## Polyacids and Lignin Used with Large Organic Cations for Soil Stabilization

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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.

• THE SUPERIOR waterproofing ability of large organic cations in soils has been demonstrated in previous studies at the Iowa Engineering Experiment Station (1,2,3). 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 Waals attraction, the larger cations are generally difficult or impossible to replace by smaller organic cations or by inorganic cations (4). Organic cations are also adsorbed between layers of the expandable lattice minerals of the montmorillonite group (5).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 (6).

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 in 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



Figure 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.

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. 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 analogous 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:

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

in which

- dW = work;
- dD = increase in distance between the two plates;

- $\gamma_{LA} =$  liquid-air interfacial tension; dS = increase in liquid-air interfacial area;
- $\gamma_{AS}$  = air-solid interfacial tension;
- $\gamma_{LS} =$ 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 (7). The value of  $P_G - P_L$  comes from

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

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 Eq. 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  $(\dot{P}_{g} - dP_{L}/dD)$  becomes negative and in Figure 1h both  $(P_G - dP_L/dD)$  and  $(\gamma_{AS} - \gamma_{LS})$  are negative. These comparisons vield

$$\frac{dW/dD_{1e}>dW/dD_{1f}>dW/dD_{1g}>}{dW/dD_{1h}}$$
(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, it may first be observed 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 Eq. 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 (Fig. 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 (Fig. 2d). A comparison of Figures 2c and 2f, which represent top views of Figures 2c and 2d, respectively, illustrates the decrease in total peripheral length of water film



Figure 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.

(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 2d than for Figure 2c and the water bond energy has been reduced. Figure 2g represents total immersion of the eight spheres in water. For this case no liquid-air interfaces exist and any water bonding must again 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 part of the mineral surfaces are coated with large organic cations because the waterorganic cation interfaces represent areas for which reduced energy is required to separate the particles. However, the presence of 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 whereas immersed strengths are greatly increased. At higher percentages of treatment, however, the immersed strengths also decrease (Fig. 8) (3).These results indicate that a percentage of treatment exists above which the beneficial effect of restricting the entrance of additional water during immersion 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 to any bonding action which can be attributed to van der Waals 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 expandable 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 (8). 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 (9, 10). 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 (11, 12, 13, 14). Mathematical expressions to characterize these systems have been developed from the classical derivation of Einstein (15, 16) and a subsequent modification by Guth and Gold (17) 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 intergranular contacts exist and where the voids are not completely filled with polymer. This is the condition in soils stabilized with polymers. For cases 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  $\theta$  is the angle of internal friction of the granular material. If there are interparticle forces operating independently of N, Eq. 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 therefore 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,



Figure 3. Comparison of the effectiveness of a nonbonded soil polymer system (a) with a bonded soilpolymer system (b) in resisting shear across the surface of bab

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 (Fig. 3b) instead of passing around the particles (Fig. 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. In Figure 4 two polymer chains crossing the shear plane b-b at an angle  $\phi$  have different lengths between fix points on opposite sides of the shear plane. 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



Figure 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.

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 Waals, 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. Havenhill et al. (18, p. 316-359) discovered that 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. By this method, the tensile strength of pure gum GR-S stocks was increased more than five-fold. Sterns and Johnson (13) found that when rubber containing carbon black is vulcanized using sulfur and accelerators extensive chemical bonding of polymer to the mineral surfaces occurs. 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 (a) direct bonding between neighboring soil particles, and (b) 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, Fig. 5) is subjected to a shear displacement dD. Inasmuch as shear fail-

ure 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 polymer having an initial average distance L between fix 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 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. Flory (20, Ch. XI) presents a comprehensive analysis of the factors governing the Young's modulus of polymer systems.

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

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



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

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

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

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

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

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

Introducing these values into Eq. 7 gives

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

As Eq. 7b indicates, the ordinate values in graph 3b (Fig. 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

$$[3c2] = S\cos\phi \qquad (9)$$

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

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

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

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

To find the components of total tension normal and parallel to the direction of

### 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 soilorganic cation system. The ionized polyacrylic acid expands from a randomly kinked configuration to an elongated configuration due to eloctrostatic 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 shear the curves in rows 3 and 4, respectively, may be integrated between the limits of  $0^{\circ}$  and  $90^{\circ}$ . Analogous to the basic Coulomb equation, the following is obtained:

$$S = C - c + N \tan \theta + \tan \theta \int_{0}^{30} [4] + \int_{0}^{90^{\circ}} [3] \quad (12)$$

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 Eq. 12 obtains a maximum.

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, presented by Flory (20, p. 584-589, 629-637) and others (21, 22, 23, 24, 25), may be explained on the basis of osmotic pressure. When a polyelectrolyte is ionized, as for example when polyacrylic acid in dilute aqueous solution is neutralized with sodium hydroxide (Fig. 6), the concentration of the mobile Na ions will always be greater in the gel than



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

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.

Katchalsky and Swick (24) found that transferring polyelectrolyte fibers from one solution to another of higher chemical potential required a larger force to maintain the length of the fibers constant. 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 Eqs. 9, 11, and 12 is one of the experimental objectives of this study.

#### Chelation of Polyacids

Whereas 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 essentially covalent bonds between neighboring ionized acid groups. The reaction, called chelation, is illustrated in Figure 7.



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

#### 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 Arguad 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 sus-

pension 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 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.

8 shows the compressive Figure strength of the silty loam as a function of Arquad 2HT as the only additive. Arquad 2HT hydroxide, represented by the solid line in 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 in Figure  $\tilde{8}$  and subsequent graphs are based on the solid weights of chemicals added in solution and on air-dry weight of the soil.



Figure 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  $1\frac{1}{2}$  times the air-dry strength of the untreated soil.

When Arguad 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 Waals 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 studied by Iler (26), Kressman and Kitchener (27), and Terayama (28).

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 in Figure 9 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 (Fig. 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-cation bonds formed between neighboring mineral particles, compressive strengths were measured for wide ranges of both Arquad 2HT hydroxide content and Acrysol A-1 con-



Figure 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.

tent (Fig. 10). It is interesting to compare the curves for immersed strength (Fig. 8) with the strength contour curves (Fig. 10). When Arquad 2HT is used alone (Fig. 8) an optimum amount of Arquad is reached for maximum immersed strength, whereas when Arquad 2HT is used with polyacrylic acid (Fig. 10) an increase in Arquad 2HT content at any point on the graph yields an in-



Figure 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.

crease in immersed strength. Apparently when Arquad 2HT and polyacrylic acid are used together the increase in strength contributed by cation-polyacid-cation bonds, as more Arquad 2HT is added, outweighs the decrease in bonding by moisture films. The strength contours over most of the area in 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-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

$$a^3 = \frac{[\eta]}{[\eta]_0} \tag{13}$$

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 (29). Viscosities were measured with an Ostwald viscometer at 30 C (flow time of water=2 min 56 sec).

In order 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. The results of these tests are presented in 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 (Fig. 12) are in close agreement with the results of the viscosity measurements (Fig. 11). It is obvious from Figure 12 that the ferric chelate is very strong, whereas 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



Figure 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 saits.



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

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

Comparison of Table 1 and Figure 13 shows that the rates at which the various 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, Fig. 13). Ferrous carbonate produces a very gradual pH drop (curves 4) and the more soluble ferrous sulfate 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 solu-

		TABLE 1		
SOLUBILITIES	OF AN	SLIGHTLY D FERRIC S	SOLUBLE	FERROUS

Salt	Water Solubility <sup>1</sup>	Temp. (°C)
FeS	0.00061	18
Fe2(SO4)3·XH2O FeCO3	0.0065	20
FeSO4(NH4)2SO4+6H2O FeSO4+7H2O	18 32.8	0

<sup>1</sup> Parts per 100 parts of water by weight.



Figure 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.

bility 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 in Figure 13.

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.

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. 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



Figure 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.

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 Arouad 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



Figure 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 2in. high specimens measured after 7-day air-drying plus 24-hr immersion.

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 anpeared 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 Arguad 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 equivalent 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 (30). 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 carbonate 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.



Figure 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 aircuring and 24-hr immersion in water.

## 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, waterinsoluble complexes with lignin and various proteins.

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 (31). It accounts for 20 to 30 percent of the weight of wood (32, 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-occurring highorganic 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 effectively bond between the positive and negative ionic groups of proteins (Fig. 17).

## 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 (33). Furthermore, lignin and proteins can both be made more resistant hydrothermally and biochemically by reactions with metals



Figure 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.) 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 chromelignin process (34) 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 (33, 35, 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



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

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 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 2 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 2 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 2 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 pH 12 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	2	
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UNCONFINED COMPRESSIVE STRENGTHS OF THE SILTY LOAM TREATED WITH COMBINATIONS OF SPENT SULFITE LIQUOR AND ZEIN WITH ORGANIC CATIONS AND METAL SALTS<sup>1</sup>

Organic Cations and Metal Salts	No Treatment	Spent Sulfite Liquor <sup>2</sup>	Zein <sup>s</sup>	Spent Sulfite Liquor and Zein 4
No treatment	Slaked	Slaked	Slaked	Slaked
CaCl <sub>2</sub>	Slaked	Slaked	Slaked	Slaked
MgCl <sub>2</sub>	Slaked	Slaked	Slaked	Slaked
CuSO4	Slaked	Slaked	Slaked	Slaked
FeCls	Slaked	Slaked	Slaked	Slaked
Co(NO <sub>3</sub> ) <sub>2</sub>	Slaked	Slaked	Slaked	Slaked
Cr2(SO4)3	Slaked	180 lb	130 lb	210 lb
Hg(O2H3O2)2	Slaked	Slaked	220 lb	230 lb
Armac T	300 lb	350 lb	290 lb	260 15
Arquad 2HT hydroxide	330 lb	370 lb	340 lb	270 lb

<sup>1</sup> 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-br immersion.

<sup>2</sup> 2 percent. <sup>3</sup> 0.5 percent

<sup>3</sup> 0.5 percent.
<sup>4</sup> 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 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





Figure 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.

Figure 20. Unconfined compressive strength of the silty loam treated with Arquad 2HT hydroxide in combination with spent sulfite liquor and sein. Strengths of 2-in. high by 2-in. diameter specimens measured after 2-day sir-drying plus 24-br immersion.



Figure 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.



Figure 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.

liquor and zein. Chromic sulfate with zein and spent sulfite liquor (curve 7 of Fig. 21) gave higher strengths than other combinations in this group.

#### SUMMARY

The mechanisms of soil stabilization with large organic cations and with high 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. Armac T and Arguad 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 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 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.

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## APPENDIX

#### TABLE A

## PROPERTIES OF CHEMICAL ADDITIVES

Commercial Name	Chemical Description	Form <sup>1</sup>	Active Fraction (%)	Supplier <sup>2</sup>
	(a) POLYACIDS AND	POLYACID SALTS		
Acrysol A-1 Acrysol A-3 Acrysol A-5 Acrysol GS Acrysol GS Acrysol ASE-75 Acrysol ASE-75 Acrysol ASE-60 Rhoplex AC-33	Polyacrylic acid Polyacrylic acid Sodium salt of polyacrylic acid Ammonium salt of polyacrylic acid A linear copolymer of acrylic ester with a carboxylic acid A very slightly cross-linked copolymer of acrylic acid An acrylic resin	Aqu. sol. Aqu. sol. Aqu. sol. Aqu. sol. Aqu. sol. Aqu. sol. Aqu. sol. Aqu. emul. Aqu. emul.	25 25 25 12 <sup>3</sup> ⁄ <sub>2</sub> 22 40 28 46	R R R R R R R
Krilium Loamaker	A hydroyzed polyacrylonitrile	Powder	¥0	M
	(b) LARGE ORGAN	VIC CATIONS		
Arquad 2HT Armac T	Di-hydrogenated tallow dimethylam- monium chloride Primary amine acetate derived from tallow fotty code	Isop. sol.	75	А
Ethoduomene Arquad 12 Polyrad 1100	N-octadecyl N, N', N'-tris-(2-hydroxy- ethyl) 1, 3 trimethylene diamine Trimethyl dodecyl ammonium chloride Reaction product of dehydroabietyl- amine and 11 moles of ethylene oxide	Pure Isop. sol.	100 50	A A A
				n
	(t) OTHER A	DDIIIVES	· · · · · ·	
Spent sulfite liquor	71% lignins, 24% sugars, 5% resins and other substances	Aqu. sol.	57% solids	s
Zein	Protein high in amide content, low in other functional groups	Powder	100	Ν

<sup>1</sup> Aqu. sol. = aqueous solution; aqu. emul. = aqueous emulsion; isop. sol. = isopropanol solution. <sup>2</sup> 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.

Item	Amount or Classification		
Themical:			
Organic matter	0.17~%		
Carbonates	10.17~%		
Iron	1.69%		
Sulfate	0.0 %		
Cation exchange capacity	8.7 me/100 gm		
pH	8.7		
extural:			
Sand	0.4 %		
Silt	79.8 %		
Clay	19.8 %		
Colloidal Clay	14.5 %		
USBPR classif.	Silty loam		

## TABLE B PROPERTIES OF THE SILTY LOAM 1

Mineral comp., clay fraction — primarily montmorillonite, with smaller quantities of illite and kaolinite

<sup>1</sup> Laboratory sample 20-2.