment with glacial acetic acid; though the former is more complete due to its higher primary amine content.

Rosin Amine D derivatives[18] Rosin Amine D is a technical grade of dehydroabietylamine with the following structural formula:

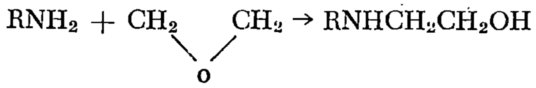


It is relatively stable up to about 100°C; decomposing at higher temperatures over extended periods of time. It is slightly soluble in water, being less than 0.5g per 100g of water at 100°C.

Rosin Amine D Acetate[18] is the acetic acid salt of Rosin Amine D. RADA, as it shall be referred to throughout the remainder of this paper, is water soluble and in the 70 percent paste form supplied by the manufacturer has a molecular weight of 338.

Monoethanol Rosin Amine D Acetate[18] is soluble in water and has a molecular weight of approximately 407. The manufacturer discusses Monoethanol RADA as follows:

Rosin Amine D reacts with ethylene oxide to form the N-substituted monoethanol derivative:



$$RNH_2 + CH_2\underset{O}{\diagdown\diagup}CH_2 \rightarrow RNHCH_2CH_2OH$$

Polyrads[18], or the Polyrad chemicals, are formed by reacting increasing amounts of ethylene oxide per mole of Rosin Amine D to form consistencies varying from balsam like liquids to wax like solids. The Polyrad chemicals used in this study and their respective approximate molecular weights are: Polyrad 0200 Acetate, 440; Polyrad 0500 Acetate, 560; Polyrad 1100 Acetate, 910; and Polyrad 2000, 1300. The number of moles of ethylene oxide per mole of Rosin Amine D is indicated by the first two numbers in the trade name. The acetate salts of the first three were used because those Polyrads containing less than 10 moles of ethylene oxide per mole of Rosin Amine D are only partially soluble in water; those with higher ethylene oxide contents are soluble.

Rosin Amine D Citrate is a salt of Rosin Amine D in which one carboxyl of citric acid has been neutralized. It is cationic, though insoluble in water, and must be pulverized and used as a powder as described in Appendix B. It has a molecular weight of approximately 466.

Rosin Amine D Citrate Solution is a mixture formulated to render the RAD Citrate water dispersible. The mixture comprises one part RAD Citrate, one part Synthetics A.F. 150, and one part Yarmor 302-W, the latter two ingredients being a pine oil and an emulsifying agent respectively.

N (3-ominopropyl) Rosin Amine D Diacetate was supplied by the manufacturer as a 100 percent active material, a very small yellowish-white aggregate varying in size from powder to small pea gravel and easily soluble in water. It has a molecular weight of approximately 550.

Vinsol resins, though not considered as cationic were included in this study for comparison with the cationic chemicals. Vinsol Resin is manufactured from residues obtained in the distillation process for turpentine[15]. Vinsol resin is a complex organic resin, phenolic in nature. It contains carboxyl, phenolic hydroxy, and methoxy groups. The two Vinsol products used in this study are Vinsol NVX and Pulverized Vinsol. The Vinsol NVX is water soluble, while the Pulverized Vinsol is insoluble in water and should be used in the powder form, as explained in Appendix B. The average molecular weights of Vinsol NVX and Pulverized Vinsol are 470 and 450 respectively.

APPENDIX B

PROCEDURES FOR PREPARING CHEMICALS FOR ADDITION TO SOIL

The following procedures were determined as being the most desirable for preparation of the chemical solutions and dispersions prior to incorporation in the soil (table II).

Procedure A.

The amount of chemical necessary to prepare a one liter volume of the concentration of chemical in water desired was placed in a 400 ml. beaker. Distilled water, previously heated to 60°C or slightly above, was mixed with the chemical until it was entirely dissolved or dispersed. The mixture was then washed into a 1000 ml. volumetric flask and diluted with the heated water to 1000 ml. To compensate for the change in volume due to temperature, it was calculated that an additional 13 ml. of water was needed to have a volume of 1000 ml. at room temperature.

Though there was little visible separation noticed in any of the physical states prepared under this procedure, each container was vigorously shaken for several minutes for complete dispersion of any separated particles before being used.

Procedure B.

Each of the six chemicals for which this procedure was used are insoluble in water in the form they are obtained from the chemical manufacturer. Upon treatment with glacial acetic acid, in the amounts previously given in Appendix A, the acetate salts formed are either entirely or partly water soluble. The amount of acid needed was added slowly to the chemical with constant stirring. This was continued until the temperature caused by the heat of reaction had decreased sufficiently to permit the acetate salt to begin to thicken to its normal room temperature status. The acetate salt was then placed in an air tight container and allowed to stand overnight before being dissolved in water. The remainder of the procedure was exactly that of Procedure A.

Except for the Crude Amine and Armeen Residue, the prepared solutions were completely dissolved; as previously stated there is incomplete water soluble acetate formation with the Crude Amine and Armeen Residue upon treatment with glacial acetic acid. Therefore the insoluble material floated to the top of the container after standing for a short time. Before each use, the containers of these two chemicals were shaken vigorously to disperse the residual material.

Procedure C.

This procedure was recommended by the manufacturer. The chemical, as supplied by the manufacturer, was placed in a large Erlenmeyer flask and was diluted with an equal quantity of distilled water at room temperature. This mixture was stirred thoroughly, yielding a heterogeneous mass, allowed to stand overnight, and with some additional stirring, yielded a homogeneous solution which was then diluted to a 10 percent stock solution by the further addition of water. The amount of stock solution needed for a desired concentration was placed in a volumetric flask and diluted to 1000 ml. with distilled water at room temperature.

Procedure D.

The Pulverized Vinsol was received from the manufacturer as a powder and required no further preparation before mixing with the soil. However, it was necessary to pulverize the RAD Citrate to a powder form. The powders thus prepared were added to the soil in the manner described in the procedure for mixing.

STABILIZATION OF LOESS WITH A PROMISING QUARTERNARY AMMONIUM CHLORIDE

by

F. B. Kardoush, Graduate Assistant
J. M. Hoover, Assistant Professor, Civil Engineering
D. T. Davidson, Professor, Civil Engineering

(Highway Research Board Proceedings 36: 736-754, 1957.)

ABSTRACT

Previously reported investigations of the Iowa Engineering Experiment Station have indicated the promising effects of a number of organic cationic chemicals as stabilizing agents for Iowa loess. From the standpoint of economic feasibility and improvement of immersed compressive strength, moisture absorption and swelling, a quaternary ammonium chloride, known commercially as Arquad 2HT, was considered especially promising.

A further evaluation of Arquad 2HT with calcareous silty loess and leached clayey loess is presented. The chemical was added to the soils as a water dispersion; for most tests a 3 percent concentration in water was used with the silty loess and a 5 percent concentration in water for the clayey loess (0.47 and 0.85 percent of the dry soil weight).

Tests were made to determine the effect of Arquad 2HT on such soil properties as plasticity, moisture and density relationship, moisture and curing time relationship, unconfined compressive strength, bearing capacity, and resistance to weathering. Results indicate that:

1. Immersed compressive strength depends to a great extent on the type of curing preceeding immersion. Air drying proved to be the best curing method.
2. Plasticity decreased.
3. Maximum dry density decreased slightly in both soils, whereas the optimum moisture content of the silty loess increased and that of the clayey loess decreased.
4. The soaked California Bearing Ratio increased and swelling decreased.
5. A considerable resistance to physical weathering was indicated.

On the basis of studies made and those reported by other investigators, a theoretical intrepretation of the mechanism of soil stabilization with organic cationic compounds is presented. Differential thermal analyses of the silty loess treated with Arquad 2HT, both under normal and nitrogen atmospheres, are evaluated.

INTRODUCTION

A means of treating the loess of Wisconsin geological age to make it suitable for use as a road base course is of great importance because of a scarcity of natural aggregates in Iowa and adjacent states. In recent years many methods of soil stabilization have been investigated by the Iowa Engineering Experiment Station with the foregoing objective in mind. One of the methods, organic cationic stabilization, which tends to give the loess greater stability through a chemical or molecular change in the surface characteristics of its clay, has shown a definite promise. Previous research has shown that treatment with large organic cations increases a soil's hydrophobic (water hating) characteristics and wetted strength[6, 7, 8, 10, 11, 12, 14].

A preliminary evaluation study by the Iowa Engineering Experiment Station of a number of organic cationic chemicals as stabilizing agents demonstrated the superiority of several of the nineteen cationic chemicals used[12]. Those designated by the trade names Arquad 2HT, Arquad 2S, Armeen Residue, Armac T and Crude Amine improved properties of the loess such as immersed compressive strength, moisture absorption and swelling; they were considered worthy of further study. One of them, Arquad 2HT, was particularly promising due to its commercial availability, economic cost in quantities used, and ease of preparation and mixing with soil.

The principal objectives of this investigation were: (1) to determine the best curing conditions for the soil-Arquad 2HT mixture; (2) to determine the effect of Arquad 2HT on such soil properties as plasticity, moisture-density relationship, and moisture-curing time relationship; (3) to evaluate the durability and bearing strength of the stabilized soils; and (4) to present a theoretical interpretation of the mechanism of soil stabilization with organic cationic compounds on the basis of studies made and those reported by other investigators.

Soils

Two samples of C horizon Wisconsin loess were used in this study to represent the average extremes in property variations of the loess in western Iowa; silty soil 20-2I and clayey soil 44A-1 were chosen because of their similarity to the friable calcareous loess and plastic leached loess (soils A and B)[12] (table I).

TABLE I. PROPERTIES OF WHOLE WISCONSIN LOESS SAMPLES

	Properties	Soil 20-21	Soil 44A-1
Physical properties	Liquid limit, %	34.2	53.1
	Plastic limit, %	26.2	25.7
	Plasticity index, %	8.0	27.4
	Shrinkage limit, %	24.6	19.9
	Specific gravity, 25°C/4°C	2.71	2.72
	Standard Proctor density test:		
	Max. dry density, lbs/ft^3	104.3	102.7
	Opt. moist. content, %	18.7	21.2
Chemical properties	Organic matter, %	0.17	0.37
	Carbonates, % $CaCO_3$	10.2	0
	Oxidation	oxidized	oxidized
	pH	7.8	6.2
	Cation exchange capacity, me./100g.	13.4[*]	24.4[*]
	Exchangeable cations, me./100g.		
	Na	1.5[*]	1.3[*]
	K	1.6[*]	1.3[*]
	Ca	10.3[*]	21.8[*]
Textural composition[†]	Sand, %	0.6	0.2
	Silt, %	80.6	58.0
	Clay: Finer than 5μ, %	18.8	41.8
	Finer than 2μ, %	14.7	31.0
Engineering classification (AASHO)		A–4(8)	A–7–6(18)

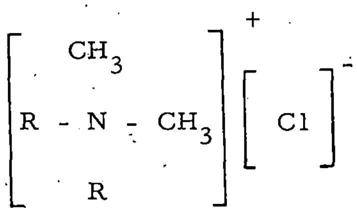
[*] These values are for soils A and B used by Hoover and Davidson (12) but are not considered representative of soils 20-2I and 44A-1, respectively.

[†] Sand—2.0 to 0.074 mm, silt—0.074 to 0.005 mm, clay—finer than 0.005 mm.

Attention is directed to the difference in cation exchange capacity of the two soils; soil 44A-1 has almost twice the exchange capacity of soil 20-2I. The predominant inorganic cations associated with the clay of both soils are calcium (Ca^{++}). Montmorillonite is the predominant clay mineral of each soil.

Chemicals

Amines and quaternary ammonium salts constitute the greatest source of organic cationic chemicals. The latter group are often described as being the organic counterpart of an ammonium salt. If the hydrogen atoms of ammonium chloride (NH_4Cl) are replaced by organic groups a quaternary ammonium salt exists. Arquad 2HT is a di-hydrogenated tallow di-methylammonium chloride and falls into a group of fatty dialkyl dimethylammonium chlorides of the following general formula (3):



$$\left[\begin{array}{ccc} & CH_3 & \\ R - & N & - CH_3 \\ & R & \end{array}\right]^+ \left[\, Cl \,\right]^-$$

It is easily dispersible in water for dispersions up to about 8 percent by weight and is supplied as 75% active in isoproponal with an average molecular weight of about 585. Arquad 2HT has been referred to by some investigators as DDAC and is also commercially available under the trade name Aliquat H226[4]. Concentrations of Arquad 2HT in distilled water as used in this study are on a weight basis of the material as supplied by the manufacturer and not on the active Arquad 2HT contained in the supplied material.

Other organic cationic chemicals refered to in this report have been described in a previous investigation[11].

Preparation of Soil-Chemical Specimens

Unless otherwise described, soil chemical specimens were prepared in the following manner:

The amount of chemical required for a desired water concentration was heated until liquified, and then diluted to 1000 ml. with distilled water previously heated to 60°C. After thorough mixing and cooling, an amount of the subsequently formed dispersion, equal to the optimum moisture content of the raw soil, was added gradually to air dried soil while being mixed in a Kitchen Aid (model K4-B) mixer at moderate speed, supplemented when necessary by hand mixing. Immediately after mixing, two inch diameter by two inch high specimens were molded to near standard Proctor density, and their heights and weights measured in a manner previously described[5, 12].

OPTIMUM CHEMICAL CONTENT

A preliminary study was made for the purpose of determining an optimum Arquad 2HT content for the soils used. The optimum for each soil was taken as the amount of chemical giving maximum unconfined compressive strength after seven days air drying and 24 hours immersion in water. Seven days air drying was found to be a reasonable length of time for the soil and Arquad mixture to dry to an equilibrium moisture content.

The data show that the air dry comprehensive strength of both soils decreased with higher concentrations of the chemical (figure 1). (The data presented are the averages of tests made on at least two specimens.) However, the immersed compressive strength of silty soil 20-2I increased to an optimum at 3 percent water concentration of chemical then tapered off, while the immersed strength of clayey soil 44-A1 increased to a leveling off point at about 5 percent water concentration of the chemical. These concentrations represent 0.47 and 0.85 percent of the dry soil weight and each is equivalent to slightly less than 5 percent of the cation exchange capacity of soils 20-2I and 44A-1, respectively. For ease of presenting the data gathered in this investigation, all chemical quantities will hereafter be expressed as a concentration in water, though the above relationships should be kept in mind.

CURING STUDIES

Since organic cationic chemicals introduced into a soil appear to maintain the soil's stability by establishing a hydrophobic condition within the soil, it was considered probable that the strength of the soil and Arquad specimens would depend to a great extent on the type of curing used prior to testing. Though only a small portion of the fourteen curing conditions investigated are likely to occur in the field, it was anticipated that information could be obtained to assist in understanding the mechanism of soil stabilization with large organic cations. To study

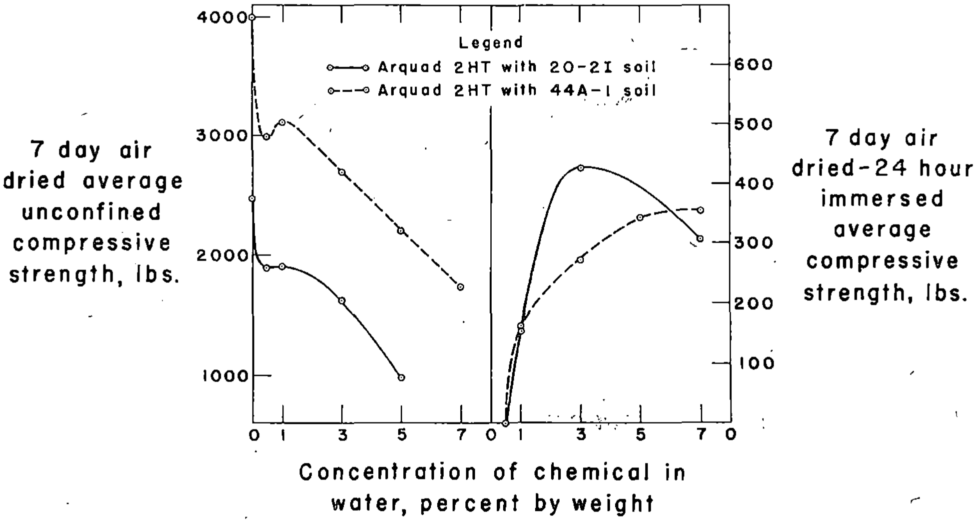


Fig. 1. Effect of amount of chemical on average unconfined compressive strength of soils 20-2I and 44A-1.

various combinations of time, humidity, and temperature which might affect curing, specimens treated with the previously determined optimum amounts of Arquad 2HT were subjected to the following curing conditions and then tested for unconfined compressive strength after 24 hours water immersion:

1. No curing.
2. Curing at room temperature.
a. In open air of approximately 30 percent relative humidity.
b. In a dessicator with approximately 65 percent relative humidity.
3. Moist curing in a moisture cabinet at 70±3° F and approximately 90 percent relative humidity.
4. Curing at elevated temperatures.
a. In 110°F oven, wrapped.
b. In 160°F oven, wrapped.
c. In 160°F oven, unwrapped.
5. Combination heat and moist curing.
a. One and two days in 90°F oven, then moist cured in a moisture cabinet at 70±3° F and approximately 90 percent relative humidity, unwrapped.
b. Same as above except in 110° F oven.
c. Same as above except in 140° F oven.
d. Same as above except in 160° F oven.

The length of curing for each condition varied from 0 to 14 days prior to immersion, except for the combination heat and moist curing. For this condition the specimens were first cured at the specified temperature, then were placed in a moisture cabinet for periods of 0 to 14 days followed by immersion for 24 hours.

Results

The curing study results (tables II, III) indicate that:

Table II. Effect of curing method and curing time on immersed strength of 20-2I specimens treated with 3 percent water concentrations of Arquad 2HT.

Curing Method	Immersed Compressive Strength, lbs. Curing Time, days						
	0	1	3	5	7	10	14
Air dry, 30% R.H.[*]	40	117	147	268	358	372	407
Aid dry, 65% R.H.	20	45	45	55	67	70	70
Moist, 90% R.H.	20	40	52	65	65	65	83
110°F, wrapped	20	62	75	77	70	83	100
160°F, wrapped	20	75	83	83	90	113	113
160°F, unwrapped	20	225	18	0	0	0	0
1 day, 90°F; moist, 90% R.H.	20	40	60	68	125	†	†
2 days, 90°F; moist, 90% R.H.	20	34	58	87	120		..
1 day, 110°F moist, 90% R.H.	20	260	255	247	247	250	242
2 days, 110°F; moist, 90% R.H.	20	93	213	213	223	243	252
1 day, 140°F; moist, 90% R.H.	20	228	243	210	197	..	..
2 days, 140°F; moist, 90% R.H.	20	20	182	183	173	..	..
1 day, 160°F; moist, 90% R.H.	20	220	205	235	250	..	..
2 days, 160°F; moist, 90% R.H.	20	45	200	195	193	..	..

[*] R.H. = Relative Humidity

† Not determined.

1. Seven days air curing at 30 percent relative humidity was the best curing method. Therefore, determination of the optimum chemical content after 7 day air curing was considered as being justifiable.

2. The effect of length of curing was different with each method used, but was more pronounced with air curing. Even with no curing, some immersed strength was gained since untreated soil specimens disintegrated within a few minutes after immersion in water.

3. The change in relative humidities from 65 to 90 percent caused little variation in the immersed strengths.

4. Wrapped specimens cured at elevated temperatures of 110° F and 160° F had immersed strengths slightly greater than those of specimens moist cured at 70±3°F. It should be remembered that moisture was preserved in wrapped specimens, and that the relative humidity inside the wrapping was at least as high as that in the moisture cabinet used for normal moist curing.

5. Prolonged oven drying of unwrapped specimens at 160° F was extremely detrimental to the silty soil specimens and caused considerable reduction in strength of the clayey soil specimens.

6. The combination of one and two days oven drying at 90° F followed by normal moist curing resulted in low immersed strengths for both soils. The strength values were about the same as those obtained by normal moist curing only.

7. Drying at temperatures of 110° F, 140° F and 160° F gave similar test results, except that the 2 day drying at 140° F and 160° F caused a reduction in the immersed strengths of specimens of both soils. This strength decrease indicates a critical moisture content-immersed strength relationship. Drying of the stabilized soils to below this critical moisture content results in a reduction of

Table III. Effect of curing method and curing time on immersed strength of 44A-1 specimens treated with 3 percent water concentration of Arquad 2HT.

Curing Method	Immersed Compressive Strength, lbs. Curing Time, days						
	0	1	3	5	7	10	14
Air dry, 30% R.H.	40	117	147	268	358	372	407
Air dry, 65% R.H.	40	75	97	85	95	70	50
Moist, 90% R.H.	40	65	90	95	85	78	80
110°F, wrapped	40	100	115	97	105	100	130
160°F, wrapped	40	112	117	95	105	123	150
160°F, unwrapped	40	202	122	130	80	60	82
1 day, 90°F; moist, 90% R.H.	40	80	100	90	108	†	†
2 days, 90°F; moist, 90% R.H.	40	72	92	68	75		
1 day, 110°F; moist, 90% R.H.	40	222	245	153	117	315	200
2 days, 110°F; moist, 90% R.H.	40	278	388	228	338	358	295
1 day, 140°F; moist, 90% R.H.	40	340	345	335	343	..	..
2 days, 140°F; moist, 90% R.H.	40	130	343	272	287	...	..
1 day, 160°F; moist, 90% R.H.	40	320	277	225	215	..	..
2 days, 160°F; moist, 90% R.H.	40	83	265	293	262	..	..

* R.H. = Relative Humidity

† Not determined.

immersed strength; dehydration of the stabilized soil by normal moist curing is highly beneficial after 1 to 3 days in a moisture cabinet.

8. The loss of strength below the critical moisture content may be caused by the increase in air voids that accompanies any reduction of moisture. Below the critical moisture value, the air void content may increase to such an extent that during immersion, water not only enters the soil rapidly but also causes compression of the air trapped within and a consequent loss of specimen strength (figure 2).

The curing studies were performed with only one Arquad 2HT treatment of each soil, the optimum treatment determined from the immersed strength of 7 day air dried specimens (figure 1) in the preliminary study. To determine the effect of curing method on the optimum chemical content, unwrapped specimens containing varying amounts of Arquad 2HT were cured one day at 140° F

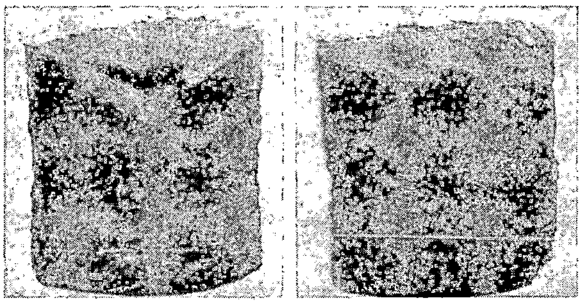


Fig. 2. Heat cured specimens following 24 hours immersion in water.

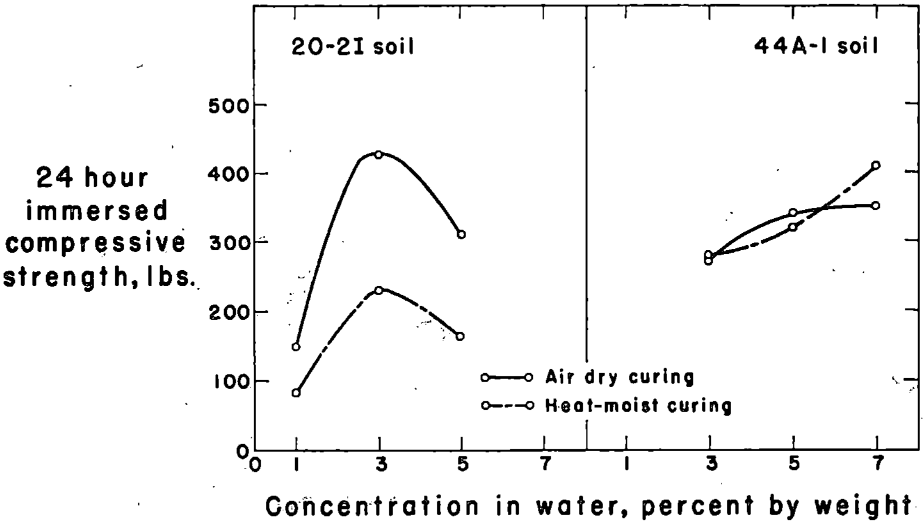


Fig. 3. Comparison of seven days air dry curing with heat moist curing for various concentrations of chemical.

followed by normal moist curing for 3 days. Strength results after 24 hours immersion are compared with those from seven day air curing (figure 3). It will be noted that for both methods of curing the optimum chemical concentration in water is about the same; 3 percent for soil 20-2I and 5 percent for soil 44A-1. There is an indication that 7 percent concentration might be slightly better than 5 percent for soil 44A-1, however, the viscosity of a 7 percent concentration is such that the ease of mixing the chemical with the soils is greatly reduced.

Arquad 2S, another quaternary ammonium salt, when tested under conditions exactly the same as described in the preceeding paragraph gave comparable immersed strength results, indicating that treatments of Arquad 2S and Arquad 2HT have similar effects on both soils.

CONSISTENCY LIMITS

To determine the effect of Arquad 2HT on the consistency limits of the two soils, soil-Arquad specimens were molded, air cured for seven days, then broken and ground by mortar and pestle to pass the No. 40 sieve. The consistency limits were then determined according to standard procedures (ASTM Designations: D423-54T and D424-54T).

The plasticity of both soils was decreased by the addition of Arquad 2HT. The amount of reduction increased as the amount of chemical in the soil increased and reached an almost constant value at 3 and 5 percent concentration for soil 20-2I and 44A-1 respectively; further increases in chemical resulted in very little change in the plasticity index of either soil.

Shown in table IV are the results of the consistency limits for raw soils and for specimens containing optimum concentrations of Arquad 2HT after subjection to two curing conditions. It will be noted that the P.I. of clayey soil 44A-1 was reduced to a greater degree than that of silty soil 20-2I while the shrinkage properties of both soils were not changed to any appreciable extent by the

TABLE IV. EFFECT OF CURING METHOD ON CONSISTENCY AND DENSITY PROPERTIES OF RAW AND ARQUAD-TREATED SOILS.

Soil No.	20-2I			44A-1		
Water Concentration Arquad 2HT, %	0	3	3	0	5	5
Curing Condition	Air Dried*	Air Dried*	Heat-Moist†	Air Dried*	Air Dried*	Heat-Moist†
Liquid Limit, %	34.2	31.5	30.1	53.1	44.1	42.6
Plastic Limit, %	26.2	24.8	24.9	25.7	28.1	27.9
Plasticity Index, %	8.0	6.7	5.2	27.4	16.0	14.7
Shrinkage Limit, %	24.6	24.2	24.2	19.9	19.9	17.1
Shrinkage Ratio	1.64	1.67	1.67	1.81	1.81	1.83
Max. Std. Proctor Density, pcf.	104.3	101.0	. . .	102.7	100.2	. . .
Optimum Moisture at Std. Proctor Density, %	18.7	19.5	. . .	21.2	19.5	. . .

* Seven days air drying at room temperature.

† One day at 140°F, 6 days moist curing at 90% relative humidity.

Arquad treatments. Also, the curing method affected the liquid limit and P.I. of both treated soils, being lower with heat-moist curing than with air drying.

MOISTURE-DENSITY RELATIONSHIP

Standard Proctor moisture density relationships (ASTM Designation: D698-42T) of raw and Arquad 2HT treated soils are compared (figure 4, table IV). There was a slight decrease of the maximum dry density of both soils when treated with the chemical; however, the optimum moisture content of the silty soil was slightly increased, and that of the clayey soil was slightly decreased. From these results, it seems permissible to use the optimum moisture content of the raw soil as a basis for estimating the amount of chemical and water dispersion to be added to the soil in preparing test specimens.

MOISTURE CURING TIME RELATIONSHIP

To compare the effect of curing on the moisture content of raw and optimum Arquad 2HT treated soil specimens, a check was made on moisture variation during air drying and during heat moist curing (one day at 140° F followed by 6 days normal moist curing). Moisture determinations, expressed as a percentage of the moisture content at the time of molding, were made at 12 hours and at 1, 3, 5, and 7 days from the time of molding (heat moist cured specimens were also checked at 4 and 8 hours). The same specimens were then immersed in water, and moisture determinations, expressed in the same manner, were made at 4 and 8 hours, and at 1, 3, 5, and 7 days after immersion (figure 5).

Only slight differences could be detected in rate of moisture loss between raw and stabilized soils. The moisture content of heated specimens was reduced to 7 or 8 percent of their optimum moisture content in 24 hours. After

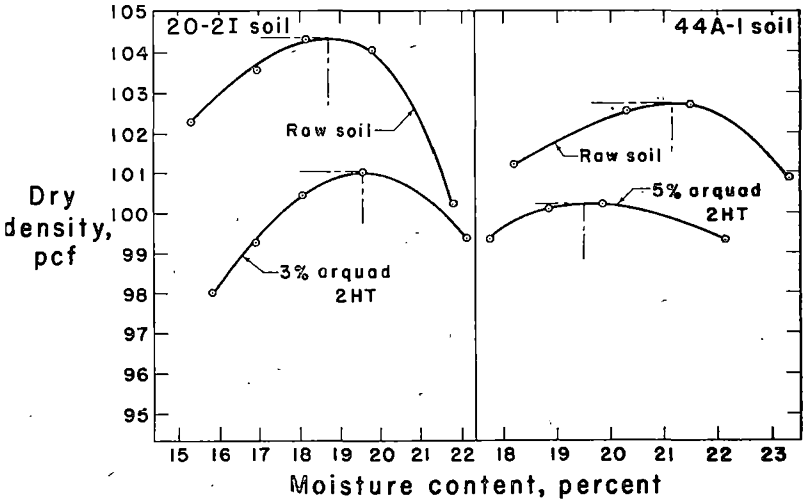


Fig. 4. Comparison of moisture density relationship of raw and stabilized soils.

placement in the moisture cabinet for 6 days, they had regained moisture up to 22 and 34 percent of the optimum moisture contents of the silty and clayey soils, respectively. After immersion, the moisture contents of both soils increased rapidly for the first day but then began to level off. Because of partial satisfaction of their affinity for moisture during the moist curing period, specimens cured in this manner absorbed less moisture during 7 days immersion than did specimens previously air dried for 7 days, indicating that elevated (140° F)

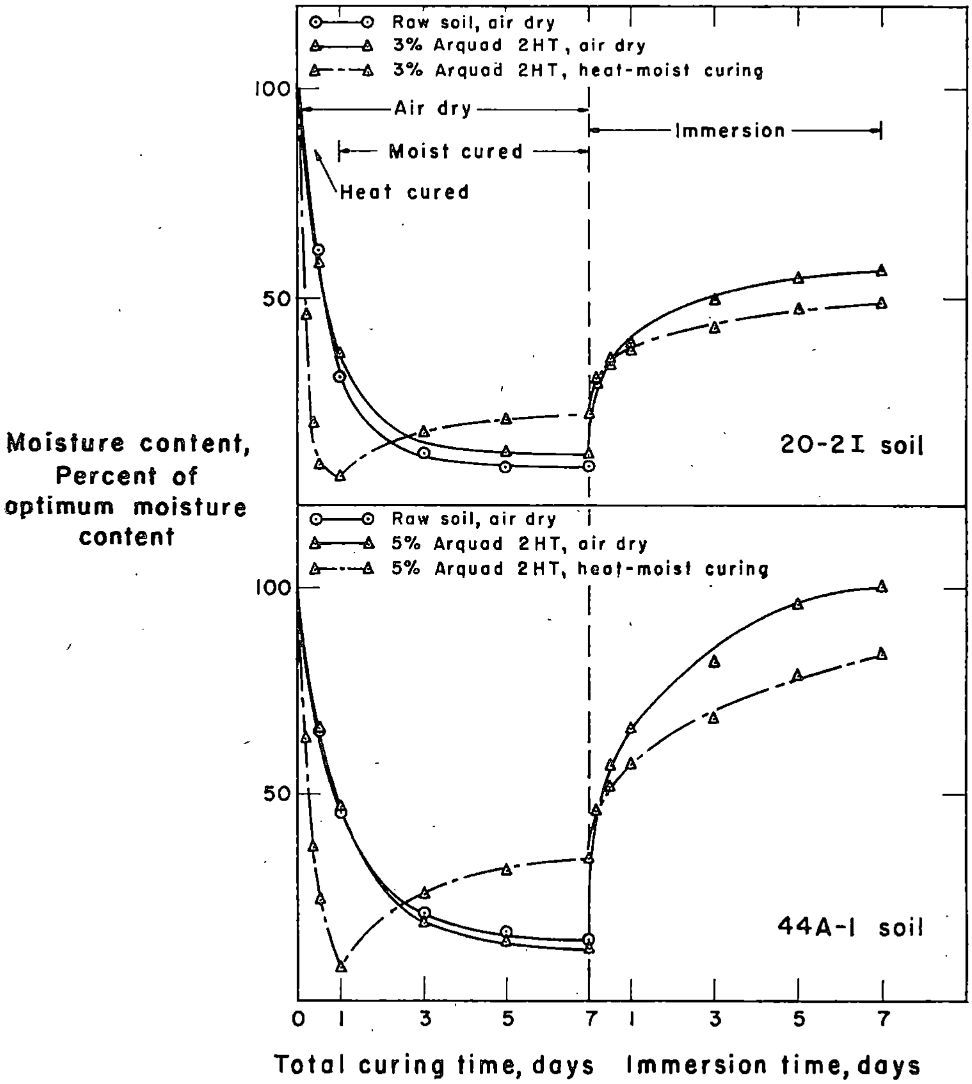


Fig. 5. Moisture curing time curves for raw and stabilized soils.

temperature during curing does not destroy the waterproofing characteristics of Arquad 2HT.

BEARING AND DURABILITY STUDIES

To further evaluate Arquad 2HT with the two soils on a basis which might be indicative of its field performance, bearing and durability tests were made.

California Bearing Ratio

C.B.R. tests were performed on uncured, unsoaked samples at standard Proctor density, and on uncured, 4 day soaked samples, using U.S. Corps of Engineers procedures[2]. Samples containing optimum amounts of Arquad 2HT were compared with raw soil samples (table V). A definite improvement was observed in the soaked strengths of the Arquad-treated soils and swelling was cut in half. It should be noted also that the treated soils gained strength during the soaking period, an indication of a benefit from moist curing that did not appear in the unconfined compression tests of the curing study.

Iowa Bearing Value

In some respects the Iowa Bearing Value test is a miniature CBR test. It has been developed at the Iowa Engineering Experiment Station and has been correlated with C.B.R.

Preparation and testing of I.B.V. specimens. Two inch diameter by 2 inch high cylindrical specimens molded to near standard Proctor density in 2 inch diameter by 5 inch brass molds are used. The specimens are retained in the molds during curing and testing. A 5/8 inch diameter rod is penetrated into the specimen at 0.05 inch per minute. The load readings, in pounds, at penetrations of 0.1 and 0.2 inch were taken as relative measures of the bearing strength of the soil.

For each soil, specimens were molded, air cured, and tested in the cured, unsoaked, and cured, 48 hour immersed conditions. Air curing was for 0, 3, and 7 days following molding. During immersion, 500 gram surcharges were kept on the specimens and measurements of swell were made. Specimens of raw soil were compared with specimens containing optimum amounts or Arquad 2HT.

TABLE V. EFFECT OF ARQUAD 2HT ON CALIFORNIA BEARING RATIO OF SOILS 20-2I AND 44A-1

	20-2I				44A-1			
	Raw		3% Arquad 2HT		Raw		5% Arquad 2HT	
	U[*]	S[†]	U	S	U	S	U	S
C.B.R. at 0.1 in. penetration, %	17.7	2.5	18.5	25.6	4.5	2.0	5.0	10.0
C.B.R. at 0.2 in. penetration, %	28.2	5.2	30.0	38.4	6.0	2.8	7.2	13.3
Swell, % of original height	..	0.5	...	0.2	..	0.8	..	0.4

[*] Unsoaked condition.
[†] Soaked for 4 days.

Results. Test results are shown in table VI. Three and 7 days of air curing prior to 48 hours immersion were extremely beneficial. Both the unsoaked and the immersed strengths of treated specimens increased approximatly 130 percent at 3 days air curing, and 400 percent at 7 days air curing, again indicating the essential role of curing in the effectiveness of soil-organic cationic chemical stabilization. The beneficial effect of the chemical treatment may also be seen in the reduction of swelling; 3 days air drying, in the case of the silty soil, caused the swell to decrease to the point where it was immeasurable.

Durability Tests

Method of test. The procedure used in this study for evaluating the resistance of Arquad 2HT treated soils to cycles of freezing and thawing and wetting and drying was as follows:

1. Two inch diameter by 2 inch high specimens were molded to near standard Proctor density using water concentrations of Arquad 2HT previously determined as being optimum for each soil.
2. Specimens were air cured at room temperature for seven days.

After curing, the procedure for freeze-thaw evaluation was:

a. Immerse specimens in distilled water for 2 hours.
b. Remove specimens from water bath and place on soaked felt pads to maintain capillary absorption.
c. With specimens on pads, place in deep freeze at —10° F for 23 hours.
d. Thaw in open air at room temperature for 2 hours.
e. Place thawed specimens in a moisture cabinet at approximately 70° F and 95 percent

TABLE VI. EFFECT OF ARQUAD 2HT ON IOWA BEARING VALUE OF SOILS 20-2I AND 44A-1

Soil	Concentration Arquad 2HT %	Length of air curing, days	Specimen Condition	Iowa Bearing Value, lbs. 0.1 in. pen.	Iowa Bearing Value, lbs. 0.2 in. pen.	Swell %
20-2I	0	0	U*	84	133	..
			S†	40	62	0.8
	3	0	U	88	155	..
			S	71	100	0.4
	3	3	U	208	312	..
			S	134	208	0
	3	7	U	424	800	..
			S	227	376	0
44A-1	0	0	U	33	45	..
			S	19	22	1.8
	5	0	U	72	96	..
			S	51	56	0.9
	5	3	U	185	244	..
			S	81	129	0.9
	5	7	U	310	574	..
			S	135	216	0.9

---

* Unsoaked, in the desired curing condition.

† Soaked for 48 hours following the desired length of curing.

relative humidity for 23 hours. This constituted the end of the first cycle. Each succeeding cycle was a repetition of steps c through e.

Three specimens of each soil were tested for unconfined compressive strength following 1, 3, 5, 7, 10, and 12 cycles of freezing and thawing.

After curing, the procedure for wet and dry evaluation was:

a. Immerse specimens in distilled water for 24 hours. This ended the first cycle.
b. Air dry specimens at room temperature for 24 hours.
c. Immerse specimens in distilled water for 24 hours. This ended the second cycle. Each succeeding cycle was a repetition of steps b and c.

Three specimens of each soil were tested for unconfined compressive strength following 1, 3, 5, 7, 10, and 12 cycles of wetting and drying.

Results. In addition to strength determinations, a visual examination of the specimens was made after each cycle. Following the sixth cycle of freezing and thawing, surface foliations appeared and steadily increased with each succeeding cycle, while vertical cracks began to appear after the sixth cycle of wetting and drying, though all specimens maintained their original shapes.

Freezing and thawing was much more detrimental to the Arquad-treated specimens than wetting and drying (table VII). Each cycle of either test caused a decrease in the unconfined compressive strengths, with the exception of wet and dry cycles with the silty soil; its strength steadily increased up to 10 cycles but began decreasing slightly at 12 cycles.

DIFFERENTIAL THERMAL ANALYSIS STUDY

Preparation of Samples

Samples of soil 20-2I were prepared at optimum moisture content with a high percentage water concentration of Arquad 2HT. An equal amount of chemical dispersion was also added to a sample of St. Peter sand. After mixing, all samples were allowed to come to equilibrium in an atmosphere controlled at 50 percent relative humidity for two weeks prior to testing.

Results

Differential thermal analysis has been shown to be a useful tool for study of clay organic chemical complexes in soils[13]. In differential thermal analysis, a sample is heated at a linear rate and the thermal reactions in the sample are recorded. In figure 6 the initial downward peak at about 100° C indicates the endothermic reaction of adsorbed water being driven from the clay. The next two curves show a reduction size of this peak due to treatment by Arquad 2HT.

Table VII. Effect of Freeze-Thaw and Wet-Dry Cycles on Unconfined Compressive Strength of Arquad 2HT-Treated Soil Specimens.

	Unconfined Compressive Strength, lbs.			
	Freeze-thaw		Wet-Dry	
No. of Cycles	Soil 20-2I, 3% Conc. Arquad 2HT	Soil 44A-1 5% Conc. Arquad 2HT	Soil 20-2I 3% Conc. Arquad 2HT	Soil 44A-1 5% Conc. Arquad 2HT
1	200	510	190	300
3	200	305	178	169
5	128	182	207	195
7	90	52	220	150
10	60	63	235	135
12	60	60	230	130

In samples run in an oxidizing atmosphere (third and fourth curves), the organic material oxidizes in a drawn-out exothermic reaction between 250 and 550° C. The reaction with sand shows a definite double peak.

A significant observation from thermal analysis study of Arquad 2HT is the lack of any delayed exotherm related to breakdown of the clay at around 600° C. Treatment of soils or clays with some organic chemicals results in a delayed exotherm believed caused by carbon adsorption on the clay[1]. When the clay structure breaks down, the carbon is released and burned. These reactions have been observed with the loess samples studied. If the interpretation is correct, the breakdown of Arquad apparently does not leave any such residual carbon attached to the clay.

A second factor in thermal breakdown of Arquad treated soil is the effect on the breakdown of calcium carbonate in soil. Thermal analysis of the natural soil gives a large, sharp endothermic peak starting at about 700° C and continuing to about 850° C. In thermal analysis of Arquad treated soils the carbonate reaction assumes a lower temperature, more rounded endotherm. At first it was believed that the Arquad might be acidic and react with the carbonates on mixing with soil. However, pH checks by titration and a measurement of CO_2 gas release from treated soil failed to verify this. Perhaps one of the high-temperature breakdown products from Arquad may be adsorbed on and catalyze the thermal decomposition of the soil carbonates.

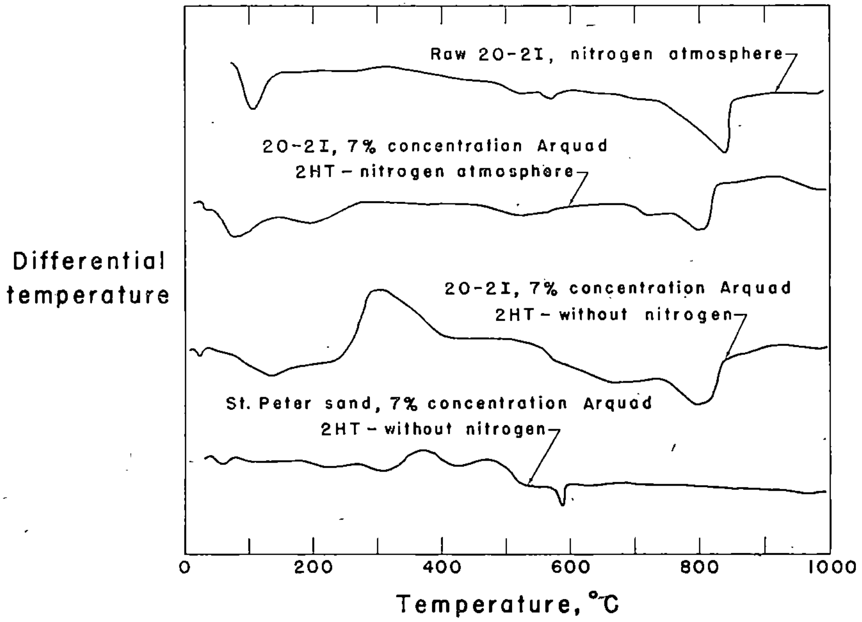


Fig. 6. Differential thermal curves of samples containing a quaternary ammonium salt.

In summary, it can be said that differential thermal analysis offers additional evidence for water-proofing of soil by organic cationic chemicals. Organic cations are preferentially irreversibly adsorbed and are substituted for water on clay, but the bond is not strong enough to retard later burning of the organic chemicals. Other observed high temperature thermal reactions appear to be related to thermal disintegration of the organic chemicals and may have no direct bearing on soil stabilization.

THEORETICAL INTERPRETATIONS

The resistance of soils to external forces is due to friction between the solid particles and the cohesion furnished by films of moisture covering these particles. When such a film thickens it performs as a lubricant, reducing the friction between adjacent particles and consequently diminishing the resistance value.

The clay-size material of both soils used in this work was predominantly montmorillonitic. Petrographic studies have shown that the clay occurs mainly as coatings on larger soil grains; in the more clayey soil, clay also occurs as separate aggregates[9]. Montmorillonitic minerals are among the most active commonly found in soil clays. Particles of montmorillonite are made up of flake-like crystal units composed of two silica sheets with an alumina sheet tenaciously held together by mutually shared oxygen atoms. The three layer structural units themselves, however, are so loosely held together that the crystal lattice is often bellows-like and expands and absorbs water readily. The strength of this bond and the amount of expansion and hydration depend to a large extent on the strength of the kind of cation present. The natural cation in the two soils used is calcium, which gives an aggregated, moderately hydrating and expanding clay. Complete substitution of organic cations for calcium would reduce the expansion and hydration to zero. Part of this effect is due to the water repellancy of the cationic Arquad 2HT once its charge is neutralized on the negative clay surface.

Arquad 2HT had waterproofing effects on the two soils. Stirring of properly treated soil in water does not result in a mud, but in a mass of water stable aggregates as in the lower photo (figure 7).

Based on experimental evidence, the possible mechanism of Arquad 2HT as a soil stabilizer may be summarized as follows:

Cation exchange and ease of mixing.

1. Mixing of water with soil is greatly facilitated if an agent is added to lower the surface tension of the water. Arquad 2HT is such an agent.

2. During or after mixing a cation exchange reaction takes place between the clay particles of the soil and Arquad 2HT. The cation exchange has the following effects:

a. Large organic cations tend to flocculate clay by reducing the clay surface charge. Flocculated clay has a lowered ability to take up water. It is also easier to mix.

b. In the amounts used, Arquad 2HT cations also partially coat the clay surfaces with a moisture repellant film. Such coated clay surfaces have little or no affinity for water.

Strength

1. The strength of soil aggregates depends in part on the structure and thickness of moisture films binding the particles. Usually the thinner the film the better the binding. For example, the strength of natural soil aggregates is usually greatly increased by air or oven drying because of the decrease in thickness of water films. Immersing such a soil in water usually results in thickening of the water films, destruction of the aggregates and reduction of the soil to a mud.

2. The water stability of aggregated soil is greatly increased by waterproofing actions of Arquad 2HT (figures 8 and 9).

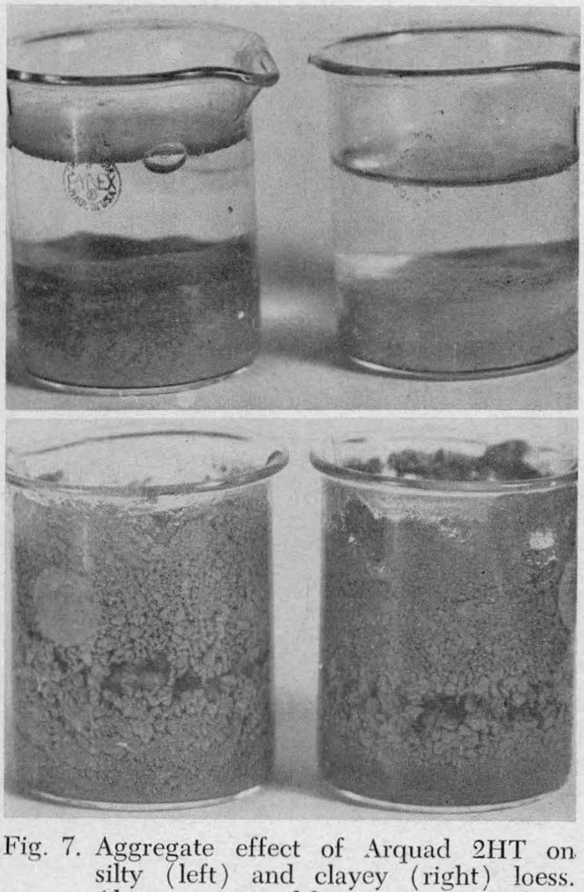


Fig. 7. Aggregate effect of Arquad 2HT on silty (left) and clayey (right) loess. Above: untreated loess in water. Below: optimum treated loess stirred in water.

3. However, because of the partial coating and waterproofing of clay particles by Arquad 2HT, binding by water films is decreased, and the strength of the air dry soil is decreased. Therefore, Arquad 2HT treatment of soil causes an increase in wet strength and a decrease in dry strength. It follows that in general the greater the amount of Arquad 2HT used the lower the air dry strength.

4. A certain minimum amount of Arquad 2HT is necessary for effective waterproofing. This amount is often an optimum; if Arquad 2HT is used in excess of this amount the strength of the water-stable aggregates may be decreased for the reason stated above.

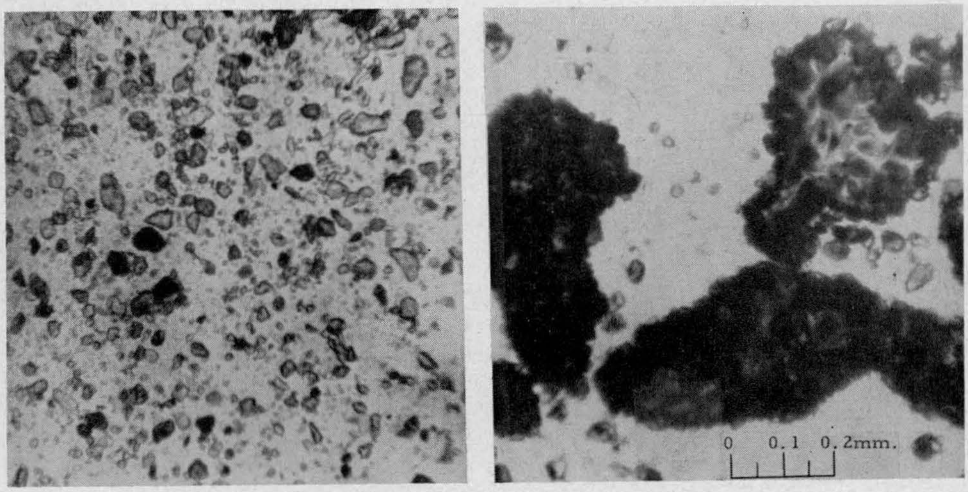


Fig. 8. Photomicrograph of 20-2I soil. At left, raw soil. At right, air dry stabilized soil.

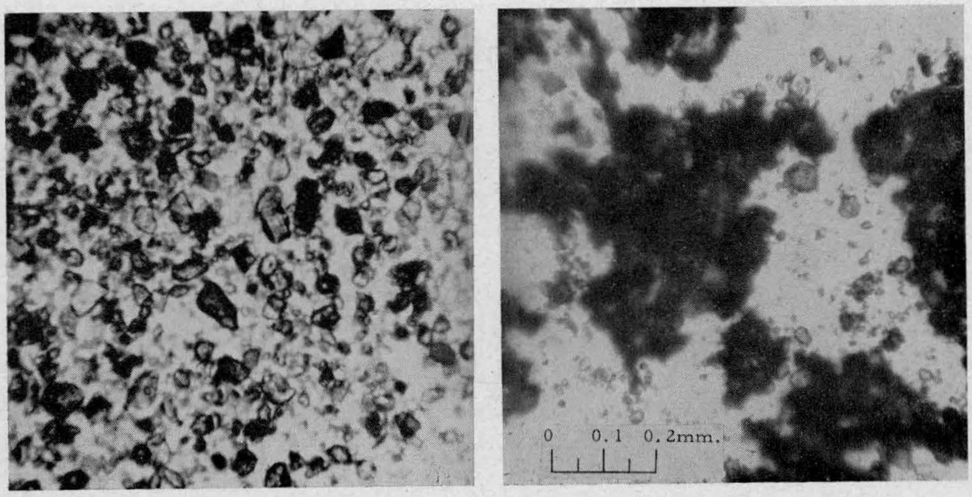


Fig. 9. Photomicrograph of 44A-I soil. At left, raw soil. At right, air dry stabilized soil.

CONCLUSIONS

Curing

Immersed compressive strengths of Arquad 2HT treated soils depend to a large degree on the curing treatment. These variations suggest a change in the disposition of the soil water and of the Arquad 2HT ions. The relations are as follows:

1. During air drying, treated soils lose water and gain strength (tables II, III and figure 5), at about the same rate as untreated soils.

2. The gain in strength of Arquad 2HT treated soils on drying is probably due to reduction in thickness of the moisture films. Curing in a humid atmosphere gives a lower strength gain.

3. Heat treatments show that an optimum degree of drying exists. Overdrying, which sometimes occurs for natural soils in hot climates and is referred to as dessication, causes such a decrease in water and an increase in air voids that sudden rewetting causes compression of the air and disruption of the specimen to occur (figure 2) and loss of strength. With Arquad 2HT treated soils this was observed after oven drying at 140° F and 160° F. However, wrapping of oven-cured specimens to prevent drying gives strength results approximating those obtained by moist curing at room temperatures.

4. Treated soils show a satisfactory recovery from oven-drying if they are subsequently aged in a humid atmosphere before immersion and testing. These moist cured strengths are much higher than those obtained without preliminary drying, showing that drying is instrumental in obtaining a better arrangement of water films.

Effects of Arquad 2HT treatment on engineering properties

1. Arquad 2HT reduces the plasticity index of soils probably by flocculating and partially waterproofing the clay. Preliminary oven drying increases this effect.

2. Arquad 2HT treatment, like lime, results in flocculation of the clays in a silty soil, giving a poorer gradation and lower compacted densities with the same compactive effort. The optimum moisture content is not greatly affected.

3. California Bearing Ratio tests show a substantial increase in soaked bearing strength after additions of Arquad 2HT. Iowa Bearing Value tests run on treated soils show further very large increases in both dry and soaked bearing strengths after air curing.

4. Data from unconfined compressive strength tests show that Arquad 2HT treatments decrease the cohesion in air dry soil. Data from the bearing tests indicate that Arquad 2HT treatments may increase the angle of internal friction.

5. Freeze thaw tests and wet dry tests on air cured Arquad 2HT treated specimens show a considerable resistance to physical weathering. The resistance of untreated soils is zero.

ACKNOWLEDGMENT

Special thanks are given to Karl M. Bierman of Armour and Company, Chemical Division, Chicago, Illinois, who generously donated organic chemicals and information concerning them.

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MINIATURE TRIAXIAL SHEAR TESTING OF A QUARTERNARY AMMONIUM CHLORIDE STABILIZED LOESS

by

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J. V. Roegiers, Student

(Iowa Academy of Science Proceedings 65: 323-331. 1958.)

INTRODUCTION

Compressive bearing characteristics of a stabilized soil may be determined by several methods, in each of which the soil specimens are loaded to failure. The resistance to failure of the stabilized soil depends on the maximum cohesion and internal friction between the soil particles after compaction. The triaxial shear test is employed to measure these two soil properties. In most highway base and sub-base design problems, or in any similar soil foundation study, the capacity of the underlying soil to withstand and support vertical and/or lateral forces is directly related to the cohesive and frictional forces present in the soil mass.

The purpose of the investigation was to determine the effect of a quaternary ammonium chloride soil stabilizing agent on the cohesive and frictional prop-

Table I. Procerties of Whole Wisconsin Loess sample

	Properties	Soil
Physical properties	Liquid limit, %	30.8
	Plastic limit, %	24.6
	Plasticity index, %	6.2
	Shrinkage limit, %	22.3
	Specific gravity, 25°C/D°C	2.71
	Standard Proctor density test:	
	Max. dry density, lbs/ft^3	108.4
	Opt. moist. content, %	18.0
Chemical properties	Organic matter, %	0.17
	Carbonates, % CaCO$_3$	10.2
	Oxidation	Oxidized
	pH	8.7
	Cation exchange capacity, m.e./100g.	13.4
	Exchangeable cation, m.e./100g.	
	Na	1.5
	K	1.6
	Ca	10.3
Textural composition°	Sand, %	1.4
	Silt, %	78.8
	Clay: Finer than 5μ, %	19.8
	Finer than 2μ, %	16.0
Engineering classification (AASHO)		A—4(8)

° Sand—2.0 to 0.074 mm, silt—0.074 to 0.005 mm, clay-finer than 0.005 mm.

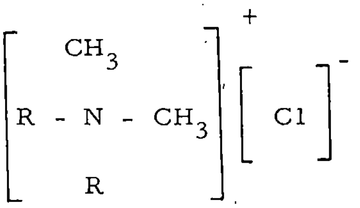
erties of a sample of western Iowa loess. A miniature triaxial shear testing apparatus, developed by the Iowa Engineering Experiment Station Soil Research Laboratory was used for the investigation.

MATERIALS

A sample of friable, calcareous, C horizon Wisconsin loess from Harrison County, Iowa, was used. X-ray diffraction analysis indicated that montmorillonite was the predominant clay mineral in the loess sample. Calcium was the predominant cation associated with the loess clay (table I).

Chemical

The quaternary ammonium chloride stabilizing agent used in this study is known commercially as Arquad 2HT[1, 2]. It is an organic cationic chemical that will retain its surface activity at either high or low pH and is not precipitated by calcium or magnesium hardness in water. Arquad 2HT is a di-hydrogenated tallow di-methylammonium chloride which is easily dispersible in water up to about 8 percent by weight and is normally supplied by the manufacturer as 75 percent active in isopropanol. It has an average molecular weight of about 585 and has the following general structural formula:



$$\left[\begin{array}{c} CH_3 \\ R - N - CH_3 \\ R \end{array}\right]^{+} \left[Cl \right]^{-}$$

Preparation of chemical. Previous research has indicated that preparation of the chemical in a water solution is desirable prior to its incorporation in the soil[4,5,6,7]. Six water concentrations of the chemical were prepared; 0, ½, 1, 2, 3, and 5 percent by weight. The relationship between chemical concentration in water, percent by dry weight of soil, and percent saturation of cation exchange capacity for each water concentration of chemical used with the loess was determined (table II).

The quantity of chemical needed for one liter of the desired concentration was

TABLE II. RELATIONSHIP BETWEEN CHEMICAL CONCENTRATION IN WATER, PERCENT DRY WEIGHT OF SOIL AND PERCENT SATURATION OF CATION EXCHANGE CAPACITY FOR FRIABLE LOESS AND ARQUAD 2HT.

Concentration of chemical in water, percent by weight	Concentration of chemical in soil, percent of dry weight of soil	Percent saturation of soil cation exchange capacity
0	0	0
½	0.08	0.8
1	0.16	1.6
2	0.32	3.2
3	0.49	4.7
5	0.81	7.8

placed in a beaker of adequate size and then was diluted with a small quantity of distilled water heated to 60° C. After the chemical was entirely dispersed, the mixture was washed into a 1000 ml. volumetric flask and was again diluted with the heated distilled water to 1000 ml. An extra 13 ml. of heated water was also added to compensate for the volume change of the mixture between 60° C and room temperature. The mixture was allowed to cool to room temperature before being mixed with the soil.

METHOD OF TESTING

The quantity of chemical solution necessary for standard optimum moisture content was added to the loess which had been air dried and passed through a No. 10 U.S. Standard sieve. Mixing was done in a Hobart model C-100 mixer at moderate speed for two minutes.

Molding

Six 1.312 inch diameter by 2.816 inch high cylindrical specimens were molded for each combination of soil and chemical concentration evaluated. The Harvard Miniature Compaction Apparatus[9] was used for molding. Each specimen produced in this apparatus is molded in two equal layers with ten 40 pound tamps per layer using a half inch diameter spring scaled rod. A compacted sample at approximately standard Proctor density results.

Curing

Six specimens of each soil chemical combination were cured under each of the following conditions:

no curing;
1 day air dry;
3 day air dry;
5 day air dry;
7 day air dry; and
5 day air dry, 24 hours immersion in distilled water.

Testing

Following the various curing periods, the cohesion, the angle of internal friction, and the modulus of compression of the stabilized soil for each combination of curing and concentration of chemical were determined by the miniature triaxial shear testing apparatus (figure 1).

The soil specimen is placed in a thin rubber membrane and sealed inside the plexiglass cylinder where it is subjected to constant lateral and dynamic axial stresses. In the triaxial compression test a liquid is ordinarily used to obtain lateral or minimum principal stresses[8]. With the I.E.E.S. apparatus compressed air is substituted for the liquid and is applied by a tire pump attached to the hose. Constant air pressures of 10, 20, and 30 pounds per square inch were used and were checked by the air pressure indicator at the base of the apparatus. At each of the three lateral pressures duplicate specimens for each curing condition and chemical concentration were run and the results were averaged. A constant rate of vertical or maximum principal stress was applied to the sample through the loading piston and was maintained until failure had occurred. Deformation of the sample was observed through the strain dial mounted on the loading piston. Applied loadings were read and recorded at each 0.01 inch of deformation.

DISCUSSION

No attempt was made to determine exactly the shearing resistance of each chemical treatment. The general effects that each treatment had on the shearing resistance through changes in the modulus of compression, internal friction angle and cohesion were noted.

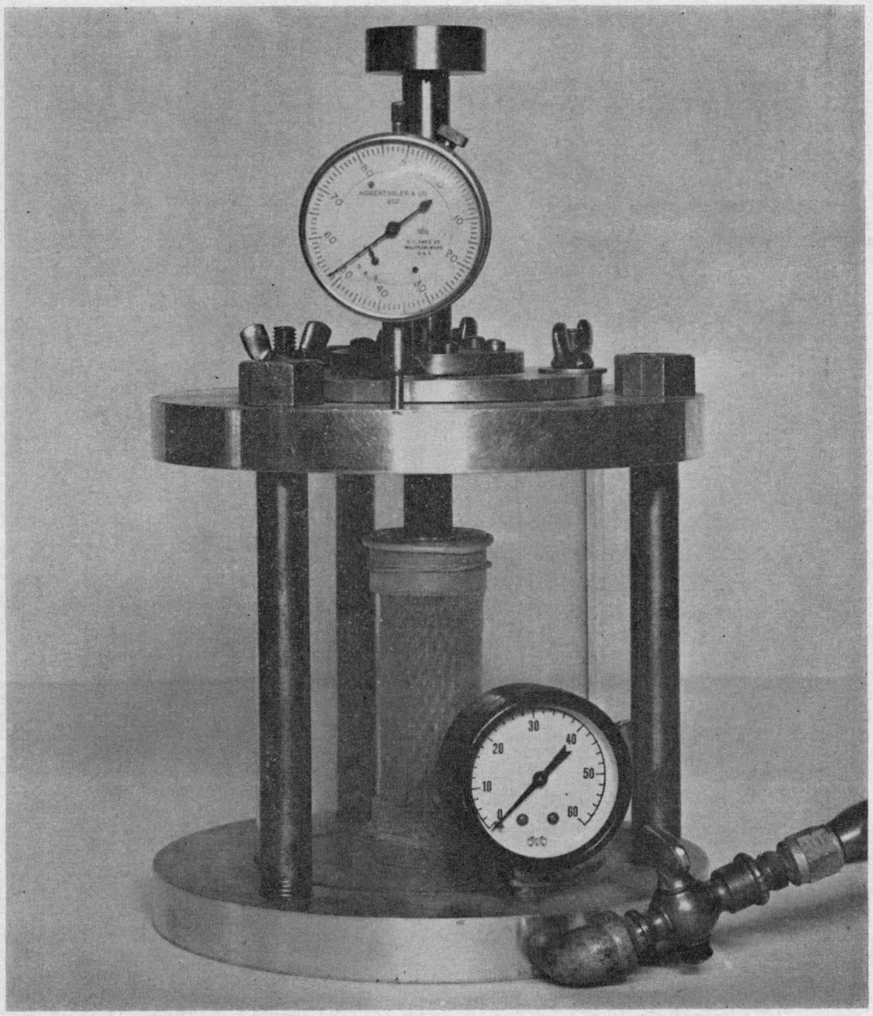


Fig. 1. Iowa Engineering Experiment Station Miniature Triaxial Shear testing apparatus.

Modulus of Compression

Loading of a specimen during a triaxial compression test produces a fairly constant ratio of unit stress to unit strain. In the early stages of the test a straight line relationship is shown in a graph of these two properties. After that the unit strain increases at a faster rate than the unit stress. The relationship of stress to strain in the straight line portion of the curve is measured as the slope of the secant line most nearly coinciding with this portion of the curve, and is designated as the modulus of compression. It is a property of soil similar to the modulus of elasticity of other engineering materials. Because soil is not elastic in the ordinary sense, the modulus of compression is only applicable during loading phases and does not apply during unloading. As the slope of the stress strain curve increases, the modulus of compression decreases indicating a greater degree of shearing resistance.

The data show that the modulus decreases considerably as the length of air drying increases for each chemical concentration (table III). Five day air drying appears to give about the minimum modulus. Five day air drying followed by 24 hour complete immersion in distilled water increases the modulus above that obtained by five day air drying only. However, at two and three percent chemical concentration, the modulus is about one-half that with no curing. This would indicate a maximum chemical benefit to the soil specimens within this range of chemical concentration and with at least five days air drying. A separate study of moisture loss versus length of air-drying gave maximum moisture losses at about five days; after five days air drying no appreciable loss in weight occurred.

Cohesion and Internal Friction

Shearing resistance S for a soil specimen subjected to the triaxial compression test is assumed determinable by the Coulomb equation, $S = C + N \tan \phi$ in which C is a constant called the cohesion, N is the stress normal to the failure surface developed in the specimen, and ϕ is the angle of internal friction. The values of C and ϕ are assumed entirely independent of the state of stress which

TABLE III. EFFECT OF VARIATION OF CHEMICAL CONCENTRATION IN WATER AND LENGTH OF AIR CURING ON THE MODULI OF COMPRESSION FOR ARQUAD 2HT STABILIZED LOESS.

	Moduli of compression for stabilized soil mixtures in lbs/in^2/ in x 10^{-4} for chemical concentration in water* shown below.					
Curing Method	0%	½%	1%	2%	3%	5%
No curing	2.23	2.20	1.30	1.83	1.93	1.30
1 day air drying	0.42	0.20	0.21	0.58	0.22	0.35
3 day air drying	0.16	0.12	0.18	0.15	0.18	0.31
5 day air drying	0.13	0.11	0.14	0.12	0.14	0.22
7 day air drying	0.11	0.11	†	†	†	†
5 day air drying and 24 hour immersion.	‡	‡	1.87	1.00	0.80	2.30

* Percent by weight of total solution.

† No specimens were molded for these concentrations.

‡ Specimens failed during immersion.

precedes failure of the soil specimen. Because of this assumption, the interpretation of a triaxial test on the basis of the foregoing equation is different for different soils. Also, the results may be slightly erratic within the same soil. It may further be assumed on the basis of the Coulomb formula that an increase in cohesion and friction angle will in turn result in an increase in shearing resistance of a soil specimen.

A graphical solution, known as the Mohr diagram, is used to determine the cohesion and internal friction angle of the tested soil specimen (figure 2). Using the difference between the averages of the total vertical stress at failure and the lateral stress on the specimen, a semicircle is drawn; the three semicircles representing the failure stress at each of the three applied lateral stresses. A line tangent to each of the semicircles is a locus of points representing failure of the stabilized soil and is a graph of the Coulomb equation. The slope of this line from the horizontal is the angle of internal friction and the intercept of the line on the ordinate of the graph is the cohesion.

With each chemical concentration air drying in general increases both internal friction and cohesion due to a decreasing thickness in the water films between the soil particles (tables IV, V). In general the chemically treated soil specimens increase to a maximum angle of internal friction at three to five days air drying. Also the friction angle tends to decrease with increasing chemical concentration. With five day air drying and twenty-four hour immersion, the friction angle increases to a maximum at about two percent chemical concentration.

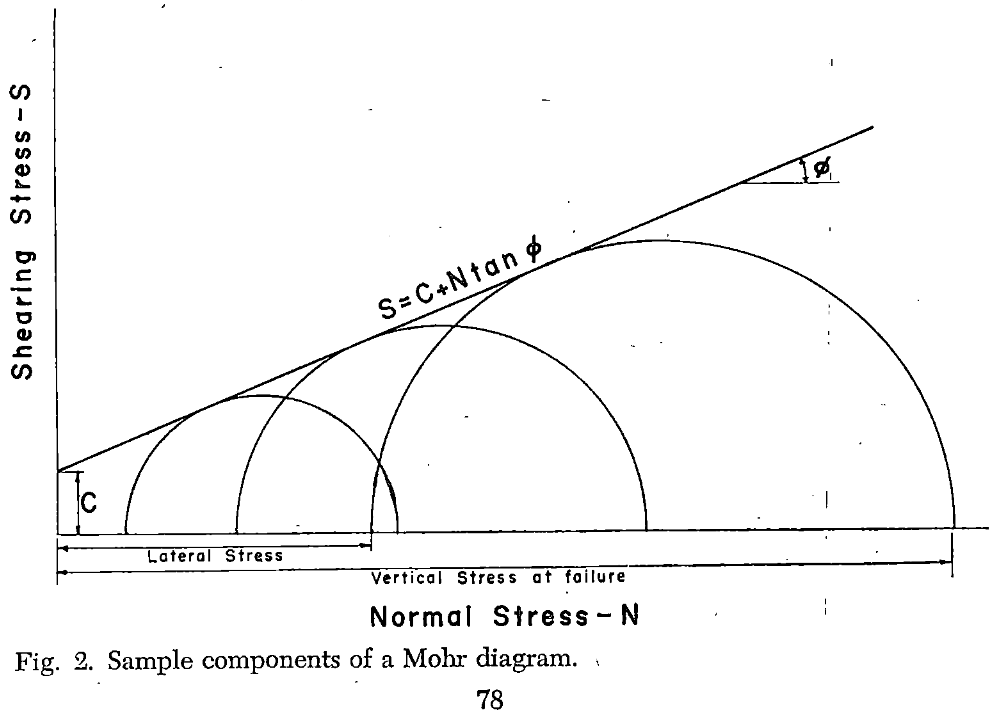


Fig. 2. Sample components of a Mohr diagram.

TABLE IV. EFFECT OF VARIATION OF CHEMICAL CONCENTRATION IN WATER AND LENGTH OF AIR CURING ON THE ANGLE OF INTERNAL FRICTION FOR ARQUAD 2HT STABILIZED LOESS.

	Angle of internal friction for stabilized soil mixtures in degrees for chemical concentration in water* shown below.					
Curing Method	0%	½%	1%	2%	3%	5%
No curing	15.0	23.5	17.5	21.0	24.5	12.5
1 day air drying	48.0	37.5	29.0	35.0	34.0	25.0
3 day air drying	44.0	42.0	39.0	30.0	37.5	41.0
5 day air drying	39.0	41.0	42.0	15.5	38.0	34.5
7 day air drying	45.0	39.0	†	†	†	†
5 day air drying and 24 hour immersion	‡	‡	21.5	42.0	29.0	20.0

* Percent by weight of total solution.
† No specimens were molded for these concentrations.
‡ Specimens failed during immersion.

TABLE V. EFFECT OF VARIATION OF CHEMICAL CONCENTRATION IN WATER AND LENGTH OF AIR CURING ON THE COHESION OF ARQUAD 2HT STABILIZED LOESS.

	Cohesion of stabilized soil mixtures in lbs/in^2 for chemical concentration in water* shown below.					
Curing Method	0%	½%	1%	2%	3%	5%
No curing	12.2	6.5	15.8	8.0	8.0	13.0
1 day air drying	18.00	82.0	98.0	27.0	27.5	37.0
3 day air drying	100.0	132.0	135.0	115.0	123.0	37.0
5 day air drying	130.0	156.0	115.0	200.0	117.0	66.0
7 day air drying	125.0	185.0	†	†	†	†
5 day air drying and 24 hour immersion	‡	‡	20.5	8.0	25.0	25.0

* Percent by weight of total solution.
† No specimens were molded for these concentrations.
‡ Specimens failed during immersion.

The apparent cohesion produced in the chemically stabilized specimens shows trends similar to those observed with the friction angle. The maximum benefits appear around two percent chemical concentration with five day air drying and at about three percent concentration with five day air drying, twenty-four hour immersion. The latter being substantially lower than at the former but also better than three times greater than that with no curing. It must be pointed out that twenty-four hours complete immersion in water is an extremely severe test with the small specimens used in this study and that all untreated specimens failed completely within several minutes after immersion.

CONCLUSIONS

When combined with about two percent water concentration of Arquad 2HT, compacted to approximately standard Proctor density and air cured for five days, the cohesion and angle of internal friction of the friable loess were increased. Similar combinations produced a reduction in the modulus of compression of the loess. By means of the waterproofing effects of Arquad 2HT, the three soil properties studied in this investigation were improved. The Arquad 2HT would probably improve the bearing capacity and shearing resistance of the loess under load if proper curing could be attained. Such benefits may also improve the adaptability of Arquad 2HT-soil mixtures as a possible supporting medium for highway surfaces.

ACKNOWLEDGEMENT

The authors take this opportunity to express appreciation to Mr. Karl M. Biermon of Armour and Company for supplying the Arquad 2HT used in this study.

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STABILIZATION OF IOWA LOESS WITH BITUMINOUS MATERIALS

by

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(Progress Report. 1955.)

INTRODUCTION

The increasing application of the principles of soil stabilization in the construction of highways, city streets, and airfields in the United States has been due largely to two factors. First, in many areas the supplies of economically available gravel and crushed stone suitable for pavement construction have been or are nearly depleted; second, the rising costs of construction have forced the use of locally available soil materials in increasing quantities.

The term *bituminous stabilization* in use at the present time covers the group of processes in which soils or soil-aggregate mixtures are stabilized by the addition of cut-back asphalts, residual oils, emulsified asphalts, or road tars. The main application of bituminous stabilized soil is in the construction of bases. Bituminous materials may also be used as admixtures to improve subgrade supporting strength. A minimum base thickness of 6 to 8 inches has been common practice, and a bituminous wearing surface is usually needed to protect the base from the abrasive effects of traffic. Some of the important information needed for the design and construction of soil-bituminous bases are the amount, the kind, and the grade of bituminous material to be used. Laboratory tests are commonly used for preliminary evaluations of the many different possibilities.

REVIEW OF PREVIOUS WORK

Development of Bituminous Soil Stabilization

The wide interest in bituminous soil stabilization stems from the economic availability of bituminous materials in many parts of the world. A review of the large volume of published information on the subject of bituminous soil stabilization leaves the reader with the impression that the method is still in its infancy, though it is one of the older and more widely used methods of soil stabilization for highways.

Bituminous stabilization is largely confined at the present time to non-plastic and feebly plastic granular soils such as gravels, sands, and soil-aggregate mixtures[6, 23, 27, 35, 44]. Where economically possible, sufficient quantities of granular borrow material, such as gravel or sand, have been added to in-place clayey soils to permit satisfactory stabilization with bituminous materials. The successful application of bituminous soil stabilization to fine-grained plastic soils without granular admixtures has been limited[6, 26, 45]. During recent years some laboratory investigations have been conducted to stabilize fine-grained soils of medium plasticity with bituminous materials[7, 20, 26, 46].

Laboratory procedures have been developed for use in evaluating the stability of soil-bituminous mixtures[2, 7, 26, 29]. It is generally considered advisable to verify laboratory results in the field by test pavements[6, 8, 14, 41]. Failures of soil bituminous roads have been reported where the soils processed had high clay contents[6, 26, 28, 32]; where the soil contained mica in appreciable amount[36, 42]; where mixtures were compacted before they had cured properly; or where surfaces were placed on the stabilized base too soon, thus trapping excess moisture and volatile materials[42].

A wide variety of bituminous materials have been tried with varying degrees of success for soil stabilization purposes. Rapid-curing and medium-curing cutbacks have been used successfully with granular soils in many different parts of the United States[6, 23, 24, 35, 41, 44] and in Great Britain and the Commonwealth Nations[14]. Grades RC-1, RC-2, MC-1, and MC-2 are mentioned most often as giving satisfactory field performance. Residual oils of the SC-1, SC-2, and SC-3 grades appear to have worked well in some hot, dry climates. Emulsified asphalts have reportedly shown promise in several states, particularly in California[9, 27, 28, 37, 45]. Some successful field results with road tars, especially with the RT-2 and RT-3 grades, have been reported in the U.S.[7, 36] and in Great Britain and the Commonwealth Nations. Laboratory evidence has been presented which indicates that tar may be superior to asphalt for soil stabilization[40]. This has not been confirmed by field experiments.

The Iowa State Highway Commission's experience with bituminous soil stabilization has been limited to a total of about 17 miles of experimental base construction in different parts of the state (table I). Among the soils processed were the following textural types: silt loam, silty clay and clay. Some of the silt loam and silty clay soils were probably loess, but all inplace soils having clay

TABLE I. BITUMINOUS STABILIZED ROADS IN IOWA

County	Location		Year	Length,	Thickness	P.I. of soil processed	Bituminous material used kind &	amount	Cost per mile of base,
	rt.	city	built	miles	In.		grade	%	dollars
Cass	83	Walnut	1935-37	1.1	6	20	TC-2*	2.92	7075
Cass	83	to	1935-37	1.2	5	17	MC-3	2.97	5878
Cass	83	Atlantic	1935-37	0.6	5	16	SC-3	3.25	5348
Cass	83		1935-37	0.5	5	14	SC-5	3.25	5737
Cass	83		1935-37	0.4	5	22	EA†	7.50	11035
Harrison	39	Portsmouth to Rt. U.S. 30	1935-37	10.5	—	—	EA†	—	—
Wayne	40		1935-37	2.0	—	—	MC†	—	—
Henry	129	Near Rome	1935-37	1.0	—	—	SC†	—	—

* Iowa State Highway Commission Standard Specification for Construction work on the Primary Road System. p. 248.
†No Record about grade is available.

contents higher than 20 percent were mixed with granular materials to bring the clay content within the range of 17 to 20 percent. Service experience with the Iowa test sections has not been very satisfactory.

The Missouri State Highway Department has had satisfactory results in stabilizing loess with a wide variety of bituminous materials. Bituminous loess stabilization has been used in Missouri for both surface course (oiled earth) and base course construction on light traffic routes. Some of the stabilized roads have tended to become spongy under traffic during the Spring break-up, but for low traffic they have been serviceable.

MECHANISM OF BITUMINOUS SOIL STABILIZATION

Bituminous materials are useful for soil stabilization purposes because of their outstanding cementing and waterproofing characteristics. The cementation property is most effective in providing increased stability in the case of non-cohesive or very slightly cohesive granular soils, such as gravels and sands. The waterproofing property is utilized to greatest advantage in the more cohesive soils or soil-aggregate mixtures, where the waterproofing assists in the preservation of the natural stability of these soils when they are dry and well compacted.

Of the many theories that have been offered to explain the mechanism of bituminous soil stabilization[7, 15, 23], the *intimate mix* and *plug* theories seem to have gained widest recognition. The *intimate mix* theory would appear to be most applicable to clean granular soils and the *plug* theory to cohesive soils or soil aggregate mixtures. According to the *intimate mix* concept, the individual particles of soil are coated with thin films of bituminous material which serve the dual function of cementing the particles together and of protecting the soil system from the adverse effects of water. The importance of thin films lies in the fact that the cementation furnished by a viscous film between two solid bodies is inversely proportional to the thickness of the film. The attainment of thin films and complete coatings on individual particles is much more feasible in the clean gravels and sands than in clayey soils where the tendency is greater for the films to coat aggregations of soil particles.

The *plug* theory was advanced to explain the waterproofing of cohesive soils or soil-aggregate mixtures by small amounts of bituminous material. Endersby visualizes the void spaces of the compacted soil bituminous mixture as being sufficiently plugged with bodies of bituminous material to prevent the entrance or exit of water.

INVESTIGATION

The work of previous investigators has shown that the stability of soil-bituminous mixtures is affected by many variables (figure 1). In the experiments reported herein investigation has been limited to some of the variables related to the soil and to the bituminous material.

Properties of Soil and Bituminous Materials

Loess samples used. Loess forms the major surficial deposit in much of Iowa.

Loess samples from two areas in the state were chosen for this study; the areas are southwestern Iowa and east-central Iowa (figure 2, table II). The property variations of loess in these areas have been given[12, 25]; the major variables are

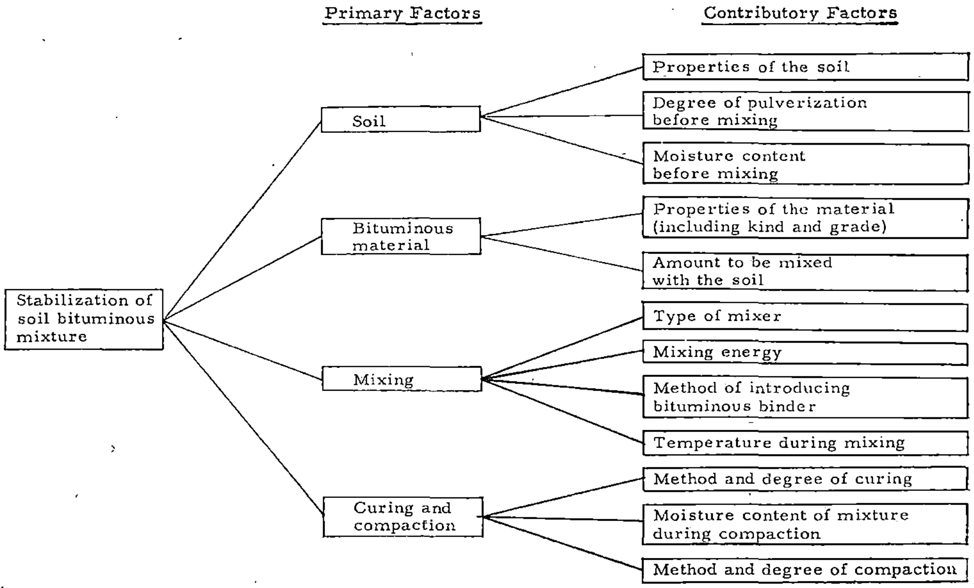

Fig. 1. Variables affecting stability of soil-bituminous mixtures.

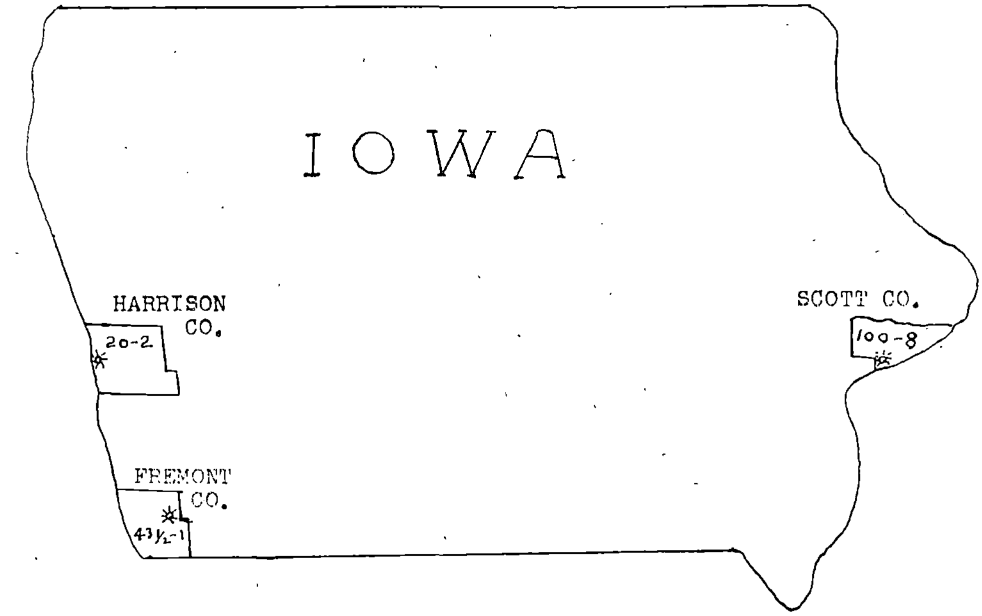

Fig. 2. Sampling locations of loess used in bituminous stabilization studies.

clay content, carbonate content and thickness. In southwestern Iowa the clay content gradually increases in a southeasterly direction from about 15 percent near the Missouri River valley to about 40 percent near the Missouri border. Carbonates occur in highest percentages near the Missouri River valley, where they commonly constitute about 15 percent of the loess. Carbonates are usually absent from the high clay loess farther east. The thickness varies from over 100 feet in the west to about 10 feet farther east.

In east central Iowa, the clay contents of loess increase and the thickness decreases southward from the Iowa River. A small area of deep calcareous loess low in clay lies adjacent to the Mississippi River floodplain. This deposit is unique in that it contains appreciable dolomite.

Three samples of C horizon loess were chosen for this study. One (20-2) is representative of southwestern Iowa loess near the Missouri River floodplain; it is calcareous and low in clay. The second (43½-1) represents the high clay, leached loess found farther east in southwestern Iowa. The third sample (100-8) is from the dolomitic, low-clay loess in east central Iowa adjacent to the Mississippi River floodplain. Petrographic data are available on all of these samples (table III). Studies indicate that significant amounts of montmorillonite are present in the clay fractions of the three samples.

Bituminous materials used. The liquid bituminous materials selected for evaluation as stabilizing agents for loess represent kinds and grades that are considered as having possible applications in soil stabilization work in Iowa. The materials used in experiments were:

1. Rapid curing cut-back asphalt of grades RC-0, RC-1, RC-2, and RC-3.
2. Medium curing cut-back asphalt of grades MC-0, MC-1, MC-2, MC-3, and MC-4.
3. Slow curing residual oil of grades SC-0, SC-1, SC-2, and SC-3.
4. Emulsified asphalt of grades RS-1, RS-2, MS-1 and SS-1, and MS-2 and MS-3.
5. Road tar of grades RT-1, RT-3, and RT-5.

Properties of the bituminous materials needed for comparison with specification requirements are given in tables IV, V, VI, VII, and VIII, in which much of the information tabulated was furnished by the manufacturer. The manufacture, general properties, and uses of these materials are discussed in readily available handbooks and text books and so will not be repeated here[2, 5, 21].

TABLE II. LOCATIONS OF WISCONSIN LOESS SAMPLES

Sample No.	County	Section	Township north	Range	Soil series	Thickness* of solum ft.	Sampling depth below surface Ft.
20.2	Harrison	S-15†	78	43-W	Hamburg	0	39-40
43½-1	Fremont	NW¼, NW¼, S-36	69	40-W	Marshall	2½	4½-5½
100-8	Scott	NW¼, SE¼, S-13	77	2-E	Fayette	3½	25-25½

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*The term solum includes the A and B horizons where both are present.

†Sample 20-2 was obtained behind the Third Ward School in the city of Missouri Valley.

TABLE III. PROPERTIES OF WISCONSIN LOESS SAMPLES

	Sample No.	20-2	100-8	43½-1
Physical properties	L. L., %	30.8	27.1	51.9
	P. L., %	24.6	19.8	18.5
	P. I., %	6.2	7.3	33.4
	C. M. E., %	19.60	———	28.5
	S. L., %	22.3	20.6	19.1
	Sp. Gr., 25°C/4°C	2.71	2.72	2.72
	Color (Munsell), moist	Dk. greyish br.	V. pale br.	Olive br.
	Color (Munsell), dry	Lt. grey	Lt. yell. br.	Pl. br.
	Lower fluff P.I., %	8	5	11.5
Chemical properties	Organic matter, %	0.17	0.2	0.37
	Carbonates, %	10.17	20.	0.5
	Iron, %	1.69	0.5	3.37
	Sulphate content, %	0	0	0
	Cat. Ex. Cap.	13.4	3.79	24.4
	pH	8.7	7.9	6.7
Textural composition percent*	Sand	0.4	2.8	0.4
	Silt	79.8	85.2	60.2
	Clay	19.8	12.0	39.4
	Collodial clay	14.5	8.9	29.8
Textural† classification (B.P.R. System)		Silty Loam	Silty Loam	Silty Clay
Engineering classification (AASHO)		A-4(8)	A-4(8)	A-7-6(18)

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*Sand—2.0 to 0.074 mm, Silt—0.074 to 0.005 mm, Clay—below0.005 mm, Colloidal clay—below 0.001 mm.

† Textural classification is based upon the Bureau of Public Roads System (36, p. 18) except that sand and silt sizes are separated by no. 200 sieve (0.074 mm).

TABLE IV. RAPID CURING CUT-BACKS (STANDARD OIL)

Properties	Test Method	Specification Designation			
		RC-0	RC-1	RC-2	RC-3
Furol viscosity at 77°F., sec.	ASTM D88	94			
Furol viscosity at 122°F., sec.			108		
Furol viscosity at 140°F., sec.				138	392
Furol viscosity at 180°F., sec.					
Specific gravity at 77°F./77°F.	AASHO T43	0.909	0.929	0.949	0.960
Distillation					
Distillate (percent of total distillate to 680°F.)					
To 374°F.					
To 437°F.	ASTM D402				
To 500°F.		66	40.3	41.7	57.8
To 600°F.		85	84.2	73	77
Residue from distillation to 680°F.					
Volume percent by difference		66	69	76	79
Tests on residue from distillation					
Pen. 77°F., 100 g., 5 sec.					
(Kopper's viscosimeter test)		125	112	96	91
Sp. gravity of residue at 77°F./77°F.	ASTM D71	1.008	1.008	1.012	1.004
Solubility in carbon tetrachloride	ASTM D4	99.56	99.63	99.72	99.56
Temperature of use for mixing		50-120	80-125	80-150	125-175
Oliensis spot test		Neg.	Neg.	Neg.	Neg.

Method of Testing

The relative stability of soil bituminous mixtures can be evaluated by various laboratory tests[2, 7, 29]. The experiments reported herein were performed mainly according to the tentative method of testing soil-bituminous mixtures recom-

TABLE V. MEDIUM CURING CUT-BACKS (STANDARD OIL)

Properties	Test Method	Specification Designation MC-0	MC-1	MC-2	MC-3	MC-4
Furol viscosity at 77°F., sec.		98				
Furol viscosity at 122°F., sec.			102			
Furol viscosity at 140°F., sec.	ASTM D88			122	340	
Furol viscosity at 180°F., sec.						154
Specific gravity at 77°F./77°F.	AASHO T43	0.939	0.95	0.959	0.966	0.978
Distillation						
Distillate (percent of total distillate to 680°F.)						
To 437°F.						
To 500°F.	ASTM D402	32.9	36.3	32.5	3.45	nil
To 600°F.		71.4	81.9			
Residue from distillate to 680°F. Volume percent by difference		65	73	78	85	90
Test on residue from distillation						
Pen. 77°F., 100 g., 5 sec. (Kopper's viscosimeter)		1000+	480	430	440	440
Sp. gravity of residue at 77°F./77°F.	ASTM D71	1.005	1.011	1.005	1.005	1.005
Solubility in carbon tetrachloride	ASTM D4	99.95	99.92	99.93	99.84	99.85
Temperature of use for mixing		50-120	80-150	100-120	150-220	175-225
Oliensis spot test		Neg.	Neg.	Neg.	Neg.	Neg.

TABLE VI. RESIDUAL OILS (STANDARD OIL)

Properties	Test method	Specification designation SC-0	SC-1	SC-2	SC-3
Flash point (C.O.C.), °F.	ASTM D92	290	300	315	310
Furol viscosity at 77°F., sec.	ASTM D88	111			
Furol viscosity at 122°F., sec.			98		
Furol viscosity at 140°F., sec.				147	
Furol viscosity at 180°F., sec.					211
Specific gravity at 77°F./77°F.	AASHO T43	1.022	0.955	0.961	0.972
Water		None	None	None	None
Distillation					
Residue from distillate to 680°F.					
Volume percent by difference	ASTM D402	88	97.5	98.5	98.5
Float test on residue at 122°F.		17	23	31	57
Solubility in carbon tetrachloride	ASTM D4	99.91	99.83	99.74	99.79
Residue of 100 penetration, %	ASTM D243	49	59	78	81
Ductility	ASTM D113	100+	100+	100+	100+
Temperature of use for mixing		50-120	80-200	150-200	175-250
Oliensis spot test		Pos.	Neg.	Neg.	Neg.

mended by the American Society of Testing Materials[2]. The principal modification is in the method of molding the specimens. The procedures used in performing the tests are as follows:

Preparation of soil bituminous mixtures. Airdry soil samples which had been pulverized to pass through the No. 10 sieve were used to prepare soil bituminous mixtures. Usually a sample of 3000 grams was mixed with a sufficient amount of water to bring the moisture content of the soil to the lower fluff point[7] (table III). The mixing of soil and water was done at moderate speed with a Blakeslee C-20 mixer, and the mixing time was five minutes. After the moist soil had been stored in a moist cabinet for 16 to 24 hours, a portion of the soil, usually about 1300 grams, was mixed at moderate speed with a desired amount of bituminous material in the same Blakeslee mixer for five minutes. The soil bituminous mixture was then cured in a moist cabinet for four hours before being used for the molding of specimens. Moisture determinations made on the moist soil and the sub-soil bituminous mixture indicated that the loss of moisture due to evaporation during the mixing, storage and curing periods was very small. Therefore, the moisture content of the soil bituminous mixture during the molding of specimens was close to the fluff point of the soil.

TABLE VII. EMULSIFIED ASPHALT (AMERICAN BITUMULS AND ASPHALT CO.)

Properties	Test method	Specification designation			
		RS-2	RS-1	SS-1 and MS-1	MS-2 and MS-3
Viscosity—S.F. at 122° F., sec.		185	36	37	131
Residue by distillation, %		66.6	59.6	61.8	66.4
Settlement after 5 days, %	AASHO M140-149	0.8	0.8	0.6	1.0
Demulsibility 35 ml. 0.02 N $CaCl_2$, %		96.0	9.0	0.0	0.0
Sieve test, 20 mesh, %		0.005	0.005	0.01	0.01
Tests on residue of emulsified asphalt					
Penetration at 77°F.		160	152	143	138
Ductility at 77°F. cms	AASHO M140-149	75	68	71	67
Solubility in CS_2		98.5	99	99.3	99.0
Ash, %		0.08	0.075	0.09	0.085

TABLE VIII. ROAD TARS (KOPPERS CO.)

Properties	Test method*	Specification designation		
		RT-1	RT-3	RT-5
Specific gravity at 77°F./77°F.		1.135	1.159	1.176
Water, % by volume		1.5	0.6	0.7
Specific viscosity, Engler				
50 cc. at 40°C.		7.1	19.2	
50 cc. at 50°C.				20.3
Distillation				
Percent by weight to 170°C.	ASTM D20	2.0	1.1	0.2
To 270°C.		27.2	23.4	18.0
To 300°C.		37.1	30.4	24.9
Residue to 300°C.		37.8	43.8	49.6

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* Type of test method used is not furnished by the company.

Molding of specimens. Specimens of soil bituminous mixtures used for all experiments reported in this paper were two inches in diameter and two inches high (figure 3). In molding the specimens, a proper quantity of soil bituminous mixture, usually about 180 grams, was poured into the cylindrical mold; and the mixture was then compacted by ten blows with a five-pound hammer dropping from a height of 12 inches. Specimens prepared in this manner were found to have a dry density nearly the same as that obtained in the standard Proctor density test. Immediately after molding the weight, height, and diameter of the specimen were measured according to the procedure given in the A.S.T.M. method D915-47T.

Curing of specimens. In the A.S.T.M. method, soil bituminous specimens are

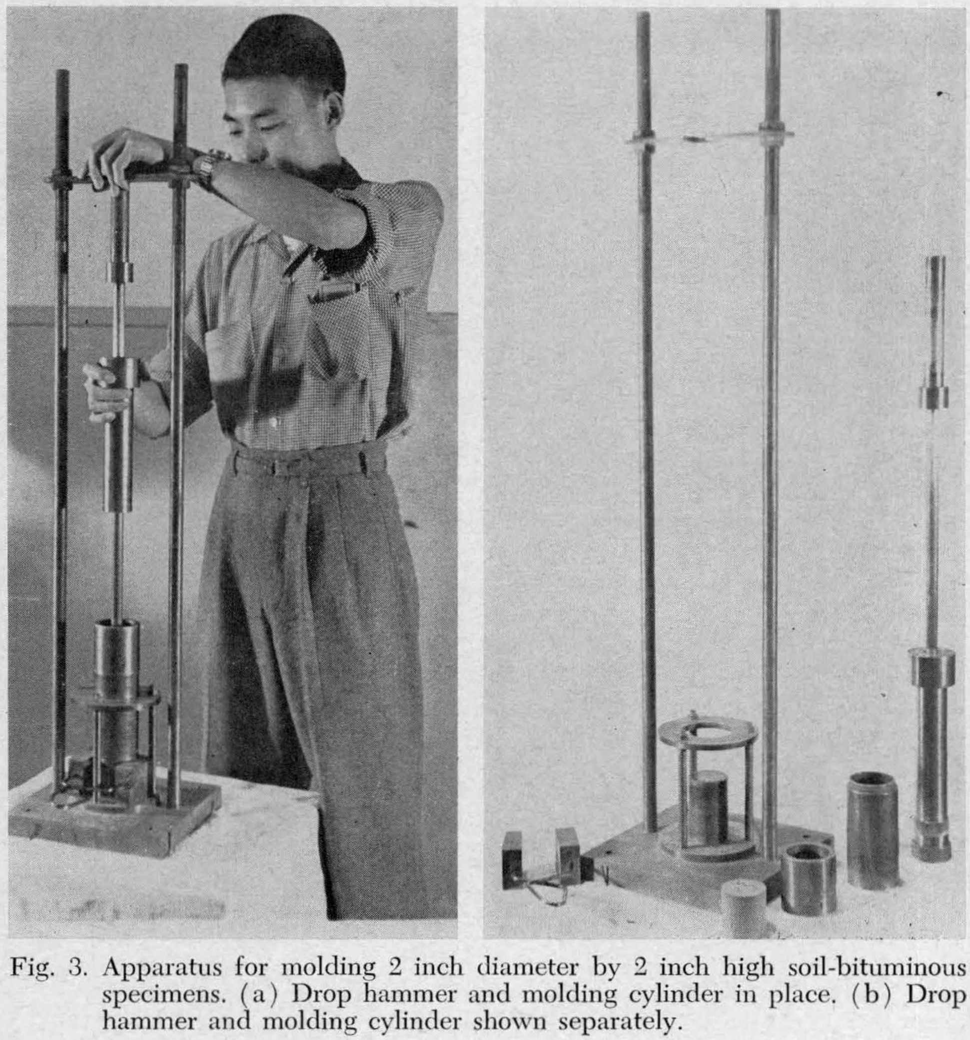

Fig. 3. Apparatus for molding 2 inch diameter by 2 inch high soil-bituminous specimens. (a) Drop hammer and molding cylinder in place. (b) Drop hammer and molding cylinder shown separately.

cured at a temperature of 140°F. All specimens used in the experiments reported in this thesis were cured at this temperature for four days. It is recognized that the curing achieved by the use of this procedure may not be obtainable under actual field conditions. For this reason, a study of various methods of curing will be made in the continuation of this research.

Absorption and extrusion test. The testing of soil bituminous specimens for water absorption, expansion, and extrusion value was also performed according to the procedure given in the A.S.T.M. method. All specimens after curing were kept in an absorption cabinet for seven days. The water in the cabinet was maintained at such a level that the lower half of each specimen was submerged in water. At the end of the absorption period, the specimens were weighed and their diameters measured. The water absorption and the expansion of each specimen were computed by using the following equations:

$$\text{Water absorption, percent} = \frac{W_2 - W_1}{Wd} \times 100$$

$$\text{Expansion, percent} = \frac{D^3{}_2 - D^3{}_1}{D^3{}_1} \times 100$$

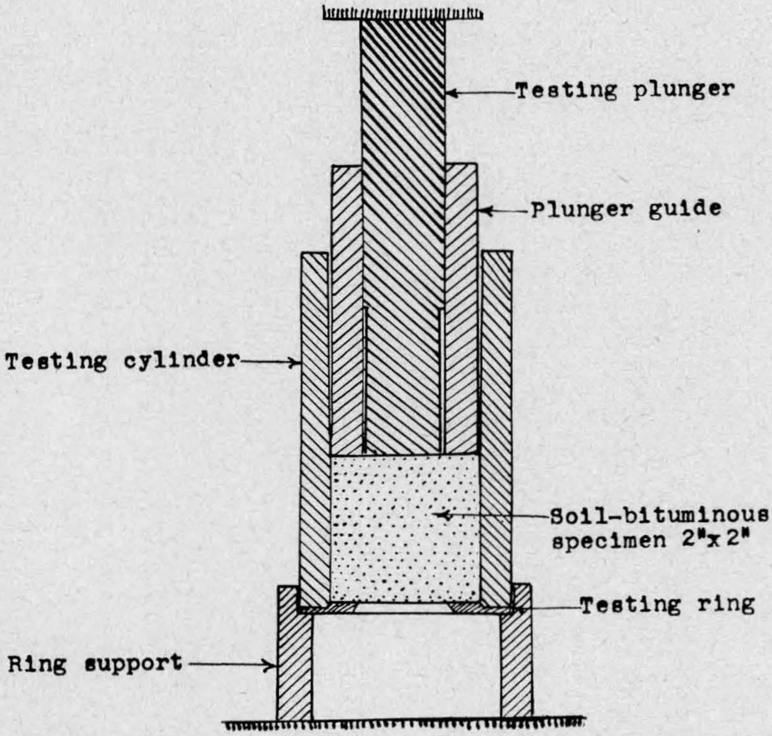

Fig. 4. Apparatus for the extrusion test of soil-bituminous specimens.

Where:

W_1 = weight of specimen before absorption,
W_2 = weight of specimen after absorption,
Wd = weigh of dry soil in specimen,
D_1 = diameter of specimen before absorption,
D_2 = diameter of specimen after absorption.

Immediately after weighing and measuring, the specimen was placed in the testing assembly (figure 4). During testing, the load was applied to the specimen through the testing plunger, which was moving at a rate of one inch per minute. The maximum load required to cause failure of the specimen was taken as the extrusion value (figure 5).

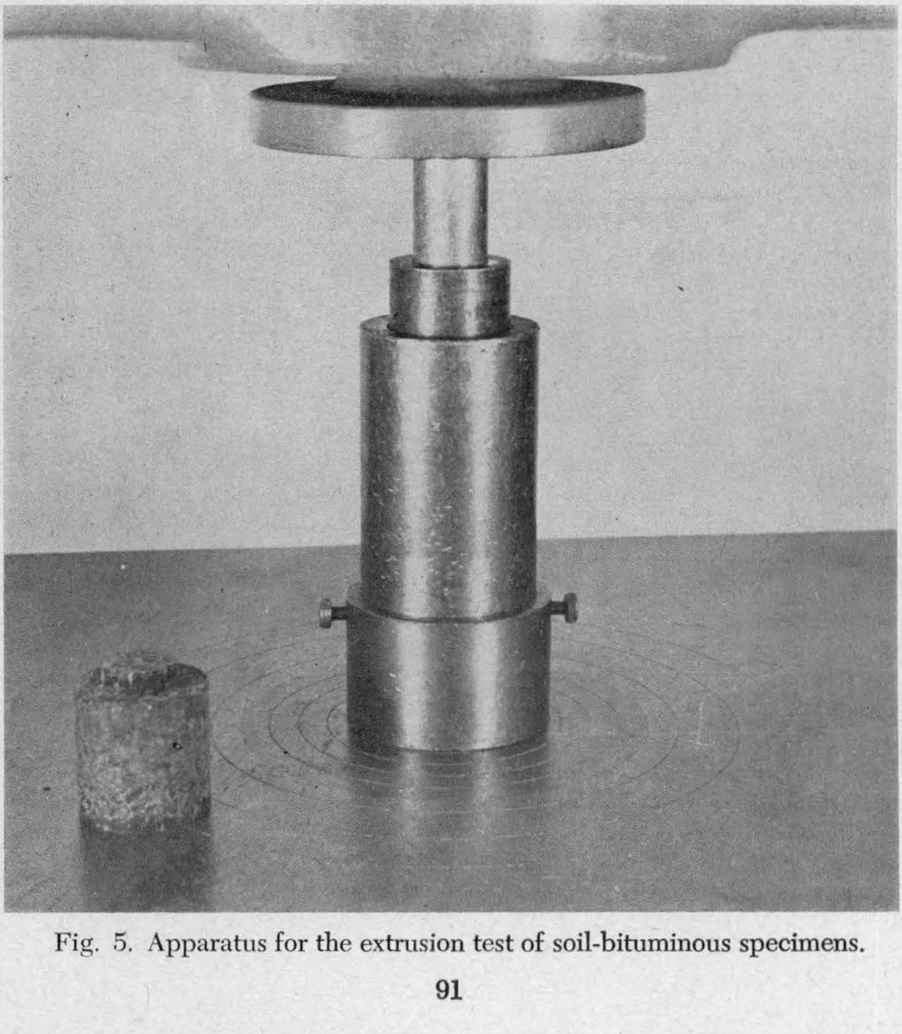

Fig. 5. Apparatus for the extrusion test of soil-bituminous specimens.

PRESENTATION AND DISCUSSION OF RESULTS

The effectiveness of the different bituminous materials as stabilizing agents for the three loess samples was compared by the previously described test method. Since the test method has not been correlated with the service behavior of soil-bituminous mixtures, it is possible only to make a relative comparison at this time.

Experiments with sample 20-2

Results obtained with mixtures of sample 20-2 and varying amounts of the different bituminous materials are presented in tables IX, X, XI, and XII. The relative stability of these mixtures may be judged from the percent of water absorption, the percent of expansion and the extrusion value of the test specimens. A mixture is considered to have a high relative stability when the extrusion value is comparatively high and the other two values are low. Each test result tabulated is the average of data for three specimens.

Data given in the tables indicate that the relative stabilities of the soil bituminous mixtures vary with the kind, the grade and the amount of bituminous materials used. Typical curves showing the relationship between the test values and the grade and amount of bituminous material are shown in figures 6, 7, and 8. These curves represent the test data obtained with medium curing cut-back asphalts. It will be noted that the asphalts having comparatively low viscosities

TABLE IX. TEST DATA FOR MIXTURES OF SAMPLE 20-2 AND RAPID CURING CUT-BACKS

Cut-back asphalt						
Kind and grade	Amount, %	Equivalent amount of Residue*, %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
RC-0	4	2.6	96.9	16.4	8.71	N.D.†
	6	3.9	96.9	15.8	7.42	235
	8	5.2	95.0	15	6.2	340
	10	6.5	95.4	11.4	5.4	703
	12	7.8	95.9	9.7	5.5	983
RC-1	4	2.8	95.0	12.6	9.9	210
	6	4.1	95.2	13.1	6.9	412
	8	5.5	92.5	9.7	6.4	480
	10	6.9	94.8	8.05	5.3	688
	12	8.3	94.4	7.5	4.9	860
RC-2	4	3.0	96.4	20.0	21.2	65
	6	4.5	94.0	14.5	7.4	440
	8	6.1	93.2	7.6	5.5	650
	10	7.6	96.2	5.0	4.8	910
	12	9.1	92.3	7.7	5.0	840
RC-3	4	3.1	94.2	N. D.	N. D.	N. D.
	6	4.7	94.0	21.7	21.3	20
	8	6.3	94.7	20.8	20.1	100
	10	7.9	95.0	13.0	13.3	400
	12	9.4	91.1	12.4	14.9	320

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* Residue from distillation to 680 F.

† The letters "N.D." indicate that the specimens could not be weighed or measured, or handled for the extrusion test.

(MC-0, MC-1, and MC-2) give relatively high stabilities, especially when the amount of bituminous material added is less than 10 percent. A similar trend of variation was found with the rapid curing cut-back asphalts, the slow-curing residual oils, and the road tars. The better results obtained with the lower viscosity grades are very likely due to a more satisfactory distribution of the bituminous material in the soil.

In figures 6 to 14, the amount of bituminous materials used is expressed in percent of the liquid bituminous material added to the soil. Since liquid bituminous materials contain varying amounts of volatile matter, it is often desirable to know the equivalent amount of residue contained in the soil. This information is given in the tables. Also shown in the tables are the dry densities obtained with the different soil bituminous mixtures. These data indicate that there is no consistent trend of variation in the dry densities of compacted soil bituminous specimens. For this reason, density data were not of much value in comparing the stabilities of the different mixtures prepared with loess sample 20-2.

Among the five kinds of bituminous materials used, emulsified asphalt was found to be ineffective for stabilizing the loess. Since emulsified asphalts vary greatly in their physical and chemical properties, different kinds of emulsified

TABLE X. TEST DATA FOR MIXTURES OF SAMPLE 20-2 AND MEDIUM CURING CUT-BACKS

Cut-back asphalt						
Kind and grade	Amount, %	Equivalent amount of Residue[*], %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
MC-0	4	2.6	91.1	N. D.[†]	N. D.[†]	N. D.[†]
	6	3.9	96.3	N. D.	7.6	380
	8	5.2	96.3	8.1	5.4	353
	10	6.5	95.7	8.6	5.4	360
	12	7.8	95.4	8.1	5.4	350
MC-1	4	2.9	96.5	14.4	17.6	65
	6	4.4	95.6	8.0	6.6	330
	8	5.8	95.3	6.2	5.7	350
	10	7.3	97.9	5.0	5.1	400
	12	8.8	94.9	4.4	4.3	355
MC-2	4	3.1	96.3	11.8	17.7	120
	6	4.7	94.9	12.2	8.0	310
	8	6.2	95.7	10.1	5.8	360
	10	7.8	96.4	5.9	5.2	420
	12	9.3	94.7	4.2	4.5	400
MC-3	4	3.4	95.8	N. D.	N. D.	N. D.
	6	5.1	95.4	N. D.	N. D.	40
	8	6.8	95.0	11.2	11.1	260
	10	8.5	94.1	6.7	6.0	330
	12	10.2	94.0	4.4	4.8	350
MC-4	8	7.2	93.2	N. D.	N. D.	N. D.
	10	9.0	93.4	10.0	13.0	220
	12	10.8	93.3	4.3	5.3	380
	14	12.6	93.1	3.7	4.6	370

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[*] For explanation refer to table IX.

[†] For explanation refer to table IX.

TABLE XI. TEST DATA FOR MIXTURES OF SAMPLE 20-2 AND RESIDUAL OILS

Residual oil						
Kind and grade	Amount, %	Equivalent amount of Residue*, %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
SC-0	4	1.9	95.2	10.1	43.8	56
	6	2.9	93.5	6.3	13.2	150
	8	3.9	93.4	2.5	6.9	240
	10	4.9	95.3	2.5	5.4	315
	12	5.9	97.3	4.7	5.3	460
SC-1	4	2.4	96.4	11.1	19.7	70
	6	3.5	96.6	9.9	6.6	290
	8	4.7	95.7	6.8	5.8	255
	10	5.9	96.0	5.6	5.5	390
	12	7.1	95.9	5.4	5.3	390
SC-2	4	3.1	93.8	N. D.†	34.1	13
	6	4.6	92.9	16.2	28.4	50
	8	6.2	92.4	5.1	7.6	240
	10	7.8	91.9	5.1	4.9	305
	12	9.4	94.7	3.0	4.7	405
SC-3	4	3.2	94.7	N. D.	N. D.	N. D.
	6	4.9	96.5	14.6	26.2	25
	8	6.5	94.1	9.3	12.9	105
	10	8.1	93.8	4.5	5.3	310
	12	9.7	92.4	4.3	4.5	310

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* Residue of 100 penetration as determined by Iowa Highway Commission specifications.

† For explanation of this symbol refer to table IX.

TABLE XII. TEST DATA FOR MIXTURES OF SAMPLE 20-2 AND ROAD TARS

Road Tars						
Kind and grade	Amount, %	Equivalent amount of Residue*, %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
RT-1	2	0.8	94.7	7.5	7.7	200
	4	1.5	96.2	4.5	4.5	430
	6	2.3	92.2	4.5	4.2	430
	8	3.0	94.0	4.5	3.4	520
	10	3.8	94.2	1.0	3.8	545
RT-3	2	0.9	94.6	N. D.†	N. D.†	N. D.†
	4	1.7	98.8	12.7	20.3	100
	6	2.6	94.3	0.3	5.2	565
	8	3.5	94.8	0.3	4.0	540
	10	4.4	93.3	0.3	3.7	500
RT-5	2	1.0	89.4	N. D.	N. D.	N. D.
	4	2.0	89.2	N. D.	N. D.	N. D.
	6	3.0	90.4	N. D.	13.0	90
	8	4.0	89.4	1.0	6.8	490
	10	5.0	94.6	1.0	4.0	580

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* Residue from distillation to 300°C.

† For explanation refer to table IX.

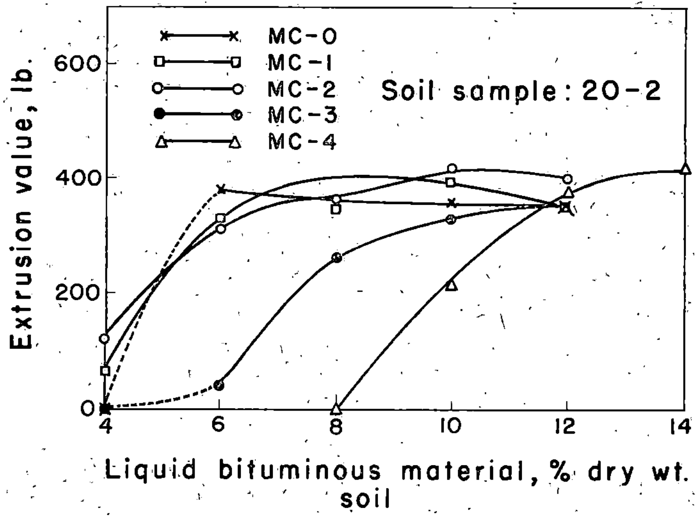

Fig. 6. Variation of extrusion value of soil-bituminous specimens with amount and grade of medium curing cut-back asphalt. Data for soil sample 20-2.

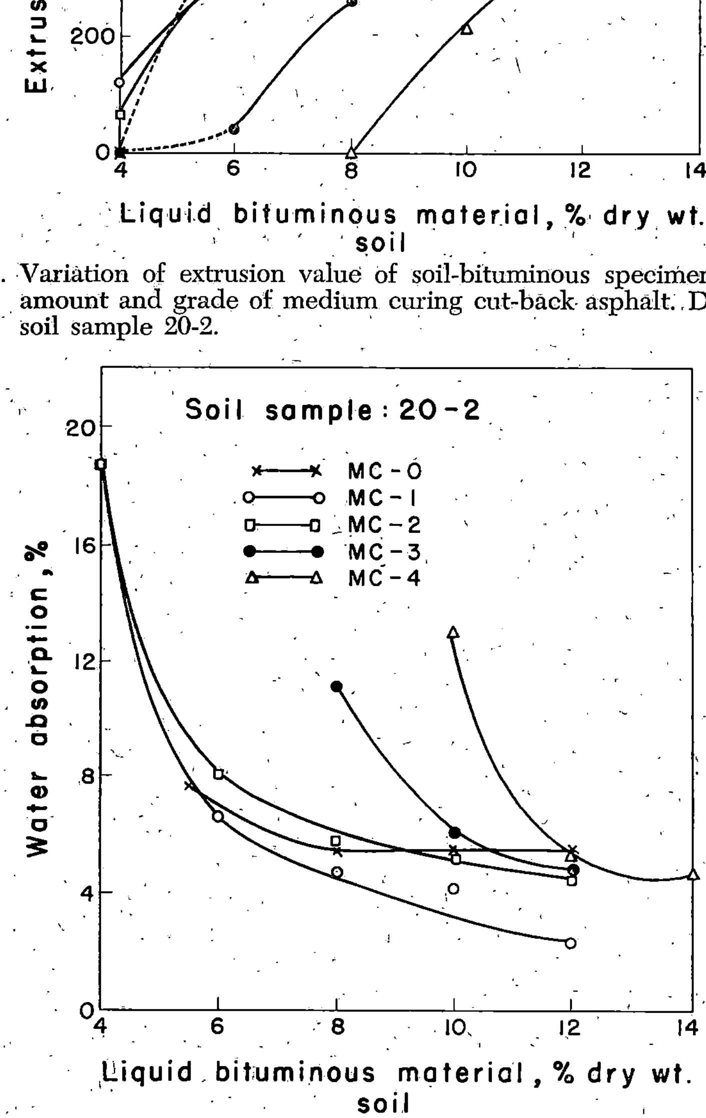

Fig. 7. Variation of water absorption of soil-bituminous specimens with amount and grade of medium curing cut-back asphalt. Data for soil sample 20-2.

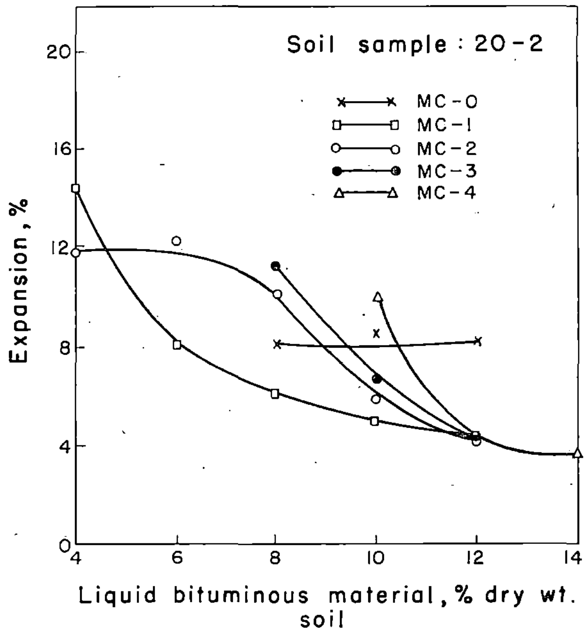

Fig. 8. Variation of expansion of soil-bituminous specimens with amount and grade of medium curing cut-back asphalt. Data for soil sample 20-2.

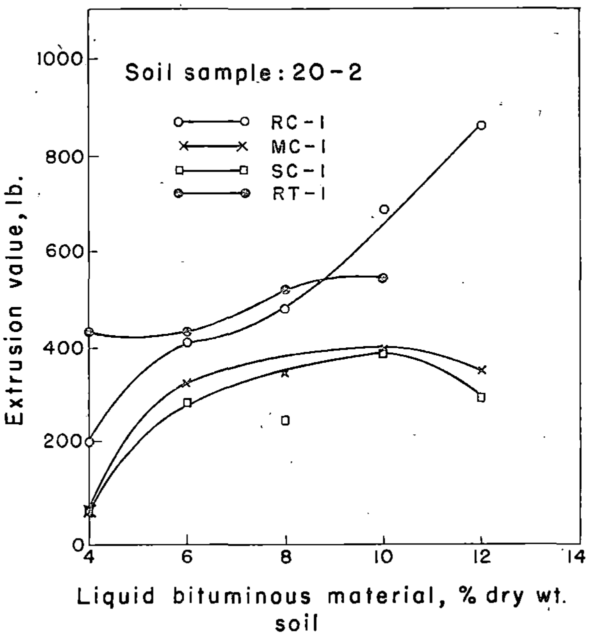

Fig. 9. Variation of extrusion value of soil-bituminous specimens with amount and kind of liquid bituminous material. Data for mixtures of soil sample 20-2 and grade 1 bituminous materials.

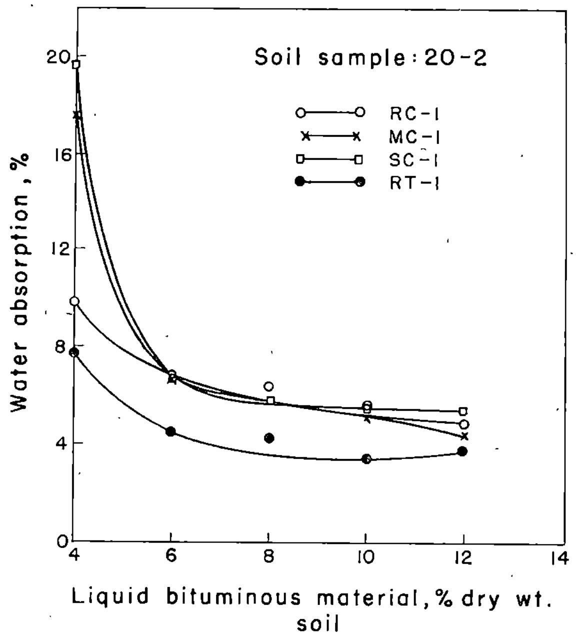

Fig. 10. Variation of water absorption of soil-bituminous specimens with amount and kind of liquid bituminous material. Data for mixtures of soil sample 20-2 and grade 1 bituminous materials.

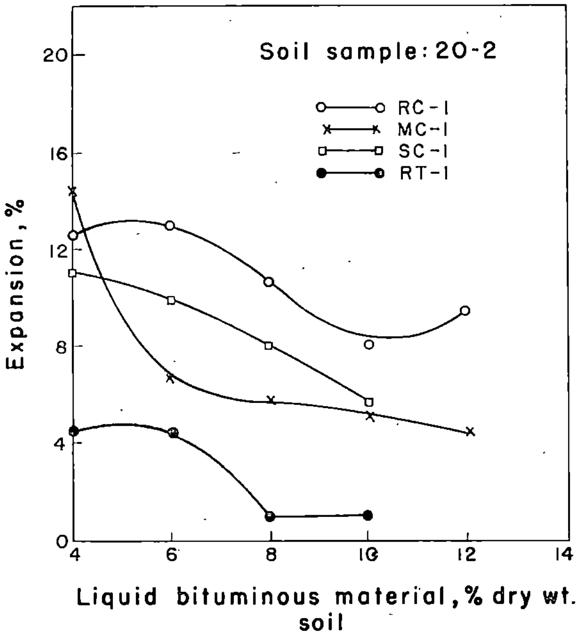

Fig. 11. Variation of expansion of soil-bituminous specimens with amount and kind of liquid bituminous material. Data for mixtures of soil sample 20-2 and grade 1 bituminous materials.

TABLE XIII. TEST DATA FOR MIXTURES OF SAMPLE 100-8 AND RAPID CURING CUT-BACKS

Cut-back asphalt Kind and grade	Cut-back asphalt Amount, %	Equivalent amount of Residue[*], %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
RC-1	4	2.8	98.5	10.7	5.4	410
	6	4.1	98.1	7.2	3.6	545
	8	5.5	99.0	5.0	3.2	795
	10	6.9	98.6	3.5	2.9	950
	12	8.3	99.3	3.0	2.8	1000
RC-2	4	3.0	97.6	N. D.	N. D.	N. D.[†]
	6	4.5	98.0	28.7	23.3	40
	8	6.1	97.5	4.5	4.2	840
	10	7.6	96.8	4.7	4.0	905
	12	9.0	96.6	2.5	3.8	1095

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[*] For explanation refer to table IX.

[†] For explanation refer to table IX.

TABLE XIV. TEST DATA FOR MIXTURES OF SAMPLE 100-8 AND MEDIUM CURING CUT-BACKS

Cut-back asphalt Kind and grade	Cut-back asphalt Amount, %	Equivalent amount of Residue[*], %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
MC-0	4	2.6	100.0	4.2	9.2	175
	6	3.9	100.0	2.9	4.1	255
	8	5.3	99.9	2.5	3.1	290
	10	6.6	100.9	2.2	3.0	260
	12	7.9	100.0	1.6	2.7	270
MC-1	4	2.9	100.1	6.4	6.4	N. D.[†]
	6	4.4	100.0	3.2	3.7	270
	8	5.8	101.0	2.5	2.9	280
	10	7.3	103.6	2.2	2.8	320
	12	8.8	101.6	1.1	2.5	295
MC-2	4	3.1	101.6	7.3	18.5	90
	6	4.7	100.9	4.8	4.9	355
	8	6.2	101.0	3.8	3.1	390
	10	7.8	103.6	1.1	2.6	360
	12	9.3	100.8	1.2	2.5	355
MC-3	4	3.4	100.7	11.1	27.4	20
	6	5.1	100.0	7.4	18.4	105
	8	6.8	100.1	3.8	3.5	390
	10	8.5	99.3	1.5	2.9	355
	12	10.2	99.3	1.1	2.8	310
MC-4	8	7.2	99.6	1.9	3.6	310
	10	9.0	97.0	3.8	7.2	220
	12	10.8	97.3	1.3	3.0	305
	14	12.6	97.8	0.9	2.6	265

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[*] For explanation refer to table IX.

[†] For explanation refer to table IX.

asphalts will be investigated in the continuation of this research. The other four kinds of bituminous material tested showed varying degrees of effectiveness as stabilizing agents for the loess. Typical curves illustrate the relationship between the three test values and the kind and amount of bituminous materials used (figures 9, 10, and 11). These curves represent the data obtained with grade 1 of each of the four kinds of bituminous material. As shown in the figures, the road tar, RT-1, gave more promising results than the three liquid asphaltic materials.

Experiments with sample 100-8

The four kinds of bituminous materials showing promise with loess sample 20-2 were studied with the friable east-central Iowa loess, sample 100-8. Tables XIII, XIV, XV, and XVI present test data obtained with all grades of medium curing cut-backs and with one or more grades of the other three kinds of bituminous materials. The grades selected for study were also those found most promising with sample 20-2. As shown in the tables, various amounts of each bituminous material were used in the evaluation experiments. The test data obtained with different grades of medium-curing cut-backs do not as clearly indicate the superiority of the lower viscosity materials as was found in the experiments with sample 20-2. However, the data does show that grades 0, 1, and 2 were considerably more effective in providing relative stability than grades 3 and 4 when the amount of cut-back added was less than eight percent.

TABLE XV. TEST DATA FOR MIXTURES OF SAMPLE 100-8 AND RESIDUAL OILS

Residual oil Kind and grade	Amount, %	Equivalent amount of Residue*, %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
SC-1	4	2.4	99.5	4.3	13.1	120
	6	3.5	100.2	1.8	3.7	200
	8	4.7	99.2	1.6	3.7	210
	10	5.9	99.0	1.6	3.6	195
	12	7.1	99.1	1.3	3.4	200
SC-2	4	3.12	99.5	22.4	22.5	50
	6	4.68	98.6	4.8	3.5	250
	8	6.24	99.8	2.5	3.2	270
	10	7.80	101.8	1.3	2.8	270
	12	9.36	100.7	1.2	2.5	225

* For explanation refer to table XI.

Figures 12, 13, and 14 show the percent of water absorption, the percent of expansion and the extrusion value of soil bituminous specimens prepared with grade 1 of each of the four kinds of bituminous materials. While no one of the materials tested is consistently superior, the data do indicate the superiority of the RT-1 and RC-1 materials. The RT-1 was apparently most effective in reducing water absorption and expansion; the RC-1 gave the highest extrusion value.

Table XVI. Test data of mixtures of sample 100-8 and road tars

Road Tar						
Kind and grade	Amount, %	Equivalent amount of Residue°, %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
RT-1	4	1.5	99.9	0.6	4.1	300
	6	2.3	100.4	0.1	2.2	350
	8	3.0	102.0	0.1	2.0	435
	10	3.8	104.0	0.1	2.2	410
	12	4.5	103.8	0.1	2.3	407

° For explanation refer to table XII.

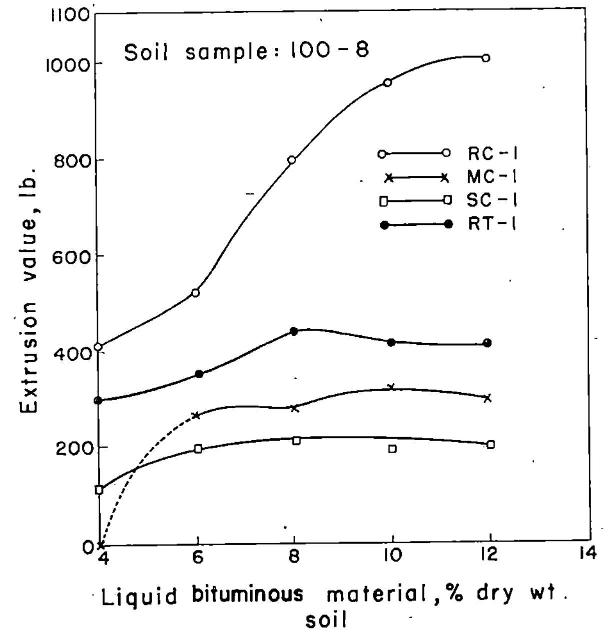

Fig. 12. Variation of extrusion value of soil-bituminous specimens with amount and kind of liquid bituminous material. Data for mixtures of soil sample 100-8 and grade 1 bituminous materials.

Experiments with sample 43½-1

As shown in table XVII, loess sample 43½-1 has a much higher clay content than the other two loess samples. Because of the difficulty of processing clayey soils with bituminous materials by conventional methods, only a limited number of evaluation experiments were performed with sample 43½-1. Medium curing cut-back asphalt of grades 0, 1, 2, and 3 were used. The test data given in table XVII illustrate the difficulty of stabilizing high clay content loess with bituminous materials.

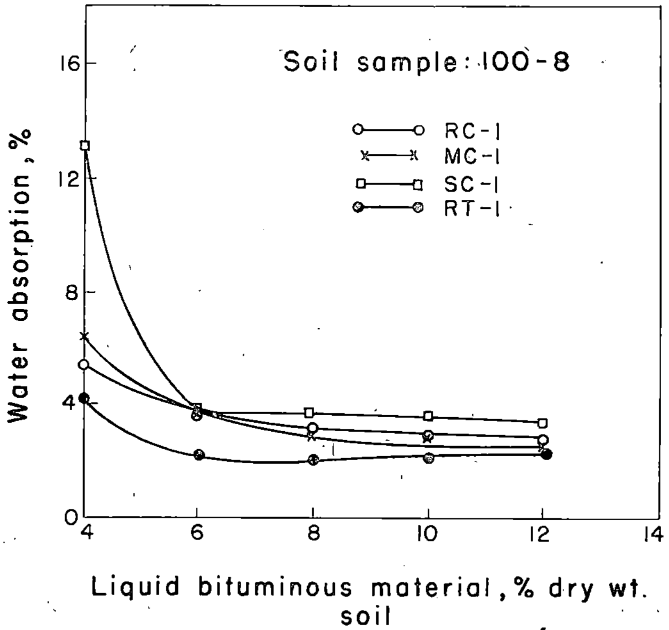

Fig. 13. Variation of water absorption of soil-bituminous specimens with amount and kind of liquid bituminous material. Data for mixtures of soil sample 100-8 and grade 1 bituminous materials.

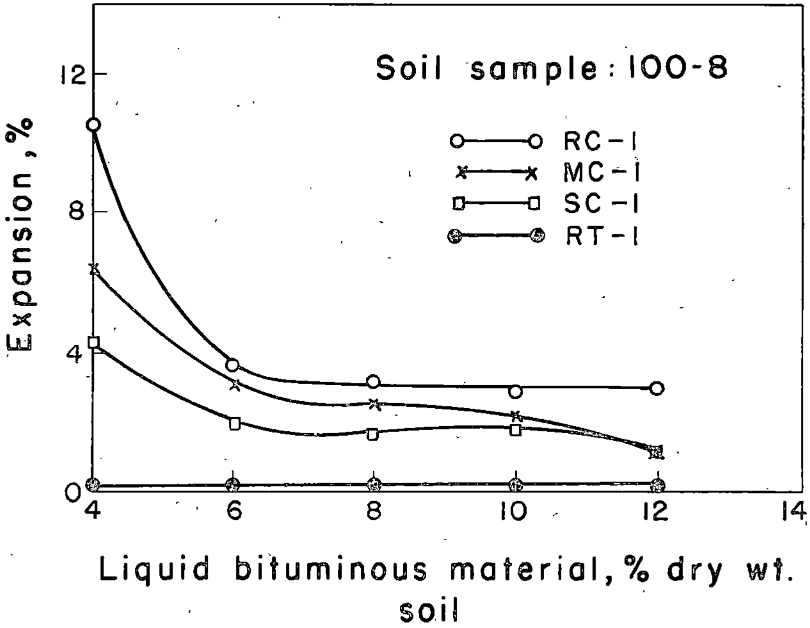

Fig. 14. Variation of expansion of soil-bituminous specimens with amount and kind of liquid bituminous material. Data for mixtures of soil sample 100-8 and grade 1 bituminous materials.

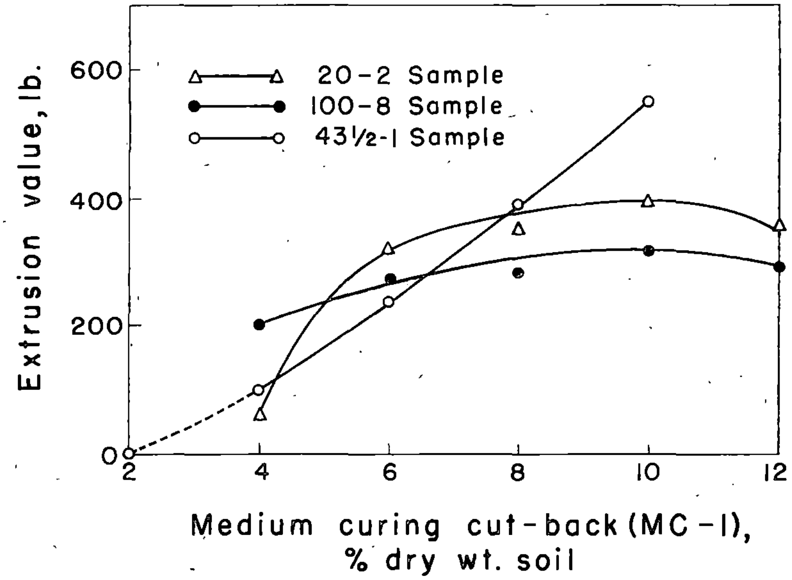

Fig. 15. Comparisons of extrusion value of soil-bituminous specimens made from mixtures of loess samples 20-2, 100-8 and 43½-1 and different amounts of MC-1 cut-back asphalt.

TABLE XVII. TEST DATA FOR MIXTURES OF SAMPLE 43½-1 AND MEDIUM CURING CUT-BACKS

Cut-back asphalt Kind and grade	Amount, %	Equivalent amount of Residue*, %	Dry density, pcf.	Expansion, %	Water absorption, %	Extrusion value, lb.
MC-0	2	1.3	90.6	N. D.†	N. D.†	N. D.†
	4	2.6	90.1	N. D.	N. D.	N. D.
	6	3.9	89.9	N. D.	N. D.	N. D.
	8	5.2	90.9	18.0	11.6	210
	10	6.5	90.9	18.7	10.2	340
MC-1	2	1.5	90.6	N. D.	N. D.	N. D.
	4	2.9	88.4	29.2	N. D.	100
	6	4.4	90.5	29.2	13.7	240
	8	5.8	90.7	20.4	10.5	390
	10	7.3	92.9	20.4	9.1	555
MC-2	2	1.6	87.2	N. D.	N. D.	N. D.
	4	3.1	87.7	N. D.	N. D.	N. D.
	6	4.7	85.6	N. D.	17.3	N. D.
	8	6.2	87.2	19.9	10.6	230
	10	7.8	87.4	19.0	9.6	285
MC-3	4	3.4	92.1	N. D.	N. D.	N. D.
	6	5.1	91.1	N. D.	N. D.	N. D.
	8	6.8	89.5	N. D.	N. D.	N. D.
	10	8.5	87.6	N. D.	N. D.	N. D.
	12	10.2	88.0	N. D.	N. D.	N. D.

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* For explanation refer to table IX.

† For explanation refer to table IX.

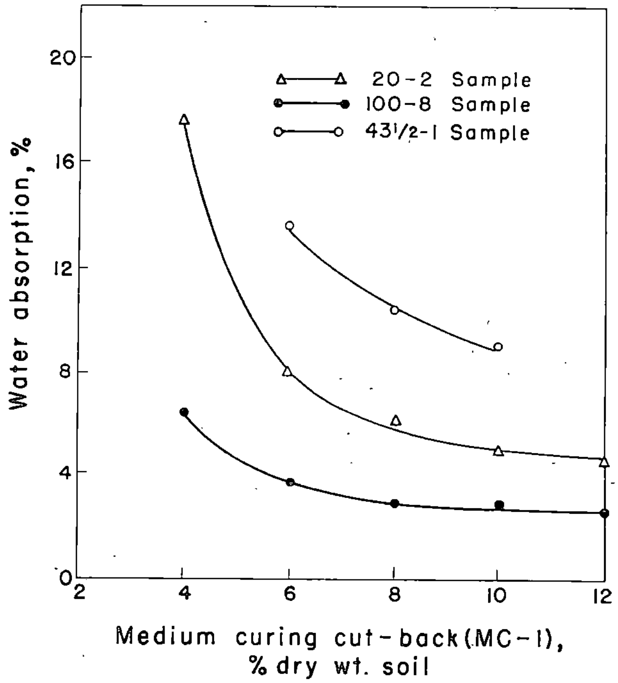

Fig. 16. Comparison of water absorption of soil-bituminous specimens made from mixtures of loess samples 20-2, 100-8 and 43½-1 and different amounts of MC-1 cut-back asphalt.

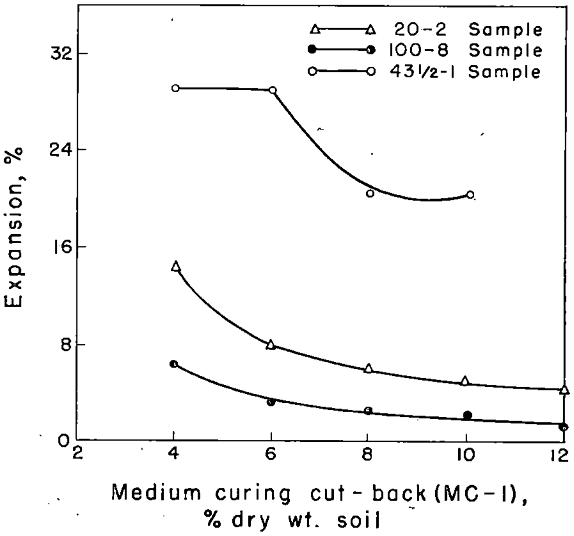

Fig. 17. Comparison of expansion of soil-bituminous specimens made from mixtures of loess samples 20-2, 100-8 and 43½-1 and different amounts of MC-1 cut-back asphalt.

Discussion of test results

A comparison of the test results for the three loess soils is made in figures 15, 16, and 17. While these curves represent data obtained with MC-1 cut-back asphalt, they are in general illustrative of the trends obtained with the other bituminous materials.

As previously mentioned, clay content is one of the major variables in the loess in southwestern and east central Iowa. The effect of this variable on the test results is most clearly shown (figures 16, 17). As would be expected, water absorption and expansion increase with an increase in clay content. The extrusion value data (figure 15) do not show such a simple relationship to clay content. The effect of amount of clay is perhaps most clearly indicated by the marked difference between the curve of the high clay content loess, sample 43½-1 and those of the more friable loess samples. The effect of the amount of clay is also reflected by the trend of the dry density data (tables IX to XVII). Regardless of the amount, kind or grade of bituminous admixture, the data show a decrease of density with increase in clay content.

A discussion of the amount of bituminous material needed to stabilize the different loess samples satisfactorily is made difficult by the preliminary nature of the experiments performed and by the lack of established criteria for evaluating the test data. It would appear from the test data of this investigation that admixtures of liquid bituminous materials in the range of 6 to 12 percent by weight of the dry soil are capable of materially improving the properties of the loess related to stability. The investigation has demonstrated the superiority of certain of the bituminous materials studied, particularly the rapid-curing and medium curing cut-back asphalts and the road tars over emulsions and road oils. The less viscous grades of these materials, grades 0, 1, and 2, seem to be most promising for loess stabilization.

CONCLUSIONS

1. Liquid bituminous materials show promise as stabilizing agents for loess.
2. The ease and adequacy of processing loess with bituminous materials is affected by the amount of clay in the loess. From this standpoint, bituminous stabilization seems more applicable to low clay content loess, represented in this investigation by samples 20-2 and 100-8.
3. Among the bituminous materials investigated, the cut-back asphalts and the road tars appear to be most suitable for stabilizing loess. The road tars are most effective in improving water absorption and expansion properties.
4. The less viscous bituminous materials, grades 0, 1, and 2, appear to give better results than the more viscous materials.
5. Admixtures of liquid bituminous materials in the range of 6 to 12 percent by weight of dry soil are capable of materially increasing the stability of loess in wet condition.

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WATER IN CUTBACK ASPHALT STABILIZATION OF SOIL

by

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ABSTRACT

Water during the mixing and the compaction phases of asphalt soil stabilization has long been recognized as an important factor. During mixing, water facilitates the even distribution of asphalt throughout the mass. The amount of moisture required for thorough distribution of cutback asphalt apparently increases as the amount of fine material in the soil increases. The amount of water becomes important during compaction mainly because of its effect on density. The amount of moisture required for maximum density of the soil-asphalt mixture is not the same as that for the soil alone.

The desirable moisture content of a soil, cutback asphalt mixture during mixing and during compaction are major factors that have been investigated. These moisture contents are controversial, to say the least. Different concepts of the relation of cutback asphalt content to water content used vary from the belief that 2% cutback asphalt replaces 1% water to the belief that cutback asphalt and water have an equivalent lubricating effect on soil grains during compaction.

Various mixtures of soil, cutback asphalt, and water were studied. Analysis of the resulting data shows that the percentage of mixing water required to produce maximum strength, maximum standard Proctor density, minimum moisture absorption during immersion, and minimum swelling is different for each property mentioned. However, a compromise moisture content (CMC) for mixing was found at which the variance of the aforementioned properties is a minimum. The CMC was found to be most advantageously determined by a minimization using the method of first powers. The CMC was also found to occur very near the mixing moisture content required to produce maximum standard Proctor density of the soil, cutback asphalt, and water system.

INTRODUCTION

Soil stabilization may be broadly defined as any regulated process that alters or controls soil properties for the purpose of improving the capacity of soil to perform and sustain an intended function. Processes by which soils may be stabilized include the use of other soil or chemical additives or cements, compaction, moisture control, or combinations of these. Asphalt is one of the cements used in soil stabilization for base or subbase courses of pavements.

Types of asphalt

Two types of asphalts, the cutbacks and the emulsions, at normal or slightly elevated temperatures, are suitable for mixing with soil. The viscosity of the asphalt cement in cutbacks is lowered by use of a solvent such as naptha, kerosene, or fuel oil. In the usual emulsions, asphalt cement is reduced to collodial size droplets and dispersed in water. Use of emulsions with soils is complicated by the fact that clays or fine silts may cause the emulsions to "break" or separate into the constituent asphalt cement and water. This causes mixing difficulties. Excellent results have been reported when the emulsions can be maintained until after mixing. The usual construction procedure is to mix, allow the emulsion to break, and aerate to reduce water in the mix prior to compaction. Usually the emulsion must be designed for the soil used.

Cutbacks are now the most practical asphalts for soil stabilization. So-called road oils are equivalent to cutbacks made with fuel oil. The road oils are usually prepared as direct residuals from fractional distillation, and they are the lowest cost asphalts. Because of their slow-curing characteristics, road oils are not the most suitable for the stabilization of soil mixes; however, they have been used for many years as surface treatments to reduce dust on gravel roads. Road oils can penetrate some oils, and continued annual treatment may build up a satisfactory stabilized mat on a light traffic road after four or five years. The use of road oil has the disadvantage that roads must be closed to traffic for long periods after treatment.

Medium curing cutbacks (called MC) and rapid curing cutbacks (RC) seem to be suitable types of liquid asphalt for soil stabilization. Different grades of cutbacks are designated from 0 to 5, depending on the percent solvent contained. MC-O and RC-O each contain about 50% solvent, and the percentage decreases to about 18% solvent for MC-5 and RC-5. RC cutbacks, in addition to having a more volatile solvent, are made with a harder asphaltic cement, contributing to better binding in the finally compacted and cured mix. The choice between MC and RC depends largely on climate, soil type, and construction practice. Cutbacks cure by an evaporation of volatiles. The higher grades of RC cutbacks may harden before mixing is completed; lower grades contain more solvent and cure more slowly.

The choice of grade MC or RC also depends on mixing conditions; usually the more solvent the greater the ease of mixing. Solvents cost about the same as the asphalt and do not directly contribute to strength. The use of high solvent content cutback asphalts may greatly prolong the curing time. For these reasons MC-0 and RC-0 are little used, MC-2 and 3 and RC-2 and 3 represent good compromises. The final choice can be made only after laboratory tests on the soil to be treated and after due consideration of climatic conditions. Usually finer-grained soils require a lower viscosity cutback asphalt for mixing.

Mechanism of stabilization

Asphalts are useful for soil stabilization because of their cementing and waterproofing qualities. The cementation property is generally considered to be most effective in providing increased stability in non-cohesive or very slightly cohesive granular soils, such as gravels and sands. The waterproofing property is utilized to greatest advantage in the more cohesive soils or soil aggregate mixtures. Waterproofing assists in the preservation of the natural stability which these soils have in a dry and well compacted condition.

Asphalt is mixed with granular soils to coat the grains and act as a waterproofer and binder. In soils containing clay the clay is a natural binder as long as water is kept out; asphalt is added as a waterproofer for the small clay cemented agglomerations.

Applications

Asphalt soil stabilization is at present limited mostly to non-plastic and mildly plastic granular soils, such as gravels, sands, and soil-aggregate mixtures[3, 14, 16, 18, 19, 20, 24]. Economics permitting, granular borrow materials have been added to fine-grained soils to obtain a mixture suitable for treatment with asphalt. Successful application of asphalt to fine grained plastic soils without granular admixtures has been somewhat limited[23, 25]. Recently laboratory investigations have been conducted on the stabilization of medium plastic soils with asphalt[5, 6, 12, 26, 27].

Need for research

Although the use of asphalt is one of the older soil stabilizing methods, less is known about the theory of asphalt soil stabilization than about some of the newer methods. Most of the knowledge on the subject has been derived from field experience, which does not allow the close control of variables which can be maintained in the laboratory. The total number of specimens required for a complete analysis and understanding of all possible interdependent variables reaches an astronomical figure. Fortunately the number of samples needed can be reduced considerably by eliminating any study of factors which have very little effect on the final result.

Role of water

The presence of water during the mixing and compaction phases of asphalt soil stabilization has long been recognized as an important factor. During mixing, water facilitates the even distribution of asphalt through the mass[7]. The amount of moisture required for thorough distribution of cutback asphalt apparently increases as the amount of fine material in the soil increases. Asphalt cement can be distributed if the amount of water used is enough to produce a slurry[22]. This phenomenon has been used to develop a surface sealing material of soil and asphalt cement[1, 8]. The use of wetting agents improves the stability of cutback asphalt treated soils[11].

During the compaction phase the amount of water becomes important mainly because of its effect on density. Usually a soil, asphalt mixture is the strongest at its maximum density. The amount of moisture required for maximum density of a soil, asphalt mixture is not the same as that for the soil alone.

Although the importance of moisture during these phases of stabilization has been recognized, a satisfactory agreement as to the amount of moisture needed has never been reached. A value of moisture content which has been proposed is called the *fluff-point* of the soil[6]. The term *fluff-point* may be misleading in that it does not always represent a specific moisture content but may be taken from a range in moisture content. The fluff-point is determined by comparison of the density of a number of samples of dry soil to each of which has been added a different amount of water. The moisture and soil are thoroughly mixed, and the moisture content of the sample exhibiting the greatest bulkiness or mealiness of texture is called the *fluff-point*. The only apparent reason for this choice of moisture content is that there is a maximum void ratio and grain separation with the minimum density. Evidently the logic of this choice was heavily influenced by great faith in the validity of the plug theory[13]. Moisture contents used in mixing asphalt with soil include: optimum moisture for maximum density of the soil, moisture content at the fluff point, optimum moisture for maximum density of the soil minus cutback asphalt content and one-half optimum moisture for maximum density of the soil. Different concepts of the relation of cutback asphalt content to water content used vary from the belief that 2% cutback asphalt replaces 1% water to the belief that cutback asphalt and water have an equivalent lubricating effect on soil grains during compaction.

The effects due to asphalt volatiles during compaction of soil asphalt mixtures are not clearly understood. Usual practice includes a period of aeration between mixing and compaction of soil cutback asphalt mixtures with a wide variance in the duration of the aeration. A reduction by aeration of the combined percentage of water and asphalt volatiles varies from one-fifth to one-half the original content. The asphalt volatile loss is thought to be responsible for an increase in strength of the compacted materials.

Purpose of investigation

The foregoing discussion emphasizes the need of this investigation which, broadly stated, is to study and interpret the effects of water during mixing and during compaction and the effects of asphalt volatiles during compaction on the stabilization of soil with cutback asphalt. A complete understanding of the effects of these variables on a compacted mix should aid in arriving at a more intelligent and efficient design of soil cutback asphalt mixtures than exists today.

TABLE I. LOCATIONS OF SOIL SAMPLES

Sample no.	County	Section	Tier North	Range	Soil series	Sampling depth, ft.	Horizon
20-2	Harrison	S-15[a]	78	43-W	Hamburg	39-40	C
100-8	Scott	NW¼, SE¼, S-13	77	2-E	Fayette	25-25½	C
S-6-2	Benton	NE¼, SE¼, S-16	86	10-W	Carrington	3-6	C
411	Page	S-27	69	36-W	Shelby	3-23	C
26-1	Shelby	S-21	81	40-W	Marshall	4-5	C
43½-1	Fremont	NW¼, NW½, S-36	69	40-W	Marshall	4½-5½	C

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[a] Sample 20-2 was obtained behind the third ward school in Missouri Valley.

MATERIALS

Soils

Soil samples were chosen from the loess, glacial till and sand materials of Iowa to represent not only widespread soil types but also textural variations of soil in general. Samples 20-2 and 100-8 represent the friable, calcareous loess in western and eastern Iowa, respectively. 20-2 was sampled from the deep loess bordering the Missouri River, and 100-8 was sampled from the deep loess along the Mississippi River. A sub-study comparing testing apparatus was made using samples 26-1 and 43½-1, which represent the plastic loess in southwestern Iowa.

Sample S-6-2 is a fine sand from east central Iowa with a low clay content of only 2 percent. This material represents the fluvial fine sand deposits of the area.

Sample 411 is Kansan glacial till from southwestern Iowa. Kansan till, one of the most abundant surficial materials in the southern part of Iowa, may be found in all parts of the state. The particle size distribution and mineralogy of Kansan till is in general similar in all areas[21].

Asphalt

Cutback asphalts of grades MC-0, MC-2 and MC-4 were used. The properties

TABLE II. PROPERTIES OF SOILS

	Sample number					
	20-2	100-8	S-6-2	411	26-1	43½-1
Physical properties						
L.L., %	30.8	27.1	N.P.	41.8	39.4	51.9
P.L., %	24.6	19.8	N.P.	14.9	26.9	18.5
P.I., %	6.2	7.3	N.P.	26.9	12.5	33.4
C.M.E., %	19.6	...	...	21.7	19.5	28.5
S.L., %	22.3	20.6	14.8	12.3	23.3	19.1
Sp. Gr.	2.71	2.72	2.68	2.67	2.71	2.72
Lower fluff point, %[*]	8	5	1.5	11.0	9.0	11.5
Std. Proct. density, pcf.	109.9		109.9	111.9	107.0	104.3
Opt. M.C., %	18.2	15.8	12.3	15.5	17.7	19.1
Chemical properties						
Organic matter, %	0.17	0.2	0.04	0.11	0.18	0.37
Carbonates, %	10.17	20.0	...		...	0.5
Cat. Ex. Cap.	3.8	13.4		20.0	18.2	24.4
pH	8.7	7.9	6.5	...	...	6.7
Textural composition, %[†]						
Sand	0.4	2.8	94.4	32.7	0.9	0.4
Silt	79.8	85.2	3.4	30.8	69.7	60.2
Clay	19.8	12.0	2.2	36.5	8.1	39.4
Colloidal clay	14.5	8.9	1.1	26.0	21.4	29.8
Textural classification[‡] (B.P.R. system)	Silty loam	Silty loam	Sand	Clay	Silty clay	Silty clay
Engineering classification (AASHO)	A-4(8)	A-4(8)	A-3(0)	A-7-6(18)	A-6(9)	A-7-6(18)

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[*] Defined by Benson[12].

[†] Sand–2.0 to 0.074 mm, silt–0.074 to 0.005 mm, clay–less than 0.005 mm, coloidal clay–less than 0.001 mm.

[‡] Classified texturally by the Bureau of Public Roads System except that sand and silt sizes are separated by the N. 200 sieve.

of the asphalts were furnished by the manufacturer (table III). Medium-curing cutback asphalts were selected for the reasons previously given.

LABORATORY PROCEDURES AND TESTS

Standard tests and laboratory techniques are not always sufficient or applicable procedures for conducting research. This was found to be true, and a number of sub-investigations were necessary to develop suitable methods of test[15].

Proportioning of materials

All additions of water and cutback asphalt were calculated as a percentage of the weight of oven dry soil with which they were mixed. Cutback asphalt percentages represent the total weight of asphalt cement plus hydrocarbon volatiles. In other words 6 percent cutback asphalt means a mixture having a ratio of 6 lb of liquid cutback asphalt to 100 lb of oven dry soil.

Moisture and hydrocarbon volatile determinations

Determinations of moisture content in samples devoid of cutback asphalt were made by drying the samples in an oven at 105° to 110°C. Moisture contents of samples containing cutback asphalt were determined by distillation of all volatile material from the sample with a subsequent separation and measurement of the amount of water and hydrocarbon volatile material[15]. The latter method determines both water content and hydrocarbon volatile content of the sample.

Mixing of materials

Test specimens were prepared from batches mixed by a Hobart C-100 kitchen mixer. The required water which varied in amount with the experiments per-

Table III. Properties of cutback asphalts[*]

Properties	Test method	MC-0	MC-2	MC-4	RC-2
		Specification designation			
Furol viscosity at 77°F., sec.	ASTM D 88	98			
Furol viscosity at 122°F., sec.			143		
Furol viscosity at 140°F., sec.				211	138
Furol viscosity at 180°F., sec.					
Specific gravity (77°/77°F.)	AASHO T 43	0.939		0.967	0.949
Distillation					
Distillate (percent of total distillate to 680°F.)	ASTM 402				
To 370°F.			2.3	0.0	
To 437°F.		71.4	20.9	9.5	41.7
To 500°F.			72.1	57.1	73
Residue from distillation to 680°F.					
Volume percent by difference		65	78.5	89.5	76
Sp. gravity of distillate (77°/77°F.)		0.79	0.83	0.84	. . .
Tests on residue from distillation,					
pen. 77°F., 100g., 5 sec.		1000	210	215	96
Sp. Gravity of residue (77°/77°F.)	ASTM D 71	1.005	1.015	1.005	1.012
Solubility in carbon tetrachloride	ASTM D 4	99.95	99.99	99.98	99.56
Temperature of use for mixing, °F.		50-120	100-120	175-225	80-150
Oliensis spot test		Neg.	Neg.	Neg.	Neg.

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[*] Properties furnished by the Standard Oil Company of Indiana.

formed and 1500 grams of soil were first machine mixed for two minutes. The sides of the mixing bowl were next scraped and the materials were mixed for an additional three minutes. The soil, water mixture was then stored in an air-tight container for 16 to 24 hours before adding the cutback asphalt. The cutback asphalt was heated to the middle of the range of temperatures recommended by the Asphalt Institute and hand mixed into the moist soil to prevent splashing. Next the materials were machine mixed in the following order: 1½ minutes of mixing, sides were scraped, 1½ minutes of mixing, sides again scraped and a final two minutes of mixing[15].

One of the sub-investigations was a study of the amount of hydrocarbon volatile material lost during the process of mixing cutback asphalt with soil. Determination of the loss of hydrocarbon volatiles while mixing 10 percent MC-0 at room temperature with oven dry soil, and with air dry soil at room temperature showed that the loss is very small; the loss after seven minutes of mixing with oven dry soil at 110°C and cooling at room temperature in a desiccator was 1.27 percent of the hydrocarbon volatiles and the loss using air dry soil was 1.21 percent. The smaller loss in the presence of hydroscopic moisture can be explained by considering the mechanism of mass transfer:

> Loss of hydrocarbon volatiles through evaporation in a system of this type is essentially a diffusional phenomenon. The system can also be considered to consist of two immiscible liquids, water and kerosene or water and gasoline. Each component liquid is in a pure state and therefore exerts its normal equilibrium vapor pressure at the existing temperature. The rate of evaporation in either a static or dynamic atmosphere is proportional to the surface exposed multiplied by the difference between the partial pressures of the evaporating component at the interface and in the surrounding atmosphere. Increased water contents do not affect partial pressures, and therefore they reduce the amount of hydrocarbon volatile loss by reducing the exposed surface area of the more volatile hydrocarbon material. Since the hydrocarbon volatile loss in the presence of a small amount of water was negligible, the loss with larger amounts of water present will be even less and for practical purposes can be considered negligible.

Ageing mixtures

Batches of cutback asphalt, soil, and water mixtures that were used for studying the amount of water required during mixing were stored four hours in an air-tight container before molding specimens. The purpose of this aging was to ensure soil mixture equilibrium conditions.

Drying-back mixtures

Batches of cutback asphalt, soil, and water mixtures that were used for studying the amount of water and hydrocarbon volatile material remaining before molding were air dried for various periods of time. The cutback asphalt, soil, and water mixtures were placed in shallow pans and covered with a layer of gauze and a one inch layer of cotton. The coverings reduced the thermal gradients and vapor concentration gradients, which in turn reduced the rate of vapor phase mass transfer from the surface of the drying material. The reduced rate of surface mass transfer causes the liquid and vapor conditions to remain static and fairly close to equilibrium throughout the drying mixture.

Molding

Following either aging or drying-back, soil cutback asphalt mixtures were molded into 2 inch diameter by 2 inch high specimens using standard Proctor compactive effort[9]. The molds were 5 inch long brass cylinders having a 2 inch inside diameter. Compacted material in excess of 2 inches was extruded from the cylinder and trimmed. The specimen remained within the cylinder through testing[15].

Testing specimens

The stability of specimens was evaluated by the Iowa Bearing Value test immediately following the soaking period. The Iowa Bearing Value test, abbreviated to IBV test, was chosen as a means of stability evaluation for several reasons[15]. The IBV test is believed to similate field conditions more nearly than other tests, it requires one-twentieth the amount of material and less than one-half the time required by the CBR test. The IBV test molds are small and require little space in humidity or storage cabinets. A singular disadvantage is the fact that the IBV test is limited to medium and fine-grained soils, although a limited amount of research indicates that materials containing up to 25 percent ¼ inch gravel may be tested[9]. The soil materials used in this study were medium and fine grained.

The IBV test is a miniature bearing test patterned after the California Bearing Ratio test. The test specimen is compacted into a 2 inch diameter mold and struck off to a height of 2 inches. A ⅝ inch penetration rod is forced into the specimen by a testing machine, and the load at various depths of penetration is recorded and graphed. In this investigation the load corresponding to 0.08 inch penetration is called the IBV.

Soaked, air-dry or after freezing and thawing specimens may be tested in the IBV test. In this investigation specimens in brass cylinders were immersed in distilled water at room temperature with a surcharge (equivalent to that used in the CBR test) and allowed to soak for seven days before testing. Seven days was chosen as the soaking period because it was found that a maximum loss in stability, as measured by strength, occurs within this period.

Review of procedure

The laboratory procedure is presented for the sake of clarity:

1. Proportion soil and water
2. Mix
3. Store 16 to 24 hours
4. Mix by hand
5. Add liquid cutback asphalt
6. Mix by hand
7. Machine mix
8. Age or dry back
9. Mold

10. Immerse in distilled water
11. Test

INVESTIGATION

Water contents during mixing and during compaction of soil cutback asphalt mixtures have marked effects on the properties of the resulting stabilized material. The amount of moisture present during mixing decidedly influences the final distribution of cutback asphalt in the soil mass. The main purpose of this investigation was to determine what moisture control should be exercised to ensure a stabilized material having an optimum combination of properties. Two processes of cutback asphalt soil stabilization were investigated: in process I, soil, cutback asphalt and water were mixed and immediately compacted; in process II, soil, asphalt and water were mixed and the mixture was dried back to some lower moisture content before compaction.

The difference between process I and process II was the stage in the process at which the water content was varied. In process I the water content was varied during mixing, and the mixture was compacted with a water content equal to that used in mixing. In process II the water content during mixing was sufficiently high to ensure good cutback asphalt distribution; the water content was then changed from that used during mixing by drying back before compaction.

Process I

The effects of moisture content during mixing on the density, IBV, absorption, expansion and the total seven day soaked moisture content were studied by testing specimens molded from different batches of soil, asphalt and water in which the water content was varied. All other quantities and qualities such as the amount and type of soil, and the amount and type of cutback asphalt were maintained constant for any one study. Each of the four soils was studied in this manner and compared using admixtures of 6 and 10 percent MC-2 and MC-4 cutback asphalt. The sand sample (S-6-2) was treated with only 3 percent MC-2, since higher percentages of MC-2 cutback asphalt produced mixtures of such a liquid consistency that molding was impossible. The use of MC-4 with the sand permitted treatments of both 3 and 6 percent. Again it is emphasized that water content was the only variable in any singular study of constant cutback asphalt content. The method of analysis can be clarified by an examination of the data presented.

Density was calculated as weight of dry soil per volume and is expressed in pounds per cubic foot. IBV was expressed in pounds; absorption was calculated as the amount of moisture gained by a specimen during the seven day immersion period and was expressed as a percentage of the oven dry weight of soil contained in the specimen. Expansion of specimens was expressed as a percentage of the original height of the specimen concerned, since the specimens were laterally confined and expansion occurred in one dimension only. Total seven day soaked moisture content was expressed as percentage of the oven dry weight of soil contained in a specimen.

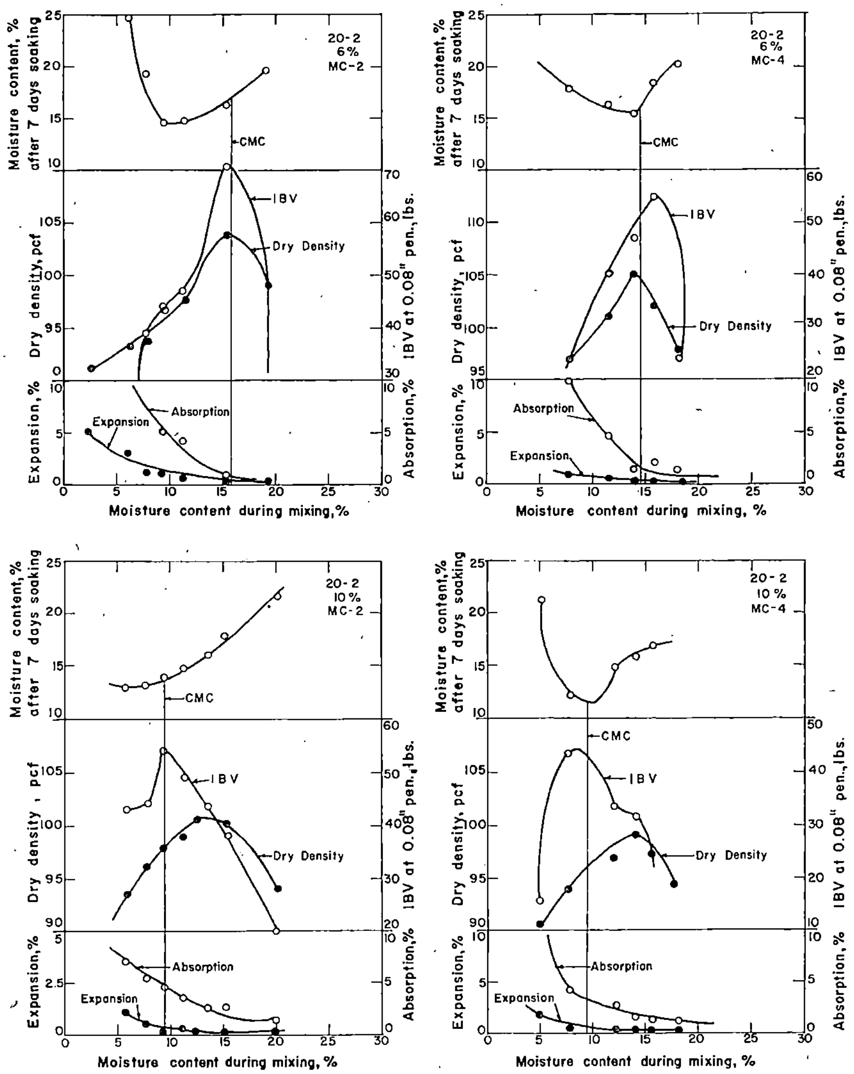

Fig. 1. Graphs of moisture content during mixing versus the IBV, dry density, absorption, expansion and total moisture content after 7 days' soaking of soil, cutback asphalt compacted specimens. The soil cutback asphalt compositions are listed on each graph. The amount of residual asphalt cement in 6 and 10 percent MC-2 is 4.93 and 8.2 percent, and in 6 and 10 percent MC-4 is 5.47 and 9.11 percent. The vertical line in the center of the graph indicates the CMC.

The data are presented in figures 1, 2 and 3 as graphs with density, IBV, absorption, expansion and total seven day soaked moisture content treated as dependent variables. The independent variable is the water content *during mix-*

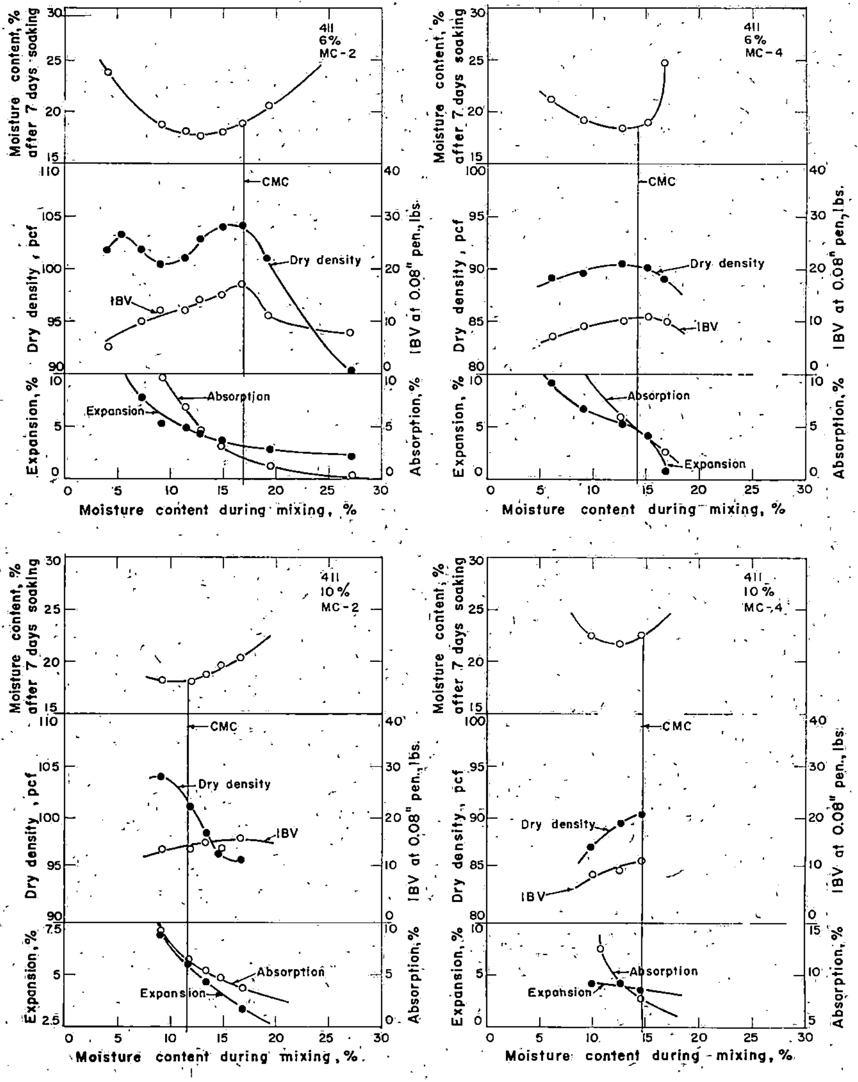

Fig. 2. Graphs of moisture content during mixing versus the IBV, dry density, absorption, expansion and total moisture content after 7 days' soaking of soil, cutback asphalt compacted specimens. The soil cutback asphalt compositions are listed on each graph. The amount of residual asphalt in 3, 6, and 10 percent MC-2 is 2.47, 4.93, and 8.2 percent, and in 3 and 6 percent MC-4 is 2.7 and 5.4 percent. The vertical line in the center of the graph indicates the CMC.

ing, expressed as a percentage of the oven-dry weight of the soil in each specimen. Each point on the graphs represents an average of three values.

The curves of IBV, density and of total moisture content after seven days'

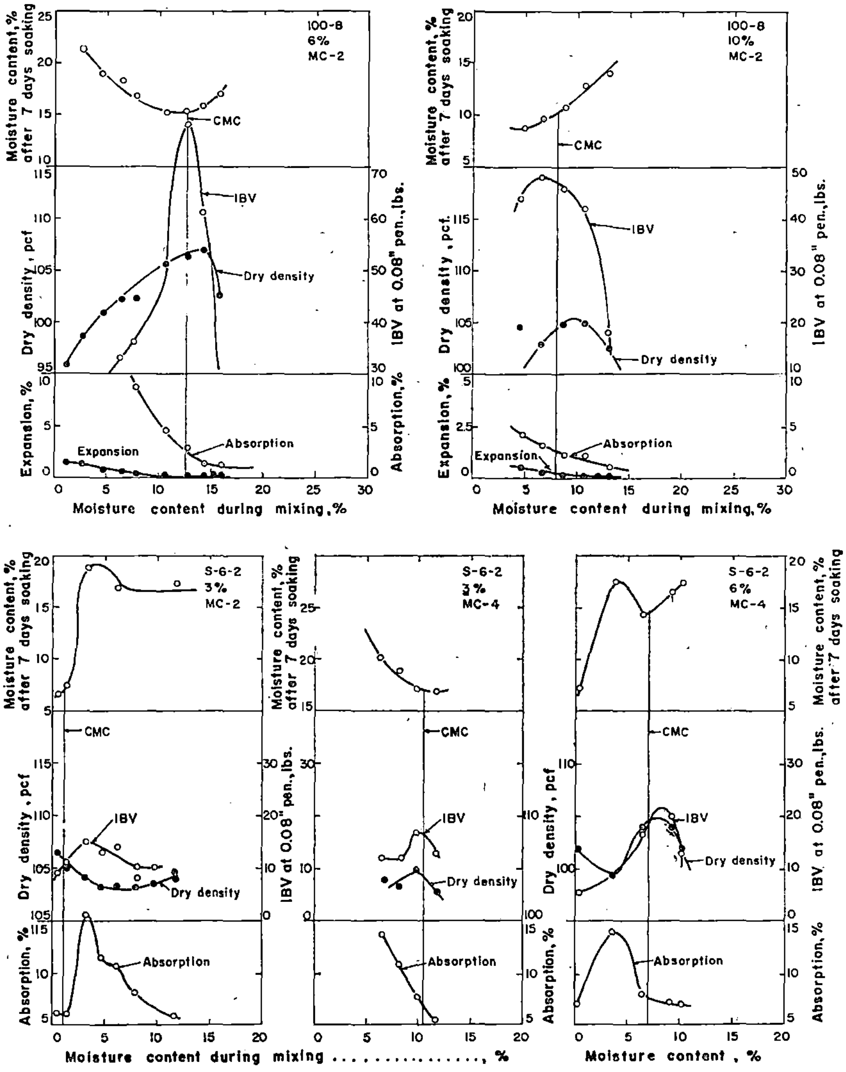

Fig. 3. Graphs of moisture content during mixing versus the IBV, dry density, absorption, expansion, and total moisture content after 7 days' soaking of soil cutback asphalt compacted specimens. The soil cutback asphalt compositions are listed on each graph. The amount of residual asphalt cement in 6 and 10 percent MC-2 is 4.93 and 8.2 percent, and in 6 and 10 percent MC-4 is 5.47 and 9.11 percent. The vertical line in the center of the graph indicates the CMC.

soaking all show either a maximum or a minimum where an optimum mixing moisture content exists for each combination of soil and type and amount of cutback asphalt. The optimum moisture contents for the foregoing seldom coincide.

The absorption and expansion curves are similar in character. Both sets of curves are, in general, a logarithmic type asymptotic to some minimum value. The curves indicate that the best absorption and expansion performances are obtained with the highest mixing water content possible. However, a gain in absorption and expansion performance by increasing the mixing water content is obtained only at the expense of other desirable properties.

Somewhere within the range of moisture studied there is a mixing moisture content which represents the best compromise when all properties are considered. The compromise point was found by graphical analysis of the data, using the method of first powers in which a minimization of the summation of individual property deviations from a datum is calculated. More accurate methods of analysis could be performed by using either the method of least squares or the method of least cubes. However, the latter methods are far more complex and require an exact knowledge of the equations of the functions relating the properties in question for accuracy. Curves could be fitted to the numerical data; but in so doing errors of a serious nature are apt to be introduced. Errors of this type offset the increased accuracy of the more complex methods, so the simplest method was used.

Each property exhibits one best value, either a maximum or a minimum, which was used as a datum. The difference between a property value and the datum value was then calculated at each moisture content as a percentage of the datum value. The percentage of deviation of all properties from their respective datums were summed at each mixing moisture content and the summations of deviations were then plotted versus mixing moisture content. The mixing moisture content corresponding to the minimum value of the summation of deviations is then the best compromise moisture content (CMC). The mixing CMC was found by this method for all soils and combinations of cutback asphalt used except for some of the sand mixes in which no definite maximum or minimum were evident. The CMC for the latter were visually estimated.

In the data resulting from the tests and calculations optimum moisture for the raw soil is included primarily as a matter of interest. The mixing moisture content corresponding to maximum IBV, maximum density and minimum total moisture content after seven days' immersion are shown for comparison with the mixing CMC at which the best over-all results are obtained (table IV).

Examination of these data show that the mixing moisture for maximum IBV and for maximum density closely correspond to the mixing CMC. Exact correspondence would produce a straight line graph passing through the origin with a slope of 45 degrees in each case. Both the plots of mixing moisture for maximum IBV and for maximum density versus CMC follow a 45 degree line fairly well

TABLE IV. DATA FROM PROCESS I—MIXED AND MOLDED

Soil	Amount and type of cutback asphalt*	Optimum moisture of soil, %	Mixing moisture content required to produce: Maximum IBV	Maximum dry density	Minimum moisture content after 7 days' soaking	Calculated MC where minimum summation of deviations occurs, CMC %
20-2	6% MC-2	18.0	15.5	15.7	10.1	15.8
	10%		9.6	13.6	7.2	9.5
	6% MC-4		16.0	14.0	13.8	14.5
	10%		8.5	13.9	10.0	9.5
100-8	6% MC-2	15.8	12.7	13.8	11.5	12.5
	10%		6.6	9.6	4.5†	8.0†
411	6% MC-2		16.6	15.8	12.3	16.3
	10%		16.5	9.0	10.4	11.6
	6% MC-4		14.7	12.5	13.1	14.2
	10%		15.2	15.7	12.3	14.6
S-6-2	3% MC-2	12.3	3.2	0.5†	0.5†	1.0†
	3% MC-4		10.0	9.8	11.7	10.5
	6%		8.5	8.0	0.5†	7.0†

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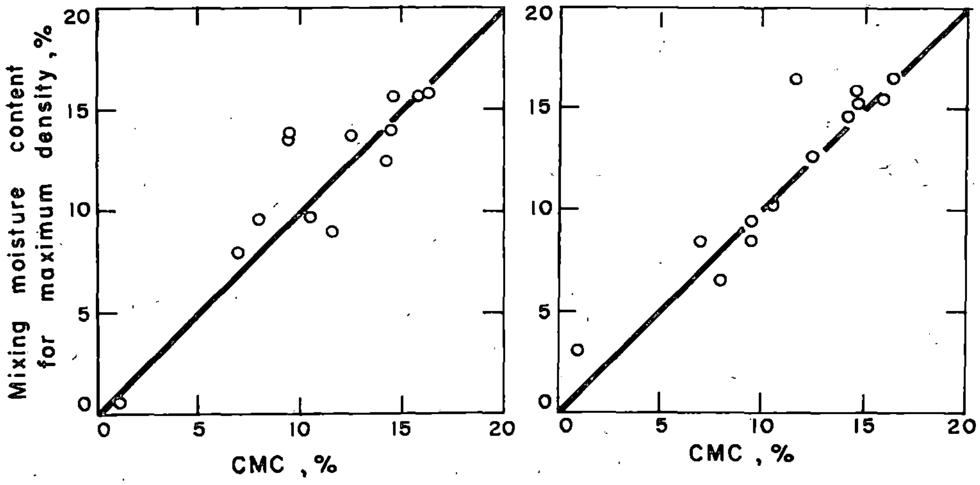
* Amount of residue in 6% MC-2 cutback asphalt is 4.93%, 10% is 8.2% and in 6% MC-4 5.47% and in 10% MC-4 9.11%.

† Visually estimated because maxima and minima were indefinite.



Process I

Fig. 4. Graphs comparing mixing moisture content for maximum standard Proctor density and mixing moisture content for maximum IBV with the compromise moisture content. Exact correlation of the experimental data would fall on the indicated 45 degree line. This relation holds true for the silty and clayey soils used in this investigation.

(figure 4). The mixing moisture for maximum IBV appears to give the best correlation; however the mixing moisture for maximum density gives a good correlation.

Absorption or expansion due to soaking cannot be used as criteria for predicting mixing moisture for maximum performance because there is no convenient control point (figures 1, 2, and 3). The only possible point of control is the minimum value in each case and the minimum values lie too far to the right of the moisture range in which maximum density, maximum IBV and minimum total moisture content after seven days' immersion occur. Inclusion of absorption and expansion in the CMC computation would displace the CMC to the right far enough to be out of the moisture range previously mentioned. These properties are determined after specimens have been soaked for one week. The properties also depend on the moisture content at the beginning of the soaking period, since the amount of absorption or expansion is partially dependent on the amount of air void space available for the entry of water. The moisture content at the beginning of the soaking period is also variable, so the amount of absorption or expansion is a relative value.

The mixing moisture for the maximum density of the soil asphalt mix is the most practical moisture content for use as a guide in determining water requirements for cutback asphalt soil stabilization. The density tests can be run in a relatively short time; the IBV test requires at least a week.

Process II

The effects of moisture content during compaction on the density, IBV, expansion and the total seven day soaked moisture content were studied by testing specimens molded from different batches of soil, asphalt and water in which the moisture and hydrocarbon volatile content had been changed by drying the material after mixing. All other quantities and qualities such as the amount and type of soil, and the amount and type of asphalt were maintained constant for any one study. Batches were mixed at either the standard Proctor optimum moisture or at the liquid limit of the raw soil and in some cases at the plastic limit. Each soil was studied in this manner and compared to other soils using 6 and 10 percent MC-2 and MC-4 cutback asphalt. The sand sample was again treated as stated in the previous section describing Process I. Property values were calculated and expressed in the same units as before.

The data are presented as graphs with density, IBV, expansion and total seven day soaked moisture content treated as dependent variables (figures 5, 6, 7, 8). The independent variable is the water content *during molding*. Each point on the graphs represents an average of three values. The data are presented in the same manner as were the data for process I. The resulting curves are of the same general type and were analyzed as were those for process I.

A close correlation, except for sand, is shown between either the moisture contents for maximum density or maximum IBV and the dried back CMC (figure 9); the results from sand tend to be erratic and the CMC must be estimated by eye. Both plots follow a 45 degree line and the same general statements apply as for Process I. The dried back moisture content for maximum

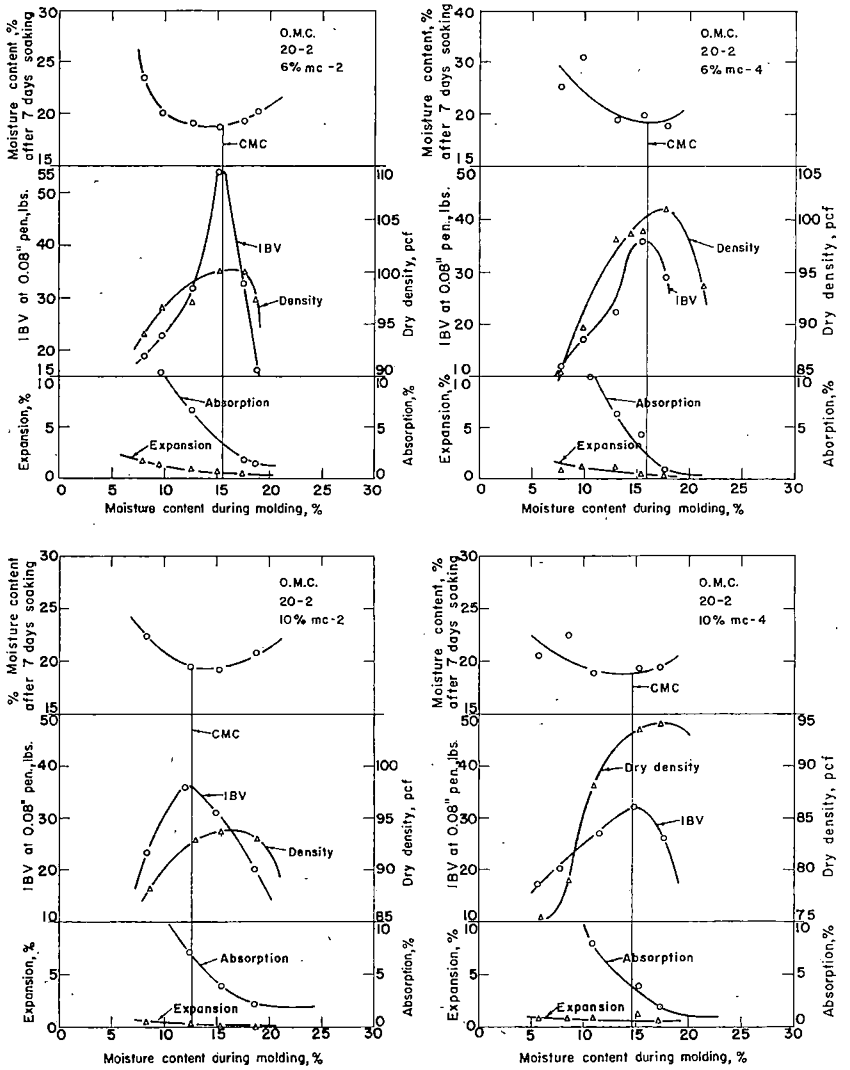


Fig. 5. Graphs of moisture content during molding versus the IBV, dry density, absorption, expansion, and total moisture content after 7 days' soaking of soil cutback asphalt compacted specimens. The soil cutback asphalt compositions and the moisture content at which the mixes were mixed are listed on each graph. The amount of residual asphalt cement in 6 and 10 percent MC-2 is 4.93 and 8.2 percent, and in 6 and 10 percent MC-4 is 5.47 and 9.11 percent. The vertical line in the center of the graph indicates the CMC.

density of the soil-asphalt mix is the most practical criterion for determining the water requirements of process II, except possibly for sand. The data indicate

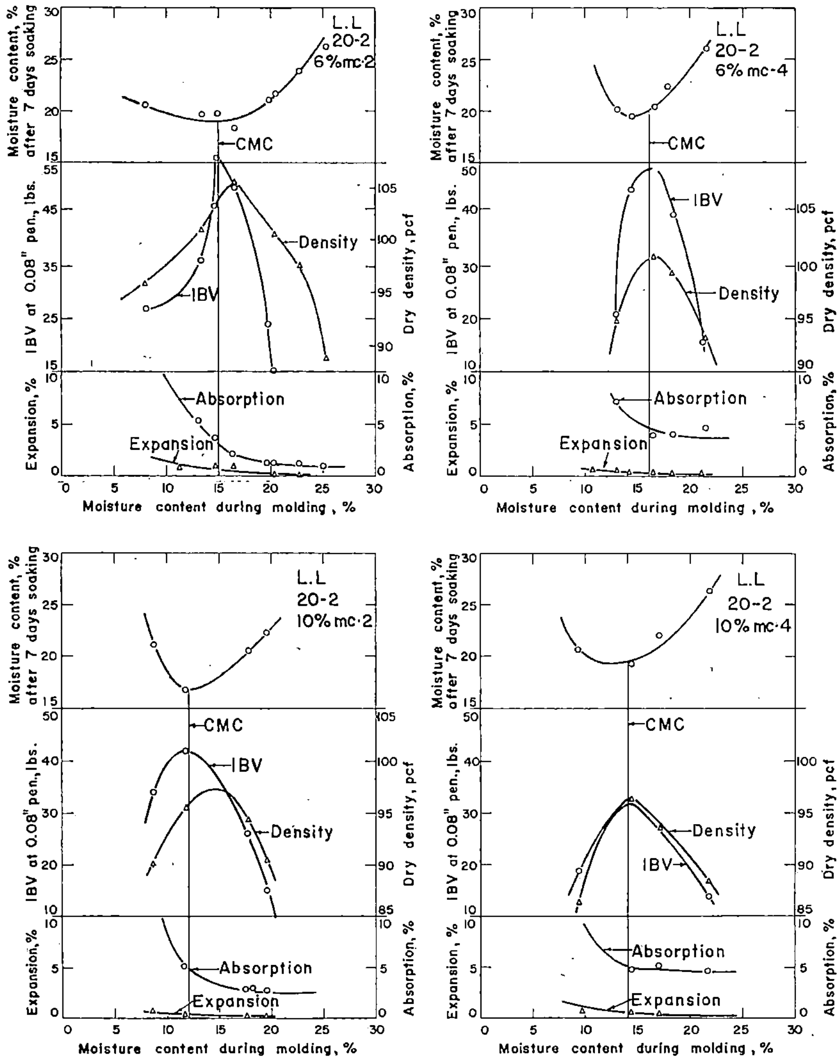


Fig. 6. Graphs of moisture content during molding versus the IBV, dry density, absorption, expansion, and total moisture content after 7 days' soaking of soil cutback asphalt compacted specimens. The soil cutback asphalt compositions and the moisture content at which the mixes were mixed are listed on each graph. The amount of residual asphalt cement in 6 and 10 percent MC-2 is 4.93 and 8.2 percent, and in 6 and 10 percent MC-4 is 5.47 and 9.11 percent. The vertical line in the center of the graph indicates the CMC.

that for sand the CMC lies on the dry side of the dried back moisture content for standard Proctor density.

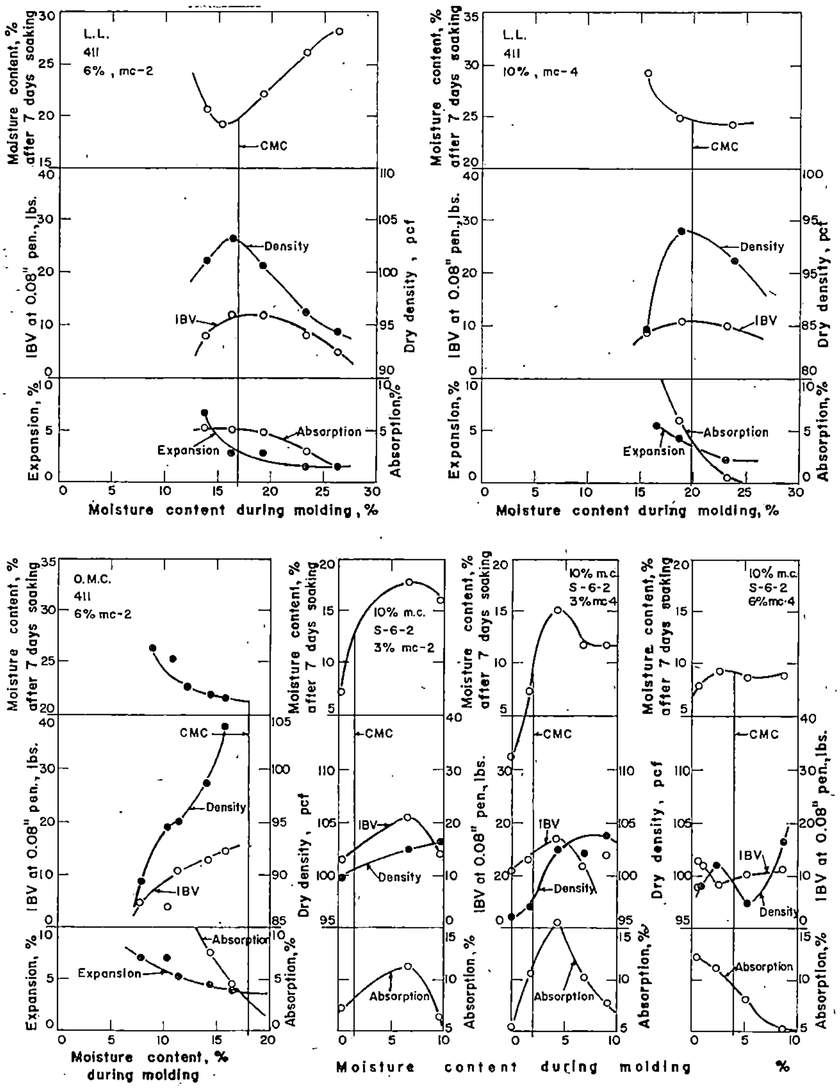


Fig. 7. Graphs of moisture content during molding versus the IBV, dry density, absorption, expansion, and total moisture content after seven days' soaking of soil, cutback asphalt compacted specimens. The soil, cutback asphalt compositions and the moisture content at which the mixes were mixed are listed on each graph. The amount of residual asphalt cement in 6 percent MC-2 is 4.93 percent. The vertical line in the center of the graph indicates the CMC.

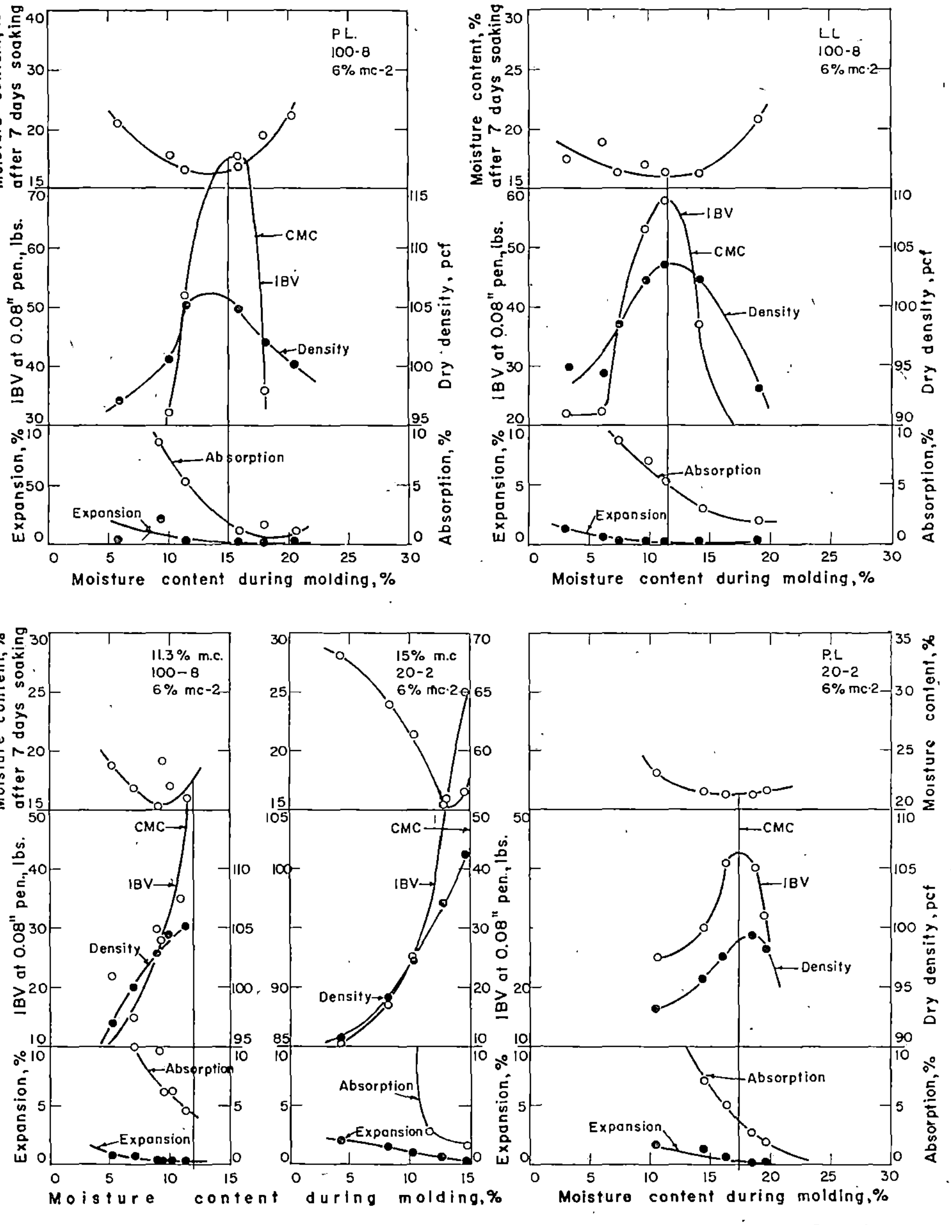


Fig. 8. Graphs of moisture content during molding versus the IBV, dry density, absorption, expansion, and total moisture content after 7 days' soaking of soil cutback asphalt compacted specimens. The soil cutback asphalt compositions and the moisture content at which the mixes were mixed are listed on each graph. The amount of residual asphalt cement in 3, 6, and 10 percent MC-2 is 2.47, 4.93, and 8.2 percent, and in 3, 6, and 10 percent MC-4 is 2.7, 5.47, and 9.11 percent. The vertical line in the center of the graph indicates the CMC.

Comparison of processes I and II

Processes I and II are compared on the basis of the values of IBV, density and total seven day soaked moisture content obtained at the CMC of each process (tables V, VI). All property values of specimens resulting from Process I were superior to those of corresponding specimens prepared by Process II except for the total seven day soaked moisture content of the sand specimens mixed with MC-4. Process I seems to produce the best results with the textural types of soil studied.

Heavier clays may require the use of process II, since the CMC of process I may lie within the plastic range of the soil. Should this be so, adequate mixing of such a soil with asphalt at the CMC of process I is impossible. The higher mixing moisture contents used in process II become the only possible solution because mixing is done easily near the liquid limit of highly plastic soils. The use of process II increases the cost, since the addition of the drying back stage may limit the application and use of cutback asphalt soil stabilization to medium to non-plastic soils.

Distribution of asphalt

The water in soil cutback asphalt mixtures not only aids in attaining maximum densities but also aids in obtaining even distribution of asphalt throughout the soil mass. A study of this was made by mixing batches of soil with a constant percentage of asphalt and varying amounts of water from one percent to percentages slightly above the liquid limit of the soil. Specimens were prepared

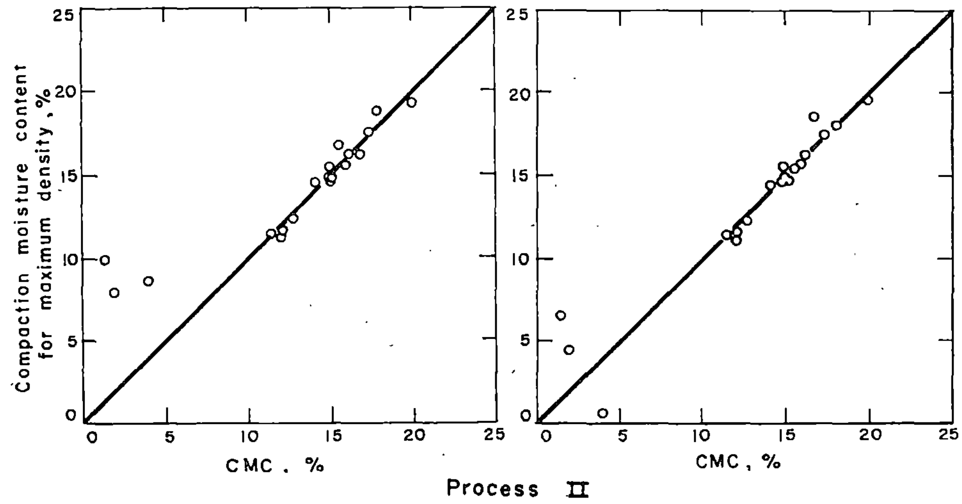


Fig. 9. Graph comparing compaction moisture content for maximum standard Proctor density and compaction moisture content for maximum IBV with the compromise moisture content. Exact correlation of the experimental data would fall on the indicated 45 degree line. This relation holds true for the silty and clayey soils used in this investigation.

by compaction and curing. Curing was done to remove moisture so that the areas containing cutback asphalt showed a high contrast with the areas containing little or no cutback asphalt (figures 10 to 15). The percentages indicated represent the moisture content that lies closest (of those shown) to the compromise moisture content as determined from the experimental data.

The asphalt tends to be locally concentrated and poorly distributed at low mixing moisture contents in the compacted cutback asphalt treated loess and glacial till, as indicated by the dark areas which contain the highest cutback asphalt concentrations (figures 10 to 14). The distribution of cutback asphalt improves as the amount of mixing water is increased, and the most uniform distribution appears to be somewhere in the neighborhood of the liquid limit of the soil. No difference in distribution pattern was noticed between MC-2 and MC-4 treatment of these soils.

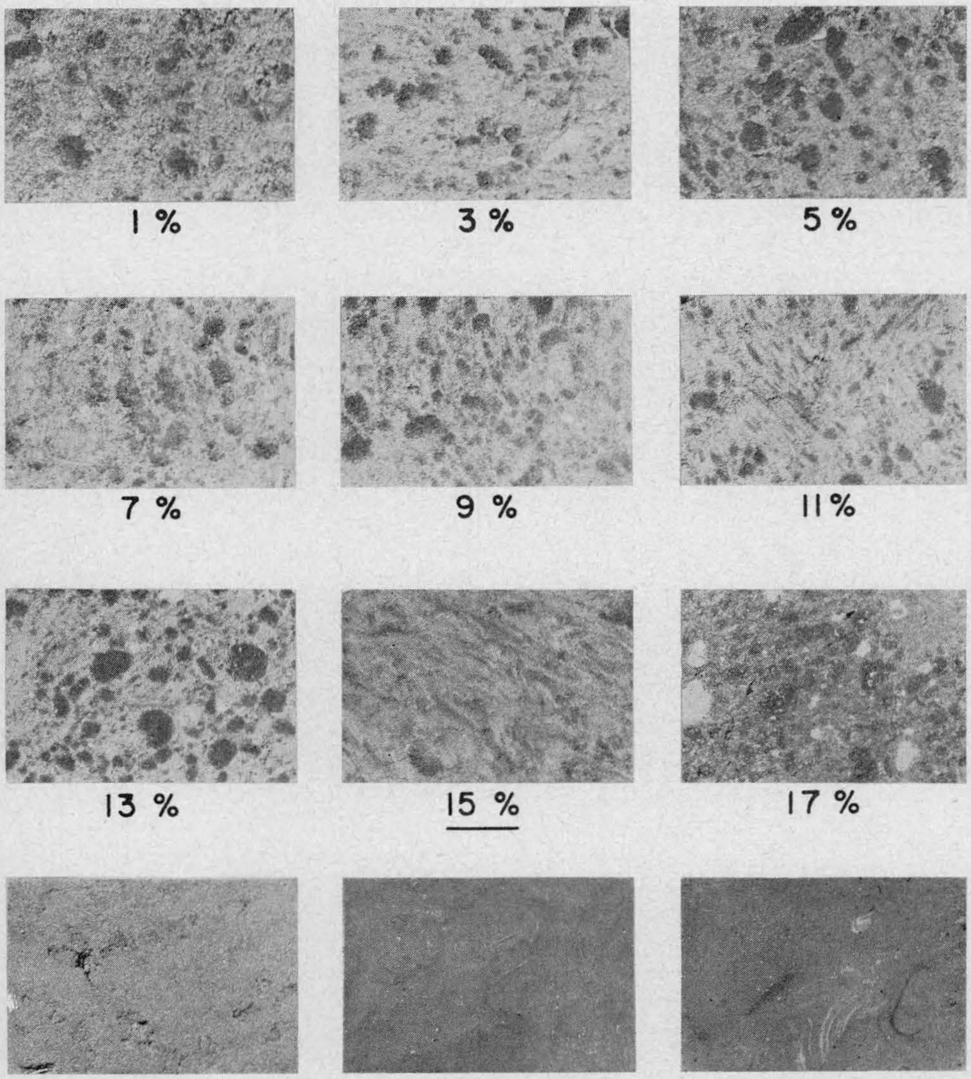
Loess. The compromise moisture content (CMC) for the two loess (20-2 and

TABLE V. BEST ATTAINABLE VALUES OF IBV, DENSITY AND TOTAL 7 DAY SOAKED MOISTURE CONTENT AT CMC USING MC-2 CUTBACK ASPHALT

	Process I					Process II			
Soil no.	Amount of asphalt, %	IBV lbs.	Density pcf.	Total moisture content, %	%	M.C. during mixing corresponds to	IBV lbs.	Density pcf	Total moisture content, %
20-2	6	71	105	16.8	15.0		65	102	17.5
						O.M.C.	54	100	18.9
						P.L.	42	99	21.2
						L.L.	56	104	19.0
	10	54	98	14.8		O.M.C.	36	93	19.4
						L.L.	42	96	16.9
100-8	6	78	107	15.3	11.3		52	105	17.6
						P.L.	75	106	16.5
						L.L.	69	104	16.0
411	6	17	104	18.3		O.M.C.	15	105	21.3
						L.L.	12	103	19.7
S-6-2	3	10	106	7.0			15	101	13.0

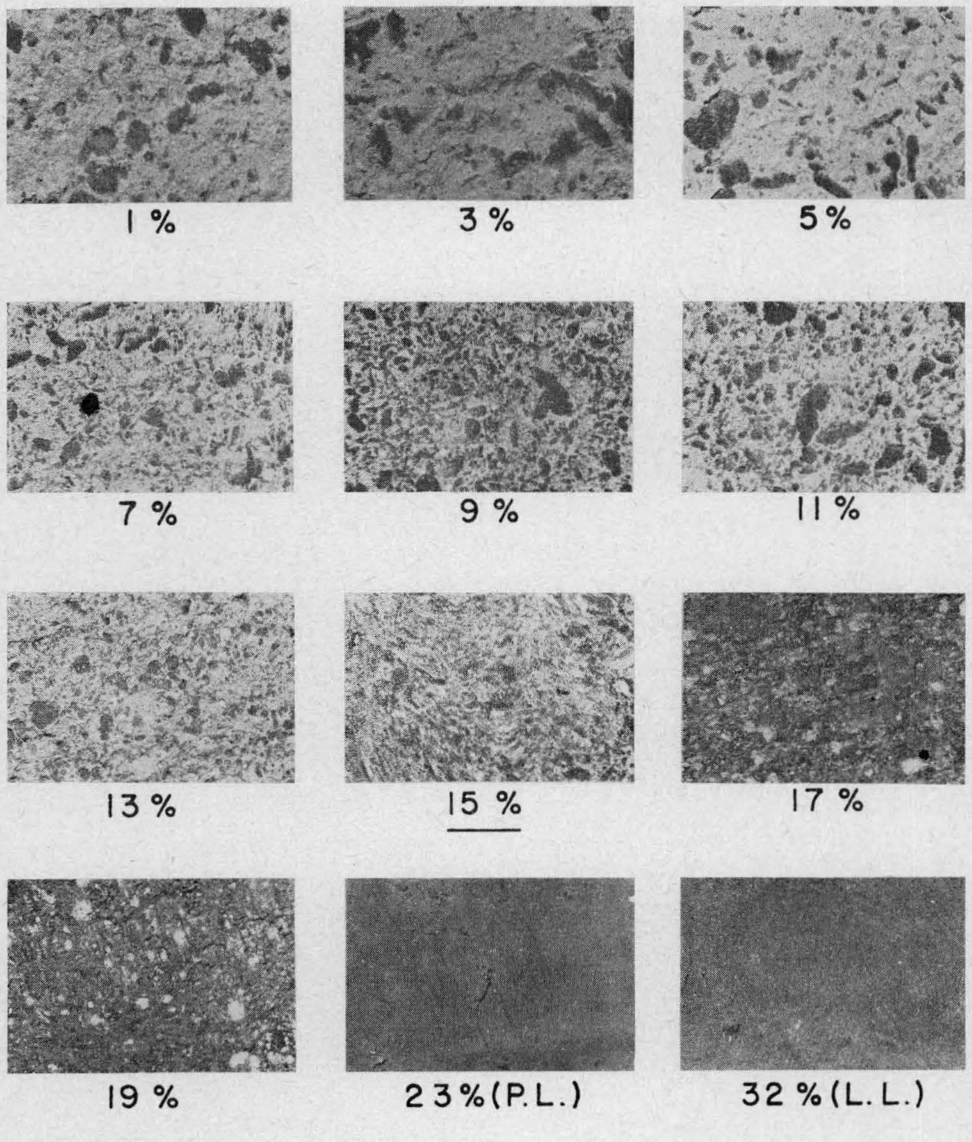
TABLE VI. BEST ATTAINABLE VALUES OF IBV, DENSITY AND TOTAL 7 DAY SOAKED MOISTURE CONTENT AT CMC USING MC-4 CUTBACK ASPHALT

	Process I					Process II			
Soil no.	Amount of asphalt, %	IBV lbs.	Density pcf	Total moisture content, %	%	M.C. during mixing corresponds to	IBV lbs.	Density pcf	Total moisture content, %
20-2	6	51	105	15.9		O.M.C.	36	100	19.2
						L.L.	50	101	20.1
	10	43	96	11.5		O.M.C.	32	93	19.8
						L.L.	32	97	19.5
411	10	12	90	22.3		L.L.	11	94	24.5
S-6-2	3	17	105	17.0	10.0		24	98	10.0
	6	19	105	14.6	10.0		10	99	9.2


1 % 3 % 5 %
7 % 9 % 11 %
13 % 15 % 17 %
19 % 23 % (P.L.) 32 % (L.L.)

20 - 2 (loess) 6 %, MC-2

Fig. 10. Photographs of Process I compacted specimens of 20-2 (loess) treated with 6 percent MC-2 and various percentages of mixing water. The percentage of mixing water is indicated below each photograph. The underlined percentage indicates the moisture content that is closest to the CMC of the mixtures shown. Photographs of specimens mixed at the plastic limit and the liquid limit of the soil are indicated by the initials P.L. and L.L. following the appropriate moisture percentages. The residual asphalt cement content is 4.93 percent.



1 % 3 % 5 %

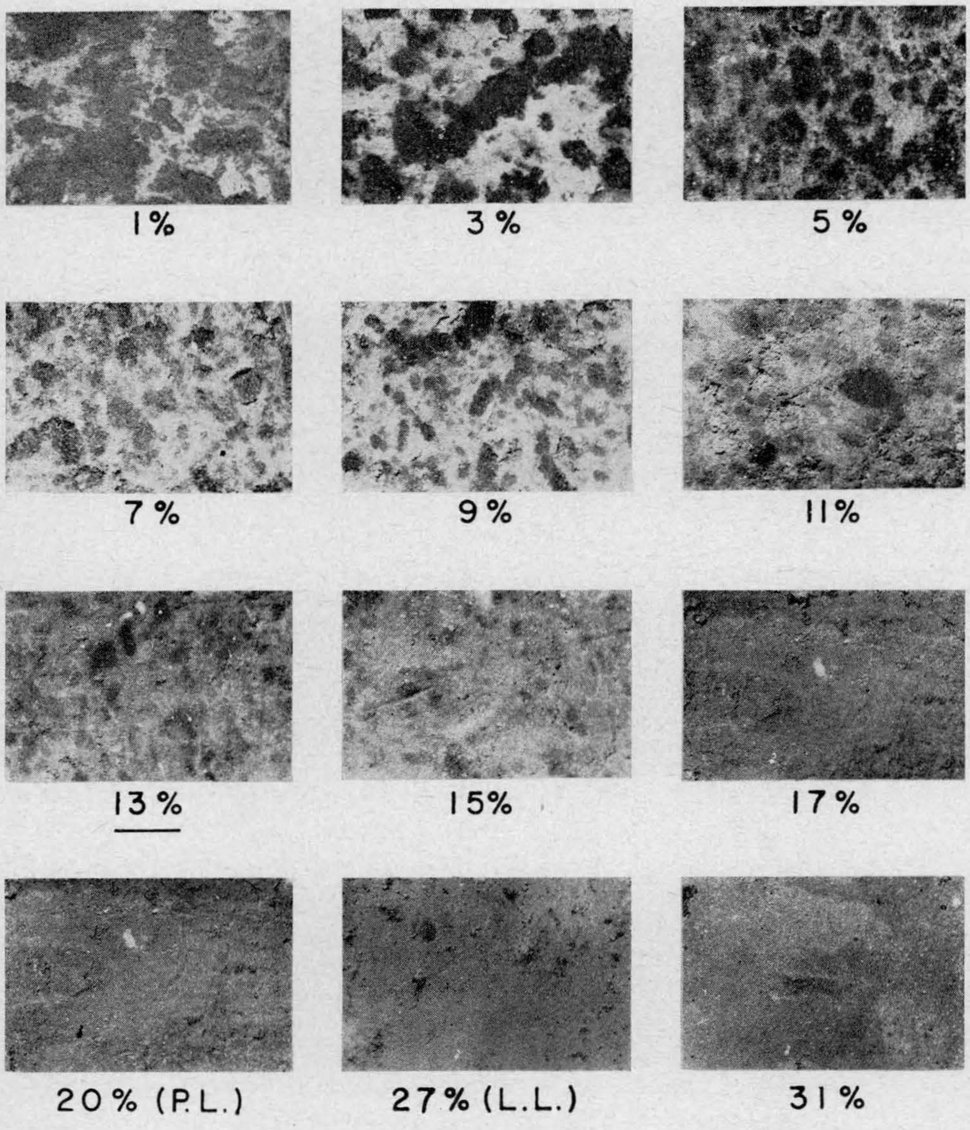
7 % 9 % 11 %

13 % 15 % 17 %

19 % 23 %(P.L.) 32 %(L.L.)

20-2 (loess) 6%, MC-4

Fig. 11. Photographs of Process I compacted specimens of 20-2 (loess) treated with 6 percent MC-4 and various percentages of mixing water. The percentage of mixing water is indicated below each photograph. The underlined percentage indicates the moisture content that is the closest to the CMC of the mixture shown. Photographs of specimens mixed at the plastic limit and the liquid limit of the soil are indicated by the initials P.L. and L.L. following the appropriate moisture percentages. The residual asphalt cement content is 5.47 percent.



1% 3% 5%

7% 9% 11%

13% 15% 17%

20% (P.L.) 27% (L.L.) 31%

100-8 (loess) 6%, MC-2

Fig. 12. Photographs of Process I compacted specimens of 100-8 (loess) treated with 6 percent MC-2 and various percentages of mixing water. The percentage of mixing water is indicated below each photograph. The underlined percentage indicates the moisture content that is the closest to the CMC of the mixture shown. Photographs of specimens mixed at the plastic limit and the liquid limit of the soil are indicated by the initials P.L. and L.L. following the appropriate moisture percentages. The residual asphalt cement content is 4.93 percent.

100-8) soils occurs at about the mixing moisture content where the asphalt appears to be streaked or smeared in the soil rather than uniformly distributed. The CMC also lies well below the plastic limit of the soil. Mixing moisture contents above the CMC produce much more uniform distribution of asphalt, but evidently the asphalt films resulting from mixing in this moisture range do not produce optimum cohesion and lower permeability. The loess soils mixed easily with asphalt at all moisture contents.

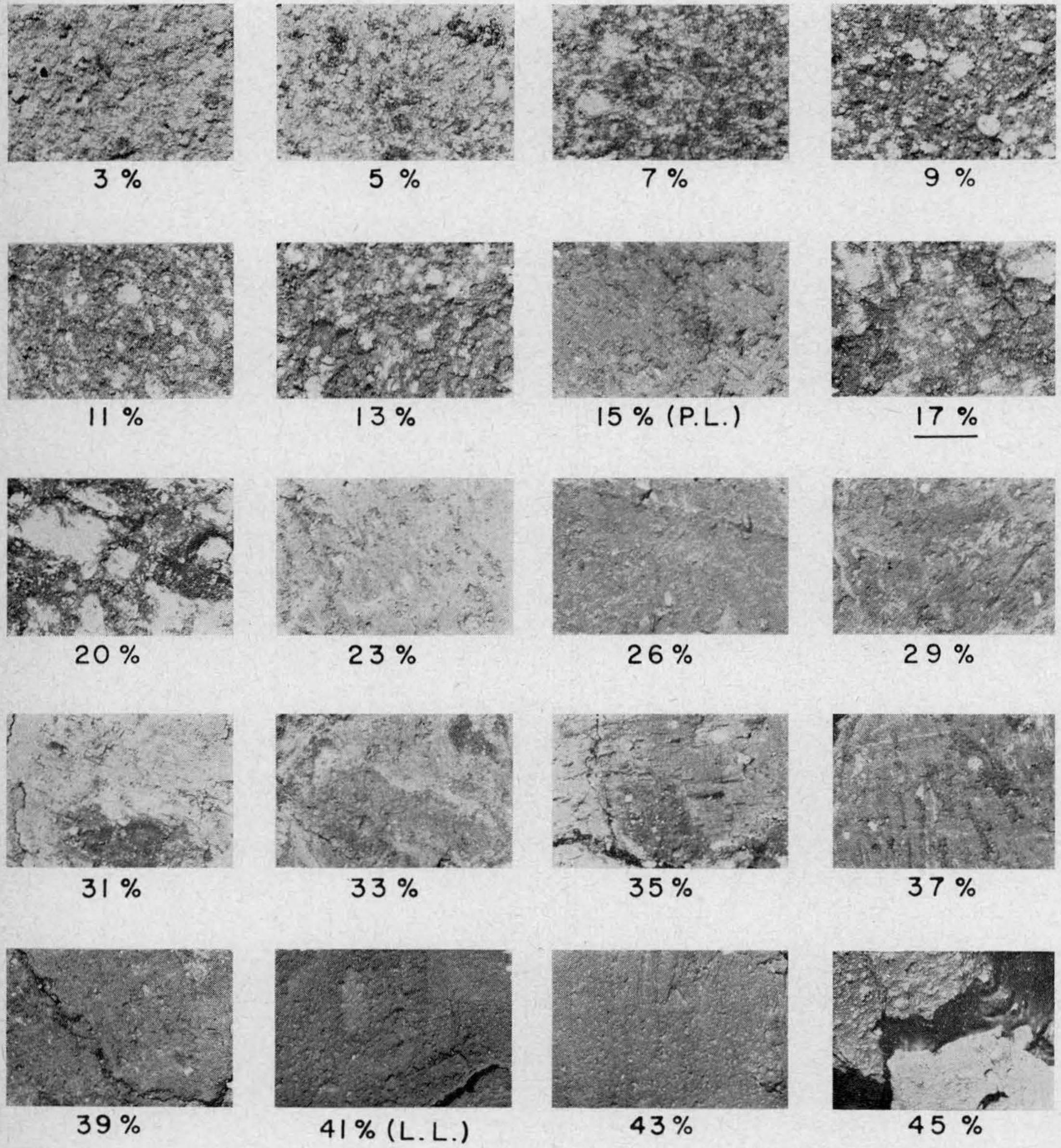
Glacial till. The photographs of the glacial till show that the asphalt is generally more poorly distributed than in the loess; but the asphalt also has a smeared appearance near the CMC, though the smeared condition is not as clearly indicated as in the loess samples. The glacial till was very difficult to mix with asphalt when the mixing moisture was in a range of 2 to 8 percent above the plastic limit of the soil. Resistance to mixing was sufficient to break the paddle of the mixing machine, and machine mixing was only carried on for about one-half a minute; no supplemental hand mixing was used. The mixing limitations imposed by the highly plastic character of this soil are, no doubt, partially responsible for the poor distribution of asphalt. Extensive planes of asphalt resulted in many mixes when the system was in a moisture produced plastic state. Specimens prepared from mixtures with moisture contents above the plastic limit showed a decided tendency to develop shrinkage cracks during drying; the amount and size of the cracks increased with the mixing moisture content (figures 13 and 14).

Sand. Figure 15 shows that a different water relationship exists in the sand (S-6-2) specimens treated with MC-2 and MC-4. The top six photographs are of sand treated with MC-2 and the bottom six are of sand treated with MC-4. The MC-2 treated specimens have an estimated CMC of 1 percent, and the MC-4 treated specimens have a CMC of 11 percent. Decreased coating of sand grains is evident as the mixing water content increased above 1 percent. With MC-4 cutback asphalt, better distribution was obtained as the mixing water content increased up to 11 percent. Evidently water is beneficial to asphalt distribution with MC-4 treatment; with MC-2 very little water is needed because MC-2 is not as viscous as MC-4.

Failure to coat some grains was also noted in the loess and glacial till specimens that were molded from batches mixed with higher water contents. The number of uncoated grains was small, since the failure to coat occurred mainly on the sand grains which are only a fraction of the total soil used.

DISCUSSION

The data indicate that cutback asphalt stabilization of the sandy, silty and clayey soils investigated is best accomplished by a process (process I) in which the soil, cutback asphalt and water are mixed for a specific period of time immediately following which the mixture is compacted. The moisture content at which the silty and clayey soils are best stabilized with either MC-2 or MC-4 asphalt corresponds closely to the optimum moisture content for maximum



3 % 5 % 7 % 9 %

11 % 13 % 15 % (P.L.) 17 %

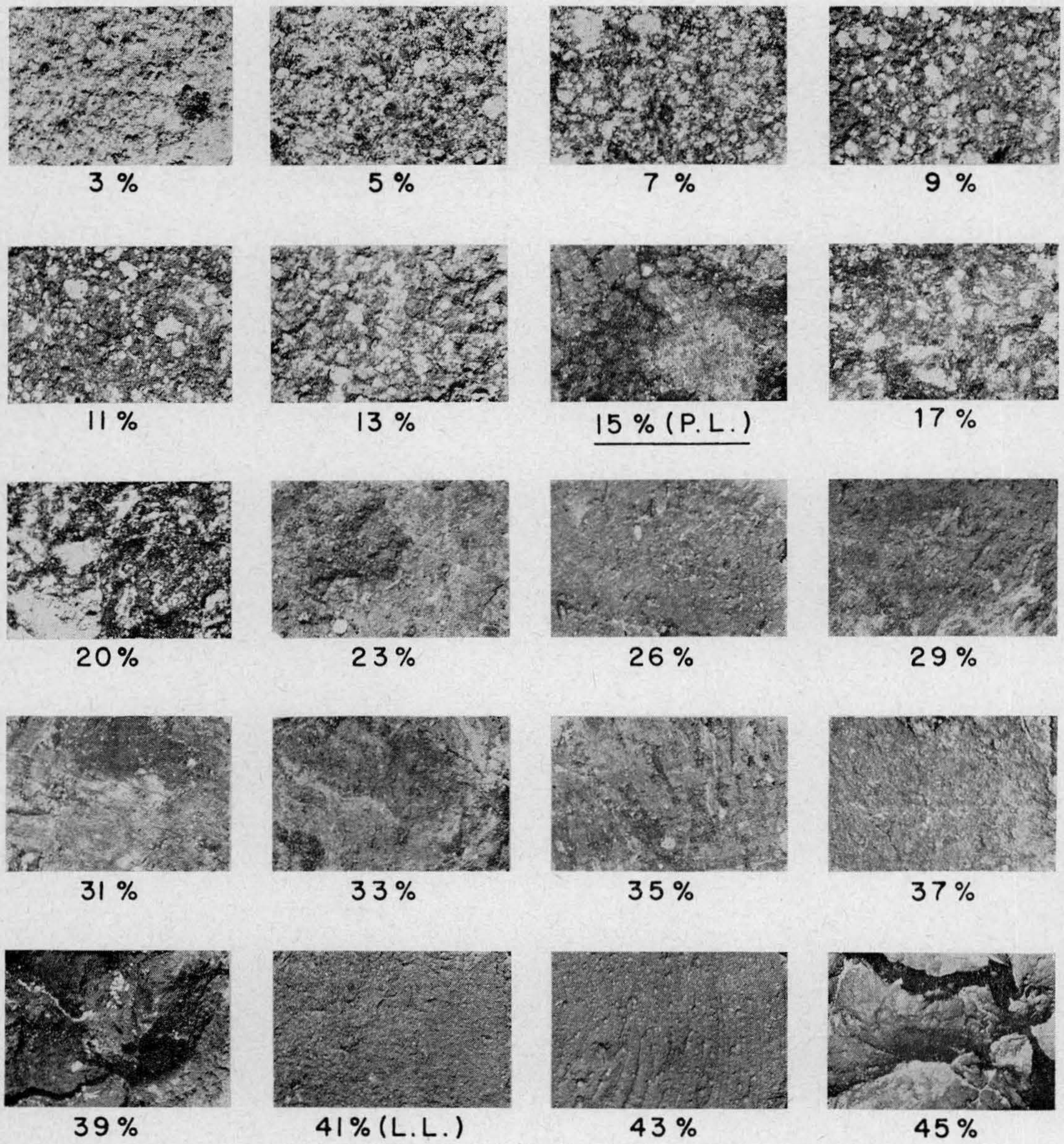
20 % 23 % 26 % 29 %

31 % 33 % 35 % 37 %

39 % 41 % (L.L.) 43 % 45 %

411 (till) 6%, MC-2

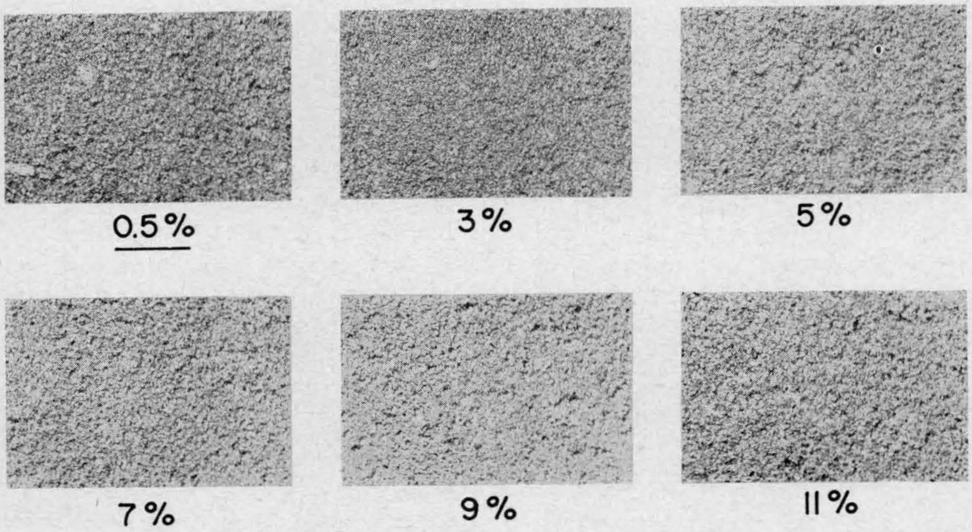
Fig. 13. Photographs of Process I compacted specimens of 411 (glacial till) treated with 6 percent MC-2 and various percentages of mixing water. The percentage of mixing water is indicated below each photograph. The underlined percentage indicates the moisture content that is the closest to the CMC of the mixture shown. Photographs of specimens mixed at the plastic limit and the liquid limit of the soil are indicated by the initials P.L. and L.L. following the appropriate moisture percentages. The residual asphalt content is 4.93 percent.



3 %
5 %
7 %
9 %
11 %
13 %
15 % (P. L.)
17 %
20%
23%
26%
29%
31 %
33%
35%
37%
39%
41% (L.L.)
43%
45%

411 (till) 6%, MC-4

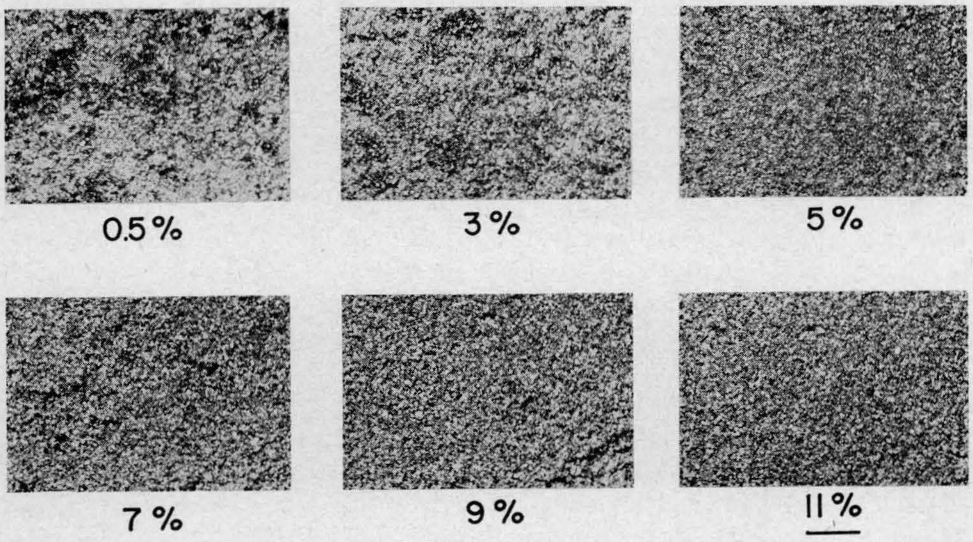
Fig. 14. Photographs of Process I compacted specimens of 411 (glacial till) treated with 6 percent MC-4 and various percentages of mixing water. The percentage of mixing water is indicated below each photograph. The underlined percentage indicates the moisture content that is the closest to the CMC of the mixture shown. Photographs of specimens mixed at the plastic limit and the liquid limit of the soil are indicated by the initials P.L. and L.L. following the appropriate moisture percentages. The residual asphalt cement content is 5.47 percent.



0.5 %   3 %   5 %

7 %   9 %   11 %

S-6-2 (sand) 3% MC-2



0.5 %   3 %   5 %

7 %   9 %   11 %

S-6-2 (sand) 3% MC-4

Fig. 15. Photographs of Process I compacted specimens of S-6-2 (sand) treated with 3 percent MC-2 and MC-4 and various percentages of mixing water. The percentage of mixing water is indicated below each photograph. The underlined percentage indicates the moisture content that is closest to the CMC of the mixture shown. The residual asphalt cement content is 2.47 percent for MC-2 mixes and 2.74 percent for MC-4 mixes.

standard Proctor density of the soil asphalt mixture. The sandy soil requires little or no moisture when stabilized with MC-2 asphalt, but it requires enough water for maximum standard Proctor density when stabilized with MC-4.

The process (process II) of mixing the materials at high moisture contents with a drying back period between mixing and compaction produced specimens inferior to those produced by process I, with the quantities of cutback asphalt used. The high mixing moisture contents resulted in a cutback asphalt distribution approaching that of an intimate mix. The drying back periods were necessary to reduce the moisture content of the mixture to that needed for maximum compacted densities. Even though process II produces better distribution of cutback asphalt than process I, and both produce comparable compacted densities, process I produces a compacted mixture that is more stable than that resulting from process II. This indicates that the most thorough cutback asphalt distribution of the percentages used does not ensure the highest stability in silty and clayey soils. Visual evidence indicates that for sandy soils the moisture content for maximum density and the moisture content for maximum cutback asphalt distribution are coincident.

The photographic study of the effect of moisture content on the distribution of asphalt is not as precise as the quantative moisture property studies, since the photograph showing best distribution of cutback asphalt must be estimated. However, the general range of moisture content in which the best distribution of cutback asphalt occurs is quite obvious.

The findings of this investigation are generally in agreement with other conclusions that the maximum stability of cutback asphalt stabilized soil is reached at some definite degree of cutback asphalt distribution less than an intimate mix[6]. The structure of the soil cutback asphalt system at the point of maximum stability is believed to consist of small irregular soil aggregates within which there is no effective waterproofing or cementing bituminous material. The surface of the soil aggregates is covered with asphalt films that vary in thickness and amount of coverage. Compaction of such a system produces a dense mass of individually waterproofed soil aggregates.

The basic structural system is thought to be established during the process of mixing. The cutback asphalt is first dispersed throughout the soil in small globules as a discontinuous phase, with the soil as a continuous phase. At this point in the mixing process paths through the soil cutback asphalt system may be found which do not pass through any cutback asphalt barriers. Continued mixing causes an inversion of the phases of the cutback asphalt and the soil; the soil tends to become discontinuous, and the cutback asphalt tends to become continuous. The continuity of the cutback asphalt is probably never complete because of the small amount of cutback asphalt that can be used economically.

A phase mixing theory based on the above observations has been proposed[6]. The proposal is in essence that the maximum protection occurs for a soil treated with asphaltic material when the thickest film of asphaltic material which can be closely and permanently held on or absorbed into the surfaces of soil aggregates must contain sufficient absorbed moisture to develop certain degrees of cohesiveness and plasticity.

The present investigation indicates that the spatial geometry of the theory is correct and that moisture must be present to produce cohesiveness and plasticity in the soil aggregates. This investigation also indicates that moisture must be present for the purpose of attaining near maximum density in the individual soil aggregates and as an aid in the distribution of cutback asphalt. Maximum density of the soil aggregates must occur at nearly the same moisture content at which maximum density of the soil cutback asphalt mass occurs since, for the percentages of cutback asphalt used, over-all density is changed very little due to differences in specific gravity. The density of the mass depends mainly on the density of the individual soil aggregates.

Any amount of water greater than that required for maximum densities serves only to aid in obtaining a degree of distribution of cutback asphalt approaching an intimate mix. The excess water must then be evaporated in order to obtain good densification by compaction. Evidently, enough mixing to give high degrees of asphalt distribution results in small soil aggregates in which some of the strength properties are destroyed. The smaller the aggregates the higher the total surface area. Coverage of a high surface area with asphalt results in asphalt films that are too thin for optimum waterproofing and cohesion.

A soil aggregate particle coated with cutback asphalt is penetrated to some depth by the constituents of the bituminous material. The core of such a particle remains in its natural untreated state and retains its inherent strength properties. The soil material of the outer layer of the particle has lost its natural cohesion, and the frictional properties have been reduced due to the waterproofing and lubricating effects of cutback asphalt. A treated particle may be weaker than an untreated particle of equivalent size; however the treated particle will be the most waterproof. The strength data and the photographs indicate that as individual soil aggregate particles grow smaller and smaller the strength of the mass also decreases. This is thought to be due to reduction in size of the natural soil cores with a proportional loss in strength, since the depth of asphalt penetration into a soil aggregate will be the same regardless of the size of the aggregate particles. A very small particle is apt to be thoroughly penetrated by cutback asphalt and will then have only the cohesive strength of the asphalt.

The following tabulation of generalized physical properties and phases of the soil and the asphalt within compacted soil cutback asphalt mixtures have been derived from the data:

SOIL		
Little or no mixing water	Intermediate amounts of mixing water	High amount of mixing water
Large aggregates	Medium aggregates	Small aggregates
Low strength	Maximum strength	Low strength
Low density	Maximum density	Low density
No shrinkage	Little shrinkage	High shrinkage

CUTBACK ASPHALT

Little or no mixing water	Intermediate amounts of mixing water	High amount of mixing water
Globules	Thick films	Thin films
Discontinuous phase	Semi-continuous phase	Continuous phase
Low cohesion	Medium cohesion	High cohesion
Low waterproofing	High waterproofing	Low waterproofing

This tabulation indicates that the optimum properties of a compacted soil-cutback asphalt mixture lie within the intermediate range of mixing moisture contents. The determination of the compromise moisture content (CMC) indicates a mixing water content at which the best combination of properties results. The degree of distribution of cutback asphalt is a function of the amount of mixing water, better distribution being obtained as the amount of water is increased with this type of mixing. The CMC also represents a mixing moisture content at which a compromise degree of asphalt distribution occurs.

Cutback asphalt stabilization of the soil types investigated is best accomplished as a general rule by mixing the moist soil and the asphalt at the water content needed for maximum standard Proctor density of the optimum results, and it is essential to maximum stability that compaction be carried out immediately following mixing.

SUMMARY AND CONCLUSIONS

The effects of water content during mixing and during compaction of soil cutback asphalt mixtures on the physical properties of the compacted product have not been clearly defined in the past. The primary objectives of this investigation have been to study and evaluate these effects.

The following conclusions concerning cutback asphalt soil stabilization are made on the basis of observations and results of the investigation. It is believed that the conclusions should apply in general to all soils of similar textural and mineralogical composition.

1. The degree of cutback asphalt dispersion in a soil mass is a function of the amount of water present during mixing. The resulting mixture varies from poor, when little water is present, to a quasi-homogenous or intimate mix when a high percentage of water is present.
2. Compaction of a soil, cutback asphalt, and water system immediately following mixing produces a more stable product than a procedure in which a drying back period is included between mixing and compaction.
3. An intimate mix does not produce the most desirable stability properties of the compacted mixture.
4. The percentage of mixing water required to produce maximum IBV maximum standard Proctor density, minimum total moisture content after seven days' immersion, and minimum expansion in compacted specimens is different for each property mentioned. However, the range of water content over which these minimum or maximum properties occur is only several percent.
5. A compromise moisture content (CMC) for mixing may be found at which the

variance from the best value of the properties will be a minimum. The CMC is most advantageously determined by the method of first powers.

6. The CMC is very close to the mixing moisture content at which maximum standard Proctor density of the soil, cutback asphalt, and water system occurs. The moisture content corresponding to maximum standard Proctor density of the soil, cutback asphalt, and water mixture provides the most convenient and easily determined moisture control point for cutback asphalt soil stabilization.
7. The value of the CMC or standard Proctor optimum moisture depends on the type of soil, the type and amount of cutback asphalt used.
8. The fluff-point moisture content and the mixing moisture content required to produce an optimum combination of stability properties do not correspond.
9. The best overall stability results for a sandy soil and MC-2 cutback asphalt are obtained when little or no mixing moisture is used; however when treating with MC-4 cutback asphalt the moisture corresponding to the CMC or standard Proctor optimum moisture content should be present during mixing.
10. Quasi-homogeneous soil cutback asphalt systems can be produced with silty and clayey soils if the amount of mixing water used is at least equivalent to the liquid limit of the soil being mixed. Mixing of clayey soil, water, and asphalt systems is nearly impossible within reasonable mechanical limitations when the moisture content lies within the plastic range of the soil-water system.
11. There is an optimum duration of mixing of soil, cutback asphalt, and water systems for each type of mixing equipment.

The foregoing conclusions seem to explain the role of water in cutback asphalt soil stabilization. The investigation should be extended to include the effects of the amount and type of cutback asphalt, emulsions, and wetting agents on the mixing water requirements of all types of soils normally found in the field of soil stabilization. Field trials of cutback asphalt soil stabilization should be conducted to adapt the findings of this investigation to the types of field equipment now in use.

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POLYACIDS AND LIGNIN USED WITH LARGE ORGANIC CATIONS FOR SOIL STABILIZATION

by

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D. T. Davidson, Professor, Civil Engineering

(Highway Research Board Proceedings 37: 517-537. 1958.)

ABSTRACT

The immersed strength and air dry strength of an Iowa silty loam treated with large organic cationic materials can be increased by the addition of various polyacids. This increase is apparently due primarily to an ionic adsorption complex in which the polyacids bond between large organic cations coating the mineral surfaces. The strength of the treated soil can be further increased by the addition of small amounts of ferrous carbonate.

Also investigated were the use of spent sulfite liquor and zein, a protein constituent of corn, with various metal salts and organic cations. Of the chemicals studied, the use of spent sulfite liquor with large organic cations appears most promising on an economic basis.

INTRODUCTION

The superior waterproofing ability of large organic cations in soils has been demonstrated in previous studies at the Iowa Engineering Experiment Station[1, 12, 17]. An investigation of methods of combining this waterproofing ability of large organic cations with the cementing capacity of high polymers is the subject of this paper. The mechanisms of waterproofing and cementing in soils also are presented.

Waterproofing soil with large organic cations

Large organic cations are adsorbed on the negatively charged surfaces of clay minerals, and their hydrocarbon groups impede the movement of water through the soil pores. Due to greater van der Waal's attraction, the larger cations are generally difficult or impossible to replace by smaller organic cations or by inorganic cations[11]. Organic cations are also adsorbed betwen layers of the expandable lattice minerals of the montmorillonite group[16]. They retard changes in the thickness of water films between these layers and thereby reduce swelling and shrinking of the expandable lattice minerals. In general, the larger the organic cation the greater its effectiveness in reducing the water absorbing capacity of the treated soil[15].

The mechanism by which large organic cations influence the bonding of soil particles by water films may be presented in the following manner.

A drop of liquid placed between two closely spaced parallel plates assumes a minimum energy configuration which depends upon the force of gravity acting on the liquid and upon interfacial tensions between the gas, liquid, and solid phases. If the distance between the two plates is small, the gravity term is negligible, and the configuration of the drop may be predicted from interfacial relationships alone.

The range of configurations which the drop may assume under the influence of varying contact angles with the two plates is illustrated by use of a soap film analogy (figure 1.) Two laboratory funnels, their rims coated with a soap solution, were brought into superposition and then separated a short distance. The upper funnel was closed to the atmosphere and a variable level water reservoir connected to the lower funnel provided a means of varying the pressure within the soap film. The law of surface tension governing the film tends to minimize its surface area for any given pressure difference across the surface of the film.

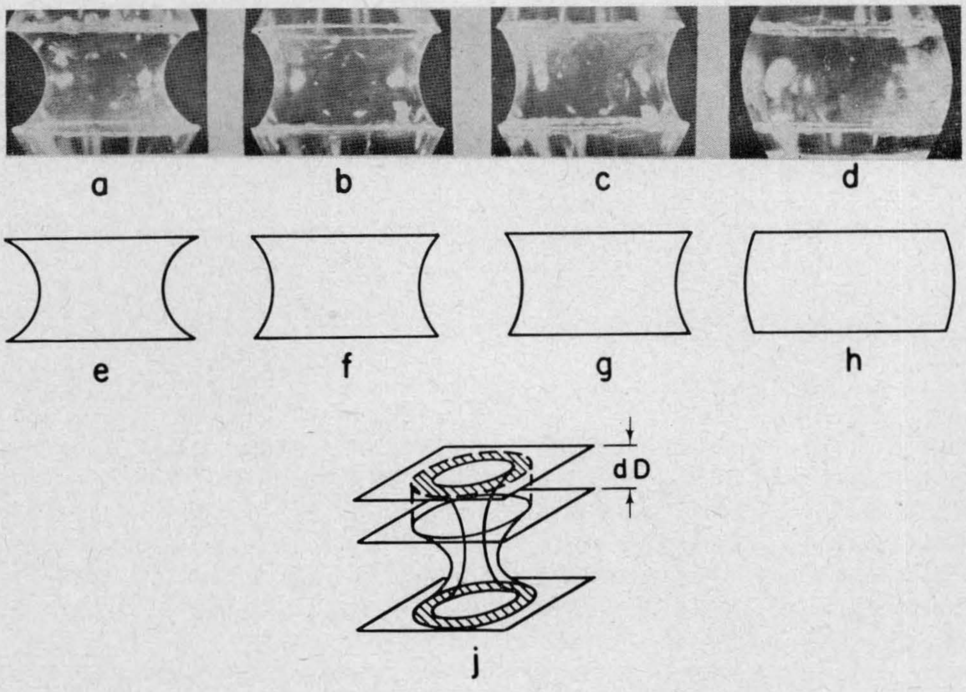


Fig. 1. Configurations assumed by liquid drops between two plates and between two spheres for various contact angles. Photographs *a* to *d* are soap film analogies for corresponding sketches *e* to *h*.

In figure 1a the film has been slightly evacuated. In figure 1b the pressure on both sides of the film is equal, and the surface becomes a catenoid, since the minimal curve of revolution is a catenary. Figures 1c and 1d illustrate successive increases of pressure within the film. Figures 1e through 1h represent liquid drops between two parallel plates having the same configurations as the analoguous soap films pictured above.

In figures 1e through 1h the work required to separate the two plates against forces which are caused by the liquid drop may be expressed by the equation:

$$dW/dD = \gamma_{LA}\,(dS/dD) + (\gamma_{AS} - \gamma_{LS})\, dA/dD + P_G - dP_L/dD)\,(dA/dD) \qquad (1)$$

in which

dW = work;
dD = increase in distance between the two plates;
γ_{LA} = liquid air interfacial tension;
dS = increase in liquid air interfacial area;
γ_{AS} = air solid interfacial tension;
γ_{LS} = liquid solid interfacial tension; and
dA = decrease in the liquid solid interfacial area as represented by the shaded portion of Figure 1j.

The pressure within the liquid differs from that in the gas and the term $(P_G - dP_L/dD)\,(dA/dD)$ accounts for the work done in moving the plates against this pressure difference[9]. The value of $P_G - P_L$ comes from

$$P_G - P_L = \gamma_{LA} \left[\frac{1}{R_1} + \frac{1}{R_2} \right] \qquad (2)$$

in which P_G is the gas pressure, P_L is the pressure within the liquid, and R_1 and R_2 are the radii of curvature of the surface film in its two principal directions, taking concavity toward the gas phase as positive.

Assuming comparable values of dS and dA for each of the conditions represented in figures 1e-1h, a quantitative comparison may now be made of the work required to separate the two plates a given distance in each of these four cases. In figure 1e both of the energy changes due to movement of the triple interface, represented by the last two terms in equation (1), are positive. The term $(\gamma_{AS} - \gamma_{LS})$ is positive because the contact angle is less than 90° and the term $(P_G - dP_L/dD)$ is positive in analogy to the evacuated soap film in figure 1a. The catenoid of figure 1f represents a special case in which $R_1 = -R_2$ and the last term of Eq. 1 drops out. In figure 1g the term $(P_G - dP_L/dD)$ becomes negative and in figure 1h both $(P_G - dP_L/dD)$ and $(\gamma_{AS} - \gamma_{LS})$ are negative. These comparisons yield

$$dW/dD_{1e} > dW/dD_{1f} > dW/dD_{1g} > dW/dD_{1h} \qquad (3)$$

showing that any increase in contact angle results in a decrease in the work required to separate the two plates.

If the two parallel plates are replaced by the curved surfaces represented in figures 1k and 1m, the foregoing expressions will still be qualitatively valid. Because the contact angle between water and most mineral surfaces is very small, figure 1k may represent a water droplet between two idealized mineral particles, and figure 1m may represent a water droplet between two similar particles which have been coated with large organic cations.

To understand the action of large organic cations as soil stabilizing agents, observe that mechanical failure of a soil mass involves shear planes along which particles roll and slide past one another. If the soil is initially in a compacted state, this process requires an increase in the void ratio and a separation of individual particles as the mass becomes dilatent. Figures 1k and 1m and equation (3) show that less work is required to separate the pair of idealized mineral particles coated with large organic cations than to separate the uncoated pair.

Next, the work required to separate a group of eight cubically-packed spherical mineral particles under different moisture conditions may be considered. In figure 2a no moisture is present, hence no bonding. In figure 2b only small annular rings of water are present around the points of contact of the mineral particles. The total liquid air interfacial area is very small, and all water molecules are in close proximity to the two mineral surfaces. Under these conditions, bonding by oriented water dipoles between the charged mineral particles may be large compared with the bond energy due to surface phenomena.

As more water is added (figure 2c) the liquid-air interfacial area is increased and the change in this area, dS, accompanying a given separation dD between the particles also increases. Thus, the water bond energy in this range of moisture content is increased by the addition of water. As more water is added, however, the interior void between the eight spheres may become filled (figure 2d). A comparison of figures 2e and 2f, which represent top views of figures 2c and 2d, respectively, illustrates the decrease in total peripheral length of water film (dotted lines) connecting the two planes of four spheres due to filling the interior void with water. The ratio dS/dD is therefore lower for figure 24 than for figure 2c, and the water bond energy has been reduced. Figure 2g represents total immersion of the eight spheres in water. There are no liquid air interfaces, and any water bonding must be due entirely to oriented water dipoles in close proximity to any two charged mineral surfaces.

Figure 2h illustrates the state of water bonding when random areas of the eight mineral spheres are coated with large organic cations. It becomes apparent that the maximum bond energy represented by figure 2c can never be realized when parts of the mineral surfaces are coated with large organic cations because the water-organic cation interfaces represent areas for which reduced energy is required to separate the particles. However, the large organic cations may prevent a transformation to the condition of figure 2d by inhibiting the entrance of additional moisture into the central void.

These interpretations appear to be substantiated by the results of strength tests performed after air drying and after immersion of soils stabilized with large organic cations. Air dry strengths are decreased by the addition of large organic cations, but immersed strengths are greatly increased. At higher percentages of treatment, however, the immersed strengths also decrease (figure 3)[17]. These results indicate that there is a percentage of treatment above which the beneficial effect of restricting the entrance of additional water during immersion

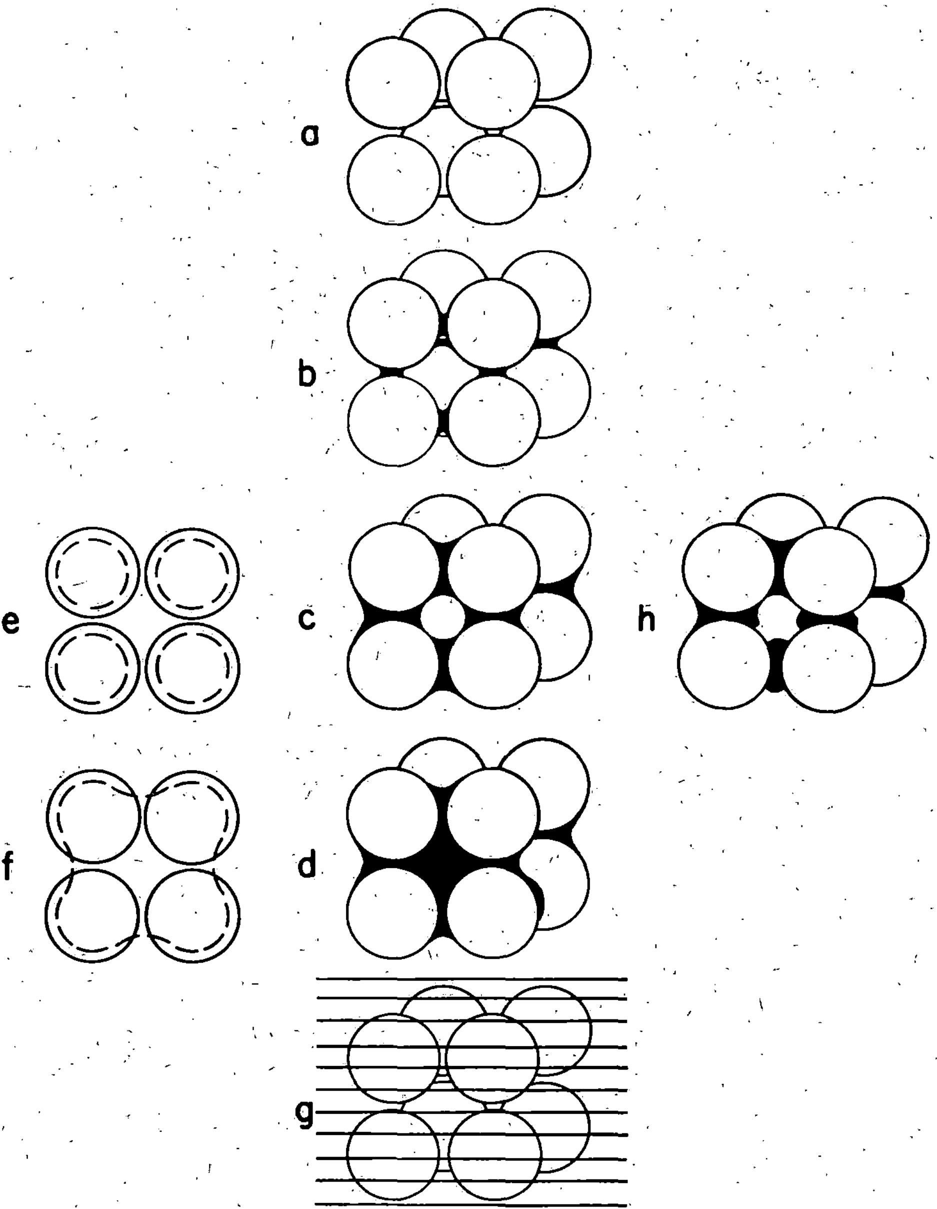


Fig. 2. Effects of moisture content and of partial coating with a surface active agent on the bonding of eight cubically packed spherical particles by water.

of the soil is exceeded by the detrimental effect of reduced bond energy resulting from the increase in water organic interfaces.

This presence of an optimum quantity of large organic cations also attests to the relatively high bond energy of water films compared with that of any bonding action which can be attributed to van der Waal's attraction between large organic cations near the points of contact of the mineral particles.

In addition to coating the exterior surfaces of mineral particles and restricting moisture movements through the soil pores, large organic cations are absorbed between layers of the expendable montmorillonite minerals. Their stabilizing action here depends upon a somewhat different principle. By minimizing changes in the thickness of water films between these layers they reduce fractures caused by differential swelling and shrinking throughout the soil mass.

CEMENTING SOIL PARTICLES WITH HIGH POLYMERS

High polymers, unlike large organic cations, increase the air dry strength of soils[27]. Bond action apparently depends upon both air water interfaces and the cementing action of the polymer.

Various authors have listed the characteristics which they believe to be important for high polymers used as cementing agents[10, 23]. It is generally agreed that the most essential characteristics are that the polymer:

1. Be water soluble or water dispersible (either in monomeric or polymeric form) when being added to the soil and during the period of mixing and compaction.
2. Be water-insoluble after the stabilization reaction is completed.
3. Bond in some manner directly between mineral particles rather than functioning as if the mineral were an inert filler.
4. Be resistant to biochemical decomposition.
5. Be cheap and/or be capable of being used in small enough quantities to make it economically feasible for large scale use.

In recent years a fairly rigorous theoretical analysis has been made of systems in which the elastic properties of high polymers are improved by the inclusion of small amounts (usually below 25 percent) of mineral fillers[7, 29, 31, 32]. Mathe-

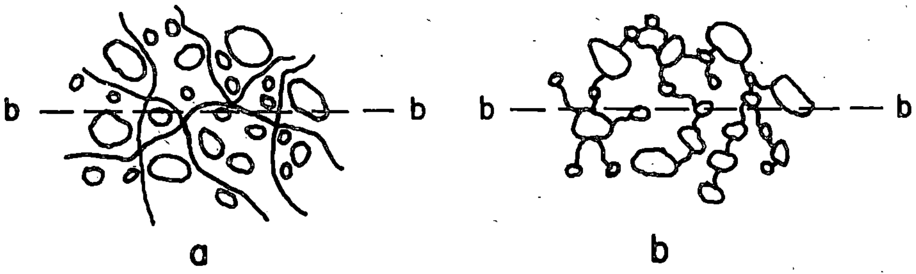


Fig. 3. Comparison of the effectiveness of a non-bonded soil polymer system (a) with a bonded soil polymer system (b) in resisting shear across the surface of b-b.

matical expressions to characterize these systems have been developed from the classical derivation of Einstein[2, 3] and a subsequent modification[8] which are based on the energy required for the displacement of a fluid around rigid disperse particles.

Apparently no similar analysis has been made of systems in which the mineral phase predominates; that is, where there are intergranular contacts and where the voids are not completely filled with polymer. This is the condition in soils stabilized with polymers. Where the mineral phase predominates, an analogous solution might be obtained by expressing the shear behavior of the rigid particles as a function of alterations due to inclusion of the polymer, rather than characterizing the fluid phase in terms of perturbations due to the inclusion of rigid particles.

The resistance to shear of a granular material may be expressed by

$$S = N \tan \theta \tag{4}$$

where S is the shear strength, N is the intergranular pressure normal to the shear plane, and θ is the angle of internal friction of the granular material. If there are interparticle forces operating independently of N, equation (4) becomes

$$S = C + N \tan \theta \tag{5}$$

the Coulomb equation, in which C is cohesion. Although the physical significance of cohesion is quite complex, a portion of this term can be attributed to the resistance to dilation during shear which is offered by the large air water interfacial areas in fine grain soils. This mechanism was discussed in the previous section.

An organic polymer in soil may decrease the total air water interfacial area, and thereby decrease that portion of cohesion attributed to water bonding. On the other hand, the polymer contributes cementing action of its own which is apparently a function of the density of polymer chains crossing the shear plane, their orientation, Young's modulus of the chains in tension, and the lengths of chains between points on each side of the shear plane which are relatively fixed, such as between branch points in a polymer network.

Methods of employing a given amount of polymer in the soil to achieve maximum shear strength may be visualized in various ways. Two theoretical advantages accrue from having the polymer chains connect directly between soil particles (figure 3b) instead of passing around the particles (figure 3a). In figure 3b the soil particles themselves constitute portions of the polymer network. According to this scheme, a polymer network may be visualized in which the branch points have been magnified many times and replaced by soil particles. The smaller the void ratio of the soil, the greater will be the effective portion of soil particles in the polymer network. Hence, a greater number of chains (composite chains comprised of both polymer and soil particles) are made to cross a unit area on any shear plane with a given amount of polymer.

A second theoretical advantage of polymer bonding directly to neighboring soil particles is the effect of such a system in decreasing the average length of polymer chains between fix points. Two polymer chains crossing the shear plane b-b at an angle ϕ have different lengths between fix points on opposite sides of the shear plane (figure 4). For a given shear displacement S, d'/d is greater than D'/D. If both chains have the same Young's modulus, the shorter chain will therefore offer the greater resistance to shear.

The realization of both of these advantages depends upon the formation of bonds between the soil particles and polymer which are at least as strong as those within the polymer. Bonds between soil particles and polymer might be van der Waal's, ionic, or covalent in nature. Interesting examples of ionic and covalent bonding between polymer and dispersed mineral particles are found in the field of rubber technology. When highly positive fillers are milled into rubber, which is itself very negative, the strong electrostatic bonds formed give rise to additional increases in modulus of elasticity and tensile strength[28]. By this method, the tensile strength of pure gum GR-S stocks was increased more than five-fold. When rubber containing carbon black is vulcanized using sulfur and accelerators extensive chemical bonding of polymer to the mineral surfaces occurs[31]. The bonds so formed constitute additional points of constraint and increase the modulus of elasticity beyond that of a system having no bonding between polymer network and mineral particles.

Another possibility may also be observed. If an initial tensile stress can be induced in the polymer, the initial shear displacement will require greater external force and the system will assume a character analogous, on an infinitesimal scale, to that of prestressed reinforced concrete.

In summary, the theoretically ideal conditions for maximum utilization of a polymer in soil appear to be direct bonding between neighboring soil particles, and pretensioning of polymer chains.

Methods of attaining these two conditions are being studied and will be described in the experimental section. General mathematical expressions for the foregoing relationships are outlined in the following.

Assume that each of three soil samples (row 1, figure 5) is subjected to a shear displacement dD. Since shear failure in granular materials takes place within a zone instead of on a unique plane, the shear planes indicated in the samples may be considered as planes within a shear zone. Assume that sample 1a is stabilized with a polymer having an initial average distance L between fix

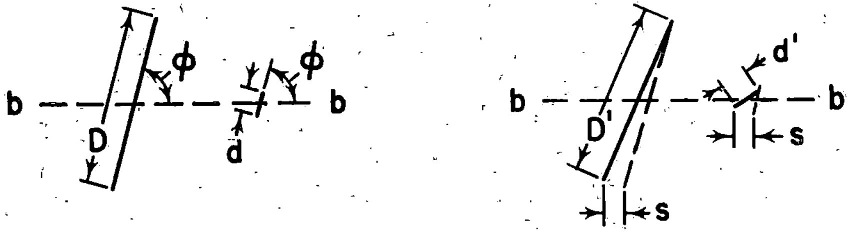
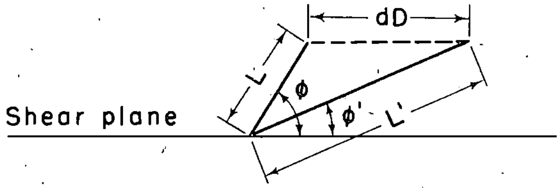


Fig. 4. Resistance offered by a single polymer chain to shear across the surface b-b as a function of length of the polymer chain between fix points.

points, which may be either branch points in a polymer network or bonds connecting the polymer to soil particles. Sample 1b is identical to 1a except that the initial average distance between fix points is less than *L*. Sample 1c will be identical to 1b except that an initial tension is placed in the polymer chains prior to subjecting the sample to the shear displacement *dD*. A random initial orientation of polymer segments in each of the three samples is assumed.

In row 2, figure 5, each polymer segment crossing the shear planes in the three samples has been projected into the plane of the paper and placed on the



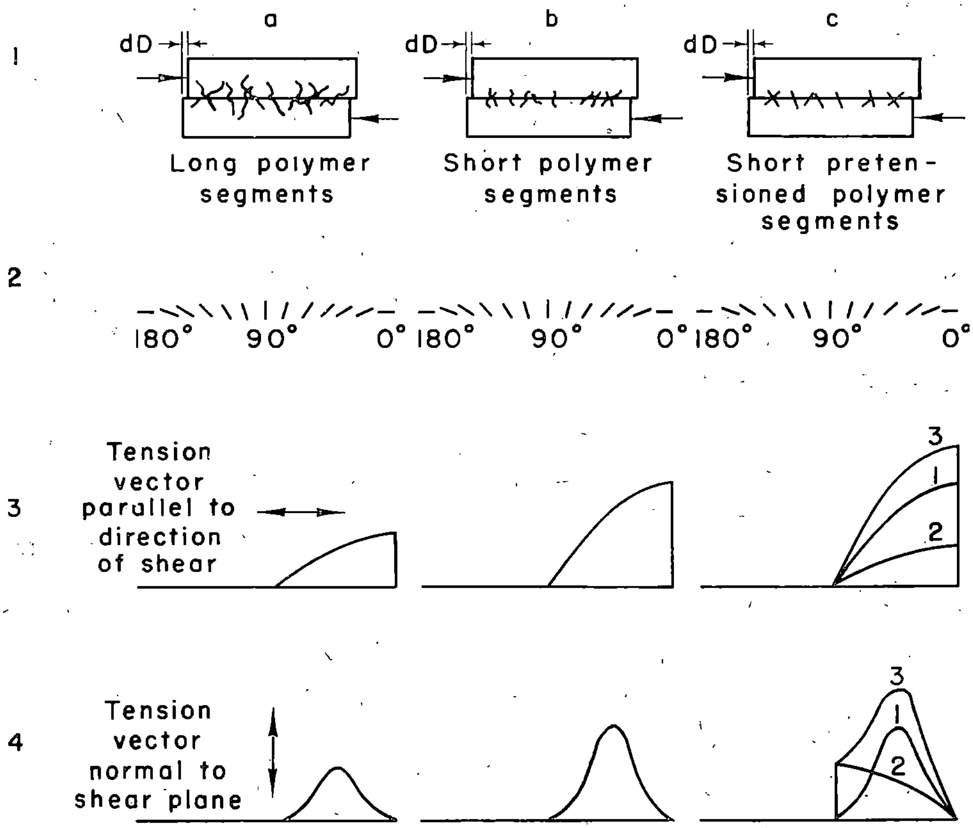


Fig. 5. Tension vectors of randomly oriented polymer segments crossing a shear plane as functions of segment length between fix points and pretensioning.

abscissa scale according to the angle which the projected segment makes with the shear plane. When the samples are subjected to the shear displacement *dD*, those segments lying between 90° and 180° (row 2) will not be lengthened and therefore will undergo no tensile stress. The tensile stress developed in segments lying between 0° and 90° can be expressed by

$$S' = \frac{L'-L}{L} Y \tag{6}$$

where S' is the tensile stress per polymer segment, L and L' are the initial and final lengths of the segment between fix points on opposite sides of the shear plane, and Y is the Young's modulus of the segment in tension[4], Ch. XI.

In row 3 the tension vectors of the polymer segments parallel to the direction of shear are shown as a function of ϕ, the angle between the projected segment and the shear plane. These curves are obtained from

$$[3] = S' \cos \phi' = \left[\frac{L'-L}{L} Y \right] \cos \phi' \tag{7a}$$

where [3] designates the tension vector parallel to the shear plane and ϕ' is the adjusted angle ϕ after the sample has been subjected to shear strain. From the sketch at the top of figure 5, and by the law of sines,

$$L' = \frac{L \sin (180-\phi)}{\sin \phi'} \tag{8a}$$

$$\text{sine } \phi' = \frac{L \tan \phi}{dD+L \cot \phi} \tag{8b}$$

$$L' = \frac{L \sin (180-\phi)}{\dfrac{L \tan \phi}{dD+L \cot \phi}} = \cos \phi \, (dD+L \cot \phi) \tag{8c}$$

$$\cos \phi' = \sqrt{1-\sin^2 \phi'} = \sqrt{1-\left[\frac{L \tan \phi}{dD+L \cot \phi} \right]^2} \tag{8d}$$

Introducing these values into equation 7 gives

$$[3] = Y \left[\frac{\cos \phi \, (dD+L \cot \phi) - L}{L} \right] \sqrt{1-\left[\frac{L \tan \phi}{dD+L \cot \phi} \right]^2} \tag{7b}$$

As equation 7*b* indicates, the ordinate values in graph 3b (figure 5) are greater than those in 3a due to the shorter polymer segment length in sample b.

Curve 2 in graph 3c represents the stress parallel to the direction of shear due to pretensioning the polymer segments, expressed by

$$[3c2] = S \cos \phi \tag{9}$$

where S is the pretension stress per polymer segment. Curve 3 in graph 3c represents the total tension parallel to the direction of shear due to pretensioning plus shear displacement, or the sum of curves 1 and 2.

Row 4 represents the tension vectors in the polymer segments normal to the shear plane, expressed by

$$[4] = S' \sin \phi' = Y \left[\frac{\cos \phi \, (dD+L \cot \phi) - L}{L} \right] \left[\frac{L \tan \phi}{dD+L \cot \phi} \right] \quad (10)$$

The contribution of the prestress tension in this case, represented by curve 2 in graph 4c, is

$$[4c2] = S \sin \phi \quad (11)$$

To find the components of total tension normal and parallel to the direction of shear the curves in rows 3 and 4, respectively, may be integrated between the limits of 0° and 90°. Analogous to the basic Coulomb equation, the following is obtained:

$$S = C - c + N \tan \theta + \tan \theta \int_{0}^{90^\circ} [4] + \int_{0}^{90^\circ} [3] \quad (12)$$

where S is the applied external shear stress, c is the reduction in water-air-interfacial bond energy due to the presence of the polymer, and the other quantities are as designated previously. Maximum shear strength is developed at the strain at which a combination of the five terms in equation (12) obtains a maximum.

SOIL STABILIZATION WITH LARGE ORGANIC CATIONS AND POLYACIDS

The stabilization method investigated in this part involves the use of large organic cations together with polymeric acids in the following manner:

1. Negatively charged clay mineral surfaces are partially coated with the large organic cations from an aqueous suspension.
2. Polyacrylic acid, ionized with potassium hydroxide, is added to the soil-organic cation system. The ionized polyacrylic acid expands from a randomly kinked configuration to an elongated configuration due to electrostatic repulsions between neighboring ionized acid groups. In addition, electrostatic attraction between the ionized acid groups of the polymer chains and the organic cations coating the mineral surfaces apparently causes orientation of the polymer chains between the organic cations and enables ionic bonding to them.
3. Addition of ferrous carbonate to the foregoing system increases the strength of the treated soil. Ferrous ions are known to cause polyacid chains to contract and become hydrophobic due to chelation with the carboxyl groups of the polyacid. The fact that the ferrous carbonate also produces a strength increase when the polyacid is omitted, however, may point to the precipitation of a hydrated iron gel which becomes a cementing agent upon dehydration.

The experimental work deals primarily with the dilation and contraction of polymeric electrolytes and with the formation of metal chelates.

Dilation and Contraction of Polymeric Electrolytes

Polymeric electrolytes, commonly called polyelectrolytes, are a class of high polymer molecules having ionizable groups as part of their repeating unit. Electrochemically, the polyelectrolytes include polyacids, polybases, and polyampholytes. The polyampholytes contain both acidic groups and basic groups.

The mechanism of swelling of ionic polymers may be explained on the basis of osmotic pressure[4, 13, 18, 19, 20, 22]. When a polyelectrolyte is ionized, as for example when polyacrylic acid in dilute aqueous solution is neutralized with sodium hydroxide (figure 6), the concentration of the mobile Na ions will always be greater in the gel than outside because of the attracting power of the fixed negatively charged carboxyl groups. Consequently, the osmotic pressure of the solution inside will exceed that of the external solution and the expansive force may be equated to these differences in osmotic pressures of the two solutions.

Transferring polyelectrolyte fibers from one solution to another of higher chemical potential required a larger force to maintain the length of the fibers constant[19]. Thus, when polymethacrylic acid fibers held at a constant length were transferred from a solution of sodium hydroxide to one of barium hydroxide, tensile stresses were induced in the fibers. Exploiting this relationship to provide the pretension stress in equations (9), (11), and (12) is one of the experimental objectives of this study.

Chelation of Polyacids

The ionic character of polyacids permits the manipulation of dilation and contraction; it is also responsible for an undesirable feature, water affinity. An ideal solution to this problem would be to find a way to bond the polymer to adjacent mineral particles, and then alter it in a way to accomplish both tensioning and waterproofing of the polymer chains. Fortunately the tensioning and waterproofing appear possible by the reaction between polyacids and transition metals such as iron, copper, zinc and nickel. These metals react to produce

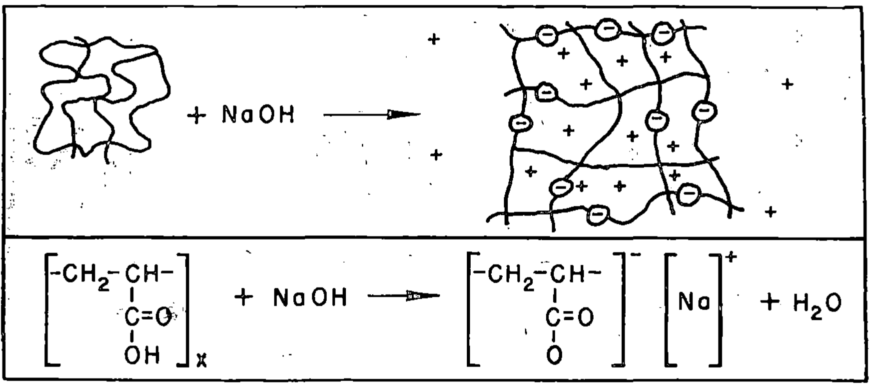


Fig. 6. Neutralization and consequent dilation of a polyacrylic acid gel in dilute aqueous solution with sodium hydroxide.

essentially covalent bonds between neighboring ionized acid groups. The reaction is called chelation (figure 7).

EXPERIMENTAL PROCEDURE AND RESULTS

The objectives of the experimental work were to evaluate the use of polyacids with large organic cations for soil stabilization and to study the possibility of chelating the polyacids at a reaction rate low enough to permit ionic bonding of the polyacids to the large organic cations coating the mineral surfaces before final waterproofing and tensioning of the polyacid chains. The effects of the following variables upon the immersed strength of a silty loam C-horizon loess were studied:

1. Type and amount of polyacid.
2. Type and amount of metal salt for chelation of the polyacid.
3. Type and amount of large organic cation.
4. Order of mixing the various additives.
5. pH adjustments in both acid and alkaline ranges.

Evaluation of Various Polyacids Used with Arquad 2HT

For the first phase of the work a single large organic cationic material, Arquad 2HT, was used. This quaternary ammonium chloride was chosen on the basis of previous tests indicating its ability to restrict moisture movements in the soil (3). The properties of the loess, of Arquad 2HT, and of nine polyacids and polyacid salts used as additives, are tabulated in the Appendix.

Soil specimens were prepared and tested by the following procedure:

1. Add Arquad 2HT in aqueous suspension to 700 g of the soil and mix in a Hobart model C-100 mixer.

2. Add the desired polyacid in aqueous solution or aqueous emulsion to the soil

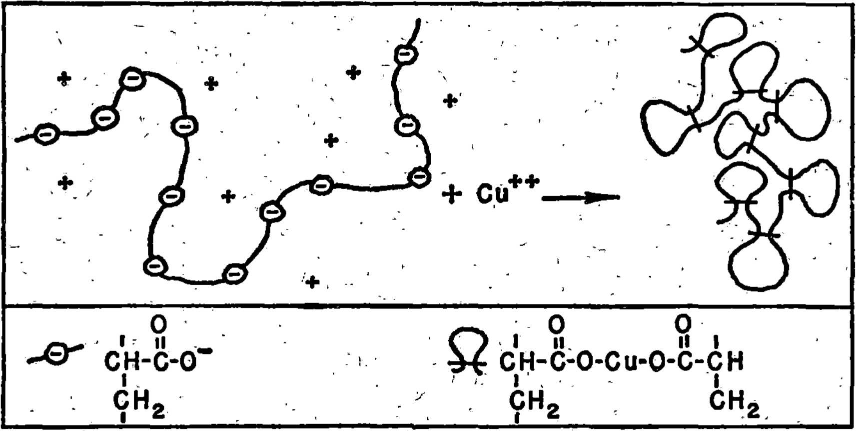


Fig. 7. Contraction and waterproofing of a polyacid chain by chelation with a transition metal.

and continue mixing; the total water added in steps 1 and 2 being enough to bring the soil to optimum moisture content for standard Proctor density.

3. Mold the soil in four 2 in. diameter by 2 in. high specimens compacted to near standard Proctor density.

4. Air cure the specimens for seven days and test two of the specimens in unconfined compression.

5. Immerse the remaining two specimens in water for 24 hr, then test them in unconfined compression.

Figure 8 shows the compressive strength of the silty loam as a function of Arquad 2HT as the only additive. Arquad 2HT hydroxide, represented by the solid line (figure 8), was prepared by mixing equivalent amounts of potassium hydroxide and the quaternary ammonium chloride in isopropanol and filtering off the precipitated potassium chloride. The percentages of treatment indicated (figure 8) and subsequent graphs are based on the solid weights of chemicals added in solution and on air dry weight of the soil.

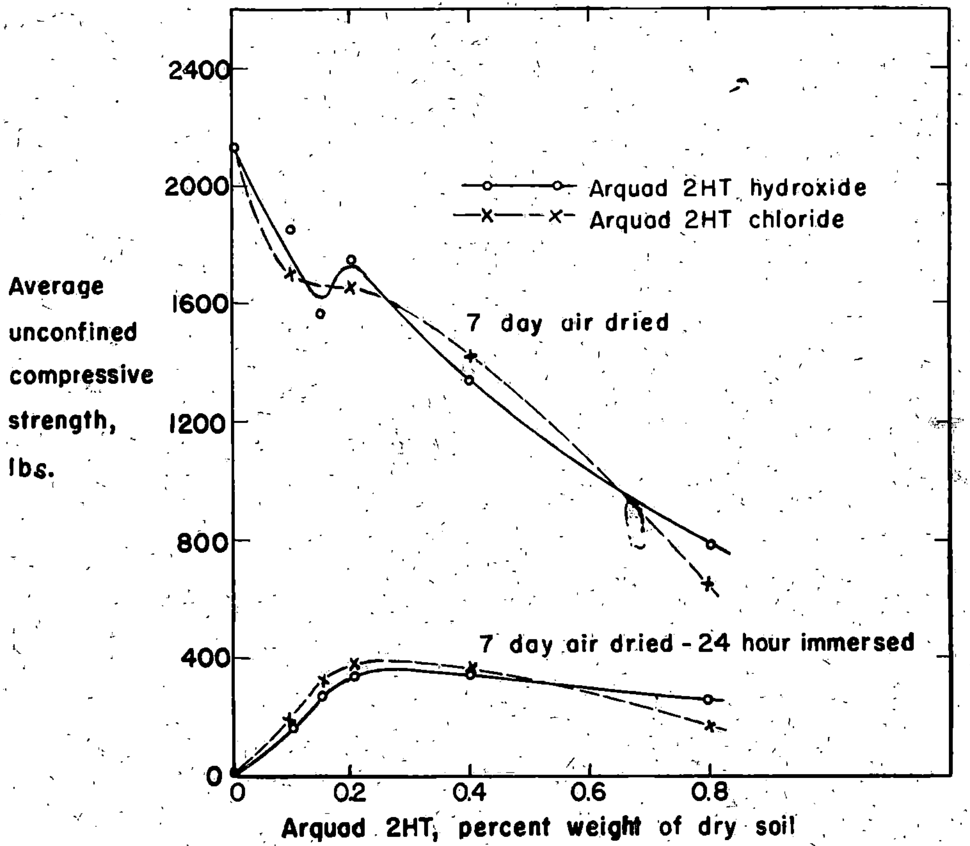


Fig. 8. Effect of amount of Arquad 2HT on unconfined compressive strength of silty loam. Test specimens were 2 in. in diameter and 2 in. high.

In contrast to the Arquad 2HT treated soil, specimens treated with 0.6 percent of the various polyacids and polyacid salts all slaked in water. The air dry strengths of most of these specimens were about 1½ times the air dry strength of the untreated soil.

When Arquad 2HT chloride was mixed in dilute aqueous solution with the various polyacids, disperse floccules were formed. When Arquad 2HT hydroxide was mixed with the polyacids the floccules formed were much denser and precipitated more rapidly than those formed with Arquad 2HT chloride, showing the added effect of ionization of the polyacid by hydroxyl ions in bringing the polyacid and organic cations together. Van der Waal's attraction between the polyacid and the long-chain cations is apparently responsible for the stability of the floccules in each case. These results are in substantial agreement with the behavior of similar systems[14, 21, 23].

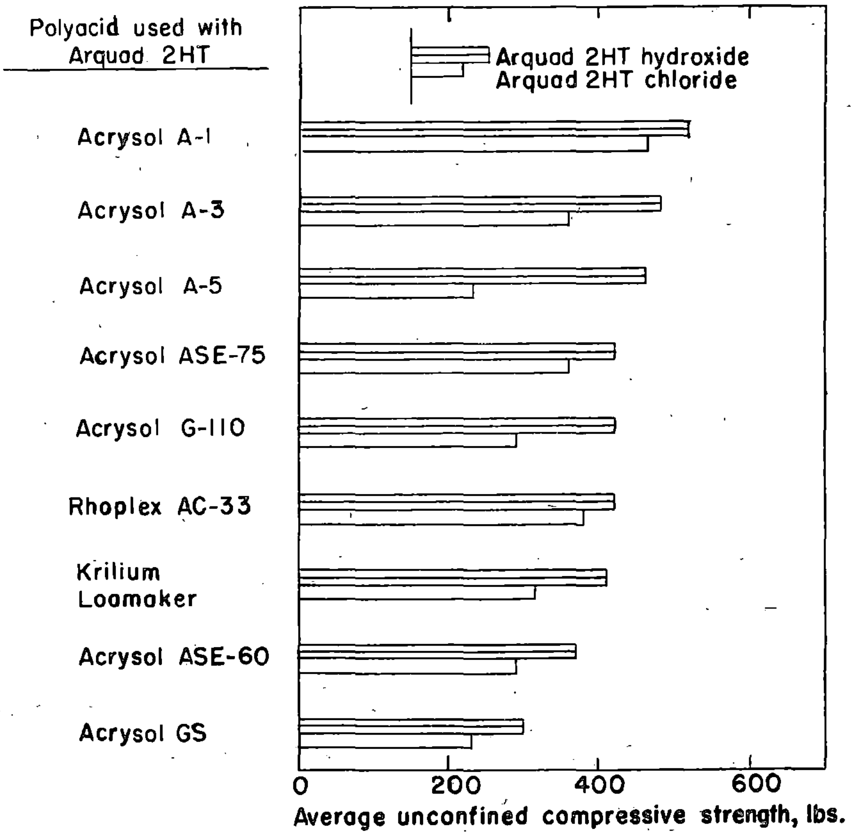


Fig. 9. Unconfined compressive strengths of the silty loam treated with 0.6 percent of various polyacids and polyacid salts and 0.2 percent of either Arquad 2HT hydroxide or Arquad 2HT chloride. Strengths of 2 in. diameter by 2 in. high specimens measured after 7 day air drying plus 24 hr. immersion.

The compressive strengths of the silty loam treated with 0.2 percent Arquad 2HT plus 0.6 percent of the various polyacids and polyacid salts are shown in figure 9. All strengths represented and the following graphs are for immersed samples. The three polyacids giving best results, Acrysols A-1, A-3, and A-5, are members of a homologous series of polyacrylic acids.

The Arquad 2HT hydroxide was found to produce greater strength with each of the polyacids than did Arquad 2HT chloride (figure 9). In agreement with the results of the flocculation studies in aqueous solution, the hydroxyl ions apparently ionize the polyacid groups and thereby increase ionic bonding between the polyacid and organic cations in the soil.

To test the theory that the strength of the stabilized soil is a function of the number of cation, polyacid, and cation bonds formed between neighboring mineral particles, compressive strengths were measured for wide ranges of both Arquad 2HT hydroxide content and Acrysol A-1 content (figure 10). It is inter-

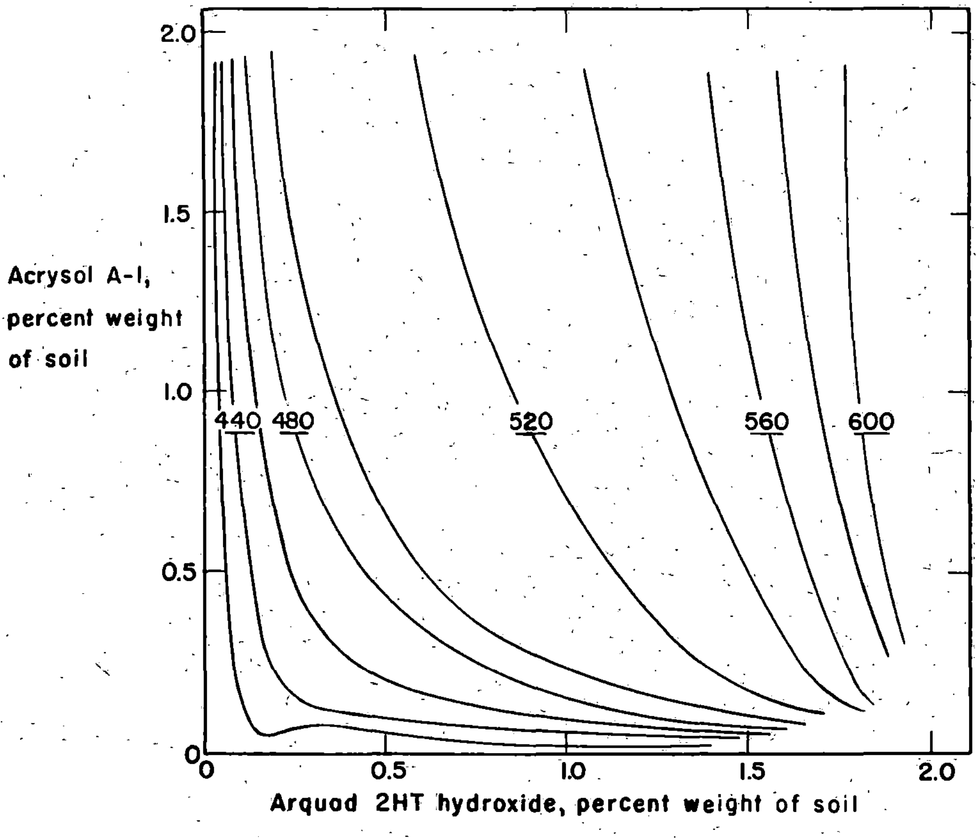


Fig. 10. Contours showing relationship of unconfined compressive strength of the soil to Arquad 2HT hydroxide and Acrysol A-1 contents. Contours indicate 20 lb increments of strength for 2 in. high by 2 in. diameter soaked specimens.

esting to compare the curves for immersed strength (figure 8) with the strength contour curves (figure 10). When Arquad 2HT is used alone (figure 8) an optimum amount of Arquad is reached for maximum immersed strength; when Arquad 2HT is used with polyacrylic acid (figure 10) an increase in Arquad 2HT content at any point on the graph yields an increase in immersed strength. Apparently when Arquad 2HT and polyacrylic acid are used together, the increase in strength contributed by cation, polyacid, and cation bonds, as more Arquad 2HT is added, outweighs the decrease in bonding by moisture films. The strength contours over most of the area (figure 10) are roughly parallel to the Acrysol A-1 axis. Apparently the concentration of organic cations is a much more critical factor in establishing cation, polyacid, and cation bonds throughout the range of additives investigated than is the concentration of polyacrylic acid.

Chelation Studies

Having obtained a sketchy understanding of the behavior of large organic cations and polyacids in the soil the next step was to study the effect of chelation on the contraction and waterproofing of polyacid molecules. Because Acrysol A-1 gave the highest strengths, this polyacid was chosen for chelation studies.

First, the degree of expansion of Acrysol A-1 molecules as a function of neutralization with sodium hydroxide, in accordance with the principle outlined under "Dilation and Contraction of Polymeric Electrolytes," was determined by viscosity measurements and use of

$$a^3 = \frac{[\eta]}{[\eta]_0} \qquad (13)$$

where a^3 is the volumetric expansion factor of the polymer molecules, $[\eta]$ is the intrinsic viscosity of the polymer in the presence of sodium hydroxide or other reagent causing a dimensional change, and $[\eta]_0$ is the intrinsic viscosity of the unperturbed polymer[5]. Viscosities were measured with an Ostwald viscometer at 30°C (flow time of water=2 min. 56 sec).

To determine which inorganic cations produce greatest contractions of the ionized polymer, and hence greatest tensile stress in the polymer chains after bonding to organic cations in the soil, viscosity measurements were made of neutralized Acrysol A-1 in the presence of various salts (figure 11). The fact that ferric chloride, added even in very small amounts, precipitates Acrysol A-1 at the concentration used is strong evidence for formation of a covalent chelate. The only ionic groups in Acrysol A-1, the $-COO^-$ groups, have apparently been rendered inactive by covalent bonding with iron, causing water insolubility.

Because metal chelates are formed by the displacement of acidic protons of the chelating agent by metal ions, the addition of a metal salt to the polyacid causes a drop in pH. The greater the tendency for the metal to combine with the polyacid, the greater the drop in pH. This constitutes a simple method of testing for chelation and it can be used to determine the tendency of different metals to combine with the polyacid.

The results of pH measurements obtained by titrating Acrysol A-1 with these same salts (figure 12) are in close agreement with the results of the viscosity measurements (figure 11). It is obvious that the ferric chelate is very strong, but the tendency for the alkaline earth metals (magnesium, calcium, and barium) to form chelates is quite weak.

Ferrous and ferric salts in the low solubility range were chosen for use with Acrysol A-1 in preparing test specimens of the soil. It was believed that slightly soluble salts would allow time for mixing the chemicals, for compacting the specimens, and for bonding between polyacid and organic cations to occur before a sufficient number of metal ions could react with the remaining acid groups to render the polymer chains insoluble.

Table I lists several slightly soluble ferrous and ferric salts in order of their solubilities.

Comparison (table I and figure 13) shows that the rates at which the various

TABLE I

SOLUBILITIES OF SLIGHTLY SOLUBLE FERROUS AND FERRIC SALTS

Salt	Water Solubility*	Temp. (°C)
FeS	0.00061	18
$Fe_2(SO_4)_3.XH_2O$	—	—
$FeCO_3$	0.0065	20
$FeSO_4(NH_4)_2SO_4.6H_2O$	18	0
$FeSO_4.7H_2O$	32.8	0

* Parts per 100 parts of water by weight.

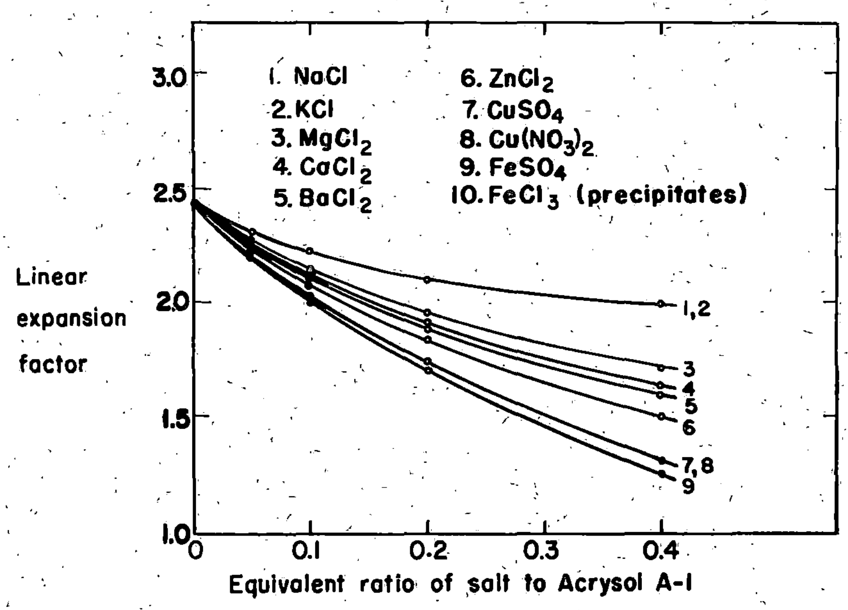


Fig. 11. Linear expansion factor of Acrysol A-1 in 0.5 percent aqueous solution 80 percent neutralized with sodium hydroxide in the presence of various salts.

salts react with polyacrylic acid to liberate hydrogen ions is in the order of their solubilities. Ferrous sulfide, being very slightly soluble, causes no detectable pH drop in the 6-hr period (curves 2, figure 13). Ferrous carbonate produces a very gradual pH drop (curves 4) and the more soluble ferrous sulphate produces a rapid drop with early leveling off in pH (curves 6).

The purpose of plotting the data of figure 13 was to determine what solubility range of iron salts would be appropriate for allowing a mixing and compacting period of approximately 30 min. and still react with Acrysol A-1 within a few hours after compaction (before loss of moisture from the soil due to air drying). Of the salts shown in figure 13, ferrous ammonium sulfate and ferrous carbonate appear optimum in this respect. The remaining three salts either react too quickly or show very little reaction at the end of 6 hr. It was recognized that the many variables in soil environment may considerably alter this time scale, causing the chelation reactions to occur either more rapidly or more slowly than shown.

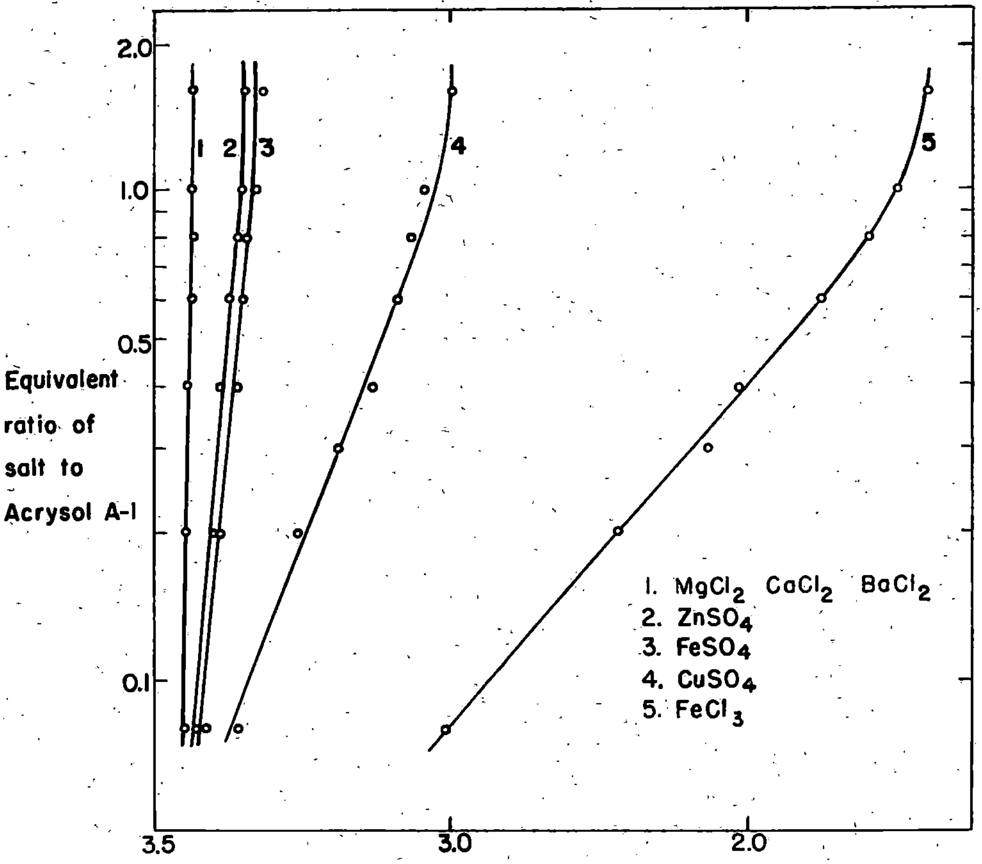


Fig. 12. pH titration curves for 0.0116 N Acrysol A-1 solution with various salts.

The immersed strengths of the silty loam treated with Arquad 2HT, Acrysol A-1, and various concentrations of the five ferrous and ferric salts, were then determined as a function of pH adjustments with hydrochloric acid and potassium hydroxide. The order of adding the chemicals to the soil was:

1. Ferrous or ferric salt in powder form.
2. Arquad 2HT hydroxide in aqueous suspension.

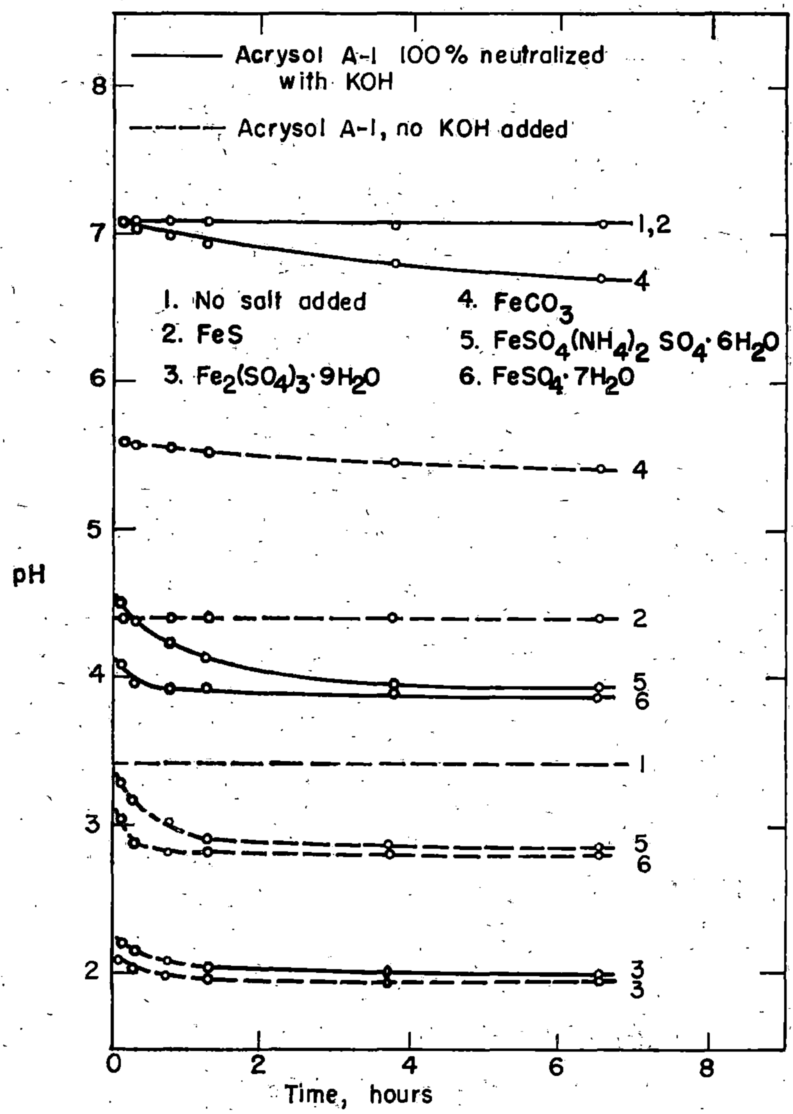


Fig. 13. pH time plots for 0.0116 N aqueous solutions of Acrysol A-1 in the presence of slightly soluble ferrous and ferric salts added in excess of their solubility limits.

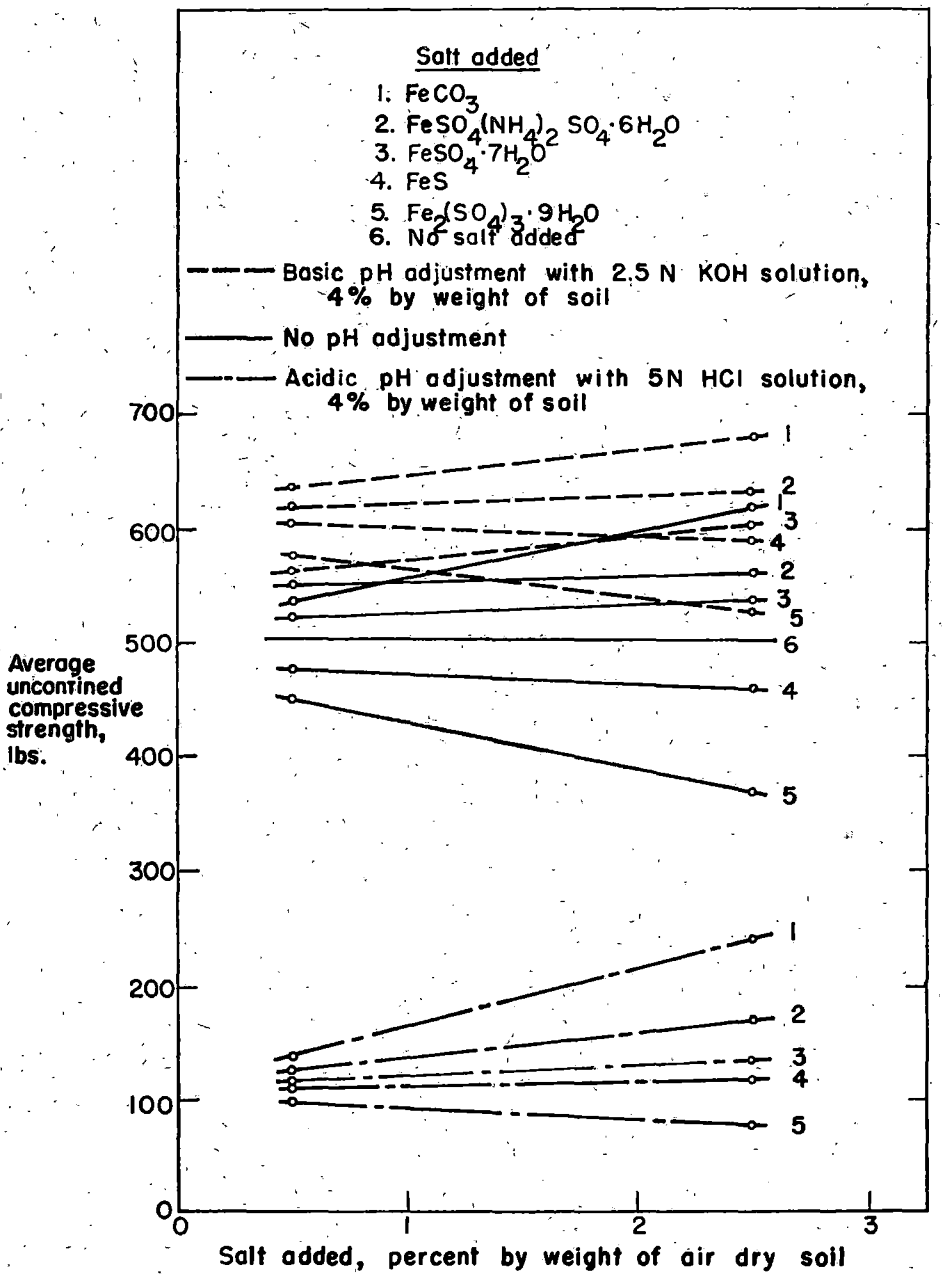


Fig. 14. Unconfined compressive strength of the silty loam treated with 0.2 percent Arquad 2HT hydroxide, 0.6 percent Acrysol A-1 and slowly soluble ferrous and ferric salts. Strengths of 2 in. high by 2 in. diameter specimens measured after 7 day air curing and 24 hr immersion in water.

3. Acrysol A-1 in aqueous solution with hydrochloric acid or potassium hydroxide.

In figure 14 each plotted point represents the average of two specimens molded from two separate mixes, or a total of four specimens. The several variables are plotted on a single graph to facilitate the observation of certain trends. It is seen that ferrous carbonate and ferrous ammonium sulfate do give slightly higher strengths than the other salts, as predicted from the pH time curves in figure 13.

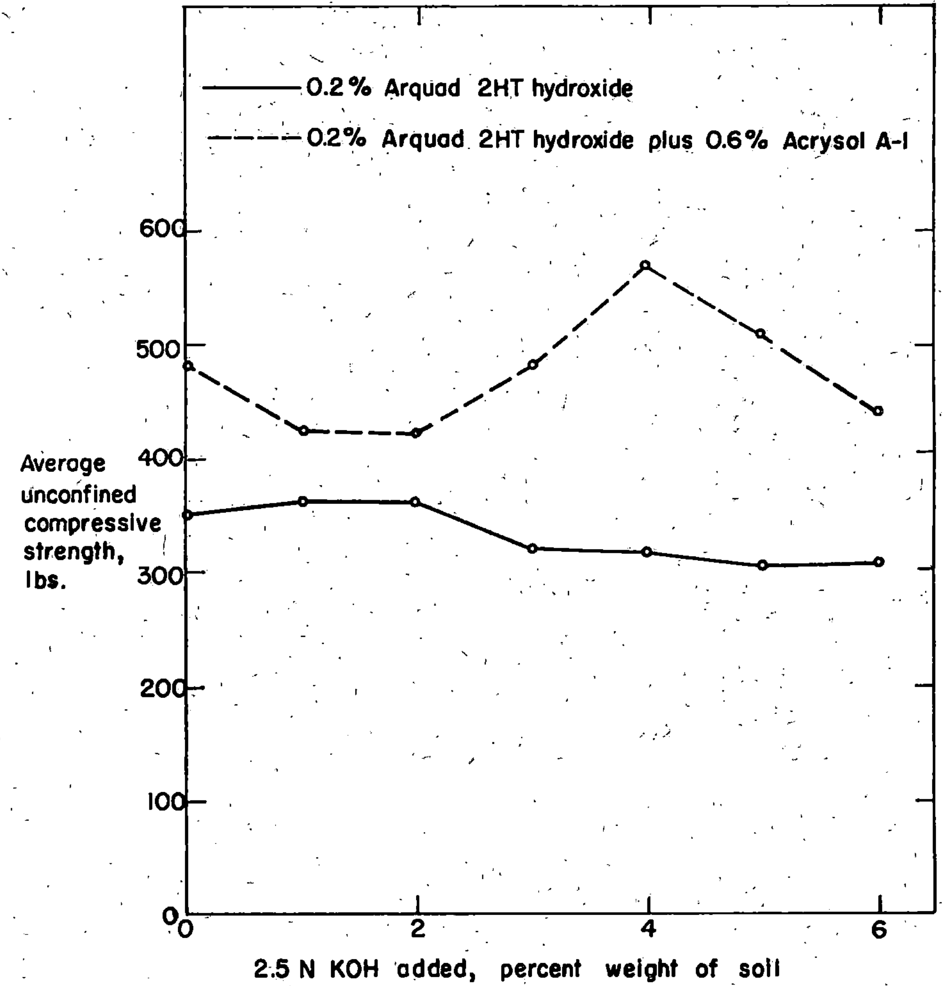


Fig. 15. Unconfined compressive strength of the silty loam treated with 0.2 percent Arquad 2HT hydroxide alone and 0.2 percent Arquad 2HT hydroxide plus 0.6 percent Acrysol A-1 as a function of basic pH adjustment with KOH. Strengths of 2 in. diameter by 2 in. high specimens measured after 7 day air drying plus 24 hr immersion.

However, no evidence has been obtained to indicate that reaction time is the only factor, or even the most important factor, causing the slightly higher strengths with ferrous carbonate and ferrous ammonium sulfate.

The most obvious trend indicated by figure 14 is that a basic pH adjustment increases strength and an acidic adjustment decreases the strength for each of the five salts added. Although this may be partly attributed to increased chelation in an alkaline environment, the fact that a basic pH adjustment also increases the strength with ferrous sulfide and ferric sulfate (curves 4 and 5), which decrease strength when no basic pH adjustment is used, seems to indicate the presence of some other phenomenon. Figure 15 shows that a basic pH adjustment has little effect on the immersed strength of specimens containing Arquad 2HT alone, but produces a prominent strength peak for specimens containing both Arquad 2HT and Acrysol A-1. Figures 14 and 15 taken together suggest that the beneficial effect of a basic pH adjustment is probably due more to increased bonding between the ionized polyacid and the large organic cations than to an increase in chelation of the polyacid by the metal ions.

Although the work to this point has been based on the hypothesis that the increase in strength due to the addition of ferrous carbonate is primarily caused by a chelation reaction with Acrysol A-1 in the soil, this fact has not been experimentally established. To determine the validity of this assumption, samples were molded containing ferrous carbonate alone, Arquad 2HT alone, ferrous carbonate with Arquad 2HT, and ferrous carbonate with Acrysol A-1. The samples containing ferrous carbonate with Acrysol A-1 slaked in water. It therefore appeared that the chelation of ferrous ions by the carboxyl groups may perform a rather minor role in contributing to strength, and that the ferrous carbonate also contributes an increase in strength by some other reaction. Samples containing ferrous carbonate alone also slaked in water and those containing ferrous carbonate and Arquad 2HT had strengths only slightly greater than samples containing equivalent amounts of Arquad 2HT alone. The greatest strength increase due to the addition of ferrous carbonate was found to occur only in the presence of both the large organic cation and the polyacid.

Other reactions were also considered as possible source of the strength increase caused by ferrous carbonate. It has been noted that carbonates contribute a weak cementing effect in some soils. The replacement of ferrous carbonate by equiva lent portions of calcium and magnesium carbonates produced strength increases, but of much smaller magnitude. Hydrous oxides of iron are also known to act as cementing agents in soil[24]. Under alkaline conditions a hydrated iron gel may be precipitated which would become a cementing agent upon dehydration, thus accounting for part of the strength increase due to the addition of ferrous carbonate. The experimental work to this point, however, leaves undetermined the nature of the reaction or reactions involving the ferrous carbonate.

Evaluation of Additional Large Organic Cations

To determine the effectiveness of Acrysol A-1 and ferrous carbonates used with structurally different large organic cations, samples were tested containing four additional types of cations. The chemical structures of the cations are indicated in the Appendix and the results of strength tests are shown in figure 16. Armac T, a primary amine acetate, gave slightly higher strength than Arquad 2HT for 0.1 percent treatment. The remaining three organic cations all gave considerably lower strengths.

SOIL STABILIZATION WITH LIGNIN-CATION AND PROTEIN-CATION COMPLEXES

In this part a study was made of lignin and protein complexed with organic cations and with metal ions for soil stabilization. The source of lignin was spent sulfite liquor, a waste product of the paper industry. The protein was zein, a byproduct of corn processing. The organic cations were the same as those studied in the previous section and the metal ions were of the heavy metal group, including chromium, iron, cobalt, copper, and mercury. These metals were chosen because they are known to be the most effective metals in forming stable, water-insoluble complexes with lignin and various proteins.

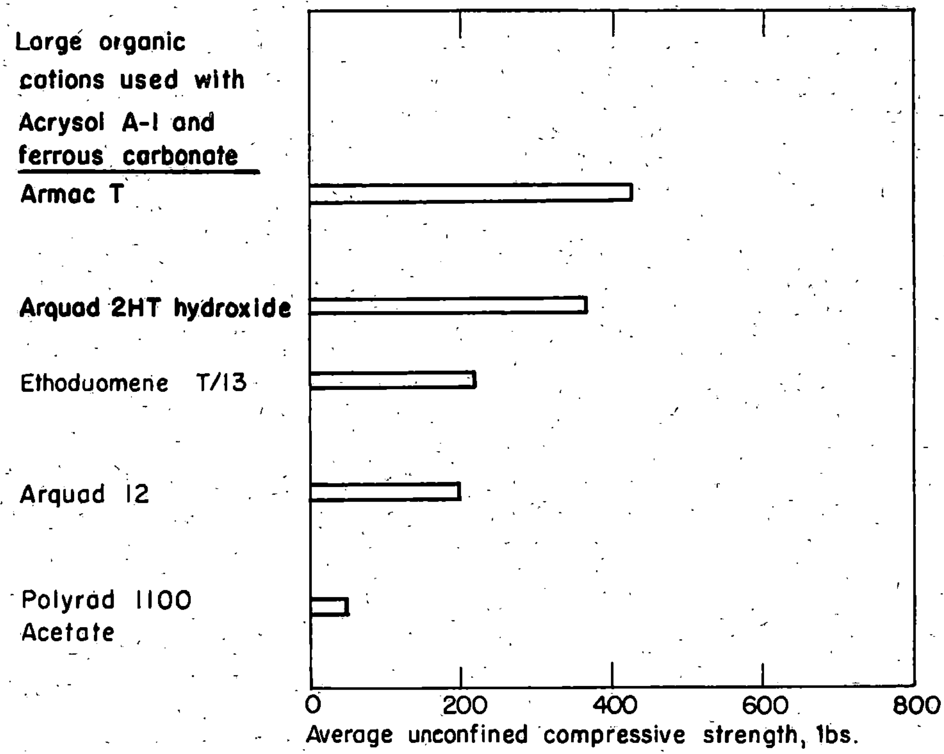


Fig. 16. Unconfined compressive strengths of the silty loam treated with 0.1 percent of various large organic cations with 0.6 percent Acrysol A-1 and 1.6 percent ferrous carbonate. Strengths of 2 in. high by 2 in. diameter specimens measured after 7 day air curing and 24 hr immersion in water.

Lignin is the organic substance which holds plant cells together. Among plant constituents, lignin is more resistant than other organic complexes to decomposition by fungi and bacteria[35]. It accounts for 20 to 30 percent of the weight of wood[26, p. 241] and constitutes a major portion of the waste liquors from paper pulp mills. Being an abundant waste material, it is a constant challenge to chemists.

Proteins are naturally occuring high organic polymers composed mainly of alpha amino acids. Because most proteins have both cationic and anionic groups they are classed as amphoteric polyelectrolytes. Similarly to the polyacids studied in the previous section, proteins react with metal ions to form stable chelates and complexes. In fact, certain metal ions, such as chromium and mercury, are known to bond effectively between the positive and negative ionic groups of proteins (figure 17).

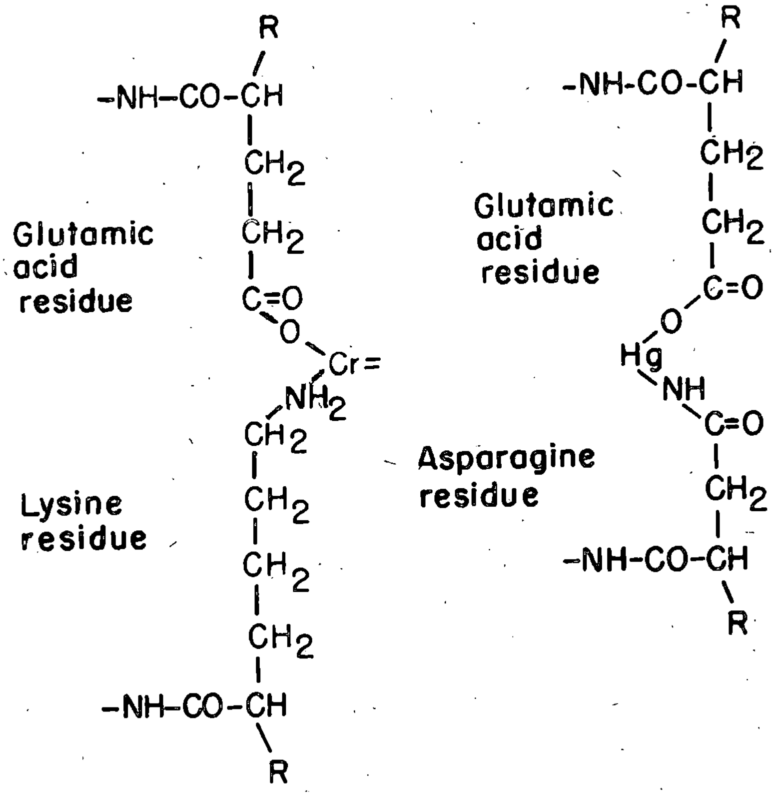


Fig. 17. Heavy metals as linking agents showing: (left) chromium linking carboxyl and amino groups, and (right) mercury linking carboxyl and amide groups. (After Wormell, R. L., NEW FIBRES FROM PROTEINS. Academic Press, New York.)

Ligno-Protein Complexes

Humus, representing the most slowly decomposable portion of organic residues in soil, is composed of from 70 to 80 percent ligno protein complexes[34]. Furthermore, lignin and proteins can both be made more resistant hydrothermally and biochemically by reactions with metals such as chromium and mercury. These facts suggest the possibility of using metal salts in conjunction with lignin and readily available plant proteins for soil stabilization.

Figure 18 has been drawn as an aid in picturing the possible combinations of reactions which may occur between mineral surfaces, lignin, proteins, and either organic cations or metal ions. Any conceivable mechanism of stabilization with these additives can be pictured by starting with the mineral surface, going outward on any series of lines and returning again to the mineral surface. For example, the lines 5-7-5 would represent a system in which lignin bonds adjacent soil particles together through metal cations at the mineral surfaces. The chrome lignin process[30] is apparently an example of this type of stabilization. Lines 6-9-6 would represent a system in which soil particles are bound together by lignin through basic proteins coating the mineral surfaces. Such ligno protein complexes in soils have been studied extensively because of their significance to agronomy[25, 34, 36]. Lines 5-7-9-6 might represent a ligno-protein complex in which lignin is bound to the mineral surfaces through both metal ions and basic amino groups. It is readily seen that a number of possibilities present themselves for study.

Of the various agricultural proteins available as surplus or waste materials, zein, a protein isolated as a byproduct in the production of corn flour, was chosen for this study. Being a readily available protein, it has been the subject of considerable investigation by companies which process corn in large quantities for starch production.

Zein has a molecular weight of about 40,000. Although it contains a relatively

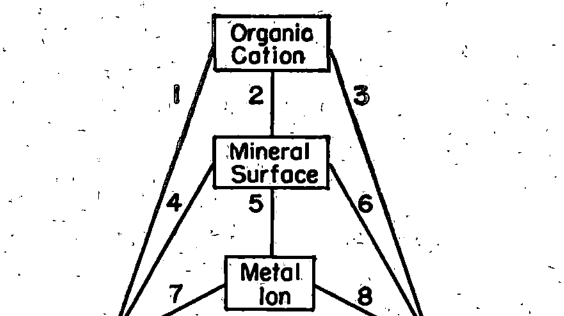


Fig. 18. Possible combinations of reactions between lignin, proteins, organic cations, metal ions, and mineral surfaces.

high proportion of amide groups, it is deficient in other active groups by comparison with most proteins. It contains no lysine and relatively little arginine, which may account for its low imbibition of water.

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental work of this part of the study was limited to a brief evaluation of the reactions represented in figure 18 by means of strength tests alone. A general survey was first made of the use of spent sulfite liquor, zein, and combinations of these two with various metal salts and organic cations. Specimens of the silty loam treated with spent sulfite liquor and zein, individually and in various combinations, slaked when immersed in water. As shown in table II additions of metal salts to the foregoing treatments were also ineffective, with the exception of the chromium and mercury salts. Of these two, mercury apparently reacts only with zein, whereas chromium reacts with spent sulfite liquor as well as with zein. The last two rows of table II show the beneficial effect of spent sulfite liquor when used with the two large organic cations. Zein did not cause a similar increase in strength. The ingredients shown in table II were added to the soil in the following order:

1. Organic cation or metal salt.
2. Zein.
3. Spent sulfite liquor.

In all cases the organic cations, metal salts, and spent sulfite liquor were added in aqueous solution. Zein was added in aqueous solution at pH12 inasmuch as it is water-soluble only in the alkaline range.

The effect of spent sulfite liquor and zein on treatments with Armac T and Arquad 2HT are shown in figures 19 and 20. The strength curves for samples

TABLE II

UNCONFINED COMPRESSIVE STRENGTHS OF THE SILTY LOAM TREATED WITH COMBINATIONS OF SPENT SULFITE LIQUOR AND ZEIN WITH ORGANIC CATIONS AND METAL SALTS[*]

Organic Cations and Metal Salts	No Treatment	Spent Sulfite Liquor†	Zein‡	Spent Sulfite Liquor and Zein§
No treatment	Slaked	Slaked	Slaked	Slaked
$CaCl_2$	Slaked	Slaked	Slaked	Slaked
$MgCl_2$	Slaked	Slaked	Slaked	Slaked
$CuSO_4$	Slaked	Slaked	Slaked	Slaked
$FeCl_3$	Slaked	Slaked	Slaked	Slaked
$Co(NO_3)_2$	Slaked	Slaked	Slaked	Slaked
$Cr_2(SO_4)_3$	Slaked	180 lb	130 lb	210 lb
$Hg(C_2H_3O_2)_2$	Slaked	Slaked	220 lb	230 lb
Armac T	300 lb	350 lb	290 lb	260 lb
Arquad 2HT hydroxide	330 lb	370 lb	340 lb	270 lb

[*] Percentages based on weight of air-dry soil and solid content of additives. Strengths of 2-in. diameter by 2-in. high specimens measured after 7 day air drying plus 24 hr immersion.

† 2 percent.

‡ 0.5 percent.

§ 2 percent spent sulfite liquor plus 0.5 percent zein.

containing Armac T generally lie somewhat higher than for samples containing Arquad 2HT. In each case the addition of 0.5 percent spent sulfite liquor increases the strength considerably, while the addition of 2 percent spent sulfite liquor produces only a small strength increase (curves 2 and 3 of both graphs). Strengths were sharply reduced by the addition of spent sulfite liquor in amounts

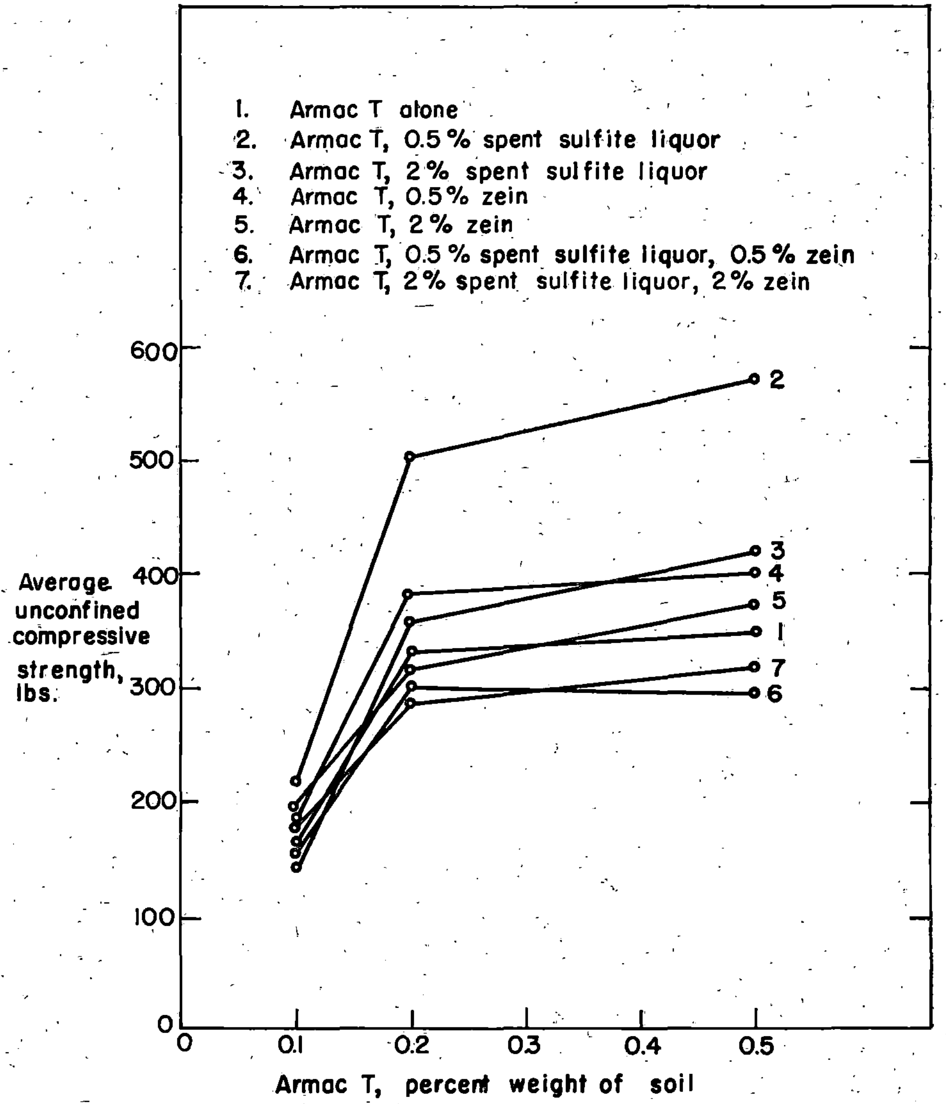


Fig. 19. Unconfined compressive strength of the silty loam treated with Armac T in combination with spent sulfite liquor and zein. Strengths of 2 in. high by 2 in. diameter specimens measured after 7 day air drying plus 24 hr immersion.

greater than 2 percent. Strength changes due to the addition of zein are negligible (curves 4 and 5) and the addition of zein and spent sulfite liquor together lowered the strengths.

Figures 21 and 22 show the relatively lower strengths obtained for treatments containing combinations of chromium and mercury salts with spent sulfite liquor

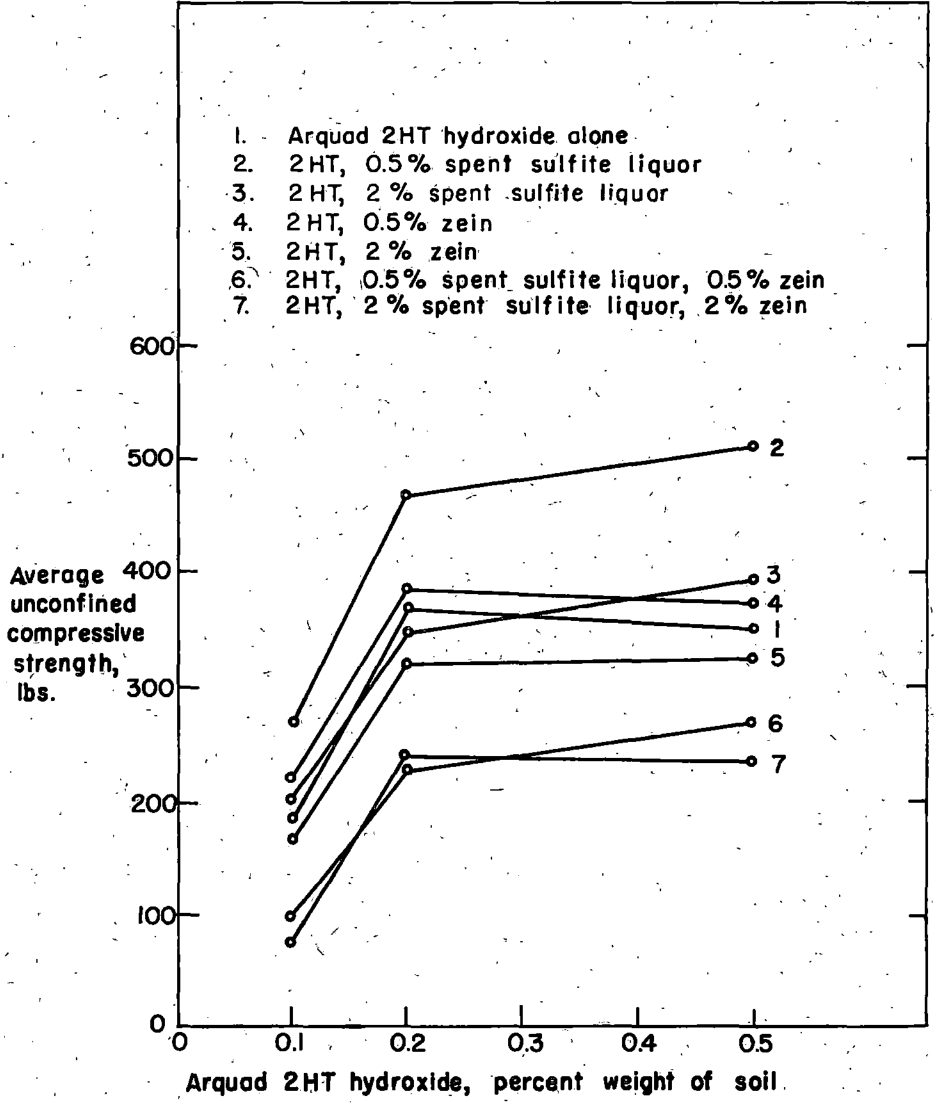


Fig. 20. Unconfined compressive strength of the silty loam treated with Arquad 2HT hydroxide in combination with spent sulfite liquor and zein. Strengths of 2 in. high by 2 in. diameter specimens measured after 2 day air drying plus 24 hr immersion.

and zein. Chromic sulfate with zein and spent sulfite liquor (curve 7 of figure 21) gave higher strengths than other combinations in this group.

SUMMARY

The mechanisms of soil stabilization with large organic cations and with high

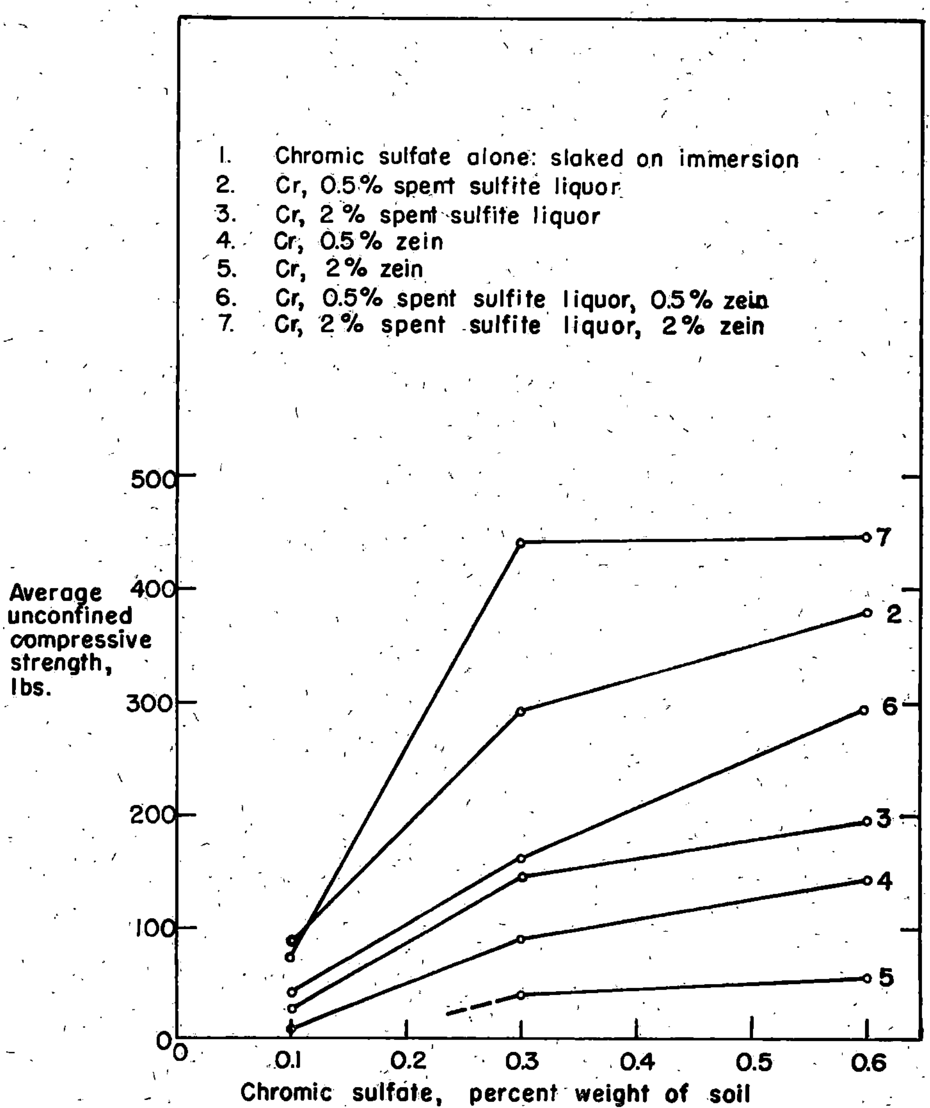


Fig. 21. Unconfined compressive strength of the silty loam treated with chromic sulfate in combination with spent sulfite liquor and zein. Strengths of 2 in. high by 2 in. diameter specimens measured after 7 day air drying plus 24 hr immersion.

polymers have been discussed and an equation has been derived for the shear strength of soil as a function of properties of the polymer.

Methods were investigated for stabilizing soil by the use of large organic cations, polyacids and metal salts. Of these, highest strengths were obtained by combinations of polyacrylic acid and ferrous carbonate with two large organic cationic materials. ArmacT and Arquad 2HT. It was believed that a chelation reaction between the polyacid and metal ions in the presence of soil might increase the strength of the treated samples by several fold. However, such strength increases were not realized and the exact degree of crosslinking by

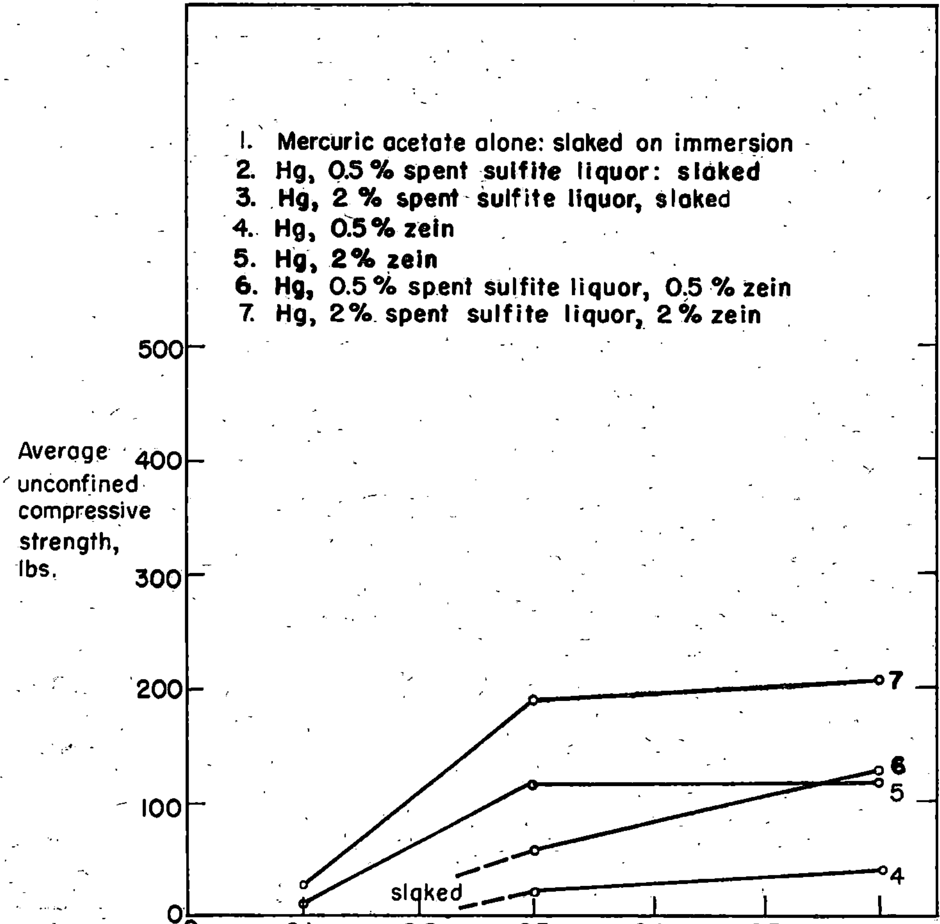


Fig. 22. Unconfined compressive strength of the silty loam treated with mercuric acetate in combination with spent sulfite liquor and zein. Strengths of 2 in. high by 2 in. diameter specimens measured after 7 day air drying plus 24 hr immersion.

chelation in the soil remains undetermined. The use of 0.2 percent of each of the two cationic materials with 0.6 percent polyacrylic acid and small amounts of ferrous carbonate produced strengths in slightly less than double those obtained with the cationic materials alone. On the basis of these tests the cost of polyacrylic acid would probably prohibit its use for most construction purposes. However, the possibility of employing other cations and polymers in similar stabilization mechanisms or of making a more thorough study of chelation reactions in the soil seems to merit further study.

The use of spent sulfite liquor with large organic cations gave smaller strengths, but appears more promising on an economic basis, particularly since the spent sulfite liquor seems to be most effective in quantities less than about 2 percent. The use of large organic cations with various waste products containing lignin definitely appears to merit further study.

Acknowledgements

Gratitude is expressed to Armour Chemical Division, Monsanto Chemical Company, and Rohm and Haas Company, for samples of chemicals used in these investigations.

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APPENDIX

TABLE III. PROPERTIES OF CHEMICAL ADDITIVES

Commercial Name	Chemical Description	Form[*]	Active Fraction (%)	Supplier[†]
(*a*) Polyacids and Polyacid Salts				
Acrysol A-1	Polyacrylic acid	Aqu. sol.	25	R
Acrysol A-3	Polyacrylic acid	Aqu. sol.	25	R
Acrysol A-5	Polyacrylic acid	Aqu. sol.	25	R
Acrysol GS	Sodium salt of polyacrylic acid	Aqu. sol.	12½	R
Acrysol G-110	Ammonium salt of polyacrylic acid	Aqu. sol.	22	R
Acrysol ASE-75	A linear copolymer of acrylic ester with a carboxylic acid	Aqu. sol.	40	R
Acrysol ASE-60	A very slightly cross-linked copolymer of acrylic acid	Aqu. emul.	28	R
Rhoplex AC-33	An acrylic resin	Aqu. emul.	46	R
Krilium Loamaker	A hydroyzed polyacrylonitrile	Powder		M
(*b*) Large Organic Cations				
Arquad 2HT	Di-hydrogenated tallow dimethylammonium chloride	Isop. sol	75	A
Armac T	Primary amine acetate derived from tallow fatty acids	Pure	100	A
Ethoduomene	N-octadecyl N, N′, N′-tris-(2-hydroxyethyl) 1, 3 trimethylene diamene	Pure	100	A
Arquad 12	Trimethyl dodecyl ammonium chloride	Isop. sol.	50	A
Polyrad 1100	Reaction product of dehydroabietylamine and 11 moles of ethylene oxide	Pure	100	H
(*c*) Other Additives				
Spent Sulfite Liquor	71% lignins, 24% sugars, 5% resins and other substances	Aqu. sol.	57%	S
Zein	Protein high in amide content, low in other functional groups	Powder	100	N

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[*] Aqu. sol. = aqueous solution; aqu. emul. = aqueous emulsion; isop. sol. = isopropanol solution.

[†] R = Rohm and Haas Co.; M = Monsanto Chemical Company; A = Armour Chemical Division; H = Hercules Powder Co.; S = Sulphite Pulp Mfr. Research League; N = Nutritional Biochemicals Corp.

TABLE IV. PROPERTIES OF THE SILTY LOAM[*]

Item	Amount or Classification
Chemical:	
Organic matter	0.17%
Carbonates	10.17%
Iron	1.69%
Sulfate	0.0%
Cation exchange capacity	8.7 me/100 gm
pH	8.7
Textural:	
Sand	0.4%
Silt	79.8%
Clay	19.8%
Colloidal Clay	14.5%
USBPR classif.	Silty loam
Mineral comp., clay fraction—primarily montmorillonite, with smaller quantities of illite and kaolinite	

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[*] Laboratory sample 20-2.

LIGNINS AS STABILIZING AGENTS FOR NORTHEASTERN IOWA LOESS

by

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D. T. Davidson, Professor, Civil Engineering
J. M. Hoover, Assistant Professor, Civil Engineering

Iowa Academy of Science Proceedings 64: 314-347. 1957.

INTRODUCTION

Lignin is the natural cement that binds the fibers of wood together in plants[37]. Because the chemical structure of lignin is still unknown, it is difficult to define. The term *lignin*, therefore, cannot be considered the designation of a constitutionally defined compound. It is rather a collective term for a group of high molecular, amorphous compounds which are chemically very closely related to other natural high molecular products[4].

Several processes, which vary with the properties of lignin, are used to isolate lignin from pulping liquor. The most common of these is the sulphite process. The lignin obtained is called "lignosulfonate" and is water soluble. It forms a major constituent of solid residue of the so-called *spent sulphite liquor.*

The lignin liquor comes from the digester in a solution having approximately 8 percent solids. In this form the liquor is commonly used on "gravel" roads and streets near pulp mills to reduce dust and the effects of frost action. When used for such purposes the spent sulphite liquor may be referred to as road binder. Concentrated road binder can be prepared by condensing the dilute liquor, largely through evaporation, to a desired percent of solids solution, usually 46 to 50 percent solids[60]. Complete drying and pulverizing produces the powdered form of lignin.

The 113 sulphite pulp mills in the United States and Canada produce over 30,000,000 gallons of spent sulphite liquor a day. A ton of pulp wood produces about 950 pounds of cellulose used for paper, and the remaining 1,050 pounds of solid is recovered in the spent sulphite liquor. This quantity of liquor contains about 750 pounds of lignins, 250 pounds of sugars, and 50 pounds of resins and other substances[50].

Since the development of uses for spent sulphite liquor is still in its infancy, the material is abundant and is very economical as a road construction material; the liquor is sold at about 6 cents per gallon in 55 percent solids form at the mill[21]. When diluted to 25 percent solids at the railroad siding, the cost would be about two cents per gallon plus freight; the latter being six cents per gallon from Appleton, Wisconsin, to Des Moines, Iowa. The northeastern Iowa area investigated for the possibility of the use of spent sulphite liquor is much nearer to the Wisconsin mills producing sulphite liquor than Des Moines, thus reducing the cost. The cost would be further reduced if the lignins were available in a more concentrated form, providing the cost of concentrating the liquor does not exceed the added cost of hauling the material at a lower concentration.

Development of Lignin Soil Stabilization

So called road binders made from a lignin base were first utilized in Sweden about 50 years ago[1, 28, 31]. The factor encouraging its use was primarily economic. Since the local supply of road binding oils was inadequate, a large quantity of road binding oils had to be impmorted. In search for a cheaper road binding material, the Swedish Government started experimenting with the sulphite liquor available in large quantities throughout the country.

The use of spent sulphite liquor as a road material in the United States resulted from a search for methods of disposing of it. Fifteen years ago, this material had no value and was wasted by dumping into streams or rivers. This brought serious objections from the public.

In the early part of this century, several patents were issued in the United States, Germany, France, and in Sweden, on the use of spent sulphite liquor as a road binding material[6, 10-15, 22, 27, 31, 35, 39, 43, 44-46, 51, 55, 56]. One of the most common uses of spent sulphite liquor in road construction has been as a dust palliative[3, 10, 15-19, 24, 28, 29, 33, 41, 44-47, 54-55, 60, 63]. It has been used to a limited extent as a stabilizer for base and surface courses[3, 12, 33, 38, 61-63], and it has been found very successful in the prevention of frost heave[17, 23]. Its action as a soil dispersant, and thereby its beneficial effects on such soil properties as density, compaction, optimum moisture content, capillarity, and permeability have been reported[12, 38]. Spent sulphite liquor used in amounts ranging from 3 to 10 percent of the soil dry weight together with a chromium salt such as potassium bichromate or sodium bichromate has been found to form a tough gel having binding and water proofing properties[22].

Spent sulphite liquor in Europe. Spent sulphite liquor has been used as a road construction material in Europe for nearly six decades, Sweden topping the list of the countries using it. Of the 55,000 miles of public roads in Sweden, 52,000 miles were gravel roads at the end of 1939. During that year, 33,000 miles of the gravel roads were treated with dust binding material[34]. The work in the beginning was confined mainly to dust control[1]. The Institute of Road Research at Stockholm found in their dust control experiments with sulphite liquor that it reacted well with dust and bound the particles together if the road surface was rich in clay. The Institute also studied the binding power of spent sulphite liquor[23], using a mixture of stone dust and the liquor. Molded specimens containing various percentages of liquor were tested for shearing strength. Good results were obtained when the amount of the liquor was 2 percent of the dry weight of the dust. It was also observed that the use of lignin in dry solid form provided higher early strength, and the concentrated liquor when thoroughly dry gave the best results after 28 days curing.

The effects of spent sulphite liquor on soils susceptible to frost action has been investigated[2]. A mixture of sulphite liquor and sodium bichromate was used as a binder. Since the addition of sodium bichromate with spent sulphite liquor forms a gel and acts as a waterproofing agent, it was observed that a solution of 9 percent concentrated spent sulphite liquor (50 percent solids) and 10 percent bi-chromate solution (50 percent $Na_2Cr_2O_7$) added to the soils in such proportions that the amounts of binder corresponded to 2, 4, 6, and 8 percent of the dry soil weight reduced significantly the intake of capillary moisture. The use of 2 percent of this binder was found to be economical as well as beneficial. Eight percent of sulphite liquor used alone reduced capillary absorption of moisture considerably[2]. During the 28 day testing period, one observation worth mentioning was that untreated soil continued to take up moisture even after 28 days, but the treated soil stopped such absorption long before the testing period was over. It was concluded that a frost susceptible soil can be made resistant to frost action through use of a binder of spent sulphite liquor and a bichromate.

Work done in America. The first published report on the use of spent sulphite liquor in this country originated with the work done by the Raylig Division, Raynier Incorporated, on the West Coast[62]. The report gives the methods of application of spent sulphite liquor for various end results.

The states of New Jersey, Washington, Maryland, and Idaho have made much use of spent sulphite liquor as a dust palliative road stabilizer, and base treatment with impervious wearing courses[38, 62]. The state of New Jersey has used spent sulphite liquor for thirty years, primarily as a stabilizer preliminary to a bituminous treatment. Spent sulphite liquor was found to be beneficial in the prevention of spring break-up of roads[62].

The state of Idaho in 1937 used concentrated spent sulphite liquor for surface treatments on several roads in the state. Inspection in the spring of 1938 revealed that the binder gave relief from dust and had conserved surface aggregate during the summer. It had slowly diffused downward, tending to produce a stabilized base course of increasing thickness[42].

The city of Spokane, Washington, reported in 1943 that diluted sulphite liquor had been used for twelve years as a dust layer on secondary city streets, and indicated the results obtained were very satisfactory[62]. Mason County, Washington, has reported on the effects of heavy rainfall on sulphite liquor treated roads. Frequent applications of sulphite binder and grading of the road surface were found to be necessary during the rainy season. The sulphite liquor treated roads did not suffer from frost heave, but untreated roads in the same neighborhood suffered badly.

The Quebec Department of Roads conducted some laboratory tests to determine the bearing capacity of raw gravel, clay stabilized gravel, and gravel treated with lignin extract[22, 26]. The bearing capacity of gravel treated with 1.2 percent lignosol was higher than that of the raw gravel and the clay stabilized gravel. Compression and absorption tests were also made. Compressive strength increased with the addition of 2 percent of lignosol. The absorption of water through capillary action was reduced, and the unconfined compressive strength of the dried lignin treated gravel increased almost proportionately with the amount of lignosol used. Moisture density relationship tests showed that an increase in the amount of sulphite liquor added to the soil increased the density and reduced the optimum moisture content.

Calcium lignosulfonate has been reported as a dispersing agent with beneficial effects on soil properties[30]. An admixture of spent sulphite liquor and bichromate in chrome lignin soil stabilization increases the stability of soil and acts as a waterproofing agent[25].

Mechanism of Lignin Soil Stabilization

The binding effect of sulphite liquor appears to be due to the lignosulfonate, which is the major constituent of the solids in it. Lignin serves as a glue[38]. Sulphite liquor is believed to have an influence on the surface properties of the fine particles of a soil system[26, 42], though there is no definite proof as to how it alters the properties which improve soil stability.

Studies of the effect of calcium and magnesium sulfonate, used in trace amounts with other additives, on the properties of soil indicated that lignin acts as a dispersing agent[30]. Because of dispersion, the largest voids are destroyed, and since the breakdown of aggregates furnishes smaller particles that can fit

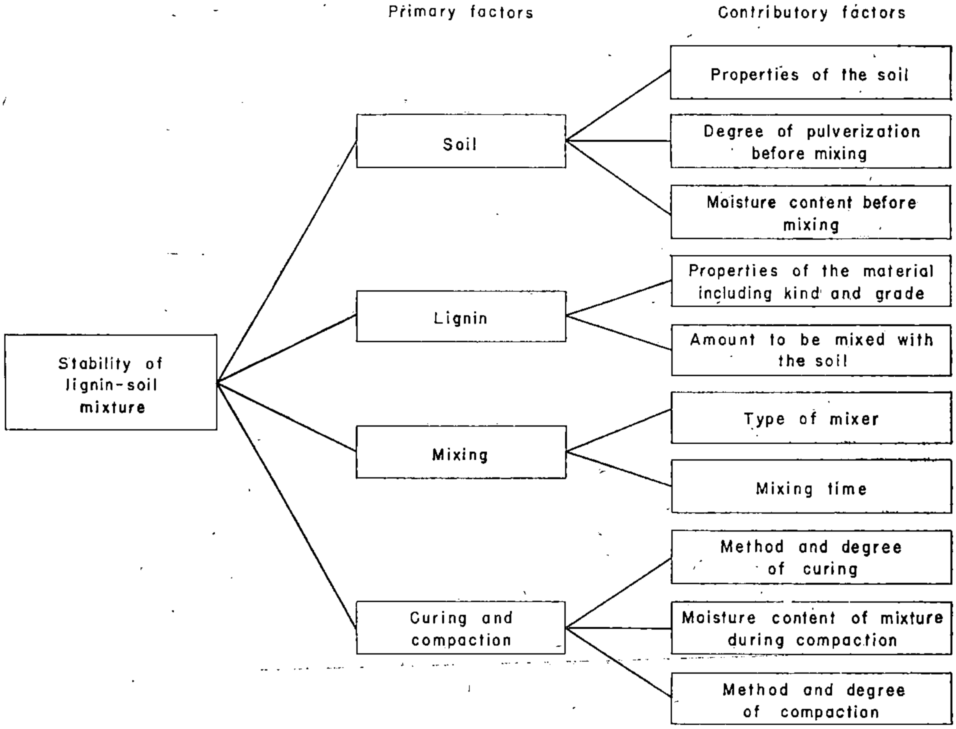

Fig. 1. Variables affecting stability of lignin and soil mixture.

into void spaces, greater density is achieved. It is also believed that the permeability of soil treated with spent sulphite liquor is decreased considerably. This helps in preventing frost heave. Research carried out at Ecole Polytechnique in Canada, under the sponsorship of the Department of Roads[26], also showed that spent sulphite liquor has a dispersing action on the soil fines and decreases the required moisture content to attain maximum density.

LABORATORY INVESTIGATION

No standard method had been developed for evaluating the stability of lignin-soil mixtures. Previous studies, however, have shown that there are several variables which affect the stability (figure 1). Time has not permitted an investigation of all the varibles shown; however, an attempt has been made to study a few of them. The results to date are given in this report.

Properties of Soils and Lignins

Three samples of northeastern Iowa loess and loess derived soil (both C horizon and solum samples) were used in this study. Loess deposits are over an area of about 4000 square miles in northeastern Iowa[34]. Northeastern Iowa loess for the most part is believed to have been deposited during the Iowan and Tazwell substages of the Wisconsin glacial stage[34]. Thicknesses of the loess are quite variable throughout northeastern Iowa. Along the Iowan drift border it is commonly 10 to 20 feet thick, but the thickness gradually decreases to a few feet in the northeastern corner of Allamakee County.

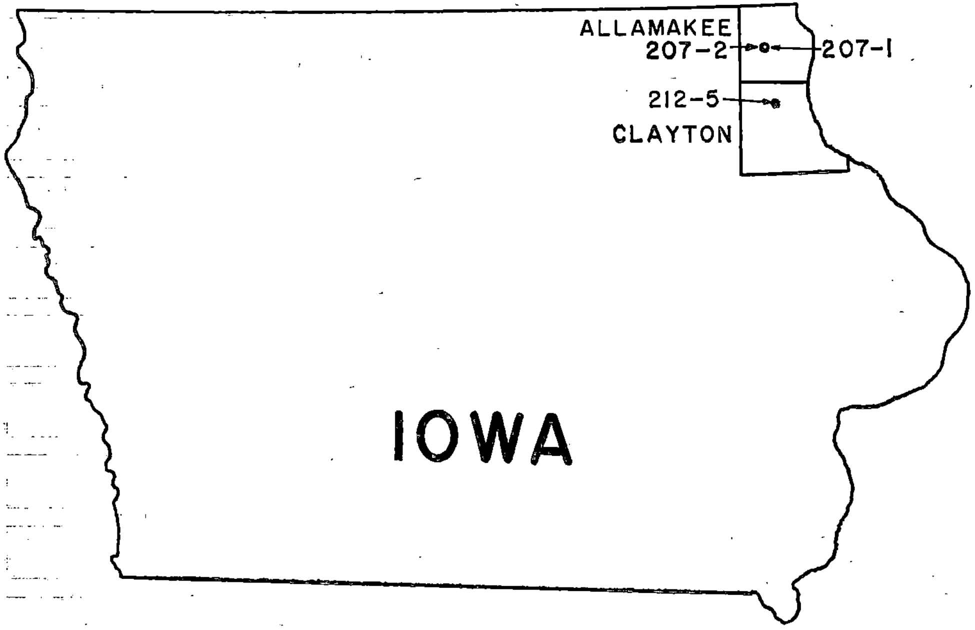

Fig. 2. Sampling locations of loess and loess derived soil used in lignin stabilization studies.

The three soil samples used in this study, Nos. 207-1, 207-2, and 212-5, are from two northeastern Iowa counties. Samples 207-1 (A horizon) and 207-2 (B horizon) came from Allamakee County, and sample 212-5 (C horizon) was obtained from Clayton County (figure 2) The reasons for selecting these soil samples are twofold: the samples represent the variations in properties of the loess in northeastern Iowa (table I, II) and the area is near the mills producing spent sulphite liquors. The second reason is purely an economic one in that, if the stabilization with lignin proves successful, it would be economical to use in northeastern Iowa.

Properties of lignins used

Five types of lignin supplied by four different companies were used in this study. The lignins used were:

1. Spent sulphite liquor, supplied by the Kansas City Star Co., Flambeau Paper Division, Park Falls, Wisconsin.

TABLE I. SAMPLING LOCATIONS OF SOIL SAMPLES

Sample no.	County in Iowa	Section	Township and range	Soil series	Horizon sampled	Sampling depth below surface
207-1	Allamakee	NE¼ SE¼ Sec. 23	Jefferson T97N-R5W	Fayette	A	0″-6″
207-2	Allamakee	NE¼ SE¼ Sec. 23	Jefferson T97N-R5W	Fayette	B	2′2″-2′8″
212-5	Clayton	SE¼ SW¼ Sec. 27	Lodomillo T91N-R5W	Tama	C	12′3″-12′9″

TABLE II. PROPERTIES OF SOIL SAMPLES

	Sample no.	212-5 (C-horizon)	207-2 (B-horizon)	207-1 (A-horizon)
Physical properties	L.L., %	33.5	43.3	39.3
	P.L., %	21.5	24.0	29.0
	P.I., %	12.0	19.3	10.3
	C.M.E., %	16.9	23.3	23.2
	F.M.E., %	22.4	22.7	24.2
	S.L., %	20.4	16.3	N.D.
Chemical properties	pH	8.0	7.1	7.5
	Chlorides, %	None	N.D.	N.D.
	Calcium carbonate, %	16.6	6.8	1.3
	Iron, %	0.50	1.49	N.D.
	Sulphate content, %	None	None	Trace
	Cation exchange capacity, m.e./100g.	15.5	18.9	19.2
	Organic matter, %	0.1	0.36	4.77
Textural composition,[*] %	Sand	4.8	0.4	1.2
	Silt	71.4	62.9	70.4
	Clay	23.8	36.7	28.4
	Colloidal Clay	18.2	29.0	18.6
Textural classification (B.P.R. system)		Silty clay loam	Silty clay	Silty clay loam
Engineering classification		A-6(9)	A-7-6(12)	A-6(8)

[*] Sand—2.0 to 0.074 mm., silt—0.074 to 0.005 mm., clay—below 0.005 mm., colloidal clay—below 0.001 mm.

2. & 3. Sulphite lignin grade A and sulphite lignin grade D, supplied by Lake States Yeast Corporation, Rhinelander, Wisconsin.

4. Bindarene flour, supplied by International Paper Company, New York.

5. Clarian extract, supplied by the New York and Pennsylvania Co., Inc., New York.

No standard specifications for the manufacture of lignins have been developed (table III).

Method of Investigation

The test methods used in this investigation to evaluate the effectiveness of the lignins as stabilizing agents for northeastern Iowa loess and loess-derived soil are of three general types: standard methods, methods in common usage but not yet standardized, and methods which have been developed and used in the soil stabilization research of the Iowa Engineering Experiment Station.

Preparation of lignin, soil mixutres. The three soil samples used in this investigation were air-dried, pulverized, and passed through a No. 10 sieve prior to preparing the lignin-soil mixtures; the whole of each of the soils passed through this sieve. Since some of the additives were solid and some were liquid, a slightly different procedure for mixing each type of additive was followed.

The soil and powdered additives were mixed dry with a trowel; the amount of additive used was calculated on the basis of the oven dry weight of soil. The resulting dry mixture of lignin and soil was then transferred to a mixing bowl.

TABLE III. PROPERTIES OF LIGNINS

Properties	Bindarene flour[*]	Clarian extract[†]	Sulphite lignin grade A[‡]	Sulphite lignin grade D[§]	Spent sulphite liquor[**]
Lignin, %	55.9	N.D.[††]	N.D.[††]	N.D.[††]	N.D.[††]
Total sugars, %	20.8	N.D.[††]	2.0	4	N.D.[††]
Moisture, %	4.0	50.0	50.0	6	N.D.[††]
Iron, %	0.02	0.25	N.D.[††]	N.D.[††]	N.D.[††]
Magnesium oxide, %	1.5				N.D.[††]
Calcium oxide, %	4.9	6.0[‡‡]	4	7.5	N.D.[††]
Sodium oxide, %	0.3	N.D.[††]	N.D.[††]	N.D.[††]	N.D.[††]
Sulfated ash, %	17.1	8.0	5	9.4	N.D.[††]
Sulfone So_2, %	5.5	N.D.[††]	N.D.[††]	N.D.[††]	N.D.[††]
Sulfur trioxide, %	0.9	N.D.[††]	N.D.[††]	N.D.[††]	N.D.[††]
Free sulfur dioxide, %	0.2	1.0	N.D.[††]	N.D.[††]	N.D.[††]
Total sulfur, %	4.1	6.0	N.D.[††]	N.D.[††]	N.D.[††]
Volatile acids, %	3.9	N.D.[††]	N.D.[††]	N.D.[††]	N.D.[††]
pH, average	5.7	7.0	5.4	5.4	N.D.[††]
Color	Light yellow powder	Dark brown viscous liquid	Dark brown viscous liquid	Light tan powder	N.D.[††]
Calcium lignosulfonate, %	80	N.D.[††]	48	90	N.D.[††]
Fe and Al as oxides, %	N.D.[††]	N.D.[††]	0.05	0.10	N.D.[††]
Specific gravity	N.D.[††]	1.26	1.25	N.D.[††]	

[*] Contains 95% non-volatile material and 5% moisture; all percentages are based on 100%.
[†] 50% solid and 50% moisture.
[‡] 94% solid and 6% moisture.
[§] 50% solid and 50% moisture.
[**] 57% solid and 43% moisture.
[††] N.D., not determined.
[‡‡] Magnesium oxides and calcium oxides are combined.

Mixing was done with a Blakeslee Kitchen Mixer, Model C-20, at moderate speed. During the first minute of mixing, distilled water was added to bring the lignin soil mixture to the optimum moisture content. The total time of mixing was five minutes.

The desired amount of liquid lignin was calculated on the basis of solids content and was diluted with enough distilled water to make the amount of liquid equal to the amount desired in the soil for compaction purposes. This additive was mixed with the soil sample.

Moisture density relationship study. The effect of amount and kind of lignin admixture on the optimum moisture content and maximum dry density of the soils was studied by using the compaction apparatus developed in the Iowa Engineering Experiment Station for molding 2 in. diameter by 2 in. high test specimens. This method of determining the moisture density relationship of soils has been correlated with the standard Proctor method (ASTM Designation: D698-42T) and gives optimum moisture contents and maximum dry densities that are very close to those obtained by the standard method[7]. With the soils and mixtures used in this investigation, five blows of a 5 pound hammer falling from a height of 12 in. on each end of the single layer of material being compacted in the mold was equivalent to standard Proctor compactive effort (figure 3). The advantages of using this test method are in the savings of time and materials as compared with the standard method.

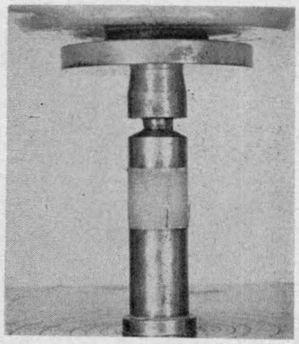

Fig. 4. above. 2 inch diameter by 2 inch high specimen being tested for unconfined compressive strength.

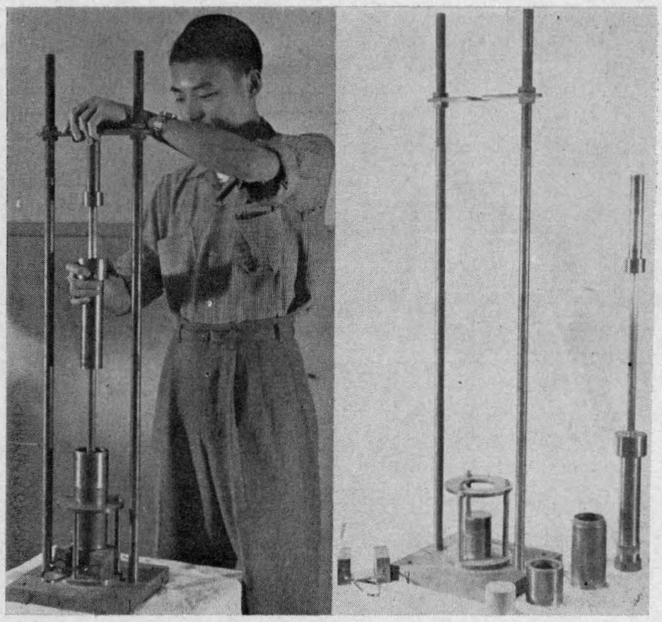

Fig. 3. above. Apparatus for molding 2 inch diameter by 2 inch high test specimens. At left, drop hammer and molding cylinder in place. At right, center, drop hammer and molding cylinder in detail.

The amounts of each lignin added to the soils were 3, 6, and 9 percent of the dry soil weight. With the liquid lignins, the dry solid content of the additives equaled these percentages. The maximum dry density and the optimum moisture content values given in this report are the average of three determinations.

Unconfined compressive strength and moisture absorption study. The five lignins were used in varying amounts with the three soils to determine the effect of lignin admixtures on the unconfined compressive strength and capillary moisture absorption of the treated soils. Test specimens 2 in. in diameter and 2 in. high were molded, cured, and tested for unconfined compressive strength and moisture absorption by the methods described below. The amounts of each lignin added to the soils were 1, 3, 6, and 9 percent of the dry soil weight.

Molding of specimens. Molding of 2 in. diameter by 2 in. high specimens was begun immediately after the completion of mixing. Approximately 200 grams of the soil mixture at optimum moisture content for maximum dry density was poured into the cylindrical mold and was compacted as previously (figure 3). Immediately after molding, the specimens were weighed and measured to the nearest 0.1 gram and 0.001 inch, respectively.

Curing of specimens. The molded specimens were air cured for seven days. This time was chosen on the basis of a supplemental air curing study. It was found that 2 in. by 2 in. lignin treated soil specimens reached approximately constant weight after seven days air curing.

Testing of specimens: After air curing. After seven days of air curing, test specimens were weighed, measured, and tested for dry unconfined compressive strength. The unconfined compressive strength was determined (figure 4). The rate of load application was 0.1 inch per minute. The maximum test load causing failure of the specimen was taken as its compressive strength. Compressive strength values are the average of values for three specimens; the same is true for moisture absorption values.

After capillary absorption. The capillary moisture absorption and its effect on the compressive strength of test specimens were determined. Both "as molded" and air-cured specimens were used in the test.

Felt pads a half inch thick were laid flat in the bottom of an air tight cabinet. The water level in the cabinet was adjusted to just below the top of the pads. The specimens were then placed on the pads with filter paper inserted between the specimens and the felt to prevent loss of soil particles from the bottom of the specimens. After three days, specimens that had not disintegrated were taken out of the cabinet, weighed, and tested for moisture absorption and compressive strength.

Consistency limits and pH study. The standard ASTM tests for liquid limit, plastic limit, and plasticity index (ASTM Designations: D423-39 and D424-39) were used in experiments to determine the effect of lignin on these soil properties. The effect of lignin on the soil pH was studied with a Leeds and Northrop pH meter. Two in. by 2 in. test specimens with and without lignin admixtures were molded and air cured at room temperature for periods of 0, 1, 2, 4, and 7 days. At the end of each curing period, the specimens were broken and ground up by mortar and pestle to pass through the No. 10 sieve and then tested. Only one additive each of two Wisconsin lignins, sulphite lignin grade A (liquid) and sulphite lignin grade D (powder), were used. The percentage admixture of each lignin, selected on the basis of the results of density, compressive strength, and moisture absorption tests, was 6 percent of the dry soil weight.

California Bearing Ratio study. Two Wisconsin lignins, spent sulphite liquor and sulphite lignin grade D, were chosen for the evaluation of their effects on the C.B.R. values of the three soils; the amount of each lignin used was 6 percent of the dry soil weight. The C.B.R. test was performed essentially according to the procedure outlined by the U.S. Corps of Engineers[52]. The raw soil and lignin treated specimens were compacted to standard Proctor density, and C.B.R. values for "as molded" and "soaked 4 days" were determined. The swelling and moisture absorption of the soaked samples were also determined.

Supplementary curing study using Iowa Bearing Value test. A supplementary curing study using the Iowa Bearing Value test was made on a mixture of soil 212-5 (C horizon) and 6 percent spent sulphite liquor. Specimens 2 in. in diameter and 2 in. high were molded at optimum moisture content to near standard Proctor density (figure 3) in a brass cylinder having an internal diameter of 2

TABLE IV. EFFECT OF LIGNIN ADMIXTURES ON THE OPTIMUM MOISTURE CONTENT AND MAXIMUM DRY DENSITY OF THE THREE SOILS

		Soil 212-5 (C-hor.)		Soil 207-2 (B-hor.)		Soil 207-1 (A-hor.)	
Kind and grade of lignin	Lignin admixture[*] % dry wt. of soil	Optimum moisture content, % dry wt. of soil	Maximum dry density of soil, pcf	Optimum moisture content, % dry wt. of soil	Maximum dry density of soil, pcf	Optimum moisture content, % dry wt. of soil	Maximum dry density of soil, pcf
Spent sulphite liquor	0	17.10	109.0	20.00	103.3	21.00	100.7
	3	15.40	114.8	18.00	107.9	17.00	103.6
	6	13.70	116.0	17.30	108.4	14.60	106.3
	9	13.30	116.1	15.62	107.3	14.10	108.2
Sulphite lignin grade A	0	17.10	109.0	20.00	103.3	N.D.[†]	N.D.[†]
	3	15.00	113.2	18.00	106.6	N.D.[†]	N.D.[†]
	6	14.90	114.2	17.30	107.5	N.D.[†]	N.D.[†]
	9	13.30	115.2	16.80	107.1	N.D.[†]	N.D.[†]
Sulphite lignin grade D	0	17.10	109.0	20.00	103.3	N.D.[†]	N.D.[†]
	3	15.00	114.7	18.70	107.2	N.D.[†]	N.D.[†]
	6	14.40	115.1	17.90	107.5	N.D.[†]	N.D.[†]
	9	14.40	115.1	17.90	107.5	N.D.[†]	N.D.[†]
Bindarene flour	0	17.10	109.0	20.00	103.3	21.00	100.7
	3	14.00	114.2	19.00	107.5	17.70	103.3
	6	13.50	116.5	18.20	107.6	16.60	105.8
	9	12.40	116.8	17.90	107.5	14.80	106.5
Clarian extract	0	17.10	109.0	20.00	103.3	N.D.[†]	N.D.[†]
	3	14.8	113.7	18.90	106.0	N.D.[†]	N.D.[†]
	6	14.7	114.7	17.70	106.2	N.D.[†]	N.D.[†]
	9	14.3	114.8	17.52	105.6	N.D.[†]	N.D.[†]

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[*] Dry solid material.

[†] N.D., not determined.

in. and a height of 6 in. The specimens were cured and tested in the cylinders in which they were molded.

Specimens were cured by two different methods. In the first, specimens were air-cured at room temperature for a period ranging from 1 to 28 days. At the end of each curing period, four specimens were weighed. Two of them were tested immediately, and the other two were immersed in water for 7 days before being tested. Before immersion, the molds were clamped to a frame (figure 5a). An annular weight, weighing 1.1 lbs. in water, which has a stem projecting above the brass specimen mold for supporting an Ames dial to measure swelling and a perforated disc at the bottom for the passage of water through it, was placed on the top of the specimens (figure 5a). At the end of seven days immersion, the specimens in their brass cylinders were taken out of water, drained, weighed, and tested. The testing procedure was the same for both air-cured and soaked

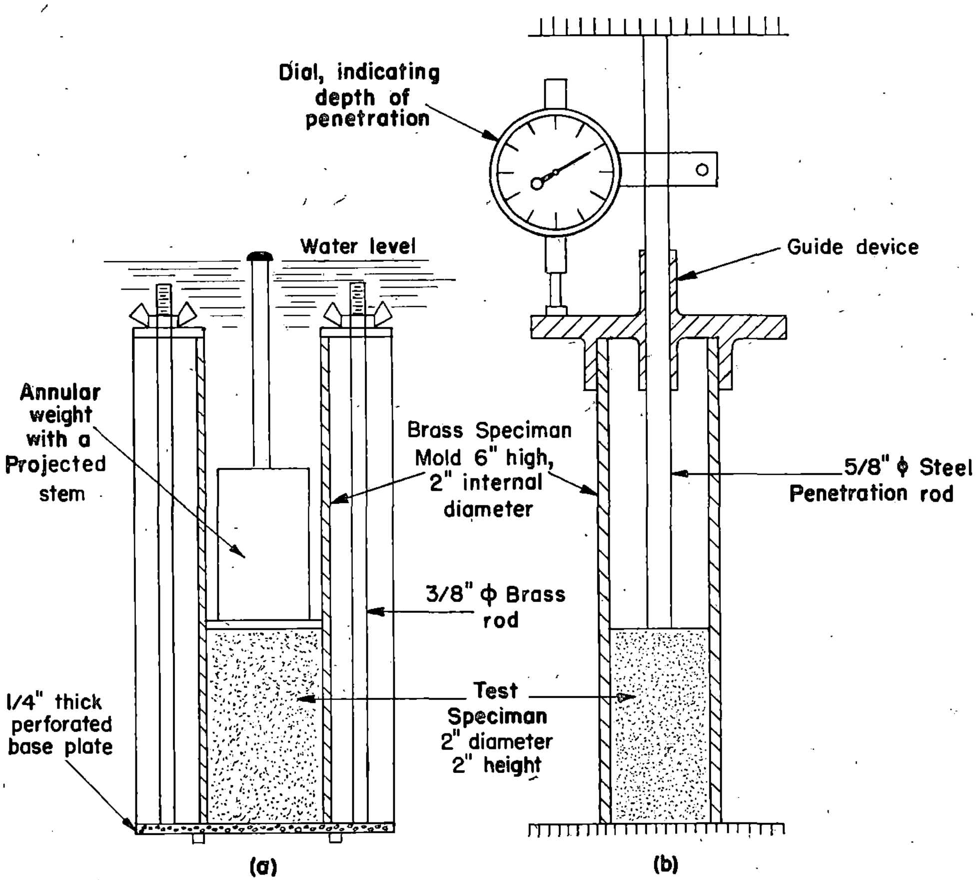

Fig. 5. The Iowa Bearing Value test apparatus. (a) Immersion of a test specimen in water bath. (b) Specimen in position for testing.

TABLE V. EFFECT OF LIGNIN ADMIXTURES ON UNCONFINED COMPRESSIVE STRENGTH AND RELATED PROPERTIES OF 7 DAY AIR DRIED SOIL 212-5 (C-HOR.) TEST SPECIMENS

Kind and grade of lignin	Lignin admixture, % dry wt. of soil	Specimen dry density, pcf	Specimen moisture content, % dry wt. of specimen	Unconfined compressive strength, lbs.*
Spent sulphite liquor	0	109.4	2.00	2847
	1	111.2	3.67	2227
	3	112.6	3.96	2125
	6	110.6	6.77	1410
	9	112.9	6.50	1255
Sulphite lignin grade A	0	109.4	2.00	2847
	1	110.0	3.51	2053
	3	110.8	3.69	1855
	6	111.2	4.80	1120
	9	111.5	7.21	988
Sulphite lignin grade D	0	109.4	2.00	2847
	1	112.3	4.20	1975
	3	110.0	5.19	1603
	6	110.8	5.87	1278
	9	113.2	5.51	1145
Bindarene flour	0	109.4	2.00	2847
	1	112.9	2.80	2300
	3	110.9	3.11	1785
	6	109.6	5.17	1602
	9	114.3	6.51	1290
Clarian extract	0	109.4	2.00	2847
	1	112.2	2.81	2188
	3	111.4	4.87	1655
	6	109.6	6.40	1565
	9	112.5	6.52	1490

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* Two inch diameter by 2 inch high test specimens.

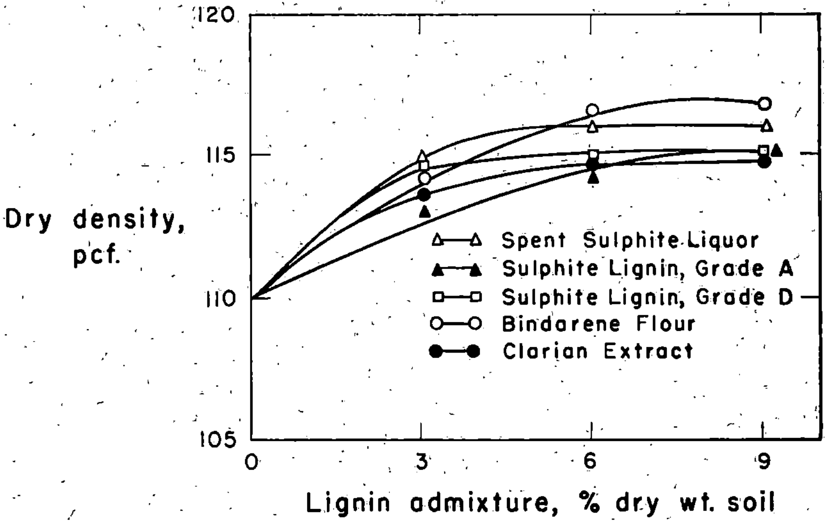

Fig. 6. Variation of maximum dry density of lignin treated C horizon loess (soil sample 212-5) with the amount and kind of lignin.

specimens (figure 5b). The rate of penetration was 0.05 inch per minute. The test load in pounds at 0.2 inch penetration was taken as the strength value of the specimens. Moisture absorption and swell during immersion were also determined. All values derived from this test are the average of at least two specimens.

Specimens were moist cured using the other method for a period ranging from one to twenty-eight days at a relative humidity of 90 to 95 percent and a temperature of about 70°F. Testing of specimens with and without immersion, after each moist curing period, was the same as in the first method.

The objectives of this study were to determine the effect of method and amount of curing on the bearing capacity of lignin treated soil. The Iowa Bearing Value test was used mainly because the large number of specimen molds required for the study and the moist cabinet space available, ruled out the use of the C.B.R. test. Other advantages of the IBV are the saving of time and materials.

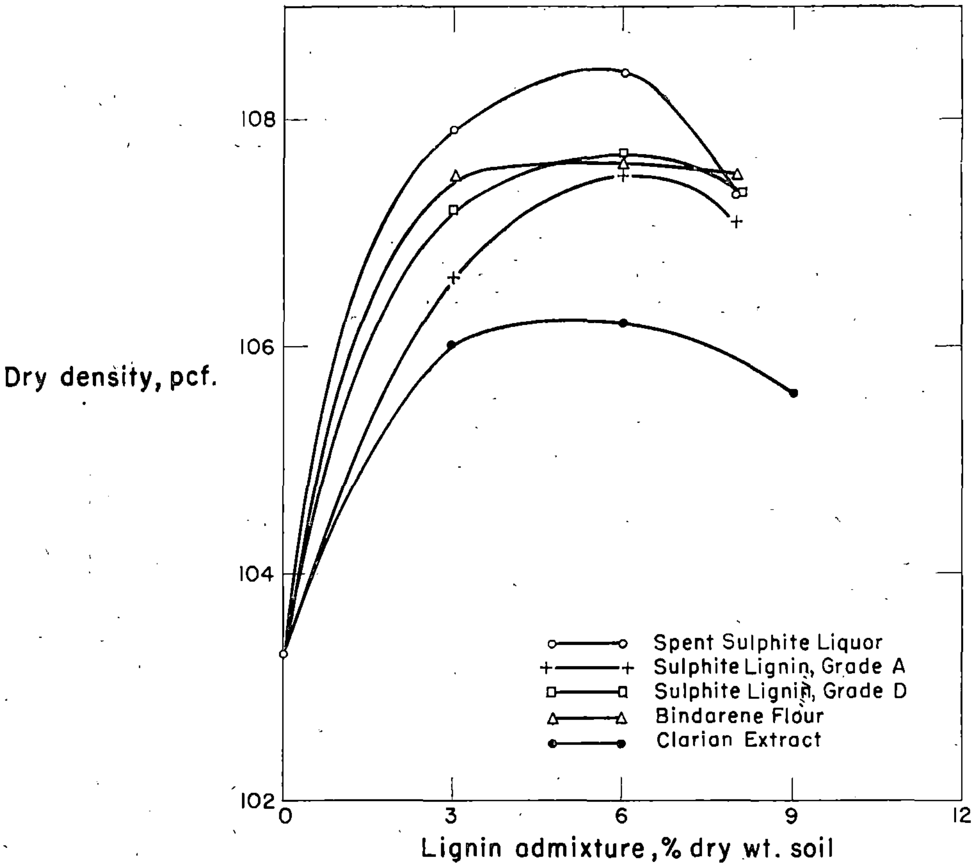

Fig. 7. Variation of maximum dry density of lignin treated B horizon loess (soil sample 207-2) with the amount and kind of lignin.

Table VI. Effect of lignin admixtures on unconfined compressive strength and related properties of 7 day air dried soil 207-2 (*B*-hor) test specimens

Kind and grade of lignin	Lignin admixture, % dry wt. of soil	Specimen dry density, pcf	Specimen moisture content, % dry wt. of specimen	Unconfined compressive strength, lbs*
Spent sulphite liquor	0	103.0	2.71	2683
	1	107.0	6.79	2152
	3	106.5	8.31	1813
	6	105.0	11.00	1100
	9	100.0	8.18	1120
Sulphite lignin grade A	0	103.0	2.71	2683
	1	106.3	4.77	2285
	3	108.0	7.86	1688
	6	106.5	7.90	973
	9	102.8	6.77	973
Sulphite lignin grade D	0	103.0	2.71	2683
	1	107.0	5.17	2292
	3	105.1	5.97	1715
	6	106.5	6.43	1655
	9	103.2	6.42	1163
Bindarene flour	0	103.0	2.71	2683
	1	105.5	3.13	2257
	3	105.0	3.87	2107
	6	104.5	3.58	1583
	9	104.4	3.60	1290
Clarian extract	0	103.0	2.71	2683
	1	106.2	7.08	1538
	3	105.8	8.25	1415
	6	105.6	9.23	1387
	9	105.7	11.28	880

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* Two inch diameter by 2 inch high test specimens.

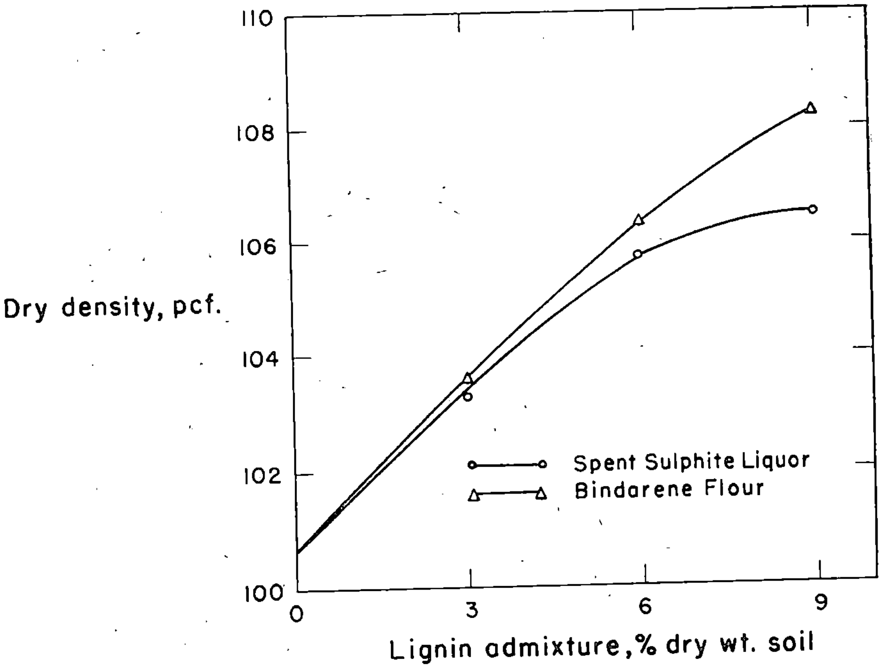

Fig. 8. Variation of maximum dry density of lignin treated A horizon loess (soil sample 207-1) with the amount and kind of lignin.

PRESENTATION AND EVALUATION OF TEST RESULTS

Effect of lignin on moisture density relationship

Work done in the past has shown that the compacted density of a soil is increased by additions of lignin[26]. This is a desirable property change, since an increase in density is usually an indication of an increase in strength.

The test results (table IV) indicate clearly that the use of lignin has a beneficial effect on the compacted density of soil, though no correction has been made in the dry-density values for the amount of lignin present in the soil. The optimum amount of lignin to produce maximum dry density for the compactive effort used lies somewhere between 6 to 9 percent of the dry soil weight (figures 6, 7, 8). No significant increase in density was shown above 6 percent in most. Though it is difficult to single out the lignin having the best effect in density, spent sulphite liquor and bindarene flour may give a slightly higher density.

All the lignin additives reduce the optimum moisture content; this reduction being of significance when the amount of lignin used was between 6 and 9 percent (figures 9, 10, 11).

Effect of lignin on unconfined compressive strength and moisture absorption

The results of the unconfined compressive strength study show that the 7 day air dried strength of the B and C horizon soils were decreased by the addition of lignins (tables V, VI, VII). This trend was not found with the A horizon

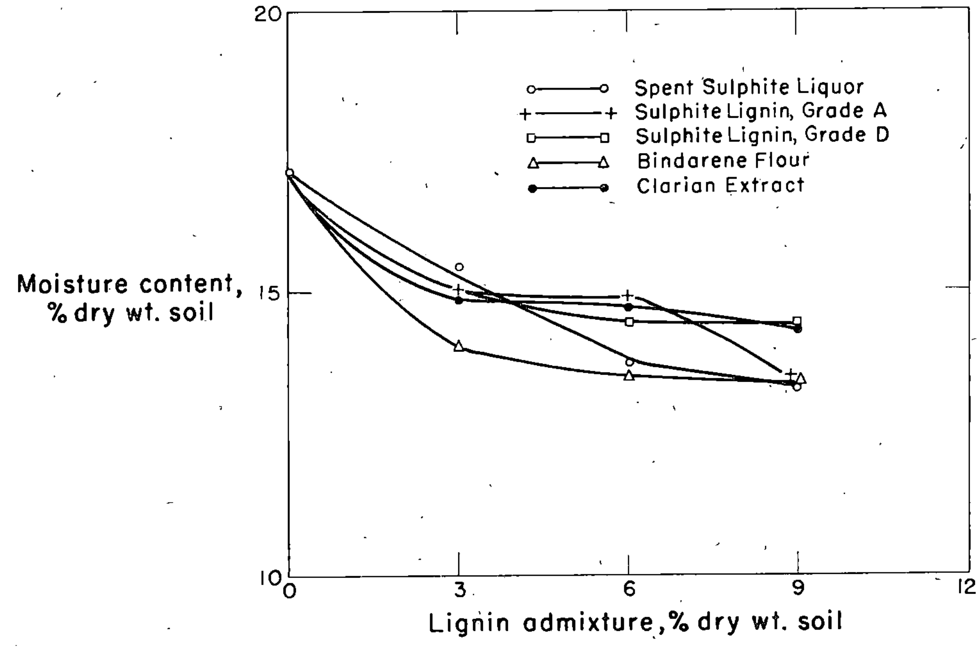

Fig. 9. Variation of optimum moisture content of lignin treated C horizon (soil sample 212-5) with the amount and kind of lignin.

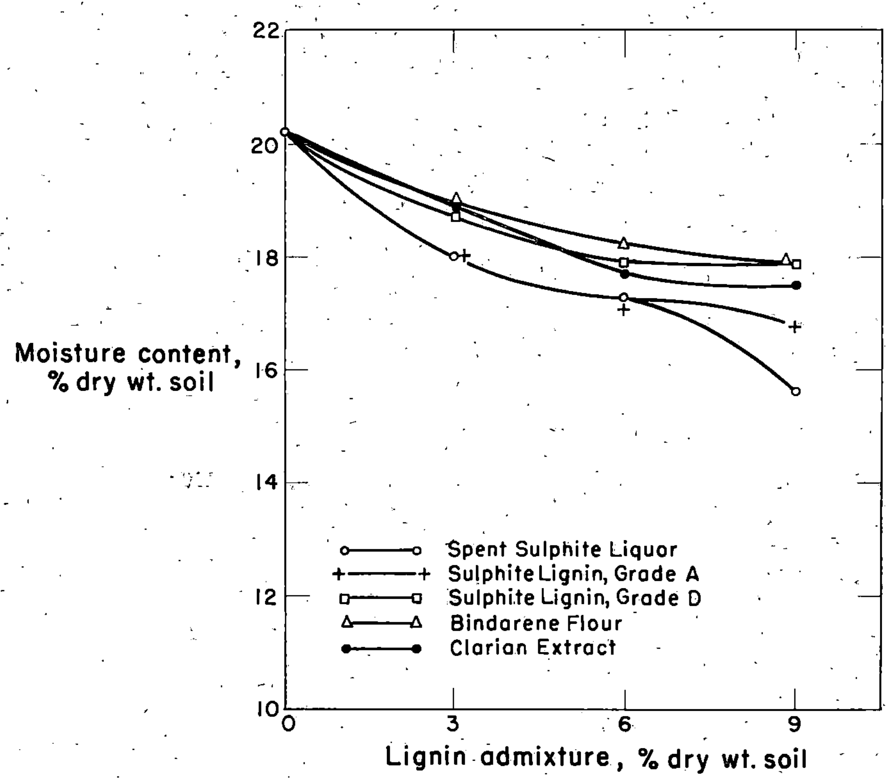

Fig. 10. Variation of optimum moisture content of lignin treated B horizon loess (soil sample 207-2) with the amount and kind of lignin.

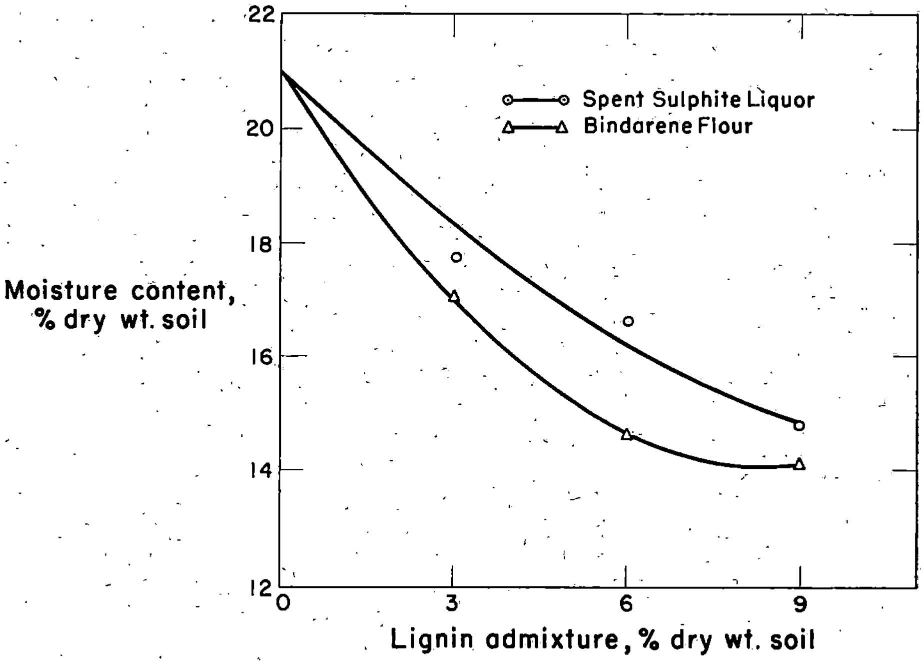

Fig. 11. Variation of optimum moisture content of lignin treated A horizon loess (soil sample 207-1) with the amount and kind of lignin.

TABLE VII. EFFECT OF LIGNIN ADMIXTURES ON UNCONFINED COMPRESSIVE STRENGTH AND RELATED PROPERTIES OF 7 DAY AIR DRIED SOIL 207-1 (A-HOR.) TEST SPECIMENS

Kind and grade of lignin	Lignin admixture, % dry wt. of soil	Specimen dry density, pcf	Specimen moisture content, % dry wt. of specimen	Unconfined compressive strength, lbs*
Spent sulphite lignin, grade D	0	99.0	6.73	1103
	1	100.2	3.35	2350
	3	100.0	2.74	2325
	6	102.5	4.40	2188
	9	98.0	7.13	1102
Bindarene flour	0	99.0	6.73	1103
	1	100.1	1.98	2668
	3	99.7	5.50	1980
	6	105.2	5.68	1687
	9	N.D.	N.D.	N.D.

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*Two inch diameter by 2 inch high test specimens.

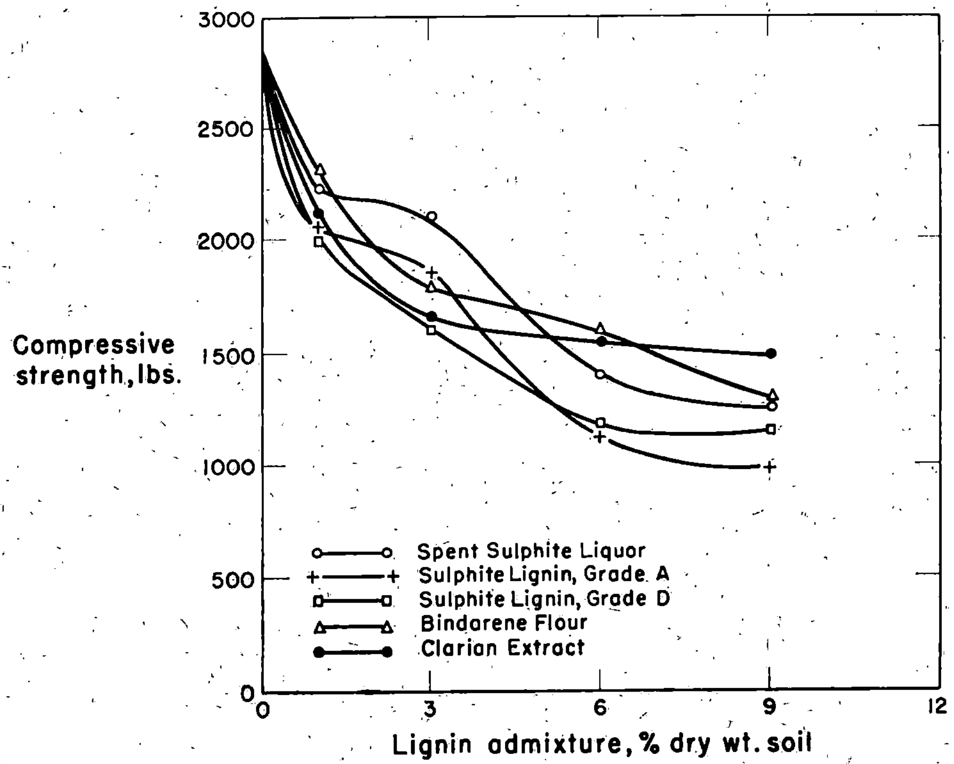

Fig. 12. Variation of 7 day air dried unconfined compressive strength of C horizon loess (soil sample 212-5) test specimens with amount and kind of lignin admixture.

soil, 207-1, whose strength was a maximum with about 1 percent of lignin additive. The reason for the decrease in compressive strength seems to be that the lignin treated soil retains more moisture than the raw soil. It is difficult to rate the lignins on the basis of the comparisons of the effect of the different lignins on the air dried compressive strength of the three soils (figures 12, 13, 14). But, since it is desirable to have as little reduction of strength as possible, bindarene flour and sulphite lignin grade D might be rated slightly higher than the others.

An increase in the amount of lignin additive increased the moisture retention capacity of the B and C horizon soils (figures 15, 16, 17). The different effect of the lignins on the A-horizon soil was undoubtedly related to the organic matter content, and no attempt at further explanation will be made.

When test specimens were air dried for seven days and then were subjected to capillary absorption of moisture for three days before being tested for unconfined compressive strength, a different trend in the compressive strength data was obtained (tables VIII, IX, X).

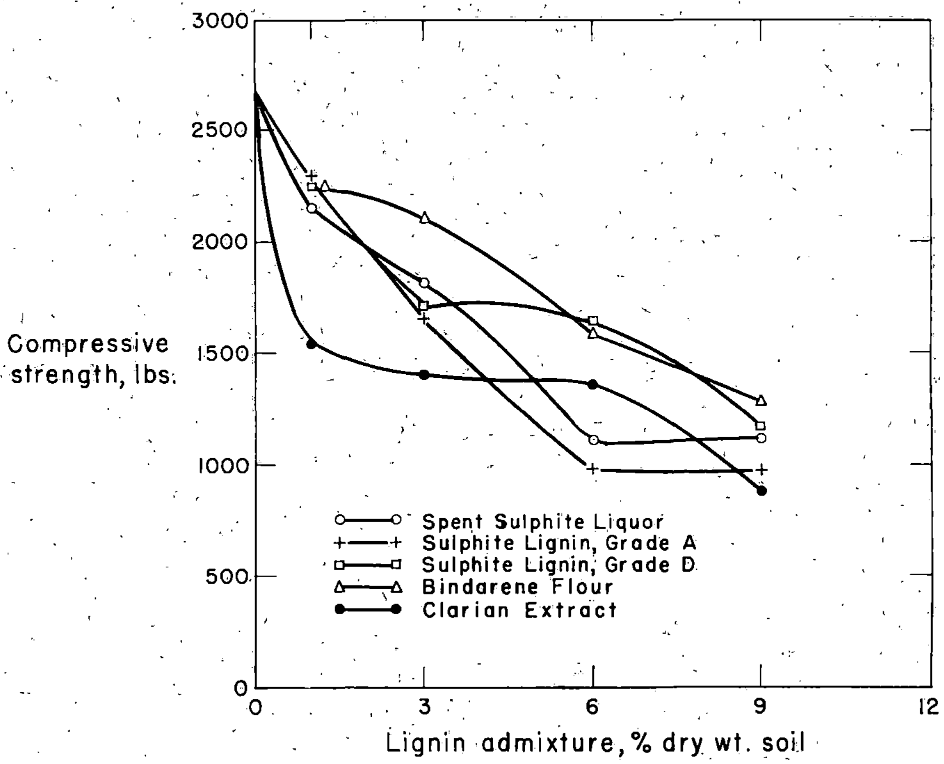

Fig. 13. Variation of 7 day air dried unconfined compressive strength of B horizon loess (soil sample 207-2) test specimens with amount and kind of lignin admixture.

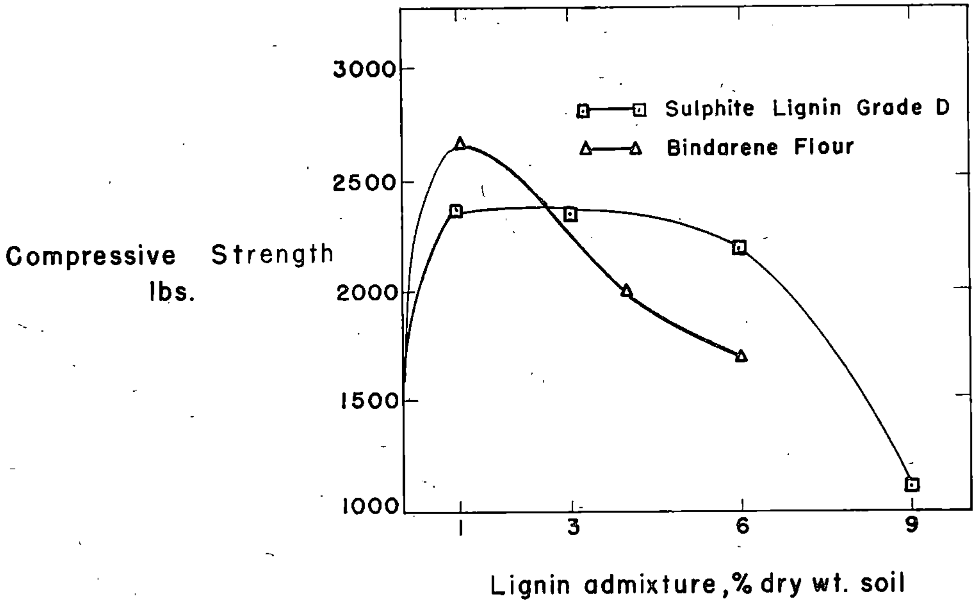

Fig. 14. Variation of 7 day air dried unconfined compressive strength of A horizon loess (soil sample 207-1) test specimens with amount and kind of lignin admixture.

TABLE VIII. EFFECT OF LIGNIN ADMIXTURES ON UNCONFINED COMPRESSIVE STRENGTH AND RELATED PROPERTIES OF 7 DAY AIR DRIED SOIL 212-5 (C-HOR.) TEST SPECIMENS SUBJECTED TO 3 DAYS CAPILLARY MOISTURE ABSORPTION

Kind and grade of lignin	Lignin admixture, % dry wt. of soil	Specimen dry density, pcf	Specimen moisture content, % dry wt. of specimen	Specimen moisture absorption, % dry wt. of specimen	Unconfined compressive strength, lbs.*
Spent sulphite liquor	0	109.4	22.40	18.70	Failed†
	1	110.7	19.83	16.21	35
	3	112.4	14.27	11.54	63
	6	110.5	10.85	4.07	124
	9	112.7	14.20	7.25	22
Sulphite lignin, grade A	0	109.4	22.40	18.70	Failed†
	1	110.7	19.48	16.10	57
	3	110.6	10.57	7.68	103
	6	109.4	8.45	2.51	262
	9	112.3	10.27	3.03	144
Sulphite lignin, grade D	0	109.4	22.40	18.70	Failed†
	1	112.2	18.07	14.08	63
	3	110.3	12.83	8.33	142
	6	111.3	8.83	2.30	183
	9	113.0	12.69	6.99	73
Bindarene flour	0	109.4	22.40	18.70	Failed†
	1	114.3	18.20	15.90	98
	3	110.7	10.40	7.30	120
	6	109.2	8.39	2.50	167
	9	113.8	12.06	5.75	20
Clarian extract	0	109.4	22.40	18.70	Failed†
	1	111.8	17.37	15.70	58
	3	111.6	10.00	5.29	105
	6	109.0	10.00	3.13	200
	9	112.5	12.10	5.98	38

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* Two inch diameter by 2 inch high test specimens.

† Test specimens failed during 3 day capillary absorption period.

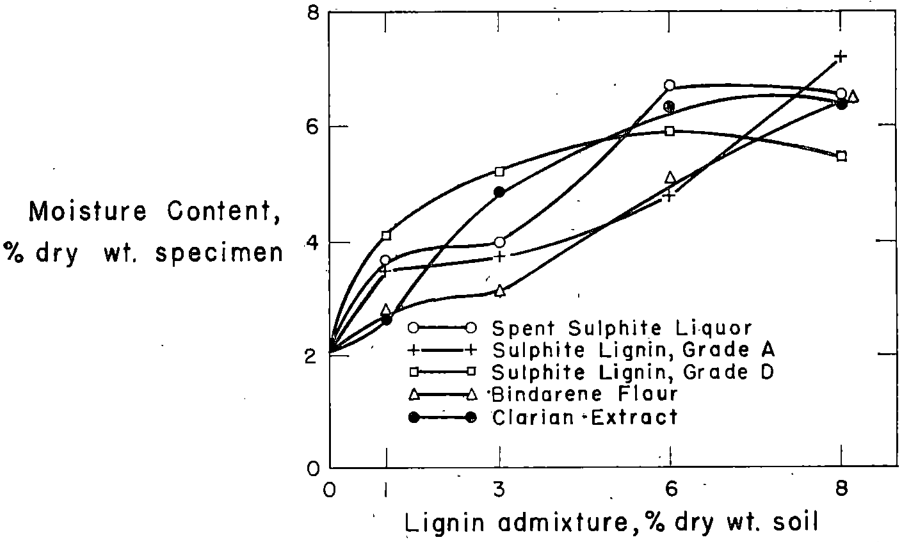

Fig. 15. Effect of amount and kind of lignin admixture on moisture retention of C horizon loess (soil sample 212-5) test specimens after 7 day air drying.

Table IX. Effect of lignin admixtures on unconfined compressive strength and related properties of 7 day air dried soil 207-2 (B-hor.) test specimens subjected to 3 days capillary moisture absorption

Kind and grade of lignin	Lignin admixture, % dry wt. of soil	Specimen dry density, pcf	Specimen moisture content, % dry wt. of specimen	Specimen moisture absorption, % dry wt. of specimen	Unconfined compressive strength, lbs.*
Spent sulphite liquor	0	103.0	26.40	22.40	Failed
	1	106.7	22.50	15.78	73
	3	105.9	15.56	6.74	142
	6	104.7	13.93	3.29	220
	9	100.0	13.00	5.64	50
Sulphite lignin, grade A	0	103.0	26.40	22.40	Failed
	1	106.1	22.70	18.10	87
	3	107.5	13.04	4.70	217
	6	106.3	16.47	2.40	228
	9	102.5	13.66	5.36	26
Sulphite lignin, grade D	0	103.0	26.40	22.40	Failed
	1	107.0	22.10	16.88	55
	3	105.0	10.07	5.16	224
	6	106.5	9.21	3.50	200
	9	103.2	15.20	6.90	58
Bindarene flour	0	103.0	26.40	22.40	Failed
	1	104.0	18.70	15.80	63
	3	103.0	8.60	4.40	234
	6	105.0	5.79	2.31	209
	9	N.D.	N.D.	N.D.	N.D.
Clarian extract	0	103.0	26.40	22.40	Failed
	1	106.2	22.80	15.50	45
	3	106.4	14.63	6.40	210
	6	105.3	12.30	3.92	232
	9	104.8	11.80	3.90	40

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* Two inch diameter by 2 inch high test specimens.

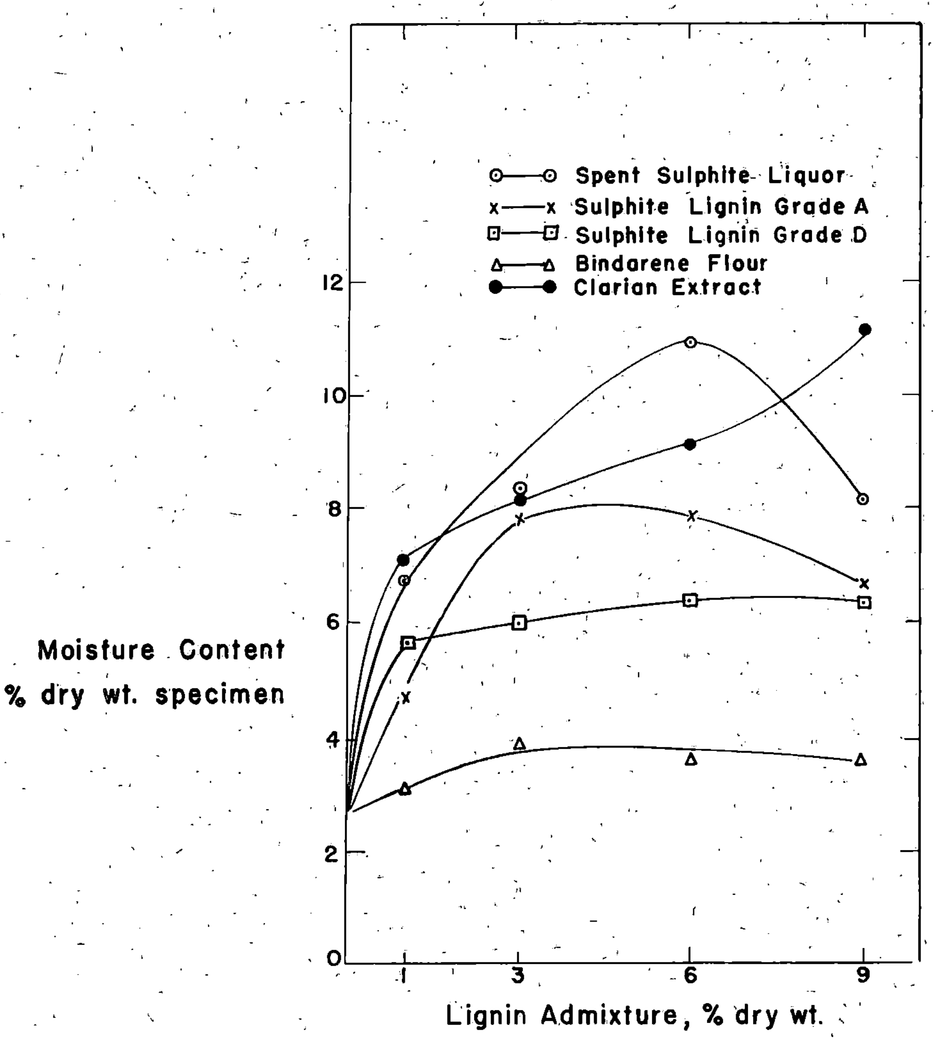

Fig. 16. Effect of amount and kind of lignin admixture on moisture retention of B horizon loess (soil sample 207-2) test specimens after 7 day air drying.

Table X. Effect of lignin admixtures on unconfined compressive strength and related properties of 7 day air dried soil 212-5 (A-hor.) test specimens subjected to 3 days capillary moisture absorption

Kind and grade of lignin	Lignin admixture, % dry wt. of soil	Specimen dry density, pcf	Specimen moisture content, % dry wt. of specimen	Specimen moisture absorption, % dry wt. of specimen	Unconfined compressive strength, lbs.[*]
Sulphite lignin, grade D	0	99.2	42.50	36.20	Failed
	1	99.5	26.80	23.60	25
	3	100.1	16.52	13.41	56
	6	102.3	11.02	6.10	200
	9	97.4	26.30	10.50	31
Bindarene flour	0	99.2	42.5	36.2	Failed
	1	99.4	27.80	25.20	26
	3	103.2	16.52	12.20	87
	6	104.3	10.31	5.68	193
	9	102.0	18.30	7.20	40

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[*] Two inch diameter by 2 inch high test specimens.

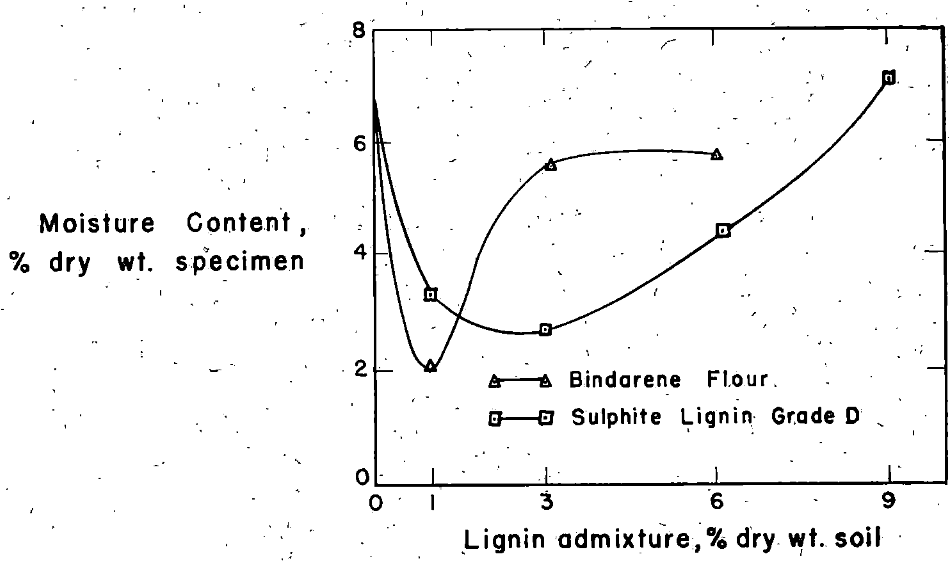

Fig. 17. Effect of amount and kind of lignin admixture on moisture retention of A horizon loess (soil sample 207-1) test specimens after 7 day air drying.

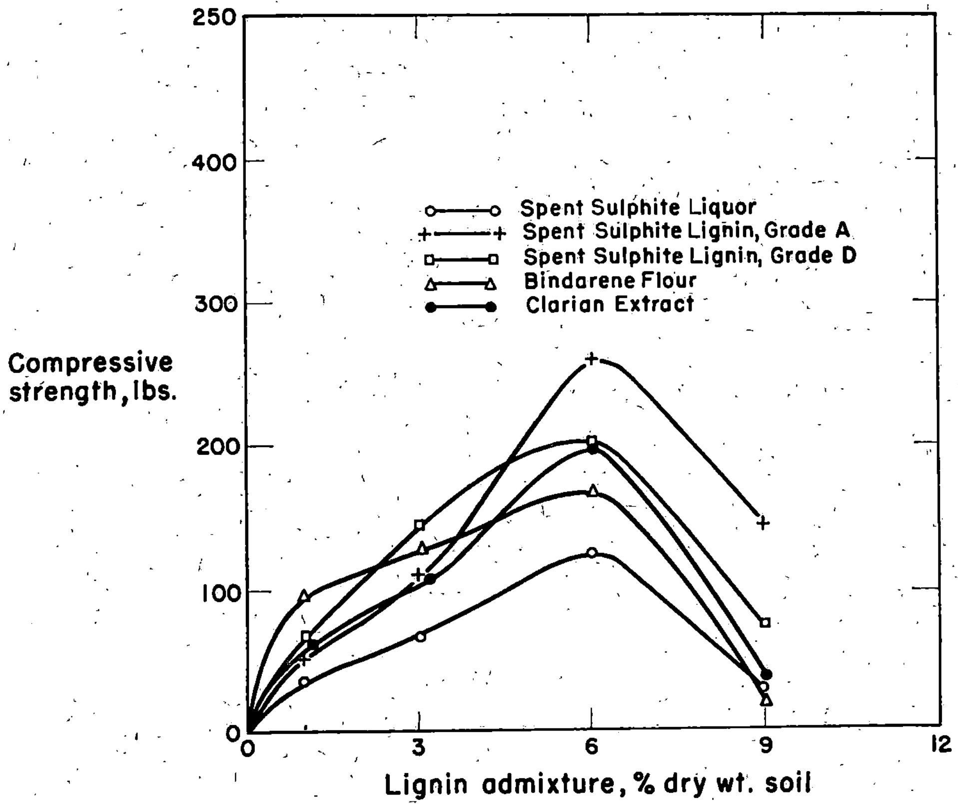

Fig. 18. Variation of 7 day air dried plus 3 day capillary moisture absorption unconfined compressive strength of C horizon loess (soil sample 212-5) test specimens with amount and kind of lignin admixtures.

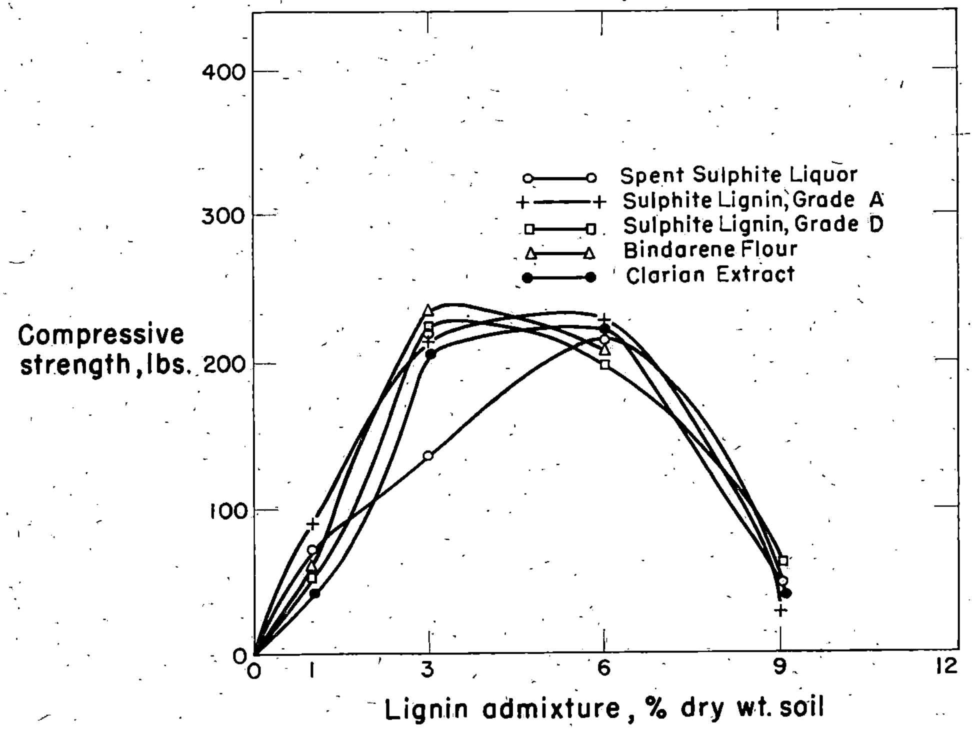

Fig. 19. Variation of 7 day air dried plus 3 day capillary moisture absorption unconfined compressive strength of B horizon loess (soil sample 207-2) test specimens with amount and kind of lignin admixtures.

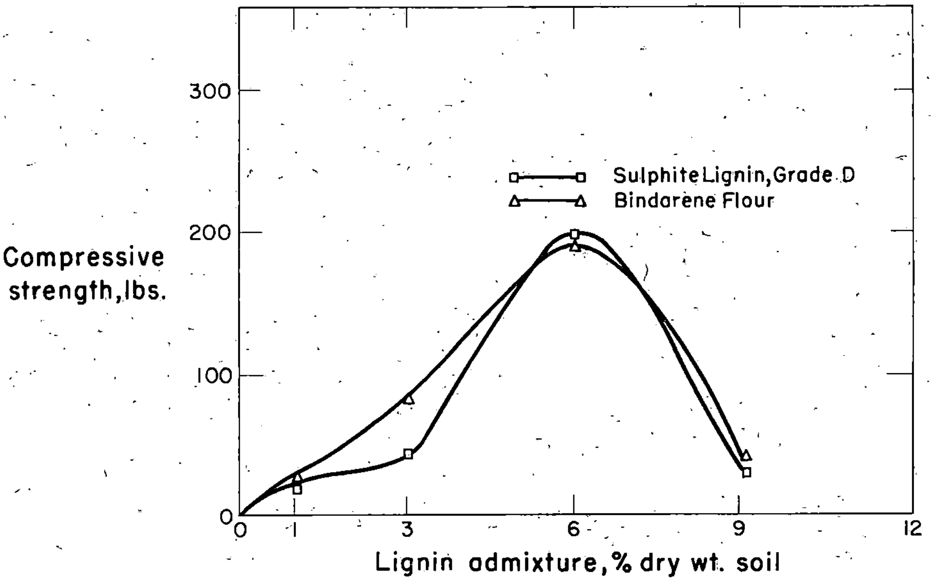

Fig. 20. Variation of 7 day air dried plus 3 day capillary moisture absorption unconfined compressive strength of A horizon loess (soil sample 207-1) test specimens with amount and kind of lignin admixtures.

Specimens containing no lignin additive fell apart in the strength tests during the capillary absorption period (figures 18, 19, 20). Though the strength of the lignin treated specimens was greatly reduced by capillary absorption, all remained intact and could be tested. Best strength results were obtained when the amount of additive was in the range of 6 to 9 percent; in most cases, about 6 percent was the optimum amount. Inspection of the moisture absorption data (figures 21, 22, 23) shows that moisture absorption was also near the minimum amount when the lignin admixture was about 6 percent. The correlation of specimen density (tables VIII, IX, X) with strength and moisture absorption is not as good as the correlation between strength and moisture absorption, but there is an indication that some of the waterproofing and strength preservation is related to the beneficial effect of lignin on soil density.

The data presented are not enough to rate the lignins as waterproofers, but note that the difference in results was least with the soil having the highest clay content, the B horizon loess; all the lignins gave this soil about the same degree of waterproofness. With the C horizon loess, sulphite lignin grade A, and clarian extract gave the best results. Only sulphite lignin grade D and bindarene flour were evaluated with the A horizon loess, and there was only a slight difference in test results.

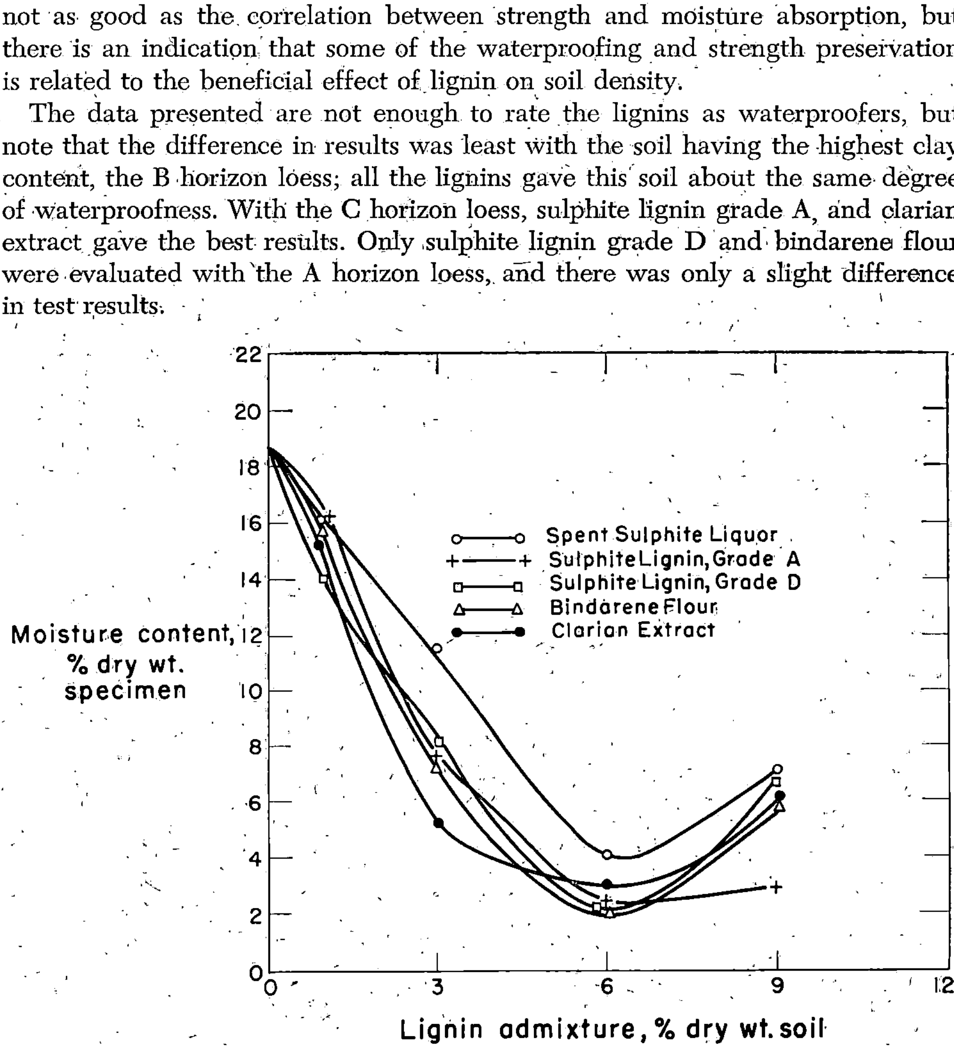

Fig. 21. Effect of amount and kind of lignin admixture on moisture content of 7 day air dried C horizon loess (soil sample 212-5) test specimens subjected to 3 days capillary moisture absorption.

TABLE XI. EFFECT OF LIGNIN ADMIXTURES ON CONSISTENCY LIMITS OF C-HORIZON AND B-HORIZON LOESS*

Types of mixture	Curing period, days	Liquid limit, %	Plastic limit, %	Plasticity index	pH
Raw soil 212-5 (C-hor.)	0	34.7	20.3	14.4	7.5
	2	33.4	20.3	13.1	7.4
	7	33.8	20.4	13.4	7.4
Soil stabilized with 6% sulphite lignin grade A	0	33.4	14.4	19.0	6.90
	1	32.6	14.8	17.8	7.4
	2	36.7	15.2	21.5	7.48
	4	35.4	14.9	20.5	
	7	36.7	16.5	20.2	
Soil stabilized with 6% sulphite lignin grade D	0	33.5	14.9	18.6	6.85
	1	32.5	14.7	17.8	7.50
	2	37.0	19.5	18.5	7.46
	4	36.5	17.9	18.6	7.62
	7	N.D.	N.D.	N.D.	7.60
Raw soil 207-2 (B-hor.)	0	47.2	22.3	24.9	6.95
	2	46.3	20.4	25.9	6.94
	7	46.2	19.8	26.5	6.93
Soil stabilized with 6% sulphite lignin grade A	0	46.0	16.1	29.9	4.71
	1	56.8	18.4	38.4	5.01
	2	53.8	19.0	34.8	5.08
	4	50.0	19.9	30.1	5.10
	7	44.6	20.1	24.5	5.18
Soil stabilized with 6% sulphite lignin grade D	0	47.9	18.6	29.3	4.56
	1	56.9	18.4	38.5	5.05
	2	52.0	19.0	33.0	4.93
	4	49.6	21.2	28.4	5.08
	7	47.0	19.2	28.8	5.10

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* Two inch diameter by 2 inch high specimens were molded, air-dried for the period indicated, then crushed to pass the No. 10 sieve prior to performing tests.

Effect of lignin on L.L., P.L., P.I., and pH

The test data definitely indicate that 6 percent admixture of sulphite lignin grade A and sulphite lignin grade D increased the plasticity indices of the C-horizon and B-horizon loess (table XI). The increase is mainly due to the lowering of the plastic limit, although there is some indication that the liquid limit increased slightly with air curing. The increase in plasticity is probably related to the fact that lignin is a dispersing agent, and when incorporated in soil it increases the effective surface area, especially that of the clay-size fraction. In general, the air curing data are too erratic for definite conclusions concerning the effect of length of curing time on the consistency limits.

The pH of the raw soil was not significantly effected by curing time (table XI); that of the lignin-treated soils showed a slight increase at 1 day curing time, but thereafter, the specimens remained more or less constant.

Effect of lignin admixtures on C.B.R.

The California Bearing Ratios of the three soils were decreased by the 6 percent admixtures of sulphite lignin grade D, and spent sulphite liquor. This was generally true for both the "as molded" and "soaked 4 days" test condition (table XII). Swelling and moisture absorption were increased by the lignin

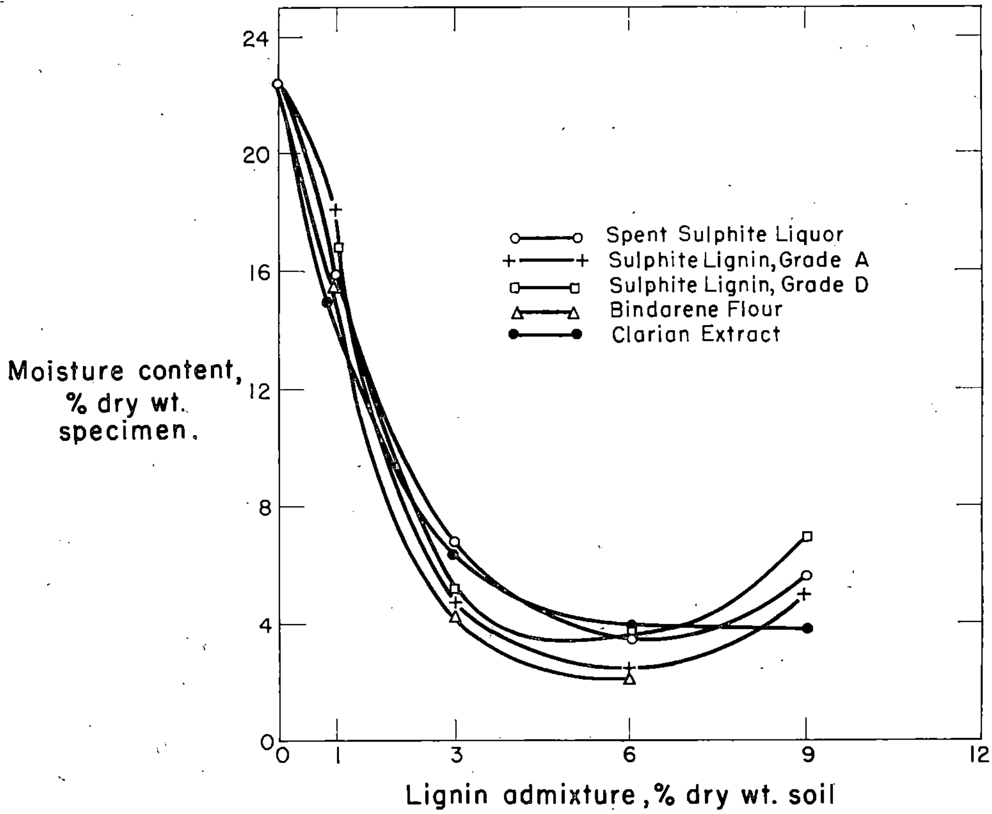

Fig. 22. Effect of amount and kind of lignin admixture on moisture content of 7 day air dried B horizon loess (soil sample 207-2) test specimens subjected to 3 days capillary moisture absorption.

TABLE XII. EFFECT OF LIGNIN ADMIXTURES ON C.B.R. AND RELATED PROPERTIES OF A, B, AND C-HORIZON LOESS

Mixture	As molded	Soaked 4 days		
	C.B.R. 0.1 in. penetration	C.B.R. 0.1 in. penetration	Swell, %	Absorption, %
Raw soil 212-5 (C-hor.)	17.8	7.7	0.36	N.D.
Soil 212-5 + 6% sulphite lignin grade D	14.2	7.9	0.34	3.2
Soil 212-5 + 6% spent sulphite liquor	14.1	4.4	0.52	5.1
Raw soil 207-2 (B-hor.)	11.4	9.0	0.52	1.9
Soil 207-2 + 6% sulphite lignin grade D	7.5	0.7	2.60	10.9
Soil 207-2 + 6% spent sulphite liquor	7.8	1.4	2.18	8.8
Raw soil 207-1 (A-hor.)	15.0	7.1	0.56	1.8
Soil 207-1 + 6% spent sulphite liquor	10.7	2.2	1.32	12.1

admixtures. The soils highest in clay and organic matter, the A and B horizon soils, were most adversely affected by the admixtures. The adverse effect of lignin on the bearing capacity of the soils, as measured by the C.B.R. test procedure used, may be due to:

1. The dispersing effect of lignin on soil,
2. The leaching out of the lignin during four days complete immersion, and
3. The lack of proper curing of the lignin treated soils prior to the C.B.R. test.

Effect of method of curing on bearing strength

The Iowa Bearing Value test study of the effect of moist and air curing on the bearing strength and related properties of lignin-treated soils was an extension of the C.B.R. study, since in the C.B.R. study the method of curing was not a variable. The reason for using the IBV test method instead of the C.B.R. has been discussed.

The data indicate that the strength of air cured specimens increased with increase of curing time (tables XIII, XIV, Figure 24). The effect of curing time is

TABLE XIII. IOWA BEARING VALUE TEST DATA FOR AIR CURED SPECIMENS OF SOIL 212-5 (C-HOR.) TREATED WITH 6 PERCENT SPENT SULPHITE LIQUOR

No. of days air-cured*	No. of days immersed	Specimen dry density,† pcf	Absorption,‡ %	Expansion,§ %	IBV strength, lbs. at 0.2 in. penetration
0	0	113.4	...	...	111
0	7	113.0	N.D.	N.D.	62
1	0	115.0	...	...	157
1	7	115.0	3.99	0.25	65
3	0	113.6	...	...	215
3	7	114.3	6.36	0.08	63
4	0	115.8	...	...	242
4	7	116.2	6.12	0.15	61
5	0	115.2	...	...	260
5	7	115.2	6.53	...	55
6	0	115.4	...	...	285
6	7	116.3	6.44	0.64	60
7	0	113.4	...	...	290
7	7	114.4	6.8	0.3	67
10	0	114.8	...	...	323
10	7	114.6	8.83	0.87	67
12	0	114.9	...	...	333
12	7	115.1	10.57	0.35	48
14	0	114.5	...		358
14	7	115.0	8.9	0.85	66
21	0	114.5	...	...	407
21	7	113.7	6.7	0.77	71

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* Curing was at room temperature which averaged about 77°F.

† No correction was made in the density for the amount of lignin present in the specimens.

‡ Absorption is the amount of water absorbed by the specimens, expressed as percent dry weight of specimens, after 7 days complete immersion.

§ Expansion is the percent increase of the specimen's height over its original height after 7 days complete immersion.

TABLE XIV. IOWA BEARING VALUE TEST DATA FOR MOIST CURED SPECIMENS OF SOIL 212-5 (C-HOR.) TREATED WITH 6 PERCENT SPENT SULPHITE LIQUOR

No. of days moist-cured[*]	No. of days immersed	Specimen dry density,[†] pcf	Absorption,[‡] %	Expansion,[§] %	IBV strength, lbs. at 0.2 in. penetration
0	0	113.4			111
0	7	113.5	2.57	0.75	58
2	0	114.5			152
2	7	114.0	2.54	0.70	76
6	0	115.5			145
6	7	114.8	2.78	0.62	65
7	0	114.8			148
7	7	115.5	5.11	0.35	76
10	0	114.2			147
10	7	115.0	1.33	0.48	79
14	0	116.2			142
14	7	113.6	3.79	0.55	77
21	0	115.8			137
21	7	115.6	1.81	N.D.	72
28	0	115.0			133
28	7	116.0	0.86	0.35	75

---

[*] Relative humidity was 90 to 95% and temperature about 70°F.

[†] Density was determined at optimum moisture content. No correction was made for the amount of lignin present in the soil sample.

[‡] Absorption is the amount of water absorbed by the specimens expressed as percent dry weight of specimens, after 7 days complete immersion.

[§] Expansion is the percent increase of the specimen's height over its original height after 7 days complete immersion.

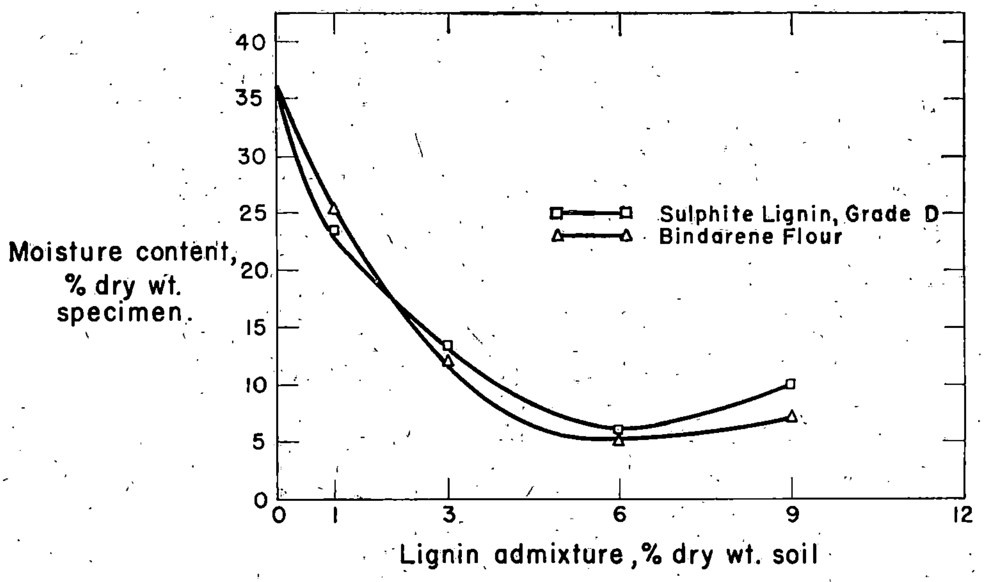

Fig. 23. Effect of amount and kind o flignin admixture on moisture content of 7 day air dried A horizon loess (soil sample 207-1) test specimens subjected to 3 days capillary moisture absorption.

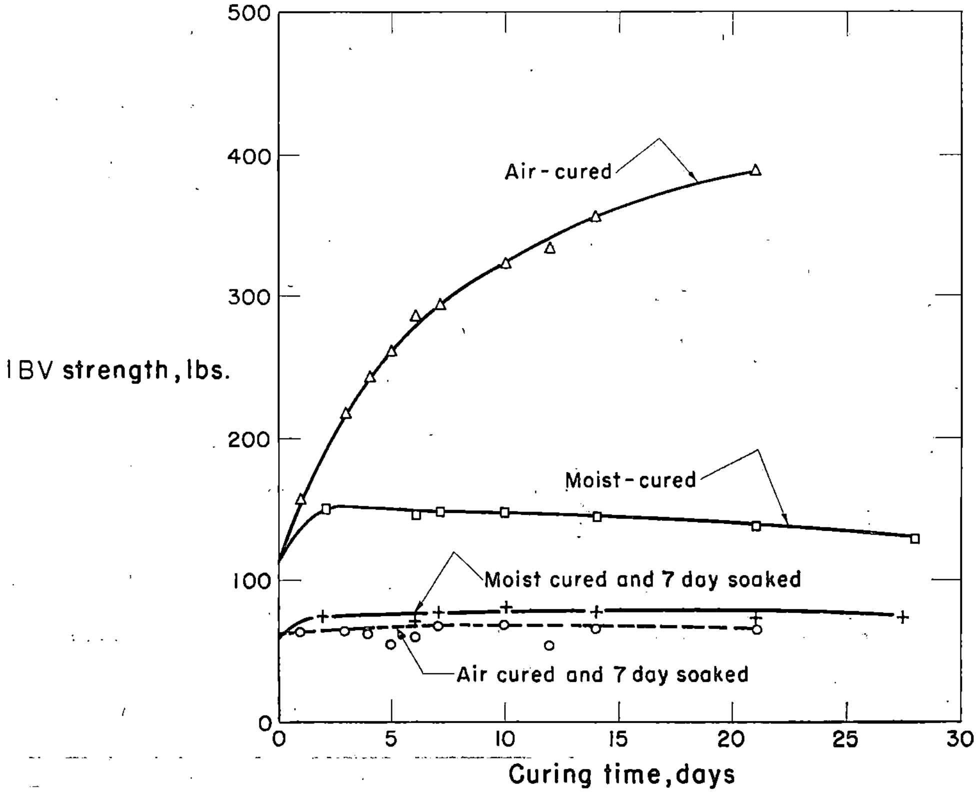

Fig. 24. Comparison of air curing and moist curing on the bearing strength (IBV) of C horizon loess (soil sample 212-5) treated with 6 percent spent sulphite liquor.

not very pronounced in the data on moist-cured specimens; they gained some strength during the first seven days of moist curing, and then gradually lost some of the strength gain throughout the remainder of the 28 day curing period. Without the 7 day immersion treatment, the strengths of moist cured specimens were much lower than those of air cured specimens.

After seven days of immersion in water, the strengths of both air cured and moist cured specimens were low; length of curing prior to immersion had little effect on the immersed strength. Moist cured specimens showed less decrease of strength and had slightly higher strength after immersion than did air cured specimens. Also, moist cured specimens absorbed less moisture than air cured specimens. The expansion data are too eratic for comparisons.

CONCLUSIONS

1. Lignins used alone as admixtures do not show much promise as stabilizing agents for loess or loess derived soils. The findings of the investigation do, however, indicate that lignins should be much more effective as stabilizing agents for granular soils or soil aggregate mixtures. This should be verified.

2. Lignin admixtures do improve some engineering properties related to stability of soil; they increase compacted density and retard absorption of moisture, though the latter benefit may be temporary if leaching out of the lignin occurs. The effect of the lignins on frost action was not investigated.

3. Lignin admixtures increase the moisture retention capacity of soil. Because of this, air dried strength of lignin treated soil may be lower than that of the raw soil dried for the same length of time. The strength of lignin treated soil increases rapidly with increase in length of air curing, and elevated temperature drying would probably be beneficial.

4. Moist curing of lignin treated soil specimens results in much lower strength than air curing, but moist cured specimens absorb less moisture and have slightly higher strength after immersion in water. The length of moist curing does not seem to have much effect on moist cured or immersed strength.

5. Lignin admixtures increase the plasticity index of soil; the amount of increase is greatest for soils having the highest clay and organic matter contents. Lignins do not appreciably change the soil pH value.

6. Lignin in powdered form was easier to use than lignin in liquid form; otherwise, the five lignins used gave much the same results.

7. There is an indication that the optimum amount of lignin admixture (dry solids basis) is about 6 percent of the soil dry weight.

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STABILIZATION OF A CALCAREOUS LOESS WITH CALCIUM LIGNOSULFONATE AND ALUMINUM SULFATE

by

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(Iowa Academy of Science Proceedings. 1960)

ABSTRACT

Spent sulfite liquor, a by-product of the paper industry, is produced in large quantities in many parts of the world. Because production far exceeds utilization, and because spent sulphite liquor pollutes water, disposal is a difficult problem. A method of disposal economical near paper mills is to use the liquor as a dust palliative for gravel surfaced roads; but the liquor is water soluble and must be periodically re-applied. Spent sulfite liquor is so used only near paper mills where the liquor is cheap. A method of producing an insoluble dust palliative or soil stabilizing agent from spent sulfite liquor would greatly increase its use in states such as Iowa, that do not have a paper industry.

INTRODUCTION

Because of its water solubility the use of spent sulfite liquor in road construction has been limited mainly to dust palliation in areas near paper mills producing large quantities of this by-product or waste chemical[4, 5, 7, 14, 19, 20, 22, 23, 24, 25, 26, 27, 28, 29, 37, 38, 41, 42, 44, 45]. Attempts have been made to reduce the water solubility by physical or chemical means. Selection of proper soil gradation and compaction of treated soils to suitable densities to reduce leaching by water are the principal physical methods which have been studied[3, 19, 32, 38, 43]. Chemical methods consist of producing insoluble lignosulfonates by use of secondary additives[12, 13, 16, 18, 31, 33, 35, 37, 39, 46]. Calcium hydroxide and chromates are the only chemicals extensively studied for insolubilizing spent sulfite liquor for soil stabilization.

Ca-lignosulfonate, the main constituent of spent sulphite liquor, forms insoluble compounds with polyvalent metallic cations in an alkaline environment[5, 18, 46]. This suggested the possibility of using salts of polyvalent metallic cations as secondary additives for spent sulfite liquor soil stabilization. A preliminary screening of such chemicals showed aluminum sulfate[15, 21] to be the most promising. The alkaline environment required for the formation of the insoluble lignosulfonate compounds was provided by $CaCO_3$ in the soil, either naturally present or added.

The effects of Ca-lignosulfonate—Al-sulfonate on the engineering properties and behavior of a calcareous, friable Wisconsin age loess were studied as the major part of this investigation. The effects of amount of additives on optimum moisture, maximum dry density, unimmersed strength, and immersed strength were studied. Optimum moisture and maximum dry density of the soil were greatly affected by the combination chemical treatment; unimmersed strength was somewhat reduced, but satisfactory immersed strength was obtained. Both strengths indicated that the degree of stabilization might be satisfactory for road base courses. The durability of untreated and treated soil specimens was evaluated by a modified standard British freeze-thaw test. Though the untreated soil specimens failed as expected, the durability of treated specimens was judged sufficient for road subbases in northern climates. Shrinkage and expansion upon wetting and drying of treated specimens were reduced.

The mechanism of the waterproofing obtained by the combination chemical treatment was analyzed as to the effect of basic aluminum lignosulfonate micelles on the surface tension of water. These micelles reduce the surface

TABLE I. DESCRIPTION AND PROPERTIES OF THE LOESS SAMPLE (LAB. NO. 20-2-VII).

Geological description:	Wisconsin age loess, oxidized; thickness over 100 ft.
Location:	Harrison Co., S.W. Iowa
Soil series:	Hamburg
Horizon	C
Sampling depth, ft.	39-40
Textural composition, %	
Gravel (> 2.00 mm)	0
Sand (2.00-0.074 mm)	0.4
Silt (0.074-0.005 mm)	80.0
Clay (< 0.005 mm)	19.6
Colloids (< 0.001 mm)	14.5
Predominant clay mineral:[*]	Montmorillonite
Chemical properties:	
Cat. ex. cap., m.e./gm[†]	13.4
Carbonates,[†] by versonate method[‡]	10.2
Fizzing when treated with N.HCl	Strong
pH	8.7
Organic matter,[†] %	0.2
Physical properties:[§]	
Liquid limit, %	30.8
Plastic limit, %	24.6
Plasticity index	6.2
Shrinkage limit, %	22.3
Classification:	
Textural[**]	Silty clay loam
Engineering (AASHO)	A-4(8)
Max. dry density, pcf	107.5
Optimum moist., %	18.0

[*] By X-ray diffraction analysis.
[†] For fraction passing No. 10 sieve.
[‡] Includes all extractable calcium.
[§] For fraction passing No. 40 sieve.
[**] From triangular chart developed by U.S. Bureau of Public Roads, but 0.074 mm was used as the lower limit of the sand fraction.

tension of the water in which they are suspended. Thus soil particles coated with a concentrated suspension have less surface free energy than those coated with a dilute suspension, and consequently absorb less water.

LABORATORY INVESTIGATION

Properties of Materials Used

Soil. The soil used is typical of the thick loess bordering the Missouri River floodplain in western Iowa. The sample was obtained from a bluff behind the Third Ward School in the city of Missouri Valley (table I).

Chemicals. Properties of the spent sulfite liquor sample used will be referred to as Ca-lignosulfonate, the principal constituent of the solids fraction (table II).

The aluminum sulfate sample ($Al_2(SO_4)_3 \cdot 18H_2O$), a chemically pure grade, will be referred to as Al-sulfate.

Method of Investigation

Mixing. Three orders of mixing chemicals with the soil were tried. In the first, an amount of spent sulfite liquor calculated to give a desired percentage of Ca-lignosulfonate was added to the soil by weight and mechanically mixed with a Hobart mixer for one minute. This was followed by a hand mixing to insure proper distribution and pulverization. Next a calculated amount of Al-sulfate solution was added to give a desired amount of Al-sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) and water. The mixture was mechanically mixed for two minutes. This was followed by a hand mixing for pulverization, and another two minutes of mechanical mixing by the Hobart mixer. After the mixing operations the mixture was kept covered with a damp cloth for fifteen minutes to allow time for reactions to be completed. At the conclusion of fifteen minutes the mixture was pulverized and mixed with an additional hand mixing. The fifteen minute reaction period was determined experimentally; if this period was not used successive molded specimens showed rapid increases in height and decreases in density, believed due to chemical reactions taking place.

TABLE II. PROPERTIES OF SPENT SULFITE LIQUOR*

Trade name	Toranil A
Concentration	50% water solution
Ca-lignosulfonate	96% of the total solid constituents
Appearance	Coffee-colored viscous liquid
Odor	Characteristic tart
Specific gravity $\frac{60°F}{60°F}$	1.24
Baumé	28.5°
Viscosity (cp) 70°C	45
50°C	130
30°C	420
pH	4.5-4.6
Boiling range	107°C-108°C
Freezing range	−4°C- −6°C
Surface tension, Dynes/cm (10% water solution)	48

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[*] From the data supplied by the manufacturer, Lake States Yeast Corporation, Rhinelander, Wisconsin.

In the second order of mixing, the sequence of adding spent sulfite liquor and aluminum sulfate solution was reversed, but the rest of the mixing procedure remained the same.

In the third order of mixing, spent sulfite liquor and aluminum sulfate solution were mixed together before adding to the soil. The same steps of mechanical mixing and hand mixing were followed.

From the effect of mixing order on the strength characteristics and related properties of a selected soil-chemicals mix, it was concluded that the first mixing order was slightly better, and this mixing order was used in the main study (table III).

Molding. Immediately after mixing, six specimens from each mixture were molded into cylinders by means of a drop hammer molding apparatus[9]. This apparatus produces a specimen two inches in diameter and two inches high. The cylindrical mold is filled with a sufficient quantity of soil, chemical, and water mixture to produce a two by two inch specimen, and the mixture is compacted by dropping a five pound hammer through a distance of one foot five times on each side of the specimen. A temporary support is placed under the mold to hold it in position and is removed after the first blow.

After compaction, specimens were ejected from the molds with a hydraulic jack. They were then weighed to the nearest 0.1 gram and their heights measured to the nearest 0.001 inch. A tolerance of ±0.05 inch in height was maintained in all specimens molded. Representative moisture samples were taken from the mixing bowl, and a moisture content for each mixture was determined, on the basis of oven dry weight of soil, to the nearest 0.1 percent. This moisture content will be referred to hereafter as "moisture at molding."

Curing. The prepared specimens were cured by air drying for seven days at room temperatures and humidities. This time was considered adequate to establish constant specimen weight[38]. Heights and weights of specimens were again measured after being cured. Three of the six specimens molded from each mixture were tested for unconfined compressive strength, and the other three were completely immersed in distilled water for a period of twenty-four hours.

TABLE III. EFFECT OF MIXING ORDER OF ADDITIVES ON STRENGTH OBTAINED BY TREATING THE LOESS WITH 6% CA-LIGNOSULFONATE AND 5% AL-SULFATE

Mixing order First additive	Second additive	Moisture at molding, %	Dry density at molding moisture, pcf	Average immersed strength,* psi	Average unimmersed strength,† psi	Average relative humidity during-curing period, %
Ca-lignosulfonate	Al-sulfate	19.1	103.4	122	556	70
Al-sulfonate	Ca-lignosulfonate	19.0	104.4	124	498	70
Mixture of the two additives	....	19.0	101.1	99	534	70

* Air cured at room temperature 7 days, immersed in distilled water 1 day.
† Air cured at room temperature 7 days.

Each specimen was weighed, measured and tested for unconfined compressive strength after it was taken from the water.

Testing for unconfined compressive strength. The unconfined compressive strengths of the specimens in dry and immersed conditions were determined by a proving ring type testing machine. Load was applied to each specimen with a rate of deformation of 0.10 inch per minute until complete failure was reached. The maximum load in pounds divided by the cross-sectional area of the specimen was recorded as the unconfined compressive strength. The unconfined compressive strengths after seven days drying in the laboratory atmosphere were referred to as "unimmersed strengths." The unconfined compressive strengths after seven days drying in the laboratory atmosphere and twenty-four hours immersion are referred to as "immersed strengths."

Determination of dry densities. Dry densities of specimens were calculated from the weight and height measurements taken immediately after molding and moisture contents during molding. This density is referred to as "dry density at molding moisture."

Determination of linear shrinkage. Linear shrinkage expressed as percentage of air dried sample height was calculated from the height measurements taken after molding and after seven days drying.

Determination of moisture retention. Moisture retention expressed as percentage of oven dry weight of sample was calculated from the weight measurements taken after molding and after seven days drying.

Calculation of linear expansion upon immersion. Expressed as percentage of air dried sample height linear expansion upon immersion was calculated from the height measurements taken after seven days drying and twenty-four hours immersion.

Calculation of total water absorption during immersion. Total water absorption expressed as percentage of oven dry weight of sample was calculated from the weight measurements taken after molding and after twenty-four hours immersion. The total water absorption is referred to as "water absorption."

Effect of relative humidity variations during the curing (drying) period. Daily records of relative humidity were taken and averaged for each curing period. Specimens of the same compositions but molded at different times and cured in atmospheres with different relative humidities varied considerably in strengths (table IV).

TABLE IV. EFFECT OF RELATIVE HUMIDITY DURING CURING ON STRENGTHS OBTAINED BY TREATING THE LOESS WITH 6% CA-LIGNOSULFONATE AND 5% AL-SULFATE

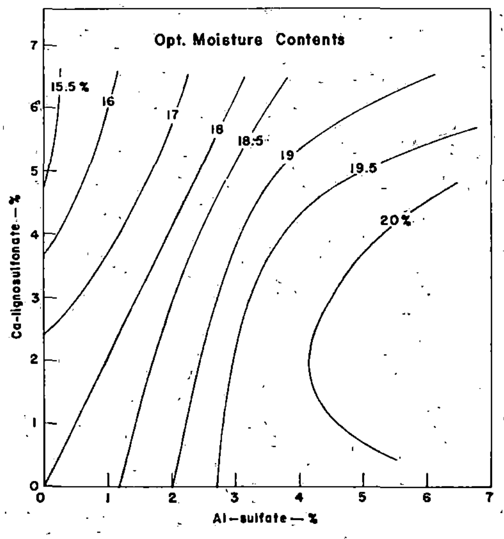
Moisture at molding, %	Dry density at molding, pcf	Time of curing at relative humidities indicated, days	Relative humidity built up by desicator solutions, %	Relative humidity ÷ 35	Moisture retention after 7-day curing, %	Average immersed strength, psi	Average unimmersed strength, psi
19.3	103	7	35	1	7	101	406
19.3	103	7	65	1.9	9	71	208
19.3	103	7	90	2.6	11	59	154

Freeze-thaw test. Six specimens from a selected mixture (6% Ca-lignosulfonate, 5% Al-sulfate, 19% water) and six specimens from untreated friable loess were molded at optimum moisture and cured for seven days in the laboratory atmosphere. After curing they were subjected to a freeze-thaw test based on the British Standard Test 1924:1957[8]. Half of the specimens prepared from the same batch were immersed for fifteen days in distilled water. The remaining specimens were immersed one day in distilled water and then were given 14 cycles of alternate freezing and thawing suspended in holders in thermos bottles (figure 7) containing enough water at 8±2°C to cover the bottom 0.25 inch of specimens. (The thermos bottle specimen container was used to cause freezing to occur from the top down and to supply unfrozen water to the bottom of the specimen throughout the test.) One freeze-thaw cycle consisted of 16 hours freezing at 5±1°C and 8 hours thawing at 25°C. At the completion of freeze-thaw cycles and immersion, all specimens were weighed, measured for height and tested for unconfined compressive strength.

PRESENTATION AND DISCUSSION OF RESULTS

Effect of the Additives on Optimum Moisture Maximum Dry Density, Immersed and Unimmersed Strengths

Percentages of Ca-lignosulfonate added to the soil were 0, 2, 4, 6, and 8 percent, and those of Al-sulfonate were 0, 1, 3, and 5 percent, all on the basis of oven-dry weight of the soil. For each combination of these percentages five sets of six specimens were prepared with different moisture contents, maintained within ±0.5 percent[1]. An average dry density was calculated for each set by



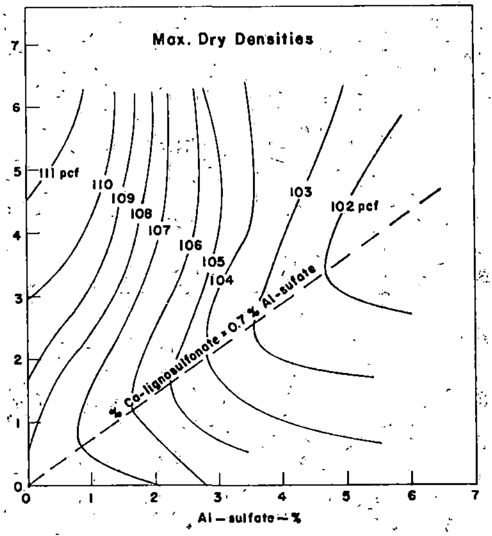


Fig. 1. Relationship of mixture composition to optimum moisture.
Fig. 2. Relationship of mixture composition to maximum dry density.

the method given in the preceding section. Dry densities of individual specimens of the same set were within ±1 pcf of each other.

After curing, three of the six specimens molded from the same batch at one moisture content were tested for unconfined compressive strength. The remaining three were immersed in water for twenty-four hours, then tested for unconfined compressive strength as in the preceding section. For each set, average unimmersed and immersed strengths were calculated. Individual unconfined compressive strengths were maintained within 10 percent of the average value or tests were repeated[2]. Dry densities, unimmersed and immersed strengths obtained for compositions tested, were plotted against molding moistures. From these density moisture and strength moisture relationships optimum moisture contents, maximum dry densities and maximum strengths for different compositions were obtained (table V). Optimum moistures for maximum dry density, immersed and unimmersed strengths were found to be nearly the same.

Optimum moistures were plotted against Al-sulfate contents at constant Ca-

TABLE V. EFFECT OF CA-LIGNOSULFONATE AND AL-SULFATE ON STRENGTH AND RELATED PROPERTIES OF THE LOESS

Ca-lignosulfonate, %	Al-sulfate, %	Optimum moisture, %	Maximum dry density, pcf	Unimmersed strength, psi	Immersed strength, psi	Moisture retention %	Linear expansion upon-immersion, %	Water absorption upon immersion, %
0	0	18.0	107.5	915	Slaked	3.0		
0	1	18.4	107.8	750	Slaked	3.0		
0	3	19.8	105.8	515	Slaked	3.5		
0	5	19.6	104.8	480	Slaked	3.7		
2	0	17.3	109.3	875	Slaked	3.5		
2	1	18.0	107.5	745	Slaked	3.6		
2	3	19.4	103.8	655	2	3.6		
2	5	20.3	102.9	620	10	4.0		25
4	0	15.8	110.7	1000	Slaked	3.8		
4	1	16.8	109.9	800	Slaked	4.5		
4	3	19.2	105.0	695	70	4.5	1.0	14
4	5	19.9	101.7	585	130	4.8	0.6	12
4	7	20.5[*] 21.1[†]	101[‡] 101.0[§]	525[**]	155[**]			
6	0	15.4	111.6	675	Slaked	5.9		
6	1	16.0	110.8	665	55	6.0		
6	3	18.1	104.8	535	125	6.5	0.5	13
6	5	19.0	103.0	520	160	5.8	0.4	11.5
6	6	19.5[*] 20.1[†]	102[‡] 102.3[§]	550[**]	180[**]			
6	7	20.0[*] 21.2[†]	101[‡] 101.2[§]	550[**]	205[**]			
6	8	20.5[*] 20.5[†]	101[‡] 102.2[§]	570[**]	260[**]			
8	0	14.5	111.9	680	Slaked	6.4		
8	3	17.5[*] 17.3[†]	104[‡] 104.4[§]	505[**]	70[**]			
8	5	19.1	103.0	520	105	7.9	0.6	13
8	6	19.1[*] 19.2[†]	102[‡] 101.5[§]	480[**]	107[**]			
8	8	19.5[*] 19.5[†]	97.3	442	83			

[*] Obtained from Figure 1.

[†] Determined at the time of molding.

[‡] Obtained from Figure 2.

[§] Actually determined density.

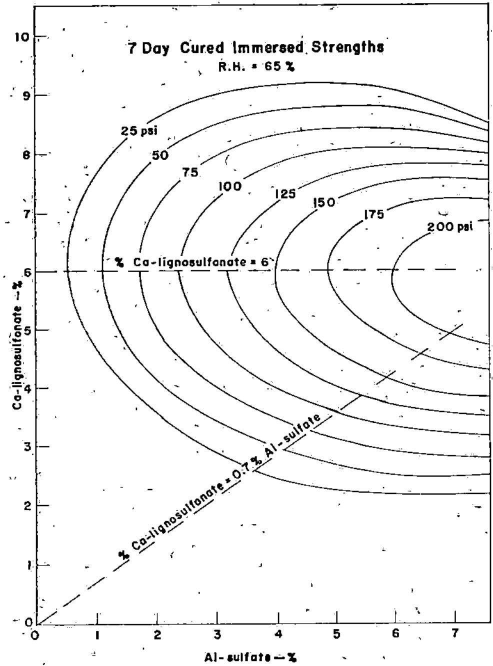
[**] Interpolated from Figure 5.

lignosulfonate contents and against Ca-lignosulfonate contents at constant Al-sulfate contents. From these curves contour graphs were constructed (figure 1) for "iso-optimum moisture contents." In the same manner curves were plotted to relate maximum dry density, unimmersed strength, and immersed strength to composition (figures 2, 3 and 4).

To check these graphs, optimum moisture contents for several compositions were estimated, and these compositions were molded and tested according to methods described in the preceding section. Maximum dry densities thus obtained were found in close agreement with those obtainable from figure 2. However, immersed and unimmersed strengths of the specimens were considerably higher than would be expected from the early results. This was believed to be due to the lower relative humidities during the second period of investigation. In the first period of the investigation the average relative humidity was 65%; in the second period it was 36%.

To check on this, three compositions studied in the first period of investigation were remolded and tested, and the strengths obtained during the first period of investigation are plotted against the strengths obtained during the second period (figure 5). These curves were used to convert the results of the latter period to the results obtained during the first period.

Examination of maximum dry density contours (figure 2) shows that for a



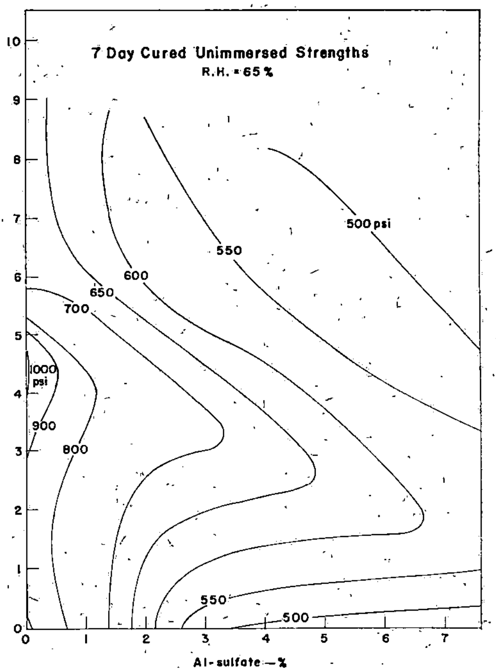


Fig. 3. Relationship of mixture composition to maximum immersed strength.
Fig. 4. Relationship of mixture composition to maximum unimmersed strength.

fixed amount of Al-sulfate, addition of Ca-lignosulfonate up to a certain percentage results in a decrease in maximum dry density. After this point is reached, further addition of Ca-lignosulfonate causes an increase in density. From this it was concluded that Ca-lignosulfonate reacts with Al-sulfate and soil and forms agglomerates, thereby decreasing density. After enough Ca-lignosulfonate is added to the mixture to complete the reaction, the excess Ca-lignosulfonate furnishes lubrication and possibly by the dispersive properties breaks the agglomerates and causes an increase in density. Further examination

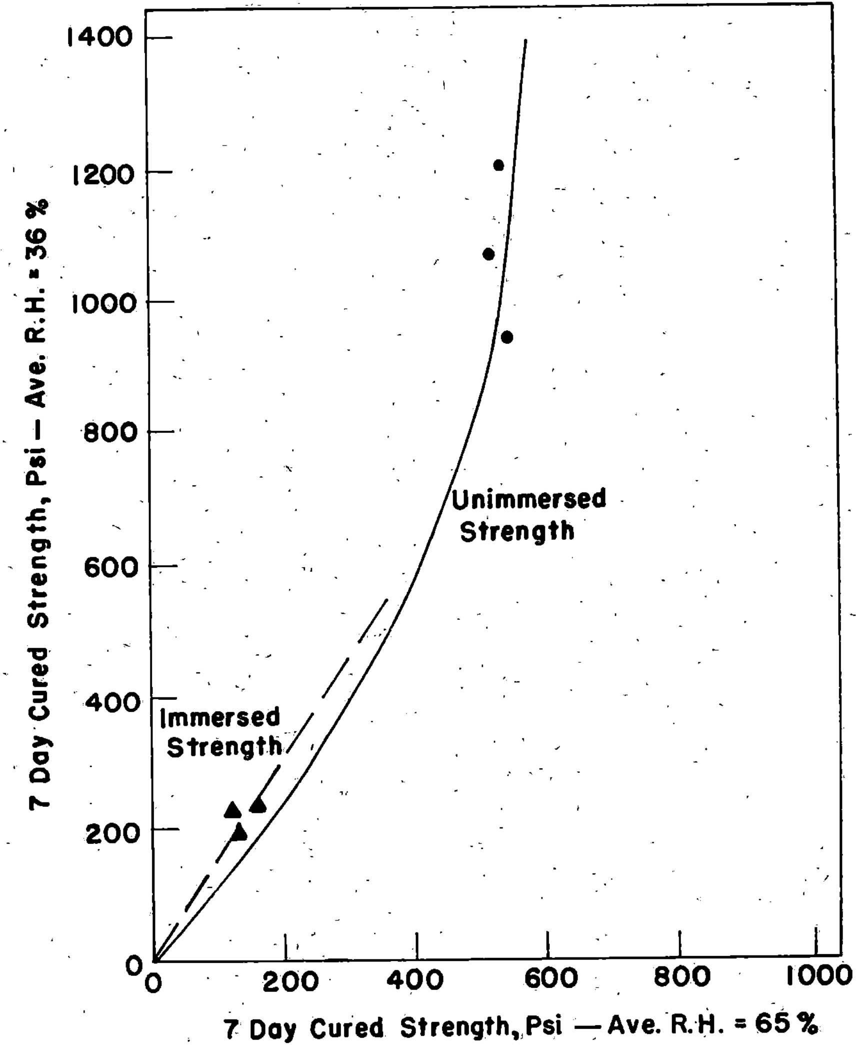


Fig. 5. Effect of relative humidity on maximum unimmersed and immersed strengths of the loess treated with Ca-lignosulfonate and Al-sulfate.

shows that the Ca-lignosulfonate—Al-sulfate relationship for minimum density which corresponds to complete reaction is a linear relationship with the equation

$$\%\ \text{Ca-lignosulfonate} = 0.7\ \%\ \text{Al-sulfate}$$

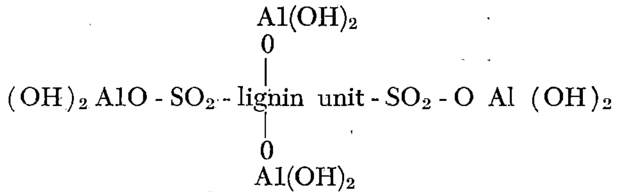
$$\text{or}\ \frac{\%\ \text{Ca-lignosulfonate}}{\%\ \text{Al-sulfate}} = 0.7$$

Conversion to molar quantities gives:

$$\frac{(1000)\ (\text{Moles of Ca-lignosulfonate})}{(666)\ (\text{Moles of Al-sulfate})} = 0.7$$

$$\frac{\text{Moles of Ca-lignosulfonate}}{\text{Moles of Al-sulfate}} = \frac{666}{1000}\ 0.7 = \frac{466.2}{1000} = 0.466 \approx 0.5$$

Therefore each mole of Al-sulfate combines with about one-half mole of Ca-lignosulfonate. (It has been established that each lignin building unit contains at least one phenolic hydroxyl group.) Assuming a Ca-lignosulfonate unit has two sulfonate groups and two phenolic hydroxyl groups[6], a basic aluminum lignosulfonate having the following composition may form:



$$\begin{array}{c} \text{Al(OH)}_2 \\ 0 \\ | \\ (\text{OH})_2\,\text{AlO - SO}_2\text{ - lignin unit - SO}_2\text{ - O Al (OH)}_2 \\ | \\ 0 \\ \text{Al(OH)}_2 \end{array}$$

Basic aluminum lignosulfonate

The condition for its formation is a basic medium[5], which would be maintained by $CaCO_3$ present in the soil. Although $CaCO_3$ is insoluble in water, when an amount of Ca-lignosulfonate solution is mixed with $CaCO_3$ in a beaker and a calculated amount of Al-sulfate solution is added into the mixture, a sol forms. Micelles of this sol are probably built up of the basic aluminum lignosulfonate and may have positive surface charges due to the partial ionization of hydroxyl groups attached to aluminum atoms surrounding lignosulfonate unit. When this sol forms in a soil, micelles of the sol would be adsorbed by negatively charged clay surfaces.

Surface tension of the sol should be considerably less than that of pure water and should decrease with increasing concentration due to the fact that dispersed micelles of the sol contain both polar hydrophilic groups and nonpolar hydrophobic groups[30] p.487. But, on the basis of the surface charges, the predominance of hydrophobic radicals, and viscosity characteristics of the sol, the solvation of basic aluminum lignosulfonate micelles is due to electrostatic repulsions rather than affinity for water; consequently the solvation energy of these micelles must be considerably less than the solution energies of true solutes and solvation energies of truly lyophilic sols[30] p. 508. Therefore the effect of the solvation energy on the free energy of the system may be considered of secondary importance as compared to that of surface tension.

Since surface tension of the adsorbed sol increases by absorption of water, surface free energy of the system also increases upon water absorption. According to laws of thermodynamics, reactions accompanied by an increase in free energy cannot proceed spontaneously; therefore water cannot enter into the system unless it is forced in.

The unconfined compressive strengths of compacted soil specimens are governed by the thickness and surface tension of a liquid film coating individual grains of the soil; strengths increase with increasing surface tensions and decreasing film thicknesses of the liquid phase[31]. When a chemically treated soil specimen is dried, film thickness decreases, and the specimen gains strength. But drying may decrease or increase the surface tension of the film, which may decrease or increase strength accordingly. Other influencing factors are that surface tension of the solid particles and interfacial tension of the solid-liquid phase affect the force with which the grains of soil are held together. The latter factor is also a measure of the affinity of the liquid to be adsorbed on the solid surfaces[11]. However, the variations in the solid to liquid interfacial tension are unpredictable, and it is doubtful that a sound speculation can be made unless sufficient experimental data is available.

In the present study the solid to liquid interface tension has been neglected, and instead of the usual practice of considering the adsorption of the solute from the solution, adsorption of the solution itself has been considered. Since the interface is excluded from the study, a concentration gradient through the adsorbed phase is not given any consideration. Such a gradient would be in the interface[30], p. 504, and this is the basis for the well-known Gibbs adsorption isotherm for liquid vapor interfaces. The simplification is believed justified because, although the interfacial tensions are of great importance in analyzing the affinity of the soil to be coated by the stabilizing solution, strengths of the mixtures are mainly governed by the characteristics of the liquid film because this film is the weakest part of the mixture. That is, a solid surface can be coated with a liquid if its surface energy is reduced by this process. This means that the surface tension of the soil-liquid interface should be less than that of the solid surface. Furthermore the interfacial tension should be greater than surface tension of the liquid.

In those solutes which increase the surface tension of water, no waterproofing is expected since absorption of water will always result in a decrease in free energy and therefore will proceed. But when the water is partially evaporated, the factors of film thickness and surface tension of the liquid phase are benefited and increase strength. Therefore dry strengths increase on drying, comparable to untreated mixtures[10].

In those solutes which decrease surface tension of water, waterproofing may or may not occur, since absorption of water results in a compromise between the factors which both increase and decrease the free energy of the system. When water is partially evaporated, surface tension of the liquid phase is affected in a direction which decreases strength whereas film thickness changes to increase the dry strength. Dry strength is decreased with the addition of chemicals (figure 4.)

A qualitative comparison of film thicknesses of treated soils can be made on the basis of moisture retentions. Chemically treated mixtures generally show a higher moisture retention than untreated mixtures under the same curing conditions, and the extent of the moisture retention depends on the amount of treatment (table V). Therefore chemically treated mixtures have thicker liquid films than untreated mixtures, causing a reduction in unimmersed strengths. Partial evaporation of water also results in increased immersed strengths. The fact that immersed strengths are considerably lower than unimmersed strengths is believed to be due to the partial penetration of water under the hydraulic head which results from complete immersion of specimens. When evaporation extends to an extreme and the solute crystallizes out as solid particles, the main role in binding the soil grains together may be played by interlocking crystals or solid particles, and dry strengths may markedly increase. When such an extreme drying takes place, the waterproofness of the stabilized soil may be destroyed because rush of water into pore spaces when the soil is suddenly immersed may break the structure before water has a chance to dissolve or disperse enough solid and form a liquid film having the least surface tension[17].

Moisture retention is a function of curing conditions, the effect of the curing condition on moisture retentions and consequently on strength characteristics (figure 5). Comparisons of strengths with those obtained by air curing showed that drying was not so effective in the desiccators prepared for controlled humidity as it had been in open air (table IV). This inconsistency is believed due to the formation of stagnant air films around specimens caused by the limited air circulation in small desiccators and inhibiting the vaporization of water. However, the results show qualitatively that low relative humidities of the curing atmosphere reduce the moisture retention and consequently increase both immersed and unimmersed strengths.

The ratio of immersed strengths of the 0.7 optimum Ca-lignosulfonate to Al-sulfate does not correspond to maximum immersed strength (figure 3). Instead, highest immersed strengths for any Al-sulfate content always occur with 6 percent Ca-lignosulfonate. This relationship is represented by the line:

$$\%\,\text{Ca-lignosulfonate} = 6$$

Ca-lignosulfonate alone furnishes some waterproofing[38] because it appreciably reduces surface tension of water (table II). Since it is highly and truly soluble in water, complete waterproofing cannot be achieved with Ca-lignosulfonate alone. Therefore, Ca-lignosulfonate contents exceeding the optimum Ca-lignosulfonate to Al-sulfate ratio, 0.7, may aid waterproofing up to a critical percentage, 6 percent, which gives an optimum coating of grains of the soil under the curing conditions maintained in this study. In other words, the percentage of Ca-lignosulfonate is as critical as the Ca-lignosulfonate to Al-sulfate ratio. If this is true, best results should obviously be expected with 6 percent Ca-lignosulfonate at 0.7 optimum Ca-lignosulfonate to Al-sulfate ratio.

A previous study of spent sulfite liquor stabilization[38] showed that two soils texturally in the same class as the calcareous loess (silty clay loam) had best waterproofness with 6 percent spent sulfite liquor solids mainly composed of Ca-lignosulfonate. In the same study 4 percent liquor solids gave best waterproofness to a silty clay soil. It is concluded that the optimum amount of Ca-lignosulfonate depends on the texture and composition of the soil to be stabilized, whereas the optimum Ca-lignosulfonate to Al-sulfate ration depends on the chemical reactions.

Nearly all unimmersed strengths are reduced by the addition of any combination of Ca-lignosulfonate and Al-sulfate (figure 4). Under the conditions studied, the maximum unimmersed strength is only slightly higher than that of raw soil and is obtainable with about 4.5 percent Ca-lignosulfonate and zero percent Al-sulfate. This slightly higher unimmersed strength is due to the formation of an optimum amount of interlocking Ca-lignosulfonate crystals which outweigh the effect of low surface tension of binder films.

Effect of the Additives on Deformation Caused by Drying and Wetting

Shrinkage and expansion upon drying and wetting of an untreated cohesive soil compacted on the dry side of optimum moisture are considerably lower than those of the same soil compacted on the wet side of optimum, but the rate of water absorption is higher for the soil compacted on the dry side[36, p. 170]. These findings led the Road Research Laboratory of Great Britain to the following conclusion:

> "It is considered inadvisable to compact cohesive soil subgrades below their optimum moisture content in cases where they are likely to be subject to the ingress of moisture during the life of the road."

But compacting cohesive soils above their optimum moisture contents may cause shear failure surfaces known as slickensides, to develop[40, p. 335].

Shrinkage caused by drying specimens of Ca-lignosulfonate—Al-sulfate treated loess compacted at moisture contents up to optimum moisture is low and constant, but when compacted above optimum moisture contents the shrinkage is greatly increased (figure 6). But expansion, caused by wetting loess specimens effectively treated with Ca-lignosulfonate and Al-sulfate and compacted at moisture contents below and above the optimum moisture, was low and of nearly the same order regardless of moisture content. Therefore it appears that Ca-lignosulfonate and Al-sulfate treated loess should be compacted at or below optimum moisture content to avoid the danger of excessive shrinkage or slickensides.

Selection of a Mixture for Further Study

Selection of the mixture for further evaluating the effects of Ca-lignosulfonate and Al-sulfate on stability was based on unimmersed and immersed strengths and economic considerations.

A mixture composed of 6 percent Ca-lignosulfonate and 5 percent Al-sulfate gave satisfactory strengths (figures 3 and 4), and cost-wise it was considered equivalent to Portland cement stabilization. A mixture composed of 6 percent Ca-lignosulfonate and 3 percent Al-sulfate gave immersed strengths of 120 psi (figure 3), and its cost would be about two-thirds that of Portland cement stabilization.

On the basis of the above reasoning, the mixture composed of 6 percent Ca-lignosulfonate and 5 percent Al-sulfate was selected for further evaluation.

Frost Susceptibility

Evaluation of frost susceptibility was based on two criteria, namely, deformation caused by alternate freezing and thawing, and the accompanying reduction

TABLE VI. EFFECT OF 14 CYCLES OF ALTERNATE FREEZING AND THAWING ON UNTREATED AND TREATED LOESS

Ca-ligno sulfonate, %	Al-sulfate, %	Moisture at molding, %	Dry density at molding moisture, pcf	Linear expansion after 14 cycles of freezing and thawing, %	Total moisture absorption after 14 cycles of freezing and thawing, %	Unconfined compressive strength after 14 cycles of freezing and thawing, psi	Unconfined compressive strength after 14 days of immersion, psi	Average relative humidity during 7 days curing period
0	0	18.4	108.2	Bulged	. .	Slaked	Slaked	70±
6	5	19.3	103.1	2	22	17.5	Cracked	70±

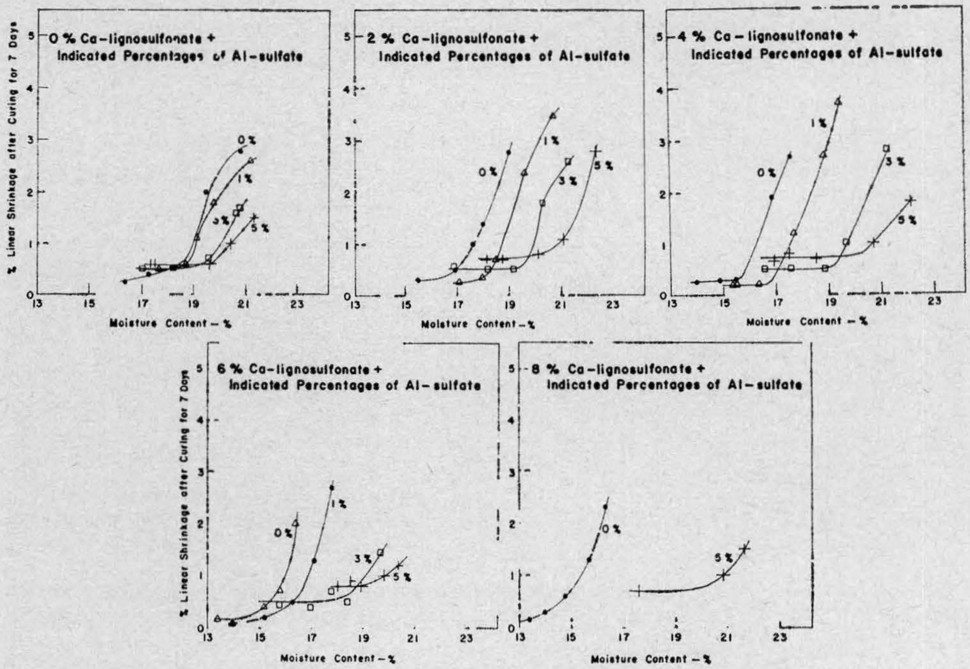


Fig. 6. Effect of Ca-lignosulfonate and Al-sulfate on linear shrinkage of specimens molded at various moisture contents.

in strength (figure 7). Untreated specimens bulged after the first cycle, but treated specimens did not show any noticeable deformation even after 14 cycles. At the end of the 14th cycle, the untreated specimens were completely destroyed, but specimens prepared from the selected mixture showed 2 percent expansion, 22 percent absorption, and gave 17.5 psi unconfined compressive strength (table VI). Specimens immersed in water for 14 days were cracked. For this method of stabilization the most severe simulated weathering condition appears to be excessive exposure to water.

CONCLUSIONS

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

1. A slightly alkaline environment or the presence of carbonates in soils is essential to this method of treatment.
2. The order of mixing the additives with soil is not critical, but best results are obtained by mixing Ca-lignosulfonate before Al-sulfonate. When both additives were combined before adding to the soil an 18% reduction in immersed strength was observed. From a constructional standpoint, the latter method of mixing is more desirable and could be used when satisfactory strengths are obtainable.
3. There is an optimum combination of Ca-lignosulfonate and Al-sulfate which gives maximum immersed strength. The optimum combination can be estimated from the effects of the additives on dry density and the effect of Ca-lignosulfonate on immersed strength. For the calcareous loess studied, this optimum combination was estimated to be 6% Ca-lignosulfonate and 8.5% Al-sulfate; this was verified by experimental results.

The optimum combination leads to the formation of a chemical compound

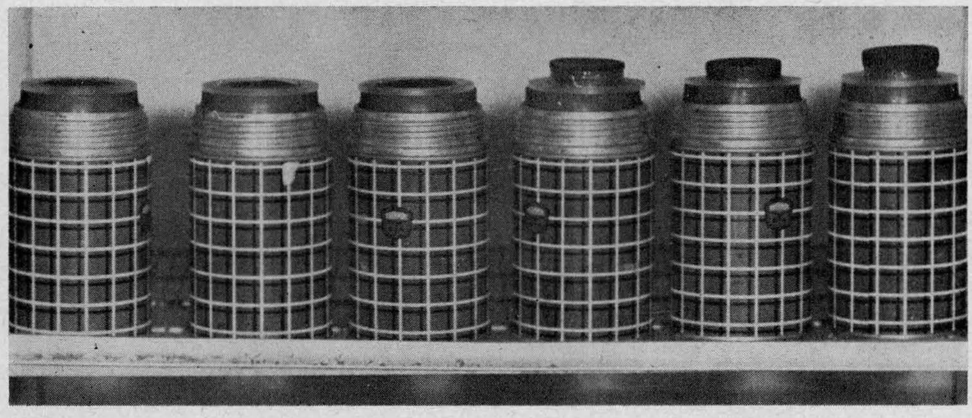


Fig. 7. Effect of Ca-lignosulfonate and Al-sulfate on frost heave. The first three vacuum flasks contained specimens treated with 6% Ca-lignosulfonate and 5% Al-sulfate; the other three contained untreated specimens. Specimens were subjected to 4 freeze, thaw cycles.

(probably a basic aluminum lignosulfonate) which is formed when the Ca-lignosulfonate to Al-sulfate ratio is 0.7. Nevertheless, the combined amount of Ca-lignosulfonate and Al-sulfate in this ratio needed to produce maximum stability varies with soil type.

4. The degree of stability obtainable by this treatment depends on the condition of the atmosphere in which the compacted mixture is cured. It was found that humid atmospheres hinder drying and strength development. The calcareous loess treated with 6% Ca-lignosulfonate and 5% Al-sulfate gave immersed strengths of 122 psi, 160 psi and 230 psi when cured in atmospheres having average relative humidities of 70%, 65% and 36% respectively. When specimens cured in the atmosphere having 70% relative humidity were subjected to 14 cycles of freeze and thaw, the unconfined compressive strength was reduced to 17.5 psi. No excessive linear expansion took place during freezing and thawing.

5. On the basis of these strength data, in humid climates having severe winter freezing and thawing, this method may be satisfactory only for subgrade or subbase stabilization of fine grained soils. In areas having dry construction seasons and mild to moderate winters, the method may also be considered for base course stabilization.

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SOIL-ORGANIC CATIONIC CHEMICAL-LIGNIN STABILIZATION

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ABSTRACT

The chemicals used in a series of tests of four Iowa soils were a quaternary ammonium chloride and a fatty amine acetate known commercially as Arquad 2HT and Armac T, respectively. The lignins used were either commercially available or in pilot plant production and contained varying sugar contents. The four soils used ranged in clay content from 10 to 74 percent.

Preliminary studies of the chemicals and lignins on one of the soils, a friable calcareous loess from southwestern Iowa, indicated the most desirable mixing chronology to be the addition of chemical solution first, followed by the addition of the lignin solution. The most beneficial lignin for each organic cationic chemical was also chosen and was used throughout the remainder of testing.

In general the use of the soil, organic cationic chemical, and lignin combination indicates increased compressive strength of the soil with reduction of moisture absorption and expansion during complete immersion in water, these benefits being somewhat greater with the combination of soil, chemical and lignin than with the soil and chemical only.

INTRODUCTION

Studies of the use of organic cationic chemicals for soil stabilization at the Iowa Engineering Experiment Station date back to 1947. Results with several Iowa soils and soil mixtures have been reported[4, 5, 6, 9, 10, 11] and two of the organic cationic chemicals appear to be promising. Known commercially as Arquad 2HT and Armac T, they are respectively a quaternary ammonium chloride and a fatty amine acetate.

It has been shown that organic cationic chemicals act primarily as waterproofing agents, which tend to maintain the bearing capacity of soil even under adverse moisture conditions. Investigations have shown that the addition of lignin to a soil and organic cationic chemical mixture may further improve waterproofing and strength characteristics[12]. Lignin, a waste product of the paper industry, is available in large quantities, and its cost depends on the distance it must be shipped.

The purpose of this investigation was further to evaluate the use of lignin in soil-organic cation mixtures. The criteria used in evaluating the effectiveness of stabilization were the air-dry and immersed unconfined compressive strengths, and moisture absorption and expansion after immersion.

MATERIALS

The soil samples used represent important soil types found in Iowa and also provide a wide range of clay content for study of this variable. The dominant clay mineral in the samples is montmorillonite (tables I, II). Because the dune sand lacked clay size particles, the plastic loess was blended and mixed with the sand to make a soil material having a clay content of about 10 percent. This dune

TABLE I. FIELD DESCRIPTION OF SOILS USED

Soil:	Dune sand lab. no. S-6-2	Plastic loess lab. no. 119-5	Friable loess lab. no. 20-2VI	Glacial till lab. no. 416-4	Gumbotil lab. no. 528-8
Location	NE¼, SE¼, S-16 T86N - R1OW, Benton County E. Iowa	NE¼, NW¼, S-31, T78N - R1OW, Iowa County E. Cent. Iowa	S-15, T78N-R43W, Harrison County, SW Iowa	SW¼, SW¼, S-6, T76N - R25W Warren County Cent. Iowa	NW¼, NW¼, S-7 T75N - R1OW Keokuk County SE Iowa
Geological description:	Wisconsin age aeolian sand, fine-grained, oxidized, leached	Wisconsin plastic loess, oxidized, leached	Wisconsin friable loess, oxidized, calcareous	Kansan glacial till, unoxidized, calcareous	Kansan glacial till, oxidized calcareous
Soil series:	Carrington	Fayette	Hamburg	Shelby	Mahaska
Horizon	C	C	C	C	Buried B
Sampling depth, ft.	2-4	6½ - 9	39 - 40	7 - 16½	7½ - 8½

TABLE II. PROPERTIES OF SOILS SELECTED FOR STUDY

Properties	Dune Sand	Plastic loess	Sand-loess Mixture	Friable loess	Glacial till	Gumbotil
Physical Properties:						
Liquid limit, %	19.0	38.4	N.D.*	32.9	38.2	87.1
Plastic limit, %	N.P.	17.2	N.P.	21.1	15.1	34.5
Plasticity index, %		21.2	N.D.	11.8	23.1	52.6
Shrinkage limit, %	12.64	17.4	N.D.	28.3	N.D.	N.D.
Specific gravity	2.64	2.70	N.D.	2.68	2.65	N.D.
Standard Proctor density:						
Max. dry density, pcf	109.9	110.3	129.0	105.0	112.1	95.2
Opt. moist. content, %	12.3	16.6	9.6	18.1	14.1	28.0
Chemical Properties:						
Organic matter, %	0.04	0.3	0.3	0.2	0.75	0.2
Carbonates, % $CaCO_3$	0.02	1.8	0.35	10.2	3.5	0.8
pH	6.5	5.7	6.3	7.8	7.4	6.5
Cation exchange capacity, me/100g	1.76	15.28	4.66	13.4	14.8	45.3
Particle size analysis†, %:						
Sand (2mm to 74μ)	95.8	1.0	70.0	0.2	32.0	17.5
Silt (74 μ to 5μ)	1.2	65.0	20.0	82.6	2.8	8.5
Clay: (< 5 μ)	3.0	34.0	10.0	17.0	40.0	74.0
(< 2 μ)	2.9	27.0	4.0	12.3	34.0	71.0
Engineering classification AASHO	A-3(0)	A-6(13)	A-2-4(0)	A-4(8)	A-6(11)	A-7-5(20)
Textural classification (BPR)	Sand	Silty clay	Sandy loam	Silty Clay loam	Clay	Clay

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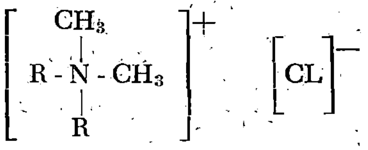
* Not determined.

† Based on that fraction of the soil material passing the No. 10 U.S. Standard sieve. Normal samples of the glacial till and gumbotil contain small quantities of gravel.

sand and plastic loess mixture (hereafter referred to as the *sand, loess mixture*) was prepared to provide a means for the cation exchange process to occur.

Chemicals

Arquad 2HT[2, 3] is a di-hydrogenated tallow di-menthyl ammonium chloride with the following general structural formula:



$$\left[\begin{array}{c} CH_3 \\ | \\ R - N - CH_3 \\ | \\ R \end{array} \right]^{+} \quad \left[CL \right]^{-}$$

in which *R* represents a fatty acid derivative. Arquad 2HT will retain its surface activity at either high or low pH and is not precipitated by calcium or magnesium in water solutions. It is easily dispersible in water up to about 8 percent by weight and is normally supplied by the manufacturer as 75 percent active in isopropanol. It has an average molecular weight of about 585. This chemical is also commercially available under the trade name Aliquat H226[8]. Concentrations referred to in this paper were calculated from the active chemical content of the material supplied.

Armac T[1, 2] is a water dispersible primary amine acetate derived from tallow fatty acids. The general structural formula is $RNH_3 + Ac^-$. Armac T has an average molecular weight of about 310 and is marketed as 100% active material.

Preparation of chemicals. Dispersions of Arquad 2HT and Armac T in water were prepared by dissolving each chemical in distilled water previously heated to 60°C. After being thoroughly mixed, the mixtures were allowed to cool to room temperature. The concentrations were adjusted to provide the desired mix water for compaction and the desired amounts of chemical in the soil. Treatments varied from 0.1 to 0.9 percent chemical by dry soil weight.

Lignins

The lignins used are labeled *A* through *E* and were obtained from several Wisconsin producers (table III).

Preparation of lignins. Solutions of the lignins were prepared by dissolving each lignin in distilled water at room temperature. The concentrations of each lignin solution were adjusted to provide for concentrations in the soils varying from 0.25 to 2.0 percent by dry weight. The concentrations of lignin are based on the total amount of solids.

METHODS OF INVESTIGATION

The investigation was divided into three phases: (1) A preliminary study with the friable loess was made to determine the best order of mixing the chemicals and lignins with the soil. One amount of each organic chemical and varying amounts of Lignin A were used. (2) Using the best mixing order, varying amounts of each of the five lignins were evaluated with mixtures of friable loess and varying amounts of the cationic chemicals. (3) The lignin producing the best results was used in the third phase, an evaluation of chemical and lignin treatments with all the soils.

Techniques for mixing, molding, curing, and testing are given in the following paragraphs.

Mixing and Molding. The mixing was with a Model C-100 Hobart mixer at moderate speed. Six 2 inch diameter by 2 inch high cylindrical specimens were molded to near standard Proctor density for each combination of soil, chemical and lignin evaluated[9, 11, 14]. The height and weight of each specimen were recorded following molding. Representative samples of the mixture were obtained from the mixing bowl for moisture content determinations after molding the second and fourth specimens.

Curing. Air drying has proved to be the best method of curing soils treated with organic cationic chemicals[11]. All specimens in this study were air cured at room temperature for seven days, weighed, and their height was measured. Three specimens for each soil, chemical, and lignin combination were then tested for unconfined compressive strength and three were immersed in distilled water for 24 hours. Following immersion the specimens were weighed, measured and then tested for strength.

Unconfined compression testing. Specimens were tested for unconfined compressive strength at a deformation rate of 0.05 inch per minute per inch height of specimen. The maximum load, in psi, causing failure of the specimen was recorded as the compressive strength. Moisture determinations were made after testing on two whole specimens of each air dry and immersed group.

TABLE III. PROPERTY ANALYSIS OF THE LIGNINS[*]

Property	Lignin A	Lignin B	Lignin C	Lignin D	Lignin E
Total solids, %	50.	52.4	51.0	94.	94.
Total sugar, %	1.2	8.84	19.9	1.2	5.70
Total sulfur, %	N.D.[†]	N.D.[†]	6.02	N.D.[†]	5.73
Ash, %	17.3	8.7	15.4	17.3	9.15
Calcium and/or magnesium oxide, %	7.50	N.D.[†]	5.68	7.50	N.D.[†]
Methoxyl	8.8	N.D.[†]	N.D.[†]	8.8	9.54
Specific gravity	1.24	1.281	1.2764	N.D.[†]	N.D.[†]
pH	4.55	4.0	4.7	4.65	N.D.[†]
Physical state	Water solution	Water solution	Water solution	Powder	Powder
Chemical name	Calcium lignosulfonate	Calcium lignosulfonate	Calcium lignosulfonate	Calcium lignosulfonate	Ammonium lignosulfonate
Trade name	Toranil A	. . . [‡]	Norlig	Toranil B	. . . . [‡]
Manufacturer	Lake States Yeast Corp. Rhinelander, Wisconsin	Consolidated Water Power and Paper Co. Wisconsin Rapids, Wisc.	Marathon Corporation Rothschild, Wisconsin	Lake States Yeast Corp. Rhinelander, Wisconsin	. . . . [§]

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[*] Mostly contributed by the manufacturer.

[†] Not determined.

[‡] Not a commercial product.

[§] Supplied by Sulphite Pulp Manufacturers Research League.

MIXING ORDER STUDY

A preliminary study was made to determine the best order of mixing the chemical, lignin and soil. Various percentages of lignin A and 0.2 percent of each chemical (dry weight of soil basis) were mixed with the friable loess. Three orders of mixing were tried:

The organic cationic chemical dispersion was mixed with the soil for one minute after which the mixture was scraped from the sides and bottom of the bowl. The lignin solution was then added and mixing was continued for one minute.

The second procedure was the same except that the lignin solution was introduced first and the chemical second.

In the third order of mixing the chemical dispersions and the lignin solutions were mixed together and then incorporated into the soil. The two time intervals of mixing were the same as in the first.

The best results were obtained from the first mixing order (figure 1). Two percent Lignin A and 0.2 percent of each chemical produced the highest air dry and immersed strengths. The second order gave slightly lower air dry and immersed strengths. The third was the least desirable procedure as shown by the reduced immersed strengths. A flocculent precipitate was formed when the chemicals and Lignin A were combined. The precipitate may indicate a poly-

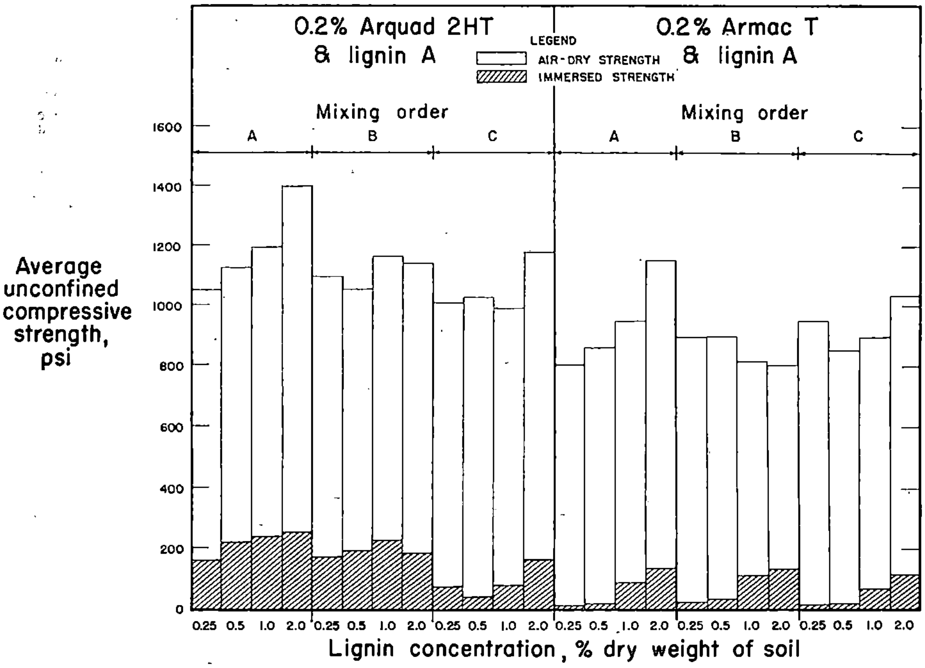

Fig. 1. Effect of mixing order on the average unconfined compressive strength of the friable loess using 0.2 percent cationic chemical and varying amounts of lignin A.

merization of lignin and cationic chemical. Moisture absorption, expansion and density variations generally followed the pattern of the immersed strength results, being most desirable with the first mixing order and least desirable with the third mixing order. The first was therefore chosen for use throughout the remainder of the study.

COMPARISON OF LIGNINS

To determine the lignin producing maximum benefits with each of the organic cationic chemicals, varying percentages of the five lignins were evaluated with the friable loess and various amounts of each chemical.

The air dry strength of the friable loess generally increased with increased lignin content for each concentration of Arquad 2HT (figure 2). The immersed strengths show the same general trend except for a few in which the effect of the Arquad 2HT was slightly better than the combined effects of chemical and lignin. This is most noticeable with Lignin A and 0.3 percent Arquad 2HT. The best overall compressive strengths were obtained at 0.2 percent Arquad 2HT for Lignins A and B; for Lignins C and D the compressive strengths remain nearly constant for Arquad percentages of 0.2 and above; very little benefit is shown for

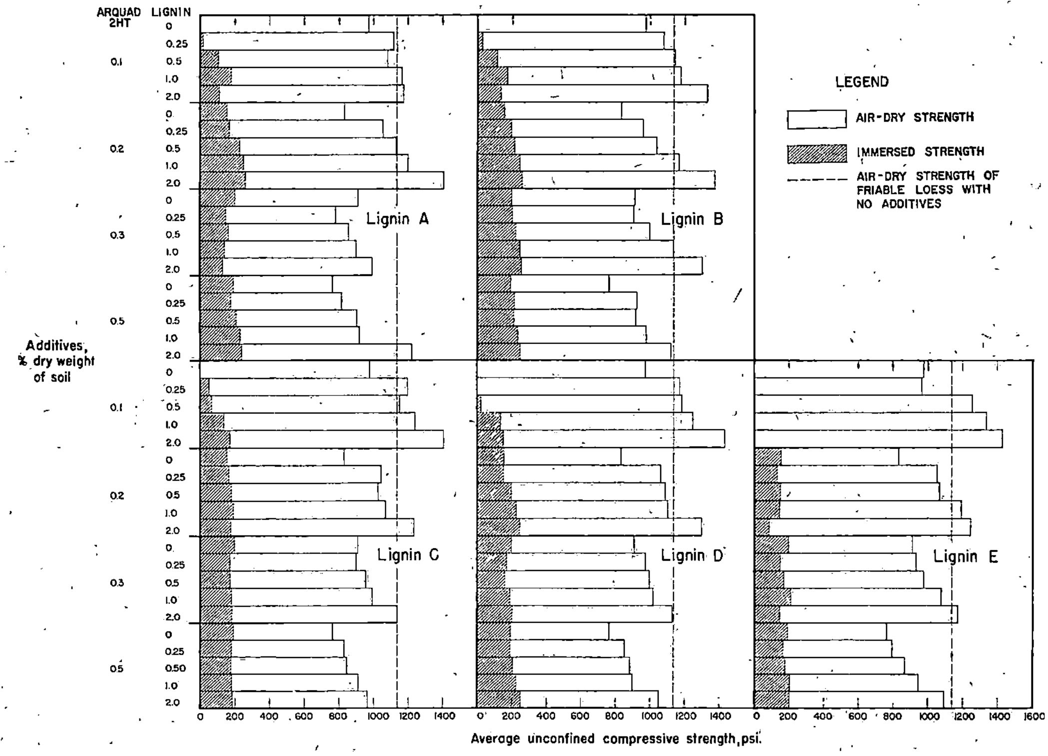

Fig. 2. Effect of amount of Arquad 2HT and each lignin on the average unconfined compressive strength of the friable loess.

Arquad percentages above 0.2 with Lignin E. The percent moisture absorption of the friable loess-Arquad 2HT-lignin combinations was generally lowest with lignins A and B; the percent expansion after immersion was a minimum with Lignin B. The dry densities were consistently greater with Lignin B, which may have contributed to the good results with this lignin. Lignin B was chosen for use with Arquad 2HT for the remainder of the investigation.

The air dry strengths of the loess, Armac T, and lignin mixtures generally increased with increasing amount of lignin, but the air dry strengths generally are not as high as those obtained with the Arquad 2HT (figure 3). In general 2.0 percent of each of the lignins gave the highest immersed strengths for each amount of Armac T. The variation of immersed strengths with additive content was much more erratic than with the Arquad 2HT. The highest immersed strength for each lignin was not obtained with the same amount of Armac T. Lignins C and E produced best immersed strength results at 0.1 percent Armac T; lignins A, B and D were best at 0.5, 0.3 and 0.2 percent Armac T, respectively. Minimum expansion and moisture absorption with each lignin appeared at or near the respective Armac T concentrations noted above. Lignin C generally

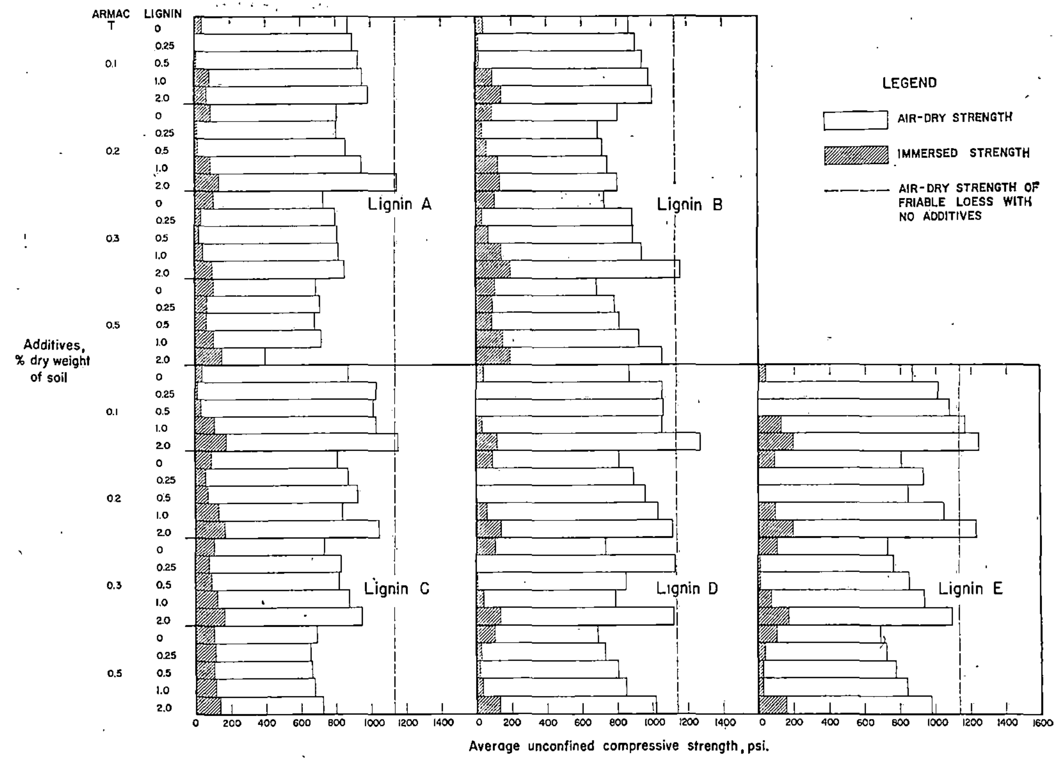

Fig. 3. Effect of amount of Armac T and each lignin on the average unconfined compressive strength of the friable loess.

gave the lowest expansion and moisture absorption, and lignin E gave the highest. The dry densities of the loess, Armac T, and lignin mixtures did not correlate well with the strengths, though lignin C generally produced the highest densities. Lignin C was chosen for use with Armac T in the remainder of the investigation.

Three known lignin variables which could have affected the results of this phase of the investigation were commercial form, total sugar content and ionic composition (table III). Lignins A, B and C were supplied in water solutions; D and E were powders. The test results do not indicate that the commercial form of the lignins prior to preparation of solutions and incorporation into the soil contribute to the variation in results.

With Arquad 2HT the total sugar content of the lignin does not appear to affect strength. With Armac T the sugar content may have affected strength results:

Lignins A and D (1.2 percent sugar) gave the lowest immersed strengths.

Lignin C (19.9 percent sugar) gave high immersed strengths at low Armac T contents.

Lignin B (8.8 percent sugar) gave slightly higher immersed strength than lignin C but only with higher Armac T contents.

Lignin E (5.7 percent sugar) gave the highest immersed strengths but also gave the greatest amount of expansion and absorption.

Lignins A, B, C and D are calcium lignosulfonates, and lignin E is an ammonium lignosulfonate. The lignin E gave the poorest results, possibly due to the ammonium ion.

EFFECTIVENESS AND CLAY CONTENT

The rest of the investigation was an evaluation of combinations of the cationic chemicals and the lignins selected for use with each chemical. The combinations were used with four soils in which the 5mu clay content ranged from 10 to 74 percent (table II).

Unconfined Compressive Strength

Unconfined compressive strength results were obtained with mixtures of the four soils and varying amounts of Arquad 2HT lignin B and Armac T lignin C and are recorded (figures 4, 5). The maximum cationic chemical content shown is 0.7 percent; with the glacial till and gumbotil, treatments of 0.9 percent showed no difference in results and were not included in these figures.

Air dry strength. Air dry strengths of all the soil and organic cationic chemical mixtures (no lignin) decreased as the amount of chemical increased. This is in agreement with previous investigations[9, 11] and is attributed to reduced bond energy due to increased amounts of the organic material on the particle surfaces.

The dry strengths of the sand and loess mixture and the friable loess generally were increased by increasing amounts of lignin when the amount of chemical was constant. This strength increase was as much as 75 percent with 2.0 percent lignin and Arquad 2HT in the sand and loess mix. Strength is decreased at equal lignin contents as the cationic chemical content increases. An exception is the maximum friable loess dry strength with 0.2 percent Arquad 2HT and 2.0 percent lignin B.

The additives produced erratic air dry strength results with glacial till and gumbotil particularly in the latter soil. Most of the erratic data may be attributed to the extreme difficulty in mixing and molding these highly plastic materials. The gumbotil exhibited considerable balling during mixing and molded samples were not uniform in quality or density. This also was true to a lesser degree with the glacial till. The addition of lignin does not materially increase the air dry strength.

Immersed strength. The cationic chemical and lignin treatments benefited immersed strengths of the sand loess mixture and the friable loess (figures 4, 5). The glacial till immersed strength was very slightly benefited by the cationic chem-

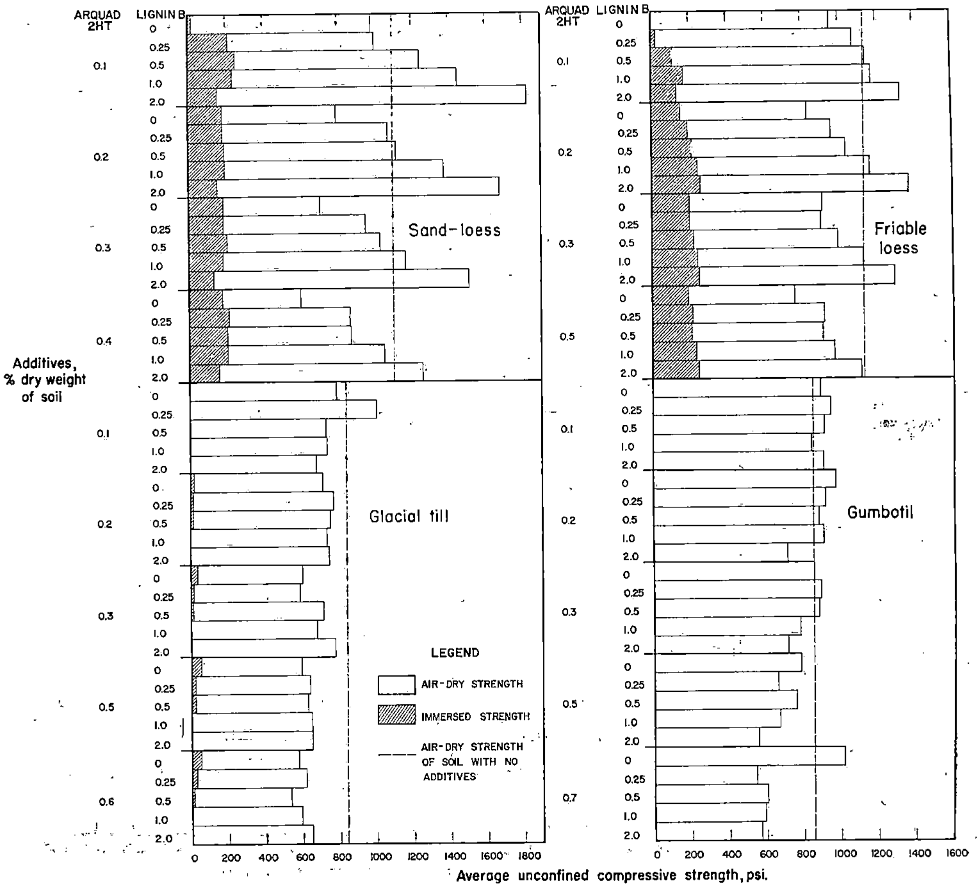

Fig. 4. Effect of amount of Arquad 2HT and lignin B on the average unconfined compressive strength of four soils with different clay content.

icals but the addition of lignin was detrimental. Gumbotil immersed strength derived no apparent benefits from the addition of either lignin or cationic chemical.

Immersed strengths of sand, loess, and friable loess treated with 0.1 percent Arquad 2HT were increased by the addition of lignin; similar benefits were obtained at 0.2 percent Arquad with the friable loess. The addition of lignin to these soils treated with Arquad percentages of 0.2 and above for the sand loess and 0.3 above for the friable loess gave little or no immersed strength increase above that obtained with Arquad alone.

Immersed strength of sand, loess and friable loess treated with 0.1, 0.2 and 0.1, 0.2, 0.3 percent Armac T, respectively, were reduced by the addition of 0.25 percent lignin. The addition of 0.5 percent lignin raised the strength to a value

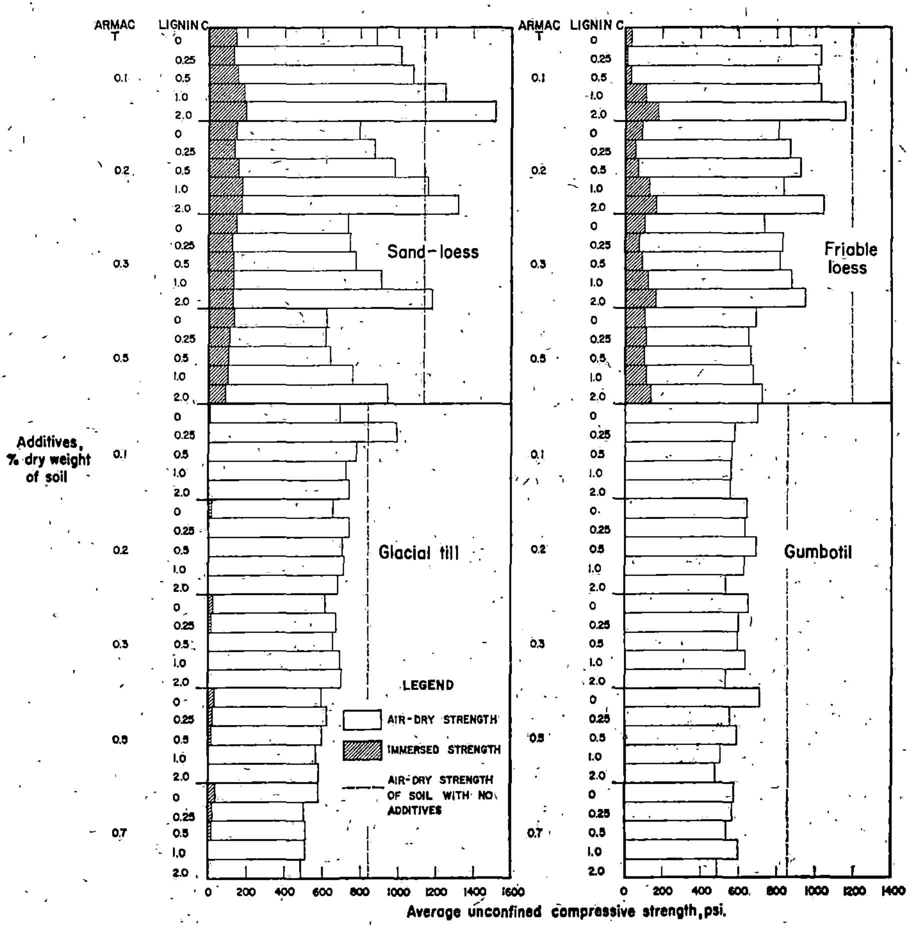

Fig. 5. Effect of amount of Armac T and lignin C on the average unconfined compressive strength of four soils with different clay content.

comparable to the value obtained with Armac T alone; higher lignin percentages increased the immersed strength to values above the original value with the exception that lignin decreased the immersed strength of sand loess treated with 0.3 and 0.5 percent Armac T. Also, the 0.5 percent Armac T treated friable loess immersed strength was benefited very little by the addition of lignin.

Moisture absorption and expansion. The amount of moisture absorption and expansion measured after 24 hours immersion in water was generally inversely related to the immersed strength and directly to the clay content; that is, as the immersed strength increased, moisture absorption and expansion decreased. As clay content increased, moisture absorption and expansion increased. The sand and loess mixture showed the least amount of moisture absorption (2 to 3 percent) at the maximum immersed strengths for each concentration of Arquad 2HT and Armac T. The amount of swelling was negligible for the sand and loess mixture and ranged from zero to about 0.3 percent for all combinations of Arquad 2HT and Lignin B. Moisture absorption and expansion of the friable loess was generally low though slightly greater than for the sand and loess mixture. The absorption and expansion of the glacial till was generally excessive; and due to the failure of all immersed specimens of gumbotil, absorption and swelling data were unobtainable.

Density. In general when cationic chemical content was constant the oven dry densities increased with increased lignin contents for the sand and loess mixture and the friable loess. The maximum density obtained with each cationic chemical content decreased slightly with increased amounts of chemical. Densities of the glacial till and gumbotil specimens decreased with increased amounts of both cationic chemical and lignin.

TABLE IV. SUMMARY OF RESULTS WITH ADDITIVES SHOWING THE BEST STABILIZING EFFECTS

	Sand-loess mixture	Friable loess	Glacial till	Gumbotil
Clay content, $< 5\ \mu$, %	10.0	17.0	40.0	74.0
Arquad 2HT, % dry wt. of soil	0.1	0.2	0.5	0.7
Lignin B, % dry wt. of soil	0.5	2.0	0.0	0.5
Air dry strength, psi	1244	1377	588	603
Immersed strength, psi	248	256	48	*
Shrinkage during curing, %	0.1	0.4	0.6	4.7
Expansion during immersion, %	0.0	0.2	2.6	*
Moisture absorption after immersion, % oven-dry wt.	2.4	6.1	15.8	*
Dry density, pcf	128.4	106.7	113.6	92.4
Armac T, % dry wt. of soil	0.1	0.1	0.5	0.5
Lignin C, % dry wt. of soil	2.0	2.0	0.0	0.0
Air dry strength, psi	1509	1158	595	713
Immersed strength, psi	192	176	31	*
Shrinkage during curing, %	0.1	0.5	1.1	5.9
Expansion during immersion, %	0.0	0.6	3.6	*
Moisture absorption after immersion, % oven-dry wt.	2.4	7.9	12.6	*
Dry density, pcf	126.2	106.3	114.0	92.4

* Specimens failed during immersion.

Discussion of effect of clay content. The results with additives showing the best stabilizing effects with the four soils of different montmorillonitic clay contents were summarized (table IV). The best treatments for the gumbotil were chosen on the basis of dry strength, shrinkage and dry density.

As reported in previous investigations the optimum amount of cationic chemicals required for maximum immersed strength increases with increasing amount of clay[9, 11]. The data presented in the summary indicate that within a range of montmorillonitic clay contents cationic chemicals and lignin are effective (figures 4, 5 and table II). The data also support the findings of previous investigations, although amounts of cationic chemical necessary to stabilize the high clay content soils were not investigated. At some clay content between 17 and 40 percent the cationic chemical and lignin treatment will produce an optimum immersed strength. Soils containing different clay minerals may exhibit different results with this type of treatment.

CONCLUSIONS

The following conclusions, based on phases one and two of the investigation, represent the use of the chemicals and lignins with the friable loess only:

1. The cationic chemical should be mixed with the soil prior to the addition of lignin.
2. Commercial form, solution or powder, of the lignin does not appear to affect the stability of the soil.
3. Total sugar content of the lignin does not affect the stability when used with Arquad 2HT. The stability of soil, Armac T, and lignin mixtures appears to be improved by higher sugar contents.
4. The use of calcium lignosulfonates appear to be more beneficial than ammonium lignosulfonates.

The remaining conclusions are based on the third phase of the investigation and represent the use of the cationic chemicals and lignins with four Iowa soils of different montmorillonitic clay contents.

5. The use of lignin and small amounts of the organic cationic chemicals is beneficial to stabilization of Iowa soils with low to medium clay contents.
6. Lignin is detrimental when used with the organic cationic chemicals to stabilize medium to high clay content soils.
7. Soils of low clay contents may be adequately stabilized with 0.1 percent Arquad 2HT-0.5 percent lignin or 0.1 percent Armac T-0.2 percent lignin.
8. Soils of moderate clay content may be adequately stabilized with 0.2 percent Arquad 2HT-2.0 percent lignin or 0.1 percent Armac T-2.0 percent lignin; the stability benefits may be higher using the Arquad 2HT.
9. Cationic chemical, lignin stabilization can be economical with low to medium clay content soils.

ACKNOWLEDGMENTS

Special thanks are given to Armour and Company, Chemical Division, Chicago, Illinois, for generously donating the organic chemicals and information concerning them, and to the various lignin producers who generously donated their products and technical information.

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USE OF PHOSPHATES IN SOIL STABILIZATION

by

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(Iowa Academy of Science Proceedings. 65: 311-316. 1958.)

INTRODUCTION

The use of phosphates for stabilizing soil to be used for road building is a new development[1]. Compacted plastic clay soils containing about 2 percent phosphoric acid greatly improved resistance to water and weathering, but the mechanism of soil-phosphoric acid stabilization was not explained. In agriculture it has been known for some time that phosphates are fixed in soil[2]. It is also known that sodium phosphates may be used to disperse soils in water for particle size analysis[3].

Laboratory Experiments

Mixtures and Materials. Four different soil, chemical mixtures were studied: soil, phosphoric acid; soil, calcium hydroxide, and phosphoric acid; soil, aluminum chloride, and phosphoric acid; and soil, magnesium acetate, and phosphoric acid. Only one soil was used, a silty clay, C horizon Wisconsin loess (table I). The phosphoric acid (75%) was commercial grade; the other chemicals were laboratory grade (table II).

Methods. The soil (passing No. 10 sieve) and the solid chemicals in powder form were first mixed in the dry state. Phosphoric acid and distilled water were then added to increase the moisture content of the soil to its optimum value for compaction. Immediately after thorough mixing, 2 inch diameter by 2 inch high specimens were molded to near standard Proctor density. The specimens were weighed, measured and wrapped in Saran Wrap. Half of the specimens were cured for seven days and half for fourteen days in a moisture cabinet at a temperature of 70 ± 3°F and a relative humidity of not less than 90 percent. At the end of each curing period the specimens were completely immersed in distilled water at room temperature for 24 hours and then were tested for unconfined compressive strength. This strength is hereafter referred to as *immersed strength.* An X-ray diffraction analysis was made on air dry, oven dry (80°C), and wet samples of some of the tested specimens to measure the basal spacing of the montmorillonite in the soil and to check for the presence of crystalline phosphates. Other specimens after testing for strength were air dried and then immersed again in distilled water to determine their resistance to soaking in the dry state.

Formation and Nature of Phosphate Gel

The development of immersed strength by treated specimens is believed due to the formation of insoluble amorphous phosphate compounds, phosphates of aluminum, iron, or alkaline earths, apparently in a gel[2, 4]. The gel concept is suported by the X-ray data, which indicated no newly formed crystalline com-

TABLE I. PROPERTIES OF SOIL USED

Textural composition %*	
Gravel (> 2.0 mm)	0
Sand (2.0 - 0.074 mm)	0.2
Silt (74 - 5 μ)	58.0
Clay (< 5 μ)	41.8
Colloids (< 1 μ)	31.0
Predominant clay mineral†	Montmorillonite and illite
Probable predominant exchangeable cation	Calcium
Specific gravity, 25° C/4° C	2.72
Chemical properties	
Cat ex. cap., m.e./100 gm‡	28.2
carbonates,§	0.8
pH	6.2
Organic matter, %	0.5
Physical properties	
Liquid limit, %	53.1
Plastic limit, %	25.7
Plasticity index	27.4
Shrinkage limit, %	19.9
Centrifuge moist. equiv., %	21.3
Classification	
Textural**	Silty clay
Engineering (AASHO)	A-7-6(18)

* Dispersed by air-jet with sodium metaphosphate dispersing agent.
† From differential thermal analysis and X-ray diffraction analysis of fraction passing No. 200 sieve.
‡ Fraction passing No. 40 sieve.
§ From differential thermal analysis.
** Textural classification is based on former Bureau of Public Roads System (8, p. 18) except that sand and silt sizes are separated on No. 200 sieve (0.074 mm).

TABLE II. EQUIVALENT TERMS EXPRESSING CONCENTRATION OF ADDITIVES

Additive	Dissociating ions		Amount of additive %	Corresponding amount expressed as milli-equivalents of positive ions per 100 grams of soil
H_3PO_4 (75%)	H+	$H_2PO_4^-$	1	7.65
	2H+	$HPO_4^=$	1	15.30
	3H+	$PO_4^{\equiv}$	1	22.95
$AlCl_3 \cdot 6H_2O$	Al+++	—	1	12.42
$Mg(CH_3COO)_2 \cdot 4H_2O$	Mg++		1	9.32
$Ca(OH)_2$	Ca++		1	27.00
$CaCO_3$*	Ca++		1	16.00

* $CaCO_3$ was not used as an additive in this study but is often present in Iowa soils. It is listed here to estimate the amount of phosphoric acid required to decompose naturally occurring $CaCO_3$.

pounds. It is not known whether the gel cements as well as waterproofs, since the effect on dry strength was not evaluated.

Treatment with phosphoric acid only. The formation of phosphate gel[4] is probably the result of the reaction between the phosphoric acid and the cations in the soil. There may be three sources of cations, exchangeable cations of clay minerals, cations of other compounds present in the soil such as Fe_2O_3 or $CaCO_3$, and cations from positions in the lattices of clay minerals. Cations from the latter source would be predominatly aluminum, magnesium, or iron. Adsorption of the H+ cations of phosphoric acid by clay minerals is believed to be of great significance in the availability of cations from the clay mineral lattices[5]. The adsorption of phosphate anions through anion exchange may also be effective in this cation migration[5].

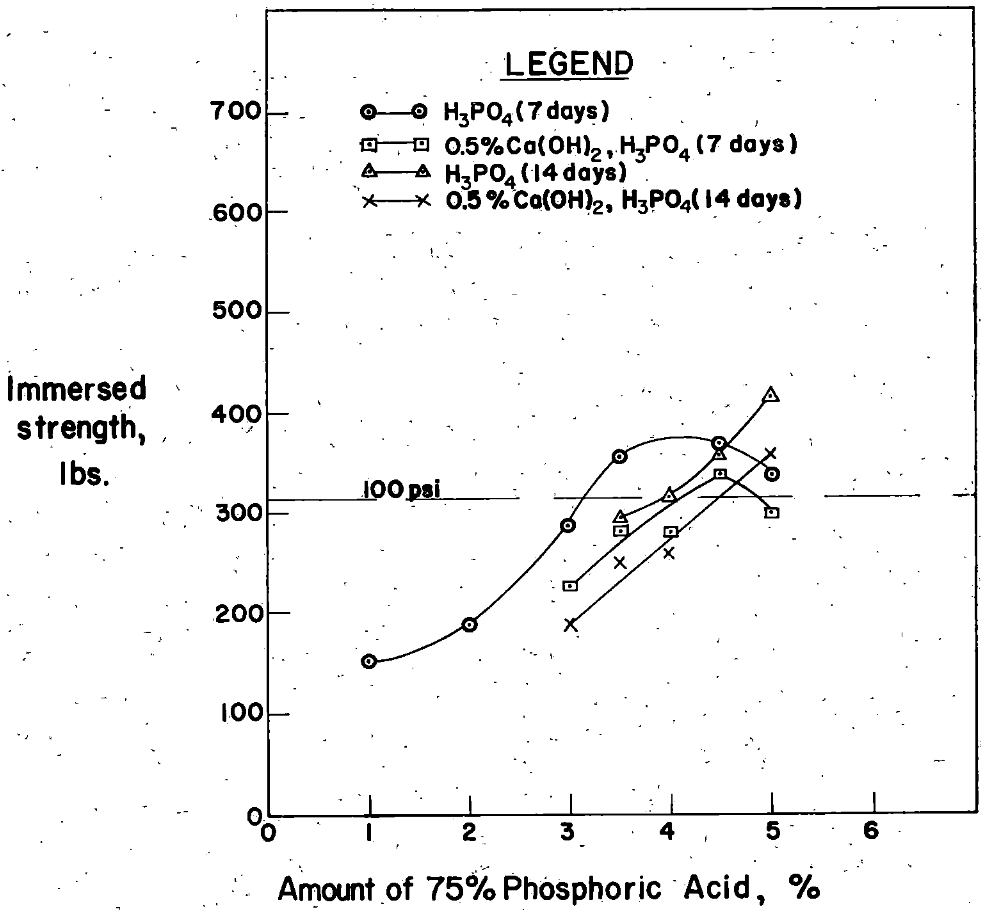

Fig. 1. Unconfined compressive strength of soil, phosphoric acid and soil, lime, and phosphoric acid mixtures after 24 hours immersion in water (2 inch diameter by 2 inch high specimens).

Since the formation of the gel must take place in solution, moist curing of the soil specimens is essential. The immersed strength of soil, phosphoric acid specimens is a function of both amount of phosphoric acid and the length of curing (figure 1). In the range of acid treatment studied an optimum strength occurred with seven day curing, but the strength increased with fourteen day curing when increased amounts of acid were used. The point of intersection of the curves may represent the minimum treatment level for satisfactory long term strength. From the data it appears that for a certain amount of phosphoric acid a certain time interval is essential for the formation of the insoluble phosphates, and the gel, once formed, undergoes either a physical or a chemical rearrangement, or both, which for small amounts of phosphoric acid may be at the expense of the immersed strength of the soil.

Use of metalic salts as an additional source of cations for phosphate gel formation. In the order of abundance the cations in the soil from any of the three sources mentioned which give insoluble phosphates, are calcium, aluminum, magnesium, and iron[2]. For this reason additives of salt of calcium, aluminum and magnesium were studied as an additional source of cations for insoluble phosphate formation in soil and phosphoric acid mixtures.

Effect of calcium hydroxide. Only 0.5 percent of calcium hydroxide was used in this experiment, and the effects on the seven day and fourteen day strengths of soil-phosphoric acid mixtures were studied (figure 1). In general the trends of data representing calcium hydroxide treated specimens are similar to those obtained for soil, phosphoric acid alone. Although strengths were slightly lowered by calcium hydroxide treatment, the differences between seven day and fourteen day strengths were less, perhaps indicating less sensitivity to curing time. The seven and fourteen day curves intersect at about the same phosphoric acid content as the curves for soil, phosphoric acid alone, lending further support to the concept of a *critical* minimum phosphoric acid content. Further study is needed to determine the effects with larger additions of calcium hydroxide.

A limited amount of experimenting was done with soil and phosphoric acid mixtures treated with 0.5 percent and 1.0 percent of aluminum chloride and magnesium acetate. Test results indicate that aluminum and magnesium cations may react with phosphoric acid to form better phosphate gels for soil stabilization than those obtained with calcium cations or with the acid alone.

Effect of air drying on immersed strength. When the immersed strength tests were completed, some soil specimens were air dried and again immersed in distilled water. All specimens thus treated, except those containing aluminum chloride or magnesium acetate, slaked in water.

The resistance to slaking is a further indication of the waterproofing effectiveness of aluminum or magnesium phosphates.

SUMMARY

Use of phosphoric acid alone or with salts of calcium, magnesium, or aluminum improves the water resistance of compacted, moist cured soil, probably through the formation of amorphous phosphates of these metals in a gel. When salts of these metals are not added with phosphoric acid, the metallic cations may be furnished by the soil.

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USE OF PHOSPHORIC ACID IN SOIL STABILIZATION

by

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(Highway Research Board Buletin 282. 1960.)

ABSTRACT

The purpose of this investigation was to determine the effect of phosphoric acid treatments on the stability of compacted calcareous and noncalcareous clay soils. Unimmersed and immersed strengths and freeze-thaw resistance of phosphoric acid treated soil specimens were used as criteria for stability.

The unimmersed and immersed strengths of phosphoric acid treated soils were studied relative to the curing conditions, carbonate contents of soils, and use of secondary additives. Moist curing was found beneficial to strength. Soils containing $CaCO_3$ required more phosphoric acid than $CaCO_3$ free soils because $CaCO_3$ reacted with the acid available for stabilization. No worthwhile benefit was found from the use of secondary additives.

X-ray diffraction analysis and quantitative chemical analyses were used to trace the chemical reactions after treatment. These analyses lead to the conclusion that phosphoric acid and clay minerals react to produce an amorphous aluminum phosphate gel which serves as a cementing agent.

INTRODUCTION

Phosphoric acid stabilization of clay soils is relatively new[5]. Compacted specimens of clayey soils treated with as little as 2% phosphoric acid were found to withstand exposure to water and to wintering.

An evaluation study by the Soil Research Laboratory, Iowa Engineering Experiment Station, showed that the water resistance of a non-calcareous plastic loess was improved by treatments with phosphoric acid, or phosphoric acid and salts of calcium, magnesium or aluminum[3]. It was hypothesized that the immersed strength of the compacted, moist cured mixtures was due to the formation of amorphous phosphates in a gel form, and that the metallic cations needed for the insoluble gel formation could be provided by the soil or by adding salts of the desired cations.

Previous work indicated that phosphoric acid, used in amounts between 1% and 10% of the dry soil weight, was a promising stabilizer for fine grained soils[6]. Strengths depended on moisture content and density; highest strengths were developed when specimens were cured under humid conditions; and certain additives accelerated the curing process and improved the strength retention after immersion. On the basis of more recent studies it was concluded that phosphoric acid with added fluorine compounds and/or amines promised low-cost stabilization of fine grained, carbonate-free soils under field conditions[7].

This investigation was undertaken to evaluate further the use of phosphoric acid for stabilizing clay soils. The principal objectives of the investigation were:

1. Determine the effect of phosphoric acid treatments on the strength of compacted clay soils.
2. Determine the resistance of phosphoric acid stabilized clay soil to alternate cycles of freeze and thaw.
3. Determine the factors and soil compositional variables, if any, which may limit the use of phosphoric acid stabilization.

To accomplish these objectives it was first necessary to determine:

1. The relationship between the molding moisture content for maximum dry density and the molding moisture content for maximum immersed strength for the phosphoric acid treated soils.
2. The best method of curing phosphoric acid treated soil specimens.

A preliminary study was made to determine whether combination treatments of a clay soil with phosphoric acid and other chemicals would give better immersed strengths than obtainable from phosphoric acid treatment alone.

MATERIALS USED

Soils

Of the seven soils investigated the first five were used in the strength studies; the leached and unleached Kansan till samples were used in supplementary studies (table I).

TABLE I. DESCRIPTION AND PROPERTIES OF SOIL SAMPLES

Sample	Plastic loess (lab. No. 528-4)	Kansan gumbotil (lab. No. 528-8)
Geological description:	Wisconsin-age loess, noncalcareous	Kansan-age gumbotil, highly weathered, noncalcareous
Location:	Keokuk County, Ia.	Keokuk County, Ia.
Soil Series:	Mahaska	Mahaska
Horizon:	C	Fossil B*
Sampling depth, ft.:	3 to 6½	7½ to 8½
Textural composition, %:		
Gravel (> 2 mm)	0	0
Sand (2-0.074 mm)	0.2	16.0
Silt (74-5 μ)	60.8	13.5
Clay (< 5 μ)	39.0	70.5
Colloids (< 1 μ)	31.0	66.0
Predominant clay minerals:†	Montmorillonite	Montmorillonite
Chemical properties:		
Cat. ex. cap., m.e./gm‡	23.5	41.0
Carbonates,§ %	0.0	0.8
pH**	5.6	6.5
Organic matter, %	0.2	0.2
Physical properties:		
Liquid limit, %	52.1	75.6
Plastic limit, %	20.0	25.6
Plasticity index, %	32.1	50.0
Classification:		
Textural††	Silty clay	Clay
Engineering (AASHO)	A-7-6(18)	A-7-6(20)

Table I, Continued.

Sample	Alluvial clay (lab. No. 627-1)	Detroit clay (lab. No. AR-4)
Geological description:	Missouri River floodplain alluvium, calcareous	Probably Wisconsin-age glacial till, calcareous
Location:	Harrison Co., Ia.	Monroe Co., Mich.
Soil Series:	None	Unknown
Horizon:	None	C
Sampling depth, ft:	0-4	Unknown
Textural composition, %:		
Gravel (> 2 mm)	0.0	0.0
Sand (2-0.074 mm)	0.5	7.0
Silt (74-5 μ)	27.5	36.0
Clay (< 5 μ)	72.0	57.0
Colloids (< 1 μ)	50.0	43.0
Predominant clay minerals:†	Montmorillonite	Illite-Chlorite
Chemical properties:		
Cat. ex. cap., m.e./gm‡	36.4	14.5
Carbonates,§ %	5.1	7.2
pH**	8.0	8.4
Organic matter, %	1.3	0.6
Physical properties:		
Liquid limit, %	65.8	44.0
Plastic limit, %	26.4	21.1
Plasticity index, %	39.4	22.9
Classification:		
Textural††	Clay	Clay
Engineering (AASHO)	A-7-6(20)	A-7-6(14)

Table I, Continued.

Sample	Virginia clay (lab. No. AR-5)	Leached Kansan till (lab. No. 416-4)
Geological description:	Residual soil over diorite, noncalcareous	Kansan-age till, noncalcareous
Location:	Virginia	Warren Co., Iowa
Soil Series:	Davidson	Shelby
Horizon:	B	C
Sampling depth, ft.:	Unknown	7 to 9
Textural composition, %:		
Gravel (> 2 mm)	0	1.3
Sand (22-0.074 mm)	21.0	32.6
Silt (74-5 μ)	37.0	29.1
Clay (< 5 μ)	42.0	37.0
Colloids (< 1 μ)	29.0	27.0
Predominant clay minerals:†	Kaolinite (Halloysite)-vermiculite	Montmorillonite
Chemical properties:		
Cat. ex. cap., m.e./gm‡	12.4	14.8
Carbonates,§ %	0.7	0.0
pH**	5.9	7.4
Organic matter, %	2.6	0.75
Physical properties:		
Liquid limit, %	43.5	38.2
Plastic limit, %	27.0	15.1
Plasticity index, %	16.5	23.1
Classification:		
Textural††	Clay	Clay
Engineering (AASHO)	A-7-6(12)	A-6(11)

The five soils were chosen so that the effects of different clay minerals and of varying calcium carbonate content could be evaluated. Three of these soils had montmorillonite as the dominant clay mineral: the noncalcareous plastic loess, the noncalcareous Kansan gumbotil and the calcareous alluvial clay. The dominant clay minerals in the calcareous Detroit clay were illite and chlorite; kaolinite (halloysite) and vermiculite were the dominant clay minerals in the noncalcareous Virginia clay.

Phosphoric Acid

The phosphoric acid used was reagent grade, 86 percent orthophosphoric acid, H_3PO_4. All additives are expressed as percentages of pure (100%) phosphoric acid, based on the oven dry weight of the soil.

Other Chemicals

The following chemicals were used with phosphoric acid. Additives of these chemicals are expressed as percentages of the oven dry weight of the soil, with no correction made for crystal water or solvents.

TABLE I, CONTINUED.

Sample	Unleached Kansan till, (lab. No. 409-12C)
Geological description:	Kansan-age glacial till, calcareous
Location:	Ringgold County, Iowa
Soil Series:	Shelby (Burchard)
Horizon:	C
Sampling depth, ft:	4½-10½
Textural composition, %:	
Gravel (> 2 mm)	0
Sand (2-0.074 mm)	31.5
Silt (74-5 μ)	30.0
Clay (< 5 μ)	38.5
Colloids (< 1 μ)	31.0
Predominant clay minerals:†	Montmorillonite
Chemical properties:	
Cat. ex. cap., m.e./gm‡	29.5
Carbonates,§ %	4.9
pH**	8.3
Organic matter, %	0.2
Physical properties:	
Liquid limit, %	42.4
Plastic limit, %	20.5
Plasticity index, %	21.9
Classification:	
Textural††	Clay
Engineering (AASHO)	A-7-6(12)

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† By X-ray diffraction analysis.

‡ For fraction passing No. 40 sieve.

§ By versenate method, includes all acid extractable calcium as calcium carbonate.

** For fraction passing No. 10 sieve.

†† From triangular chart developed by U.S. Bureau of Public Roads, but 0.074 mm was used as the lower limit of the sand fraction.

* Underlies C horizon loess of Mahaska series.

Aluminum sulfate. Reagent grade aluminum sulfate with 18 moles of crystal water, $Al_2(SO_4)_3 \cdot 18H_2O$, was dissolved in distilled water before adding to the soil.

Arquad 2HT. Suspensions of Arquad 2HT in distilled water were prepared from chemical supplied by Armour and Company, Chicago, Illinois. This chemical contained 75% active Arquad 2HT.

Sodium fluoride. Reagent grade sodium fluoride, NaF, was added to the soil in powdered form.

Aluminum hydroxide. Reagent grade aluminum hydroxide, $Al_2O_3 \cdot 3H_2O$, was used in powdered form.

Calcium Chloride. Reagent grade anhydrous calcium chloride, $CaCl_2$, was dissolved in distilled water before being added to the soil.

Sodium metasilicate. Reagent grade sodium metasilicate with 9 moles of crystal water, $Na_2SiO_3 \cdot 9H_2O$, was dissolved in distilled water before being added to the soil.

Calcium carbonate. Reagent grade calcium carbonate, $CaCO_3$, was added to the soil in powdered form.

METHODS OF PREPARING AND TESTING SPECIMENS

Preparation of Mixtures

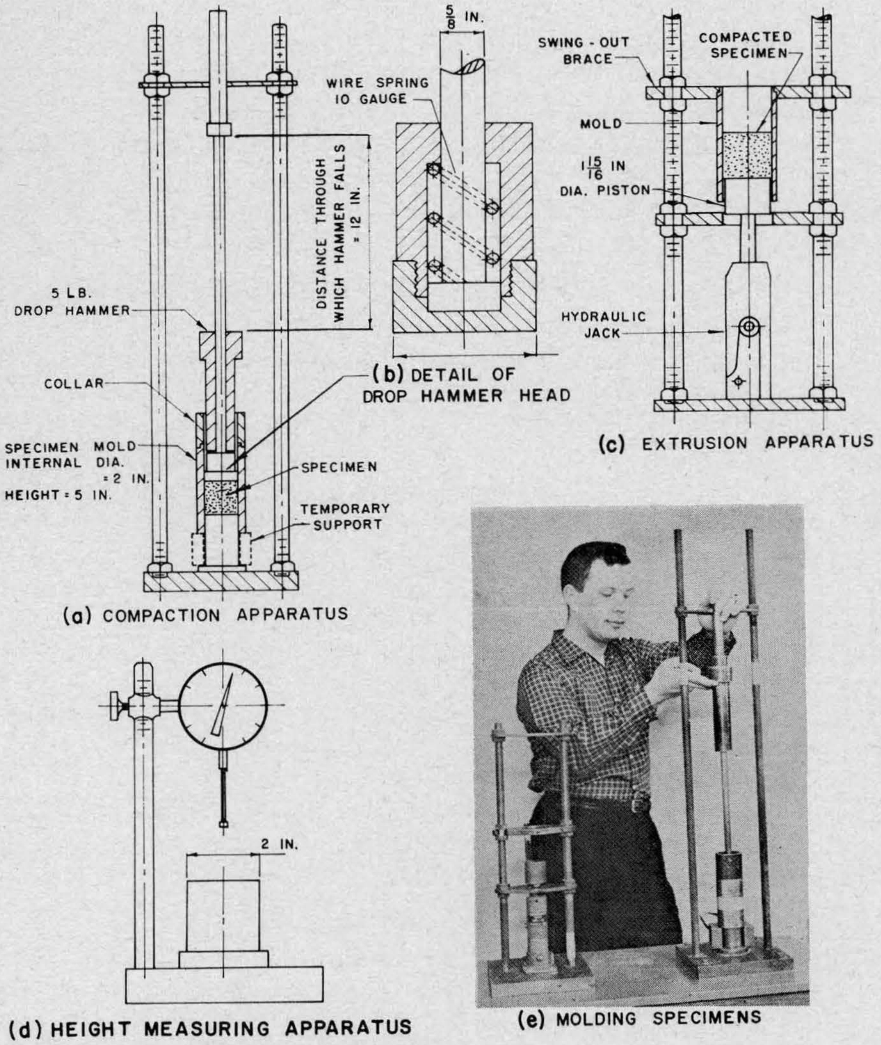
Air dried soil passing the No. 10 sieve was weighed and placed in an aluminum mixing bowl. Distilled water for the specified moisture content was added slowly to the soil while it was being mixed with a Hobart Model C-100 mixer. (Allowance was made for the water in the 86% phosphoric acid and the hygroscopic water of the soil in calculating the mix water needed for a specified moisture content.) After adding the water, phosphoric acid in the required amount was added slowly as mixing continued. This mixing of water and phosphoric acid took about one minute. The mixture was then machine mixed for an additional one minute, hand mixed for thirty seconds to insure that no unmixed soil adhered to the bottom of the bowl, machine mixed for another minute, and finally hand mixed for approximately thirty seconds.

Chemicals used in the dry form were dry mixed with the soil for one minute prior to the addition of water. The other chemicals were added to the soil in the mix water before adding the phosphoric acid.

A two minute period of machine mixing following the addition of phosphoric acid was chosen because longer mixing produced a hard and lumpy mix. A shorter period of machine mixing did not properly mix all the ingredients with the soil.

Molding

From each mix, six 2 inch diameter by 2 ± 0.05 inch high test specimens were prepared by use of the molding apparatus (figure 1). The 5 lb. hammer was dropped a distance of twelve inches. The specimen was compacted by five blows of the hammer on each end of the specimen for a total of ten blows. This gave a compactive effort approximately equal to the standard ASTM (Proctor) compactive effort (ASTM Method D 558-57) when the molding is done on a wooden table[9]. Immediately before molding the first specimen and immediately after molding the last specimen, a sample was taken from the mix for moisture content determination, and the two moisture contents were averaged. A moisture content of ± 1 percent of the specified moisture content was maintained. All specimens were weighed to the nearest 0.1 gram and measured for height to the nearest 0.001 inch.



(a) COMPACTION APPARATUS

(b) DETAIL OF DROP HAMMER HEAD

(c) EXTRUSION APPARATUS

(d) HEIGHT MEASURING APPARATUS

(e) MOLDING SPECIMENS

Fig. 1. Apparatus for molding 2 inch diameter by 2 inch high test specimens.

Mixtures of plastic loess and varying percentages of phosphoric acid were used to determine the optimum molding moisture content for maximum immersed strength. Specimens of each mixture were molded at different moisture contents to determine the dry density versus moisture content relationship. After the specimens had been weighed and measured for density calculations, they were

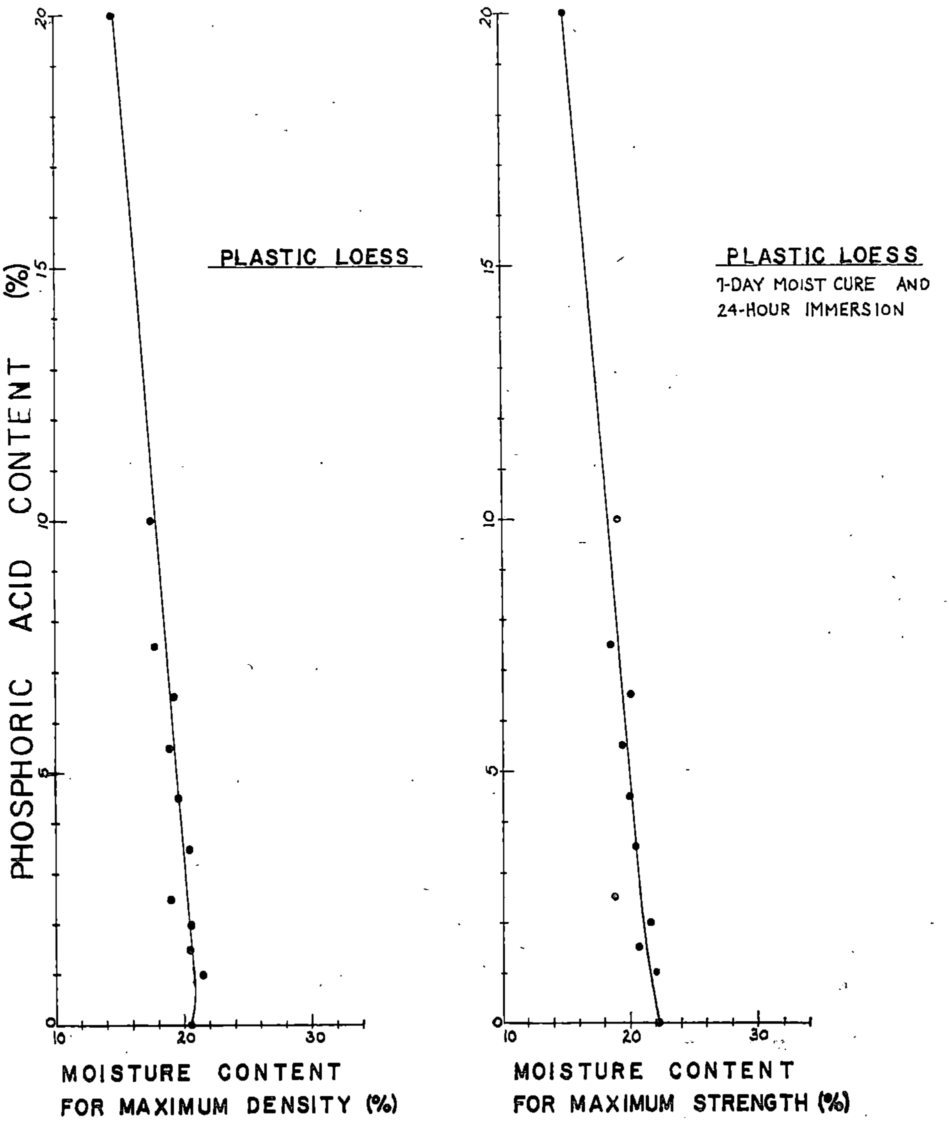


Fig. 2. Effect of phosphoric acid content of mixtures with plastic loess on the optimum moisture contents for maximum standard Proctor density and for maximum immersed strength.

moist cured for seven days and then were immersed for twenty-four hours in distilled water before being tested for unconfined compressive strength. Optimum moisture contents for maximum dry density and for maximum immersed strength of each mixture were interpolated from graphs of density versus molding moisture content, and of immersed strength versus molding moisture content.

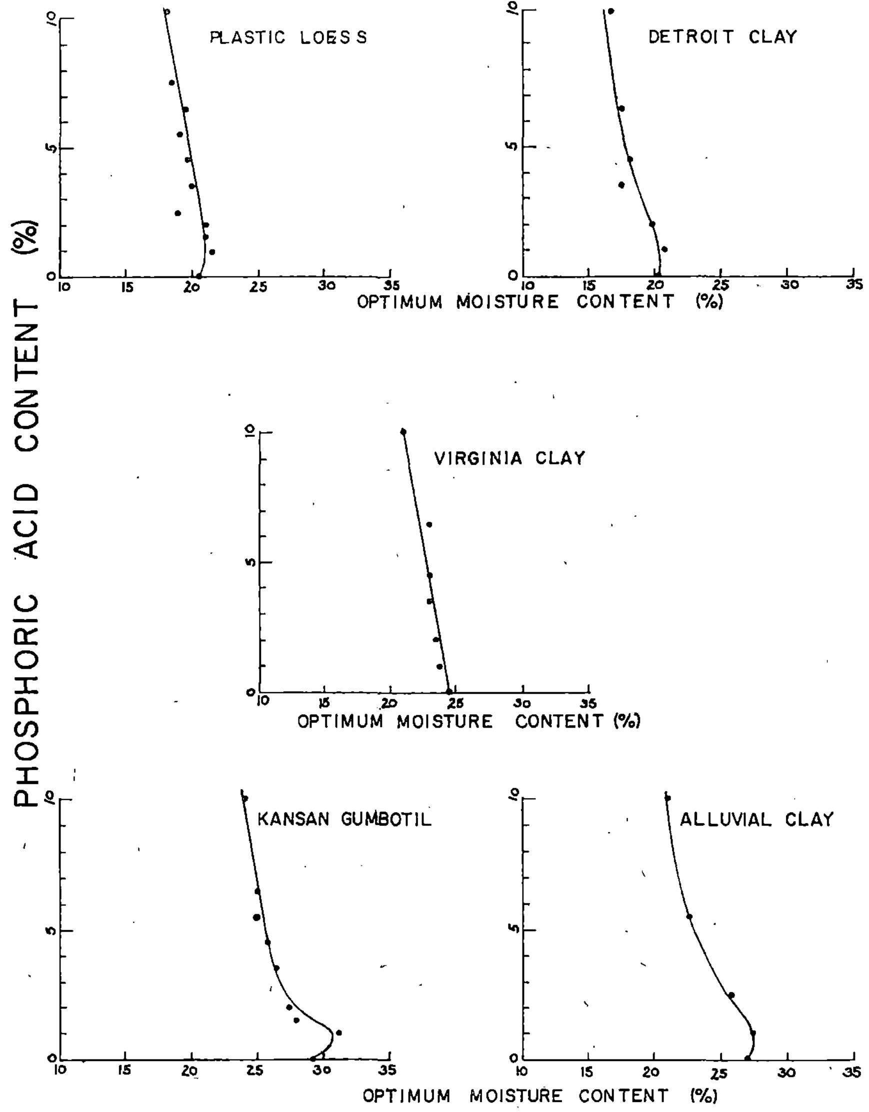


Fig. 3. Effect of phosphoric acid content of mixtures with plastic loess, Detroit clay, Virginia clay, Kansan gumbotil, and alluvial clay on optimum moisture content for maximum standard Proctor density.

These optimum moisture contents were then plotted against phosphoric acid content (figure 2). The two optimum moisture contents are nearly identical; hence optimum molding moisture contents for mixtures of phosphoric acid and each of the other soils used in the main study were interpolated from dry density versus moisture content curves and specimens for strength studies were molded at these optimum moistures. The effect of phosphoric acid content on the optimum molding moisture contents so selected was determined for each of the five soils (figure 3). The data indicate that there is an inverse relationship between optimum moisture content and phosphoric acid content, with optimum moisture decreasing about 3 to 5%, based on the dry soil weight, as the phosphoric acid content is increased to 10%. The untreated soil generally had a slightly lower optimum moisture content than after treatment with 1 to 2% acid.

Curing

Two methods of curing phosphoric acid-treated soil were compared before selecting a curing method for the main study. The test specimens for the comparative study were prepared from a mixture of plastic loess and 7.5% phosphoric acid. In both curing methods the molded specimens, wrapped in wax paper and sealed with cellophane tape, were first placed in a curing room at 70 ± 4°F and 95 ± 5% relative humidity for 7, 14 or 28 days. In one method the specimens were unwrapped after each moist curing period and immersed in distilled water for 24 hours before testing for strength. In the other method, after moist curing 7, 14 or 28 days the specimens were unwrapped and placed in open air for 7 days and then immersed for 24 hours in distilled water before testing for strength.

The specimens cured by the first method were molded at optimum moisture for maximum dry density because maximum density gives near maximum immersed strength as previously discussed. In the second curing method the specimens were molded at various moisture contents for 7 days moist curing and 7 days air curing; all specimens cured in this manner slaked upon immersion. The last specimens to slake were those molded at optimum moisture for maximum dry density. For this reason all the specimens prepared for 14 or 28 days moist curing and 7 days air curing were molded at optimum moisture content; however, these specimens also slaked upon immersion.

On the basis of these results it was decided to cure all specimens in the humid room for most of the investigation, and immediately after each curing period either to test them for unimmersed strength or to immerse them in distilled water for 24 hours before testing for unconfined compressive strength. Immersion in water before testing was to simulate the detrimental effect of water on inadequately stabilized soil in the field, although complete immersion for 24 hours is a more severe treatment than usually encountered in roads.

Unconfined Compressive Strength Testing

The specimens were tested for unconfined compressive strength by a testing machine having a load travel rate of 0.1 inch per minute. The compressive strength was taken as the maximum test load in psi sustained by a specimen. Unless otherwise indicated, strengths reported in this paper are averages for three specimens. In only a few did the difference between the individual values and the average value exceed 10% of the average value.

Freeze Thaw Testing

The resistance of phosphoric acid stabilized soil to alternate cycles of freeze and thaw was evaluated by the modified British standard freeze-thaw test[2]. Only one soil, the plastic loess, treated with 2, 4.5 and 7.5% phosphoric acid was used in this study. For each curing period, two identical 2 inch diameter by 2 ± 0.05 inch high specimens were molded from each mixture at optimum moisture content; the curing periods were seven and fourteen days. One specimen was designated the control specimen and the other the freeze thaw specimen[1, 2, 4]. After moist curing the top flat surface of both specimens was spray painted with a resin base paint to a thickness of approximately 1 mm. The control specimen was immersed for fifteen days in distilled water at a temperature of 77 ± 4°F and then tested for unconfined compressive strength. The freeze-thaw specimen was immersed in distilled water at a temperature of 77 ± 4°F for 24 hours, then was exposed alternately to temperatures of 23 ± 2°F and 77 ± 4°F for 14 cycles, each cycle lasting 24 hours, and finally tested for unconfined compressive strength. (A vacuum flask specimen container was used to cause freezing to occur from the top down and to supply unfrozen water to the bottom of the specimen throughout the test.)

PRELIMINARY STUDY

Previous work had indicated the possibility that metallic salts or amines with phosphoric acid might give better results than phosphoric acid alone. A preliminary study was made to check on this. The soil used was the leached (noncalcareous) Kansan till (table I).

In the 14 day cured immersed strengths produced by soil-phosphoric acid mixtures with and without aluminum sulfate, at 0.6% phosphoric acid, 3% aluminum sulfate increased immersed strength; at 2% phosphoric acid, 3% aluminum sulfate decreased immersed strength, and 10% caused a further decrease; at 4% phosphoric acid, 1% aluminum sulfate only slightly increased immersed strength (figure 4).

The 7 day cured immersed strength results obtained with treatments of the other chemicals show that the highest immersed strength was obtained with 2% phosphoric acid and 0.2% Arquad 2HT; but it is probably only slightly better than obtainable with 2% phosphoric acid alone (figure 5). The other additives also did not produce promising results.

STRENGTH STUDIES

Unimmersed Strength

The phosphoric acid treatment on the unimmersed specimen strengths of the five soils after 7, 14 and 28 days moist curing resulted in the montmorillonitic clay soils (Kansan gumbotil, alluvial clay, and plastic loess) generally reaching a maximum strength with from 2 to 10% phosphoric acid (figure 6). More chemical generally caused a decrease in strength.

No optimum phosphoric acid content was observed with the illitic-chloritic clay soil (Detroit clay). Up to 10 percent phosphoric acid, strength increased slowly at a uniform rate with increased acid content; but at 10 percent or above, the rate of strength gain increased sharply, and at all curing times it continued

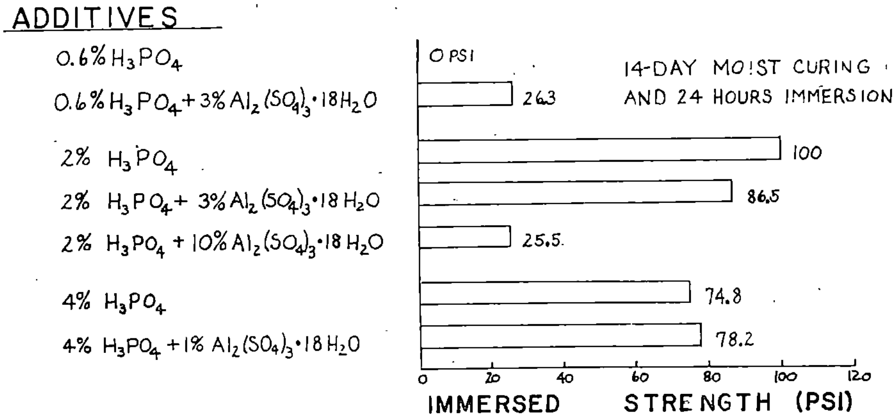


Fig. 4. Immersed strengths of 14 day cured specimens of noncalcareous Kansan till treated with phosphoric acid and with phosphoric acid plus aluminum sulfate.

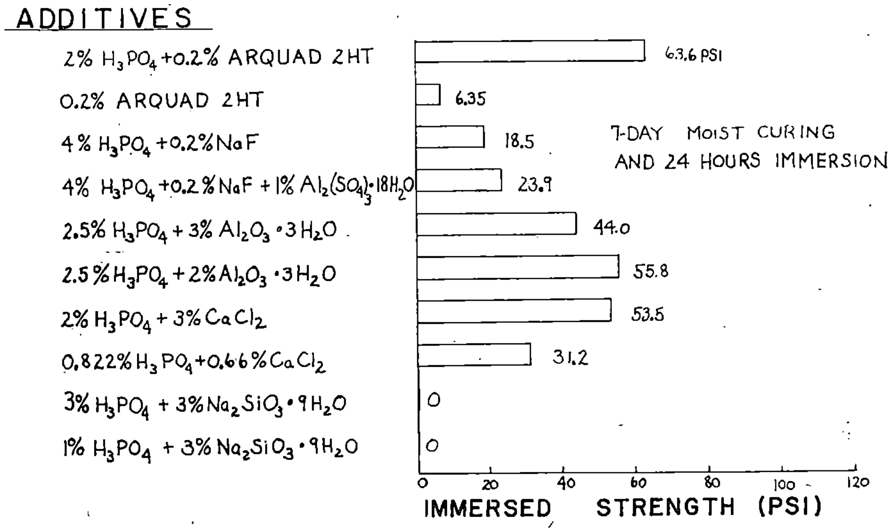


Fig. 5. Immersed strengths of 7 day cured specimens of noncalcareous Kansan till treated with phosphoric acid plus various other chemicals.

at the increased rate up to 18% acid, the largest amount used. This change in the rate of strength increase, discussed later, was due to the calcium carbonate content of the soil.

The strengths of the phosphoric acid treated kaolinite-vermiculite clay soil (Virginia clay) specimens were low, and did not reach a maximum with from 1 to 14% acid. At 14% phosphoric acid, the 14 and 28 day strengths were still increasing, indicating that use of more acid might further increase strength.

Since the unimmersed strength of a stabilized soil is an indicator of cementing action derived from the stabilizer, phosphoric acid treatment of soil can be said to produce a cementing agent.

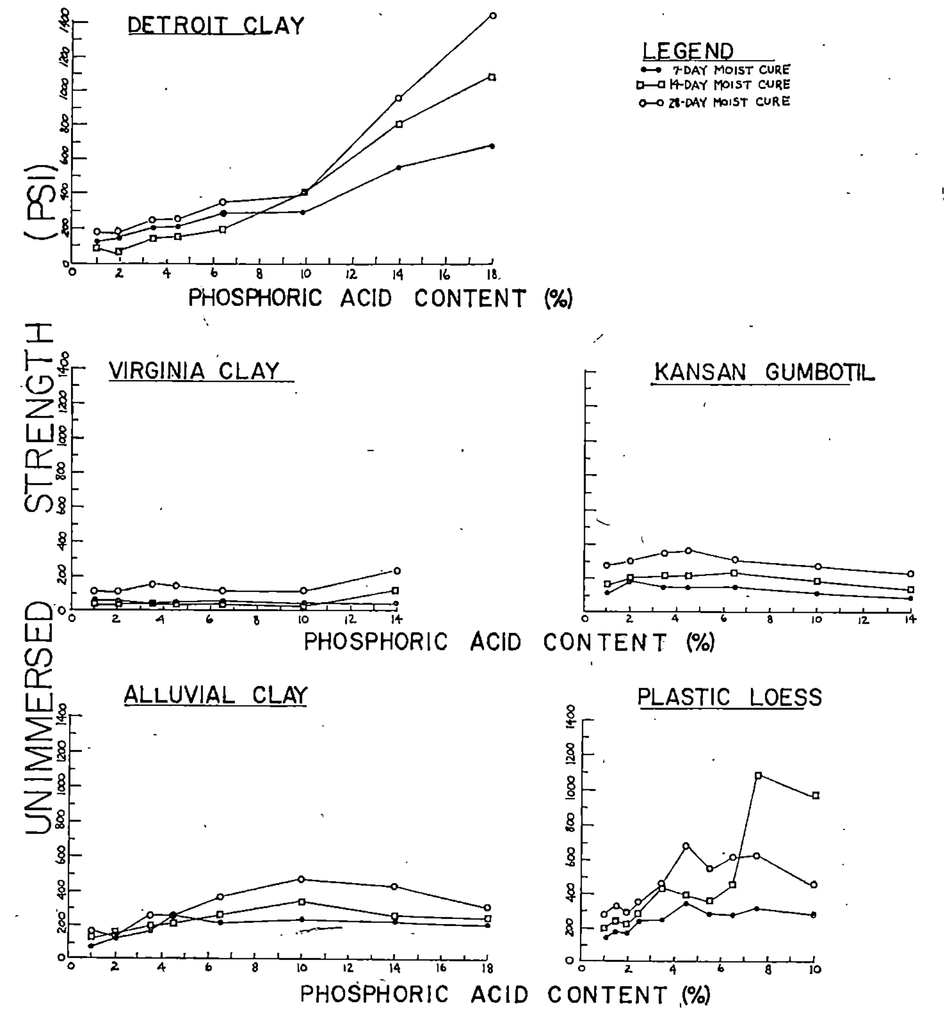


Fig. 6. Effect of phosphoric acid content of clay soils on unimmersed strengths of 7, 14, and 28 day cured test specimens.

Immersed Strength

The phosphoric acid treatments on the immersed strength of the five soils after 7, 14 and 28 days moist curing resulted in the montmorillonitic clay soils (Kansan gumbotil, alluvial clay, and plastic loess) reaching a maximum or near maximum immersed strength at each curing time with from 4 to 14% phosphoric acid (figure 7). More than the optimum amount of acid generally caused a decrease in strength.

Specimens of the illitic chloritic clay soil (Detroit clay) containing less than 10% phosphoric acid failed during immersion. However strength gain was rapid

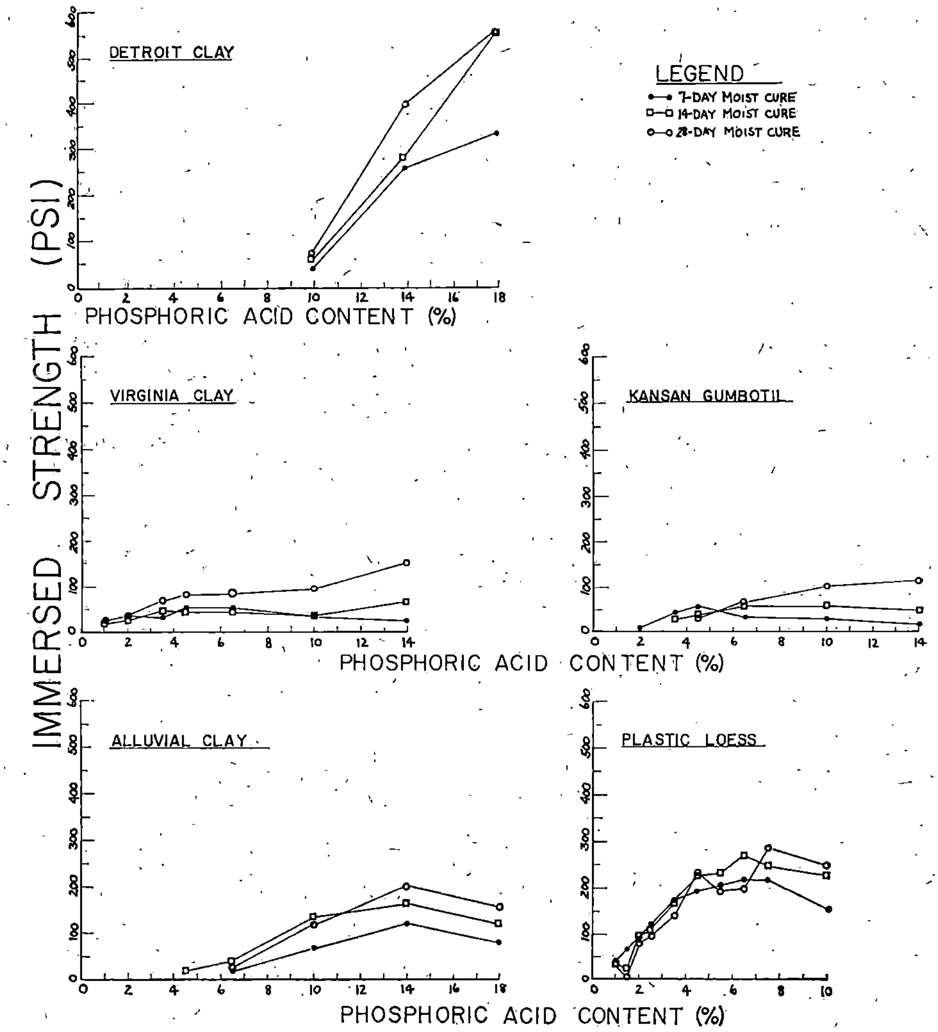


Fig. 7. Effect of phosphoric acid content of clay soils on immersed strengths of 7, 14, and 28 day cured test specimens.

as acid content was increased above 10%, and at 18% the strength probably had not reached a maximum.

The 14 and 28 day strengths of the kaolinite and vermiculite clay soil (Virginia clay) specimens generally showed gradual increase with from 1 to 10% phosphoric acid without reaching to a maximum, and above 10% the rate of strength gain was somewhat greater. The 7 day strength reached a maximum at 4 to 5% acid, and strength slowly decreased with use of more acid.

The immersed strengths obtained in these tests indicate that the cementing product produced by the interaction of phosphoric acid and soil is water insoluble.

The use of small percentages of phosphoric acid with Detroit clay and alluvial clay did not produce immersed strength (figure 7). This is due to the calcium carbonate content of these soils, as explained later. Here it is enough to say that phosphoric acid reacts with calcium carbonate and this increases the amount of phosphoric acid necessary to obtain immersed strength.

Analysis of the Strength Data

The different responses of different soils to phosphoric acid treatments (figures 6, 7) may be hypothesized as being due to differences in the rapidity and the extent of the chemical reactions which furnish the reaction products that cement soil grains together and thus increase strength. Any remaining unreacted phosphoric acid lubricates the soil particles and tends to decrease the strength. Therefore, when the ratio of unreacted phosphoric acid to the reaction product is excessive, a net decrease in specimen strength occurs. The relative amounts of unreacted phosphoric acid and the reaction product depend on how far the reaction has progressed towards equilibrium, which for any given time depends on the rapidity of the reaction.

Generally both a maximum unimmersed and immersed strength were obtained with montmorillonitic clay soils; but with the range of treatment, maxima were not reached with the illite and chlorite and the kaolinite and vermiculite rich clay soils. The highest strengths were obtained with the illite and chlorite rich soil and the lowest strengths with the kaolinite and vermiculite rich soil. The three montmorillonitic soils gave mid-range strengths.

The rapid attainment of high strengths with the illitic-chloritic clay soil (Detroit clay) (figures 6, 7) may be due to the rapid and complete reaction of phosphoric acid with the chlorite in the soil. As discussed later, X-ray diffraction analysis (figure 11) showed that chlorite is much more highly reactive with phosphoric acid than the other clay minerals; therefore it is believed that the chlorite in the Detroit clay reacted completely with phosphoric acid, which was largely responsible for the high strengths obtained.

Phosphoric acid treated montmorillonitic clay soils attained moderate strengths rapidly (figures 6, 7). This indicates that the rate of reaction may be as rapid in the montmorillonitic clay soils as it is in the illitic-chloritic clay soil, but the extent of the reaction is not as great in the montmorillonitic clay soils. Consequently with the montmorillonitic clay soils an appreciable amount of unreacted phosphoric acid was always present when equilibrium was reached, and its lubricating action tended to detract from the cementation effects of the reaction product. When the amount of unreacted phosphoric acid at higher levels of treatment became excessive, a net decrease in strength resulted. It also appears that both the amount of the optimum phosphoric acid treatment and the maximum strength depend on the amount of clay-size material present in the montmorillonitic clay soils. Generally, the higher the clay content the more phosphoric acid was required for optimum results and the lower the maximum strength value. Reduction of the maximum strength with increasing clay content may be due to the resulting decrease in coarser grained fractions which contribute to internal friction in the stabilized soil and oppose the lubricating action of unreacted phosphoric acid.

Phosphoric acid-treated kaolinite-vermiculite clay soil (Virginia clay) specimens generally showed a gradual increase in strength with longer curing time and with increased phosphoric acid contents. This may be attributed to a slow rate of reaction and the equilibrium conditions in favor of the products. The continued progress of the reaction more than compensates for the lubricating effect of the unreacted phosphoric acid as well as reducing the amount of unreacted material. Thus the slow but continuous strength gain results.

It is believed that the reaction product which furnishes cementation is essentially the same for all clay minerals and is a complex amorphous aluminum phosphate in the form of a gel—a conclusion also reached more or less by others[3, 6, 7].

Chlorite clay minerals seem to be the most reactive of clay mineral groups investigated in this study. Montmorillonitic minerals react rapidly with phosphoric acid but the reaction does not proceed very far. Kaolinite and vermiculite react slowly with phosphoric acid, and the reaction may proceed to an appreciable extent. An accelerator or a catalyst may aid the stabilization of kaolinite or vermiculite rich soils by speeding the reaction but can hardly benefit montmorillonite rich soils, since the reaction is already rapid. This conclusion is substantiated by the results reported[7], which show that fluorides and fluosilicates do not affect the phosphoric acid-clay reaction in montmorillonitic soils; however, they do accelerate the reaction in illitic soils. Thus, in all probability, illite reacts similarly to kaolinite or vermiculite. The general behavior of the illite group minerals can not be predicted from the data of the present study, since the reaction was obscured by the presence of chlorite.

FREEZE-THAW STUDY

The modified British freeze-thaw test[2] was used to evaluate the durability of seven and fourteen day cured specimens of selected mixtures of plastic loess and phosphoric acid. Bar graphs (figures 8, 9) show unconfined compressive strengths after curing and 1 day immersion; after curing and 15 days immersion (control specimen, p_c); and after curing, 1 day immersion, and 14 cycles of freeze-thaw (freeze-thaw specimen, p_f).

Criteria of Durability

Two criteria have been used for the evaluation of the freeze-thaw test results[2]. The first criterion is the value of the index of resistance to the effect of freezing (R_f), defined by the following equation and expressed as a percentage to the nearest 5%

$$R_f = \frac{100\, p_f}{p_c}$$

The minimum R_f value considered indicative of satisfactory field performance of

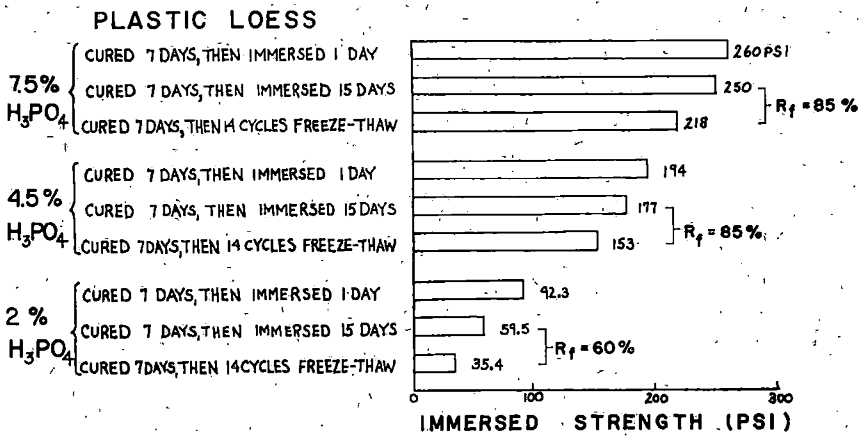


Fig. 8. Results of modified British freeze-thaw tests of 7 day cured specimens of phosphoric acid treated plastic loess.

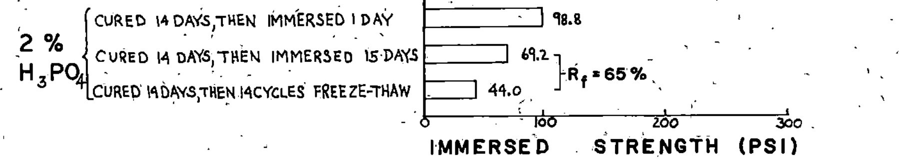


Fig. 9. Results of modified British freeze thaw tests of 14 day cured specimens of phosphoric acid treated plastic loess.

stabilized soils in road base courses in Great Britain is 75%. This same minimum value was adopted for the present study.

The second criterion requires a minimum value for the unconfined compressive strength of the control specimen (p_c) and the freeze-thaw specimen (p_f). The tentative minimum requirement for both p_c and p_f, for stabilized base course mix design in Iowa, is 250 psi, the value used in the present study[2].

Discussion of Results

Specimens cured 7 days. Resistance to the damaging effects of immersion and of freezing and thawing showed marked increases with increased phosphoric acid content in the treatment range 2% to 7.5% (figure 8), but judged on the basis of 7 days curing, none of the mixtures would be considered adequate for road bases in Iowa. However, the mixture with 7.5% phosphoric acid came close to being satisfactory, in that $R_f = 85\%$, $p_c = 250$ psi and $p_f = 218$ psi, the latter value being the only one that did not meet the minimum requirements for durability.

Specimens cured 14 days. If mix design was based on fourteen day curing of test specimens, 7.5% phosphoric acid would satisfactorily stabilize plastic loess for road bases in Iowa (figure 9). Lesser amounts of phosphoric acid probably would not provide adequate durability.

Time of immersion. A comparison of the strengths of the specimens immersed for one day with those of similar specimens immersed for 15 days (figures 8, 9) shows that as phosphoric acid content was increased the amount of strength reduction due to the longer time of immersion was generally reduced.

LIMITATION STUDY

The presence of calcium carbonate in many soils can be one limitation to the use of phosphoric acid stabilization. The cost of phosphoric acid stabilization can be another.

Calcium Carbonate

In a preliminary study of phosphoric acid stabilization using the calcareous (unleached) Kansan till (table I) no immersed strengths were obtained, that is, the specimens failed by slaking. Because of this it was decided to study the effect of calcium carbonate content on the immersed strength of phosphoric acid stabilized soil. Two experimental approaches were used. In one, natural soils that contained known amounts of calcium carbonate were used to evaluate the effect of calcium carbonate on immersed strength. The five soils used contained amounts of calcium carbonate varying from 0 to 7.2% (table I). The second approach was to use the noncalcareous plastic loess and add specific amounts of calcium carbonate and study the effect on immersed strength.

Natural soils. The effect of calcium carbonate content on immersed strength is shown by the curves for the five soils (figure 7). Noncalcareous plastic loess showed an immediate increase of immersed strength with the addition of 1% phosphoric acid. Alluvial clay with 5.1% $CaCO_3$ did not develop immersed strength until about 6.5% phosphoric acid was used. Detroit clay which contained 7.2% $CaCO_3$ did not develop immersed strength until the phosphoric acid content was at least 10%. Therefore it seems that the amount of phosphoric acid necessary to obtain immersed strength is increased as the calcium carbonate content is increased.

Plastic loess plus $CaCO_3$ additives. The effects on 7, 14 and 28 day cured

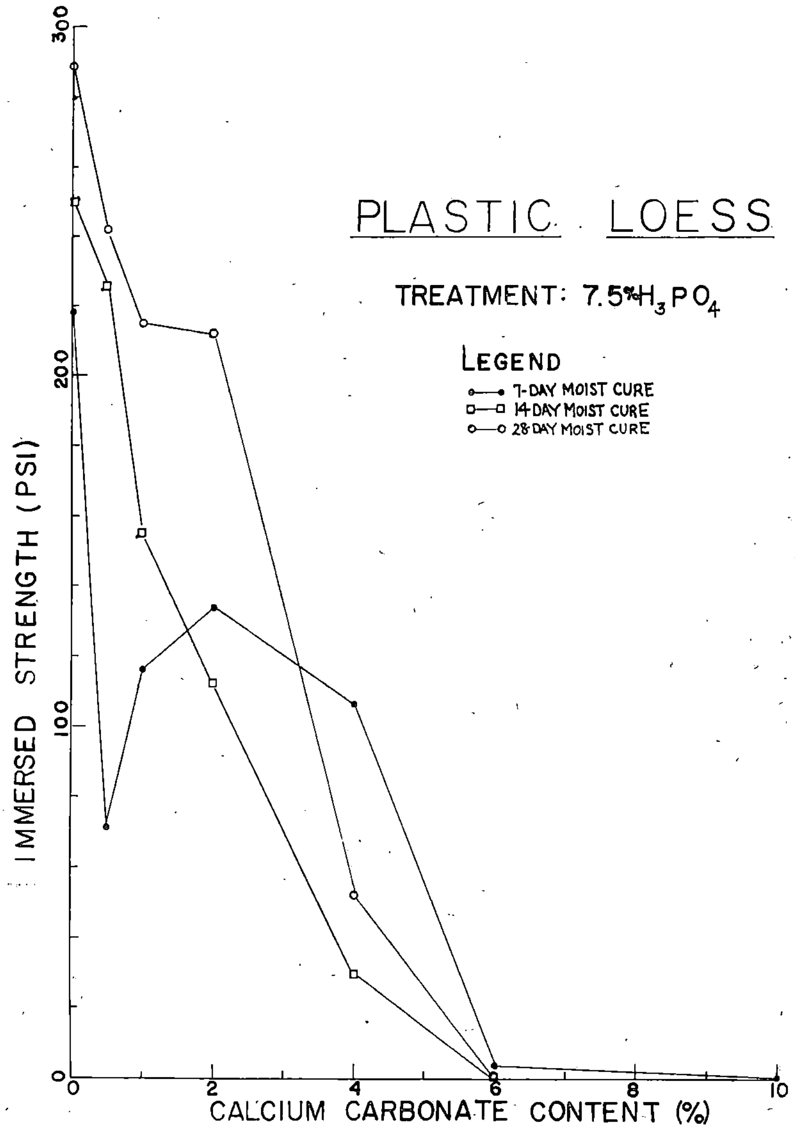


Fig. 10. Effect of calcium carbonate additives to plastic loess on the immersed strengths of 7, 14, and 28 day cured specimens containing 7.5% phosphoric acid, based on the dry weight of the loess $CaCO_3$ mixture.

immersed strengths of adding different amounts of calcium carbonate to plastic loess are shown (figure 10). (The phosphoric acid treatment was held constant at 7.5% based on the dry weight of the soil-$CaCO_3$ mixtures.) Increasing the amount of calcium carbonate decreased the immersed strengths, until at about 6% $CaCO_3$ the strengths were zero or close to it.

Phosphoric acid (H_3PO_4) gives three principal calcium salts: Tricalcium diphosphate, $Ca_3(PO_4)_2$; calcium hydrogen phosphate, $CaHPO_4$; monocalcium tetra hydrogen diphosphate, $Ca\,H_4\,(PO_4)_2$. Formation of these salts from $CaCO_3$ and H_3PO_4 may be represented stoichiometrically, by the following equations:

$$3CaCO_3 + 2H_3PO_4 = Ca_3(PO_4)_2 + 3CO_2 + 3H_2O \quad (1)$$

$$CaCO_3 + H_3PO_4 = CaHPO_4 + CO_2 + H_2O \quad (2)$$

$$CaCO_3 + 2H_3PO_4 = CaH_4(PO_4)_2 + CO_2 + H_2O \quad (3)$$

These reactions are governed by the acid and base strengths of the reactants and the products. Since $Ca_3(PO_4)_2$ is a much stronger base than $CaCO_3$, the first reaction can hardly take place. However, if the pH of the medium in which $CaCO_3$ and H_3PO_4 are reacting is controlled, any of these reactions may be possible. Constituents of a soil may furnish such a control and make any one of these reactions possible.

An indirect approach was used to decide which of these reactions takes place when a calcareous soil is treated with phosphoric acid. The ratio of the weight of phosphoric acid to calcium carbonate based on the above three stoichiometric equations is respectively 0.987, 1.98 and 2.96. The ratio of phosphoric acid to calcium carbonate at which immersed strengths were obtained with the calcareous soils studied was as follows: alluvial clay, 1.18; Detroit clay, 1.25. For the plastic loess with different amounts of calcium carbonate added the ratio of phosphoric acid to calcium carbonate content at the point where the immersed strength was zero was 1.25. These three ratios are very close to one another and to the ratio of phosphoric acid to calcium carbonate, 0.987, equation (1). The slight difference between the first three values and the latter may be because phosphoric acid reacts with the calcium carbonate to a small extent according to the second reaction in equation (2), and also because small amounts of phosphoric acid may react with other soil constituents.

Calcium carbonate in soil increases the amount of phosphoric acid necessary to stabilize the soil. This appears to be due to the phosphoric acid acting to neutralize the calcium carbonate before reacting with the other soil constituents. The amount of phosphoric acid necessary to neutralize the calcium carbonate in the soils studied was about 1.25 times the amount of the calcium carbonate present. The neutralization of the calcium carbonate in a soil apparently contributes nothing to strength but would of course add to the cost of the stabilization.

Cost. Cost is another factor that may limit the use of phosphoric acid for soil stabilization. Phosphoric acid currently costs about 7.5 cents a pound[8]. For comparison, Portland cement costs about 1 cent a pound, and is used in soil stabilization of fine grained soils in amounts of from 12 to 20%. To compete cost-wise with cement, the amount of phosphoric acid that can be used must be from 1.6 to 2.7%. This estimate is based only on the cost of the additive, and does not take into account methods of construction. The adding of phosphoric acid to the water for compaction might be advantageous. Also phosphoric acid might be cheaper to handle than Portland cement, due to the smaller amount of ad-

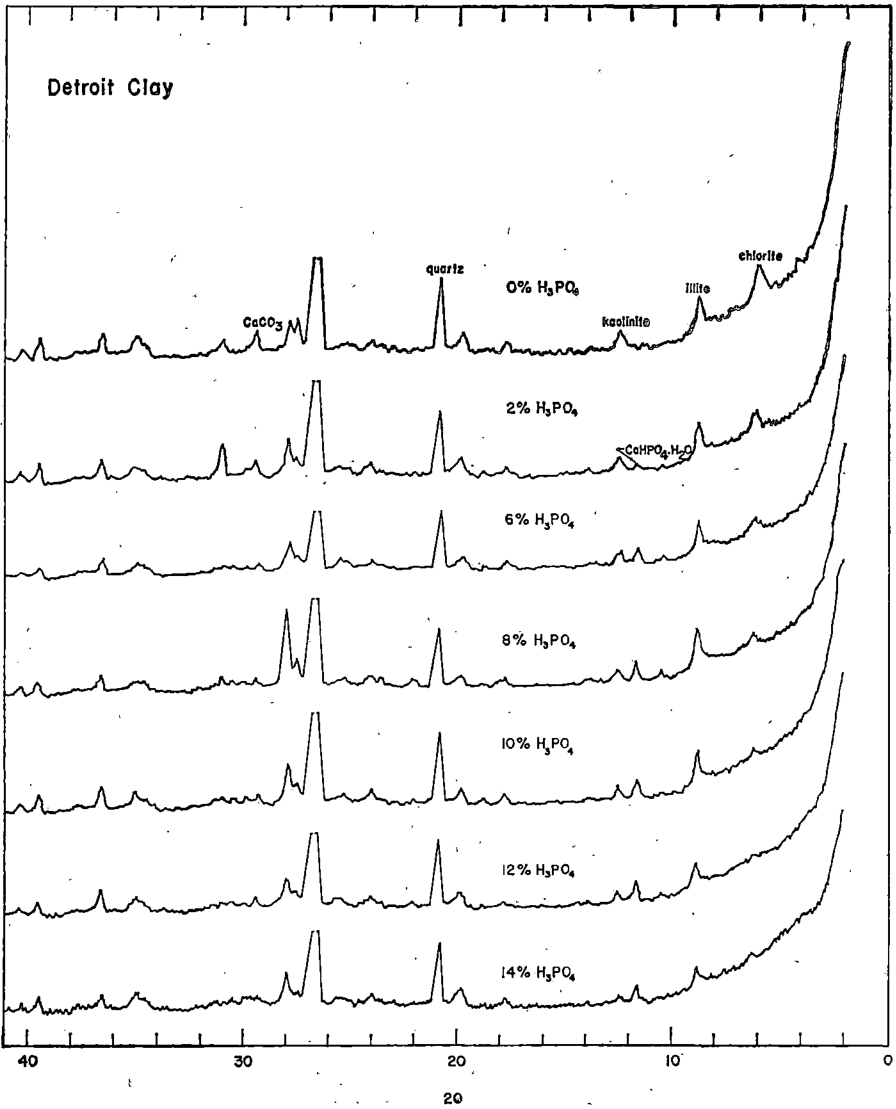


Fig. 11. X-ray diffractometer chart showing the effect of various percentages of phosphoric acid on the clay minerals of the Detroit clay.

ditive involved. These are matters to be investigated, and field trial is necessary before a final decision is made.

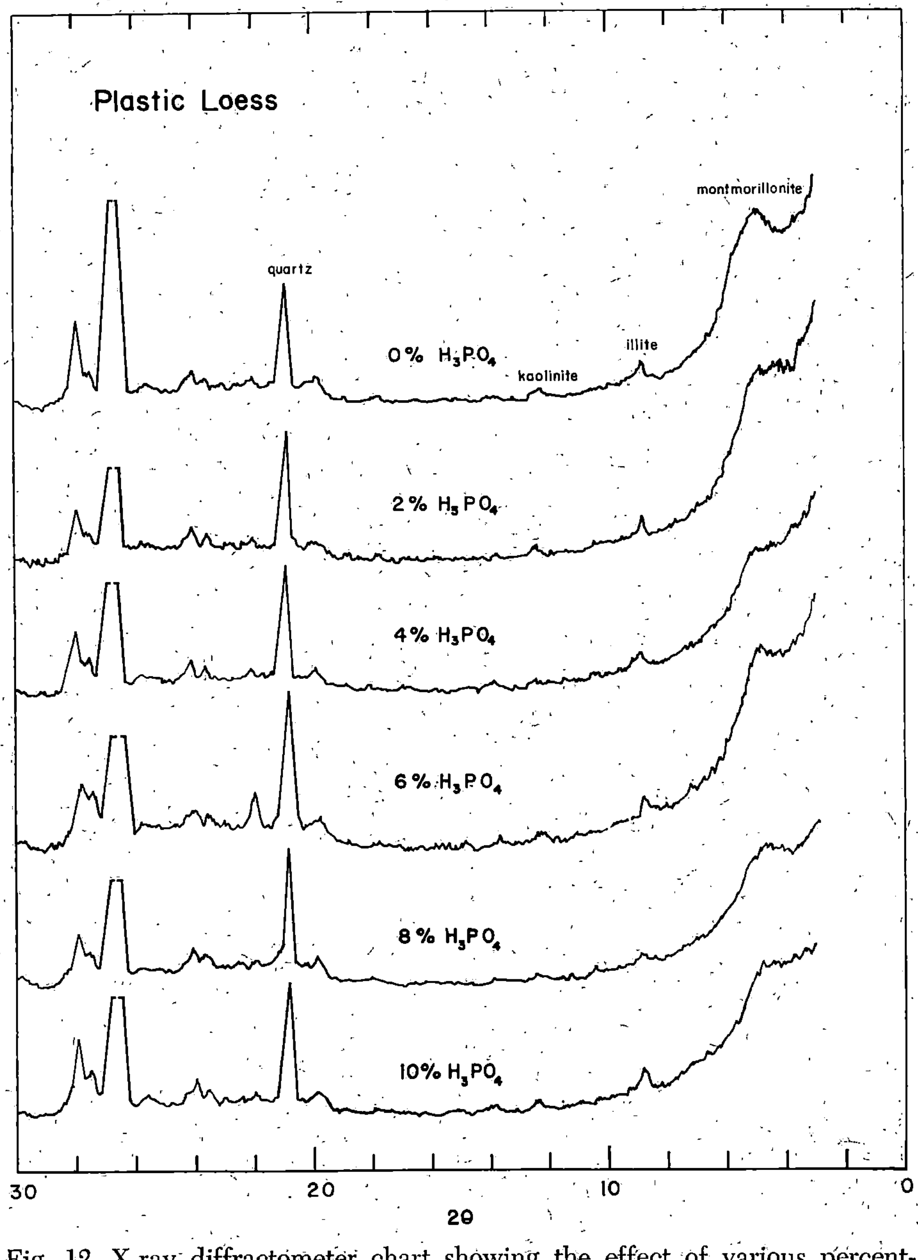


Fig. 12. X-ray diffractometer chart showing the effect of various percentages of phosphoric acid on the clay minerals of the plastic loess.

MECHANISM

The mechanism if phosphoric acid stabilization is in chemical changes taking place upon treating soils. In the present study X-ray diffraction analysis and quantitative chemical analysis were used for tracing the chemical changes. X-ray diffraction charts show the three soils, Detroit clay, plastic loess, and Virginia clay, all treated with various percentages of phosphoric acid and cured 7 days in a humid atmosphere (figures 11, 12, 13). X-ray diffractometer charts show the minus 5 micron fraction of the kaolinite-vermiculite rich soil (Virginia clay) before and after treatment with an equal amount of phosphoric acid by weight, diluted approximately to liquid limit consistency with water, and cured in a humid atmosphere for 7 days (figure 14). The purpose of this 1:1 treatment was to assist the changes taking place in the phosphoric acid treatment.

The X-ray charts indicate an amorphous halo and no newly formed crystalline substances resulting from phosphoric acid treatment, except that the calcareous Detroit clay gives calcium phosphate peaks resulting from the reaction between calcium carbonate and phosphoric acid. All three treated soils showed a decrease in the intensities of clay mineral peaks depending on the level of the treatment, suggesting that phosphoric acid had reacted with clay minerals. The amorphous halo is attributed to the reaction products.

Quantitative chemical analyses made on Detroit clay treated with phosphoric acid showed an appreciable increase in HCl-soluble aluminum compounds depending on the level of the phosphoric acid treatment (table II). The cation exchange capacity of Detroit clay and plastic loess treated with various percentages of phosphoric acid increased, depending on the level of the treatment.

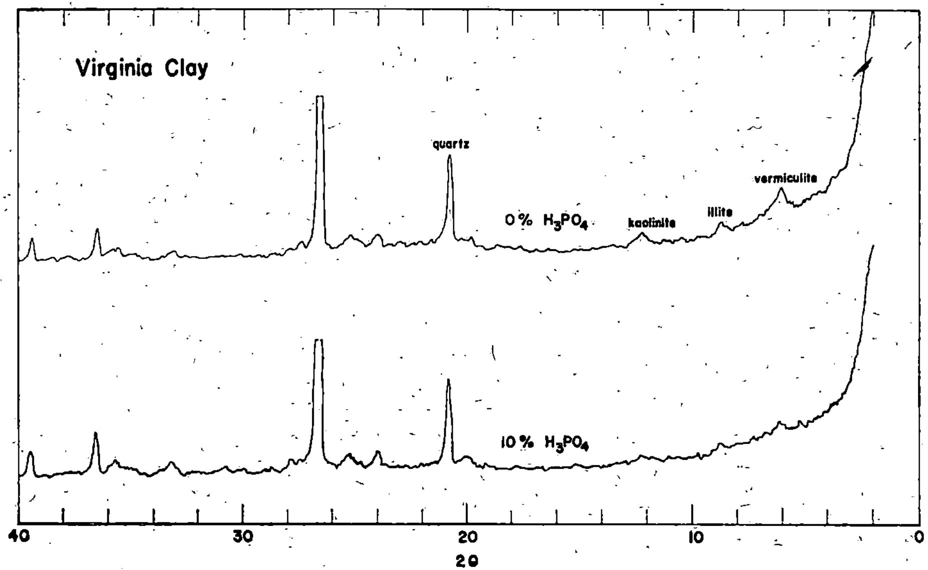


Fig. 13. X-ray diffractometer chart showing the effect of 10% phosphoric acid on the clay minerals of the Virginia clay.

Based on these data it is hypothesized that phosphoric acid releases aluminum ions from clay mineral lattices by destroying the clay mineral structure. Alumi-

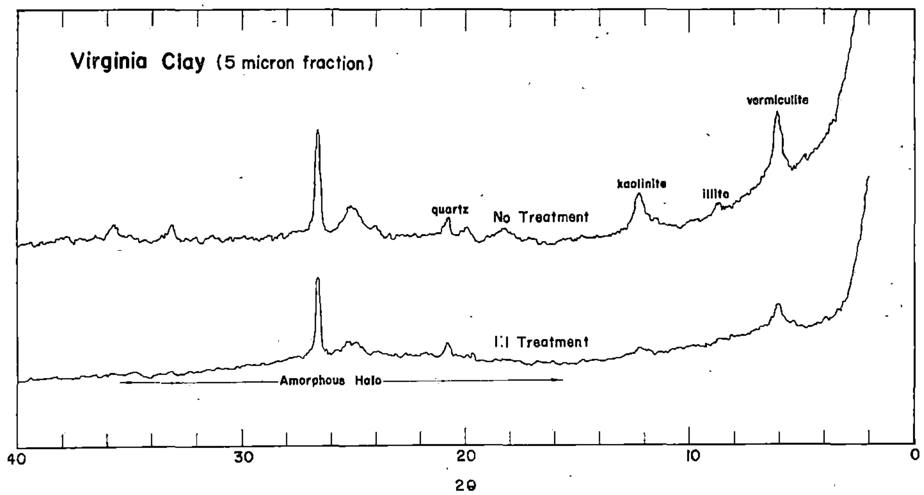


Fig. 14. X-ray diffractometer chart showing the effect of phosphoric acid on the clay minerals of the minus 5 micron fraction of the Virginia clay.

Table II. Effect of phosphoric acid on the cation exchange capacities of Detroit clay and plastic loess, and on the amounts of hydrochloric acid extractable aluminum compounds of the Detroit clay.

Soil	H_3PO_4*, %	Cation exchange capacity†, me/100 g		N. HCl extractable aluminum†, %	
		On the basis of the total weight of the mixture	On the basis of the soil fraction of the mixture	On the basis of the total weight of the mixture	On the basis of the soil fraction of the mixture
Detroit clay	0	14.5	14.5	1.1	1.1
	2	18.9	19.3		
	4	21.6	22.5		
	6	27.9	29.7		
	8	28.8	31.3		
	10	29.4	32.7		
	12	38.0	43.2		
	14	45.9	53.4	1.7	1.9
Plastic loess	0	23.5	23.5		
	1	40.4	40.8		
	2	43.4	44.3		
	4	45.0	46.9		
	6	52.5	55.9		
	8	52.3	56.8		
	10	50.3	55.9		

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[*] Expressed as percentage of pure (100%) phosphoric acid based on the oven-dry weight of the soil.

[†] Determined after moist curing for 7 days, and expressed as a percentage of the oven-dry weight of the sample.

num ions released combine with the phosphate anions to form an irreversible gel having a high cation exchange capacity. This gel acts as a cementing agent by bonding to the surfaces of other mineral constituents of the soil.

CONCLUSIONS

1. Phosphoric acid treatment improves the strength and durability characteristics of compacted, moist cured, clayey soils. The degree of the improvement depends on the amount of phosphoric acid used and on the types and amounts of clay minerals in the soil. Chlorite appears to be much more reactive with phosphoric acid than montmorillonite, illite, kaolinite, or vermiculite type clay minerals.

2. There is an optimum amount of phosphoric acid which produces the highest unimmersed and immersed strengths in stabilized soils.

3. Moist curing phosphoric acid stabilized soils gives higher immersed strengths than curing in open air.

4. The molding moisture content for maximum dry density of soil and phosphoric acid mixtures correlates closely with molding moisture content for maximum immersed strength.

5. For each combination of phosphoric acid and soil there is a curing time beyond which there is no further increase in immersed strength. This time is a function of the amount and the type of clay minerals reacting and the amount of phosphoric acid available for the reactions.

6. The resistance of phosphoric acid stabilized soil to alternate cycles of freeze and thaw increases with increasing percentages of phosphoric acid.

7. Phosphoric acid acts to neutralize the calcium carbonate in a soil before reacting with the other soil constituents; this increases the amount of phosphoric acid necessary to stabilize the soil. Each percentage of calcium carbonate consumes about 1.25% phosphoric acid.

8. Based on the (1959) relative costs of Portland cement and phosphoric acid, the maximum percentage of phosphoric acid that can be used economically in soil stabilization is about 3%, based on the dry soil weight. Soils containing more than 2.5% calcium carbonate may consume more than 3% phosphoric acid in the neutralization of calcium carbonate without gaining in stability. Therefore, in such regions as Iowa where calcareous soils are abundant phosphoric acid stabilization may not be an economical method of stabilizing soils for roads. A reduction in the price of phosphoric acid, however, could make it economical to use for stabilizing calcareous clayey soils.

9. In reacting with clay minerals phosphoric acid produces a water insoluble cementing compound. Based on chemical and X-ray diffraction analyses it is believed that this cementing compound is an irreversible gel composed of amorphous aluminum phosphates.

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REACTIONS OF PHOSPHORIC ACID WITH CLAY MINERALS

by

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(Highway Research Board Proceedings. 1961.)

ABSTRACT

Commercial clays comprised of montmorillonite, vermiculite, illite, chlorite, or kaolinite were treated with various amounts of phosphoric acid in the presence of water. Progress of the reactions was checked by X-ray diffraction analysis performed at certain intervals. Lowering of treated clay mineral X-ray diffraction peak intensities was used for estimating the extent of the reaction.

INTRODUCTION

When soils which contain different clay minerals are stabilized with phosphoric acid different strength characteristics are developed[1]. Differences in strength characteristics were attributed to different responses of each class of clay mineral toward phosphoric acid. It was hypothesized that these different responses were due to the differences in rapidity and extent of the chemical reactions which took place between clay minerals and phosphoric acid. Analysis of strength data utilizing this hypothesis lead to the conclusions that the reaction between chlorite and phosphoric acid was rapid and complete, the reaction between montmorillonite and phosphoric acid was rapid but incomplete, the reaction between kaolinite and phosphoric acid and the reaction between vermiculite and phosphoric acid were slow but continuous. These conclusions may leave the way open to some doubts because they were not directly deduced, and some of the soils contained more than one clay mineral.

The present study was undertaken to compare further the reactivities of various clay minerals with phosphoric acid. Commercially available monomineralic clays were treated with distilled water and phosphoric acid, and the mixtures were analyzed by X-ray diffraction at various intervals. Changes in the height of major diffraction peaks of the clay mineral were used as an index of reactivity with phosphoric acid. However, this technique cannot be used to predict the chemical mechanism of the complex heterogeneous clay mineral, phosphoric acid reaction or its extent in a thermodynamical sense; but the results obtained can be compared with each other. Thus relative measures of reactivities with regard to the rapidity and the extent of reactions may be established; they may also be compared with the previous conclusions obtained from the analysis of strength data.

MATERIALS USED

Clays

The commercially available clays used are listed in table I.

Chemicals

The phosphoric acid used was reagent grade, 86 percent orthophosphoric acid, H_3PO_4. All additives are expressed as percentages of pure (100 percent) phosphoric acid, based on the oven dry weight of the soil. Distilled water was used to bring the clays up to liquid limit consistencies. The hydrochloric acid used to extract the reaction products was prepared from 36 percent reagent grade hydrochloric acid. The ammonium hydroxide used for precipitation was diluted reagent grade concentrated ammonia solution. Aluminum chloride used to obtain reference precipitates was reagent grade, $AlCl_3 \cdot 6H_2O$.

METHODS OF PREPARING SAMPLES AND TESTING

Preparation of Mixtures

Distilled water was mixed with clay samples to bring them to liquid limit consistencies. After addition of each increment of water and thorough mixing, consistencies of the mixtures were checked by a liquid limit device. When the liquid limits were reached, the mixtures were placed in polyethylene containers and were tightly covered. Then from each clay-water mixture, samples corresponding to 10 grams of oven-dry clay were taken and mixed with enough phosphoric acid to give the desired acid percentage. Mixing was done using a spatula for 20 minutes in a small polyethylene container. Immediately after mixing, a slide was prepared from each mixture and analyzed by X-ray diffraction. (In this study nickel filtered copper radiation was used.) Then the slide and the container containing the clay-water-phosphoric acid mixture were placed

TABLE I. DESCRIPTION OF COMMERCIAL CLAY SAMPLES

Sample	Producer	Clay mineral		Other constituents	Fineness	Liquid limit, %
		Type	%			
Florida clay (Kaolin)	Edgar Plastic Kaolin Co., Edgar, Florida	Kaolinite	84	14% loss on ignition	100% finer than 44μ 55% finer than 1μ	71.6
Volclay (Bentonite SVP)	American Colloid Co., Skokie, Illinois	Montmorillonite	92-95	Feldspar	96% finer than 74μ 86% finer than 0.5μ	524.6
Concentrated vermiculite ore	Zonolite Co., Chicago, Illinois	Vermiculite	...		Wet ground and sieved through 325 mesh (44μ) screen	70.4
Prochlorite	Wards Natural Science Establishment, Inc., Rochester, New York	Chlorite	...		Wet ground and sieved through 325 mesh (44μ) screen	32.7
Grundite	Illinois Clay Products Co., Chicago, Illinois	Illite	...		100% finer than 420μ 75% finer than 5μ	55

in a chamber maintained at an average temperature of 73± 3°F and 100 percent relative humidity. At intervals of time, X-ray diffraction analyses were repeated on the slides stored or on freshly prepared slides from clay, water, and phosphoric acid mixtures stored. Some of the mixtures after a period of storage were extracted with 2N HCl and the extracts were titrated with dilute ammonium hydroxide to various pH values; the precipitates obtained were filtered and washed with distilled water. X-ray analysis as made on these precipitates along with the reference precipitate obtained from the titration of a mixture of aluminum chloride solution and an excess of phosphoric acid with dilute ammonium hydroxide.

PRESENTATION AND DISCUSSION OF RESULTS

The precipitate obtained from the HCl extract at pH 4 was amorphous and gave an X-ray diffraction chart similar to the one obtained by the reference precipitate. However, the precipitate obtained between pH 4 and 7 from the HCl extract of the prochlorite sample was crystalline (figure 1). The crystalline compound or compounds have not yet been identified. It is believed that these precipitates form in phosphoric acid-stabilized soils as the pH rises upon curing. The pH of phosphoric acid treated soils increases with age^2.

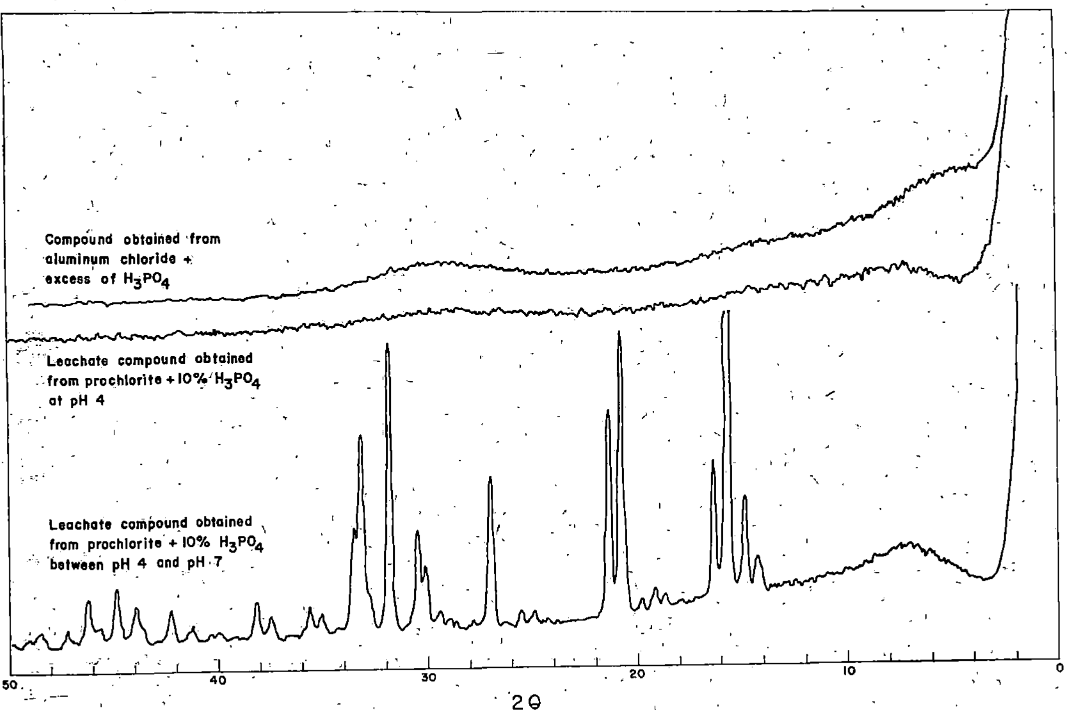

Fig. 1. X-ray diffractometer charts of the precipitates obtained by titrating HCl leachate of prochlorite + 10 percent phosphoric acid sample and aluminum chlorite + phosphoric acid solution with ammonium hydroxide.

Amounts of phosphoric acid used were 5, 10, 15, and 40 percent with all clay samples except bentonite. Only 40 percent phosphoric acid was used with bentonite due to difficulties in mixing lower amounts at liquid limit consistency. Treated samples were analyzed by X-ray diffraction two to four times during the first week of their preparation; thereafter they were analyzed at periods of two weeks, one month and four months after they had been prepared. A series of X-ray diffractometer charts were obtained, and all of the diffraction peak intensities corresponding to various "d" spacings were lowered by the treatment (figures 2 to 8). The major diffraction peaks of the clay minerals used for tracing the reactions are indicated. After each analysis, heights of the major peaks were measured (figure 2) and plotted against time (figure 9). From the curves of figure 9, diffraction peak heights at certain intervals of time were read and each was divided by the original height also obtained at zero time. This ratio is termed the "relative extent of reaction." The relative extent of the reactions against time were plotted (figure 10). Rapid and extensive reactions are shown by chlorite and vermiculite clays. The reaction with kaolinite was rather slow and incom-

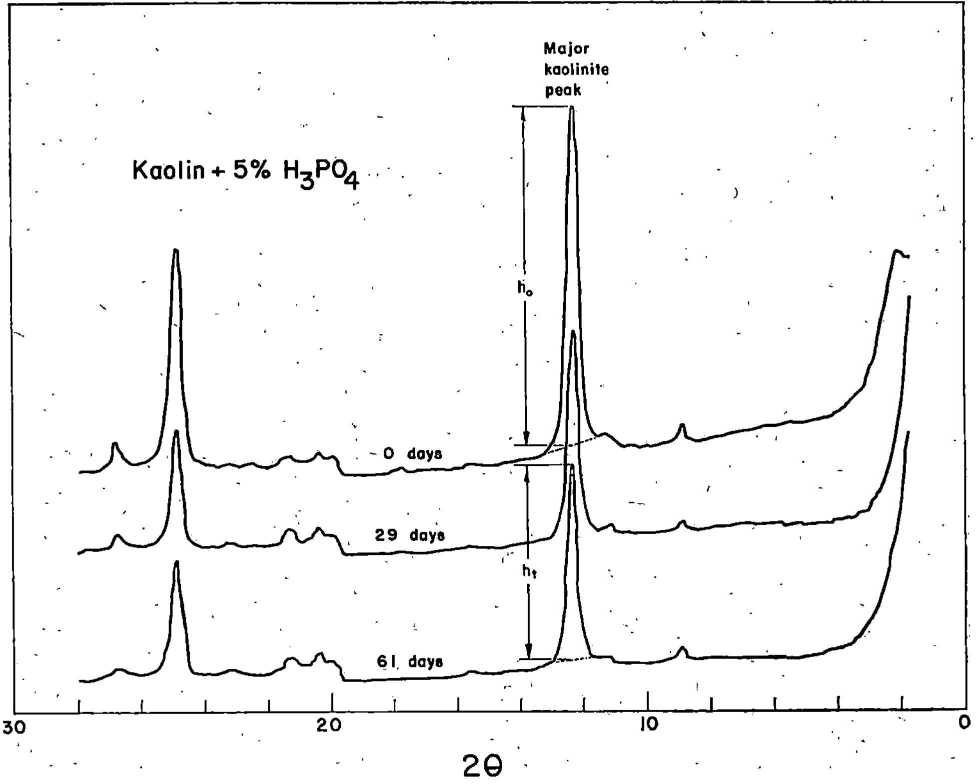

Fig. 2. X-ray diffractometer chart showing the changes in peak intensities of kaolin + 5 percent phosphoric acid mixture with time.

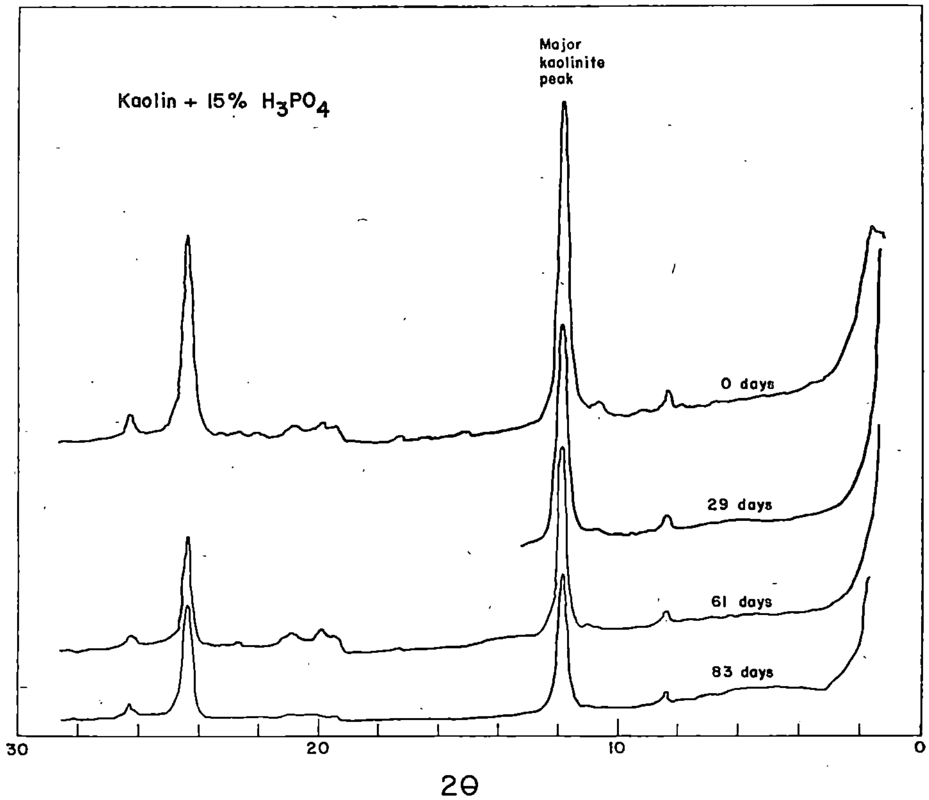

Fig. 3. X-ray diffractometer chart showing the changes in peak intensities of kaolin + 15 percent phosphoric acid mixture with time.

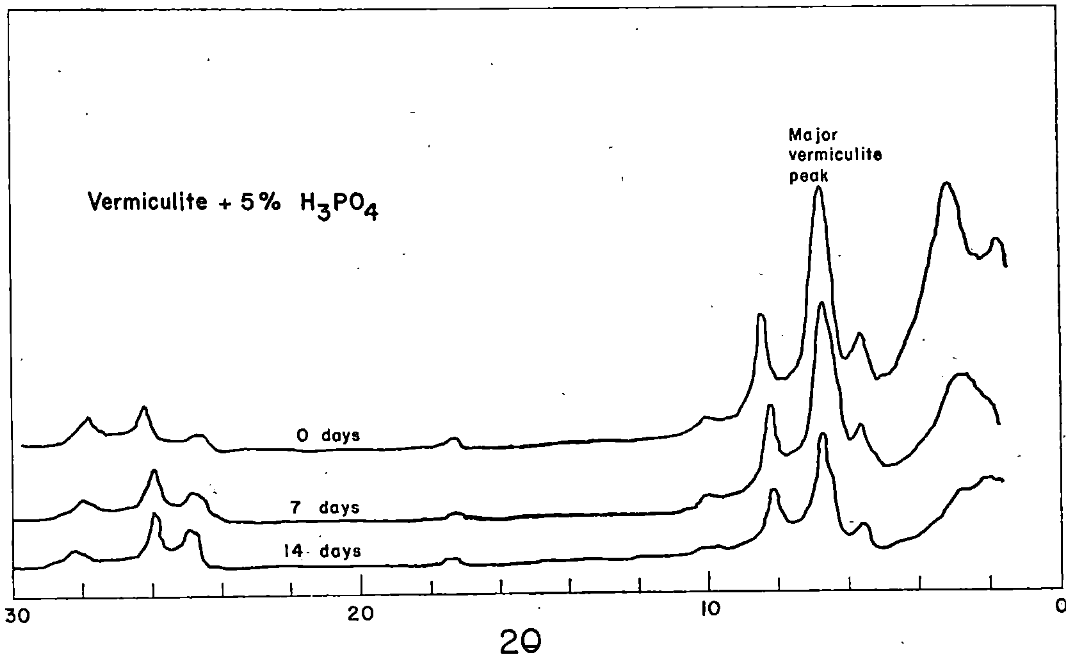

Fig. 4. X-ray diffractometer chart showing the changes in peak intensities of vermiculite + 5 percent phosphoric acid mixture with time.

plete. Montmorillonite clay gave a rapid but incomplete reaction. Illite clay appeared to react slowly and continuously. Except for the conclusion reached for kaolinite and vermiculite, these results closely agree with the conclusions reached by the authors upon analyzing the strength characteristics of phosphoric acid stabilized soils. The disagreement concerning kaolinite and vermiculite is believed due to the presence of both of these minerals in the same soil investigated in the strength study[1]. Their response toward phosphoric acid is masked by interference.

The stored slides were carefully and frequently examined for surface irregularities which occurred due to chemical reactions. Surface irregularities occurred more frequently with prochlorite and vermiculite than with other clay samples, which is another indication of their reactivities. When surface irregularities were observed, fresh slides were prepared from the stored samples. With some of these new slides, peak heights of the original slide were not reproducible. Therefore,

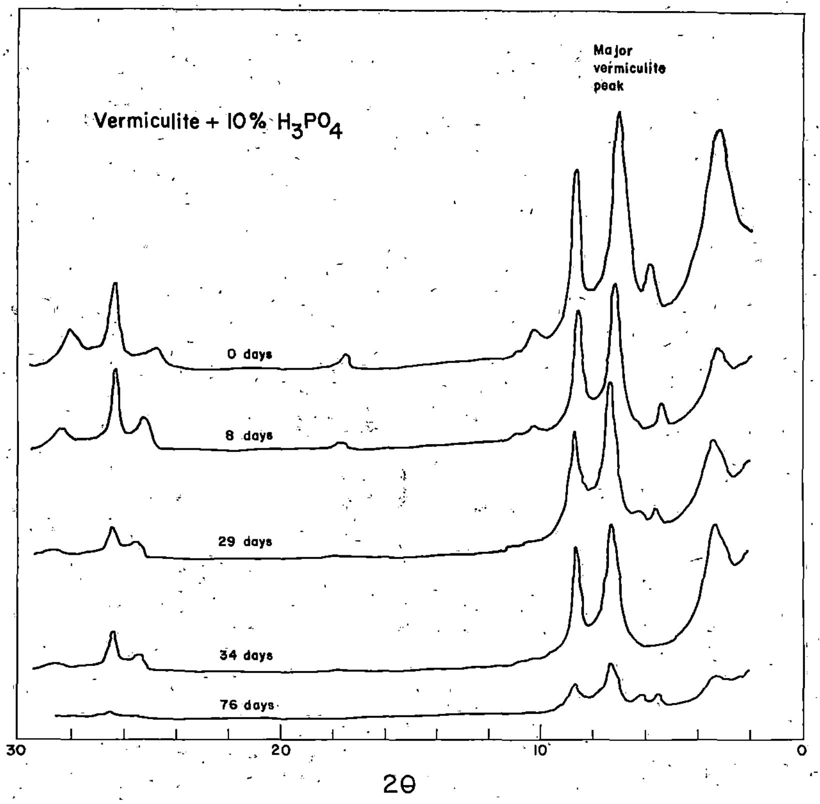

Fig. 5. X-ray diffractometer chart showing the changes in peak intensities of vermiculite + 10 percent phosphoric acid mixture with time.

when this occurred, use of X-ray diffractometer charts in preparing "relative extent of reaction" versus time curves (figure 10) was discontinued.

A water insoluble crust was formed on the surface of prochlorite samples. This crust was most pronounced with 10 percent phosphoric acid treatment; however there was no crust on the prochlorite sample treated with 40 percent phosphoric acid. X-ray analysis of the crust isolated from the 10 percent phosphoric acid sample 132 days after preparation showed new peaks in addition to weak chlorite peaks indicating that a crystalline compound or compounds had formed (figure 11). Identification of newly formed compounds is presently being undertaken.

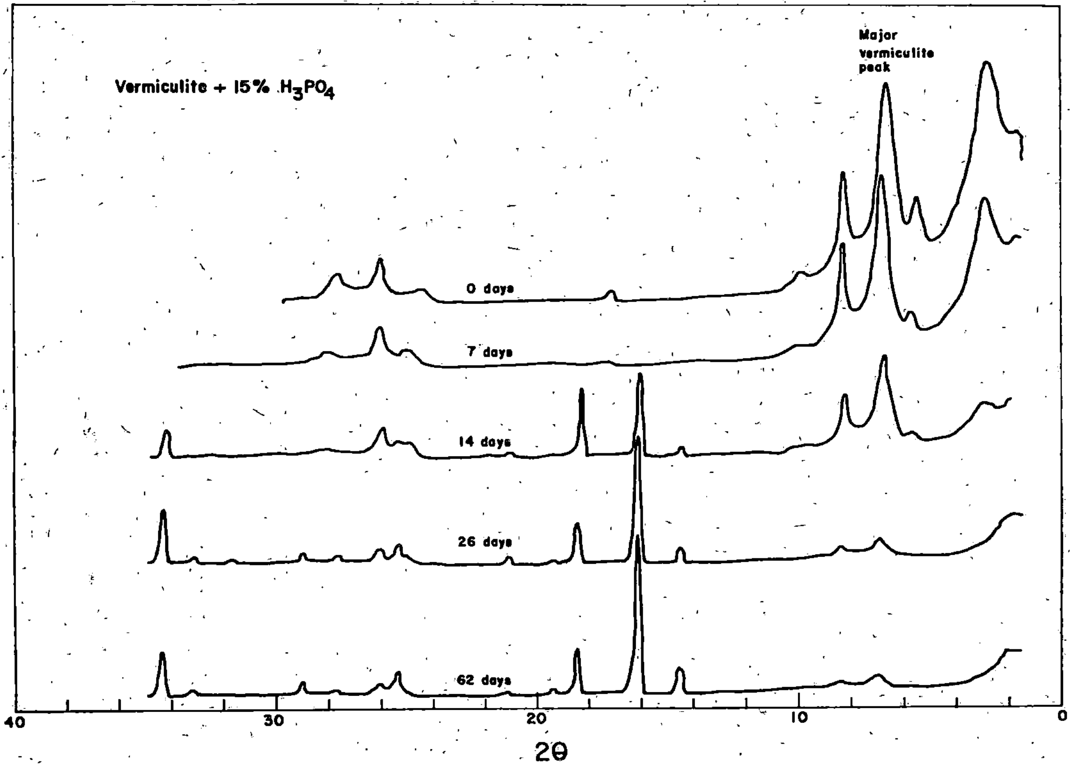

Fig. 6. X-ray diffractometer chart showing the changes in peak intensities of vermiculite + 15 percent phosphoric acid mixture with time.

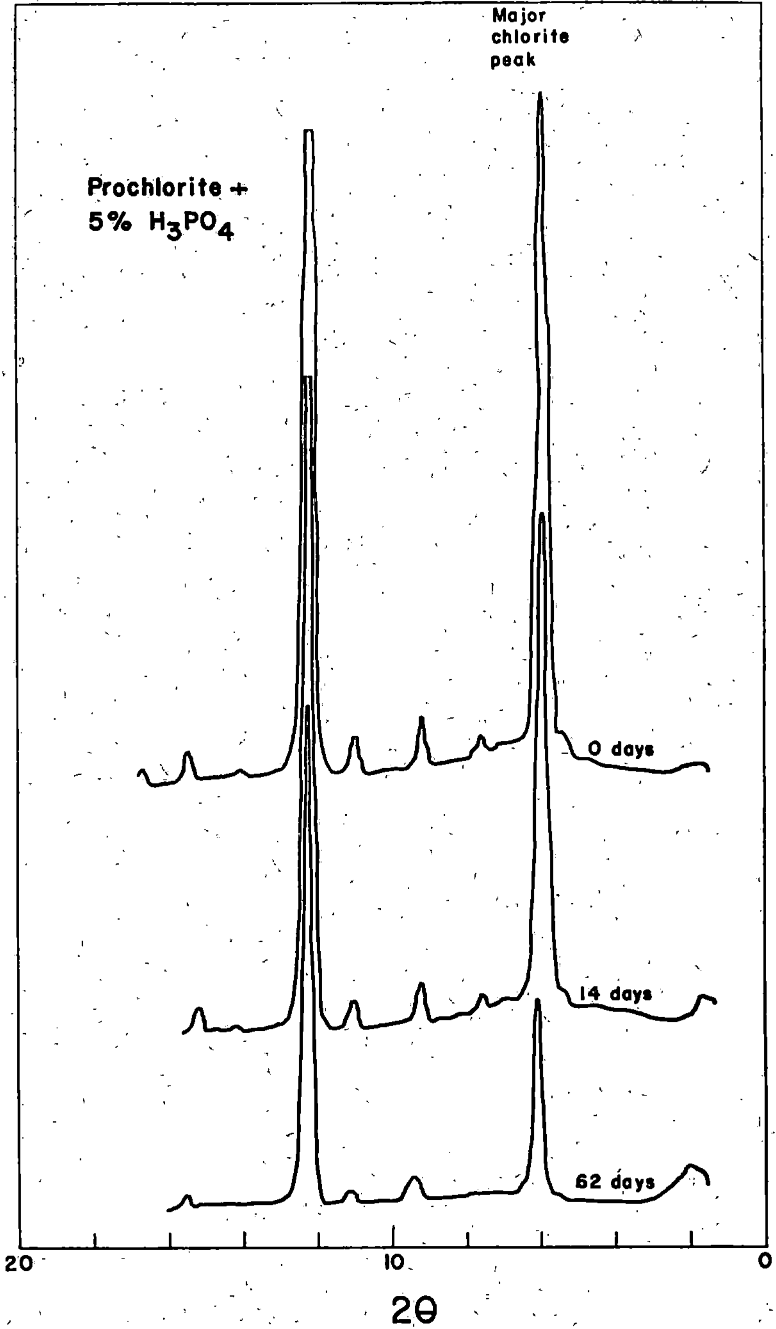

Fig. 7. X-ray diffractometer chart showing the changes in peak intensities of prochlorite + 5 percent phosphoric acid mixture with time.

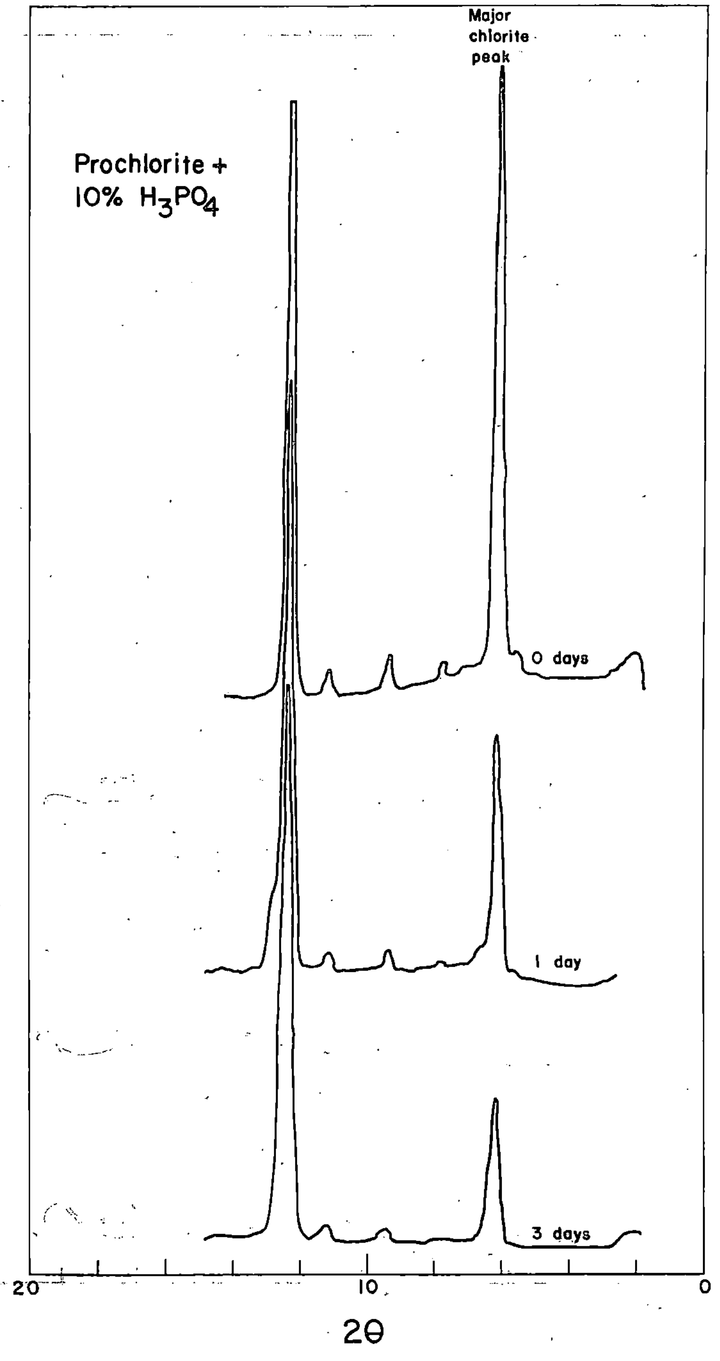

Fig. 8. X-ray diffractometer chart showing the changes in peak intensities of prochlorite + 10 percent phosphoric acid mixture with time.

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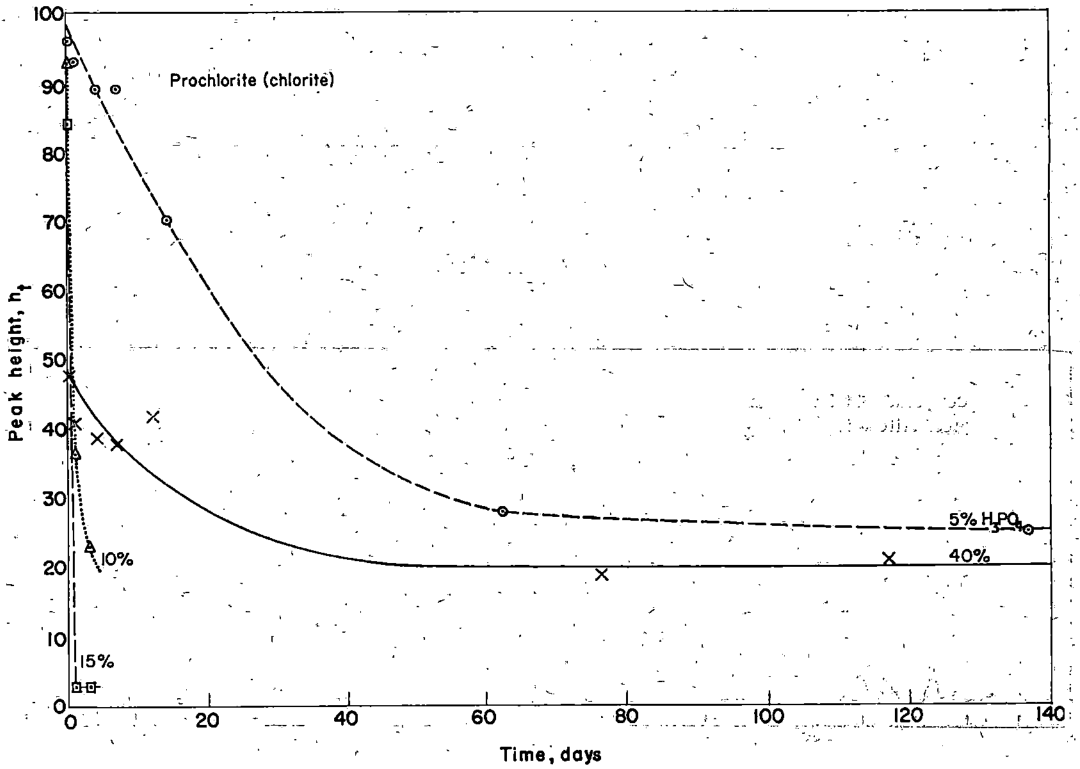

Fig. 9. Major peak heights plotted against time for prochlorite treated with 5, 10, 15, and 40 percent phosphoric acid.

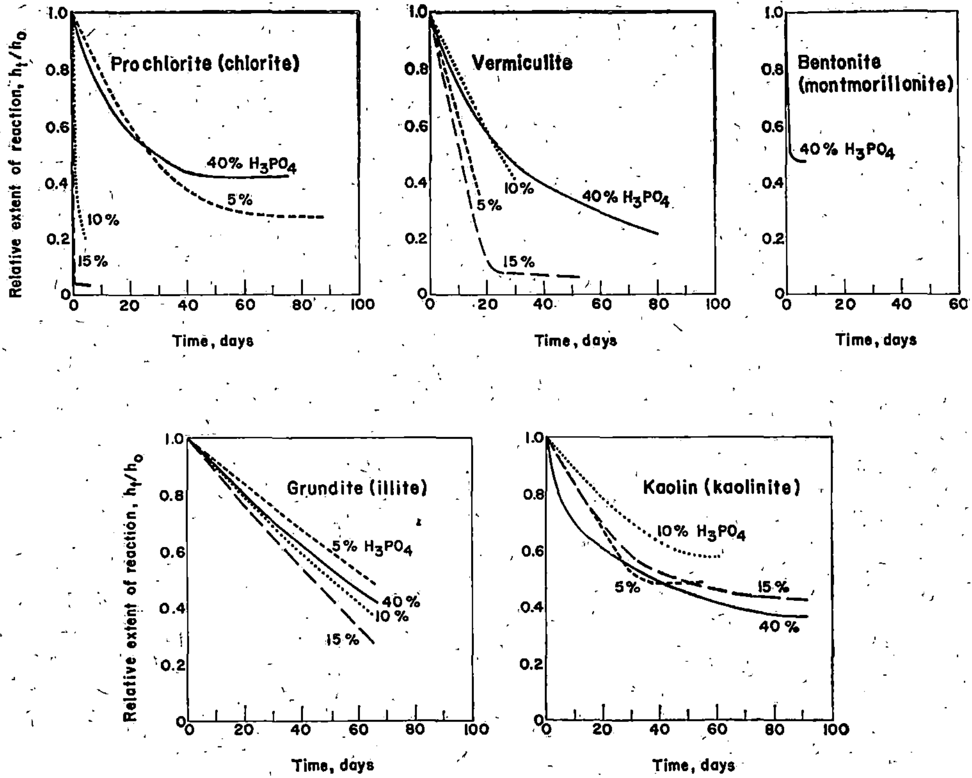

Fig. 10. Relative extent of the reaction plotted against time for all clays and phosphoric acid percentages studied.

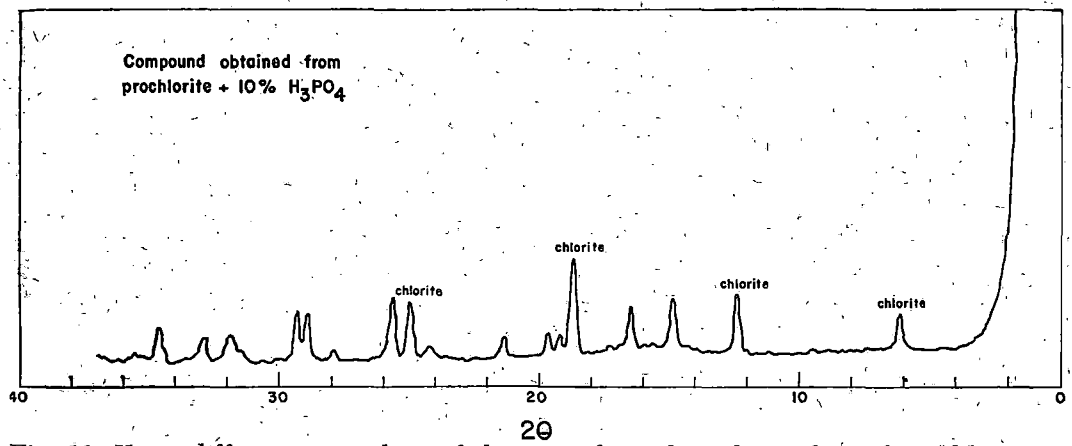

Fig. 11. X-ray diffractometer chart of the crust formed on the surface of prochlorite + 10 percent phosphoric acid.

STABILIZATION OF LOESS WITH ANILINE AND FURFURAL

by

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ABSTRACT

Aniline and furfural are organic liquids that when mixed, spontaneously form a resin known as aniline furfural resin. A ratio of 2 mols of aniline to 1 mol of furfural produces the most superior resin. Soil may be stabilized by mixing with aniline, furfural, and water, followed by compaction of the mass and an adequate curing period. Different amounts of resin produce different results with any one soil.

The loess of southwestern Iowa is excellent for studying the effect of amount of clay on the stabilizing efficiency of chemical treatments. The minerologic content of the loess is very nearly the same, except that the amount of clay increases systematically. Several loess samples were chosen as representative of the variation in clay content and used in the aniline, furfural evaluation studies. These soils were stabilized with different percentages of aniline, furfural resin. Laboratory tests were performed to determine changes in soil properties. The results of the laboratory tests were then treated as dependent variables with the clay content and the aniline, furfural content treated as independent variables. This treatment of the test results makes it possible to draw contour lines representing soil properties on a plot of aniline, furfural versus clay content.

The aniline and furfural stabilized soils were evaluated from unconfined compressive strength determinations in a wet and in a dry state, moisture absorption, differential thermal analysis and microscopic studies, Atterberg limits, and artificial laboratory weathering. All studies seem to indicate that the excellent stability resulting from aniline and furfural resin is mainly due to the clay and organic complexes formed. These complexes appear to be the cause of the soil and resin mass becoming considerably more hydrophobic. There is also evidence of soil grains and of grain aggregates. Differential thermal analysis shows a very distinct relationship between the resin and the clay present in the soils.

INTRODUCTION

The Iowa Engineering Experiment Station has been conducting studies of fundamental properties and stabilization methods on Iowa soils in an effort to solve the problem of shortage of gravel. These studies have been directed toward efficient and economic methods of suitable base and surface course construction of secondary roads.

Early stabilization studies indicated that artificial resins were a means for accomplishing a practical stabilization with satisfactory results. The most effective of these artificial resins was the resin formed by the reaction of two parts of aniline to one part of furfural.

Aniline and furfural are two liquid organic chemicals that polymerize on contact to form a resin known as aniline furfural resin or AF. Aniline was discovered in 1826[23] and furfural in 1830[9]. The first report of the aniline and furfural reaction was probably around 1850[22]. Aniline reacts with aldehydes to form a group of compounds that are known as "Schiff" bases in honor of Dr. Hugo Schiff of Florence, Italy.

Resins have many useful applications, among which is that of an impregnating agent. Impregnation may best be distinguished from coatings or the application of adhesives by the fact that the entire body of the material treated is altered in character rather than just the surface.

One of the best examples of the use of an agent of this type is in the impregnation of soft wood with methylol urea, the monomeric unit of ureaformaldehyde resins, and then carrying out the polymerization reaction in the cells of the wood. The product will not swell, shrink, or warp with humidity changes, and the grain will not rise on wetting. The material can be worked, turned, and finished to give a product superior to the hardwoods.

Aniline furfural resin plays a role of this type in the stabilization of soil. The chemicals are mixed into the soil separately and polymerize slowly thereafter. The resin is thus formed within the soil mass.

The use of aniline furfural resin as a soil stabilizing agent was reported in 1947[24]. The resin was used in a weight ratio of 70 parts of aniline to 30 parts of furfural and was found to be most successful with medium plastic soils. Resin also acts both as a binder and as a waterproofing agent. The work was successfully extended in 1949 to beach sands.

MATERIALS

Wisconsin loess in southwestern Iowa

The soils employed in this investigation came from the southwestern portion of Iowa where composite Wisconsin loess forms a massive surface deposit that mantles older loesses and pre-Wisconsin glacial deposits. The loess varies in thickness, as measured on ridges and hilltops, from 60 to over 100 feet along the Missouri River bluffs to about 17 feet toward the south-central part of Iowa.

Over one hundred samples of Wisconsin loess have been taken along the five traverses (figure 1). Control samples for determining areal property variations were taken at a depth of two or three feet below the top of the C horizon. Areal and stratigraphic variations in properties were determined by comparison and correlation of results from some 25 to 30 physical and chemical tests[6].

Test data indicate that physical and chemical properties along the east valley wall of the Missouri River are remarkably uniform both areally and stratigraphically. With increasing easterly distance away from the east valley wall the test data reflect a marked increase in plasticity, shrinkage, water-holding capacity, and in-place density. These property changes appear to be chiefly due to an increase in the amount of clay in the loess[8].

The mineralogical nature of this Wisconsin loess seems to be quite uniform. Organic matter and soluble sulfate contents are low or absent. Aside from the variation in amount of clay, the principal variable in the loess appears to be carbonate content which varies both areally and stratigraphically. Carbonate contents, expressed as percent calcium carbonate by weight, were as high as 18 percent along the Missouri River to as low as one percent in inland samples.

The loess may be conveniently divided into two fractions of minus 2 micron material and plus 2 micron material. In general the plus 2 micron material contains mostly quartz, feldspar, and calcite, along with a minor amount of heavy minerals. These minerals are considered to be non-reactive with large organic cations.

The minus 2 micron material in the loess is very similar throughout and is mainly of clay minerals. The clay minerals in this fraction are thought to be a randomly interstratified mixture of montmorillonite and illite types. X-ray diffraction data indicate an increase in the montmorillonite:illite ratio with increasing clay content in the loess. Microscopic examination of the loess has shown that the clay is mainly as coatings on larger grains.

Cation exchange capacity is one of the most important properties of soil, a

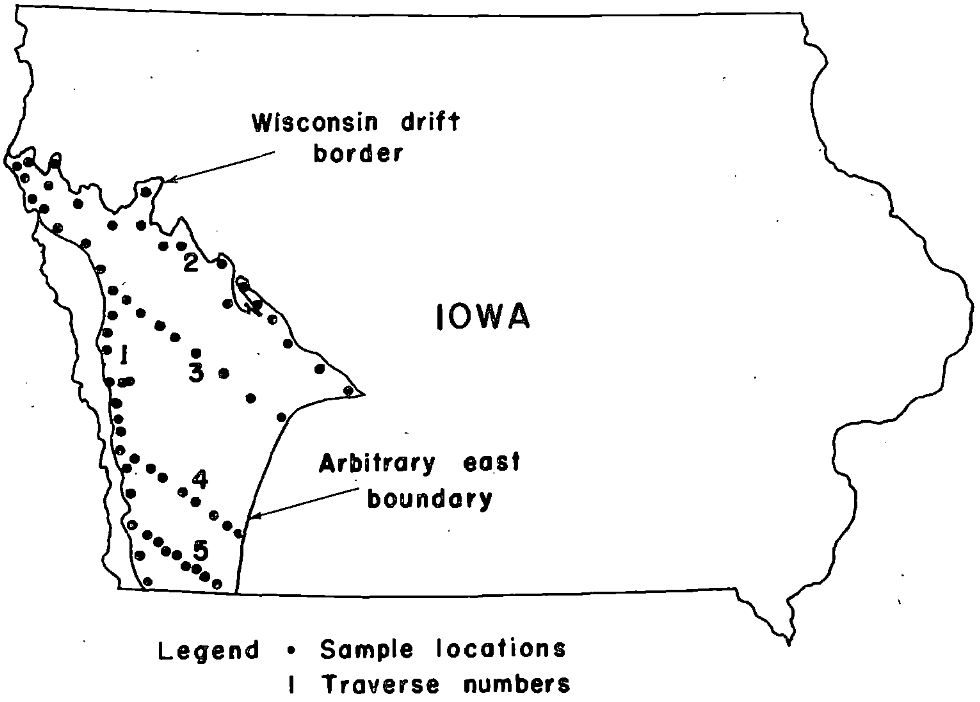

Fig.1. Locations of loess sampling traverses in southwestern Iowa.

fact that has long been recognized by agricultural soil scientists[14]. It can be measured quantitatively and is closely related to the physical and chemical behavior of soil. It has been related to engineering properties of Wisconsin loess[7]. Southwestern Iowa loess exhibits a range in cation exchange capacity, expressed as milli-equivalents per 100 grams of soil, from 7 along the Missouri River to 26 further inland. This increase is mainly attributed to an increase in the amount of clay in the loess.

Because of the orderly variation of the areal and stratigraphic properties of the southwestern Iowa loess and the apparent qualitative mineralogic continuity, it was decided to investigate the effectiveness of aniline furfural stabilization on this soil by studying a few samples representing the entire area. The property study has indicated that the principal variable in the loess is the amount of clay. The soil samples were therefore selected to provide a range in clay content from 7 to 37 percent.

Several hundred pounds of each soil were obtained from the C horizon with the exception of sample 503-2, which was from the B horizon (table I). Samples 20-2 and 44A-1 were used in obtaining basic data necessary for further study. Sample 20-2-II is from a different stratigraphic position than 20-2 and was used because it affords a better position in the overall representation of the range in soil properties (table II)[4, 5].

The soil samples were selected from data obtained from small laboratory samples used in the initial property studies. The selections were made to present a range in 2 micron clay content that increased in increments of approximately 5 percent. Subsequent analysis of representative samples taken from the larger samples used in the stabilization studies show the 5 percent increments to be correct. The lone exception was sample 46-1 which has a clay content very close to that of 36-1.

Aniline and Furfural

The chemicals used in this investigation were obtained from Iowa State University chemistry stores. The aniline was made by the Baker Chemical Company in Phillipsburg, New Jersey, and the furfural by the Quaker Oats Company in Cedar Rapids, Iowa.

TABLE I. LOCATION OF LOESS SAMPLES

Sample no.	County	Township	Section	Soil series	Thickness of solum,* ft.	Sampling depth below surface, ft.
55-1	Harrison	Little Sioux	8	Hamburg	½	2½-3
20-2	Harrison	St. Johns	15	Hamburg	0	60-61
20-2II	Harrison	St. Johns	15	Hamburg	0	34½-35½
26-1	Shelby	Grove	21	Monona	2	4-5
36-1	Montgomery	Grant	14	Marshall	3½	5½-6½
44A-1	Page	Morton	21	Marshall	3	4-5
46-1	Page	Amity	30	Marshall	3	5-6
503-2	Taylor	Jefferson	17	Sharpsburg	4	1½-2

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* *Solum* includes the A and B horizons where both are present.

TABLE II. PROPERTIES OF LOESS SAMPLES

SAMPLE NUMBERS	55-1	20-2	20-2III
Sand (2.0 to 0.074 mm), percent	0.5	1.4	0.7
Silt (0.074 to 0.005 mm), percent	91.1	78.8	78.9
Clay (below 0.002 mm), percent	7.4	15.1	17.8
Colloidal clay (below 0.001 mm), percent	6.5	14.5	17.5
Liquid limit, percent	29.6	30.8	33.2
Plastic limit, percent	27.3	24.6	24.0
Plasticity index, percent	2.3	6.2	9.2
pH	8.0	8.7	7.8
Cat. Ex. Cap. (m.e./100 gm)	10.0	13.4	12.6
Carbonates, percent	7.6	10.2	6.9
Organic matter, percent	0.21	0.17	0.19
Textural Classification (B.P.R. System)[*]	silty loam	silty loam	silty clay loam
Engineering Classification (AASHO)	A-4(8)	A-4(8)	A-4(8)

TABLE II. (Continued)

SAMPLE NUMBER	26-1	36-1	44A-1
Sand (2.0 to 0.074 mm), percent	0.5	0.4	0.2
Silt (0.074 to 0.005 mm), percent	74.8	69.6	58.9
Clay (below 0.002 mm), percent	21.7	26.3	30.6
Colloidal clay (below 0.001 mm), percent	21.4	25.0	29.4
Liquid limit, percent	34.7	39.0	53.1
Plastic limit, percent	24.0	25.6	25.7
Plasticity index, percent	10.7	13.4	27.4
pH	7.9	6.5	6.2
Cat. Ex. Cap. (m.e./100 gm)	15.3	19.6	23.1
Carbonates, percent	6.4	0.7	0.8
Organic matter, percent	0.25	0.14	0.52
Textural Classification (B.P.R. System)[*]	silty clay loam	silty clay	silty clay
Engineering Classification (AASHO)	A-6(8)	A-6(9)	A-7-6(19)

TABLE II. (Continued)

SAMPLE NUMBER	46-1	503-2
Sand (2.0 to 0.074 mm), percent	0.4	2.0
Silt (0.074 to 0.005 mm), percent	67.9	55.2
Clay (below 0.002 mm), percent	26.3	37.0
Colloidal clay (below 0.001 mm), percent	24.2	34.5
Liquid limit, percent	54.7	56.7
Plastic limit, percent	22.0	26.4
Plasticity index, percent	32.7	30.3
pH	5.9	6.4
Cat. Ex. Cap. (m.e./100 gm)	23.6	28.1
Carbonates, percent	0.9	0.8
Organic matter, percent	0.23	0.72
Textural Classification (B.P.R. System)[*]	silty clay	clay
Engineering Classification (AASHO)	A-7-6(19	A-7-6(19)

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[*] Textural classification is based upon the Bureau of Public Roads System except that sand and silt are separated by the No. 200 sieve.

METHODS OF EVALUATION

The evaluation of the ability of AF to stabilize loess was accomplished by testing 2 inch high by 2 inch diameter specimens that were molded to standard Proctor density.

The order of mixing chemicals and water into the soil and the method of moisture determination are discussed in the appendix.

Preparation of mixtures

The chemicals and water were mixed into 1200 grams (oven dry basis) of air dry soil which produces sufficient mixture for six specimens. The entire quantity of furfural and about one half of the distilled water required was added and folded into the soil with a mixing spoon. Initial mixing by hand is required to dampen the soil for the prevention of dusting. The balance of the furfural was added and mixed with the soil and furfural with a Hobart Model C-100 mixer at low speed. After mixing for one minute the mixer was stopped, and the mixture was hand mixed for another minute. The aniline was then added and the mixer was allowed to run for two minutes. Another minute of hand mixing followed and final mixing was done with another minute of machine mixing. The hand mixing is necessary because of a tendency for the mixture to adhere to the bowl and consequently pile up.

The ratio of aniline to furfural was kept on a 2:1 molar basis because all prior[24, 25] and present research has indicated that this is the best stoichiometric relation for the formation of optimum quality AF resin. The chemicals were added volumetrically with an accuracy of measurement correct to the nearest 0.1 milliliter. The volumes were computed on a weight basis using the specific gravity values of each chemical at 70°F. Desired percentages of chemical composition were produced by addition of appropriate volumes. Heights and weights of all specimens were recorded immediately after molding.

Specimen Molding and Curing

Specimens of soil AF mixtures were molded in 2 inch diameter cylinders by means of a drop hammer apparatus[2]. Five blows on each end of a specimen produces the most uniform density throughout the specimen; this compaction effort also produces near standard Proctor density. After compaction the molded specimen was extruded from the cylinder, weighed, and measured to the nearest 0.001 inch in height.

A curing time of ten days was chosen on the basis of drying studies and strength studies. Drying is shown to reach a constant value after 7 or 8 days and strength also increases rapidly during the first few days of air curing and attains a constant value after 7 to 8 days (figure 2).

Unconfined Compression Testing

Unconfined compression tests were made with a Riehle, 60,000 pound capacity, hydraulic testing machine, and all data were read to the nearest ten pounds. The compressive load was applied at a rate of 0.1 inch deformation per minute. The maximum load causing a specimen to fail was recorded as the unconfined compressive strength.

Heights and weights of all specimens were recorded after a ten day air curing period, and even numbered specimens were immersed in distilled water for 24 hours at room temperature. Odd numbered specimens were tested for unconfined compressive strength immediately following their physical measurements and the results reported as dry strength.

The immersed specimens were blotted dry on the surface with paper towels, measured, and weighed after the 24 hour immersion period. The specimens were then reimmersed to avoid drying during the delay period between measurement and testing. Individual specimens were removed from the immersion bath and placed in the testing machine dripping wet. The results of this test were reported as wet strength.

Atterberg Limits

Atterberg limits were determined by ASTM designations: D 423-54T and D 424-54T[1] with the exception that values were reported as percentages of the stable weight. Since the specimens to be tested were stabilized cylinders, it was necessary to break them up and grind the material with a mortar and pestle until

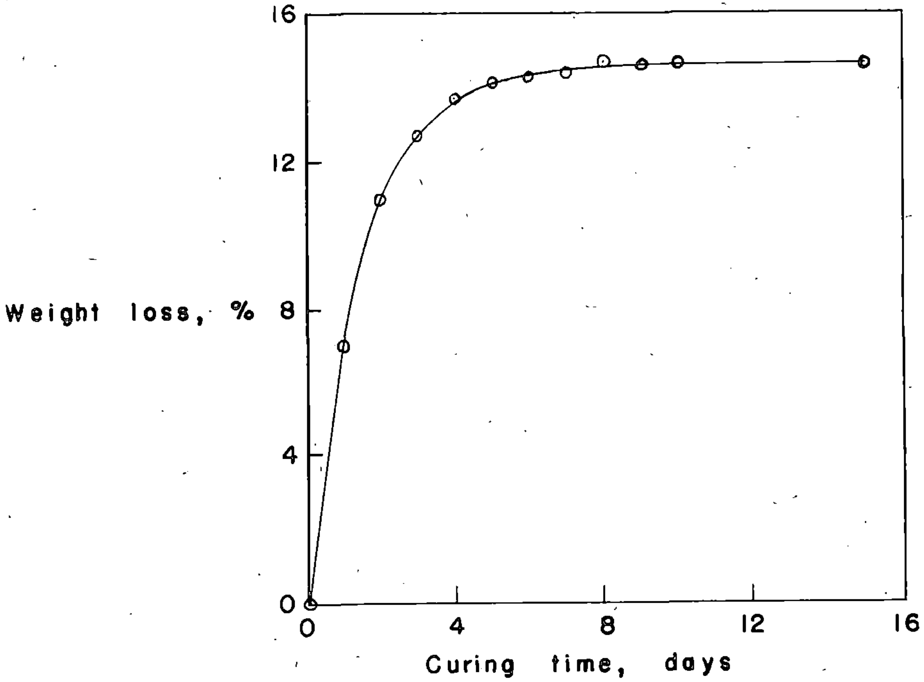

Fig. 2. The total weight percent of volatile material lost in curing versus the time of curing in days for soil 20-2 using 5 percent AF. Similar curves were obtained for other percentages of resin.

100 percent passed a no. 40 sieve. Though mixing the material with water was very difficult, it was continued until the mass was homogeneous.

Freezing and Thawing

After curing for ten days, the specimens to be evaluated in freeze-thaw studies were immersed in distilled water for two hours before starting the freeze-thaw cycles. The specimens were then placed on water saturated felt pads in pans and frozen at —10°F for 23 hours. The pans, containing the specimens, were then removed and were partially filled with distilled water to a level just below the top of the felt pads. The specimens were allowed to thaw, exposed, at room temperature for two hours. The pan was then covered with Saran wrapping and kept at room temperature for another 23 hours. The foregoing 48 hours treatment was considered to be one cycle. Three specimens were tested after each cycle by weighing, measurement of height change, and immediate unconfined compression testing.

Three specimens of each soil and treatment were allowed to air dry for 30 days after nine cycles had been completed. They were then subjected to a final cycle of freezing and thawing and tested by the aforementioned procedure.

Wetting and Drying

A complete cycle of wetting and drying consisted of 24 hours of air drying followed by 24 hours immersion in distilled water. The three specimens to be tested after each cycle were blotted dry on the surface with paper towels and their heights measured. They were then placed in open, individual moisture cans, and were weighed and tested for unconfined compressive strength while resting in the cans. The use of cans while testing insures the confinement of all flakes or chips resulting from testing. The moisture can containing the entire sample was placed in an oven at 100-110°C for 24 hours, cooled for one hour in a dessicator, and weighed. This procedure provides an accurate average moisture content determination since water does not permeate a specimen completely.

Three specimens of each soil and treatment were allowed to air dry for 30 days after nine cycles had been completed. They were then subjected to a final cycle of wetting and drying and tested.

Differential Thermal Analysis

Differential thermal analysis is a technique generally used as an aid in the identification of clays, minerals, and other crystalline materials. The unknown sample is heated simultaneously with an inert material such as calcined alumina. Both sample and inert material are heated at a constant rate, and their temperature difference is recorded on a strip chart by means of a differential thermocouple. The temperature of the sample block is recorded on a separate strip chart.

Each mineral or chemical undergoes characteristic reactions that occur at specific temperatures. These reactions are either endothermal or exothermal in nature and are revealed together with the temperature at which they occur when the two strip charts are correlated[15].

Differential thermal curves were obtained from a number of AF stabilized specimens. The samples varied in amount of clay contained as well as in the amount of AF content. These samples were material salvaged from unconfined compression tests. The coarse fragments were gently ground to pass a no. 40 sieve before placing directly into the differential thermal apparatus. Curves were also obtained from a nonstabilized sample of each soil.

DISCUSSION OF RESULTS

Standard methods for the evaluation of the effectiveness of soil stabilizing chemicals have not been established and correlated with field performance. Since such criteria are lacking, it is not possible to make any specific predictions concerning the field use of aniline furfural stabilized soils. Laboratory investigations, however, do produce mixture designs that appear to give the most efficient performance for any one soil.

Contour Graphs

Exploratory work led to the conclusion that many properties of stabilized loess depend on the amount of analine and furfural introduced and on the amount of clay contained by the native soil. (Clay content is all material smaller than 2 microns equivalent spherical diameter as determined by the hydrometer technique.) Properties of stabilized loess could be related to the two variables, amount of analine and furfural (AF) and amount of clay, by three dimensional diagrams, using the z-axis for the dependent variable or property to be studied, the y-axis for the AF content, and the x-axis for the less than 2 micron clay content. Three dimensional graphs are difficult to present clearly by planar diagrams; however, the use of contour lines such as are used in topographical mapping makes this possible. The AF content was plotted as the ordinate and the clay content as the abscissa. Stabilized loess has a definite numerical value for each property in any set of coordinates. These values were written over their coordinates, and all equal values were connected, thus creating iso-property lines.

Density

The dry density of AF stabilized loess may be expressed either as the weight of oven dry soil particles per unit volume of stabilized soil, or as the weight of the oven dry soil particles plus AF per unit volume of stabilized soil. Herein the former is referred to as the *dry density*, the latter as the *stable density*.

A three dimensional figure of the data for dry density would show a surface similar to a sugar loaf hill (figure 3). By holding the AF variable constant and making a plot of density versus clay content, the resulting curves show peaks near 22 percent clay. Apparently this effect is due to the graduation of the loess samples. Since about 98 percent of loess is silt and clay size material, the amount of silt in a sample is closely equal to 100 minus the clay content.

The AF variable also has a pronounced effect on the dry density. If the clay variable is held constant, the dry density drops slowly as AF is added. Aniline furfural displaces some of the soil, as can be shown by plotting the volume of soil displaced against the volume of AF added. This plot is not linear because

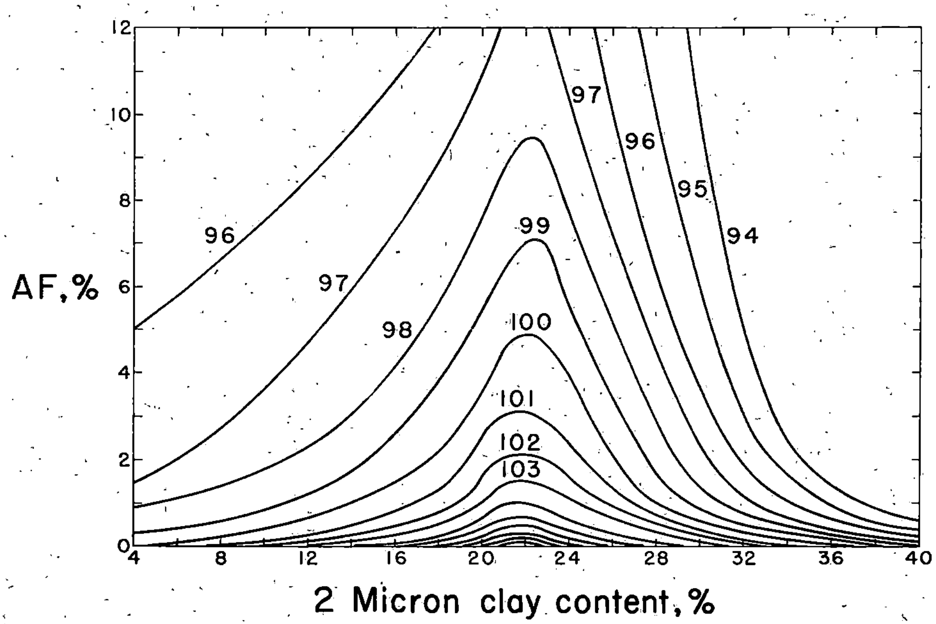

Fig. 3. Dry density contours showing the relationship of dry density to AF content and clay content in loess. The values of the contours are in lb. per cu. ft.

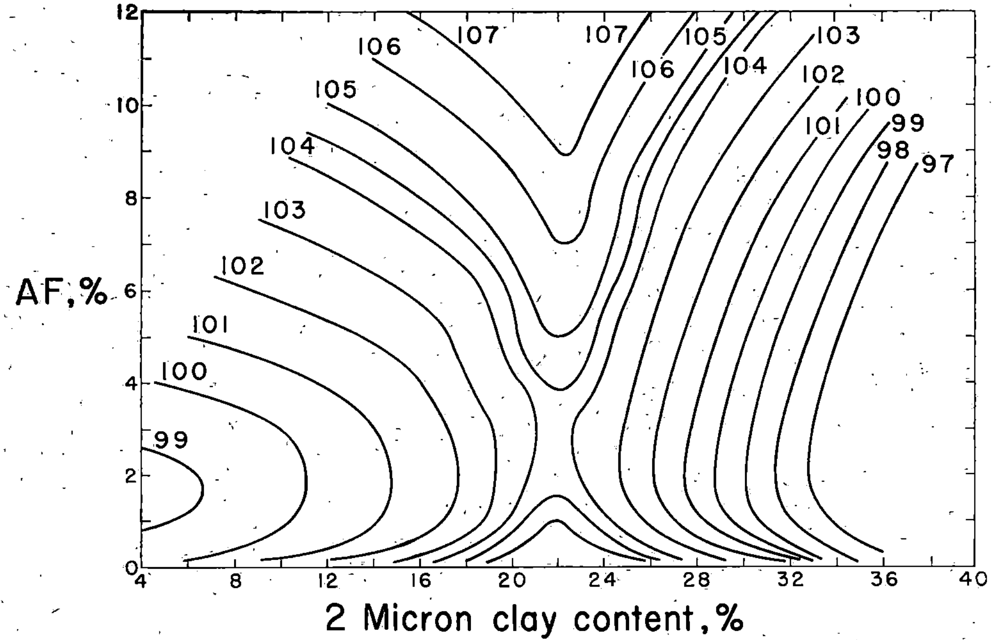

Fig. 4. Stable density contours showing the relationship of stable density to AF content and clay content in loess. The values of the contours are in lb. per cu. ft.

some of the AF fills the void spaces rather than displacing soil. The reduction in dry density is partially due to aggregation caused by the association of large organic cations, developed in the resinification reaction, and the clay minerals.

The influence of gradation is much the same but the influence of AF content on the stable density is very different from its influence on dry density (figure 4). Instead of causing the stable density to decrease steadily for any given clay content, the AF causes the stable density to decrease at first and to then increase. Evidently the weight loss due to displacement of soil by AF is more than overcome by the added weight of the AF contained in the voids. The net effect of the two variables, AF and clay, is the formation of a ridge near 22 percent clay due to gradation effects, the formation of a narrow sloping trough to the left of the ridge, and a wide sloping trough to the right of the ridge. A saddle point at a clay content of 22 percent and an AF content of 2.5 percent results at the concurrence of the ridge and the sloping troughs.

Optimum Moisture

A comparison of the contours for dry density (figure 4) and the optimum moisture content contours for standard Proctor density (figure 5) shows a striking resemblence between their contour lines. Closer examination reveals that the surfaces formed are the exact opposite of each other. Figure 5 shows a valley along the 22 percent clay line and a ridge closely following the 2 percent AF line. The liquid chemicals appear to replace some of the moisture required for com-

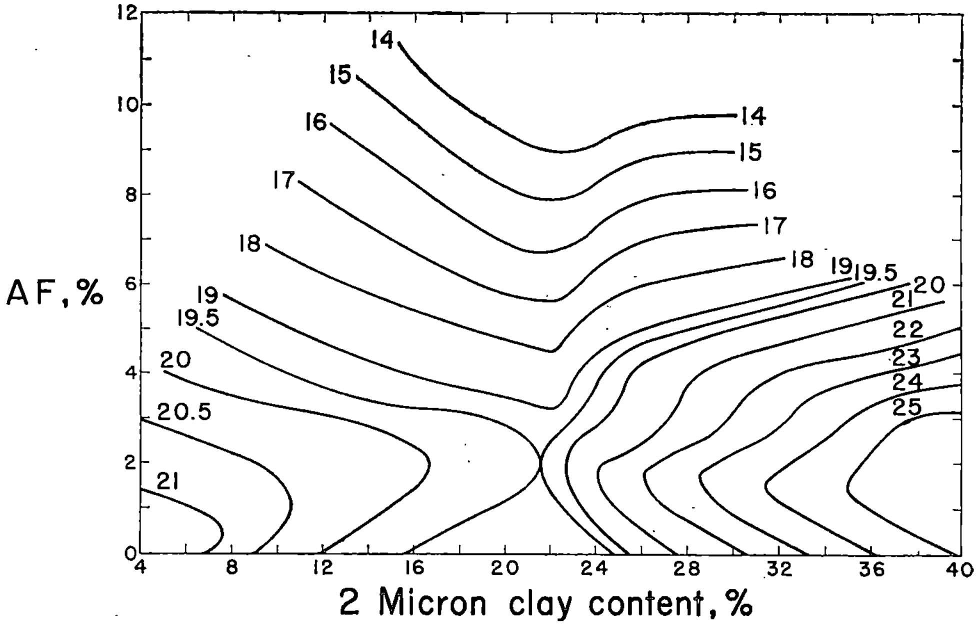

Fig. 5. Optimum moisture contours showing the relationship of optimum moisture to AF content and clay content in loess. The values of the contours are in percent of the dry weight of soil in the stabilized specimens.

paction so that less moisture is needed to cause the soil to flow for proper compaction. The total liquid added in all is greater than the amount of water required for natural soil.

Compressive Strength

Specimens tested for unconfined compressive strength after air curing were always higher in strength than those of equal AF treatment and equal clay content that were tested after 24 hours immersion in distilled water. The surface presented by the contour lines for immersed strength of AF stabilized loess is best described as a sugar loaf hill remarkably symmetrical to an axis along the 21 percent clay line (figure 6). Here gradation also has an important influence on the property being studied. The influence of gradation is probably an indirect effect acting through the medium of density, and density has a profound influence on strength. An examination of the surface shows that the rate of strength increase with increased AF content is much lower for low and high percentages of clay than it is in the mid range of clay. Again this is probably primarily due to the influence of gradation on density.

Moisture Absorption

Clay content is seen to have very little influence on moisture absorption until more than 23 percent clay is reached (figure 7). Past this point the AF content does not exert much influence. Below 23 percent clay the AF content is more

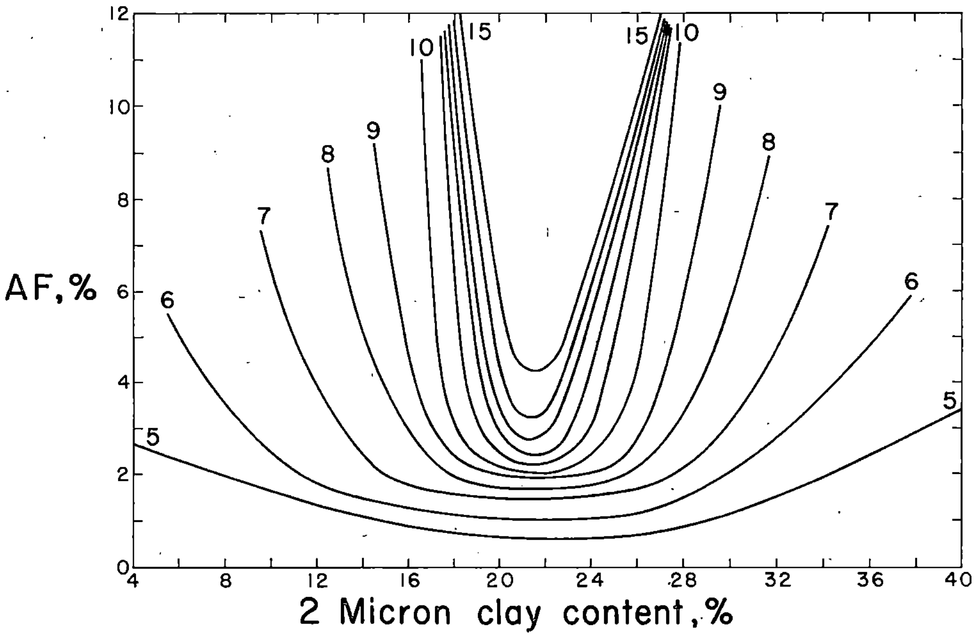

Fig. 6. Immersed strength contours showing the relationship of immersed strength to AF content and clay content in loess. The values of the contours are in hundreds of pounds.

in evidence. Below 18 percent clay the influence of AF is almost the same for all clay contents, in that a minimum moisture absorption occurs with a 2 to 3 percent AF treatment. In the 18 to 23 percent clay range a treatment of 1.5 to 7 percent AF appears to be quite satisfactory. The small effect of the amount of AF on moisture absorption in the higher clay ranges is most likely due to the difficulty of mixing, with, with a consequent poor intimacy of contact between the clay and the AF. The higher clay content loess samples showed a definite tendency to aggregate which contributed to the difficulty of mixing.

Atterberg Limits

The data for the effect of AF treatment on the Atterberg limits show that a small amount of AF greatly reduces the plasticity index in all cases (table III). Additional AF further reduces the plasticity index until the material finally becomes non-plastic. The Atterberg limits are a basis for comparison of soil stabilizers as to their relative waterproofing ability. During the preparation of the AF stabilized specimens for the Atterberg determinations, considerable difficulty was experienced in obtaining a good mixture of water and stabilized material in all cases. As much as thirty minutes of kneading with a spatula was required.

Freezing and Thawing

Samples were subjected to freezing and thawing cycles, and three samples

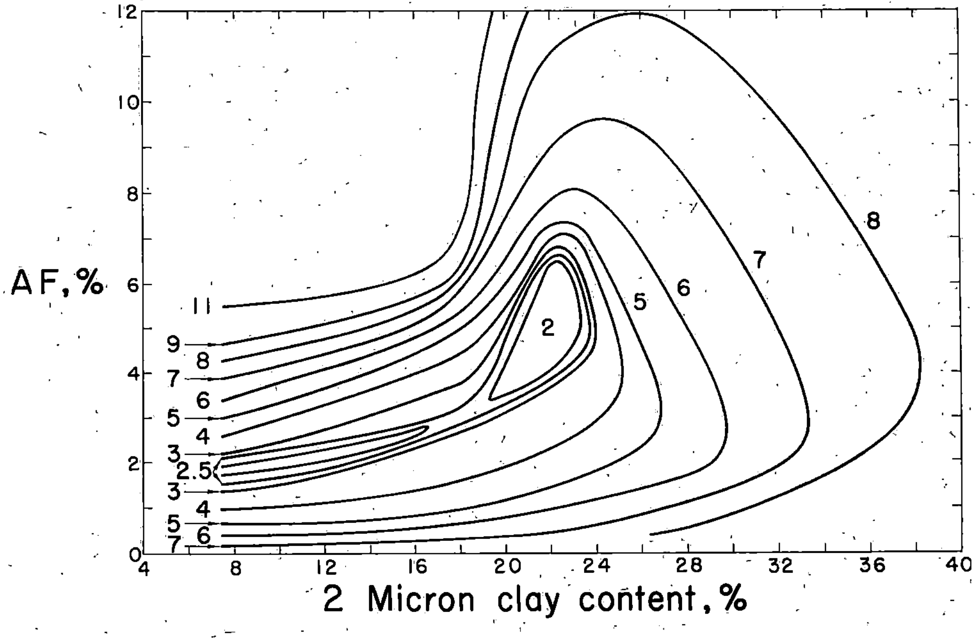

Fig. 7. Moisture absorption contours showing the relationship of moisture absorption of AF content and clay content in loess. The values of the contours are in percent of the weight of the soil plus the weight of the AF.

were tested after 1, 2, 3, 4, 6, and 9 cycles. Three other samples were set aside after the ninth cycle and allowed to air dry for 30 days before being subjected to a tenth and final cycle. The strength tabulated as zero cycles is the air dry strength of the soil (table IV).

The moisture absorbed was calculated as the gain in weight above the air dry weight of the sample and was based on the stable weight. The small amount of moisture absorption is thought to account for the remarkable durability of the specimens. There was no spalling or noticeable sample disintegration. Some samples became slightly soft where they were in contact with the moist felt pads and suffered mechanical abrasion if they were handled roughly.

The strength of the specimens decreases considerably with the first cycle but appears to trend toward a constant value thereafter. The 30 day period of drying after the ninth cycle caused the strength following the tenth cycle to revert to a value near that found after the first cycle.

Wetting and Drying

The specimens employed in this study were subjected to an identical number of wet and dry cycles as were used in the freeze-thaw study (table V).

TABLE III. ATTERBERG LIMITS OF STABILIZED AND NON-STABILIZED SOILS

Sample no.	Aniline-furfural content %	Liquid limit %	Plastic limit %	Plasticity index %
55-1	0	29.6	27.3	2.3
	2	NP[a]	—	NP
	5	NP	—	NP
20-2II	0	33.2	24.0	9.2
	1	27.6	24.0	3.6
	2	25.0	22.4	2.6
	3	26.3	24.3	2.0
	5	NP	—	NP
	7	NP	—	NP
	11	NP	—	NP
26-1	0	34.7	24.0	10.5
	2	26.6	25.1	1.5
	5	24.8	21.0	3.8
36-1	0	39.0	25.6	13.4
	1	32.0	23.0	9.0
	2	30.9	24.2	6.7
	3	29.7	24.8	4.9
	5	NP	—	NP
	7	NP	—	NP
	11	NP	—	NP
46-1	0	54.7	22.0	32.7
	2	33.8	26.4	7.4
	5	29.8	25.1	4.7
503-2	0	56.7	26.4	30.3
	2	37.7	29.5	8.2
	5	31.9	27.9	4.0

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[a] Non-plastic.

TABLE IV. DATA OBTAINED FROM FREEZING AND THAWING TESTS

Soil and amount of resin treatment		Cycle no.	Moisture absorbed %	Height increase inches x 1000	Strength lbs.
20-2II	5%	0			2600
		1	1.4	4	1320
		2	1.7	1	1450
		3	1.8	4	1210
		4	1.7	4	1030
		6	2.5	5	1080
		9	2.6	4	970
		10*	0.8	0	1360
20-2III	2%	0			2090
		1	2.0	1	490
		2	2.3	0	500
		3	2.8	4	390
		4	2.9	6	390
		6	3.1	5	420
		9	3.7	8	290
		10*	1.4	2	460
36-1	5%	0			3380
		1	1.8	4	1930
		2	2.3	3	1730
		3	2.6	9	1460
		4	2.9	10	1370
		6	3.9	13	1080
		9	4.3	16	970
		10*	1.6	7	1770

---

* 30 days of air-drying between cycles 9 and 10.

TABLE V. DATA OBTAINED FROM WETTING AND DRYING TESTS

Soil and amount of resin treatment		Cycle no.	Moisture absorbed %	Height increase inches x 1000	Strength lbs.
20-2II	5%	0			2600
		1	3.7	6	860
		2	4.2	9	730
		3	5.1	9	750
		4	3.7	12	780
		6	4.1	11	760
		9	3.8	12	770
		10*	4.0	11	740
20-2II	2%	0			2090
		1	3.9	8	395
		2	4.0	9	330
		3	4.9	12	310
		4	4.5	11	290
		6	5.0	9	280
		9	4.6	11	320
		10*	4.9	9	260
36-1	5%	0			3380
		1	2.8	13	1250
		2	5.7	25	870
		3	7.6	23	650
		4	6.7	25	700
		6	7.8	28	570
		9	8.1	28	500
		10*	7.4	24	590

---

* 30 days of air-drying between cycles 9 and 10.

The strength, like that of the freeze-thaw specimens, drops considerably with the first cycle and remains relatively constant thereafter. After a 30 day drying period and a tenth cycle of wetting and drying, the specimens did not show any significant changes over the ninth cycle. Apparently some of the resin, products of the reaction, or unreacted chemicals are leached from the specimens during the periods of immersion. A distinct amber color was noticed in the immersion water with the depth of coloring increasing with each cycle. The discoloration is probably due to the unreacted chemicals, because resins are usually insoluble in water. An odor typical of aniline furfural also emanated from the immersion water. Some wet-dry specimens had minor shrinkage cracks, but these cracks did not appear to be serious.

The number of cycles used in both of the foregoing durability studies are considered to be very severe weathering tests for 2 inch by 2 inch specimens. Four cycles with 2x2 specimens are reported as about equivalent to 12 cycles with the 4x4½ standard Proctor specimens used in freeze-thaw and wet-dry tests for evaluating soil cement[26]. The durability of the AF treated loess after nine cycles in both tests is therefore quite outstanding.

Differential Thermal Analysis

Reported results of differential thermal analysis of AF stabilized loess show that the aniline furfural resin and the clay are very intimately associated, and that some of the resin is formed on and within the clay mineral lattice with the remainder filling the voids and cementing the loess particles together[21].

Microscopic Examination

Examination of stabilized specimens under a low power binocular microscope showed the soil particles to be well aggregated with the degree of aggregation and size of aggregates increasing with clay content. The aggregates also appeared to be surrounded and interlaced with resin.

The homogeneity of the overall soil and resin mass is excellent in the lower clay ranges. Higher clay content soils contain some aggregates that are surrounded by resin but are devoid of resin in their centers. Fracture planes that were examined revealed that both the bonding resin between aggregates and the aggregates themselves failed in shear. These planes appear to be like a cobble street when viewed under a microscope.

Economics

Availability and cost are two of the most important factors in any contemplated use of chemical materials. Since the use of aniline and furfural in soil stabilization would involve considerable quantities of both chemicals, the question of availability arises. A preliminary report of the Tariff Commission shows an aniline production of 132 million pounds in 1955[19]. Production of furfural is now about 50 million pounds per year.

Aniline and furfural in carlots were priced at $0.22 and $0.13 per pound respectively in March of 1956[19]. This places the cost of a 2:1 resin at 19 cents per pound. A table of cost comparisons (table VI) for various stabilizing agents has been prepared from data supplied by personnel of the Iowa Engineering Experiment Station who have been working with the different chemicals listed. Stabilization of loess with AF is one of the most expensive treatments listed. However, the benefits derived from the use of AF could well justify the extra cost. It is conceivable that AF could be used in conjunction with a cheaper method of stabilization in building roads, the more economical method making up the majority of the stabilized material and the AF being used in areas of critical moisture.

Lower grades of either aniline or furfural are not available because of the nature of the processes by which they are made. Manufacturers find that they are able to sell the purest products cheaper than they can sell the chemicals contaminated with water because of the cost in transporting the inert water.

Furfural plants are located in Memphis, Tennessee; Omaha, Nebraska; and Cedar Rapids, Iowa.

Toxicity of Aniline and Furfural

The toxicity of aniline has been studied in considerable detail because of its industrial importance and uses^{20}. The symptoms produced by the inhalation or ingestion of aniline are headache, nausea, prostration, giddiness, mental confusion, and violent neuralgic pains. If the dose has been large enough, these symptoms are followed by cyanosis, excessive perspiration, loss of reflexes and voluntary movement, hurried weak pulse, rapid or irregular respiration, hemoglobinuria, and coma with dilation of the pupils. Sufficiently long survival of a large dose of poisoning produces jaundice with a great increase in the biliary pigment of the skin.

Cases of chronic poisoning develop anemia, skin eruptions, nervous symptoms, and amblyopia. Chronic cases lasting a number of years occasionally develop bladder carcinomas as a result of continuous irritation of that organ. Aniline

TABLE VI. ECONOMIC COMPARISONS OF VARIOUS STABILIZING TREATMENTS FOR SOIL 20-2

Stabilizing material	Treatment %	Cost Cents per lb.	Strength after 24 hours immersion lbs.	Stabilization cost cents per 100 lbs. of soil
Aniline-furfural	1	19	530	19
	2	19	810	38
	3	19	980	57
Cutback asphalt	10	2.41	220	24
Portland cement	15	1.111	1780	16.7
Lime-Fly ash (1:2)	18	0.58	485	10.5
Hydrated lime	6	1.125	250	6.7
Arquad 2S	0.16	43	310	6.7
Crude amine	0.30	18	260	5.3
Armeen residue	0.38	9	330	3.5
Arquad 2HT	0.08	36	330	2.7

workers have a high incidence of popillomas and carcinomas of the bladder, and these may develop several years after exposure.

Ingestion of as little as 0.25cc. of aniline may produce symptoms of poisoning[20]. Recovery has followed ingestion of 75 cc., and ingestion of 25 cc, has proved fatal. The maximum allowable vapor concentration is 5 parts per million[17].

Furfural has very mild toxic effects compared with those of aniline. Furfural at 280 parts per million causes only slight irritation to the mucous membranes of lower animals[10]. Furfural is less apt to produce contaminated atmospheres than aniline because a higher concentration is required for toxic effects. Continued exposure to furfural can produce chronic effects, so unnecessary exposure should be avoided.

SUMMARY

The mechanism of aniline furfural resin formation within the loess may be explained by the theorization that the phenomena of absorption and adsorption of the chemicals by the predominent montmorillonitic type clay minerals is of primary significance. Absorbed chemicals form part of the resin within the expanding lattice of the clay minerals, and the remainder of the final resinous products are formed by a reaction between absorbed and free chemicals. The formation of resin from absorbed chemicals produces a link through the crystal lattice of the clay minerals. The resin formed by the reaction between adsorbed and free chemicals produces a covering over the clay and a cementation between the clay and surrounding particles with a consequent aggregating effect.

The overall result of this type of mechanism is the formation of several types of bonds in addition to those in the natural soil. The natural bonds in loess are primarily those of clay to silt and clay to clay as several investigators have found the clay to exist mainly as a covering on the larger silt particles. The bonds resulting from the resinification reaction are those of resin to clay, resin to silt, resin to large organic cations adsorbed on the clay, and resin to resin.

The reaction between aniline and furfural produces large organic cations[12], p. 75. A 2 percent treatment of soils should be sufficient to saturate all soils except those of the very highest cation exchange capacities. Large organic cations of AF held in the exchange positions should enter into polymerization reactions by their unsaturated double bonds and therefore be linked to other aniline furfural cations held in other exchange positions. This would create a bond between clay minerals and aggregates of soil particles.

Furfural is more highly absorbed by clay minerals than aniline[13]. Furfural is also more soluble in water than aniline. The mixing study (Appendix) shows that the introduction of water and furfural before aniline produces the most satisfactory results. More resin is probably formed between the unit layers of the clay minerals when this mixing procedure is used. Since furfural is more soluble in water than aniline, the introduction of furfural first should tend to provide the most uniform distribution and absorption of chemicals.

The low shrinkage during drying and the low amount of swelling on immersion may be explained by this theory. The formation of a resin between the unit layers of the clay minerals tends to hold the layers apart in an expanded position even after moisture removal, accounting for the low amount of shrinkage exhibited. However, the reentry of moisture provides little or no expansion, since the clay minerals are already in an expanded state.

The low moisture absorption and hydrophobic character of the AF stabilized soils are also consistent with the theory. Saturation of the cation exchange sites with large organic cations to produce hydrophobic qualities has been discussed [3, 12], p. 75. The AF reaction products include such cations, and the hydrophobic character of loess stabilized with AF is well illustrated by the Atterberg limits and weathering tests previously discussed. Moisture does find its way into the clay minerals but in small quantities only. The volume of available space is no doubt a large contributing factor to the amount of water absorbed. Any resin formed between the unit layers of the clay minerals and in the void spaces of the soil mass prevents moisture from occupying these positions. Therefore the amount of moisture absorption is reduced below that possible before stabilization.

The formation of resins between the unit layers of the clay and on the clay is supported by the results of the differential thermal analysis, which indicate that the resin is formed in close association with the clay. The steady gain of immersed and dry strength with increased AF content supports the reasoning that an enclosure and cementing of soil grains and aggregates occurs. Increased resin content tends to increase the thickness of the enclosing and cementing wall, thus increasing the overall strength of the stabilized soil.

According to this theory stability should increase with an increase in clay content. However, the data indicate that the optimum stability occurs in the mid range of clay content. There is an indication that aggregation of treated soil also increases with clay content. In soils having clay contents above that which produces maximum stability the aggregation appears to be increased so that total or near total saturation of the clay minerals with the resin is prevented. This tends to reduce the effectiveness of the overall stabilization of a soil with a high clay content by leaving some soil in the aggregates untreated as was found to be true by visual inspection of fracture planes. Possibly, the use of a small amount of sodium ion in the mixing water would aid this situation by dispersing the clay particles so that contact between the resin and more clay would be possible.

The contour curves that have been plotted (figures 3, 4, 5, 6, 7) should aid in the design for any contemplated use of AF. The use of these curves requires a knowledge of the clay content of the soil only. Primary consideration should be given to strength and moisture absorption which then fix the amount of resin needed. Should the amount of material needed for proper stability be too high, the use of AF must necessarily be discarded in favor of a more economical means of stabilization.

The close agreement of the findings of this investigation with others[24] are interesting to note. Particularly significant is the agreement that the mid-range clay content soils derive the greatest benefits from the resin treatment and that the resin is both a waterproofing agent and a binding agent. The results of the present study also indicate that a minimum of about 2 percent AF is needed for resistance to weathering. Since the earlier studies, which were performed on a variety of soils other than loess, and the loess studies agree so closely, it seems plausible to assume that the results may be extrapolated to still different soils with a reasonable degree of accuracy.

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APPENDIX

The order of mixing of aniline, furfural, and water into soil has an important influence on the final stabilizing effectiveness of the AF treatment. The determination of moisture content in samples containing unreacted chemicals is a difficult problem and is considered here because of its obvious influence on the moisture density relationships.

Ratio of Aniline to Furfural

A study of the effects of the ratio of aniline to furfural was made in which this ratio was varied from 1:4 to 3:1. The total amount of aniline and furfural was held constant at 5 percent and mixed with soil 20-2 to have a common basis for comparison. The dry and soaked unconfined compressive strengths were determined along with the total volatile loss during drying and the moisture absorption during soaking.

The data clearly indicate that a weight ratio near 2 parts aniline to 1 part furfural is an optimum ratio (table VII). Plots of the data indicate that maxima or minima occur slightly below the 2:1 weight ratio. These results agree closely with those of other investigators. A weight ratio of 1.93:1 is a 2:1 mol ratio which is the exact stoichiometric relation between aniline and furfural as proposed[25, 27]. Ratios as low as 3:2 and as high as 5:2 could be used without a drastic departure from optimum conditions.

Order of Mixing

Batches of soil in which all possible combinations of the order in which the chemicals and the water should be introduced were mixed. The resulting mixtures were molded and air cured for ten days and then tested for dry unconfined compressive strength, soaked compressive strength, deformation at failure when tested dry and after soaking, water absorption, swelling, loss of volatiles and shrinkage during air curing. The results were tabulated, and an arbitrary value of 10 was assigned to the best performance in each test, 9 to the second best, 8 to the third, and so on. The results of the first five tests mentioned were used as evaluation criteria because the results of the last three tests did not vary significantly.

The ratings revealed that the mixing order of water, furfural, and then aniline

TABLE VII. ANILINE-FURFURAL RATIO STUDY DATA

Weight ratio of aniline to furfural	Dry strength lbs.	Wet strength lbs.	Weight loss during curing %	Moisture absorption after 24 hrs. immersion %
1:4	1530	190	17.3	15.3
1:2	1630	390	16.6	14.2
2:2	1310	400	15.5	16.1
3:2	2430	1090	15.2	2.9
4:2	2790	1240	15.4	2.2
5:2	2540	1070	15.3	2.6
6:2	2100	580	15.7	10.7

produced the best all around product. The second best mixing order was found to be furfural, water, and aniline. Mixing furfural in last produces fair results, but mixing water in last was definitely shown to be poor procedure.

The results are only very slightly better when water is mixed in first than when furfural is mixed in first. In any case it is important that the aniline be mixed in last. This is probably because furfural is more soluble in water than aniline, and furfural is also absorbed by clay to a greater degree than aniline[13].

All mixtures were henceforth made by mixing the water and furfural simultaneously into the soil until the mass was homogeneous. Aniline was mixed in last, just prior to molding.

Determination of Moisture Content

The moisture content of soil is defined as the ratio of the weight of water contained in the soil to the weight of the dry soil: it is expressed as a percentage and is determined by drying a sample to equilibrium moisture content in an oven at 100-110°C. The difference between the weights of the sample before drying and after drying is taken as the amount of moisture contained in the soil.

Moisture determination in samples containing unreacted aniline and furfural presents a difficult problem, since both aniline and furfural are volatile. Some loss of these chemicals occurs along with the normal loss of water, although the resin forming reaction begins immediately on contact between the aniline and furfural. The rate of resin formation depends on many factors including temperature and catalysis, but the rate of volatilization depends mainly on temperature and the amount of unreacted material present. Research done on this problem has indicated that the loss of unreacted chemicals also depends on the amount of water present at the time of mixing.

The weight of the material after oven drying includes both the original amount of soil and the residual aniline and furfural that have reacted to form the nonvolatile resin. Since varying percentages of resin were studied, all moisture contents for molding purposes were computed as a percentage of the weight of the oven dry soil. This places the moisture contents at the time of molding on a common basis and permits a comparison of all mixtures, including those composed of only soil and water.

After air curing most of the original mix water has been lost through evaporation and the residue is soil, hygroscopic moisture, and AF resin. Moisture is absorbed when treated specimens are immersed or otherwise brought into contact with water or water vapor. Since this moisture is apparently absorbed by both the soil and the stabilizing resin the percentage absorption is computed on the basis of the combined weights of the oven dry soil and resin.

The moisture content of specimens molded from a prepared batch may be determined by adding the hygroscopic moisture of the soil used and the amount of water incorporated into the mixture. This method of moisture determination is subject to the errors of evaporation during mixing, evaporation during the process of molding, and the limitations of quantitative measurements prior to mixing. A correction was introduced to compensate for evaporation loss during mixing by adding a predetermined amount of extra water to the mass before mixing. Evaporation during molding was kept at a minimum by covering the mixing bowl containing the batch of soil, water, and AF with a water saturated cloth. This keeps the partial pressure of the water vapor in the atmosphere above the mixture at a maximum and evaporation from the mixture at a minimum. Errors due to volumetric apportionment of fluids are easily kept within limits of ½ a gram. Since the soil mass weighs over 1000 grams, the error due to volumetric measurement is less than 0.05 percent of the soil weight.

As a check on the accuracy of this method for moisture determination, some tests were made in which small individual samples of 2:1 aniline, furfural, water, soil systems were oven dried at 100-110°C. The soil was first weighed in a small aluminum weighing can, after which furfural was added and mixed into the soil. The can and contents were again weighed to determine, by difference, the amount of furfural added. Water was then added and mixed with the soil and furfural. The can and total contents were again weighed. Finally aniline was added and mixed into the system, the total amount was again weighed and placed in an oven for 24 hours. All of these weighings, together with a separate determination of hygroscopic moisture in the soil, permitted an accurate material balance to be made. The oven dried sample was weighed, and the amount of AF lost was determined.

A number of similar samples were prepared, varying the amount af aniline furfural and the amount of water in each sample. It was found that a plot of the percentage of the AF lost in drying versus the weight ratio of initial amount of water to initial amount of AF was very close to a straight line with a slope of one and an intercept of 17. The equation of this line permits the derivation of a moisture content equation dependent only on the variables of total loss after oven drying and the total residue after oven drying.

A similar study found that the moisture may be determined, without appreciable error, by expressing the total volatiles lost as a percentage of the total residue[18]. This was subject to the condition that the moisture sample be held in a covered can for 30 minutes before placing in the oven. The 30 minute period appears to be sufficient for the aniline and furfural to react to a degree that minimizes losses in the oven or at least makes the losses consistent. The previous method requires samples to be placed in the oven immediately.

Both of the above methods of moisture determinations are time consuming. Samples containing unreacted AF must be placed in an oven to dry with a consequent volatilization of some of the chemicals. These volatile chemicals have a tendency to be absorbed by other samples and thus produce contamination. The change in weight due to absorbed vapors proved to be quite serious in some cases. It was therefore decided to use the method of moisture determination in which the moisture is calculated by the amount of water introduced prior to mixing.

RELATIVE EFFECTS OF CHLORIDES, LIGNOSULFONATES, AND MOLASSES ON PROPERTIES OF A SOIL AGGREGATE MIX

by

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(Highway Research Board Bulletin 282. 1960.)

ABSTRACT

Selection of the most economical stabilizing agent for a desired effect on the properties of a soil should be based on knowledge of relative effects of the agent rather than on personal prejudice or the publicity given to an agent. The objective here is to provide a starting point for cost-effect comparisons by showing the effects of four agents on certain properties of a single soil aggregate surface course mix.

Properties compared were: moisture-density relations as determined by standard Proctor density tests; strength as determined from California Baring Ratio studies; moisture retention as determined by a non-standard test; and the plastic properties of the mix as determined by the Atterberg Limits tests. Additives, used in treatments of 0, 0.5, 1, 1.5 and 2%, were: Peladow calcium chloride pellets, Sterling FC and CC salts, Toranil A and Lignin Liquor spent sulphite liquors, and a 79.5 Brix molasses.

The mechanism of stabilization with each agent was discussed to permit extrapolation of effectiveness to other soils. No selection of the "best" agent was made since this is a function of the desired effect on properties and available funds.

INTRODUCTION

Scarcity and costs of better grade road aggregates combined with ever increasing demands for low cost secondary roads have focused the attention of highway engineers on the use of chemical additives to conserve available aggregate and to improve the performance of inferior materials. Despite the extensive research conducted relative to chemical stabilization, no record is available reflecting a direct comparison of the effects of the additives selected for this study on the properties of a specific soil.

Since logical selection of the most economical additive for a desired effect can not be made without a basis for comparison, this study was initiated to provide a starting point for cost-effect comparisons. The objective of the paper is to compare the effects of calcium chloride, sodium chloride, lignosulfonates, and molasses on the moisture-density relationships, strength, moisture retention and plasticity characteristics of a soil-aggregate surface course mix.

MECHANISM OF STABILIZATION

The two main factors contributing to the stability (resistance to lateral flow) of a granular road are internal friction and cohesion[10]. Internal friction in a soil-aggregate mix is attributed to the granular fraction, and is a partial function of density. Cohesion, on the other hand, is a function of soil fines, moisture films, and cementing agents[8].

Chloride Stabilization

Increased stability of granular road bases has been attributed to the use of chlorides to the following seven effects[5]:

1. *Lubrication.* Based on the unctuous nature of a chloride solution, increased densities of 1 to 7% are cited in comparison with an untreated soil. This increase in density may logically be expected to increase internal friction and reduce the rate of moisture loss. Although this effect is less pronounced with sodium chloride than with calcium chloride, the deficiency may be negligible since sodium chloride contributes to dispersion of the binder preventing localized concentrations and thus eliminating soft spots.

2. *Flocculation of clays.* Presence of certain amounts of sodium or calcium ions in the mix will flocculate the binder into silt sized particles. This amounts to changing the grain size distribution and may have the effect of reducing the plasticity index. Other concentrations of ions (more or less) will cause electrical imbalances which will tend to disperse the clay. Crystallization of the salt or leaching by rainfall will change the concentration of ions, permitting dispersion of the clay, with consequent plugging of voids contributing to watertightness.

3. *Moisture retention.* Because of the deliquescence of calcium chloride and the hygroscopicity of sodium chloride, the rate of evaporation of soil moisture will be reduced. As a result, cohesion will be retained and the binder fraction will function as desired rather than being lost as dust.

4. *Solubility of road aggregate.* This effect is mentioned as a possible means of cementation within the mix and is based on the solubility of limestone and dolomite in chloride solutions, resulting in precipitation of cementitious carbonates. The effectiveness of this reaction is unevaluated.

5. *Freezing point depression.* By lowering the freezing point of the mixture, resistance to temperature effects is obtained with the use of chlorides. For complete freezing, road temperature must be —59.8°F with calcium chloride treatment or —6°F with sodium chloride treatment; thus the creation of ice lenses is inhibited.

6. *Surface tension.* The increase of this property due to the presence of chlorides results in strengthening water film bonds between soil grains, adding to apparent cohesion. With evaporation, the chloride concentration increases, causing a further increase in surface tension. The degree of increase may be such that increased densities will result.

7. *Crystallization.* This effect is present only with sodium chloride and may compensate for the lesser effectiveness of salt altering other properties. Advantages which result from the formation of salt crystals are: the crystals plug voids

thus retarding evaporation and shrinkage, they act as a cement which prevents aggregate losses, and they provide a hard, tightly knit traffic surface.

Lignosulfonate Stabilization

The principal effects of lignosulfonates on a soil aggregate mixture are those of cementation and dispersion of clay[5].

Cementation is derived from the fact that the lignosulfonates, being water soluble polymers, act in the soil similarly to a glue. Best results are obtained with mixes rich in binder soil, since open type mixes permit rapid leaching of the lignosulfonate. Hygroscopicity of the wood sugars present may also contribute to strength by retarding evaporation, thus benefiting cohesion.

Dispersion of the clay fraction benefits stability of the soil-aggregate mix by: plugging voids and consequently improving watertightness and reducing frost susceptibility, eliminating soft spots caused by local concentrations of binder soil, filling voids with fines thus increasing density, and increasing the effective surface area of the binder fraction which results in a greater contribution to strength from cohesion.

Molasses Stabilization

The principal effects of molasses in a soil-aggregate mix are increased moisture retention and cementation[7]. Moisture retention effects may be attributed to the hygroscopicity of the molasses and to reduced vapor pressure. From this description of the cementation effect, it would appear that the actual effect is not cementation, which implies a rigid bond between particles, but rather an increase in surface tension with consequent increase in apparent cohesion. As with lignosulfonates, best results may be anticipated with a high percentage of binder soil owing to the ease with which molasses will enter solution and be leached from the mix.

INVESTIGATION

Materials Used

Soil-aggregate mix. Three natural soils containing about 6% moisture, were blended in a two cubic foot cement mixer to give a soil-aggregate mix conforming to Iowa State Highway Commission specification 4111[6] for stabilized surface course materials. The three soils used were: a pit-run gravel from a glacio-fluvial deposit north of Ames, Iowa; a silty clay loam (Monona Series, C horizon) from Shelby County, Iowa; and a C horizon oxidized Wisconsin-age (Cary) glacial till from near Ames, Iowa.

The gradation of the resultant mix is shown in table I; other physical properties of the soil-aggregate mix are as follows:

Liquid limit, 25.5%
Plastic limit, 16.8%
Plasticity index, 8.7
Optimum moisture, 9%
Std. Proc. dens., 129.2 pcf
Specific gravity, 2.69

Carbon content, 0.1%
Carbonate content, 21.2%
Cation exchange capacity, 7.5 me/100 gm
Exchangeable cation, Ca++
pH, 8

X-ray analysis of the fraction passing the no. 200 sieve revealed the presence of quartz, calcite, dolomite, and feldspars, as well as the clay minerals illite, kaolinite, montmorillonite and vermiculite, although recent work indicates that the latter may be a non-expanding 14 angstrom montmorillonite. No quantitative analysis of these minerals was attempted but the predominant clay mineral was montmorillonite.

Results of a petrographic analysis of the remaining portion of the soil-aggregate mix are shown in table II.

Calcium chloride. Calcium chloride for this study was provided in the form of Peladow pellets (tables I, III). In this form the chloride is anhydrous, contains about 95% $CaCl_2$, and costs approximately $30 per ton undelivered.

Sodium chloride. Rock salt was provided in two gradations (tables I, III). The larger size salt is designated by the manufacturer as Sterling CC, and the smaller as Sterling FC. Identification in this paper will be by the letter designations CC and FC respectively. Costs at the mine for these salts vary from about $8 to $13 per ton depending on the size shipment and the packaging requirements.

Lignosulfonates. Two types of spent sulphite liquor were used in the study. The first, Toranil A, is a desugared calcium lignosulfonate which was provided

TABLE I. MECHANICAL ANALYSES OF DRY MATERIALS USED IN STUDY

Sieve size	Weight percentage retained on sieve Soil-aggregate	$CaCl^2$ (Peladow)	NaCl (CC)	NaCl (FC)
3/4"	0	—*	—	—
3/8"	—	Nil	0	—
#4	18.55	0.2	35.0	—
#8	—	37.0	48.0	0
#10	18.0	—	—	—
#12	—	—	—	5.0
#16	—	—	15.9	—
#20	—	62.8	—	42.0
#40	29.15	—	—	—
#80	—	—	—	43.0
#200	11.20	—	—	—
Pan	23.20	0.1	1.1	10.0

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* Indicates sieve not used in analysis.

TABLE II. PETROGRAPHIC ANALYSIS OF PORTION OF THE SOIL-AGGREGATE MIX COARSER THAN THE #200 SIEVE

Sieve retaining material	Weight percentage Quartz*	Feldspar	Heavy†	Carbonates‡	Aggregate§
#4	0	2	0	51	47
#10	21	1	0	38	40
#40	~78	trace	0	~6	~16
#200	73	6	7	7	7

---

* Includes quartz and quartzite.
† Includes turmaline, augite, magnetite, and opaque minerals.
‡ Includes limestone and calcite.
§ Includes all rock fragments, e.g. granite, etc.

in the concentrated form (50% solids). The other, lignin liquor, is also a concentrate rich in calcium lignosulfonate, but contains a higher percentage of sugars (table IV). Costs are about 4.5c per gallon undelivered.

Molasses. Although the Brix reading of the molasses used in the study was 79.5, representing a sugar content of 79.5%, evaporation to constant weight at 70°C revealed a solids content of only 50% by weight (table V). Current cost is $35 per ton in eastern Iowa..

Method and Procedure

To permit direct comparison of effects, test specimens were prepared con-

TABLE III. TYPICAL CHEMICAL ANALYSES OF CHLORIDES

Constituents	Weight percentage $CaCl^2$ (Peladow)	 NaCl (CC)	 NaCl (FC)
$CaCl_2$	95.2	0.053	0.071
NaCl	1.15	98.220	98.236
KCl	2.96	—[*]	—
$Ca(OH)_2$	0.068	—	—
$CaCO_3$	0.024	—	—
$CaSO_4$	—	0.643	0.651
$MgCl_2$	133[†]	0.052	0.085
Heavy metals as Pb	0.5	—	—
S as SO_4	0.009	—	—
Fe	16[†]	—	—
Water insolubles	—	1.041	0.957

[*] Indicates not determined.
[†] Indicates parts per million.

TABLE IV. PROPERTY ANALYSIS OF SPENT SULPHITE LIQUORS AS GIVEN BY PRODUCERS

Property	Toranil A	Lignin Liquor
Total solids, %	50	52.4
Total sugar, %	0.6	11.5
Total sulfur, %	—[*]	3.21
Ash, %	8.65	8.58
Calcium oxide, %	3.75	3.40
Specific gravity	1.24	1.267
pH	4.55	4.0
Manufacturer	Lake States Yeast Corp., Rhinelander, Wis.	Consolidated Water Power & Paper Co., Wisconsin Rapids, Wis.

[*] Indicates not determined.

TABLE V. TYPICAL ANALYSIS OF 79.5 BRIX MOLASSES

Constituent	Weight percentage
Minimum invert sugar	48
Reducing sugar	16-20
Sucrose	28-35
Nitrogen as crude protein	2-4
Ash	7-12

taining 0, 0.5, 1.0, 1.5, and 2.0% of each of the previously described additives. The percentages were based on the weight of solids contained in the additive, and the oven dry weight of the soil, aggregate mix. Duplicate specimens were prepared for each phase of testing.

Daily readings of temperature and relative humidity from a psychrometer located in the laboratory were recorded throughout the test periods to permit correlation with effects.

Mixing was in a model CC20 Blakeslee mixer in the sequence soil, additive, water. Materials were mixed mechanically for about three minutes, then transferred to a shallow pan where final mixing was done by hand. Next the mix was compacted to a depth of about two inches using a 5.5 pound rammer. Curing for about five minutes while covered with a damp cloth (to retard evaporation) permitted more uniform absorption of the moisture.

Standard Proctor moisture-density relationships. These tests were performed in accordance with method D. ASTM tentative method of test D 698-57 T[2], except that the height of the molded specimens was five inches instead of the specified 4.584 inches.

California Bearing Ratio. These tests were performed in accordance with the procedures of the U.S. Corps of Engineers[9]. For each percentage of additive, four specimens were prepared at optimum moisture content and maximum density as determined by moisture density tests. Two specimens were tested immediately to determine the CBR values. Then, after four days immersion using a 5 pound surcharge, the soaked CBR values were obtained from the opposite ends of the specimens. The second pair of specimens was permitted to air cure under room conditions for a week prior to being subjected to the same tests. Expansion of the specimens during the periods of immersion was also determined.

Moisture retention. This property was determined through a non-standard method of testing. Two specimens, identical to those for the CBR tests, were prepared for each percentage of the various additives. Specimens were extruded and stored on open shelves under room conditions. The weight of the specimens was recorded after extrusion and after lapses of 1, 2, 7, 15, 30, 60, and 90 days.

Atterberg limits tests. These tests were performed in accordance with ASTM tentative methods for test D 423-54 T(1) and D 424-54 T(3). Material for testing was obtained from specimens used in the moisture retention tests.

RESULTS OF INVESTIGATION

Moisture-density Relationships

Effect of calcium chloride. Marked increases in density were realized with the addition of calcium chloride to the mix. The dry densities obtained are shown in figure 1. Of particular interest is the fact that maximum dry density was obtained at 1% calcium chloride, and that addition of more chloride tended to decrease the density.

This phenomenon may be explained by reference to the diffuse double layer concept, which considers that the clay particles have negative surface charges caused either by isomorphous substitution of lower valence cations within the lattice or by adsorbed hydroxyl ions due to broken valence bonds. These negative surface charges cause repulsive forces between clay particles thus increasing the compactive effort required for a given density, or conversely lessening the density which might be attained with a given effort. Introduction of Ca^{++} ions will give two beneficial effects. First, the negative surface charges may be neutralized, thus eliminating the repulsive forces, and secondly, because the calcium

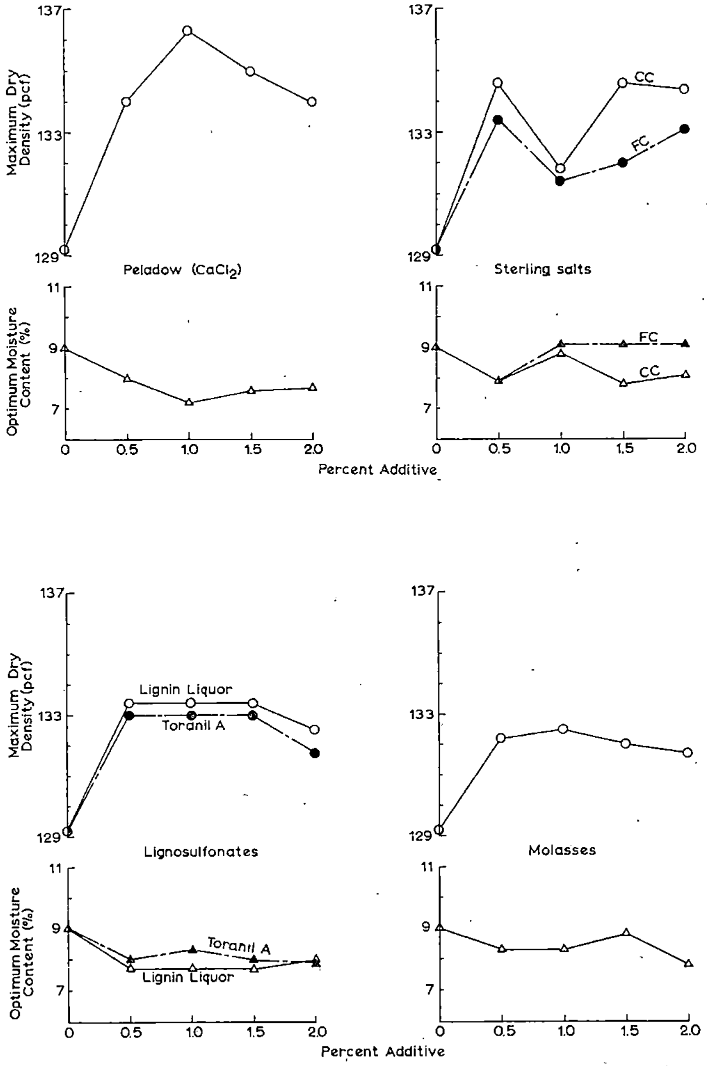


Fig. 1. Variation of optimum moisture content and maximum dry density with percent treatment of indicated additives.

ion carries a double positive charge, valence bonds may be set up between neighboring clay micelles. Both of these effects will mean greater densities with the given compactive effort.

Continued addition of calcium ions will give increased benefits only until the negative surface charges are satisfied. Beyond this optimum point additional ions will be detrimental since the media will then assume a positive charge and repulsive forces will be reinstituted. This, apparently, is the explanation of the lower densities obtained in this study with the higher percentages of calcium chloride.

An additional point of interest in this phase of the investigation is the apparent inverse relationship between optimum moisture content and maximum dry density, indicating the need for greater lubrication to assist in overcoming the repulsive forces.

Sodium chloride. As with calcium chloride, densities obtained with the addition of sodium chloride exceeded the maximum obtained with the untreated soil-aggregate mix. Unlike the specimens treated with calcium chloride, those treated with sodium chloride were not restricted to a single optimum chloride content. Whether the salt used was CC or FC, a minimum dry density (treated material) was observed at 1% salt (figure 1).

Since the hydrated sodium ion is larger and more reactive than the calcium ion, and since a gram of sodium chloride contains almost twice as many cations as a gram of calcium chloride, it is reasonable to expect an effective neutralization of the negative surface charge of clay by a lower weight percentage of sodium chloride. At 0.5% salt, a maximum density was attained probably because of an effective neutralization of negative surface charges on clay particles. This maximum density was not as great as that for 1% calcium chloride treatment since valence bonding of clay micelles is less probable, and since the size of the hydrated sodium ion precludes as close an approach of the neutral clay particles. At 1% sodium chloride content, the repulsive forces were active because of the excess sodium cations, and lower densities resulted. Because the repulsive forces are related inversely to the square of the distance between charges, and because of the imposition of aggregates and voids, a maximum effective value of repulsive forces is attained which is relatively unaffected by the addition of mere salt to the mixture. Thus, in effect, the increased densities which were observed at 1.5 and 2% sodium chloride may be partially attributed to the additional weight of salt contained within the specimens.

That all densities resulting from FC salt treatment are less than those resulting from corresponding percentages of CC salt may be explained by the gradation differences. The FC salt, being finer grained, went into solution more rapidly than the coarser grained CC salt. Instances were noted where the CC salt crystals were not completely dissolved at the time of molding. Thus the number of active sodium ions was greater in the specimens prepared with FC salt.

The inverse relationship between moisture content and maximum dry density was again evident in the case of sodium chloride treatment, with the exception of samples containing 1.5 and 2% FC salt. This may have resulted from incomplete dissolution or from experimental error.

Lignosulfonates. Densities obtained with the use of lignosulfonates as additives were higher than those obtained for the untreated soil-aggregate mix. The lignin liquor showed a slight advantage over Toranil A in all percentages. The maximum dry densities are given in Figure 1.

With the lignosulfonates constant maximum densities were obtained at 0.5, 1, and 1.5 % additive, and a decrease in density was obtained with 2% additive.

Speculation as to the cause of density variations has lead to the conclusion that the initial density increase at 0.5% lignosulfonate treatment is caused by better lubrication derived from the decrease of surface tension. Since the lignosulfonates are assumed to coat the soil particles, the addition of further lignosulfonates should lead to thicker films and consequent separation of the soil grains. The specific gravity of the liquor is lower than that of the soil so that displacement of soil by lignin should lead to lower densities. Presumably, at 1 and 1.5% liquor, the beneficial effect of lubrication compensates for the thicker films and the overall density remains constant. At 2% lignosulfonate, the effect of thicker films predominates and density decreases.

The difference in densities obtained with lignin liquor and with Toranil A is believed to be caused by the different specific gravities of the liquors. Lignin liquor, having a slightly higher specific gravity, gave greater maximum dry densities. Other possible reasons for this difference might be found in the difference in lubricating properties because of the differing sugar contents, or in experimental error.

The inverse relationship between maximum dry density and optimum moisture content was again apparent with lignin liquor, but was not shown by the Toranil A treated specimens. A possible explanation is that the clay lumps may have been coated in aggregated masses with the higher percentages of Toranil A, preventing water intrusion, thus changing the effective gradation of the mix and lessening the moisture requirement for optimum lubrication.

Molasses. Although density increases were appreciable with the addition of molasses to the soil-aggregate mix (figure 1), they were not as great as with any of the other additives. As with lignosulfonates, density increases are attributed to the lubricating effects accompanying reduced surface tension.

Optimum molasses content for maximum dry density occurred at 1% additive, with only slight deviation at contents of 0.5 and 1.5%. The same mechanism, as was proposed for the variation of density with lignosulfonates, is believed applicable to the molasses treated specimens; benefit from lubrication being overridden at higher percentages of additive by dispersion caused by thicker films.

The erratic nature of variation of optimum moisture with percent molasses is believed to be due to causes discussed for Toranil A.

California Bearing Ratio

Although CBR tests as performed included obtaining values for specimens permitted to air dry for seven days, direct comparison of these results would not be realistic since all specimens were not subjected to similar conditions of relative humidity and temperature. For this reason the discussion of results will center on test values for specimens tested immediately, and after four days immersion, with only occasional mention of curing effects.

Effects of calcium chloride. CBR values were increased in all cases by the addition of calcium chloride, the trend both in immediate and soaked values apparently correlating with the density of the specimen. The highest immediate CBR value was that with 1% calcium chloride (table VI). This value (103.0%) represents an increase in strength of more than 600% when compared to the value obtained for the untreated soil-aggregate mix. After four days immersion, the strength is 490% that of the untreated mix tested under the same circumstances. After seven days curing, all of the calcium chloride treated specimens reflected an increase in unimmersed strength with only the 1% specimens failing to give higher immersed strengths than the corresponding uncured specimens. Expansion of the specimens during soaking was negligible (table VI).

Effects of sodium chloride. Marked increases in immediate CBR values were obtained with 0.5, 1.5, and 2% CC salt treatments, but only the 0.5% FC salt treatment gave values exceeding the untreated value. At 1% CC salt, and at both

TABLE VI. RESULTS OF CALIFORNIA BEARING RATIO TESTS

Additive		California Bearing Ratio, %				Expansion, %	
		Uncured specimens		Cured specimens			
Kind	%	Immediate	Immersed	Dry	Immersed	Uncured	Cured
Untreated	—	15.3	9.8	40.5	22.5	0.19	0.51
$CaCl^2$	0.5	42.0	35.0	129.0	67.0	0.20	0.31
(Peladow)	1.0	103.0	48.0	160.0	48.0	0.26	0.40
	1.5	51.0	43.0	82.0	53.0	0.21	0.19
	2.0	38.0	27.5	44.0	30.0	0.25	0.19
NaCl (CC)	0.5	56.5	45.0	90.0	52.5	0.33	0.11
	1.0	12.5	6.5	31.5	21.0	0.09	0.03
	1.5	51.0	36.0	120.0	57.0	0.05	0.09
	2.0	34.0	25.0	54.5	43.5	0.10	0.09
NaCL (FC)	0.5	51.7	42.0	61.0	44.0	0.29	**0.20**
	1.0	16.8	10.3	21.0	17.7	0.22	0.16
	1.5	12.0	8.3	20.0	18.0	0.06	0.15
	2.0	8.6	6.4	14.5	10.0	0.05	0.08
Lignin	0.5	71.0	49.5	97.5	36.5	0.23	0.18
Liquor	1.0	53.0	35.5	76.0	42.0	0.21	0.26
	1.5	47.0	33.0	56.5	33.8	0.24	0.26
	2.0	16.0	12.0	24.0	13.5	0.04	0.32
Toranil	0.5	64.0	52.0	97.0	46.0	0.17	0.29
A	1.0	39.0	32.5	64.0	30.0	0.10	0.13
	1.5	42.0	29.0	56.0	28.0	0.14	0.24
	2.0	26.5	20.0	35.5	21.3	0.13	0.54
Molasses	0.5	32.0	24.5	48.0	30.0	1.07	0.39
	1.0	28.0	20.5	50.0	23.5	0.70	0.57
	1.5	12.0	11.5	25.0	19.0	0.52	0.61
	2.0	23.0	26.0	46.5	32.0	0.13	0.33

1.5 and 2% FC salt, though densities exceeded that of the untreated soil-aggregate mix, CBR values were lower than the untreated CBR. If one considers the 1.5 and 2% CC salt treated specimens to be not truly representative (because of incomplete dissolution of the salt), then the loss of strength may be attributed to loss of internal friction due to the lubricating properties of the chloride solutions, and to loss of cohesion due to repulsive forces caused by excess sodium ions.

Loss of strength on immersion was less in the case of 0.5% sodium chloride treatment than in the case of 1% calcium chloride treatment, probably because of the lower percentage and the lesser hygroscopicity of the salt. Considering both the accuracy of the test, and the CBR curve corrections required, the best four day immersed CBR values (no curing) of the three chlorides tested (FC, CC, and Peladow) are esentially equal.

As was true for calcium chloride, the CBR values of rock salt treated specimens reflected strength gains after curing, both dry and immersed. Of note were the increases associated with 1.5 and 2% CC salt specimens, indicating rapid evaporation, and again supporting the assumption of incomplete dissolution of the salt.

Expansion of the salt treated specimens on immersion was negligible (table VI).

Effects of lignosulfonates. All percentages of lignosulfonates used in this study increased the strength of the specimens over the strength obtained with the untreated soil aggregate mix. The greatest immediate gain was at 0.5% lignin liquor, with the greatest immersed strength (uncured and considering all additives) associated with 0.5% Toranil A. Immediate CBR values generally decreased with increase in lignosulfonate content, indicating the detrimental effects of increased lubrication. The exception in this trend was found at 1.0% Toranil A treatment. This may be attributed to the higher moisture content at molding and the consequent increase of lubrication.

Strength loss on immersion of the Toranil A treated specimens was generally less than that of the specimens treated with liqnin liquor possibly due to the lesser hygroscopicity of Toranil A. Another factor which may account for the strength loss associated with immersion of lignin liquor treated specimens was the fact that fungal consumption of the lignin was indicated by the presence of a mold on the surface of the specimens.

Curing either benefited immersed strength or left it unchanged except in the case of 0.5% lignin liquor. This loss may have been caused by lower waterproofing potential at this content or may have been caused by loss of lignin due to fungal consumption. Expansion on immersion was negligible.

Effects of molasses. With CBR strength as a criterion, molasses was the least beneficial of the additives tested. Maximum immediate strength gain was with 0.5% molasses treatment, which gave approximately a twofold increase over the untreated soil-aggregate mix strength (table VI). At 1.5% molasses content, a loss of strength was apparent.

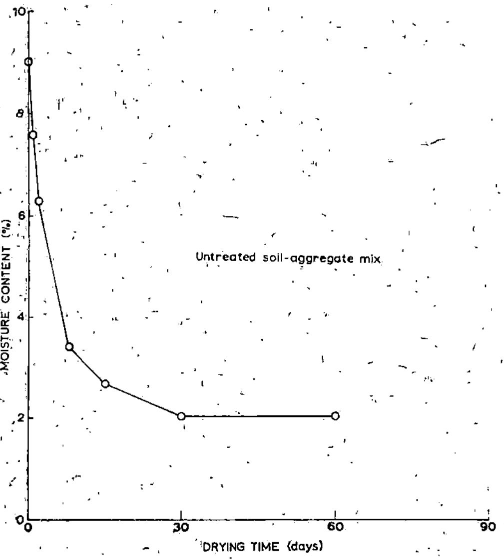
Results of this phase of the investigation are not considered to be very reliable because the treated specimens were subject to rapid fungal action, becoming moldy both during the curing and immersion periods. This factor, combined with the degree of expansion (particularly at 0.5% molasses content), indicates that the use of molasses as a stabilizing agent should be limited to areas with extremely dry climates.

Moisture Retention

A direct comparison of the moisture contents of the various specimens as a function of time of curing proved inadequate as a means of determining the relative effectiveness of the additives. Direct comparisons are inadequate since they show inconsistencies even amongst various percentages of the same additive, as well as showing higher equilibrium moisture contents for the untreated soil-aggregate mix than for specimens containing hygroscopic additives (figures 2, 3, 4, 5, 6, 7, 8). The reason for this apparent discrepancy is that the conditions under which samples dried varied; therefore a more complete analysis is required in order to compare the effectiveness of the additives.

The process of drying may be divided into four phases during which the rates of drying will differ because of changes in the governing properties[4].

Phase 1. During this phase of drying, the water content of the specimen is at a maximum (near saturation) and thus evaporation may be considered as essentially that from a free water surface. The area of escape for water vapor can be considered to be the exposed surface area of the specimen. This period is one of instability because the specimen is adjusting to the temperature of the drying medium.



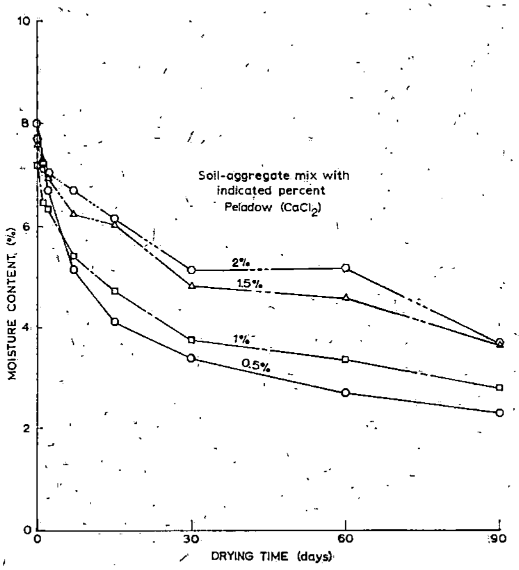
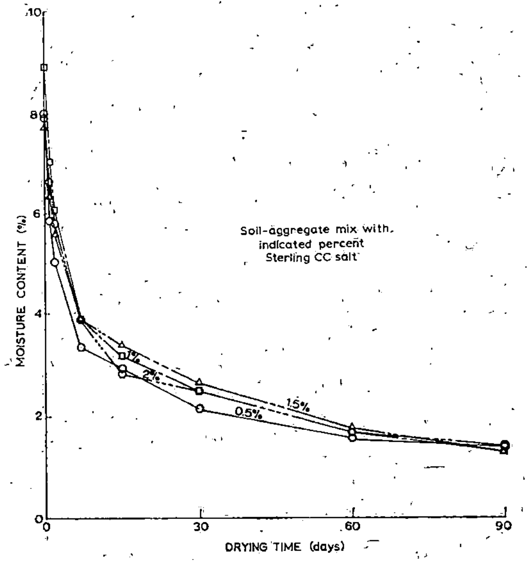


Fig. 2. Variation of moisture content with drying time, untreated soil-aggregate specimens.

Fig. 3. Variation of moisture content with drying time, calcium chloride treated specimens.

Phase 2. This is a period of steady rate drying which, owing to the lower moisture content, is governed by the rate of capillary movement of moisture, and the rate of flow into the soil voids. During this phase the area of escape is some portion of the exposed area of voids.



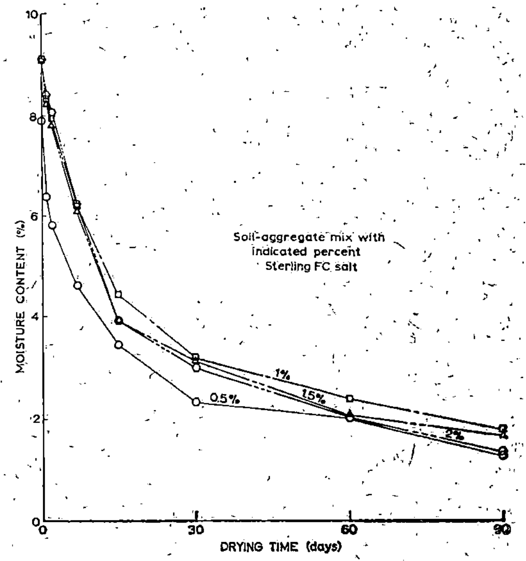
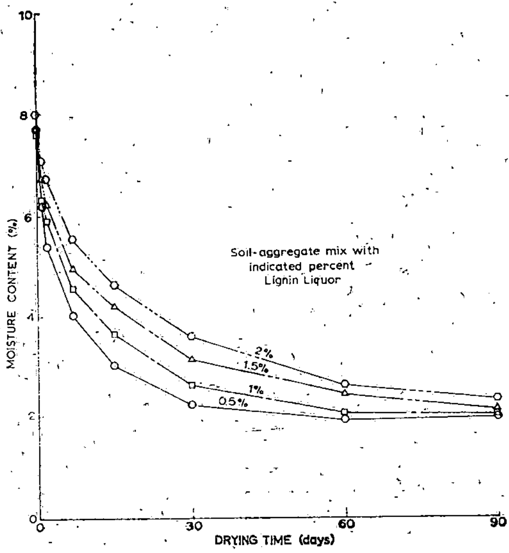


Fig. 4. Variation of moisture content with drying time, CC salt treated specimens.
Fig. 5. Variation of moisture content with drying time, FC salt treated specimens.



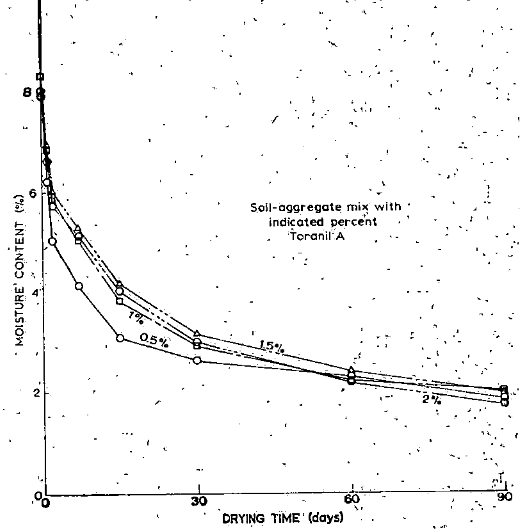


Fig. 6. Variation of moisture content with drying time, lignin liquor treated specimens.
Fig. 7. Variation of moisture content with drying time, Toranil A treated specimens.

Phase 3. This period of drying is characterized by a constantly decreasing rate of evaporation more or less proportional to the moisture content of the specimen. Because of the low water availability, the rate of evaporation is governed by the rate of diffusion within the specimen. The area of escape is essentially the exposed surface area of the voids.

Phase 4. The final phase of drying again is characterized by a decreasing rate of moisture loss. During this period, the rate of loss is governed by the water retention forces of the soil, vapor pressure of water on clay, with the area of escape remaining unchanged.

From comparison of natural evaporation formulae and constant condition drying formulae, it is apparent that the rate of evaporation is proportional to the vapor pressure difference between the vapor pressure of the moisture in the soil and the partial pressure exerted by the air. This may be expressed as:

$$dX/dt = -k \triangle p$$

where X = moisture content
t = time
$\triangle p$ = vapor pressure differential
k = a constant of proportionality for any given moisture content.

Based on this equation, the effectiveness of the additives was evaluated (figures 9, 10, 11, 12, 13, 14). The figures show a plot of k versus moisture content. In preparing the figures, several approximations were required. First, data for the early periods were discarded because of the unstable nature of this phase of

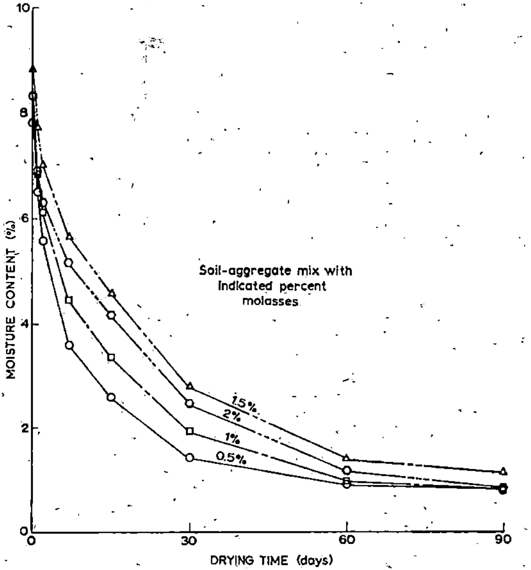
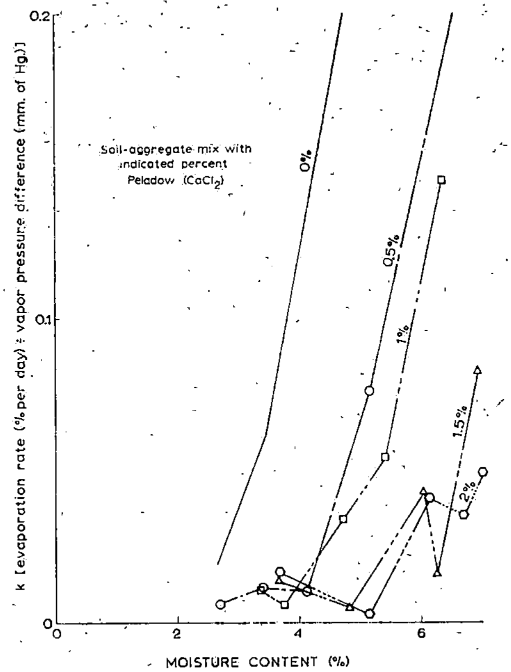


Fig. 8. Variation of moisture content with drying time, molasses treated specimens.



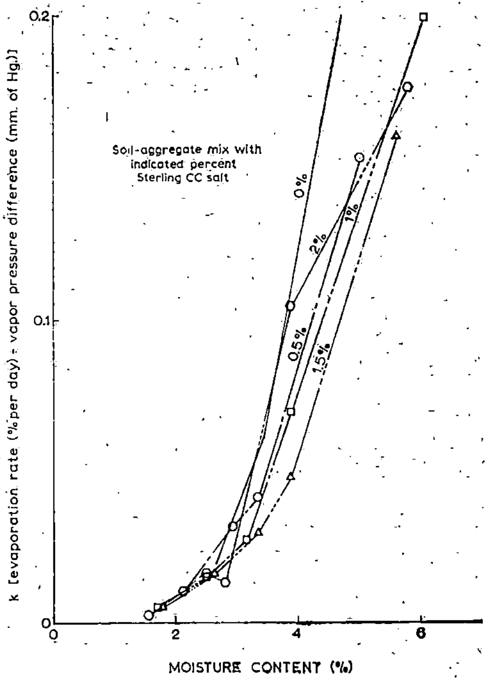
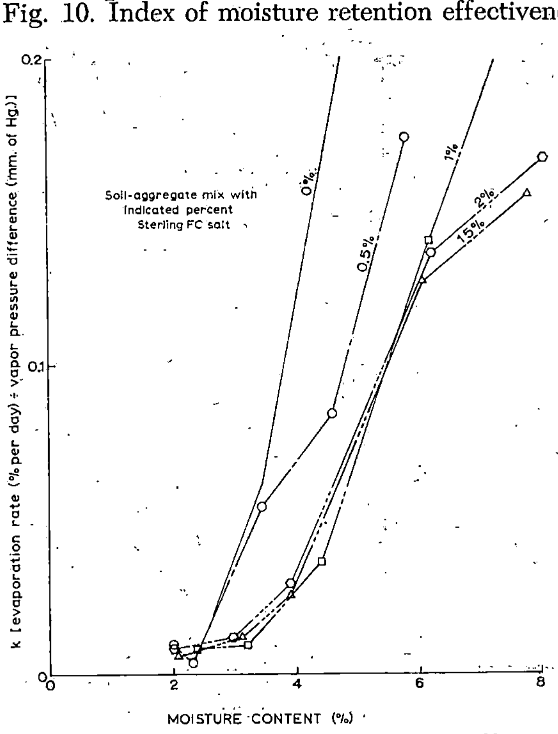


Fig. 9. Index of moisture retention effectiveness for calcium chloride treated specimens.

Fig. 10. Index of moisture retention effectiveness for CC salt treated specimens.



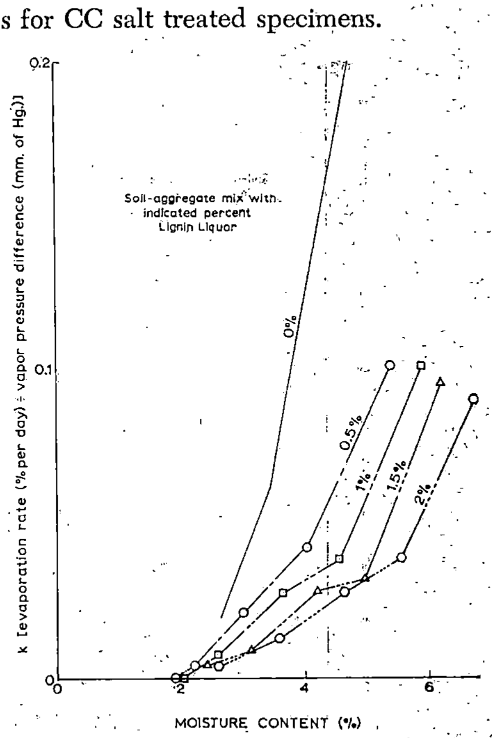


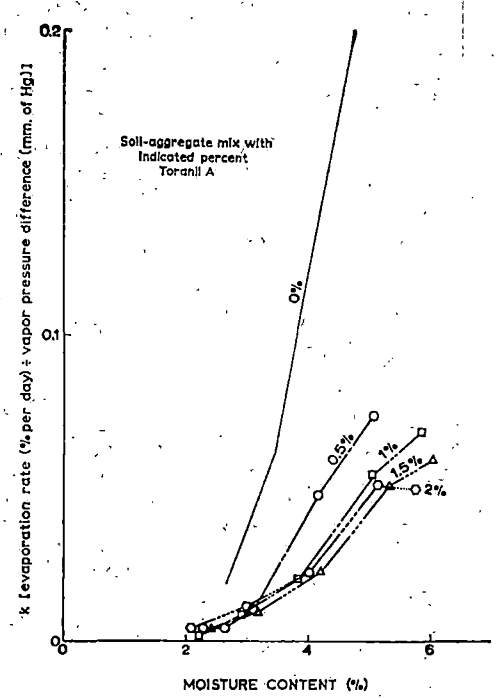
Fig. 11. Index of moisture retention effectiveness for FC salt treated specimens.

Fig. 12. Index of moisture retention effectiveness for lignin liquor treated specimens.

drying and because the temperature of the specimens could not logically be estimated as air temperature. Next, since the vapor pressure differential was not constant throughout the drying periods, the assumption was made that the average of differences for the day of weighing and the two previous days would be representative of the conditions for the entire period. In this respect, the vapor pressure of moisture in the specimen was based on pure water since there was no knowledge of the concentration of chemicals in the solution. By doing this no serious error is introduced, since the net result is that of reflecting the vapor pressure effects of the chemicals in the calculated values of k.

Based on these assumptions, the formula was solved for k, and the resultant values were plotted against the moisture content of the specimen at the start of the time period associated with the incremental loss of moisture. Although certain irregularities appear in the curves as a result of the approximations, sufficient consistency exists to permit comparison.

Relative moisture retention capacity of the additives may be determined from the curves by comparing the value of k for the various additives at a given moisture content; the greater the value, the less effective the additive. Less credence should be given to the lower ends of the curves since weighing errors would have greater effects in this range, and since specimens may have reached equilibrium moisture content before lapse of the time increment used.



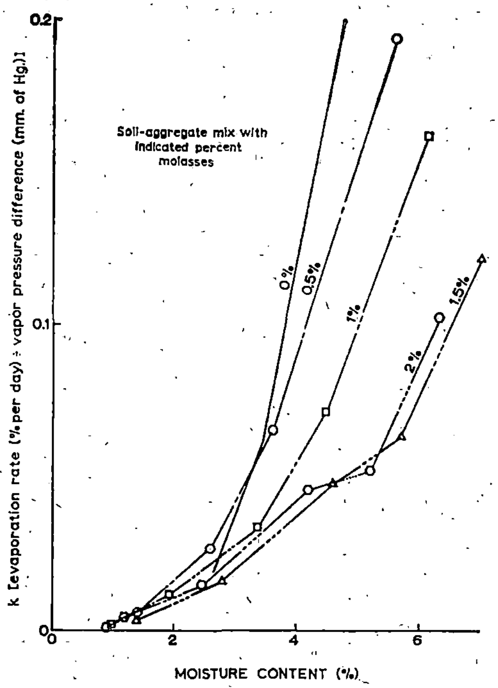


Fig. 13. Index of moisture retention effectiveness for Toranil A treated specimens.
Fig. 14. Index of moisture retention effectiveness for molasses treated specimens.

No discussion of the actual results obtained is deemed necessary since the relative effectiveness may be readily observd from the curves. However, the poor showing of the salt treated specimens does merit some discussion. Factors which should be considered because they are not reflected in the curves are: under traffic salt crystals which grew out from the surface of the specimens would be packed into void spaces (figure 15); the exposed surface area per unit volume of the specimens was greater than for comparable material in a road; the crystalization was less dense at the surface, and moisture retention was therefore less.

Atterberg Limits Tests

The Atterberg limits give an indication of the plastic and cohesive properties of soils. Specifically, these tests give: the liquid limit of the soil, or the minimum moisture content at which the soil water mixture reacts as a viscous liquid; the plastic limit, or the minimum moisture content at which the mixture acts as a plastic solid; and the plasticity index, which is the range of moisture content through which the mixture exhibits plastic behavior[8]. From this it is possible to assume that improved lubrication will tend to decrease both the plastic and liquid limit. Increased viscosity would have the opposite effect.

Effect of chlorides. Because of the amount of individual judgment involved in these tests, the degree of change in limits caused by incorporation of chlorides

TABLE VII. RESULTS OF ATTERBERG LIMITS TESTS

Additive		Plastic limit	Liquid limit	Plasticity index
Kind	%	%	%	
Untreated	—	16.8	25.5	8.7
$CaCl_2$	0.5	15.6	26.1	10.5
	1.0	16.0	26.3	10.3
	1.5	16.5	24.9	8.4
	2.0	15.0	25.5	10.5
NaCl (CC)	0.5	16.2	24.7	8.5
	1.0	16.5	26.1	9.6
	1.5	17.0	25.3	8.3
	2.0	16.3	26.1	9.8
NaCl (FC)	0.5	17.2	26.2	9.0
	1.0	17.3	25.4	8.1
	1.5	17.5	24.9	7.4
	2.0	16.7	24.7	8.0
Lignin Liquor	0.5	16.4	26.5	10.0
	1.0	15.7	29.0	13.3
	1.5	14.6	28.4	13.8
	2.0	14.2	27.5	13.3
Toranil A	0.5	15.8	28.9	13.1
	1.0	16.2	30.1	13.9
	1.5	15.3	27.2	11.9
	2.0	14.9	29.0	14.1
Molasses	0.5	17.0	32.5	15.5
	1.0	16.4	31.7	15.3
	1.5	17.5	31.6	14.1
	2.0	17.9	31.2	13.3

in the mix is not significant. Results (table VII) are erratic and establish no definite trend. One contributing factor in the case of sodium chloride treated specimens evolves from the fact that the salt migrated to the surface of the specimens and caused changes in salt concentration in the material tested.

Effect of lignosulfonates. A consistent decrease of plastic limit coupled with consistent increase in liquid limit was observed with increased lignosulfonate treatment. This trend led to the natural consequence of increasing the plasticity index, irrespective of the spent sulphite liquor involved. In the results of the Atterberg limits tests there is no consistent difference between decrease in plastic limit and increase in liquid limit, the increased plasticity index can not be attributed to either lubrication or viscosity changes alone, but must be considered as a combination of both effects (table VII).

Effect of molasses. The results also indicate that molasses had the greatest effect on the plasticity index of the mixture. Since significant changes were not noted in the plastic limits, but marked increases were noted in the liquid limits, the increased range of plasticity is attributed to higher viscosity because of the presence of molasses.

CONCLUSIONS

Conclusions are based on the use of additives of Peladow calcium chloride pellets, Sterling FC and CC salts, Toranil A, lignin liquor spent sulphite liquors, and a 79.5 Brix molasses with a single soil-aggregate surface course mix.

1. Using standard Proctor compactive effort the value of maximum density is increased by all of the additives. There is an inverse relationship between maximum dry density and optimum moisture content when the additives are used. Density is sensitive to the amount of additive in chloride stabilization.

2. Calcium chloride is the most effective agent for densification. In order of decreasing effectiveness the other additives evaluate as Sterling CC salt, Sterling FC salt, lignin liquor, Toranil A, and molasses.

3. Strength of the soil-aggregate mix can be improved by any of the additives. Immersed strength with optimum amount of additives are approximately equal for all additives except molasses. Molasses is subject to bacterial action and only improves strength about half as much as the other additives.

4. Calcium chloride is the most effective of the additives for moisture retention. Lignosulfonates and molasses have moderate effects, while rock salt is relatively ineffective.

5. Chlorides have little effect on the plastic properties of the mix; lignosulfonates and molasses raise the plasticity index.

RECOMMENDATIONS

Recommendations based on the results of this study are:

1. That additional studies of the effect of these additives be initiated to provide a basis for comparison applicable to other soils.

2. That the effects of the additives on moisture retention be investigated in a controlled humidity room to permit immediate comparison of results.

3. That curing of specimens for CBR tests be conducted under controlled conditions of relative humidity and temperature to permit equitable comparison of results.

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SODIUM CHLORIDE STABILIZED ROADS IN IOWA

by

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(Highway Research Board Bulletin 282. 1960.)

ABSTRACT

Sodium chloride has been used as a secondary road stabilizer for a number of years and the performance of salt stabilized roads has been reported periodically. These reports have differed widely as to success, costs, maintenance methods, riding qualities and other items. The Iowa Engineering Experiment Station has undertaken a project to clarify and better understand the usage and mechanism of sodium chloride stabilization in this state.

The counties in Iowa which have existing salt stabilized roads were contacted and each county engineer was interviewed. This paper reports a summation of these interviews and gives the composition and dimensions of the salt stabilized roads as well as maintenance practices, present physical conditions of surfaces, effects of winter and comments of county engineers.

INTRODUCTION

Sodium chloride has been used in varying degrees as secondary road wearing surface stabilizers for many years. The successes or failures of this stabilizing agent have been reported periodically, but these reports differ widely as to degree of success, maintenance requirements, costs, riding qualities, and other items. County engineers in Iowa have discussed sodium chloride stabilization without reaching any general conclusion as to effectiveness or economic value. However, each county engineer has proceeded according to his own convictions, which are generally based on experience and opinion. As a consequence, some counties use large amounts of NaCl and others use none.

The Iowa Engineering Experiment Station has undertaken a project designed to understand better the usage and mechanism of chemical stabilization in this state. The purpose of the project is to study the physical and chemical characteristics of chemically treated roadway surfaces, particularly those which have been treated either with sodium chloride or calcium chloride, or both, in the original construction of the roadway. The main objectives are

(1) the determination of the reasons for differences in results from a given method of treatment for a series of aggregate and soil mixtures and for different aggregates and soils;

(2) the evaluation of the benefits derived from chemical treatment of any given mixture of aggregate and soil and for different aggregates and soils.

In the initial phase of the study counties using salt treatment of secondary roads were located and the county engineer in each was interviewed. The results of the interviews are presented under the various headings. Counties using salt stabilization are shown on the accompanying state map (figure 1).

SODIUM CHLORIDE

Composition and Dimensions

Fourteen counties using salt for chemical stabilization were found to have a total of 524 miles of salt stabilized roads. Jones County has the least mileage with only 4 miles of salt stabilized roads, and Franklin and Linn counties are high with 106 miles. Some salt stabilized roads have been blacktopped and are included in total mileage.

Table I shows counties using salt and information pertinent to the material content of stabilized roads. Nearly all stabilized wearing courses are deep in the middle and feathered to the edge. The average depth of stabilized material varies from two to four inches, the width varies from 22 feet to 28 feet. Nine counties use soil-aggregate-salt mix, and four counties use salt and aggregate only. The amount of salt used is generally expressed on a ton per mile basis and varies from five to twenty tons per mile. Some engineers express salt contents as pounds of salt per ton of soil material, the amounts quoted on this basis varied from 8 to 12 pounds per ton. The quotations in Table I are expressed on a ton per mile basis by estimating the soil material used per mile

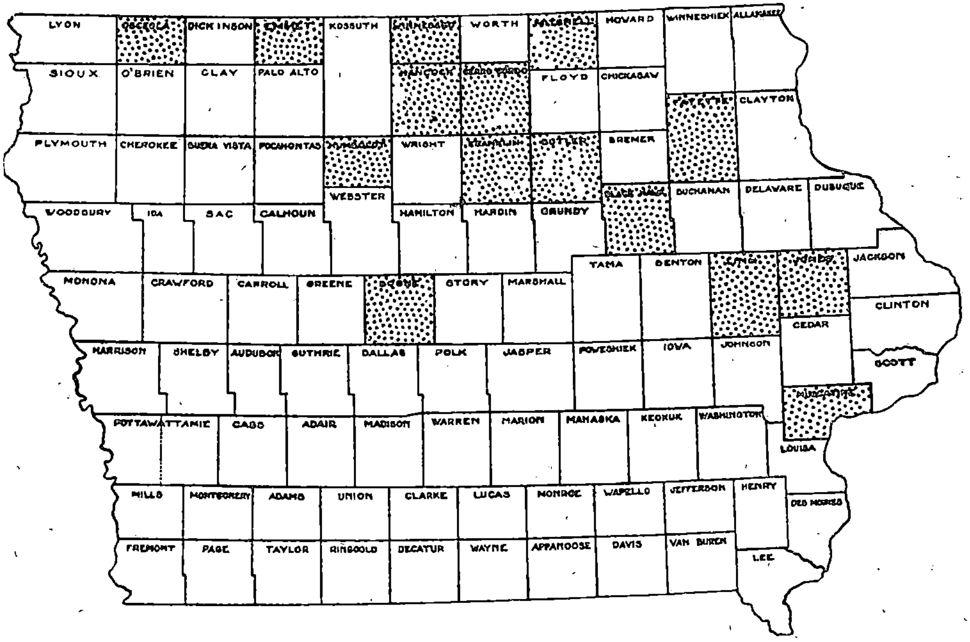

Fig. 1. Counties using NaCl stabilization.

and the density of the in-place material. Estimates comparable with 8 to 12 pounds per ton are twelve to nineteen tons per mile. Aggregates used were either pit run gravel or crushed stone. Glacial clay was used in all soil--aggregate roads. Seven counties include a surface application of about five tons of calcium chloride per mile per season to aid in surface moisture retention and dust palliation.

Mitchell County uses a mixture of 75% salt and 25% calcium chloride, initially applied at a rate of 4½ tons per mile. Subsequent applications bring the total chemical application up as high as 17 tons per mile. The primary purpose of chemical stabilization is to hold the material in place prior to blacktopping.

Construction Procedure and Costs

Most roads are constructed from materials mixed in the field either by blade or by a Seaman Pulvimixer. In general the gravel and soil materials are windrowed and bladed several times, salt is distributed and bladed in, water is added, the material is uniformly spread and compacted to 90 or 95% standard Proctor density. The clay is either pulverized before spreading or pulversized on the road bed before bladding. A few counties use plant mixed materials exclusively and some use plant mixed material occasionally. The plant mix method is preferred by many although it is considered somewhat more expensive. One man thought the plant mix was cheaper than a road mix. The general belief is that increased road quality compensates for any added expense.

Cost data proved to be rather scarce. Reports varied from 2500 to 4000 dollars

TABLE I. COUNTIES USING SODIUM CHLORIDE STABILIZATION AND DATA RELATIVE TO SURFACE COURSE COMPOSITION.

County	Miles of NaCl Stabilized Roads	Amount of original chemical treatment T/mi	Annual additional treatment with CaCl	Average thickness inches	Width feet	Aggregate	Binder
Black Hawk	38	6-10	———	2	22	Class A Crushed limestone	Glacial Till
Boone	4	20	4 T/mi	4	24	¾" Pit Run	Glacial Till
Butler	88	10	Some	3	24	1320 T⅝" gravel 600 T⅝" Rock	300 yd Glacial Clay
Cerro Gordo	25	5-9	———	3	24	Rock and Gravel	Glacial Clay
Fayette	16	16-20*	Some	3-5	26	2200 T ¾" Crushed Rock	About 1" from old surface
Franklin	106	9-10	Some	4	26	Gravel	Glacial Till
Hancock	50	16*	2 lb/sq yd	—	27	Pit Run	18-20% Glacial Till
Humboldt	25	13*		4	26	¾" Pit Run	20% Glacial Clay
Jones	4	20*	5T/mi	—	28	¾" Crushed Rock 40% dust	None
Linn	106	——	———	—	——	¾" Crushed Rock	None
Muscatine[1]	1	——	———	—	——	———————	—————
Mitchell	32	4½	———	—	——	¾" Crushed Rock	None
Osceola	11	9	———	3	26	Pit Run	None
Winnebago	19	15	2-3 times a year	4	27	Pit Run	12-16% Glacial Clay

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* Estimated from width, depth and assumed density. Originally expressed in lbs. salt per ton of material.

per mile of completed road. One engineer reported a cost of two dollars per ton of laid material, and another reported a cost of 450 dollars per mile for materials alone (gravel, clay and chemical).

Maintenance Practice

Blade maintenance following a rain was common in all counties, with most engineers expressing the opinion that a shallow cut is essential to good performance. A deep cut destroys the crust that has formed on the immediate wearing surface and thus allows undue traffic abrasion until a new crust is formed. The formation of a new crust may come too late or not at all, and the road then has a short life.

All county engineers seem to have a problem in educating the blade men. Most maintenance men have the idea that they are not accomplishing their purpose unless they carry a large roll of material in front of the blade. Local citizens are also guilty of this misconception and voice such an opinion in no uncertain terms. Harassing like this can cause improper blading, since maintenance men are prone to slide back into old ways under pressure.

Many of the counties use supplemental applications of calcium chloride for dust paliation and retention of the binding surficial clay and dust. Potholes are hand patched in some counties with mixtures of clay, gravel and calcium chloride. This seems to produce better results than filling the potholes with bladed material and depending on traffic compaction for stability. The first method is evidently only a temporary measure at best because the bladed material does not have sufficient binding material.

Most engineers are agreed that this type of road needs maintenance attention to ensure a good riding surface. Surprisingly, attention to maintaining crowns was mentioned very little. One engineer said that it is necessary to rebuild the crown every spring.

Present Physical Condition of Surfaces

County engineers reported everything from smooth to rough when asked to describe the present riding qualities of their salt stabilized roads. The descriptions have little meaning since they depend on the type of surface with which the salt road is compared. However, every county reports that salt roads exhibit a decided tendency to pit. The amount of pitting appears to depend on the traffic volume, maintenance methods and the amount of moisture in the road. The moisture content depends mostly on rainfall since salt is not deliquescent.

Engineers were asked to describe the dust conditions on the salt roads as either dust free, slightly dusty, dusty, or very dusty. None of the roads were described as dust free or very dusty, and in most cases they were called slightly dusty. Sodium chloride thus appears to have some value as a dust palliative.

Every engineer agreed that salt stabilized roads exhibit excellent aggregate retention. This is especially a favorable recommendation since traffic on these roads ranges up to 450 cars per day, with an average of about 200 cars per day.

Effects of Winter

Comments on the effects of winter freezing were favorable to salt roads. Most engineers said that treated roads have less tendency to form frost boils than untreated roads, and several county engineers have noticed a few adverse effects due to freezing. Butler and Franklin county engineers have noticed that treated roads do not soften during the usual spring break-up period.

A very interesting and unusual phenomenon was reported in Fayette county where both salt stabilization and calcium chloride stabilization are used. Calcium chloride roads were observed to ice over during winter, but salt roads either do not or have less tendency to ice over.

As previously mentioned, Mitchell county uses a mixture of salt and calcium chloride for stabilization of soil aggregate material. The county engineer has found that the calcium chloride content must be held down to minimize the effects of freezing and thawing.

COMMENTS

Many interesting comments concerning salt stabilized roads resulted during casual conversations and are listed by county as follows:

Black Hawk—Most everyone is well satisfied, and gravel is conserved.

Boone—Salt road gets hard when dry, road was slippery because of too much clay, addition of pea gravel corrected the slipperiness. Some pits developed. The road was rolled before blacktopping.

Butler—Three-fourths of the clay is effective, and one-fourth is lost in construction. Formerly added lime dust in maintenance, but this created a layer of different texture which tended to scale. Road bed was tested and found dry and hard in the spring. The road material broke up fairly easily when hit with a pick. Salt stabilization saves about 250 tons per mile per year on a heavily traveled road. A new road is built after an old road wears out. A road lasts on an average about five years.

Cerro Gordo—Roads were built in 1954 and 1957. No additional maintenance material either salt or calcium, has been applied since the roads were built.

Fayette—Most of the trouble develops on heavily traveled roads. Surface applications of calcium chloride to the mid 16 feet helps to hold the gravel. This type of road works best on roads carrying about 125 cars per day. Salt and calcium stabilization are responsible for large saving on both maintenance and gravel.

Franklin--Salt roads hold moisture longer than untreated roads. Salt roads also develop a surface crust and stay hard through the spring. Roads don't hold up too well when traffic exceeds 150 cars per day, tend to grind up. Stabilized roads are in better all-around condition than untreated roads, and therefore save gravel on adjacent roads by drawing traffic.

Hancock—Salt stabilized roads are used in a 2 to 3 stage blacktop construction. Bad spots appear and are corrected before blacktopping. Roads are in service for two to four years before the blacktop is applied. Find plant mix cheaper than road mix.

Humboldt—Sheepsfoot is not as satisfactory as a rubber tire roller. Tried chemical in solution but had spraybar trouble. Costs less to keep aggregate over a period of time and conserves aggregate.. Gravel requirements on all roads appear to be reduced due to better surfacing of blacktop over chemically stabilized material.

Jones—Trial road. Added 1500 tons of aggregate per mile to old road before chemical stabilization. Moisture added at quarry and by water wagon on the road. Constructed in one 4 inch lift.

Linn—Road work is contracted and chemical is pug mill mixed at quarry. Costs are quite accurate and vary from 2.19 to 2.98 dollars per ton.

Economics

Mr. O. W. Zack maintains records of roads in Butler county which indicate that an untreated gravel road initially requires 1250 tons of soil-aggregate per mile, followed by 250 tons of aggregate per mile per year for maintenance

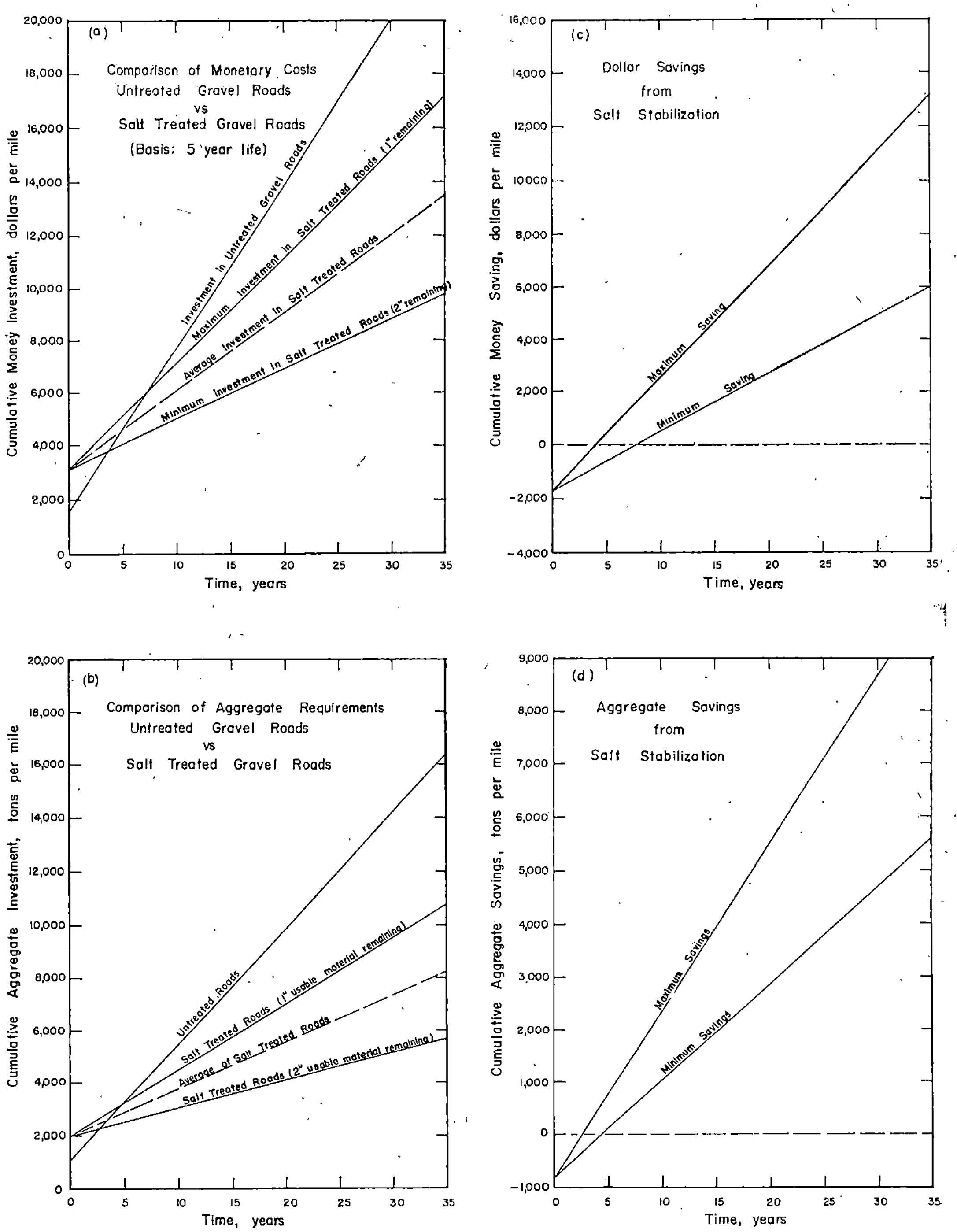

Fig. 2. Comparison of cumulative monetary and aggregate investments required to maintain untreated and salt treated secondary soil-aggregate roads in Butler County, Iowa.

and that such a road lasts about 4 years. Little or no gravel remains after the 4 year life of the road so that the road must be entirely rebuilt with new material.

Mr. Zack's records also indicate that salt treated roads constructed with 2200 tons of soil-aggregate-salt per mile last 5 to 7 years before they require rebuilding. Layers of 1 to 2 inches of material remain at this time but the material is rather loose and lacking in binder. The road must then be rebuilt but only a fraction of the original material requirement is needed.

These data have been used to compute cumulative road investments of money and aggregate for an economic comparison of both types of road construction in Butler County. The cumulative cost of each type of road is a stepwise function, yearly for the untreated road and every 5 to 7 years for the treated roads. The average cost per year has been used in both cases to give a continuous rather than a stepwise function. Costs for the treated road have been computed for a 5 year life and for both 1 and 2 inches of remaining material.

In a comparison of the cumulative investment for both types of road, the initial cost of a salt stabilized road is almost twice that of an untreated road; but the cost rate of an untreated road is higher than that for a treated road (figure 2). The net result is that after a period of 3½ to 7¼ years (depending on material retention in the treated roads) the same amount of money has been spent to have either type of road. Henceforth the treated road becomes considerably cheaper to maintain. The same trend is shown in the amount of aggregate used.

In the first few years an untreated road is cheaper and requires less aggregate than a treated road (figure 2). But if 500 miles of county roads were constructed with salt stabilized soil-aggregate (1½ inches retention) rather than untreated soil-aggregate, the county would save about $2,400,000 and a little over 2 million tons of aggregate over a period of about 20 years.

The savings in dollars over this 20 year period is very important to a county treasury and to each individual taxpayer. Perhaps of more importance is the savings in natural resources which is equivalent to a block of solid stone which would cover a 160 acre farm to a depth of 4 feet.

DISCUSSION

The summarized testimony of the county engineers interviewed shows general agreement that salt treatment improves the performance of soil-aggrgate roads in several ways, the most important being the long range conservation of natural resources and reduction in road improvements. Iowa's deposits of gravel and stone are being rapidly depleted and are entirely gone in some areas. Should aggregate consumption continue at the present rate the cost of secondary roads will rise still higher because extinction of gravel pits and stone quarries will necessitate long hauls in addition to high prices at the sources of supply. Taylor County in southern Iowa is now faced with this situation. Gravel mus tbe trucked in from outside the county and costs are over two dollars a ton at the pit.

Salt roads further improve the overall secondary road picture by presenting a smoother and less dusty riding surface than non-treated roads. Such surfaces attract traffic from adjacent roads and are thus responsible for still more savings in gravel and money by reducing the wear on these adjacent roads. Salt roads also retain a good riding surface longer than untreated roads and therefore require less blade work. Salt roads also show better resistance to winter and spring breakup.

Why do salt roads have all these advantages over non-treated soil-aggregate roads? A listing of reasons includes high density, low permeability due to clay to a number of reasons, none of which have been completely proven or disproven. A listing of reasons includes high density, low permeability due to clay expansion following leaching, moisture retention, lowered freezing point of water, recrystallization of salt, increased solubility of calcium carbonate, gel formation, flocculation and increased cohesiveness of clay due to sodium ions.

The Iowa Engineering Experiment Station now has a project underway which plans investigation of the physico-chemical phenomena of salt treated soil aggregate road materials and the effects of these phenomena on the performance of roads constructed of such material. The project is sponsored by the Iowa Highway Research Board and supported by funds from the Iowa State Highway Commission.

DENSITY—COMPACTIVE ENERGY—CALCIUM CHLORIDE CONTENT RELATIONSHIPS FOR AN IOWA DOLOMITE

by

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(Highway Research Board Proceedings 40. 1961.)

ABSTRACT

The effects of calcium chloride content and the amount of compactive effort on the density of a crushed limestone were determined by laboratory experiments. The data were analyzed on the basis of energy cost or savings due to the presence of calcium chloride. The results indicate that the expenditure of compactive energy to obtain a given density depends on the calcium chloride content. The results also show that there is an optimum calcium chloride content for a given density which will produce the density with a minimum compactive effort. The optimum calcium chloride content varies with the density.

INTRODUCTION

Soil stabilization today is based on the application of mechanical principles, either alone or in combination with the addition of chemicals or of materials whose principal properties are of a chemical nature. Whether the method of stabilization is purely mechanical or chemical, compaction is always used. However, the effects of additive chemicals or materials on the compaction characteristics are not well understood.

The applied mechanical principles leading to mechanical stability are gradation, binding properties of the fine material, and the compaction characteristics of the system. The addition of chemicals to soil material changes all of these. Gradation is changed, since the lower limit of particle size becomes the size of a molecule or a crystal of the chemical used. The binding properties are changed due to ion exchange and other surface chemical phenomena. The compaction characteristics are also changed due to intermolecular forces in the soil and a change in the liquid used from water to a solution. Pure water is seldom used except in the laboratory.

An investigation was undertaken to understand better the mechanism causing changes in the compaction characteristics of a crushed dolomite when calcium chloride is added. The basis of computation used in the analysis was somewhat different than is usually used in density studies. Ordinarily the basis is a cubic foot. Here the basis is weight, since the volume of a mold is a constant and the weight of material forced into a mold is variable. All energy values are expressed as energy per pound of compacted crushed rock plus calcium chloride or per pound of compacted crushed rock.

MATERIALS

The calcium chloride used was a commercial product known as **Peladow** and was supplied by the Dow Chemical Company. The material contains a minimum of 94.0 percent calcium chloride and less than one per cent water. The magnesium chloride content is less than 0.5 percent, and the alkali chloride content (e.g. sodium chloride) is less than 5.0 percent.

The crushed rock was obtained from Cook's quarry, about five miles northeast of Ames, Iowa. The rock is a buff to brown calcitic dolomite of Mississippian age and has physical properties similar to limestone. The material was crushed at the quarry to pass a ¾ inch screen (table I).

EXPERIMENTAL PROCEDURE AND DATA

Moisture density relations were determined for batches of dolomite containing 0, ½, 1, 1½ and 2 percent calcium chloride (based on the oven-dry weight of the rock) by the AASHO standard method, T-99-57. The compactive effort used was 20, 25 or 30 blows per layer, the amount being constant for any one study.

Initial studies indicated that the crushed rock suffered degradation when used repeatedly in the density determinations. This was reflected by data which gave erratic density correlations. Therefore each density determination was conducted with fresh material; material was discarded after being compacted once, and all data reported in this paper were derived from fresh material.

About 1000 pounds of dolomite, crushed to pass a ¾ inch screen, was separated into three size fractions. Each density determination was made with a 2000 gram sample composed of the appropriate quantities of the size fractions necessary to produce a mixture having the original mechanical analysis. This procedure was followed to reduce errors due to segregation of fine material (table I).

Batches were prepared from the indicated quantities of crushed rock. Appropriate amounts of calcium chloride solutions were mixed with the dolomite in a Hobart C-100 kitchen mixer until the material appeared to be uniform. A density test was then conducted according to AASHO designation T-99-57.

Moisture samples were taken from the molds and dried for 24 hours at 105 ± 2°C and were redried for an additional 24 hours to check the initial determination. All checks showed 24 hours drying time to be sufficient.

TABLE I. SIZE FRACTIONS OF CRUSHED DOLOMITE AND AMOUNTS USED FOR INDIVIDUAL BATCHES.

Passing Sieve	¾ inch	½ inch	No. 16	Totals
Retained on sieve	½ inch	No. 16		
Air-dry Wt., gms.	85,737	182,835	51,910	319,482
Moisture content, %	nil	0.1495	0.4762	0.1622
Oven-dry wt., gms.	85,737	182,562	51,664	319,693
Fraction, %	26.80	57.05	16.15	100.00
		Batch composition		
Oven-dry wt., gms.	536.00	1,141.00	323.00	2,000.00
Wt. of moisture, gms.	nil	1.71	1.54	3.25
Air-dry wt., gms.	536.00	1,142.71	324.54	2,003.25

Iso-optimum moistures and iso-density curves were plotted from the data as a function of the compactive energy and the calcium chloride content (figures 1, 2). The compactive energy values are expressed as foot pounds of potential energy per pound of dry material (rock + Cal_2), and the densities are expressed as pounds of dry material (rock + $CaCl_2$) per cubic foot. The data in figure 2B is based on a pound of rock only and excludes the $CaCl_2$ content. The optimum moisture values and calcium chloride contents are expressed as a percentage of the dry weight of the soil.

ANALYSIS OF DATA

An exact accounting of all material and energy that enters or leaves the system is made by computing all quantities on some arbitrary basis. Quantities may be added or subtracted if the basis establishes equivalent amounts of material or energy. Mass is used as the basis for computation in this study, since compactive energy is absorbed by the mass rather than by the volume. The energy is expended in the rearrangement of particles as a heat loss due to friction and as a force causing fluid flow.

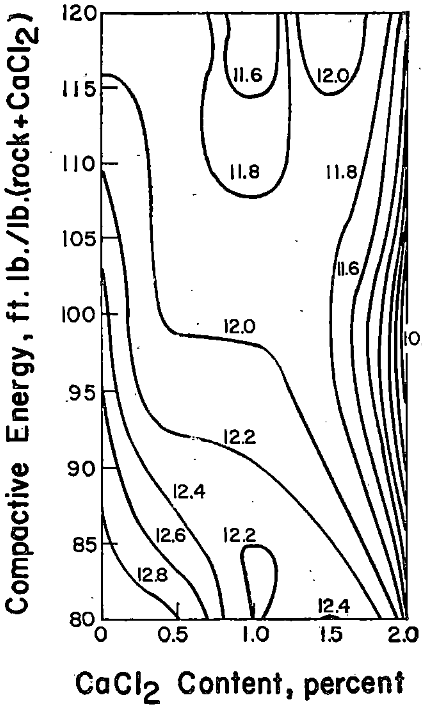

Fig. 1. Optimum moisture requirements for the various combinations of compactive energy and calcium chloride content.

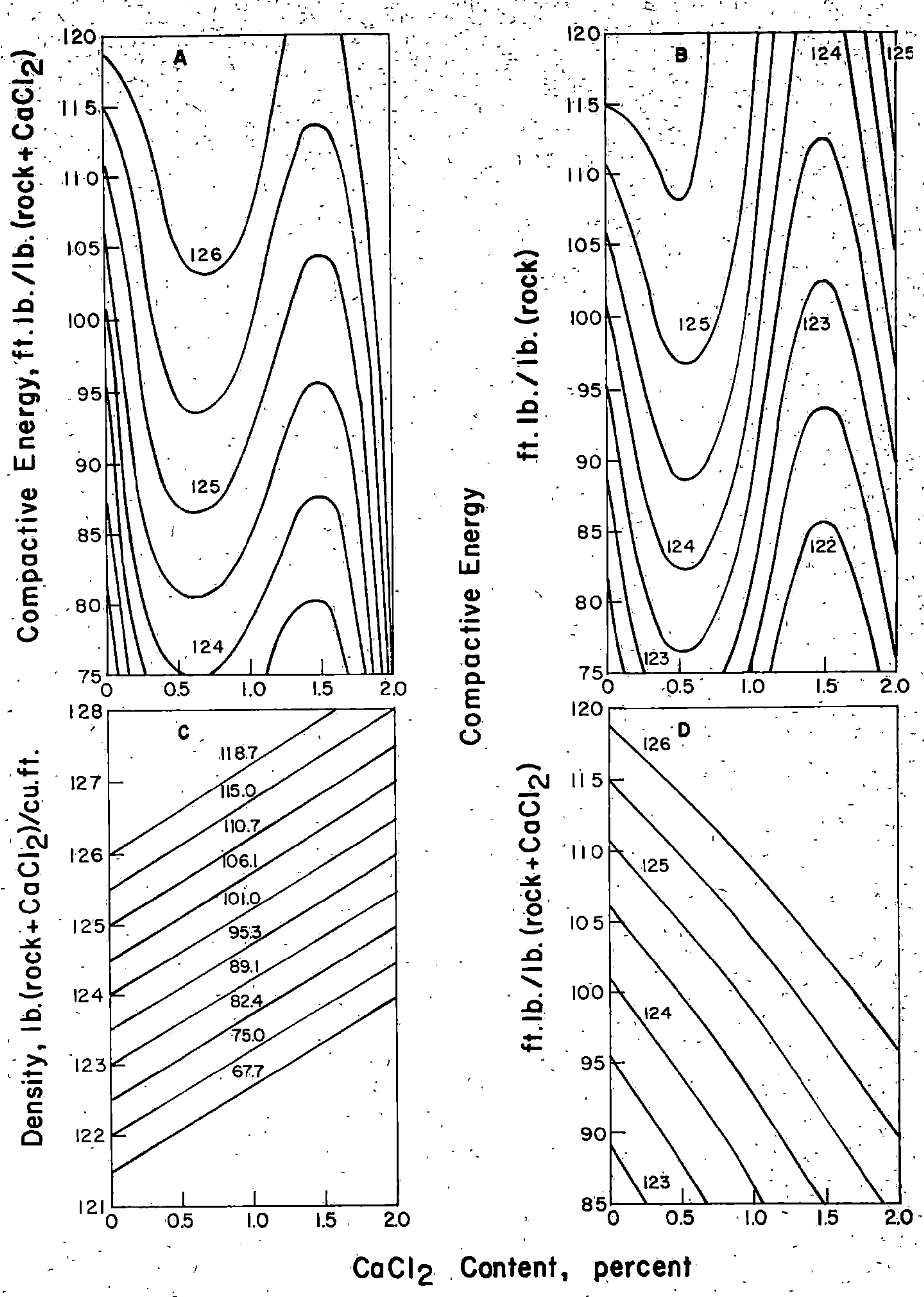

Fig. 2A. Iso-density curves as a function of compactive energy and calcium chloride content. Energy and density values are based on pounds of crushed rock plus calcium chloride.

B. Data from figure 2A plotted with energy and density values based on pounds of crushed rock plus calcium chloride.

C. Theoretical iso-energy curves showing the increase in density due to the physical presence of calcium chloride.

D. Curves from figure 2C replotted.

The use of mass as a basis for computations also allows easier and readily apparent comparison of values. For instance using 30 blows per layer and 3 layers in 1/30 of a cubic foot may produce a density of 120 pounds per cubic foot for one percentage of calcium chloride and 125 pounds per cubic foot for another. Using the cubic foot basis, these two densities result from the same compactive effort. On a pound basis one received 123 foot pounds per pound of material and the other 118 foot pounds per pound. This then represents a difference of 5 foot pounds of energy less per pound of material to attain a higher density, rather than the same compactive effort to attain a higher density.

The introduction of calcium chloride to the dolomite, water system affects the density that results from any given compactive effort. The variations in density are caused by the physical presence of the calcium chloride and by the chemical influence of the calcium chloride on the system. The amount of energy involved in the chemical influence can be indirectly found, since the total effect on energy requirements in known (figure 2A) and the physical effect can be calculated for any amount of calcum chloride added. The difference between these two therefore represents the amount of chemical influence.

Consider a cubic foot of dry compacted crushed rock (specific gravity 2.70) weighing 126 pounds per cubic foot. The volume of solid material is 0.750 cubic foot, and the volume of voids is 0.250 cubic foot. The weight of such a cubic foot of material can be increased through partially filling the voids by allowing a solution of calcium chloride to seep into the material and then evaporating the water. Theoretically the void space could be completely filled by hexahydrate calcium chloride, thereby increasing the density of 152.2 pounds per cubic foot, the increase in density being accomplished by the calcium chloride. A plot of density versus calcium chloride content for the above is a linear function. The maximum calcium chloride content theoretically possible is limited by the void space available, which is dictated by the initial density. The top limit for the above is 20.8 percent hexahydrate calcium chloride or 10.5 percent anhydrous calcium chloride.

Figure 2C shows a series of iso-density lines plotted from the energy value required to produce arbitrarily chosen densities for zero percent calcium chloride. Assuming that the presence of calcium chloride causes only a physical effect (any increase is due to added weight of calcium chloride in the voids) and shows no chemical influence, the lines should represent the densities attainable with the same compactive effort that was required to achieve the initial density (0% $CaCl_2$). The required compactive efforts for initial density may be obtained from figure 2A and are shown on figure 2C for each line. Values from figure 2C can be replotted as an iso-density chart with the same coordinates as used for figure 2A. This chart (figure 2D) represents the combinations of compactive energy and calcium chloride content theoretically necessary to achieve a given density *if and only if* the effect due to calcium chloride is purely physical. The differences in the amounts of energy, necessary to produce a given density with a given calcium chloride content (figure 2A, 2D) then represent the amount

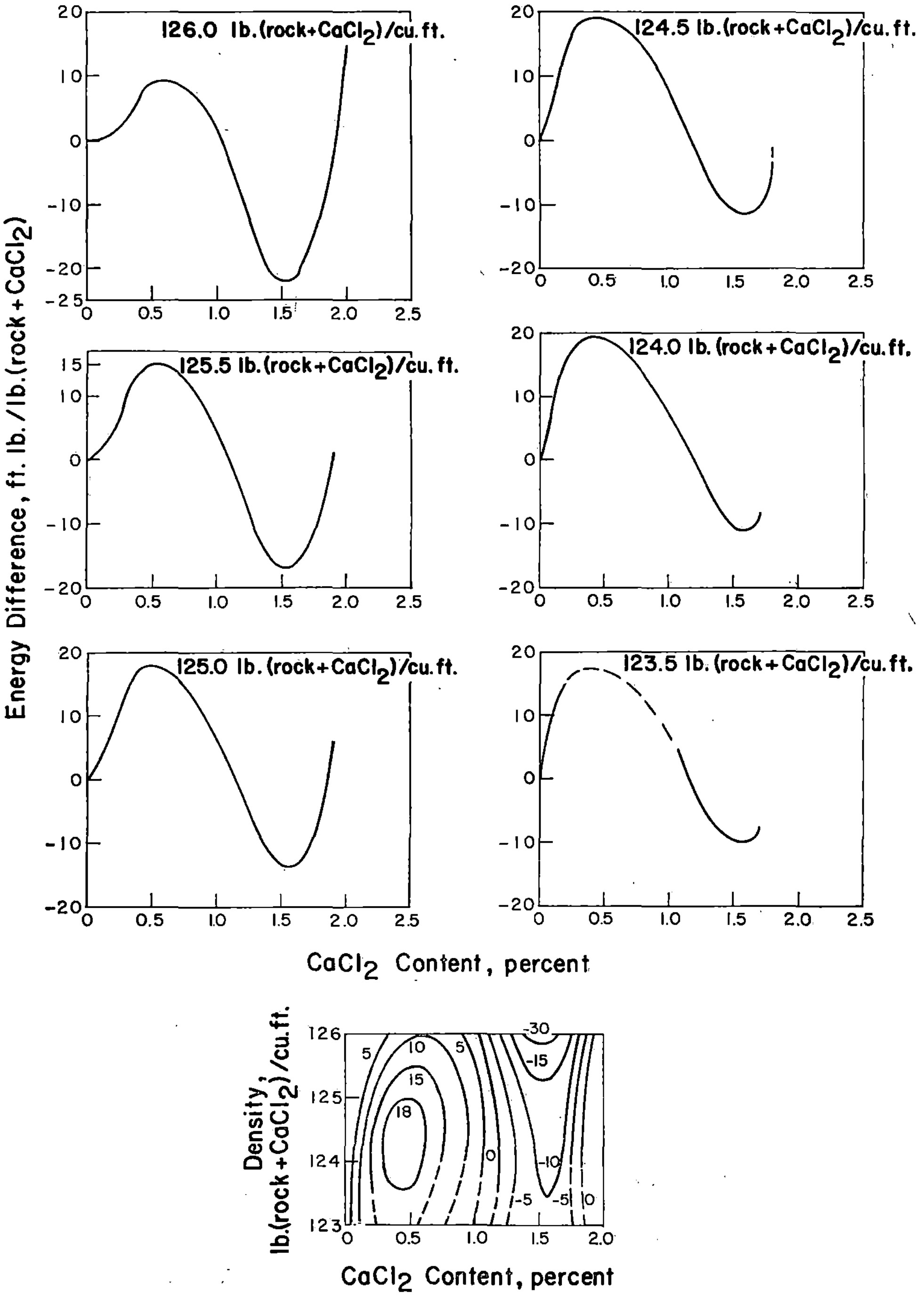

Fig. 3. Energy saving or cost due to the chemical influence of calcium chloride. The upper six graphs are for the indicated density and are combined in the lower iso-energy chart. Positive values indicate saving and negative values indicate cost.

of energy saved or the extra energy requirements due to the chemical effects of the calcium chloride (figure 3). The iso-energy cost-saving chart was drawn from the upper six graphs.

The minima near 0.5 percent $CaCl_2$ show that to achieve a specific density with a minimum expenditure of compactive effort, the amount of $CaCl_2$ required varies with the specified density (figure 2A). This does not imply that a combination of compactive effort and $CaCl_2$ content chosen from these minima will be the most economical combination.

Economic analysis of the data is necessarily limited to a relative status by the lack of compaction cost data. Such an analysis can be made from figure 2D by using a pound of compacted crushed rock for a basis as follows:

Let E = ft lb per lb rock
C = lb $CaCl_2$ per 100 lb rock
A = cost per lb $CaCl_2$
B = cost per ft lb energy

The total cost due to compaction needs and the inclusion of calcium chloride is

$$\text{Cost} = BE + (AC/100) \qquad (1)$$

Since B is unknown

$$\text{Let } R = A/100B \qquad (2)$$

Substitute equation (2) in equation (1) and the total cost becomes

$$\text{Cost} = B\,(E + RC) \qquad (3)$$

By rearranging equation (3) the total costs are expressed as relative costs

$$\text{Relative costs} = \frac{\text{cost}}{B} = E + RC \qquad (4)$$

Equation (4) relates the variables through the relative ratio R which may be assigned any arbitrary value for the purpose of study. Values of E and C must be read from Figure 2B to be comensurate. Curves of equation (4) using data from Figure 2B are shown in Figure 4 with the arbitrary values of R indicated for each curve.

DISCUSSION

The iso-density curves (figure 2A) show that the compacted density of the dolomite-calcium chloride system depends on the amount of compactive energy expended and on the amount of calcium chloride in the system. The lowest densities result from the lowest expended energy and the lowest amount of $CaCl_2$; the highest densities result from the highest values of energy and $CaCl_2$ within the ranges studied. Between these limits are maxima and minima in the family of curves. These maxima and minima are interesting in that they reflect the chemical influence of the $CaCl_2$.

The curves also indicate that the statement "less compactive effort is required to obtain a required density when calcium chloride is incorporated in the mix" does not hold true for all values of $CaCl_2$ content. The statement is certainly upheld by the data between 0 and 1.0 percent, but the curves for 125.5 and 126.0 pcf near 1.5 percent show that the same or more effort is required than

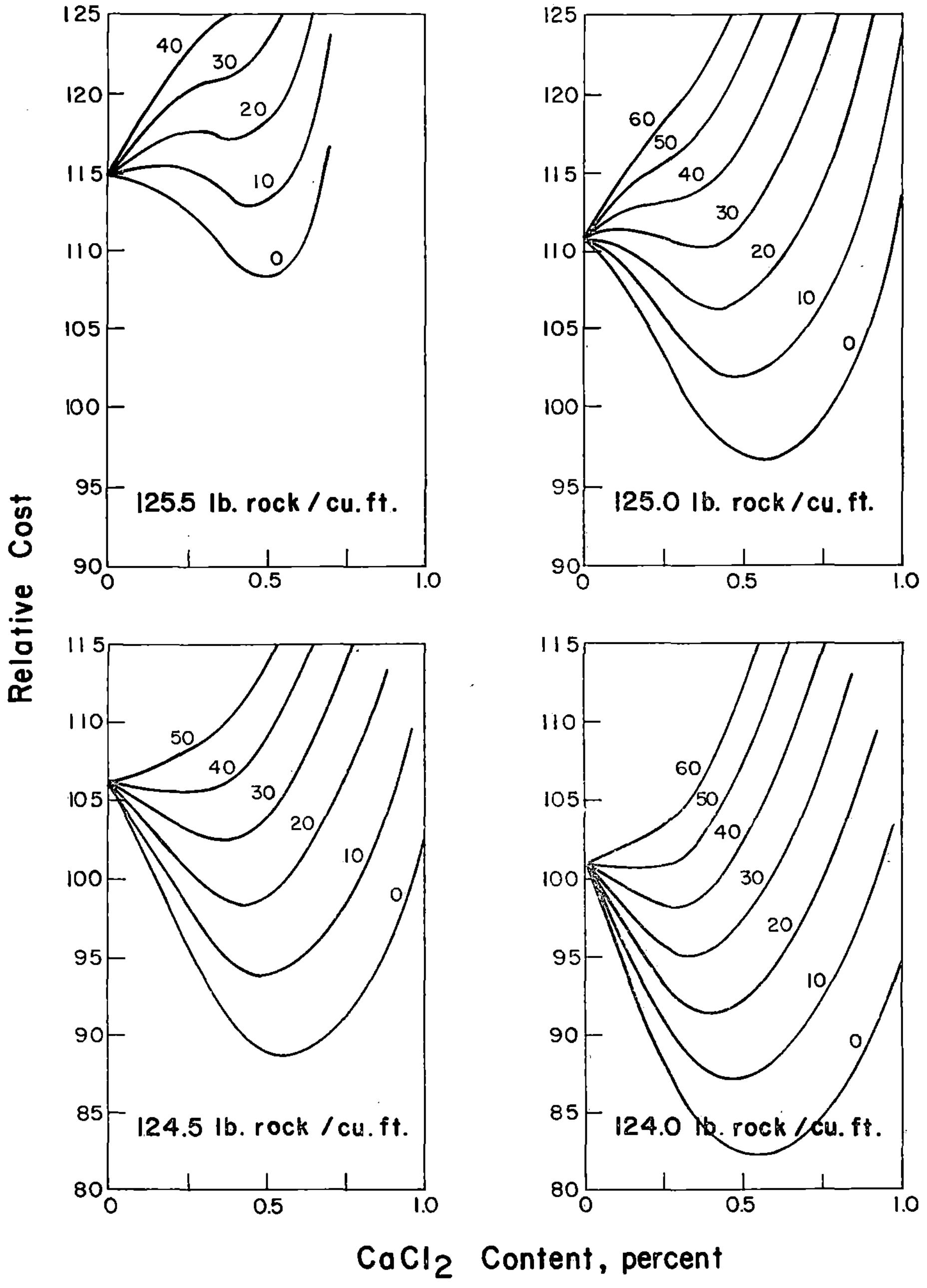

Fig. 4. Curves showing relative cost as a function of the calcium chloride content for the density listed. The number identifying each line is the ratio of unit cost per pound of calcium chloride to the unit cost per foot pound of compactive energy.

at zero percent. However, 1.5 percent is generally out of the economic range and would therefore seldom be used.

The changes in energy requirements to achieve a given density are caused by the physical presence and the chemical influence of th $CaCl_2$. The degree of change depends on the amount of $CaCl_2$ contained in the system. The $CaCl_2$ reduces the energy requirements in a near linear relationship with the amount of $CaCl_2$ (figure 2D). The changes in energy requirements due to the chemical influence are of a more complex nature and vary greatly with the amount of $CaCl_2$ and with the density of the system.

Proper analysis of the curves of the variations in energy requirements due to the chemical influence requires a knowledge of the chemical properties of the $CaCl_2$ solutions that are present during compaction (figure 3). These properties vary with the molar concentrations of $CaCl_2$. Molar concentrations may be calculated from the optimum moisture data (figure 1). Viscosity, surface tension, lubrication, zeta potential, streaming potential and crystallization are properties or phenomena that are dependent on molar concentrations.

The molar concentration in the ranges studied is nearly a linear function of the $CaCl_2$ content because the molarity is more affected by the amount of $CaCl_2$ than by the amount of water. The optimum moisture contents vary only over the limited range of 12.9 to 10.6 percents whereas the $CaCl_2$ content varies from 0 to 2.0 percent.

Since the viscosity and the surface tension of the solutions are both linear functions of the molarity, the resistance to compaction should increase linearly with $CaCl_2$ content, as demonstrated by investigators who have made studies of fluid flow through porous media. The compaction of soil materials is essentially a problem of the forces involved in the flow of fluids through or from porous media since in the process of rearrangement of particles, the fluid (water or a solution) must move relative to the solid particles. Plots of energy versus density, at constant $CaCl_2$ content, show that the energy requirements increase with density and that slopes of the energy-density lines also increase as the $CaCl_2$ content increases.

The quality or the amount of lubrication is a property that has not been determined for any liquid so far as is known. Zeta potential and streaming potentials are probably of little influence in the present system, since clay minerals and ion exchange are virtually absent.

Preferential absorption of water by the dolomite, which would increase the concentration of the solution, could cause crystallization before compaction was completed if enough water were absorbed to cause the solution to become supersaturated. The hexahydrate would crystallize and the crystals would increase the resistance to compaction somewhat.

The foregoing discussion points out various factors that are primarily dependent on the molarity of the $CaCl_2$ solutions involved. The total resistance to compaction is in turn a summation of the various contributions of these factors. If all factors were clearly understood, their various contributions could be separated and a summation of these should produce favorable cost curves (figure 4). This analysis is limited by ignorance of these factors, but this discussion may stimulate further investigation of this problem.

A question often posed is whether or not the added cost due to the inclusion of $CaCl_2$ is offset by a reduced cost of compaction. The relative cost curves indicate the added cost is lowered, provided the ratio of the unit cost of $CaCl_2$ to the unit cost of compactive energy is low. A value of R exists, for each density, above which the inclusion of $CaCl_2$ is not economical. This value of R may be defined as a permissible cost ratio, R_p. The value R_p is then the maximum value of R that will permit the economical use of $CaCl_2$. The curves show that R_p decreases with an increase in density from 50 for 124.0 cu/ft to about 12 for 125.5 lb/cu ft. The economical use of $CaCl_2$ is therefore dictated by the density desired.

A general statement as to whether or not the cost of $CaCl_2$ is offset by reduced compaction costs can not be made until data for many other materials become available and until a permissible cost ratio is determined. Finally, laboratory data and field data should be correlated to form a realistic basis for conclusions.

EVALUATION OF GYPSUM AS A SOIL STABILIZING AGENT

by

D. T. Davidson, Professor, Civil Engineering

Manuel Mateos, Research Associate

(Progress Report. 1960.)

Recent information released by the Soils Laboratory of Cornell University states that gypsum treated soils do not expand when placed in a freezer[1]. Another source of information indicates that 1.5 percent gypsum in a mixture of 90 parts of sand and 10 parts of lime is the optimum amount of gypsum for maximum strength and that gypsum improves the resistance of sand-lime mixes to repeated freezing[2].

Although some unpublished research done at the Soil Research Laboratory of the Iowa State University Engineering Experiment Station had shown gypsum to be a poor soil stabilizer, much inferior for this purpose than other commonly used products such as lime, lime-fly ash, cement, etc., the promising claims of the Cornell investigators were responsible for another investigation, presented here, of the effect of gypsum on the stability of compacted soil.

MATERIALS

A friable loess, mostly silt-size, was used as the soil. Compacted specimens of this soil containing no chemical additive have very low resistance to alternate freezing and thawing cycles exhibiting a large amount of heave after only one cycle. The lime used was dolomitic monohydrate (Type N), brand-name Kemidol, produced by U. S. Gypsum Company. The gypsum was reagent calcium sulfate ($CaSO_4 \cdot 2H_2O$).

METHODS

The soil lime, soil gypsum and soil lime gypsum mixtures evaluated (table I) were mixed with the optimum amount of water for maximum density, and cylindrical 2 inch by 2 inch specimens were molded to near standard Proctor density (ASTM D 698-58T).

Five specimens of each mixture were cured for 28 days in a moist room at 70±3°F, and then were immersed in distilled water for 24 hours. After 24 hours immersion three specimens of each mixture were tested for unconfined compressive strength; the fourth specimen, designated the control specimen, was left immersed for 10 more days; and the fifth specimen, designated the freeze-thaw specimen, was exposed alternately to temperatures of 20±2°F (16 hours) and 77±4°F (8 hours) for 10 cycles, each cycle lasting 24 hours. A vacuum flask

TABLE I. TEST RESULTS

Mix No.	Materials, %			As molded dry density, psi	Strength, psi			R_f, %
	Soil	Lime	Gypsum		28-day cured, 1-day immersed	p_f	p_c	
1	98	0	2	104.3	0	ND[*]	0	—
2	96	0	4	104.8	0	ND	0	—
3	94	0	6	103.5	0	ND	0	—
4	98	2	0	101.0	169	Failed @ 7 cycles	187	—
5	96	4	0	101.0	350	Failed @ 8 cycles	356	—
6	94	6	0	99.9	348	343	396	87
7	98	1	1	101.5	Partially disintegrated	ND	ND	—
8	96	2	2	99.9	139	Failed @ 4 cycles	122	—
9	94	3	3	99.3	256	Failed @ 7 cycles	254	—

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[*] Not determined because specimens failed during immersion.

specimen container was used to cause freezing to occur from the top down and to supply unfrozen water, kept at 35±2°F by a light bulb, to the bottom of the specimen throughout the freeze-thaw test. After these addiional treatments, the unconfined compressive strength of the freeze-thaw specimen (p_f) and the control specimen (p_c) were determined. These values were used to evaluate the durability of the stabilized soils. The Index of Resistance to the effect of freezing (R_f) was calculated from the formula:

$$R_f = \frac{100\,p_f}{p_c}\ (\%).$$

INVESTIGATION

Presentation of Results

Soil specimens treated with up to 6 percent gypsum failed completely during the 24-hour immersion period (table I). Consequently it was not possible to submit them to freezing and thawing.

Specimens treated with lime and gypsum in a 50:50 ratio showed better stability than those treated with gypsum alone. The mixture with 2 percent combined additives failed during immersion, but those with 4 and 6 percent withstood immersion and a number of freeze-thaw cycles.

Lime treated mixtures were better than those with gypsum alone or those with gypsum and lime. All the lime mixtures withstood immersion even for such a low lime content as 2 percent. Mixtures wtih 2 and 4 percent lime failed after 7 and 8 freeze-thaw cycles, respectively, which is good performance with such small amounts of lime. Six percent lime gave very good strengths, over 300 psi after any treatment, withstood all 10 freeze-thaw cycles, and showed an Index of Resistance of 87 percent.

Discussion

An unconfined compressive strength of 300 psi after 10 cycles of freeze and thaw in the Iowa freeze-thaw test is considered indicative of satisfactory resistance to frost action. Addition of 6 percent dolomitic monohydrate lime to the silty soil gave a strength of well over 300 psi after immersion in water or freezing and thawing to specimens cured for 28 days. Another criterion of satisfactory freeze-thaw resistance is an Index of Resistance of at least 80 percent. The mixture with 6 percent lime had an Index of Resistance of 87 percent, very satisfactory for base courses of roads in Iowa. The use of gypsum or lime gypsum as additives in the silty soil did not produce satisfactory freeze-thaw resistance for base courses of roads in Iowa.

It is strongly felt that stabilized soils used in pavement base courses in climates of the severity of Iowa should pass the above requirements. Otherwise base course and pavement stability may be impaired. It is of course possible that gypsum treated silty soils subjected to a less severe freeze-thaw or freezing test may stand up; however, it is likely that a much smaller lime treatment of equal or less cost would produce equal or better results.

Unless otherwise demonstrated, the use of gypsum does not appear to be promising for counteracting the destructive freezing and thawing effects in silty soils to be used in pavement base courses.

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