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Stabilization of a Calcareous Loess With Calcium Lignosulfonate and Aluminum Sulfate

T. DEMIREL¹ and DONALD T. DAVIDSON²

Abstract. This paper describes a promising method of stabilizing calcareous Wisconsin-age loess with a combination treatment of spent sulfite liquor and aluminum sulfate. The stabilization is thought to be due to formation of water-insoluble basic aluminum lignosulfonate in the compacted soil.

Because of its water solubility and the consequent need for its periodic replenishment, 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. Attempts have been made to reduce its water solubility by physical or chemical means. Selection of a proper soil gradation and compaction of treated soils to suitable densities to reduce leaching by water have been the principal physical methods studied (3, 19, 32, 38, 43). Chemical methods have consisted 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 which have been extensively studied for insolubilizing spent sulfite liquor for soil stabilization.

Ca-lignosulfonate, the main constituent of spent sulfite 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-sulfate 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

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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. 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 on the basis of the effect of basic aluminum lignosulfonate micelles on the surface tension of water. These micelles reduce the surface 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.

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. Sampling location and properties of the sample are given in Table 1.

Chemicals. Properties of the spent sulfite liquor sample used are given in Table 2. It will be referred to as Ca-lignosulfonate, the principal constituent of the solids fraction.

The aluminum sulfate sample ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) was chemically pure grade. It will be referred to as Al-sulfate.

METHOD OF INVESTIGATION

Mixing. Three orders of mixing chemicals with the soil were experimented with. In the first, a calculated amount of spent sulfite liquor 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 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

Table 1
Description and Properties of the Loess Sample (Lab No. 20-2-VII)

Geological description:	Wisconsin age loess, oxidized; thickness over 100 ft.	Classification: Textural ^e Engineering (AASHO)	Silty clay loam A-4(8)
Location:	Harrison Co. S. W. Iowa	Max. dry density, pcf	107.5
Soil series:	Hamburg	Optimum moist, %	18.0
Horizon:	C		
Sampling depth, ft.	39-40		
Textural composition, %			
Gravel (>2 mm)	0		
Sand (2-0.074 mm)	0.4		
Silt (74-5 μ)	80.0		
Clay (<5 μ)	19.6		
Colloids (<1 μ)	14.5		
Predominant clay mineral ^a :	Montmorillonite		
Chemical properties:			
Cat. ex. cap., m.e./gm ^b	13.4		
Carbonates, ^b by versenate method ^c	10.2		
Fizzing when treated with N.HCl	Strong		
pH	8.7		
Organic matter, ^b %	0.2		
Physical properties ^d :			
Liquid limit, %	30.8		
Plastic limit, %	24.6		
Plasticity index	6.2		
Shrinkage limit, %	22.3		

^aBy X-ray diffraction analysis

^bFor fraction passing No. 10 sieve

^cIncludes all extractable calcium

^dFor fraction passing No. 40 sieve

^eFrom triangular chart developed by U. S. Bureau of Public Roads, but 0.074 mm was used as the lower limit of the sand fraction

Table 2
Properties of Spent Sulfite Liquor^a

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 $\frac{60^\circ \text{ F}}{60^\circ \text{ F}}$	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

^aFrom the data supplied by the manufacturer, Lake States Yeast Corporation, Rhinelander, Wisconsin

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 to be due to chemical reactions taking place.

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.

Table 3 shows 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.

Molding. Immediately after mixing, six specimens from each mixture were molded into cylinders by means of a drop-hammer molding apparatus developed by Davidson and Chu (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-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 per cent. 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). After curing, heights and weights of specimens were again measured. 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. After being taken from the water each specimen was weighed, measured, and tested for unconfined compressive strength.

Table 3
Effect of Mixing Order of Additives on Strength Obtained by Treating the Loess With 6%
Ca-lignosulfonate and 5% Al-sulfate

Mixing order		Moisture at molding, %	Dry density at molding moisture, pcf	Average immersed strength, ^a psi	Average unimmersed strength, ^b psi	Average relative humidity during curing period, %
First additive	Second additive					
Ca-ligno- sulfonate	Al-sulfate	19.1	103.4	122	556	70
Al-sulfate	Ca-lignosul- fonate	19.0	104.4	124	498	70
Mixture of the two additives	—	19.0	101.1	99	534	70

^aAir cured at room temperature 7 days, immersed in distilled water 1 day

^bAir cured at room temperature 7 days

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 are referred to as "unimmersed strengths" while 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. Linear expansion upon immersion expressed as percentage of air dried sample height was calculated from the height measurements taken after seven days drying and after 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 having the same compositions but molded at different times and cured in atmospheres having different relative humidities showed considerable variation in strengths as illustrated in Table 4.

Freeze-thaw test. Six specimens from a selected mixture³ and six specimens from untreated friable loess were molded at optimum

³6% Ca-lignosulfonate, 5% Al-sulfate, 19% water.

Table 4
 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 desiccator solutions, %	Relative humidity \div 35	Moisture retention after 7- day cur- ing, %	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

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 subjected to fifteen days immersion in distilled water. The remaining specimens were given one day immersion in distilled water followed by 14 cycles of alternate freezing and thawing suspended in holders in thermos bottles containing enough water at $8 \pm 2^\circ$ 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 $-5 \pm 1^\circ$ C. and 8 hours thawing at $25 \pm 1^\circ$ C. At the completion of freeze-thaw cycles and immersion, all specimens were weighed, measured for height and tested for unconfined compressive strength.

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 per cent, and those of Al-sulfate were 0, 1, 3, and 5 per cent, 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 per cent (1). An average dry density was calculated for each set by the method described 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 described in the preceding section. For each set, average unimmersed and immersed strengths were calculated. Individual unconfined compressive strengths were maintained within 10 per cent 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 5). 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-lignosulfonate contents and against Ca-lignosulfonate contents at constant Al-sulfate contents. From these curves con-

Table 5
Effect of Ca-lignosulfonate and Al-sulfate on Strength and Related Properties of the Loess

Ca-ligno- sulfonate, %	Al- sulfate, %	Optimum moisture, %	Maximum dry density, pcf	Unimmersed strength, psi	Immersed strength, psi	Moisture retention, %	Linear expansion upon im- mersion, %	Water absorption upon im- mersion, %
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 ^a 21.1 ^b	101 ^c 101.0 ^d	525 ^e	155 ^e			
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 ^a 20.1 ^b	102 ^c 102.3 ^d	550 ^e	180 ^e			
6	7	20.0 ^a 21.2 ^b	101 ^c 101.2 ^d	550 ^e	205 ^e			
6	8	20.5 ^a 20.5 ^b	101 ^c 102.2 ^d	570 ^e	260 ^e			
8	0	14.5	111.9	680	Slaked	6.4		
8	3	17.5 ^a 17.3 ^b	104 ^c 104.4 ^d	505 ^e	70 ^e			
8	5	19.1	103.0	520	105	7.9	0.6	13
8	6	19.1 ^a 19.2 ^b	102 ^c 101.5 ^d	480 ^e	107 ^e			
8	8	19.5 ^a 19.5 ^b	97.3	442	83 ^e			

^aObtained from Figure 1

^bDetermined at the time of molding

^cObtained from Figure 2

^dActual determined density

^eInterpolated from Figure 5

four graphs are constructed in Figure 1 for "iso-optimum moisture contents." In the same manner curves are plotted to relate maximum dry density, unimmersed strength, and immersed strength to composition. These contour graphs are shown in Figures 2, 3 and 4.

To check these graphs, optimum moisture contents for several compositions were estimated by use of Figure 1, 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 and Table 5. 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 prevailing during the second period of investigation. In the first period of the investigation the average relative humidity was 65 per cent, whereas in the second period it was 36 per cent.

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 in Figure 5. These curves were used to convert the results of the latter period to the results obtained during the first period.

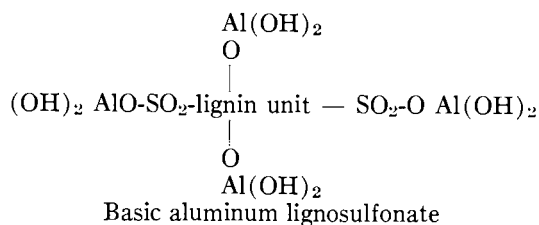
Examination of maximum dry density contours of Figure 2 shows that for a fixed amount of Al-sulfate, addition of Ca-lignosulfonate up to a certain percentage results in a decrease in maximum dry density. After this point is reached, further addition of Ca-lignosulfonate causes an increase in density. 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 of Ca-lignosulfonate furnishes lubrication and possibly by its dispersive properties breaks the agglomerates and causes an increase in density. Further examination of Figure 2 shows that the Ca-lignosulfonate-Al-sulfate relationship for maximum density which corresponds to complete reaction is a linear relationship with the equation

$$\begin{aligned} \% \text{ Ca-lignosulfonate} &= 0.7 \% \text{ Al-sulfate} \\ \text{or } \frac{\% \text{ Ca-lignosulfonate}}{\% \text{ Al-sulfate}} &= 0.7 \end{aligned}$$

Conversion to molar quantities gives:

$$\begin{aligned} \frac{(1000) (\text{Moles of Ca-lignosulfonate})}{(666) (\text{Moles of Al-sulfate})} &= 0.7 \\ \frac{\text{Moles of Ca-lignosulfonate}}{\text{Moles of Al-sulfate}} &= \frac{666}{1000} \cdot 0.7 = \frac{466.2}{1000} = 0.466 \approx 0.5 \end{aligned}$$

Therefore each mole of Al-sulfate combines with about one-half mole of Ca-lignosulfonate. Assuming a Ca-lignosulfonate unit has two sulfonate groups and two phenolic hydroxyl groups⁴ (6), a basic aluminum lignosulfonate having the following composition may form:



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 to the mixture, a sol forms. It is believed that micelles of this sol are 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 are absorbed 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). On the other hand, on the basis of the presence of surface charges, the predominance of hydrophobic radicals, and viscosity characteristics of the sol, it is believed that 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.

⁴It has been established that each lignin building unit contains at least one phenolic hydroxyl group.

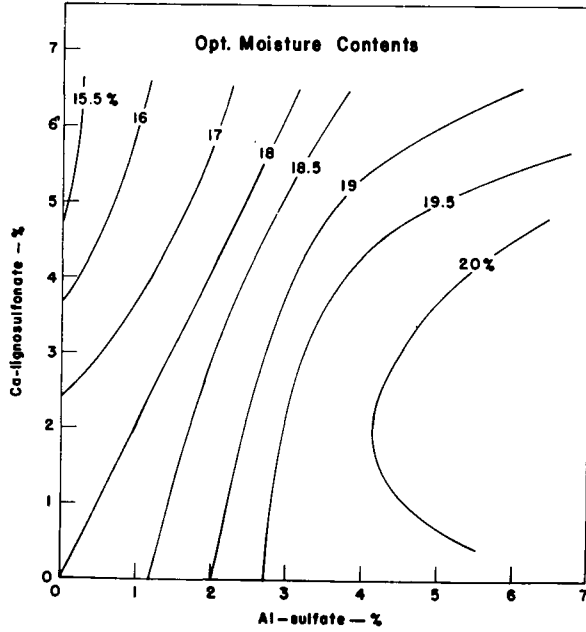


Figure 1. Mixture composition—optimum moisture relationship.

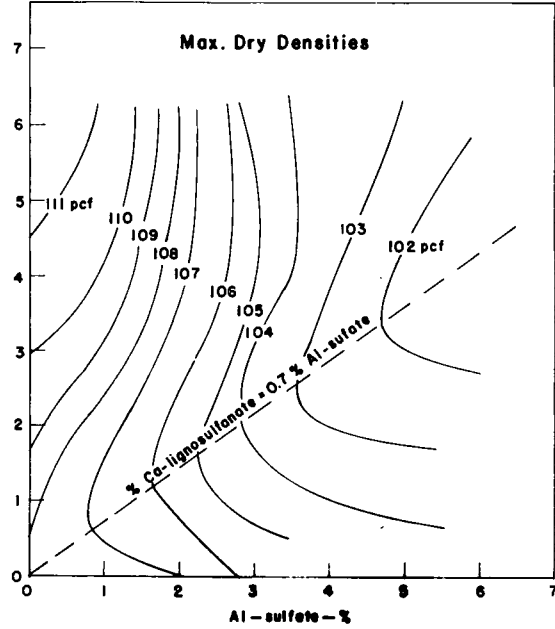


Figure 2. Mixture composition—maximum dry density relationship.

As explained by Nicholls and Davidson (31), 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. On the other hand, 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, variations in the solid-liquid interfacial tension are unpredictable with present knowledge, and it is doubtful that a sound speculation can be made unless sufficient experimental data are available.

In the present study the solid-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, existence of a concentration gradient through the adsorbed phase is not given any consideration. Such a gradient would exist in the interface as demonstrated by Helmholtz or Stern models (30 p. 504), and also forms 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, which 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 the case of 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. On the other hand, upon partial evaporation of water 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 the case of 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. Upon partial evaporation

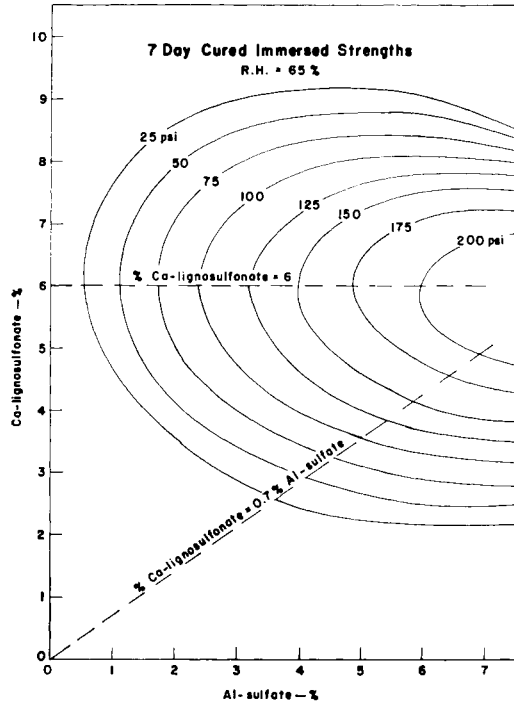


Figure 3. Mixture composition—maximum immersed strength relationship.

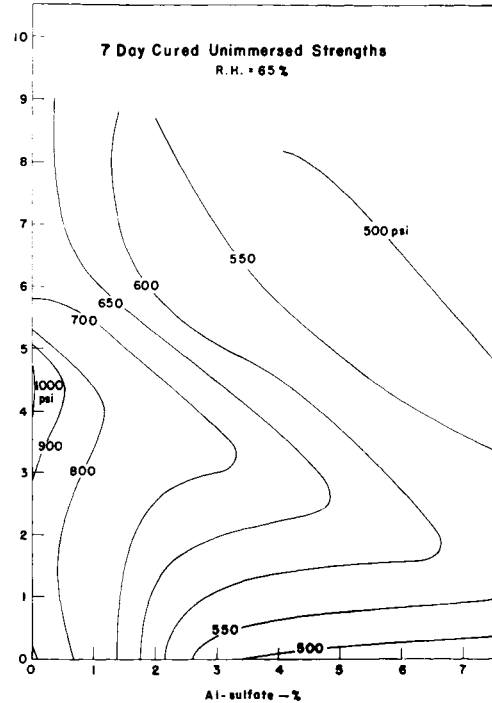


Figure 4. Mixture composition—maximum unimmersed strength relationship.

of water, surface tension of the liquid phase is affected in a direction which decreases strength whereas film thickness changes to increase the dry strength. A decrease in dry strength from the addition of chemicals is indicated in 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 5). 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 due to the fact that rush of water into pore spaces upon the sudden immersion 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. This fact was observed by Kardoush, Hoover, and Davidson (17) in studying the effects of large organic cations on soils. Oven-dried specimens which once had been waterproofed with a large organic cation slaked upon immersion in water, but when similar oven-dried specimens were stored in a humid atmosphere for a sufficient period of time waterproofing was restored (17 p. 740). This indicates the existence of an optimum range of moisture retention, which gives satisfactory liquid film thicknesses for adequate unimmersed and immersed strengths.

Moisture retention is a function of curing conditions; the effect of the curing condition on moisture retentions and consequently on strength characteristics can be seen from Figure 5. Table 4 shows the relative effect of the curing conditions on strengths. However, comparisons of strengths in Table 4 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. 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.

Examination of immersed strengths in Figure 3 shows that the 0.7 optimum Ca-lignosulfonate to Al-sulfate ratio does not correspond to maximum immersed strength. Instead, highest immersed strengths for any Al-sulfate content always occur with 6 per cent Ca-lignosulfonate. In Figure 3 this relationship is represented by the line:

$$\% \text{ Ca-lignosulfonate} = 6$$

Ca-lignosulfonate alone furnishes some waterproofing (38), due to the fact that it appreciably reduces surface tension of water, Table 2. 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 per cent, 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 per cent Ca-lignosulfonate at 0.7 optimum Ca-lignosulfonate to Al-sulfate ratio.

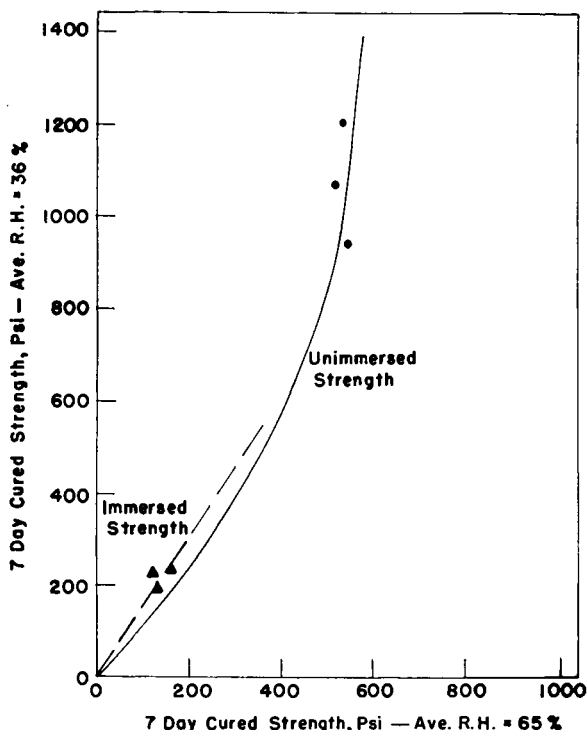


Figure 5. Effect of relative humidity on maximum unimmersed and immersed strengths of the loess treated with Ca-lignosulfonate and Al-sulfate.

Graphical solution of this is represented in Figure 3 by intersecting the lines:

$$\begin{aligned} \% \text{ Ca-lignosulfonate} &= 6 \quad \text{and} \\ \% \text{ Ca-lignosulfonate} &= 0.7 \times \% \text{ Al-sulfate.} \end{aligned}$$

Examination of the figure shows that the intersection is located at a point of highest strength contours, verifying this theory.

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 per cent spent sulfite liquor solids mainly composed of Ca-lignosulfonate. In the same study 4 per cent 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 ratio depends on the chemical reactions.

Examination of Figure 4 shows that nearly all unimmersed strengths are reduced by the addition of any combination of Ca-lignosulfonate and Al-sulfate. Under the conditions studied, the maximum unimmersed strength is only slightly higher than that of raw soil and is obtainable with about 4.5 per cent Ca-lignosulfonate and zero per cent Al-sulfate. It is believed that 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."

On the other hand, compacting cohesive soils above their optimum moisture contents may cause shear failure surfaces to develop, known as slickensides (40 p. 335).

Figure 6 shows that 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. On the other hand, 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 excess 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.

Six per cent Ca-lignosulfonate was selected, as it gave best immersed strengths (Figure 3).

The cost of spent sulfite liquor delivered to Ames, Iowa, is about 2.2 cents per pound of solid constituents. It is believed that this extremely high price for an essentially waste product is due to small scale usage and consequent restricted transportation facilities. Only about 3 to 5 per cent of sulfite liquor production has been put to commercial use. Undoubtedly a major cause for its high cost is the expense involved in the disposal of the remaining 95 per cent waste product. If it were not for this waste, the cost of the spent sulfite liquor might be considerably less than that of Portland cement, which costs about 1.0 cent per pound.

The cost of Al-sulfate is about 2.0 cents per pound.⁵ From a cost comparison the amount of Al-sulfate used should not exceed one-half of the amount of Portland cement requirement for the stabilization.

The engineering classification of the loess used in this study is A-4, and the cement requirement for an A-4 soil is about 12 per cent (34). Therefore the maximum percentage of Al-sulfate to be economically comparable with Portland cement is 6 per cent. If 5 per cent Al-sulfate is used, the 1 per cent saved can be replaced by an amount of spent sulfite liquor cost-wise equivalent to 2 per cent Portland cement. Since 6 per cent spent sulfite liquor solids gave best results, the cost of spent sulfite liquor based on its solid constituents should be less than one-third of the cost of Portland cement, or 0.33 cents per pound.

⁵Taken from Chemical and Engineering News' Quarterly Report on current prices.

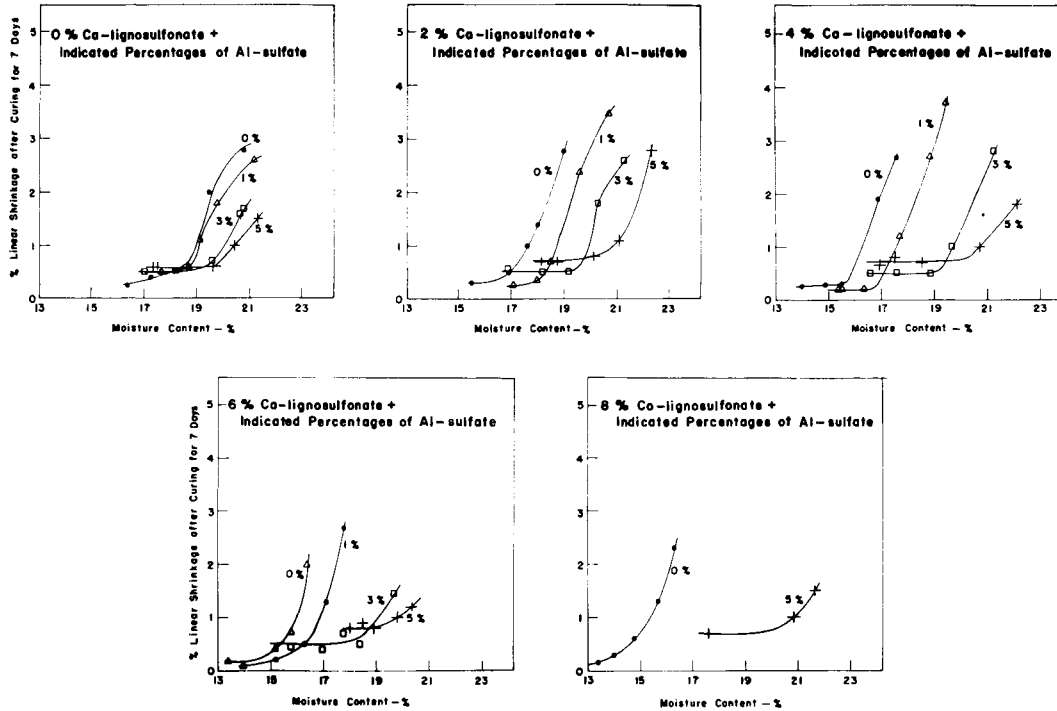


Figure 6. Effect of Ca-lignosulfonate and Al-sulfate on linear shrinkage of specimens molded at various moisture contents.

A mixture composed of 6 per cent Ca-lignosulfonate and 5 per cent 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 per cent Ca-lignosulfonate and 3 per cent 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 per cent Ca-lignosulfonate and 5 per cent 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 in strength. Table 6 shows the effect of alternate freezing and thawing on specimens prepared from the untreated loess and the selected mixture. Untreated specimens bulged after the first cycle, whereas 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 whereas specimens prepared from the selected mixture showed 2 per cent expansion, 22 per cent absorption and gave 17.5 psi unconfined comprehensive strength. Specimens immersed in water for 14 days were cracked. Thus, it appears that for this method of stabilization the most severe simulated weathering condition is 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-sulfate. When both additives were combined before adding to the soil an 18 per cent 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

Table 6
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±

strength. For the calcareous loess studied, this optimum combination was estimated to be 6 per cent Ca-lignosulfonate and 8.5 per cent Al-sulfate; this was verified by experimental results.

The optimum combination leads to the formation of a chemical compound (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 per cent Ca-lignosulfonate and 5 per cent Al-sulfate gave immersed strengths of 122 psi, 160 psi, and 230 psi when cured in atmospheres having average relative humidities of 70 per cent, 65 per cent, and 36 per cent, respectively. When specimens cured in the atmosphere having 70 per cent 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 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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