1957

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Recommended Citation

Nicholls, Robert Lee, "Soil stabilization with organic cations and high polymers " (1957). *Retrospective Theses and Dissertations*. 2229.
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SOIL STABILIZATION WITH ORGANIC CATIONS AND HIGH POLYMERS

by

Robert Lee Nicholls

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Soil Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1957

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INTRODUCTION

The rapid growth of automotive and air transportation is creating increased demands for the construction of new highways and air fields. The rising costs of these facilities have been attributed largely to three factors: increased construction volumes, more stringent design requirements resulting from heavier wheel loads, and the growing shortage of readily available aggregate for pavement surfaces and base courses. The last of these factors, shortage of aggregate, has stimulated a keen interest among soil engineers and chemical manufacturers in the development of methods for strengthening or stabilizing soils by the addition of chemicals.

Chemical soil stabilizing agents are often classed in one of two categories: chemicals which serve primarily to cement mineral particles together and those which serve primarily to inhibit the entrance of large amounts of moisture into a relatively dry soil, thus preserving the natural bonding force exerted between soil particles by thin water films. The cementing agents include portland cement, lime, lime and fly ash, and organic polymers such as aniline-furfural and calcium acrylate. The water-proofing agents include surface active compounds which coat the mineral surfaces and whose hydrophobic groups inhibit the movement of moisture through the soil pores.

Previous studies at the Iowa Engineering Experiment Station have demonstrated the superior water-proofing ability of large organic cations in soils (1, 2, 3). An investigation of methods of combining this water-proofing ability of large organic cations with the cementing capacity of high polymers is the subject of this thesis. The mechanisms of water-proofing and cementing in soils will be presented in the following paragraphs.

WATER-PROOFING 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 descriptively 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 the photographs, Figure 1a to 1d. Two laboratory funnels having their rims coated with a soap solution were brought into superposition and then separated a short distance.[1] The upper funnel was closed to the atmosphere and a variable level water reservoir connected to the lower funnel provided a means of varying the pressure within the soap film. The law of surface tension governing the film tends to minimize its surface area for any given pressure difference across the surface of the film. 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

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[1] A stable soap solution can be made with 60% distilled water, 30% glycerine and 10% triethanolamine oleate. A small amount of titanium dioxide powder gives the film a high index of refraction for better photographic results. This formula was developed by Mr. Ray Bonanno of the Theoretical and Applied Mechanics Department, Iowa State College.

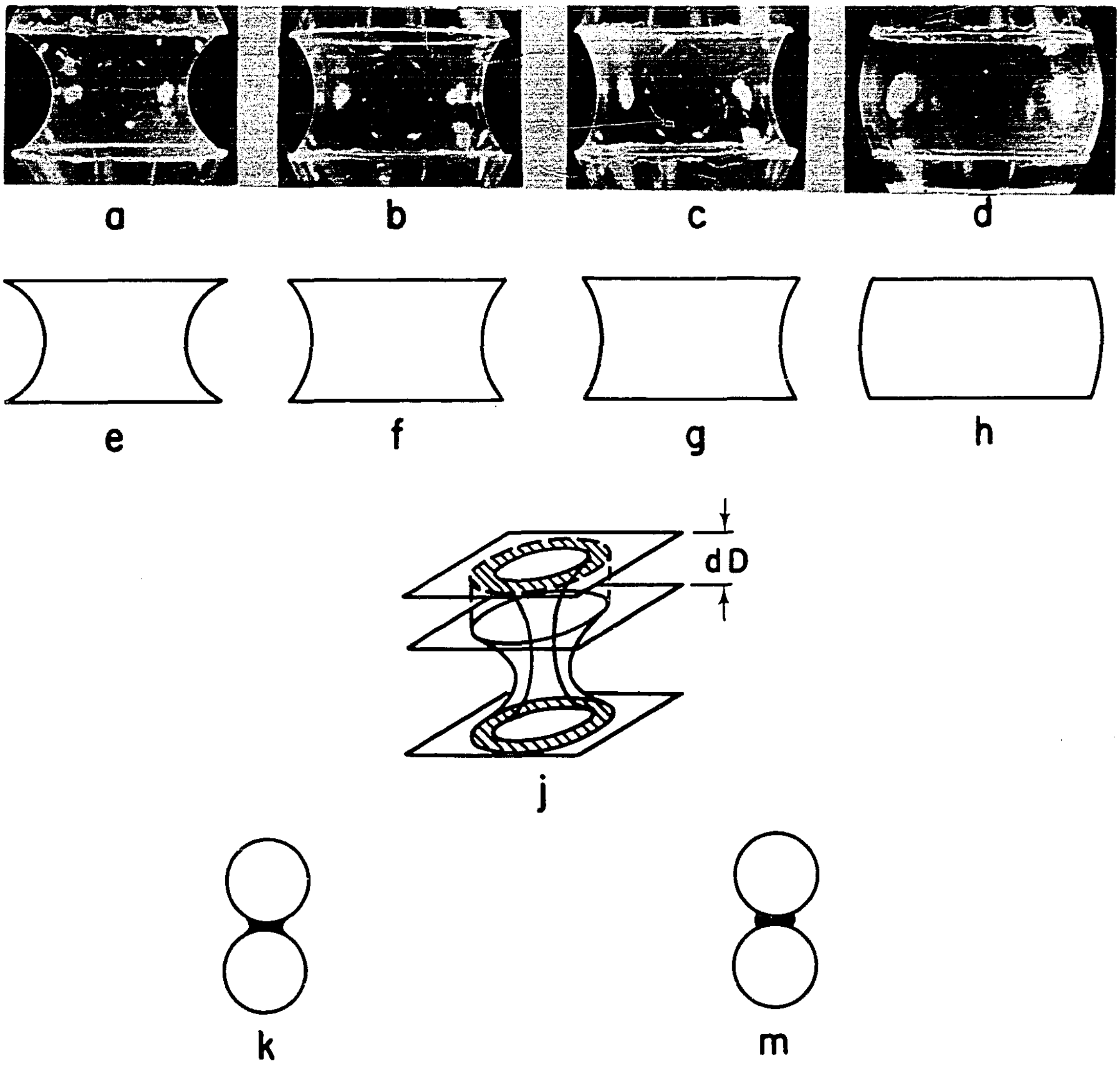


Fig. 1. Configurations assumed by liquid drops between two plates and between two spheres for various contact angles. Photographs a to d are soap film analogies for the corresponding sketches e to h.

the two plates against forces which are caused by the liquid drop may be expressed by the equation:

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

where dW = work

dD = increase in distance between the two plates

γ_{LA} = liquid-air interfacial tension

dS = increase in liquid-air interfacial area

γ_{AS} = air-solid interfacial tension

γ_{LS} = liquid-solid interfacial tension

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 the expression:

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

where 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. If the liquid perfectly wets the two plates, *i.e.*, no contact angle, the liquid-solid interfacial area does not decrease when the two plates are separated. For this special case the second and third terms on the right-hand side of equation (1) drop out.

Assuming comparable values of dS and dA for each of the conditions represented in Figures 1e through 1h, a quantitative comparison may now be made of the work required to separate the two plates a given distance in each of these four cases. In Figure 1e both of the energy changes due to movement of the triple interface, represented by the last two terms in equation (1), are positive. The term ($\gamma_{AS} - \gamma_{LS}$) is positive because the contact angle is less than 90° and the term ($P_G - dP_I/dD$) 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 equation (1) drops out. In Figure 1g the term ($P_G - dP_I/dD$) becomes negative and in Figure 1h both ($P_G - dP_I/dD$) and ($\gamma_{AS} - \gamma_{LS}$) are negative. These comparisons yield the following relationship:

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

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

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

In order 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 expression (3) show that less work is required to separate the pair of idealized mineral particles coated with large organic cations than to separate the uncoated pair.

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

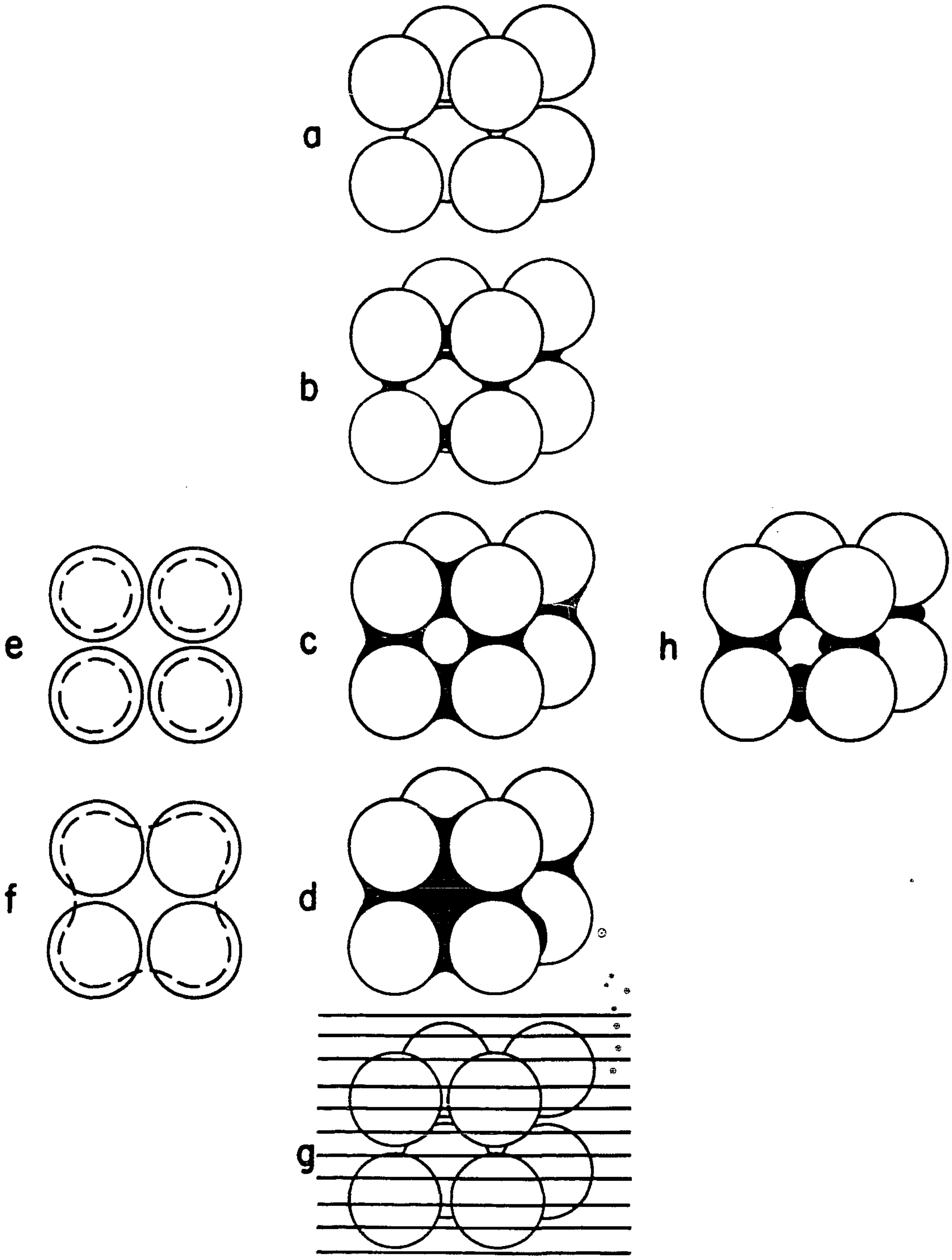


Fig. 2. Effects of moisture content and of partial coating with a surface active agent on the bonding of eight cubically-packed spherical particles by water.

increased and the change in this area, dS, accompanying a given separation dD between the particles also increases. Thus the water bond energy in this range of moisture content is increased by the addition of water. As more water is added, however, the interior void between the eight spheres may become filled (Figure 2d). A comparison of Figures 2e and 2f, which represent top views of Figures 2c and 2d respectively, illustrates the decrease in total perpherial length of water film (dotted lines) connecting the two planes of four spheres due to filling the interior void with water. The ratio dS/dD is therefore lower for Figure 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 water-organic 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 mechanical 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 (Figure 10 and reference 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 upon 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.

The following table shows three processes which might be used to produce water-insoluble polymers in the soil.

Table 1. Methods of producing water-insoluble polymers in soils

Starting material	Process	Final product	Example
1. Water-soluble monomer	Addition polymerization	Water-insoluble polymer	Calcium acrylate
2. Monomer	Condensation polymerization	Water-insoluble polymer	Aniline-furfural
3. Water-soluble polymer	Chelation or complex formation with metal salts	Water-insoluble polymer	Polyacrylic acid plus iron salts

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%) of mineral fillers (11-14). 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 (17a) 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, i.e., 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 the equation:

$$S = N \tan \theta \qquad (4)$$

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

$$S = C + N \tan \theta \qquad (5)$$

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.

A typical stress-strain curve from a direct shear test on dense sand is illustrated in Figure 3. As indicated, the maximum shear stress of a dense sand often occurs about midway between zero strain and the strain at which maximum dilatency is developed. This behavior is typical of dense

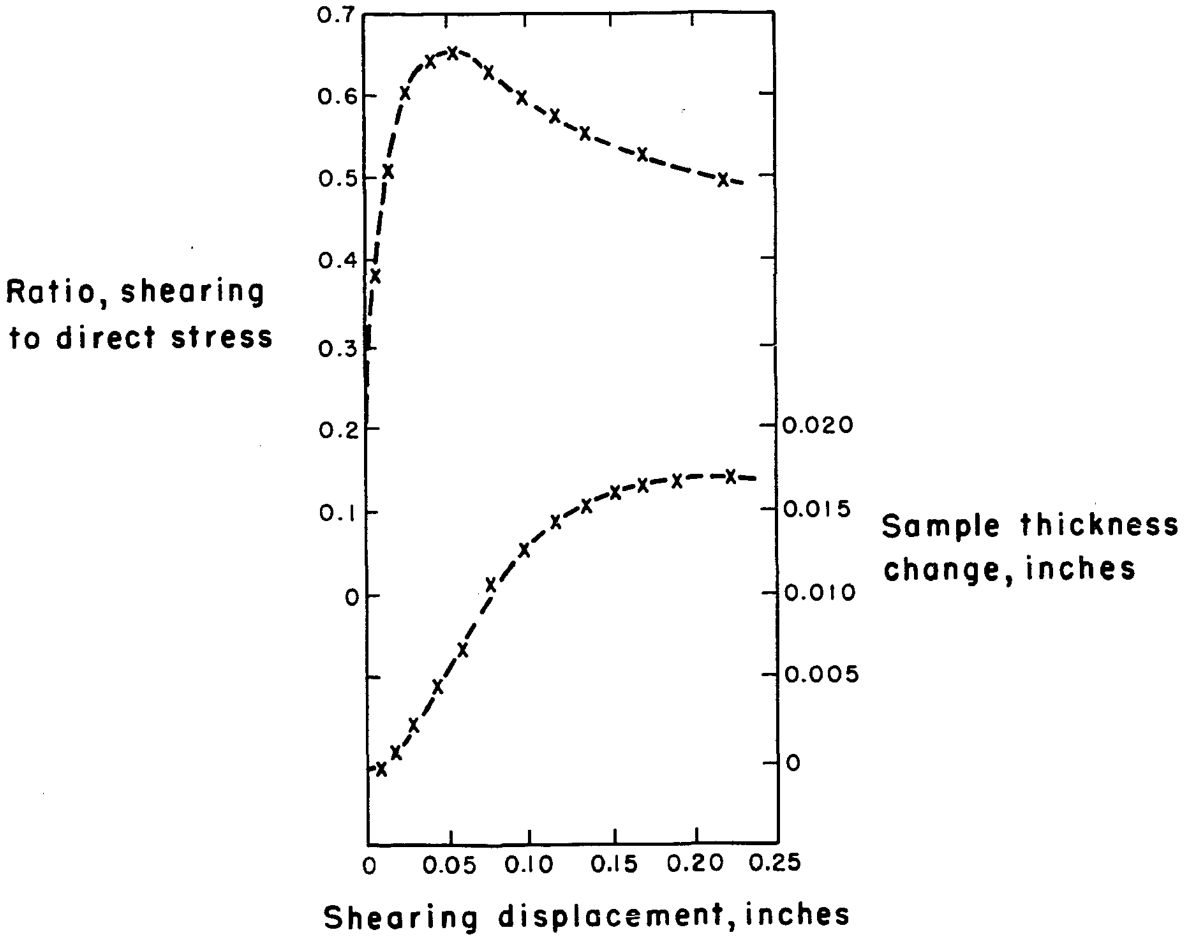


Fig. 3. Typical plot of a direct shear test for dense sand. (Taken from Fundamentals of Soil Mechanics, by Donald W. Taylor (17b).)

fine grain soils as well.

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, 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, as in Figure 4b instead of passing around the particles, as in Figure 4a. In Figure 4b, 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 any shear plane with a given amount of polymer.

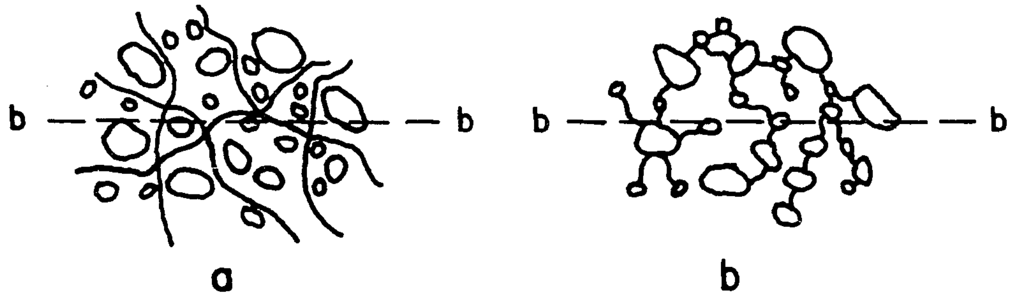


Fig. 4. Comparison of the effectiveness of a non-bonded soil-polymer system (a) with a bonded soil-polymer system (b) in resisting shear across the surface b-b.

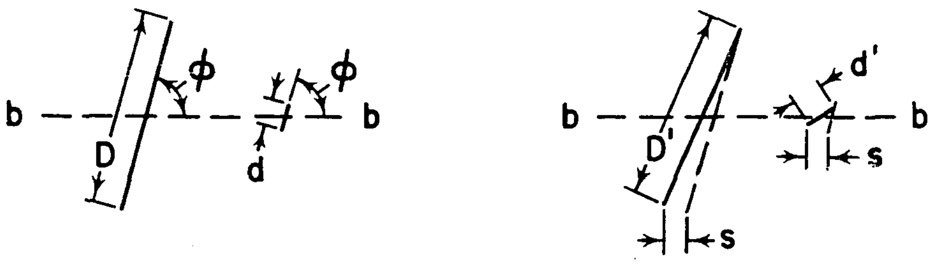


Fig. 5. Resistance offered by a single polymer chain to shear across the surface b-b as a function of length of the polymer chain between fix points.

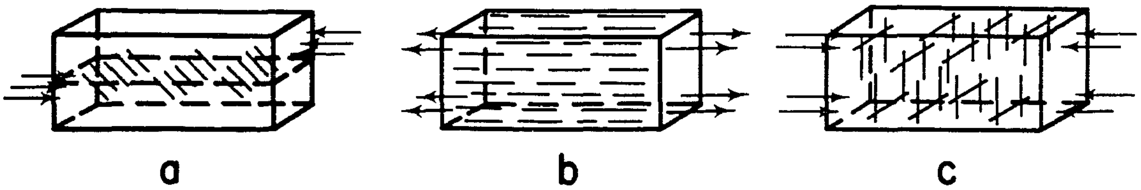


Fig. 6. Optimum orientations of polymer chains in a soil subjected to different types of stress: (a) shear, (b) tension, and (c) compression.

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 5 two polymer chains crossing the shear plane b-b at an angle ϕ have different lengths between fix points on opposite sides of the shear plane. For a given shear displacement S, d'/d is greater than D'/D. If both chains have the same Young's modulus the shorter chain will therefore offer the greater resistance to shear. Ideally, a relationship may exist in which the average length of polymer segment between fix points is such that maximum retractive stress of the polymer will be attained at the same shear strain at which the maximum internal friction stress indicated in Figure 3 is developed.

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 and coworkers (18, pp. 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 fivefold. Stearns 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.

In connection with this relationship, in which maximum retractive tensile stress of the polymer and maximum frictional shear resistance between mineral particles are developed simultaneously, 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.

Finally, greater strength might be obtained with the same amount of polymer if the polymer chains could be oriented in such a manner as to most effectively resist a given type of applied stress. In the field of rubber technology the phenomena of chain orientation due to imposed strains has received considerable attention. For example, Flory and coworkers (19) have developed an equation for the proportion of randomly distributed chains which are lengthened as a function of deformation in a stretched rubber and have studied the relationships between degree of cross-linking, orientation due to strain, and maximum tensile strength of rubbers.

For a soil-polymer system subjected to direct shear, preferential orientation of the polymer chains might be represented by the slanted lines in Figure 6a. The orientations shown for simple tension (Figure 6b) and simple compression (Figure 6c) are apparent from a consideration of elementary mechanics.

In summary, the theoretically ideal conditions for maximum utilization of a polymer in soil appear to be:

1. Direct bonding between neighboring soil particles.
2. Pretensioning of polymer chains.
3. Orientation of polymer depending upon the external stresses to be resisted.

Methods of attaining the first two of these three conditions are being studied and will be described in the experimental sections. General mathematical expressions for the above relationships are outlined in the following paragraphs.

Imagine that each of three soil samples, row 1 of Figure 7, is subjected to a shear displacement dD. Since shear failure in granular materials takes place within a

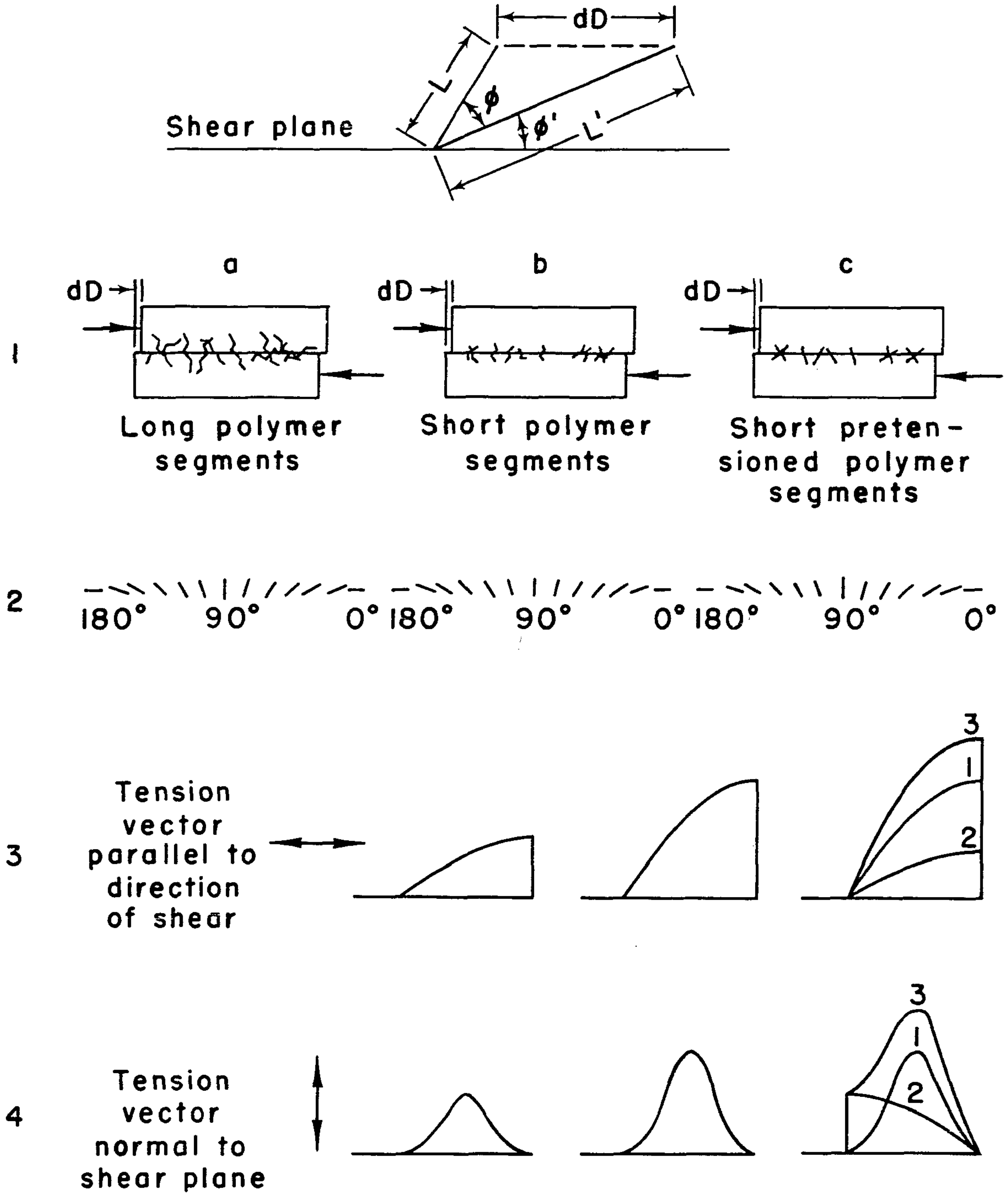


Fig. 7. Tension vectors of randomly oriented polymer segments crossing a shear plane as functions of segment length between fix points and pretensioning.

zone instead of an a unique plane, the shear planes indicated in the samples may be considered as planes within a shear zone. Imagine that sample 1a is stabilized with polymer having an initial average distance L between fix points. The fix points may be either branch points in a polymer network or bonds connecting the polymer to soil particles. Sample 1b will be identical to 1a except that the initial average distance between fix points will be less than L. Sample 1c will be identical to 1b except that an initial tension shall be placed in the polymer chains prior to subjecting the sample to a shear displacement dD. A random initial orientation of polymer segments in each of the three samples will be assumed.

In row 2, Figure 7, 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 the equation:

$$S' = \frac{L'-L}{L} Y \qquad (6)$$

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 ϕ, the angle between the projected segment and the shear plane. These curves are obtained from the expression:

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

where [3] designates the tension vector parallel to the shear plane and ϕ' is the adjusted angle ϕ after the sample has been subjected to shear strain. From the sketch at the top of Figure 7, and by the law of sines,

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

$$\sin \phi' = \frac{L \tan \phi}{dD + L \cot \phi}$$

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

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

Introducing these values into equation (7),

$$[3] = Y \left[\frac{\cos \phi \, (dD + L \cot \phi) - L}{L}\right] \sqrt{1 - \left(\frac{L \tan \phi}{dD + L \cot \phi}\right)^2} \qquad (8)$$

As this equation indicates, the ordinate values in graph 3b 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 the equation:

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

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.

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

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

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 shear the curves in rows 3 and 4 respectively may be integrated between the limits of 0° and 90°. Analogous to the basic Coulomb equation we then obtain:

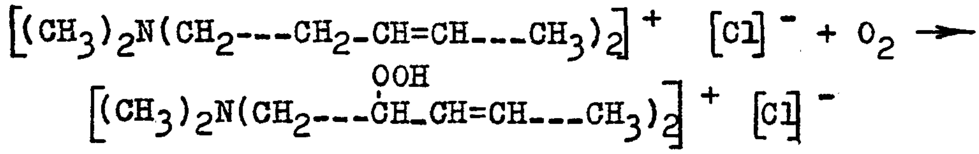
$$S = C - c + N \tan \theta + \tan \theta \int_{0^{\circ}}^{90^{\circ}} [4] + \int_{0^{\circ}}^{90^{\circ}} [3] \qquad (12)$$

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

PART I. INVESTIGATION OF A GRAFT POLYMERIZATION METHOD FOR SOIL STABILIZATION

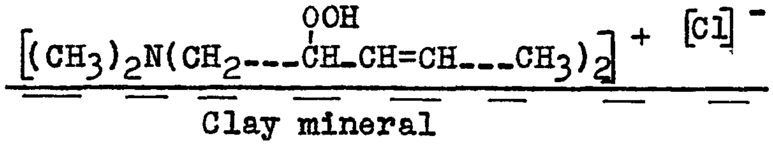
For the first phase of the study an attempt was made to employ a graft polymerization process for soil stabilization which would consist of the following steps:

1. Oxidize an unsaturated quaternary ammonium salt to obtain hydroperoxide groups on carbon atoms alpha to the double bonds.



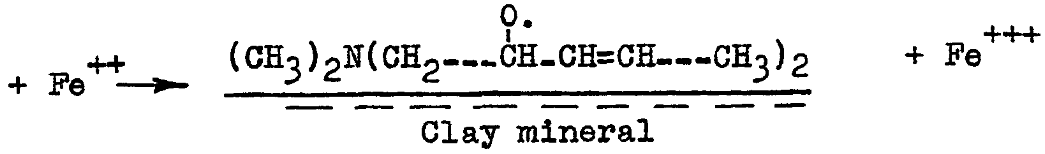
$$[(CH_3)_2N(CH_2{-}{-}{-}CH_2{-}CH{=}CH{-}{-}{-}CH_3)_2]^+ \quad [Cl]^- + O_2 \rightarrow$$
$$[(CH_3)_2N(CH_2{-}{-}{-}\overset{OOH}{CH}{-}CH{=}CH{-}{-}{-}CH_3)_2]^+ \quad [Cl]^-$$

2. Partially coat the negatively charged clay mineral surfaces with the oxidized cation of the salt.



$$\underset{\text{Clay mineral}}{\underline{[(CH_3)_2N(CH_2{-}{-}{-}\overset{OOH}{CH}{-}CH{=}CH{-}{-}{-}CH_3)_2]^+ \quad [Cl]^-}}$$

3. Add a water-soluble reduction activating agent to convert the hydroperoxide groups to free radicals from which polymer chains can be initiated.



$$+ Fe^{++} \rightarrow \underset{\text{Clay mineral}}{\underline{(CH_3)_2N(CH_2{-}{-}{-}\overset{O\cdot}{CH}{-}CH{=}CH{-}{-}{-}CH_3)_2}} \quad + Fe^{+++}$$

The polymer chains extending outward from the organic cations coating the mineral surfaces might then be joined by molecular entanglements or by chemical cross-linking.

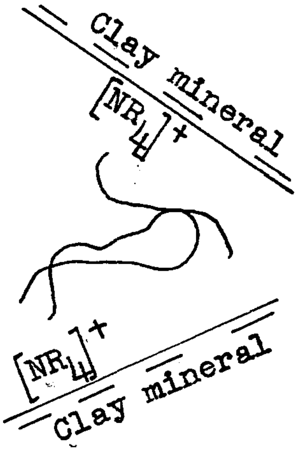


Figure 8. Proposed bonding of mineral particles by polymer chains initiated from organic cations coating the mineral surfaces.

Figure 8 represents the final stabilized soil system which it was hoped this process would produce.

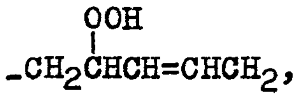
While the results of this phase of the work were largely negative it is possible that the general principle may be revamped and used in some way not recognized by the author. A recapitulation of the method is presented for possible future development.

Review of Literature

Since the experimental work of this part is divided into two stages, the oxidation of an olefinic compound to form a hydroperoxide and the use of this hydroperoxide to initiate graft copolymers, the review of literature will deal with these two fields.

Oxidation of olefins to hydroperoxides

The formation of hydroperoxides in unsaturated fatty acids as a result of the reaction with molecular oxygen is important in the development of rancidity in fats and in connection with the behavior of drying oils used for the manufacture of paints, varnishes and linoleum (21, pp. 424-428). In the case of mono-olefins, as oleic acid, and in the case of unconjugated diolefins, as linoleic acid, mild oxidation generally produces



$$-CH_2\overset{\overset{\large OOH}{|}}{C}HCH{=}CHCH_2,$$

displacing the hydrogen on the alpha carbon and leaving the double bond intact (22, 23). More intense or prolonged oxidation may involve either direct addition to the double bond and final cleavage of the double bond (23) or the formation of disubstituted cyclic and polymeric peroxides (24).

Gunstone and Hilditch (23) found that in the case of 1:4-diene structures ($-CH{=}CHCH_2CH{=}$), as for example in linoleic acid, uniting of molecular oxygen with the central CH_2 group takes place much more readily than with the CH_2 group alpha to a single double bond.

With conjugated double bonds ($-CH{=}CH-CH{=}CH-$) a different phenomena is usually observed. Farmer (25) states:

> . . . experiment shows that all investigated conjugated compounds, including those in which the unsaturated centers are flanked by alpha-methylene groups, undergo peroxidation additively at the double bond systems, leaving the adjacent alpha-methylene groups intact.

The significance of these relationships to the present study will be made apparent on the following page.

Graft copolymerization

A number of methods have recently been developed for the preparation of copolymers by addition polymerization, which, instead of the two components being distributed in the molecule according to their reactivity ratios, have chains in which branches containing only one monomer species are attached to a substrate or "backbone" containing only the second monomer species. Such copolymers are called graft copolymers (26). For example Metz and Mesrobian (27) have used hydroperoxides of polystyrene derivatives as the substrate upon which polymers of methyl methacrylate were grafted.

Although much data has been obtained on the efficiency of structurally different hydroperoxides used as polymerization initiators, the underlying causes apparently are not well understood yet. The concentration of the hydroperoxides in the aqueous phase is known to be an important factor in the case of emulsion and solution polymerizations (28).

Experimental Procedure and Results

The study was divided into two steps to answer the following questions:

1. Can unsaturated quaternary ammonium salts be oxidized to hydroperoxides by any of the common methods used for the peroxidation of linoleates and similar unsaturated compounds (22-25)?

2. If step 1 is successful, can the resulting hydroperoxides be used with any of the reducing agents commonly employed in redox systems (28) to initiate polymerization of ethylenic monomers such as the acrylic esters and acrylonitrile?

Oxidation tests

The olefinic compound chosen for the investigation was Arquad 2S (Armour and Company trade name), a quaternary ammonium chloride having two methyl groups and two long alkyl groups. Arquad 2S was chosen for the oxidation studies because it is the most highly unsaturated of a group of quaternary ammonium salts which were previously found effective in water-proofing soils (2, 29). The long alkyl groups of Arquad 2S are derived from soybean oil, one of the common drying oils whose reactions with oxygen have been discussed. Soybean oil is sometimes referred to as a semi-drying oil because, although unsaturated, it contains only a small percentage of the conjugated linolenic structure most conducive to polymerization. The long alkyl groups of Arquad 2S contain mean values of 54% linoleic acid and 28% oleic acid with smaller percentages of linolenic, palmitic and stearic acids (29). The predominant group, linoleic acid, contains two double bonds in 1:4-diene structure and therefore should be quite easily oxidized. Oleic acid, containing one double bond, might be oxidized with greater difficulty.

The method of obtaining the hydroperoxide of Arquad 2S was essentially the same as those used by Metz and Mesrobian (27) and Gunstone and Hilditch (23). Molecular oxygen was dried in a calcium chloride tube, preheated in a flask supported on a heating mantle, then passed into a three neck flask containing the Arquad 2S in carbon tetrachloride solution at reflux temperature (76° C.). The apparatus used for oxidation is shown in the Appendix, Figure 44. An oxidation period of twelve hours was used and samples were withdrawn every two hours for determination of hydroperoxide content.

Isoproponol, the solvent in which Arquad 2S is obtained commercially, was removed by vacuum distillation to approximately 2% by weight of the Arquad 2S and the Arquad 2S was redissolved in carbon tetrachloride. Carbon tetrachloride was used as solvent for the oxidation studies instead of isoproponol for two reasons. First, several investigators have reported the inhibiting effect of alcoholic substances on the induction period in autoxidation systems (30). Evidently alcohols can seriously affect chain-starting processes when the systems contain too little hydroperoxide to provide a steady supply of free hydroxyl radicals. By removing most of the alcohol any inhibiting action of the alcohol would be reduced. The second reason for conducting oxidation tests in carbon tetrachloride instead of isoproponol is that infrared absorption spectra were used to confirm the presence of hydroperoxides and the tertiary alcohol bands of isoproponol centering in the region 850-910 cm^{-1} might have masked the absorptions due to C-O for peroxides in this region (31, 32).

Peroxide numbers of the oxidized Arquad 2S samples were determined by a modification of the method used by Armour Chemical Division to determine the oxidative rancidity of fats. This method is outlined in the Appendix. Qualitative confirmation of peroxides was obtained by infrared absorption analysis. Iodine numbers of Arquad 2S determined before oxidation and after twelve hours of oxidation indicated no decrease in unsaturation, showing that oxidation was not intensive enough to cause addition to the double bonds which might have led to oxidative degradation or the formation of polymeric peroxides. The peroxide content, expressed as moles of peroxide per mole of Arquad 2S is shown as a function of time of oxidation in Figure 9. The plotted points represent average values for two separate oxidations.

Polymerization tests

The ethylinic monomers chosen for these investigations include acrylonitrile, methylacrylate and methyl methacrylate. These monomers were chosen because they are known to give high polymer yields with a variety of reduction activating agents (33). All three are successfully initiated by redox systems having hydroperoxides as catalyst and various metal salts as activator. Also, the monomers are considerably more soluble in water than most ethylenic compounds and it was therefore unnecessary to complicate the investigations by working in emulsion. In the case of acrylonitrile, the polymer is insoluble in water, so that the beginning of polymerization is sharply defined by the appearance of a white turbidity in the solution, which enables the length of the induction period to be measured accurately. Acrylonitrile was obtained in pure form. Methyl acrylate and methyl methacrylate contained polymerization inhibitors and these were removed by methods given in the Appendix.

The reduction activating agents investigated for polymer initiation include sodium bisulfite ($NaHSO_3$), sodium metabisulfite ($Na_2S_2O_5$), silver nitrate ($AgNO_3$) and copperas ferrous sulfate ($FeSO_4 \cdot 7H_2O$). The first three of these

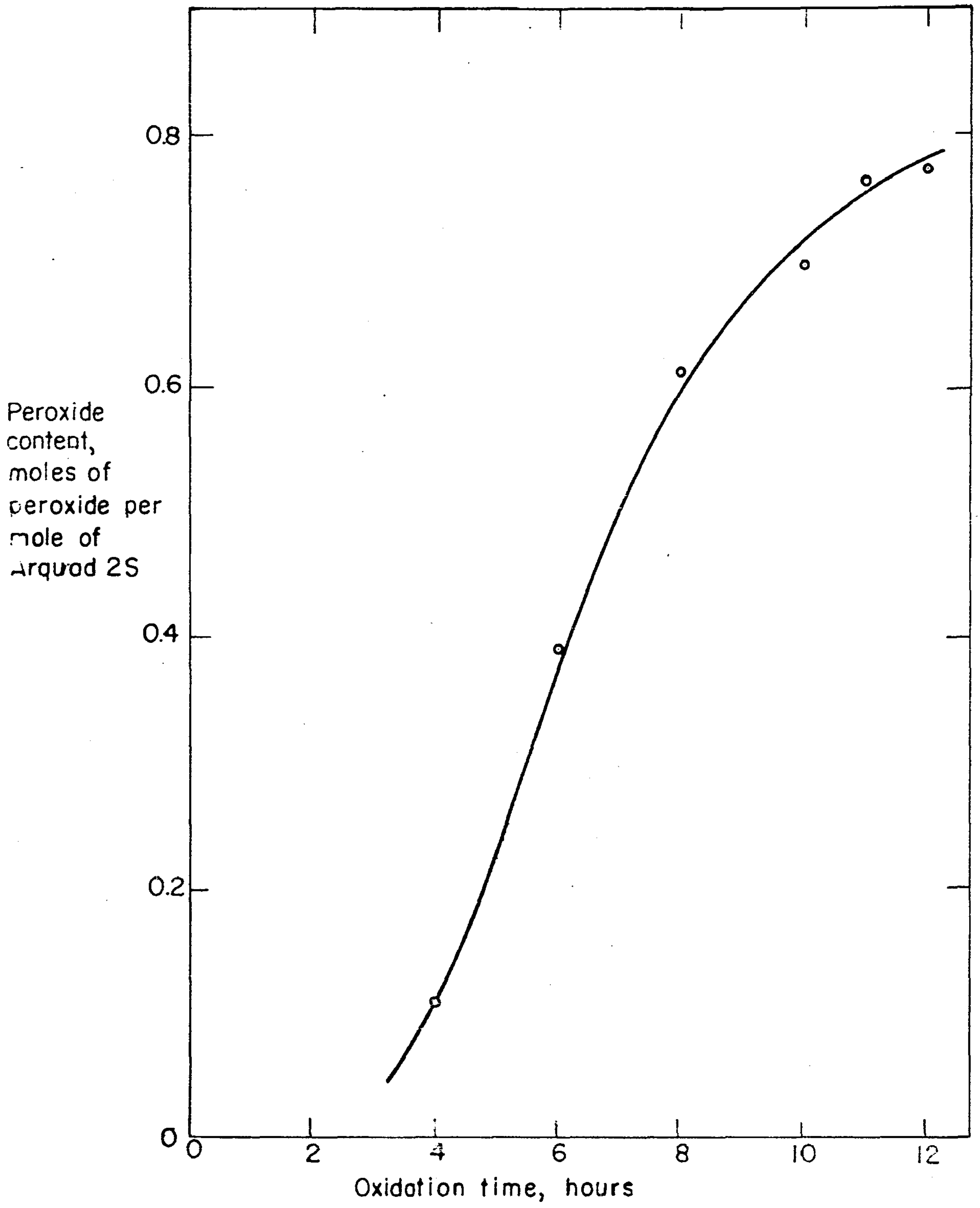


Fig. 9. Peroxide content of Arquad 2S as a function of time of oxidation with molecular oxygen. 20% Arquad 2S in carbon tetrachloride at 76° C.

reducing agents are among those found most effective by Bacon (33) for initiating polymerizations with a number of structurally different hydroperoxides.

The polymerization tests were conducted in a special apparatus described in the Appendix. All polymerizations were in aqueous solution at 30° C. Induction period (time of turbidity) was observed visually and per cent conversion of monomer to polymer at the end of two hours was determined by filtering the contents of the polymer reaction bottles on a Buchner funnel, washing first with distilled water, then with isoproponol to remove the occluded monomer, and drying to constant weight in a 60° C. oven. Since these investigations were exploratory in nature no studies were made of time-conversion characteristics or molecular weight distributions of the resulting polymers.

In order to test the adequacy of the polymerization apparatus and to provide a standard of comparison for Arquad 2S initiated polymers, polymerizations were first conducted using standard recipes for the three monomers. The standard recipes and the corresponding percentages of monomer-to-polymer conversion are shown in Table II.

A number of recipes were then prepared using Arquad 2S hydroperoxide as initiator together with the three monomers and four reducing agents. Variables included the ratios in which Arquad 2S, the three monomers and four reducing agents

Table 2. Per cent monomer-to-polymer conversion at the end of two hours for acrylonitrile, methyl acrylate and methyl methacrylate monomers using standard recipes. Per cent conversions represent the average of two polymerizations

Monomer	Acrylonitrile	Methyl acrylate	Methyl methacrylate
Polymerization recipe	100 ml distilled water	100 ml distilled water	100 ml distilled water
	15 ml 2.0% aqueous potassium persulfate	0.5 gm ammonium persulfate	0.5 gm ammonium persulfate
	10 ml 1.0% aqueous sodium bisulfite	0.5 gm ferrous sulfate	0.7 gm silver nitrate
	7 gm acrylo-	5 ml inhibitor-free methyl acrylate	5 gm inhibitor-free methyl methacrylate
Reference for polymerization recipe	(33, p. 141)	(68, p. 54) (Standard recipe calls for ethyl acrylate)	(28)
Per cent conversion after two hours	84%	92%	58%

were combined and pH adjustments by the addition of HCl and NaOH. Most of the recipes investigated yielded no polymer after two hours. The few recipes which did yield measurable polymer are shown in Table 3. The highest conversion

Table 3. Per cent monomer-to-polymer conversions at the end of two hours for ethylenic monomers initiated with Arquad 2S hydroperoxide and various reducing agents. Arquad 2S contained approximately 0.8 mole hydroperoxide per mole. All polymerizations conducted at 30° C. in 100 ml distilled water

Recipe	1	2	3
Monomer	Methyl acrylate (7 gm.)	Methyl acrylate (7 gm.)	Acrylonitrile (15 gm.)
Reducing Agent (added in aqueous solution)	$FeSO_4 \cdot 7H_2O$ (0.2 gm.)	$NaHSO_3$ (0.1 gm.)	$FeSO_4 \cdot 7H_2O$ (0.5 gm.)
Arquad 2S Hydroperoxide	0.5 gm.	0.7 gm.	0.5 gm.
pH	4.0	4.0	5.5
Per cent conversion, 2 hr.	5.1%	4.2%	8.7%

obtained, that for recipe 3 in Table 3, represents a maximum polymer yield for variations in the acrylonitrile-ferrous sulfate-Arquad 2S ratio and for variations in pH. Extension of the polymerization period to six hours for recipe 3 failed to give a measurable increase in polymer yield.

Conclusions

In view of the low polymer yields with Arquad 2S hydroperoxides these studies were discontinued in favor of subsequent investigations.

PART II. SOIL STABILIZATION WITH LARGE ORGANIC CATIONS AND POLYACIDS

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

1. Negatively charged clay mineral surfaces are partially coated with the large organic cations from an aqueous suspension.

2. Polyacrylic acid, ionized with potassium hydroxide, is added to the soil-organic cation system. The ionized polyacrylic acid expands from a randomly kinked configuration to an elongated configuration due to electrostatic repulsions between neighboring ionized acid groups. In addition, electrostatic attraction between the ionized acid groups of the polymer chains and the organic cations coating the mineral surfaces apparently causes orientation of the polymer chains between the organic cations and enables ionic bonding to them.

3. The addition of ferrous carbonate to the above system increases the strength of the treated soil. Ferrous ions are known to cause polyacid chains to contract and become hydrophobic due to chelation with the carboxyl groups of the polyacid. The fact that the ferrous carbonate also

produces a strength increase when the polyacid is omitted, however, may point to the precipitation of a hydrated iron gel which becomes a cementing agent upon dehydration.

Review of Literature

As the experimental work deals primarily with the dialation and contraction of polymeric electrolytes and with the formation of metal chelates a brief outline of these two fields will be presented.

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, pp. 584-589, 629-637) and others (34-38), may be explained on the basis of either of two mutually related phenomena: electrostatic repulsion and osmotic pressure. Expressions for the swelling of linear ionic polymers based upon the electrostatic repulsion concept have been derived by Katchalsky *et al.* (35). For the sake of brevity the osmotic pressure concept developed by Flory will be presented here.

When a polyelectrolyte is ionized, as for example when polyacrylic acid in dilute aqueous solution is neutralized with sodium hydroxide (Figure 10), the concentration of the mobile sodium ions will always be greater in the gel than outside because of the attracting power of the fixed negatively charged carboxyl groups. Consequently the osmotic pressure of the solution inside will exceed that of the external solution and the expansive force may be equated to these differences in osmotic pressures of the two solutions. The osmotic pressure (20, p. 587) arising from the difference in mobile ion concentrations between the gel and the external solution will be:

$$\pi_i = RT\left[C_+ + C_- - (C_+^* + C_-^*)\right] \tag{13}$$

where π_i = the difference in osmotic pressure caused by the difference in mobile ion concentrations

R = gas constant

T = absolute temperature

$C_+ + C_-$ = total mobile ion concentration inside the gel at equilibrium

$C_+^* + C_-^*$ = total mobile ion concentration outside the gel.

If a polyacid gel is highly ionized the C_+ term (in the case of our example, the sodium ions within the gel) will increase in an effort to maintain electro-neutrality within the gel, causing a greater expansive force π_i. When a small concentration of a salt such as sodium chloride is added to the solution the concentration of the external mobile ions $C_+^* + C_-^*$ increases relative to the concentration of the internal mobile ions $C_+ + C_-$ and the expansive force π_i is greatly reduced. The gel, though still ionized, returns to the randomly kinked configuration indicated at the left of Figure 8.

Katchalsky and Swick (37) 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 equations 9, 11 and 12 is one of the experimental objectives of this study.

Chelation of polyacids

Whereas the ionic character of polyacids permits a 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 water-proofing 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 as illustrated in Figure 11.

Many cations other than the transition metals react with strong electron donors such as nitrogen, sulfur and oxygen to form similar ring structures in which the metal bonds are essentially ionic. The term chelate is applied to these ring structures whether the metal bonds are essentially ionic or covalent. Chelates in which the metal bonds are essentially covalent are termed inner-complex salts (39).

Martell and Calvin (39, p. 183) point out that the factors which govern the relative tendencies for various metals to combine with a given electron donor may be divided into two classes: (1) the ionic forces which are related to both charge and radius of the metal ion, and (2) the relative tendencies of various metals to form homopolar bonds with electron donors. Regarding class (1), studies of ion exchange equilibria in polyelectrolytes (40) have shown general agreement with the results of the classical Hoffmeister-series investigations. More highly charged ions are generally adsorbed in preference to those of less charge and among ions of the same charge, those having smaller hydrated radii are usually adsorbed in preference to those of larger hydrated radii. Regarding class (2), Mellor and Maley (41) point out that as a first approximation the stability of metal chelates seems to decrease with increasing basicity of the metal,

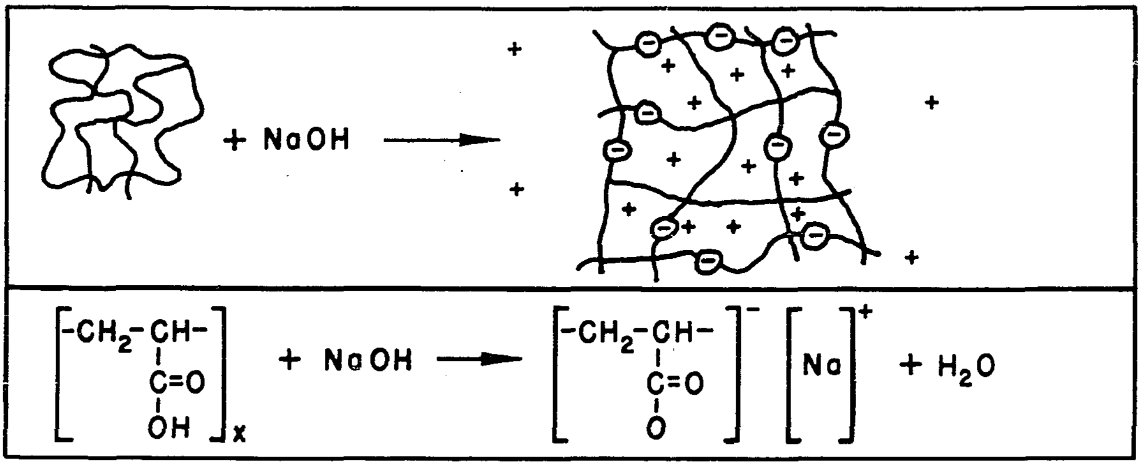


Fig. 10. Neutralization of a polyacrylic acid gel in dilute aqueous solution with sodium hydroxide.

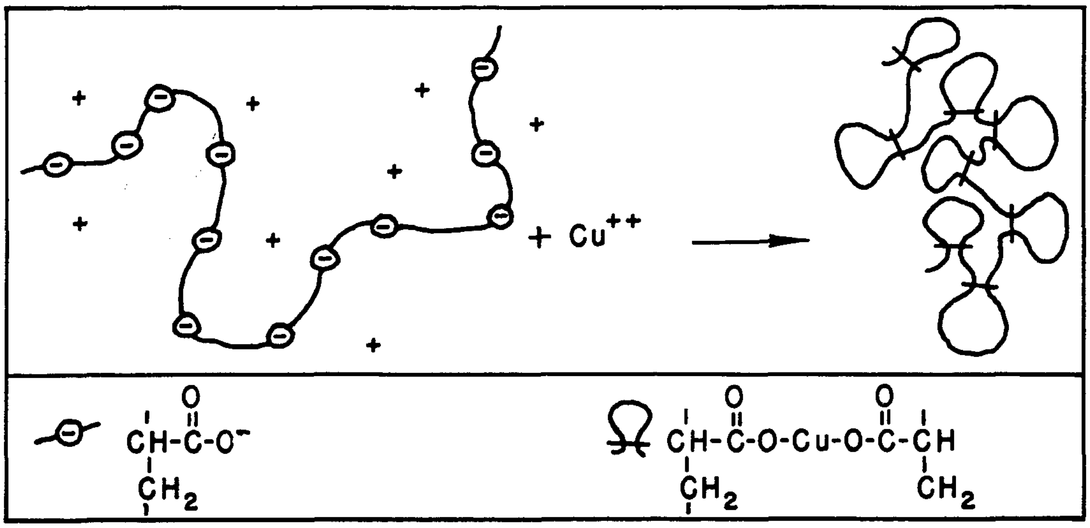


Fig. 11. Contraction and water-proofing of a polyacid chain by chelation with a transition metal.

weakly basic copper forming the strongest, and the most strongly basic metal, magnesium, forming the weakest chelates. Thus the metals which can form the strongest homopolar bonds generally form the most stable chelates.

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 water-proofing and tensioning of the polyacid chains. The effects of the following variables upon the immersed strength of a silty loam C-horizon loess were studied:

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

Evaluation of various polyacids used with Arquad 2HT

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

Soil specimens were prepared and tested by the following procedure:

1. Add Arquad 2HT in aqueous suspension to 700 grams 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-inch diameter by 2-inch 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 hours before testing them in unconfined compression.

Figure 12 shows the compressive strength of the silty loam as a function of Arquad 2HT as the only additive. Arquad 2HT hydroxide, represented by the solid line in Figure 12, was prepared by mixing equivalent amounts of potassium hydroxide and the quaternary ammonium chloride in isoproponol and filtering off the precipitated potassium chloride. For later investigations Arquad 2HT hydroxide was obtained from Armour and Company, Chicago, Illinois. As indicated in Figure 12 the chloride and hydroxide forms of Arquad 2HT yield approximately equal strengths, a slight decrease in the immersed strengths occurring above 0.2% treatment in each case. The percentages of treatment indicated in Figure 12 and subsequent graphs are based on the solid weights of chemicals added in solution and on air-dry weight of the soil.

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

When Arquad 2HT chloride was mixed in dilute aqueous solution with the various polyacids disperse floccules were formed. When Arquad 2HT hydroxide was mixed with the polyacids the floccules formed were much denser and precipitated more quickly 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 (42), Kressman and Kitchener (43) and Terayama (44). Iler found that mixtures of long chain quaternary ammonium ions with polymetaphosphoric acid were readily precipitated from aqueous solutions as gummy solids. Kressman and Kitchener observed that the affinity of certain large organic cations, including quaternary ammonium salts, for a polyanionic resin increases with increasing size of the cation, also suggesting the importance of van der Waals attraction.

The compressive strengths of the silty loam treated with 0.2% Arquad 2HT plus 0.6% of the various polyacids and polyacid salts are shown in Figure 13. All strengths in Figure 13 and the following graphs are immersed strengths. The three polyacids giving best results, Acrysols A-1, A-3 and A-5, are members of a homologous series of polyacrylic acids. Acrysol A-1, having the lowest molecular weight, gave the greatest strength, whereas Acrysol A-5, having the highest molecular weight, gave the lowest strength of the three.

One factor which may contribute to this inverse relationship between molecular weight of the polyacid and strength of the stabilized soil is the effect that polyacid chain length would have on the probability of a polyacid molecule coming to rest between two organic cations. Assuming the mineral surface area for one cation exchange position is 80 A^2 (30, p. 134) and that the organic cations lying flat on the mineral surfaces (4) each occupy 120 A^2, the organic cations cover only 5.8% of the area represented by exchangeable cation positions alone. Although no distinction was made between

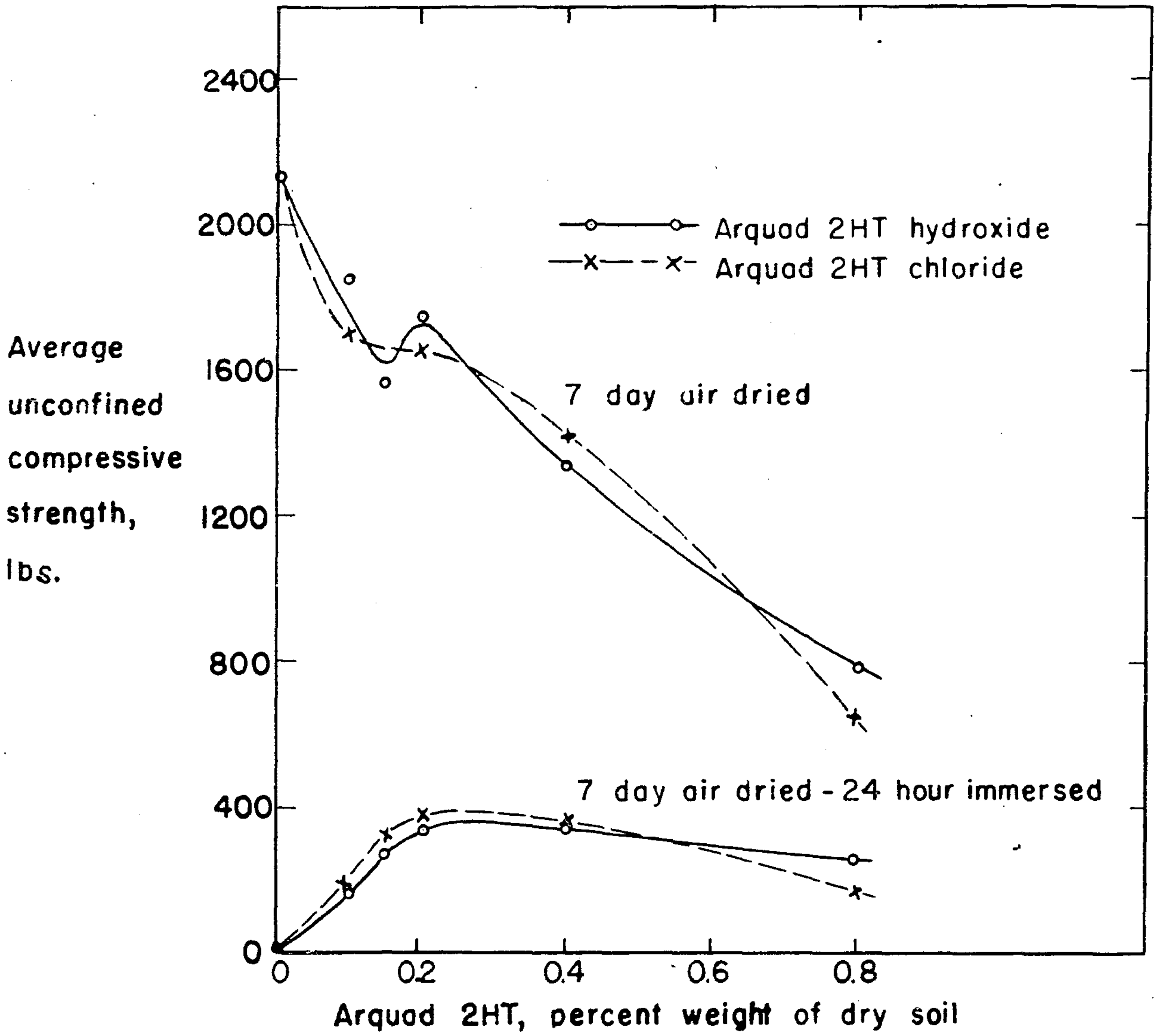


Fig. 12. Effect of amount of Arquad 2HT on unconfined compressive strength of the silty loam. Test specimens were 2 inches in diameter and 2 inches high.

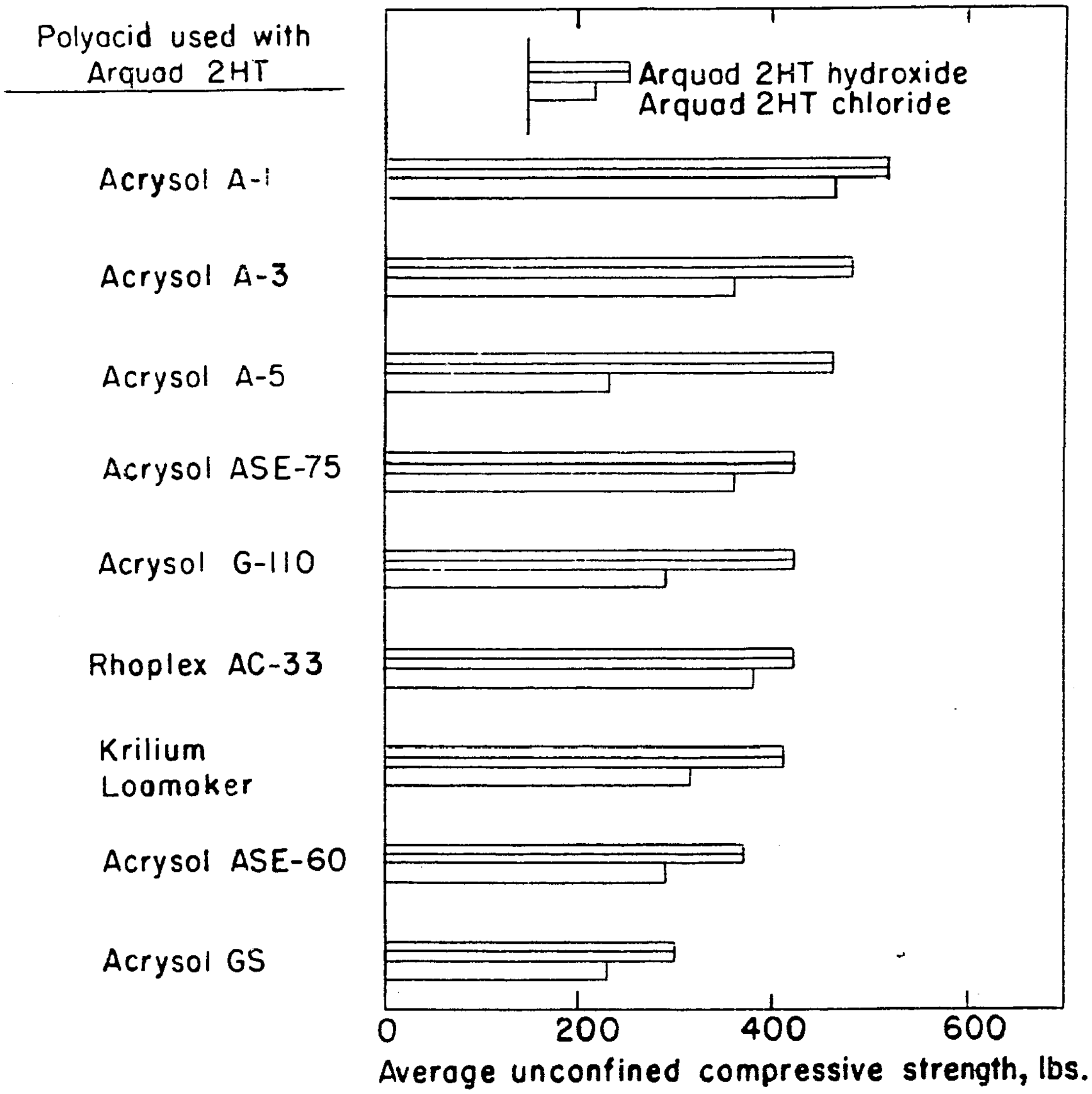


Fig. 13. Unconfined compressive strengths of the silty loam treated with 0.6% of various polyacids and polyacid salts and 0.2% of either Arquad 2HT hydroxide or Arquad 2HT chloride. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

interlayer cation exchange positions and cation exchange positions on the exterior surfaces in arriving at this value, it may, nevertheless, give some idea of the area covered by the organic cations. It is significant in illustrating that, for a random distribution, the probability of two organic cations on neighboring mineral particles being in close proximity is quite small. In the process of mixing, the number of cation-polyacid-cation bonds formed would seem to be a function of the number of polyacid molecules, the portion of mineral surface area covered by the organic cations, and the type of mixing and length of mixing time. For a given weight of polyacid added to the soil the number of molecules coming to rest between adjacent organic cations will be statistically greater for the lower molecular weight fraction of polyacid. Theoretically, it would seem that for a given weight of polyacid the strength of the treated soil should increase with decreasing molecular weight to a point where the average polymer chain becomes shorter than the length required to bridge the mean gap between two neighboring organic cations.

The Arquad 2HT hydroxide was found to produce greater strength with each of the polyacids than did Arquad 2HT chloride (Figure 13). In agreement with the results of flocculations 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.

Since Arquad 2HT is commercially available as a chloride salt the possibility of using the chloride form and adding inorganic bases such as sodium hydroxide and potassium hydroxide was investigated as an alternative to using Arquad 2HT hydroxide. Figure 14 shows the strength of the soil treated with 0.2% Arquad 2HT chloride plus 0.6% Acrysol A-1 as a function of the amounts of sodium and potassium hydroxides added with the Acrysol A-1. In comparing the sodium hydroxide and potassium hydroxide curves it may be recalled that sodium ions, being highly hydrated at high moisture contents, act as a strong dispersing agent in most soils whereas potassium ions do not. In the case of sodium hydroxide the increased bonding of polyacid to cations caused by ionization of the polyacid by hydroxyl ions is apparently offset by the dispersing action of sodium ions. The lower strength of the soil treated with Arquad 2HT and Acrysol GS, the sodium salt of Acrylic acid (Figure 13) might also be partly due to this phenomena. Potassium on the other hand is not a strong dispersing agent and higher strengths occur throughout the entire potassium hydroxide range, indicated by the solid line in Figure 14.

For comparison with the results of Figure 14 similar curves were obtained by replacing the Arquad 2HT chloride with Arquad 2HT hydroxide (Figure 15). As indicated, the Arquad 2HT hydroxide gave strength values slightly greater

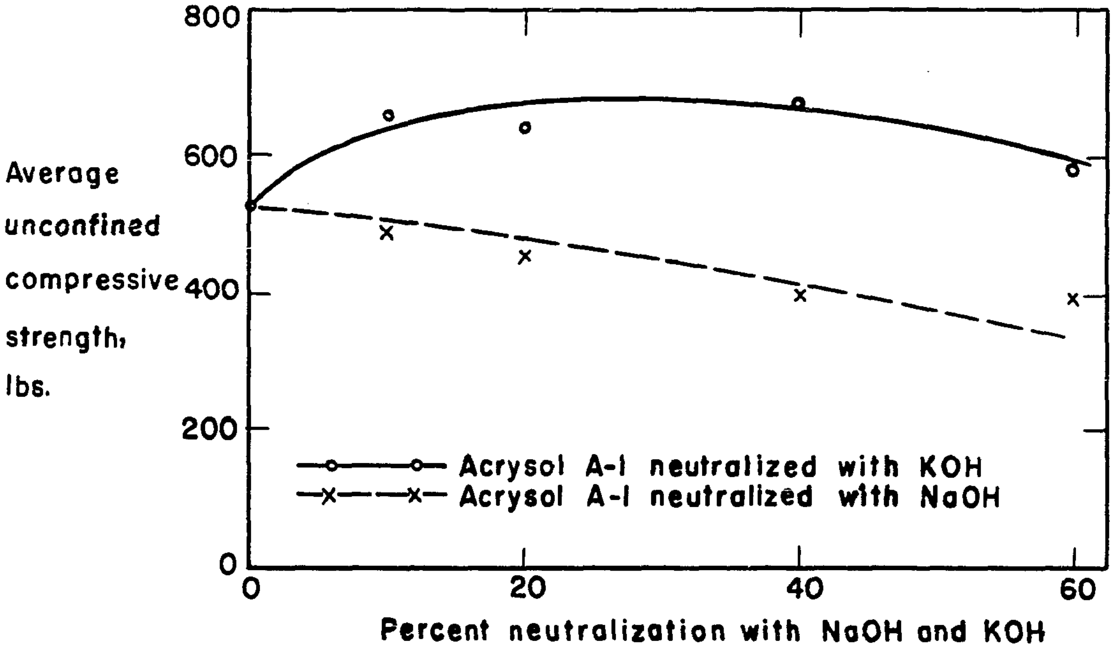


Fig. 14. Unconfined compressive strengths of the silty loam treated with 0.2% Arquad 2HT chloride and 0.6% Acrysol A-1 as a function of per cent neutralization of Acrysol A-1 with NaOH and KOH. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

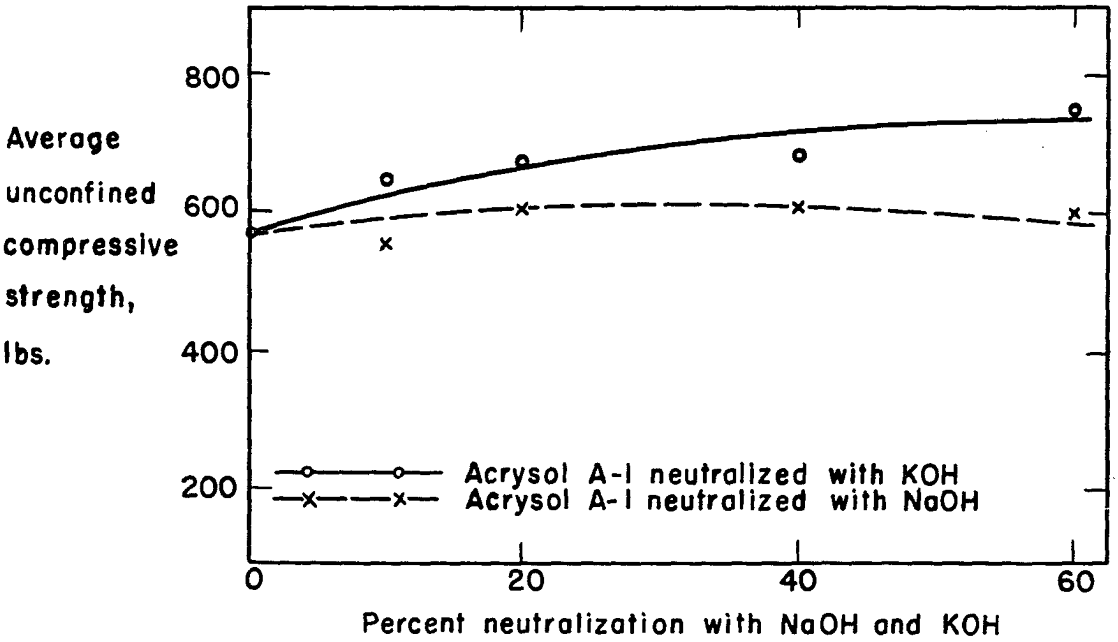


Fig. 15. Unconfined compressive strengths of the silty loam treated with 0.2% Arquad 2HT hydroxide and 0.6% Acrysol A-1 as a function of per cent neutralization of Acrysol A-1 with NaOH and KOH. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

than those for Arquad 2HT chloride.

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 content (Figure 16). It is interesting to compare the curves for immersed strength in Figure 12 with the strength contour curves in Figure 16. When Arquad 2HT is used alone (Figure 12) an optimum amount of Arquad 2HT is reached for maximum immersed strength whereas when Arquad 2HT is used with polyacrylic acid (Figure 16) an increase in Arquad 2HT content at any point on the graph yields an increase in immersed strength. Apparently when Arquad 2HT and polyacrylic acid are used together the increase in strength contributed by cation-polyacid-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 16 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.

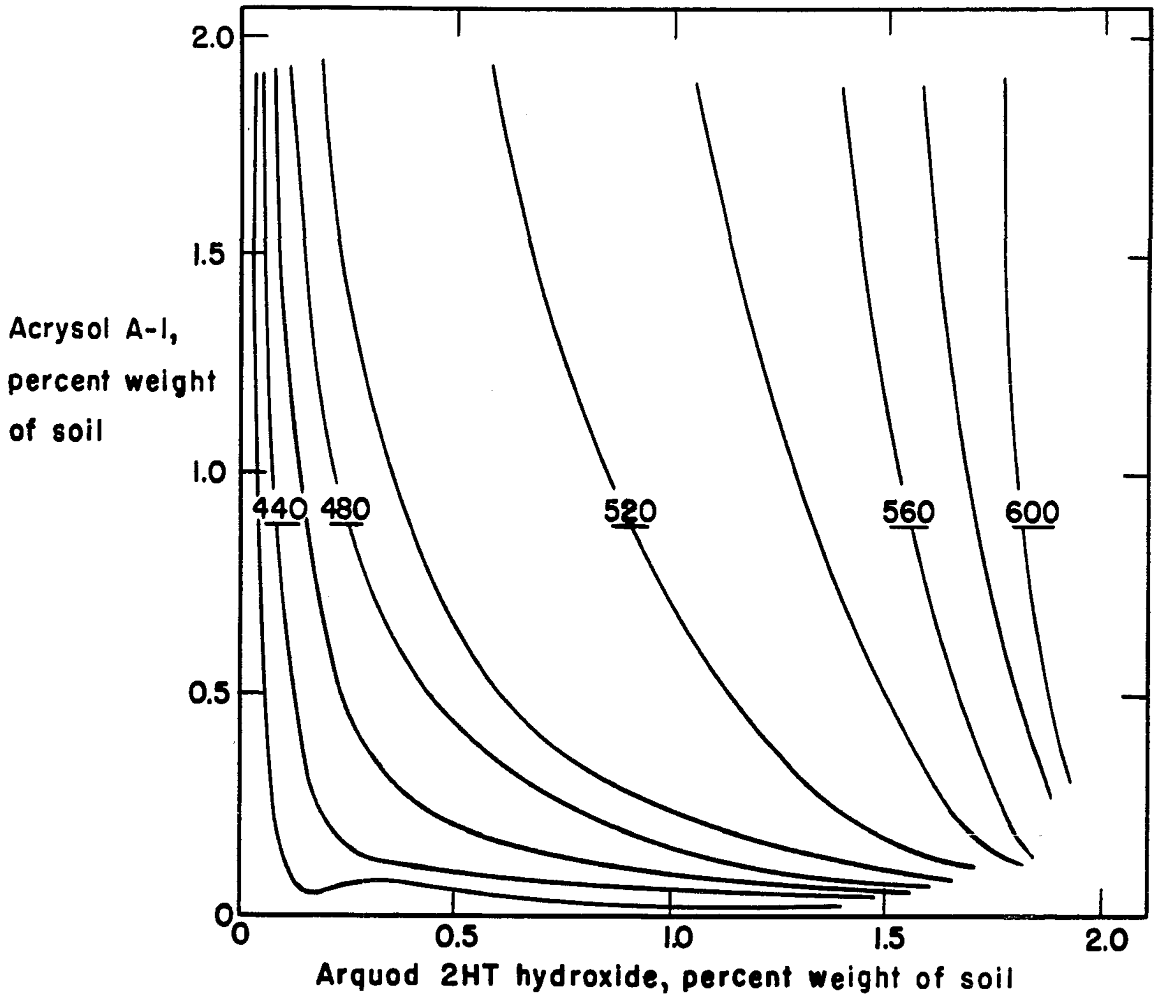


Fig. 16. Contours showing the relationship of unconfined compressive strength of the soil to Arquad 2HT hydroxide and Acrysol A-1 contents. Contours indicate 20 lb. increments of strength for 2 inch high by 2 inch diameter soaked specimens.

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 water-proofing of polyacid molecules. Since 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 principal outlined on page 41, was determined by viscosity measurements and by use of the equation:

$$\alpha^3 = \frac{[\eta]}{[\eta]_0} \qquad (14)$$

where α^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 (46). Viscosities were measured with an Ostwald viscometer at 30° C. (flow time of water = 2 min. 56 sec.). Figure 17 shows the linear expansion factor α as a function of the per cent neutralization with sodium hydroxide and Figure 18 shows the expansion factor for 100% neutralized Acrysol A-1 extrapolated to zero concentration.

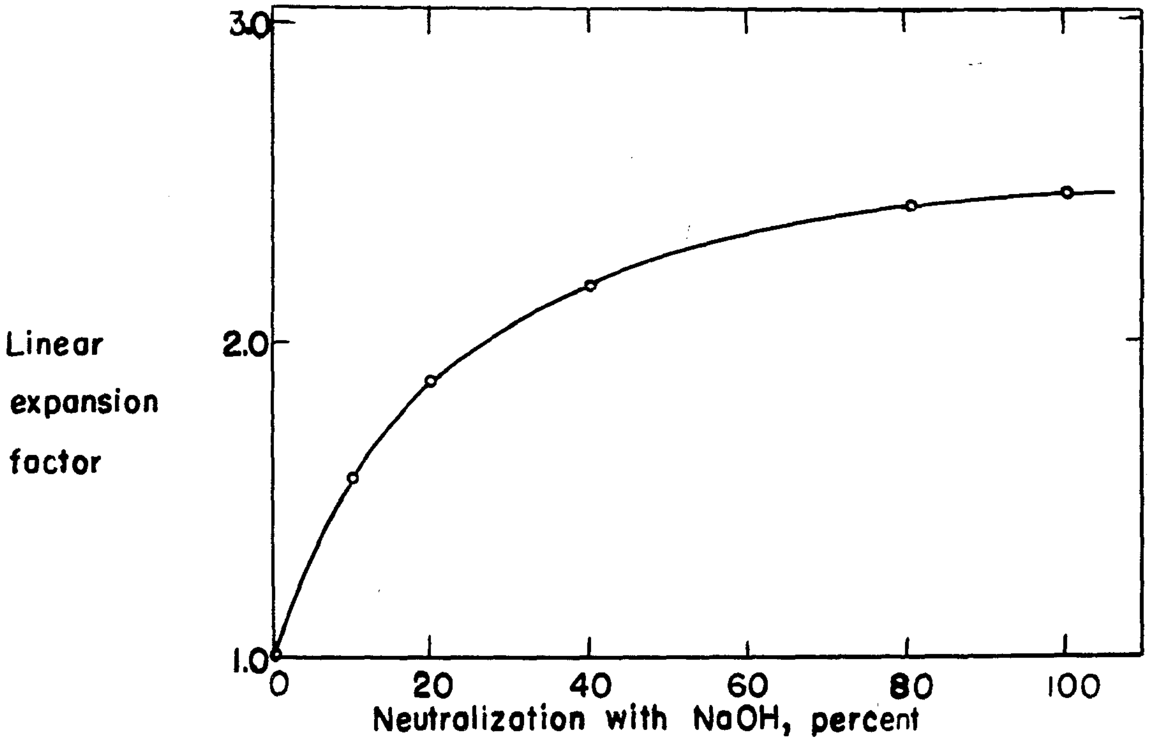


Fig. 17. Linear expansion factor of Acrysol A-1 in 0.5% aqueous solution as a function of per cent neutralization with sodium hydroxide.

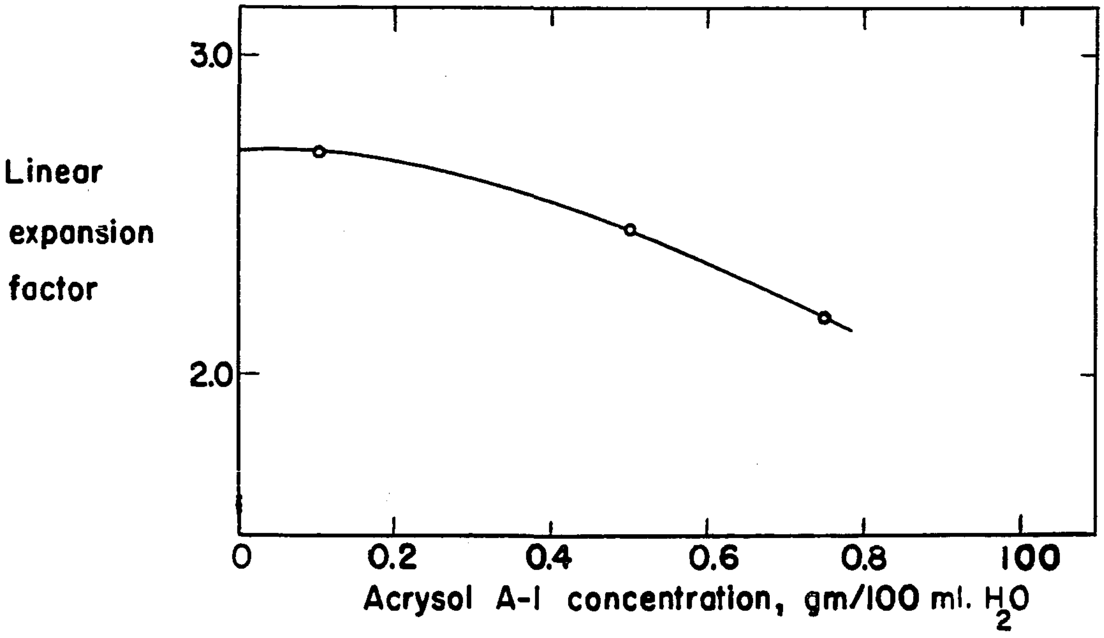


Fig. 18. Linear expansion factor of Acrysol A-1 100% neutralized with NaOH as a function of concentration.

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 19. 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 an inner complex salt. The only ionic groups in Acrysol A-1, the $-COO^-$ groups, have apparently been rendered inactive by covalent bonding with iron, causing water-insolubility.

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

The results of pH measurements obtained by titrating Acrysol A-1 with these same salts, Figure 20, are in close agreement with the results of the viscosity measurements, Figure 19. It is obvious from Figure 20 that the ferric chelate is very strong whereas the tendency for the alkaline

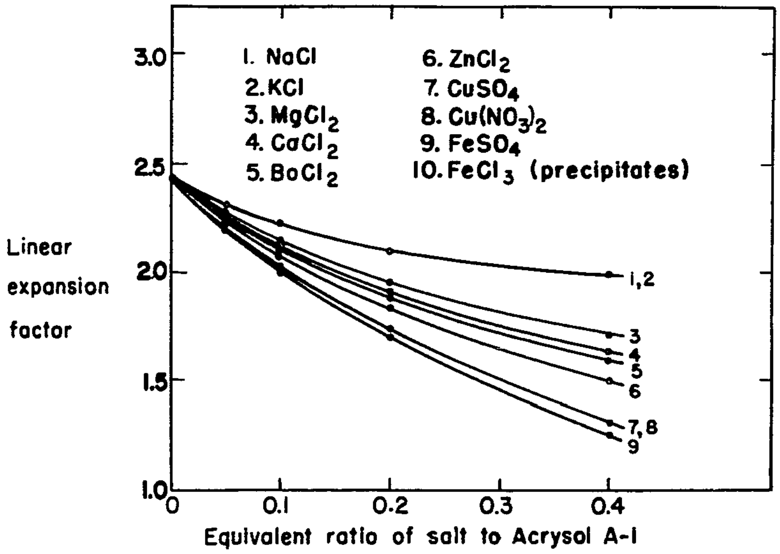


Fig. 19. Linear expansion factor of Acrysol A-1 in 0.5% aqueous solution 80% neutralized with sodium hydroxide in the presence of various salts.

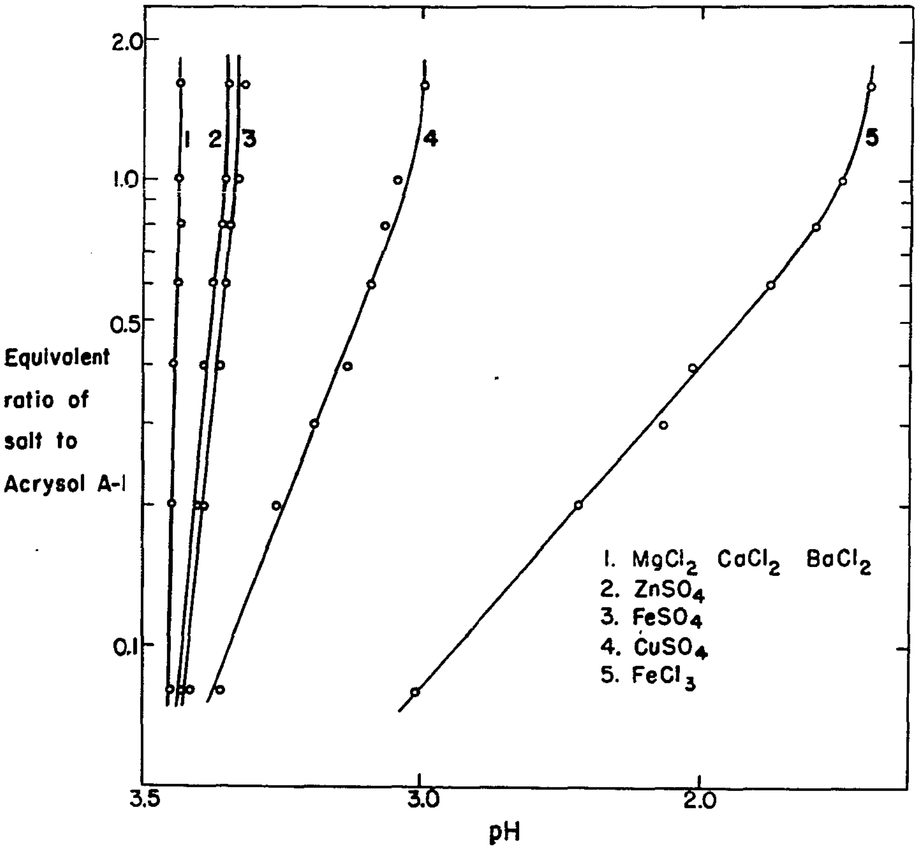


Fig. 20. pH titration curves for 0.0116 N. Acrysol A-1 solution with various salts.

earth metals, magnesium, calcium and barium, to form chelates is quite weak. All metal ions assume approximately the same relative positions in Figures 19 and 20 with the exception of the ferrous ion. Since the data in Figure 19 were obtained for 80% neutralization of the polyacid whereas Figure 20 represents no neutralization, this displacement of the ferrous curve may indicate a greater pH dependency for ferrous chelate formation than for chelation with the other ions investigated.

A comparison of the distances H_1 and H_2 in Figure 21 indicates that a given amount of copper causes greater contraction of the polyacid molecules at low percentages of neutralization. H_1 is the contraction occurring with a copper-Acrysol A-1 equivalent ratio of 0.05 for 80% neutralization. H_2 is the contraction for the same equivalent ratio of salt to polyacid at 10% neutralization. If the polyacid is first neutralized to enable ionic bonding to the organic cations in the soil and subsequently chelated to stretch the polyacid chains, this relationship between H_1 and H_2 may be significant from the standpoint of economy of the chemicals used to elongate and contract the polyacid chains.

In Figure 22 the contraction caused by copper ions at 10% neutralization is compared with the contractions caused by ferrous and ferric ions. The fact that the ferrous curve

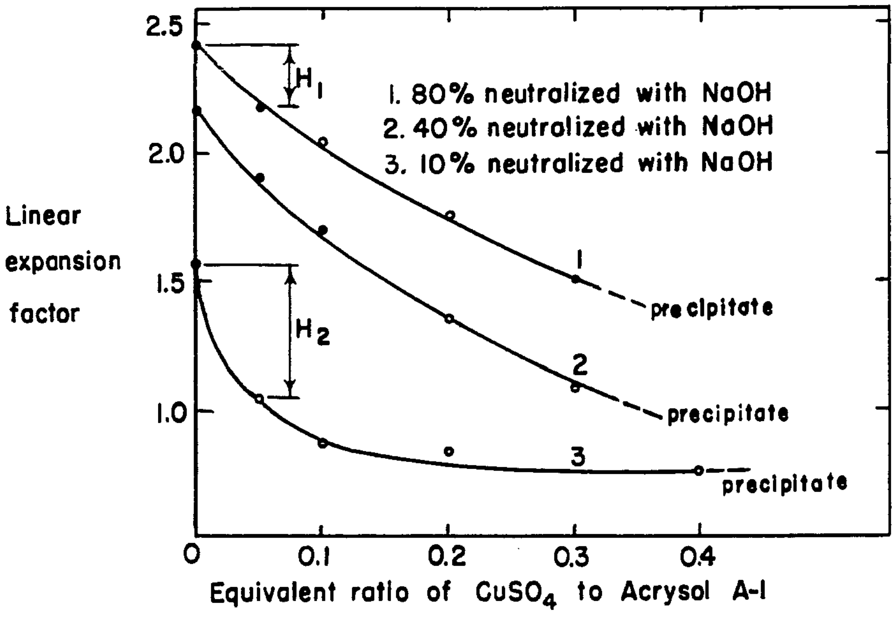


Fig. 21. Linear expansion factor of Acrysol A-1 in 0.5% aqueous solution as a function of per cent neutralization with sodium hydroxide and of copper sulfate concentration.

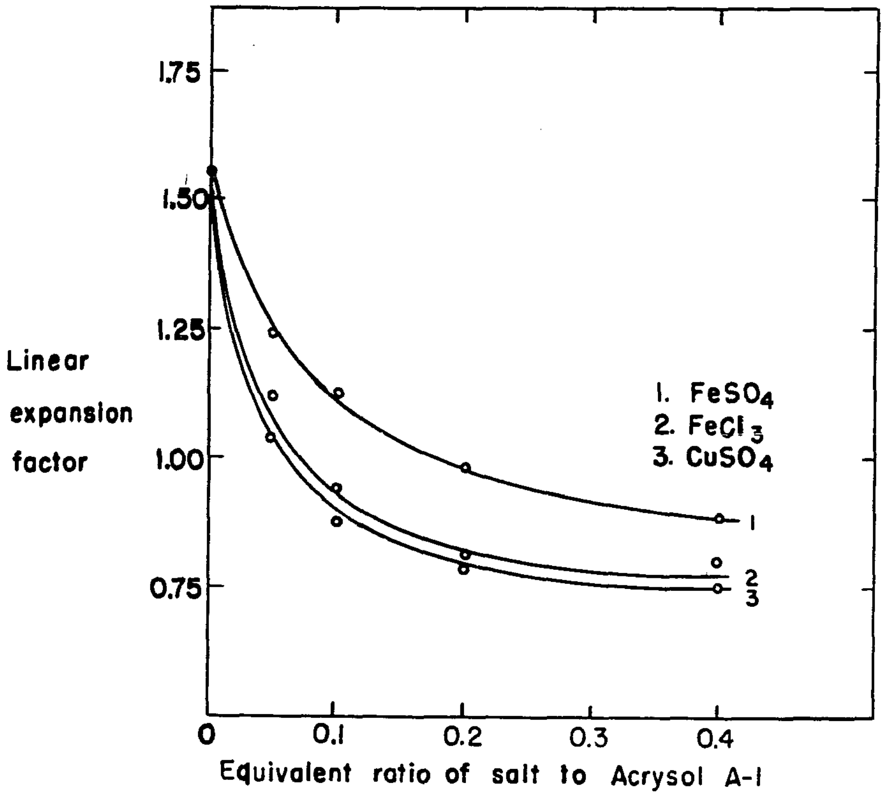


Fig. 22. Linear expansion factor of Acrysol A-1 in 0.5% aqueous solution 10% neutralized with sodium hydroxide in the presence of copper and iron salts.

now lies above the copper curve, corresponding more closely to the results in Figure 19 than to those in Figure 18, seems to again indicate a greater pH dependency of ferrous chelate formation.

As mentioned previously, the fact that ferric ions precipitated Acrysol A-1 under the conditions represented in Figure 19 is suggestive of inner complex salt formation. To learn more about the water-proofing nature of copper, ferrous and ferric ions with polyacrylic acid optical density measurements were made. The use of optical density measurements, now a common identification test for metal chelates, is based on the work of McKenzie _et_ _al_. (47a) and others who found that ionic chelates have adsorption spectra similar to those of the two reactants whereas covalently bonded chelates have adsorption bands characteristic of the chelate and hence of the metal bond.

Figures 23 and 24 show curves obtained by plotting optical density against the per cent neutralization of Acrysol A-1 with sodium hydroxide in the presence of various amounts of ferrous, ferric and copper ions. The optical densities shown are the differences between readings of the chelates and of the metal salts. Readings were taken with a Klett Immerson model 800-3 photoelectric colorimeter using a blue filter.

It is interesting to compare the optical density curves

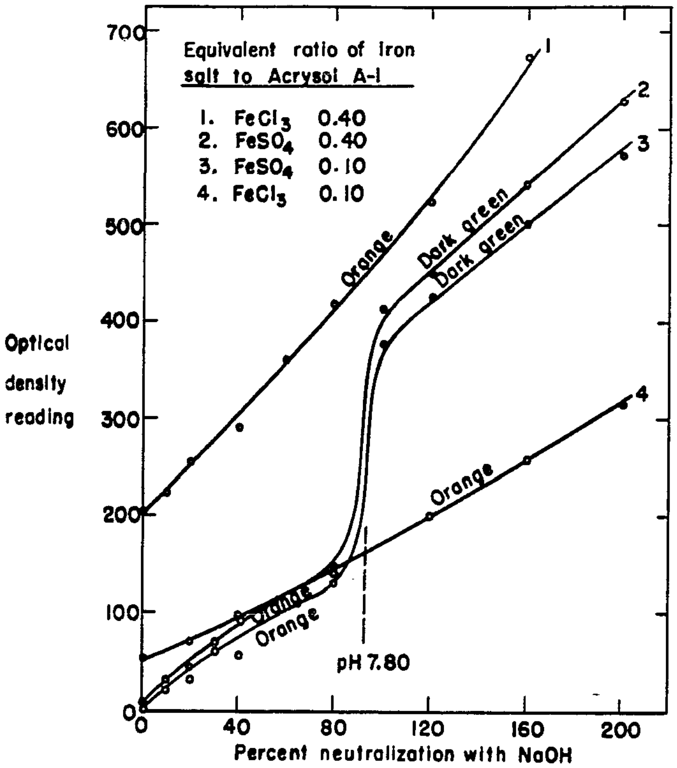


Fig. 23. Optical densities of Acrysol A-1 in 0.25% aqueous solution equilibrated with various concentrations of $FeSO_4$ and $FeCl_3$ as a function of neutralization with NaOH.

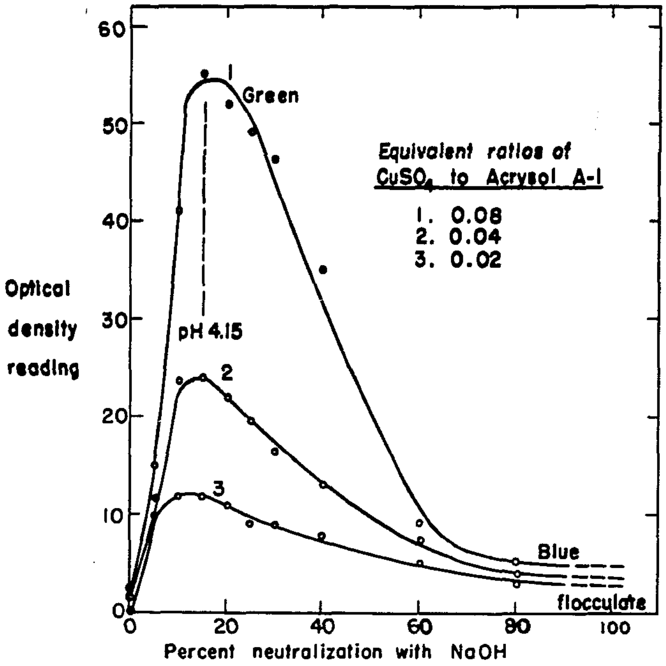


Fig. 24. Optical densities of Acrysol A-1 in 2.5% aqueous solution equilibrated with various concentrations of $CuSO_4$ as a function of per cent neutralization with NaOH.

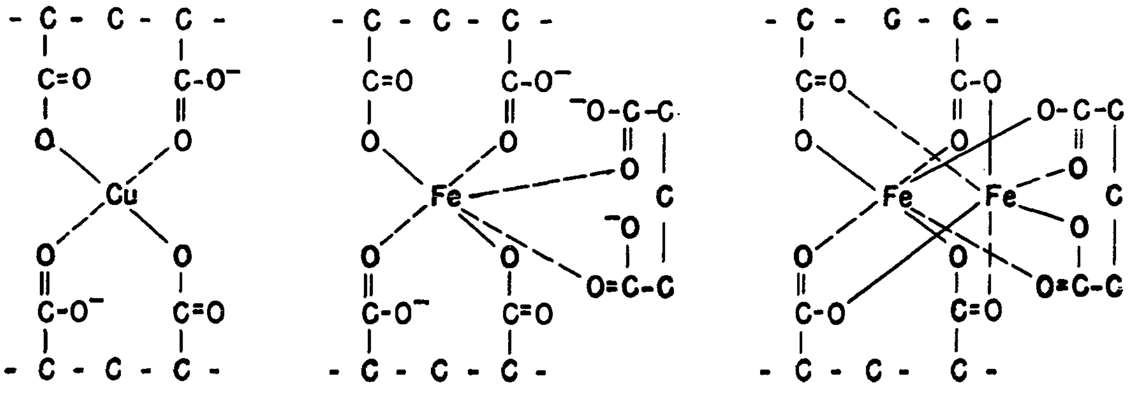
of Acrysol A-1 in the presence of ferrous and ferric ions, Figure 23. The sudden color change in the presence of ferrous ions at approximately 100% neutralization with sodium hydroxide is apparently caused by an alternate resonance form in the ferrous chelate.

The optical density of the copper chelate (Figure 24) passes through a maximum at about 15% neutralization of Acrysol A-1 with sodium hydroxide. At higher percentages of neutralization the green color of the chelate is gradually replaced by the blue color of copper hydroxide. These curves illustrate the critical dependence of copper chelate formation upon pH, an important factor to consider if it were used for soil stabilization. The low concentration of the chelate at low percentages of neutralization is apparently due to the competition of hydrogen ions with copper ions for the polyacrylic acid, whereas at pH values above the optimum for chelation the equilibrium is shifted from the copper chelate to copper hydroxide.

In general, the number of chelate donor groups which can combine with a metal ion corresponds with the coordination number of that ion. Copper, with a coordination number of four, is almost always found in a square planar configuration whereas iron, with a coordination number of six, assumes octahedral coordination (39, p. 246). Suggested structures for the copper, ferrous and ferric chelates are shown in Figure 25. In the ferrous chelate (Figure 25b) a color change may be caused by displacement of the C=O double bond when a proton is removed from the carboxylate group by sodium hydroxide. In the structure suggested for the ferric chelate (Figure 25c) there are no carboxylate groups from which protons can be removed and therefore no color change would be possible. The fact that the ferric chelate precipitates more readily than the ferrous chelate (Figure 19) also seems to suggest a structure less polar than that of the ferrous chelate, in accordance with Figures 25b and 25c. Steric limitations to the structure in Figure 25c however have not been investigated.

Whether chelation with copper, ferrous and ferric ions is intramolecular, as represented for the copper ion in Figure 25d, or intermolecular, as in Figure 25e, is probably statistical, depending upon the concentration of the polyacid chains. If the polyacid were used in sufficient concentration in the soil to permit gelation, *i.e.*, formation of a continuous network structure by intermolecular chelation, the bonding of soil particles would be effected by a continuous macromolecule, providing greater rigidity.

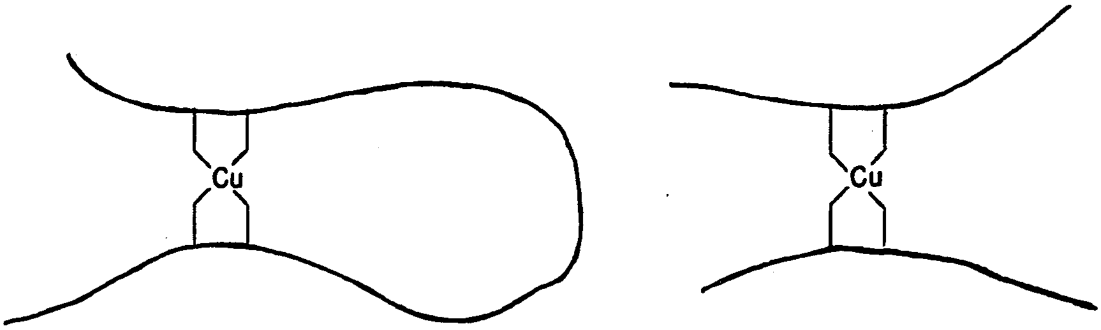
Ferrous and ferric salts in the low solubility range were chosen for use with Acrysol A-1 in preparing test specimens of the soil. It was believed that slightly soluble salts would allow time for mixing the chemicals, for



a. Copper-polyacrylic acid chelate

b. Ferrous-polyacrylic acid chelate

c. Ferric-polyacrylic acid chelate



d. Intramolecular chelation with copper

e. Intermolecular chelation with copper

Fig. 25. Suggested chelate structures for polyacrylic acid with copper, ferrous and ferric ions.

compacting the specimens and for bonding between polyacid and organic cations to occur before a sufficient number of metal ions became available to react with the remaining acid groups, rendering the polymer chains insoluble.

Several slightly soluble ferrous and ferric salts are listed in order of their solubilities in Table 4a.

Table 4a. Solubilities of slightly soluble ferrous and ferric salts

Salt	Water solubility, parts per 100 parts of water by weight
FeS	0.00061 @ 18° C.
$Fe_2(SO_4)_3 \cdot XH_2O$	-
$FeCO_3$	0.0065 @ 20° C.
$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$	18 @ 0° C.
$FeSO_4 \cdot 7H_2O$	32.8 @ 0° C.

A comparison of Table 4a and Figure 26 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 six hour period (curves 2, Figure 26). 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 26 was to

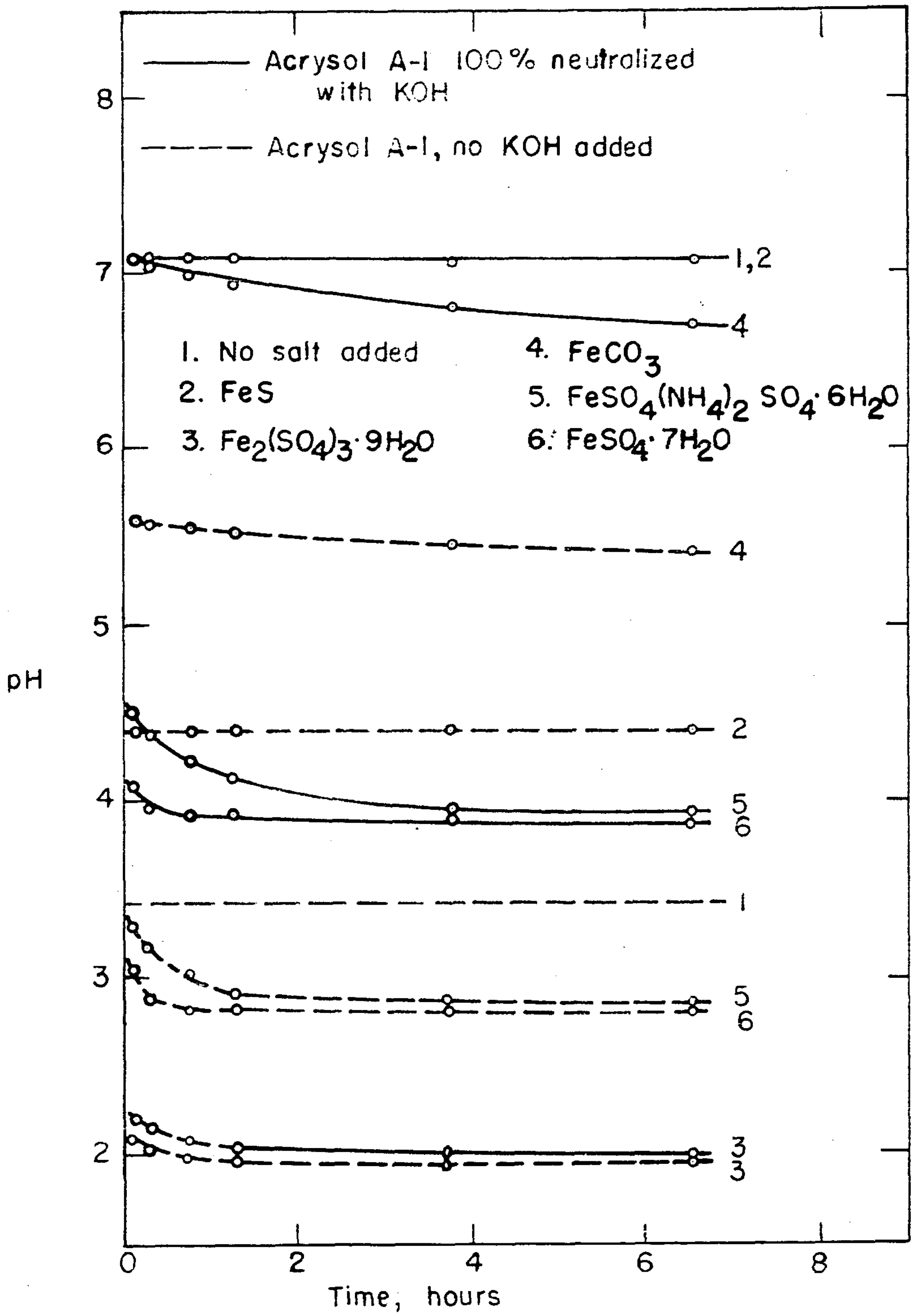


Fig. 26. pH-time plots for 0.116 N aqueous solutions of Acrysol A-1 in the presence of slightly soluble ferrous and ferric salts. Salts added in excess of their solubility limits.

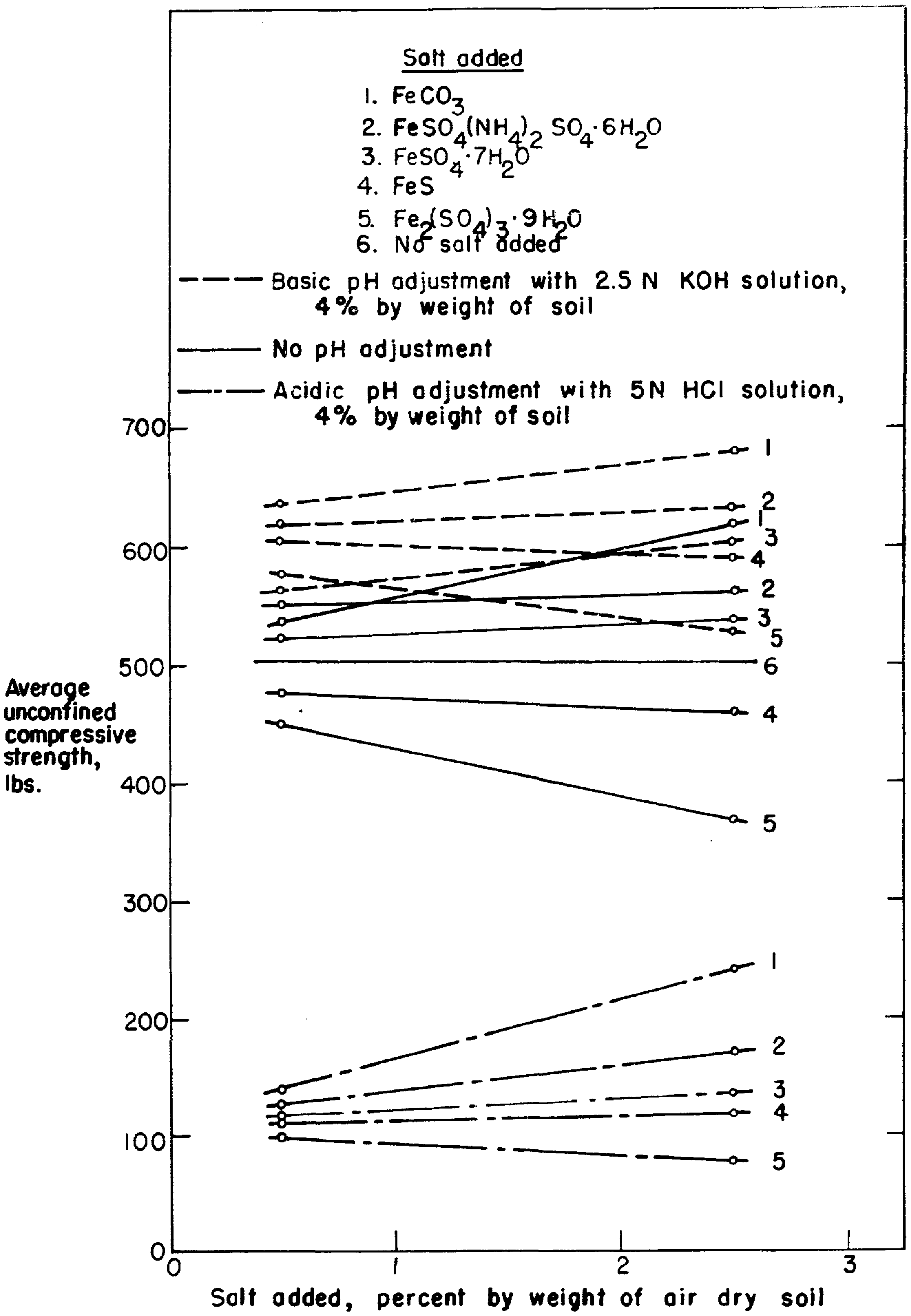
determine what solubility range of iron salts would be appropriate for allowing a mixing and compacting period of approximately half an hour and still react with Acrysol A-1 within a few hours after compaction (before loss of moisture from the soil due to air drying). Of the salts shown in Figure 26 ferrous ammonium sulfate and ferrous carbonate appear optimum in this respect. The remaining three salts either react too quickly or else show very little reaction at the end of six hours. 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 26.

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 27 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

Fig. 27. Unconfined compressive strength of the silty loam treated with 0.2% Arquad 2HT hydroxide, 0.6% Acrysol A-1 and slowly soluble ferrous and ferric salts. Strengths of 2 inch high by 2 inch diameter specimens measured after 7 days air curing and 24 hours immersion in water.


Salt added
1. $FeCO_3$
2. $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$
3. $FeSO_4 \cdot 7H_2O$
4. FeS
5. $Fe_2(SO_4)_3 \cdot 9H_2O$
6. No salt added
Basic pH adjustment with 2.5 N KOH solution, 4% by weight of soil
No pH adjustment
Acidic pH adjustment with 5N HCl solution, 4% by weight of soil
Average unconfined compressive strength, lbs.
0
100
200
300
400
500
600
700
0
1
2
3
Salt added, percent by weight of air dry soil
1
2
1
3
4
2
3
5
6
4
5
1
2
3
4
5

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

The most obvious trend indicated by Figure 27 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 (see Figure 21) 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 28 shows that a basic pH adjustment has little effect on the immersed strength of Arquad 2HT treatments but produces a prominent strength peak for samples treated with both Arquad 2HT and Acrysol A-1. Figures 27 and 28 taken together suggest that the beneficial effect of a basic pH adjustment is probably due more to increased bonding between the ionized polyacid and the large organic cations than to an increase in chelation of the polyacid by the metal ions.

An additional study of the Arquad 2HT-Acrysol A-1-ferrous carbonate system indicated immersed strength varies directly

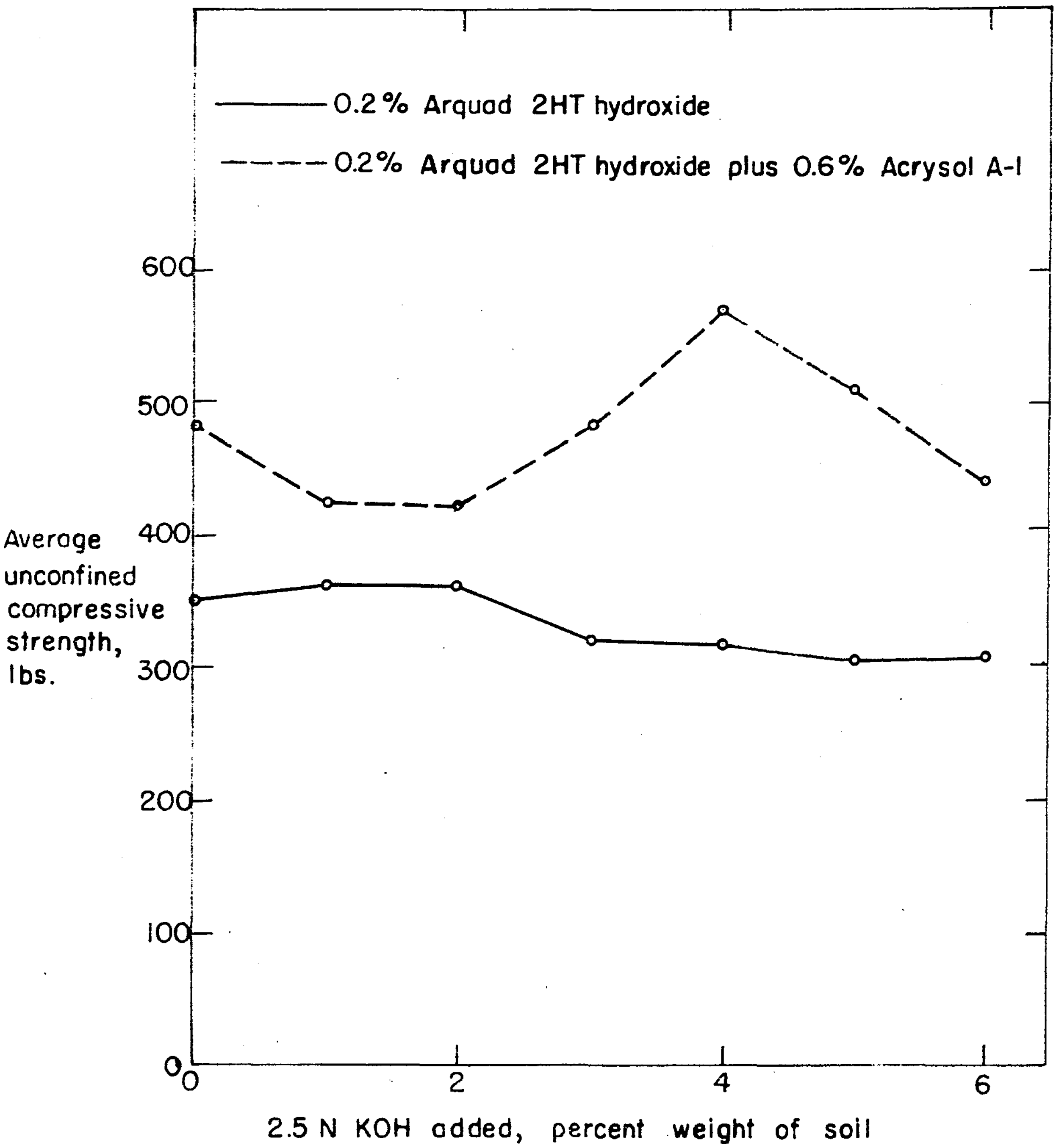


Fig. 28. Unconfined compressive strength of the silty loam treated with 0.2% Arquad 2HT hydroxide alone and 0.2% Arquad 2HT hydroxide plus 0.6% Acrysol A-1 as a function of basic pH adjustment with KOH. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

with Acrysol A-1 and ferrous carbonate contents and inversely with Arquad 2HT content to a minimum limit of 0.1% of Arquad 2HT (Figure 29). Samples containing less than 0.1% Arquad 2HT have reduced strengths. Strength values for the combination of admixtures giving maximum strength in Figure 29, represented by the dotted circle, are shown as a function of alkalinity adjustment with potassium hydroxide by the solid line in Figure 30. Figures 28 and 30 show that the optimum amount of 2.5N potassium hydroxide is about 4% by weight of soil regardless of whether or not ferrous carbonate is added. The strength peak for samples containing ferrous carbonate (Figure 30), however, is higher than for samples not containing ferrous carbonate (Figure 28).

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. All samples containing ferrous carbonate alone and ferrous carbonate with Acrysol A-1 slaked in water. On the basis of these results it appears that the chelation of ferrous ions

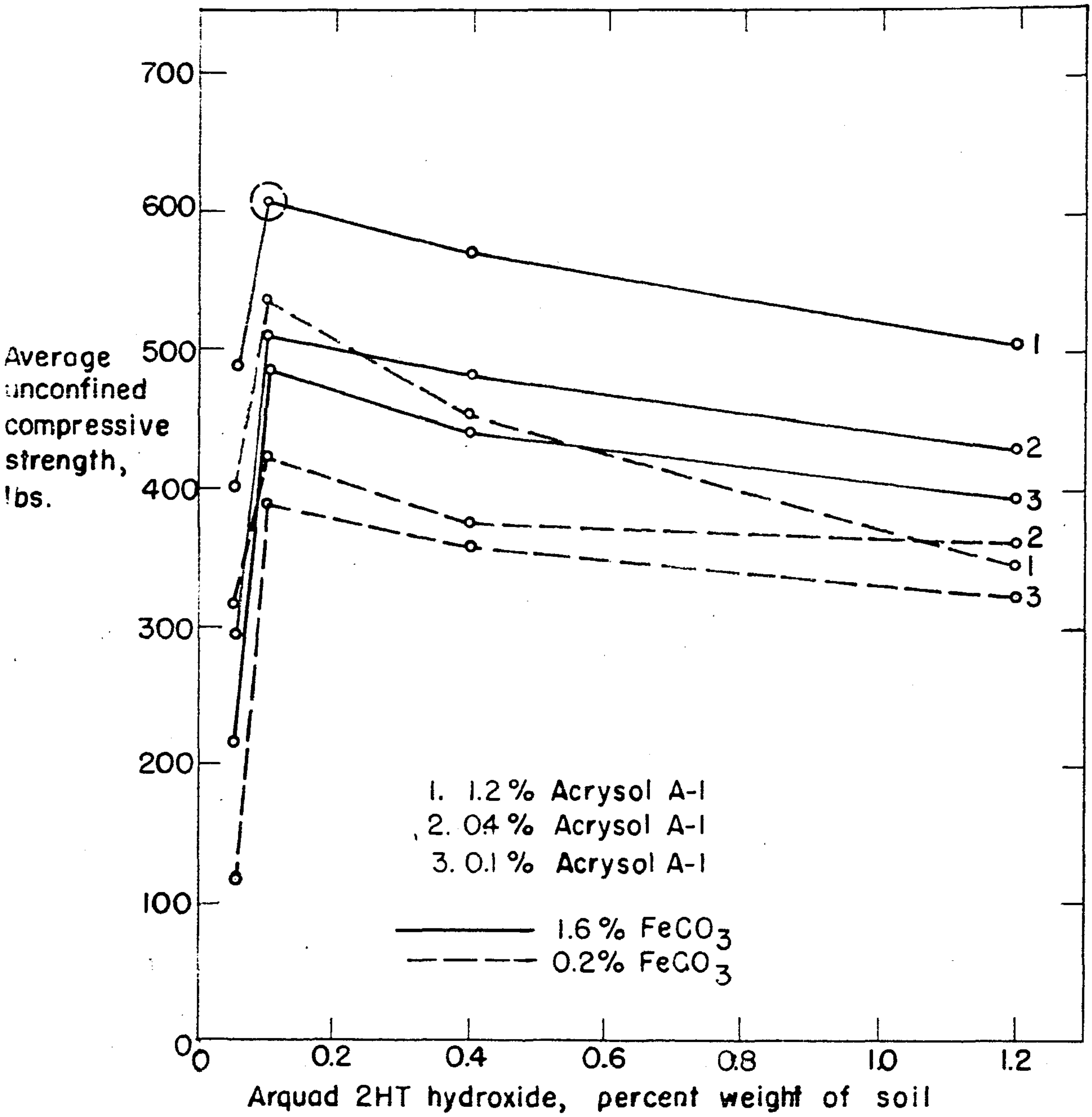


Fig. 29. Unconfined compressive strength of the silty loam treated with various percentages of Arquad 2HT hydroxide, Acrysol A-1 and ferrous carbonate. Strengths of 2 inch high by 2 inch diameter specimens measured after 7 days air-curing and 24 hours immersion in water.

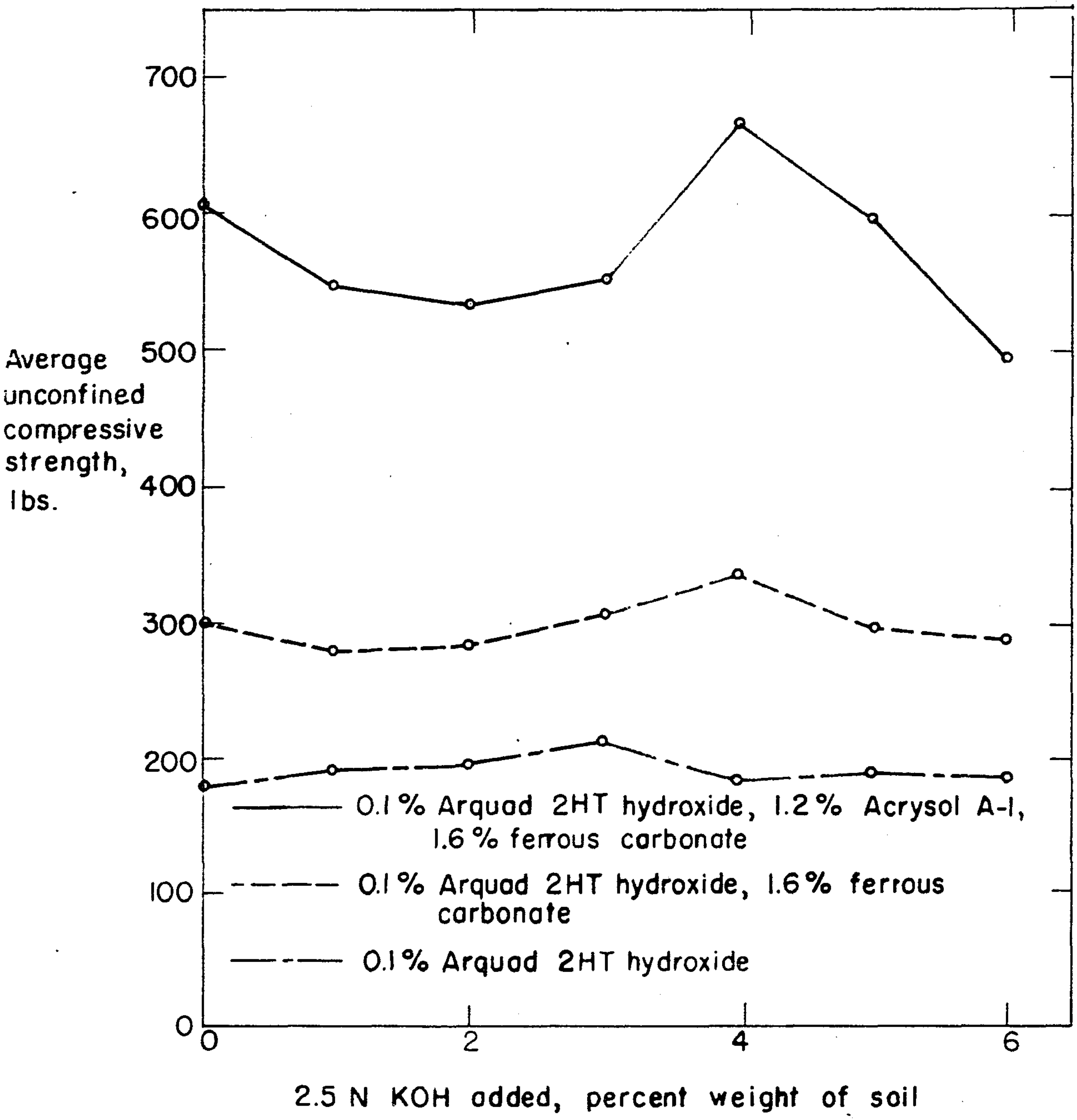


Fig. 30. Unconfined compressive strength of the silty loam treated with Arquad 2HT hydroxide, Acrysol A-1 and ferrous carbonate as a function of alkalinity adjustment with KOH. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

by the carboxyl groups performs a rather minor role in contributing to strength, and that the ferrous carbonate also contributes an increase in strength by means of some other reaction. It has been noted in some soils that carbonates contribute a weak cementing effect. The replacement of ferrous carbonate by equivalent portions of calcium and magnesium carbonates produced strength increases but of smaller magnitude. Hydrous oxides of iron are also known to act as cementing agents in soil (47b). Under basic 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.

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 tabulated in the Appendix and the results of strength tests are shown in Figure 31. Armac T, a primary amine acetate, gave slightly higher strength than Arquad 2HT for 0.1% treatment. The remaining three organic cations all gave considerably lower strengths.

The strength of the silty loam as a function of

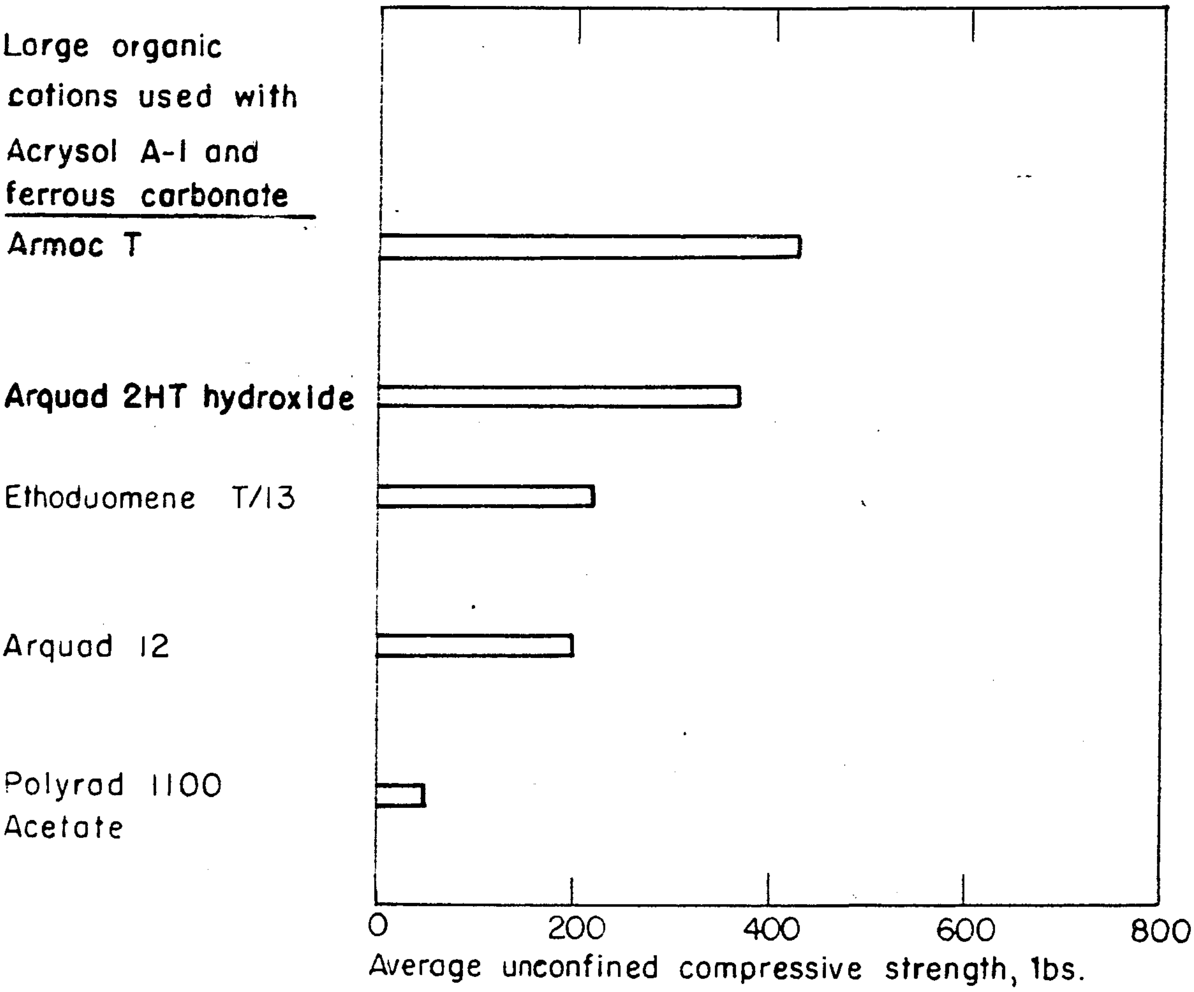


Fig. 31. Unconfined compressive strengths of the silty loam treated with 0.1% of various large organic cations with 0.6% Acrysol A-1 and 1.6% ferrous carbonate. Strengths of 2 inch high by 2 inch diameter specimens measured after 7 days air-curing and 24 hours immersion in water.

variations in amounts of Armac T, Acrysol A-1 and ferrous carbonate is shown in Figure 32. Slightly higher peak strengths were obtained with Armac T than with Arquad 2HT but the amount of Armac T required to obtain maximum strength was also greater (compare Figures 29 and 32). In Figure 33 the effect of basic pH adjustments on Armac T treatments is shown. As with Arquad 2HT, the addition of about 4% of 2.5 normal potassium hydroxide slightly increases the strength of samples treated with Armac T, Acrysol A-1 and ferrous carbonate. Figure 34a shows the variation in strengths of the treated silty loam with time of air drying prior to immersion.

To determine the effectiveness of the Armac T-Acrysol A-1-ferrous carbonate combination with a soil having low clay content an Iowa sand was treated. The properties of the sand are tabulated in the Appendix. Although the general trends were the same as for the silty loam, *i.e.*, increasing strength with increasing Acrysol A-1 and ferrous carbonate contents, the optimum amount of Armac T was much less for the sand (Figure 34b). The fact that strengths of the treated sand were all much lower than those of the treated silty loam may be partly due to the lack of cohesion in the natural sand. Sand specimens containing only Acrysol A-1 and ferrous carbonate absorbed large volumes of water when immersed and had negligible strength.

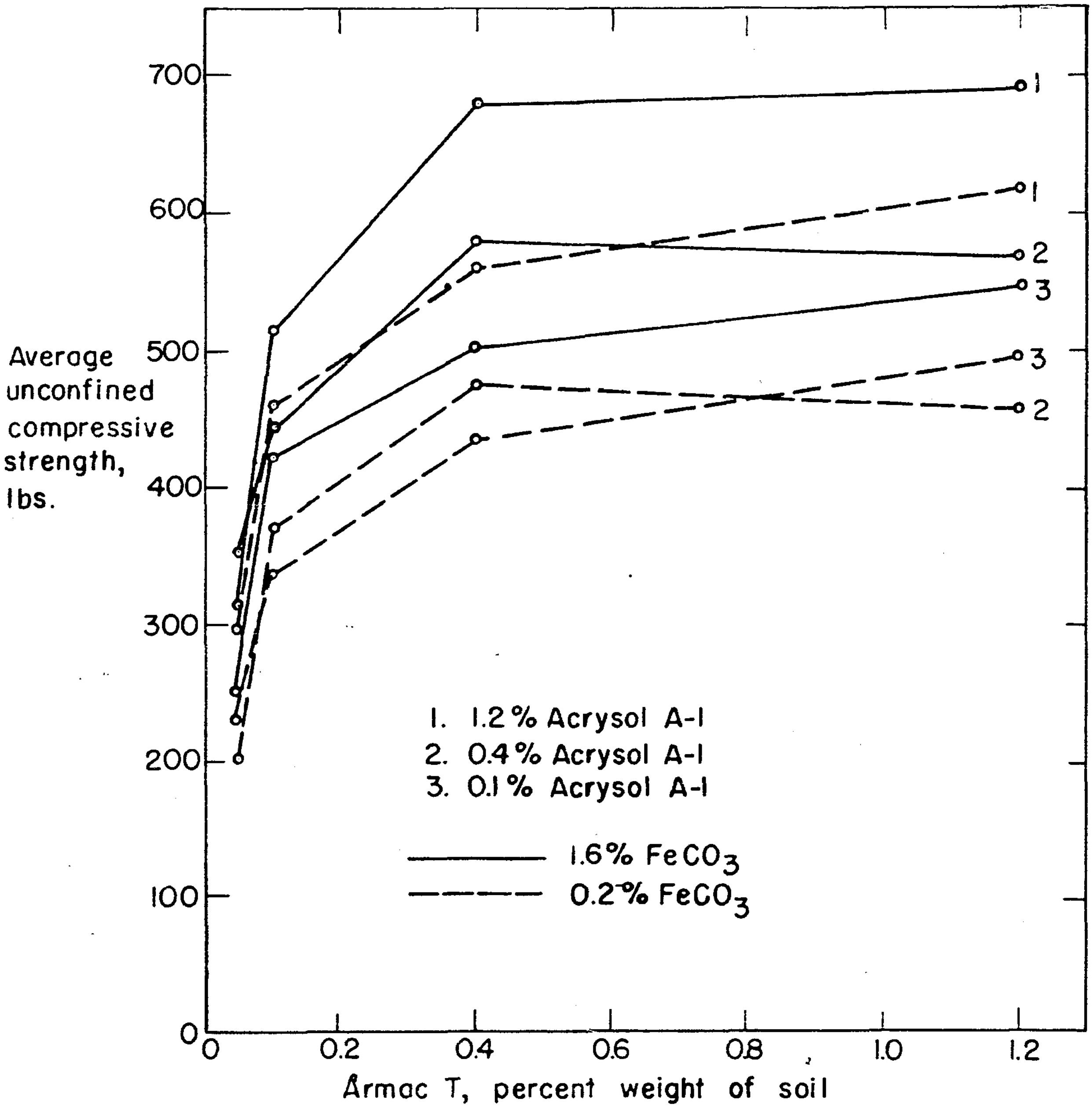


Fig. 32. Unconfined compressive strength of the silty loam treated with various percentages of Armac T, Acrysol A-1 and ferrous carbonate. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

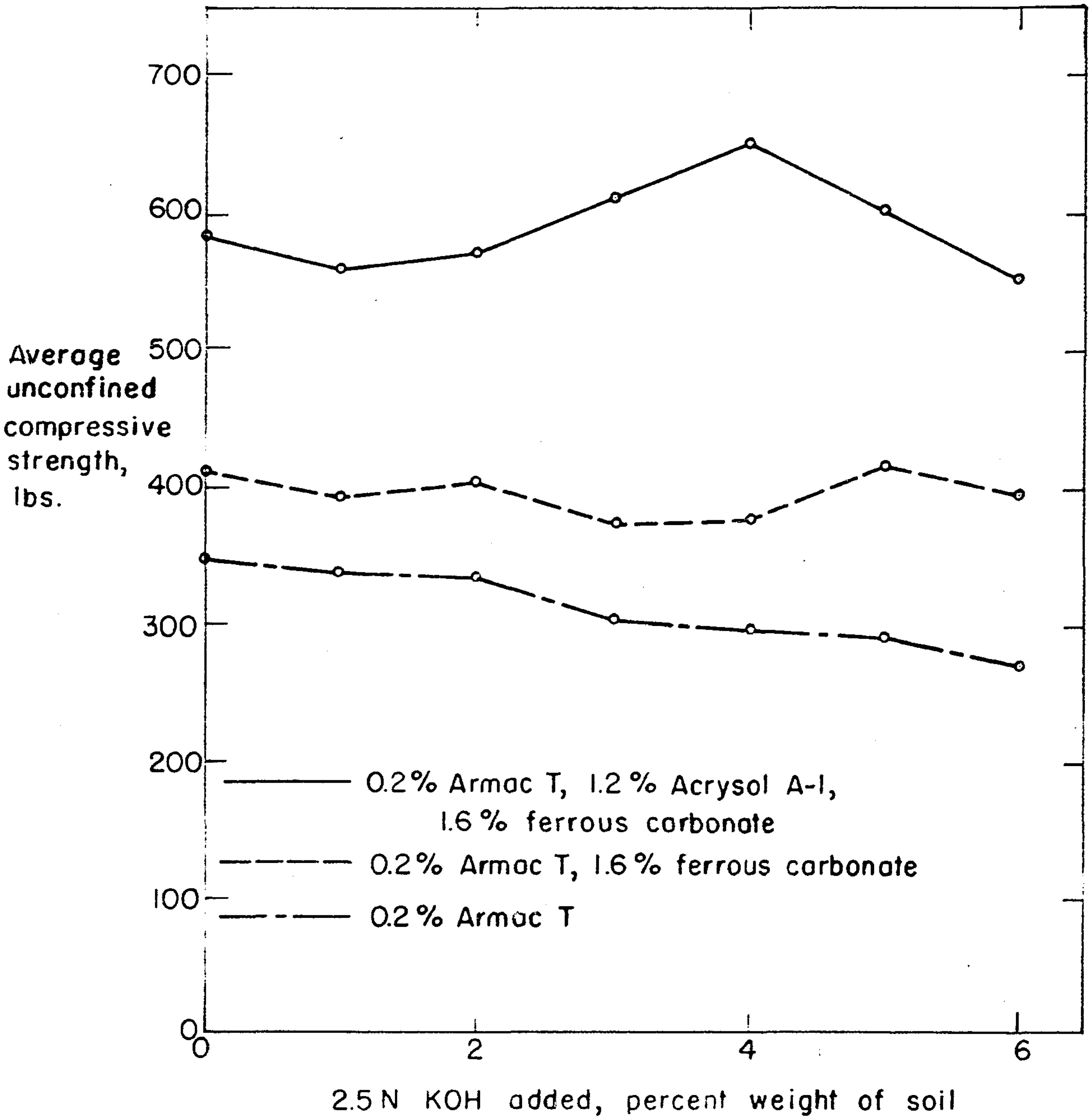


Fig. 33. Unconfined compressive strength of the silty loam treated with Armac T, Acrysol A-1 and ferrous carbonate as a function of alkalinity adjustment with KOH. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

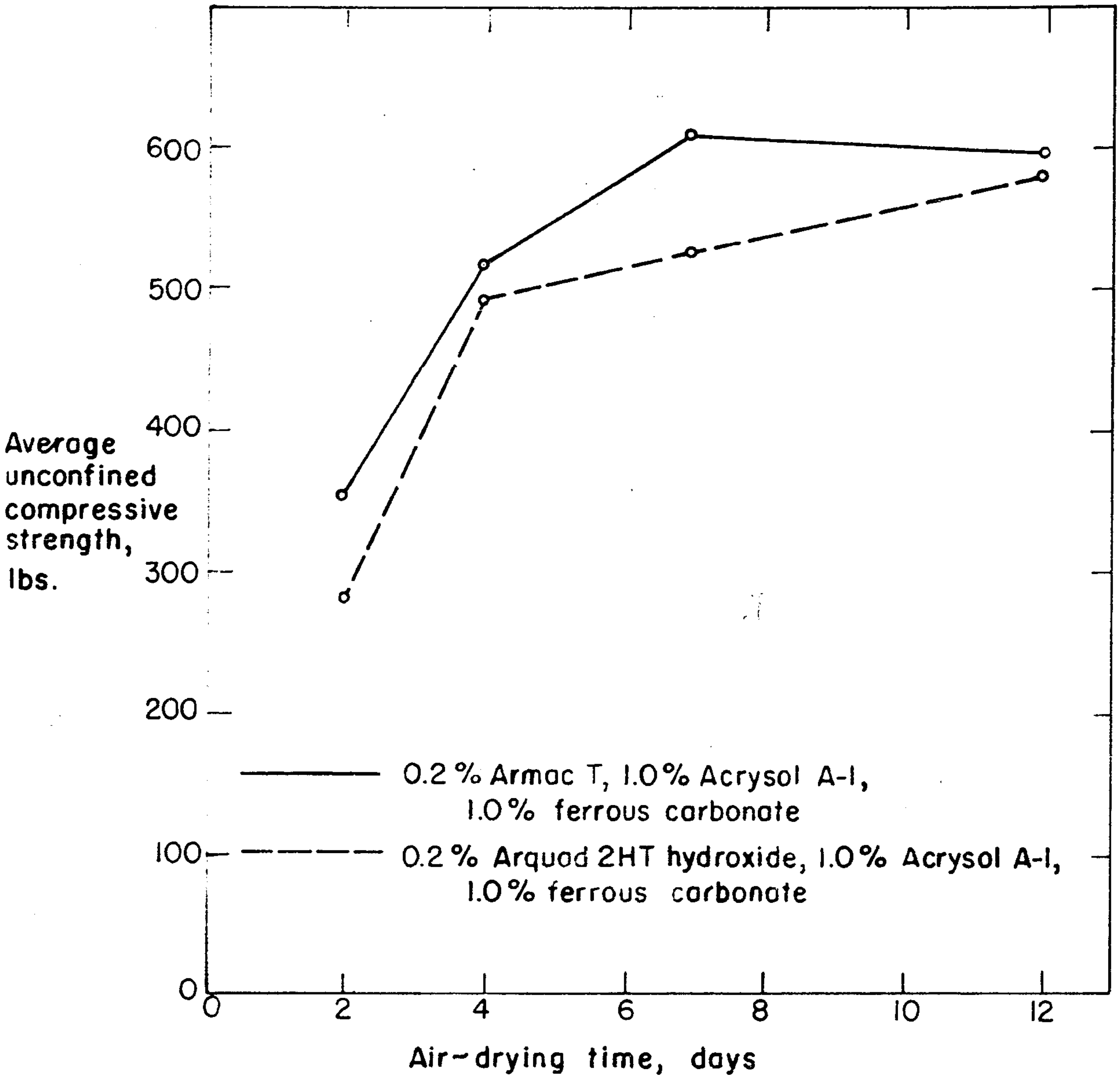


Fig. 34a. Effect of air-drying time on the unconfined compressive strength of the silty loam treated with Armac T and Arquad 2HT hydroxide with Acrysol A-1 and ferrous carbonate. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

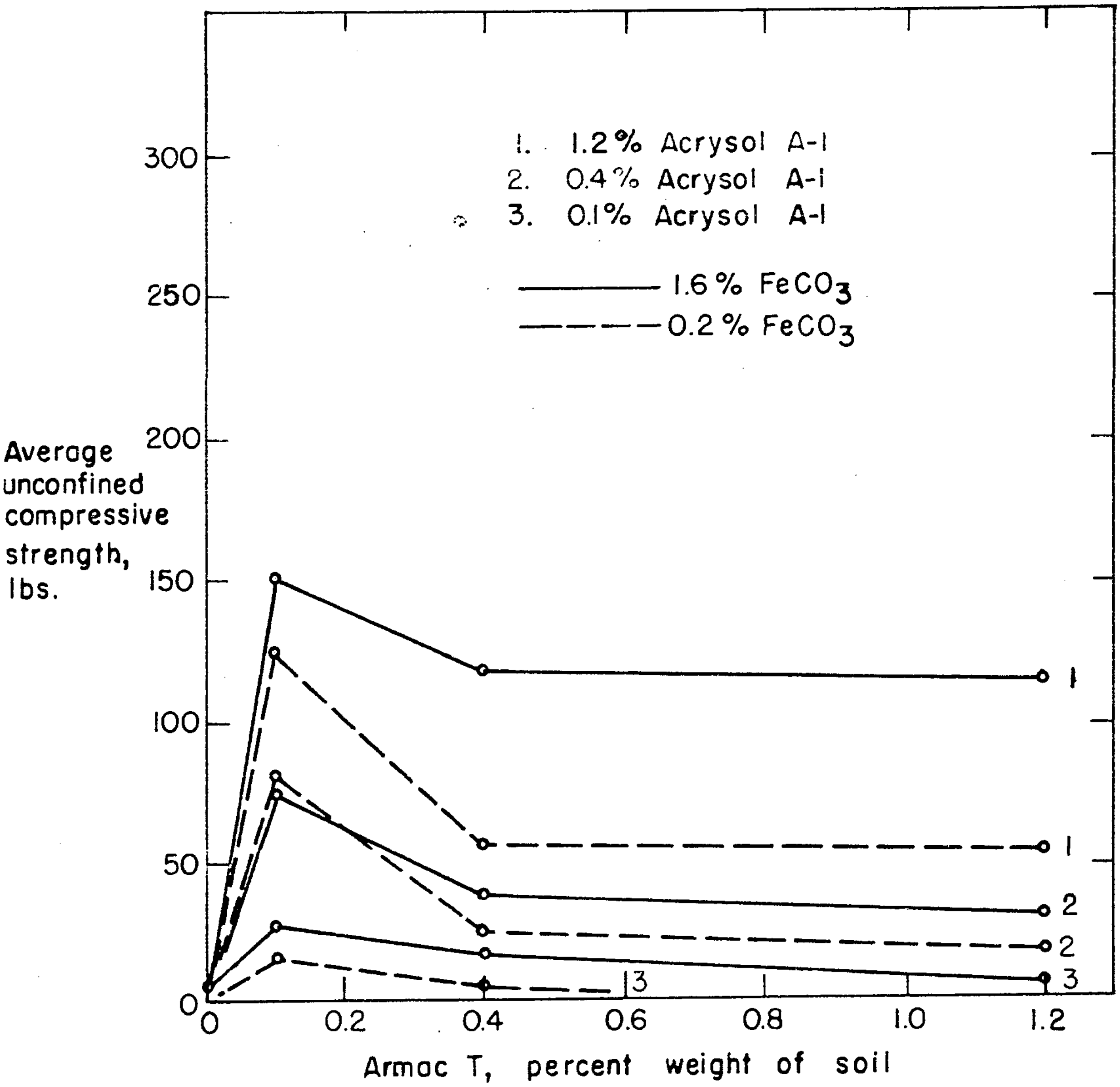


Fig. 34b. Unconfined compressive strength of an Iowa sand treated with various amounts of Armac T, Acrysol A-1 and ferrous carbonate. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion.

Conclusions

From the experimental work of Part II it may be concluded that:

1. The immersed strength and air-dry strength of a silty loam treated with quaternary ammonium cations can be increased by the addition of polyacrylic acid. This increase is apparently due primarily to an ionic adsorption complex in which the polyacrylic acid bonds between organic cations coating the mineral surfaces.

2. The effectiveness of the polyacrylic acid is dependent upon its molecular weight. Three samples having average intrinsic molecular weights ranging from 75,000 to 250,000 give slightly increasing strengths with decreasing molecular weight.

3. The hydroxide form of the quaternary ammonium cation used with polyacrylic acid gives greater strength than does an equal amount of the chloride form.

4. The strength of the cation-polyacid treated soil can be slightly increased by partial ionization of the polyacid with potassium hydroxide.

5. Cupric, ferrous and ferric ions form inner complex salts with polyacrylic acid, the ferric ion being the most active of the three.

6. The immersed strength of the soil can be slightly increased by the addition of ferrous carbonate. The

beneficial effect of the ferrous carbonate, however, seems to be primarily due to some reaction other than chelation of the ferrous ions with polyacrylic acid. The precipitation of an iron gel may account for part of this increase in strength.

7. An alkali pH adjustment increases the strength of the silty loam treated with the organic cation-polyacrylic acid-ferrous carbonate combination.

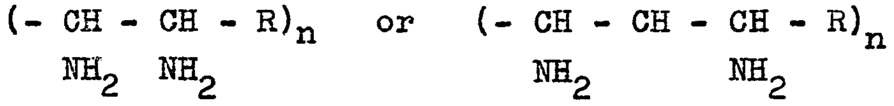
8. Of five structurally different large organic cations used with polyacrylic acid and ferrous carbonate, a primary amine acetate and a di-methyl di-hydrogenated tallow ammonium hydroxide give greatest strengths.

9. When the organic cation-polyacrylic acid-ferrous carbonate combination is used for stabilizing a sandy soil the optimum organic cation content is much lower.

PART III. INVESTIGATION OF POLYCATIONS AS SOIL STABILIZING AGENTS

As an alternative to the use of polyacids with large organic cations for soil stabilization a brief study was made of two polycations. These were the salt of a polymeric tertiary amine and the corresponding polymeric quaternary ammonium salt. Whereas organic acids such as Acrysol A-1 may be adsorbed by clay through organic or inorganic cations, basic organic compounds such as polycations should be adsorbed directly by clay. As shown in Figure 16, the effectiveness of a polyacid is critically dependent upon the concentration of large organic cations through which bonding with the mineral surfaces is apparently accomplished. One theoretical advantage of polycations as soil stabilizers is that their effectiveness in bonding to mineral surfaces should be independent of the concentration of a second additive.

A polycation-stabilized soil would conceivably consist of polycation chains bonding neighboring mineral particles together, some of the cationic groups being attached to mineral surfaces and others occupying positions on the polymer chains in the interstices between mineral particles. As with polyacids these unattached ionic groups would need to be complexed in some way to render them water-insoluble. Chelation may again be considered as a possible solution. Cobalt and copper ions are known to preferentially form chelates with basic nitrogens (39, p. 169). For optimum results with chelation the ligand should be a primary aliphatic amine capable of forming five or six member rings with the metal ions; for example,



$$(-\underset{NH_2}{CH}-\underset{NH_2}{CH}-R)_n \quad \text{or} \quad (-\underset{NH_2}{CH}-CH-\underset{NH_2}{CH}-R)_n$$

The primary aliphatic amines are better chelate formers than other amines (39, p. 168) and the five and six member chelate rings are the most stable (39, p. 137). Since the primary aliphatic amines are stronger bases than secondary, tertiary or aromatic amines (21, p. 222) they would also be more strongly attracted to the mineral surfaces.

From replies to inquiries sent to five major producers of resins and polymers it was learned that there are apparently no polycations of the above form commercially available. Therefore a tertiary amine salt and the corresponding quaternary ammonium salt, produced by Rohm and Haas under the trade names Acrysol CA and Acrysol CQ respectively, were chosen as alternative products to study.

Experimental Procedure and Results

A comparison of the cation exchange capacities of Wyoming Bentonite H-25, an American Petroleum Institute reference clay mineral, before and after treatment with Acrysols CA and CQ shows that the two polycations are irreversibly adsorbed (Table 4b). The bentonite was treated with the polycations in excess of its cation exchange capacity and the unattached polycation molecules were then removed by repeatedly washing the treated bentonite with distilled water, centrifuging and decanting until the supernatent liquid was free of polycations as determined by a color indicator test. Cation exchange capacities were measured by washing the samples with neutral normal ammonium acetate solution and analyzing the soil for the amount of cations exchanged. This procedure is given in the Appendix. The values in Table 4b are for treatments at pH 7. Although treatments at lower pH values may yield greater decreases in cation exchange capacity due to slightly increased ionization of the polycation salt, it is expected that the reduction would never be large due to inability of the large polycations to migrate completely throughout the interlayer spaces.

To determine if the polycations bond adjacent mineral particles together through cation exchange positions measurements were made of the cation exchange capacities of

Table 4b. Reduction in cation exchange capacity of Wyoming Bentonite by treatments with Acrysols CA and CQ

Untreated Bentonite	Bentonite treated with Acrysol CA	Bentonite treated with Acrysol CQ
73 me/100 gm	61 me/100 gm	66 me/100 gm

mixtures of the treated and untreated bentonites. The reduction in total cation exchange capacities of the treated and untreated bentonites due to mixing should be an indication of the additional number of indigenous cations irreversibly replaced by the polycations and hence an indication of the degree of bonding between mineral particles by the polycations. Table 5 shows the results of these tests.

Table 5. Reduction in cation exchange capacities by mixing the untreated bentonite with equal portions of the treated bentonites

Untreated bentonite	73[a]	Untreated bentonite	73
Bentonite treated with Acrysol CA	61	Bentonite treated with Acrysol CQ	66
Average	67	Average	69.5
Untreated bentonite mixed with equal portion of treated bentonite	63	Untreated bentonite mixed with equal portion of treated bentonite	67
Difference	4	Difference	2.5

[a] me/100 gm

Powder X-ray diffraction data (Figure 35) show that Acrysols CA and CQ reduce the swelling of montmorillonite by water in a manner similar to single large organic cations but to a much smaller degree.

For plotting Figure 35 Wyoming Bentonite was ground to pass the #60 U.S. Standard sieve and divided into five portions. One portion was left untreated and the remaining four were treated with 1:1 ratios by weight of 10% aqueous solutions of Armac T, Arquad 2HT hydroxide, and Acrysols CA and CQ. The treated samples were dried at 60° C., reground to pass the #60 sieve and X-rayed. The samples were then soaked in water for two hours and X-rayed again.

Figure 35a shows the peak for untreated dry montmorillonite at approximately 13 Angstroms. After soaking in water for two hours an almost random distribution of the (001) spacings occurs with the exception of a minor peak 3 Angstroms to the right of the peak for dry montmorillonite, representing a lattice expansion by one molecular layer of water.

In Figures 35b to 35e treatments with the four cationic materials are arranged in order of decreasing water-proofing effectiveness. The 13 Angstrom peak before soaking and the smaller 16 Angstrom peak after soaking occur for the last three treatments but not for treatment with Armac T. Apparently Armac T completely penetrates the expandable

Figure 35. X-ray powder diffraction plots showing the relative effectiveness of Armac T, Arquad 2HT hydroxide and Acrysols CA and CQ in preventing the swelling of Wyoming Bentonite by water. Copper K alpha radiation with nickel filter

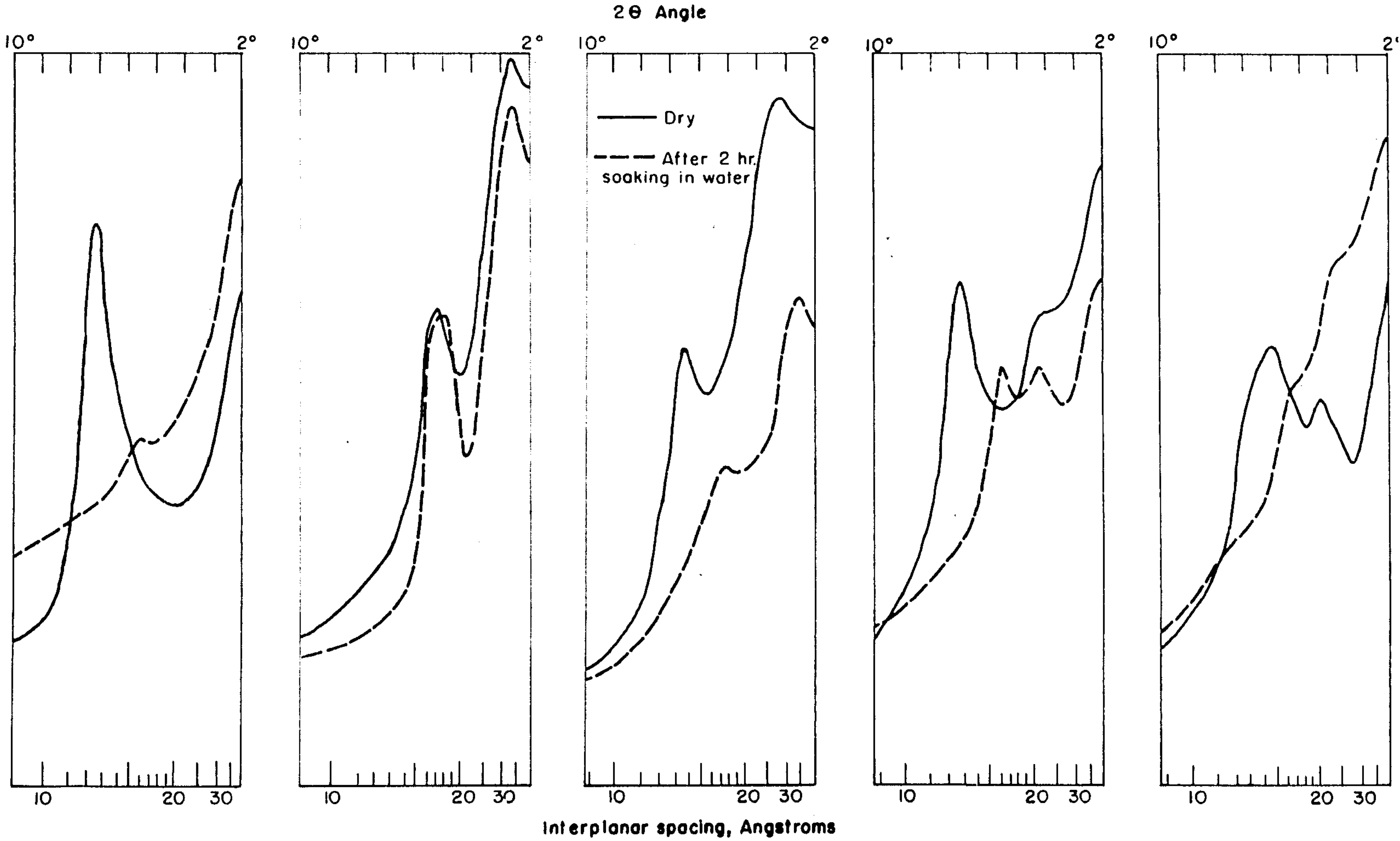
a. Untreated

b. Treated with Armac T

c. Treated with Arquad 2HT hydroxide

d. Treated with Acrysol CA

e. Treated with Acrysol CQ


2θ Angle
10°
2°
Dry
After 2 hr. soaking in water
10
20
30
Interplanar spacing, Angstroms

interlayer spaces. The wet and dry curves of Armac T are practically superimposed, indicating its high water-proofing ability. The peak at 17 Angstroms represents a displacement of 4 Angstroms (17 minus 13), or the van der Waal's thickness of one hydrocarbon chain. The second peak, occurring at 32 Angstroms, is less easily explained. It may be that a multiple layer structure of Armac T molecules is required for stability at greater interlayer thicknesses.

For the samples treated with Acrysols CA and CQ minor peaks occur at 20 and 21 Angstroms respectively, showing interlayer adsorption of these two polycations. The close similarity between the curves in Figures 35a and 35e indicate the very minor water-proofing ability of Acrysol CQ. The low interlayer water-proofing ability of Acrysols CA and CQ compared with the two single organic cations may be due to either the large molecular size of the polycations, causing limited mobility within the interlayer spaces of montmorillonite, or to the higher ratio of ionic to hydrophobic groups in the polycations.

The soil treated with Acrysols CA and CQ alone had strengths similar to those treated with the various polyacids studied in Part II. All immersed strengths were zero and air-dry strengths ranged from one to almost two times the strength of the untreated air-dry soil, depending upon amount of treatment. That a polycation-treated soil slakes in water whereas single large organic cations are effective water-proofers may be due to a large number of cations in the polycation being left unattached to mineral surfaces and hence remaining strongly hydrophillic.

Admixtures studied with Acrysols CA and CQ included ferric chloride, cobaltous nitrate, ferrous carbonate, copper sulfate and chromic sulfate. Samples treated with all of the metal salts slaked when immersed in water. The use of the two polycations with the various polyacids studied in Part II was also briefly evaluated. All samples treated with combinations of polycations and polyacids slaked when immersed in water.

Conclusions

The results of cation exchange capacity and X-ray studies show that the two polycations are adsorbed by montmorillonite, interlayer adsorption being much less than in the case of single large organic cations. The average molecular weights of the polycations (over 1,000,000) should enable single polymer chains, even in tightly coiled configurations, to bind together large numbers of clay-size particles. That this is true appears to be substantiated by a reduction in the cation exchange capacity when treated and untreated Wyoming Bentonites are mixed. This leads to the question as to why a polycation-treated soil slakes whereas the soil treated with single large organic cations does not. As suggested earlier, one possible explanation is that a large number of cationic groups in the polycation-treated soil are left unattached to the mineral surfaces and hence remain strongly hydrophillic. In the case of polymeric tertiary amine and quaternary ammonium salts, apparently little can be done to render these hydrophillic groups insoluble. If polymeric primary amines could be used, as pointed out in the review of literature, chelation with metal ions might offer a possible solution.

PART IV. SOIL STABILIZATION WITH LIGNO-PROTEIN-CATION COMPLEXES

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

Review of Literature

Lignin

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 (48). It accounts for 20 to 30% of the weight of wood (49, 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.

Lignin is a polynuclear compound containing benzol rings with carboxyl (COOH), hydroxyl (OH) and methoxyl (OCH_3) groups attached. It is characterized primarily by its molecular size (between 5,000 and 10,000) and the large number of acidic carboxyl groups on the molecule (50). The chemical structure of native lignin varies in different plant materials and also in different parts of the same plant. The structure of derived lignins depends on the process by which they are obtained from the plant materials.

Proteins

Proteins are naturally occurring high organic polymers which are composed mainly of alpha-amino acids. The attachment of one amino acid to another is by an amide linkage between the alpha-amino group of one molecule and a carboxyl group of the other. Proteins are commonly classed as fibrous and globular. The fibrous proteins most commonly serve as the structural material in animal tissues very much as cellulose serves for plants. All fibrous proteins are characterized by insolubility in neutral solvents. The globular proteins occur primarily in plants, especially in plant seeds, and are also known as soluble proteins. Individual proteins are chemically differentiated primarily on the basis of the chemical nature of side chains attached to the main polymer chain.

Since most proteins have both cationic and anionic groups they are amphoteric polyelectrolytes. The extent of the anion or cation reactivity depends on the environmental pH and on the number and reactivity of each type of functional group present in the polymer. A high hydrogen ion concentration increases the degree of ionization of amino or basic groups and at the same time represses the ionization of acidic groups. A low hydrogen ion concentration increases ionization of the acidic groups. The hydrogen ion concentration at which the acidic and basic ionization is equal is called the isoelectric point.

Proteins are generally bound intramolecularly through dissociable salt linkages, hydrogen bonds and disulfide bonds (Figure 36). The ease with which proteins are manipulated chemically depends upon the nature and distribution of these bonds (51).

Similarly to the polyacids and polycations studied in Parts II and III, 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 (59).

Proteins possess a theoretical advantage over polyacids and polycations as soil stabilizing agents because their

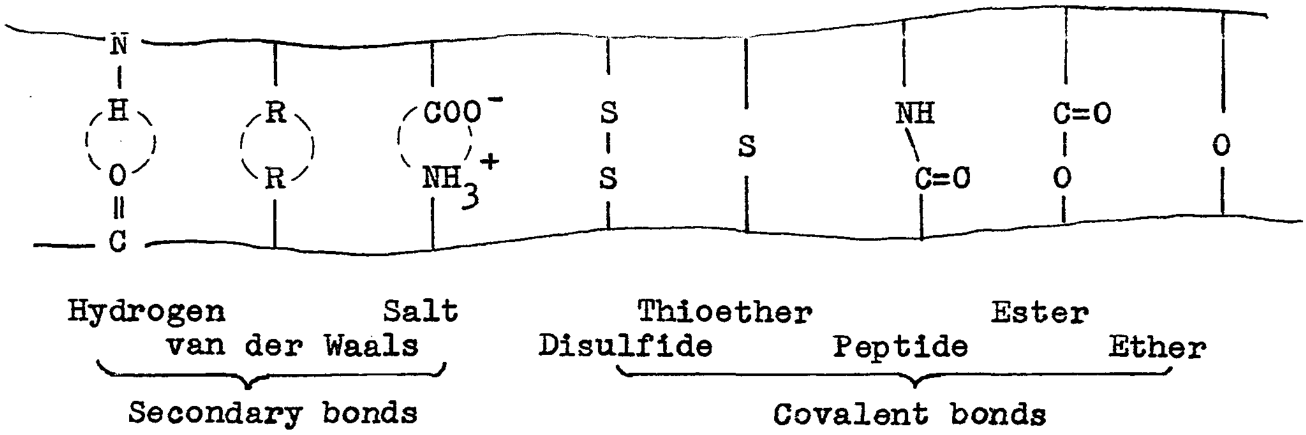


Fig. 36. Possible cross linkages between protein chains. Hydrogen, van der Waals, salt and disulfide bonds are the most common. (From Lundgren, H. P. Synthetic fibers made from proteins. Advances in Protein Chemistry. Vol. 5, pp. 305-351. 1949)

acid-base reactivity may be manipulated by pH adjustments. Anionic and cationic groups may thereby be used to perform different linking functions. For example, at a pH slightly below the isoelectric point of the protein basic amine groups may link with the acidic mineral surfaces. By a small pH adjustment through the isoelectric point the carboxyl groups might then be ionized for subsequent chelation or complex formation with metal ions.

Ligno-protein complexes

Humus, representing the most slowly decomposable portion of organic residues in soil, is composed of from 70 to 80% ligno-protein complexes (52). Furthermore, lignin and proteins can both be made more resistant hydrothermally and biochemically by reactions with metals such as chromium and mercury. These facts suggest the possibility of using metal salts in conjunction with lignin and readily available plant proteins for soil stabilization.

The line chart, Figure 37, has been drawn as an aid in picturing the possible combinations of reactions which may occur between mineral surfaces, lignin, proteins and either organic cations or metal ions. Any conceivable mechanism of stabilization with these additives can be pictured by starting with the mineral surface, going outward on any series of lines and returning again to the mineral surface. For example, the lines 5-7-5 would represent a system in which lignin bonds adjacent soil particles together through metal cations at the mineral surfaces. The chrome-lignin process, studied by Smith (53) is an example of this type of

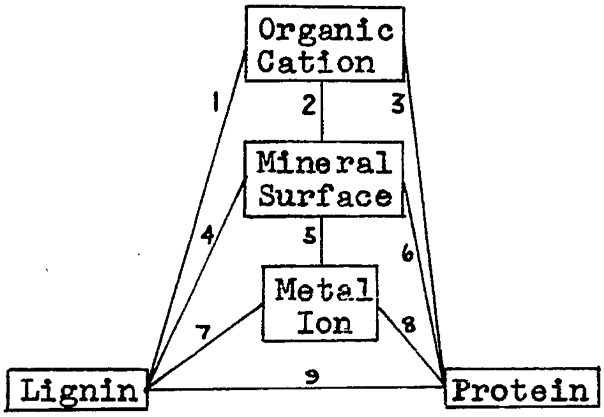


Fig. 37. Line chart showing possible combinations of reactions between lignin, proteins, organic cations, metal ions and mineral surfaces.

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 (52, 54, 55). Lines 5-7-9-6 might represent a ligno-protein complex in which lignin is bound to the mineral surface through basic amino groups. It is readily seen that a number of possibilities present themselves for study. To facilitate organization of this study, Figure 37 will be referred to throughout the review of literature and the experimental work.

Reactions involving clay, lignin, proteins and cations

Information available in the literature on each of the nine reactions represented in Figure 37 will be briefly reviewed.

1. Lignin-organic cation reactions

No published information was found on lignin-organic cation reactions. The numerous carboxyl groups of lignin may provide a means of linking in a manner similar to the formation of polyacrylic acid-organic cation complexes.

2. Organic cation-mineral surface reactions

These reactions were discussed earlier.

3. Organic cation-protein reactions

No published information was found.

4. Lignin-clay mineral reactions

No published information was found on reactions directly between lignin and clay minerals. Both are primarily acidic and the possibility of the formation of a complex or co-ordination compound of any type seems small.

5. Metal ion-clay mineral reactions

Although extensive studies have been made of exchange reactions of clay minerals with the alkali and alkaline earth metals, apparently no work has been published on reactions between clay minerals and the transition metals. Generally, but not invariably, the replaceability of alkali and alkaline earth metals on clays obeys the Hoffmeister series. That is, an ion is replaced by another of smaller hydrated radius and greater surface charge density. If ions of the transition metal group follow this pattern the replaceabilities of the metals to be studied would be in the order $Cr < Fe < Co < Cu < Hg$, mercury being the most firmly bound ion.

6. Protein-clay mineral reactions

Proteins can be bound directly to clays through linkage by their basic groups. Demolon and Barbier (56) found that certain humic colloid proteins are strongly adsorbed by clays when the hydrogen ion concentration of the system is high. Ensminger and Geiseking observed from powder X-ray diffraction studies that gelatin and albumen were adsorbed within the lattice layers of montmorillonite, resulting in larger (001) spacings (57). The adsorption was greater at higher hydrogen ion concentrations, indicating these proteins are adsorbed as cations. Untreated gelatin was more completely adsorbed than nitrous acid-treated gelatin, indicating the reaction was partly due to the presence of the free amino groups of the protein. Mattson observed that the isoelectric point of proteins is lowered by bentonite (55). He believed this was due to the formation of a non-ionized compound between bentonite and proteins.

7. Metal-lignin complexes

Very little is known about the reaction of lignin with various metals. Chromium ions are known to form water-insoluble co-ordination complexes with lignin but the nature of these complexes is still very vague (53). No published work could be found indicating similar complexes with other metal ions.

8. Metal-protein compounds

The reaction of metal ions with proteins is apparently very similar to the reaction of metals with polyanions and polycations, discussed in Parts II and III. The large number of both positive and negative co-ordinating groups in proteins, however, makes the interpretation of results more difficult. Two types of metal-protein reactions are commonly recognized. These are the protein complexes and the protein chelates (58). In the protein complexes the number of donor groups is identical to the number of ligands and in the protein chelates two or more donor groups form a ring structure with one molecule of ligand, providing additional stability.

Metal-protein compounds have been studied extensively in connection with leather tanning. Collagen, the protein of animal hide, is made microbiologically and hydrothermally resistant by crosslinking with certain metal ions or with organic crosslinking agents such as formaldehyde. Some of the metals used for tanning protein fibers are exceptional in that they have the power to combine with both carboxyl and amino groups (59). When protein fibers are treated with chromium salts for example, stable cross links between carboxyl and amino groups are formed (Figure 38). Increasing the basicity of the chromic salt will lower the hydrogen ion concentration and ionize a greater number of carboxyl ions which can then react with the chromic ions (60). A second type of union with metals is that of mercury. Mercury forms stable cross links between carboxyl and amide groups (Figure 39). Mercury is also valuable in that it discourages the growth of fungi and bacteria (59, p. 87).

9. Ligno-protein complexes

a. Chemical nature of ligno-protein complexes

Several possibilities exist for reactions between

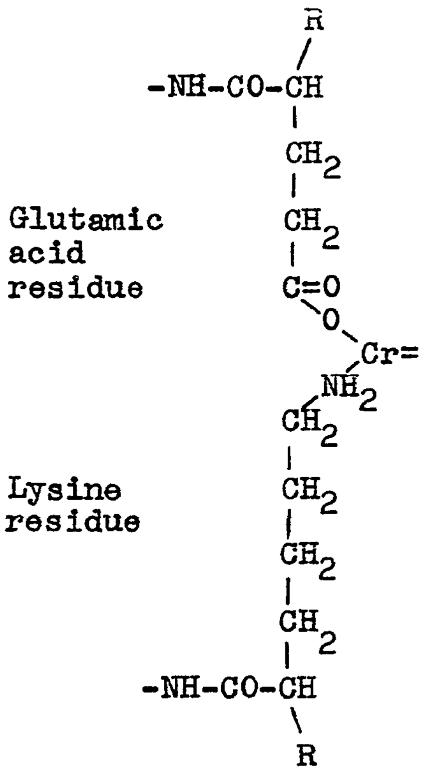


Fig. 38. Chromium as a linking agent between carboxyl and amino groups.

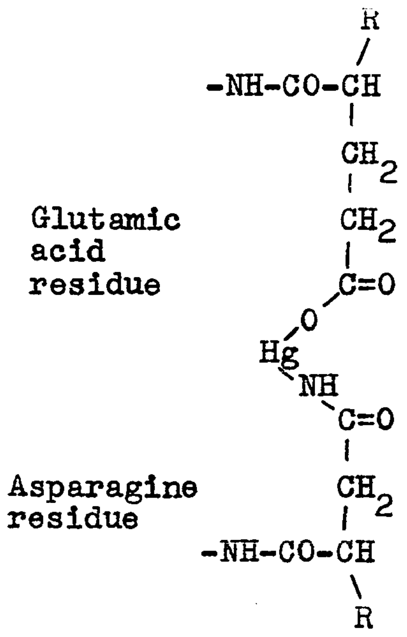


Fig. 39. Mercury as a linking agent between carboxyl and amide groups.

(Figures 38 and 39 taken from Wormell, R. L. New fibres from proteins. Academic Press, Inc. New York. 1954.)

lignin and proteins (50). These are based upon the fact that lignin possesses carboxyl, hydroxyl, carbonyl and methoxyl groups. Salt formation takes place when the NH_2 group of protein reacts with the COOH group of lignin. A reaction between the NH_2 group of protein and the carbonyl group may also occur, forming a Shiff's base type compound.

$$\underset{\text{Lignin}}{C_{52}H_{46}O_{10}(OCH_3)\cdot(COOH)\cdot(OH)_4\cdot CO} + \underset{\text{Protein}}{H_2N\cdot R\cdot COOH} \longrightarrow$$

$$C_{52}H_{46}O_{10}(CH_3)\cdot(COOH)\cdot(OH)_4\cdot C{=}N\cdot R\cdot COOH + H_2O$$

This complex is stable and possesses a high base exchange capacity, a phenomenon characteristic of humus. Other combinations between proteins and lignins may also occur (50).

Ensminger (61) prepared ligno-gelatin complexes to determine what effect lignin has on the basic properties of gelatin. He found that increasing the amount of lignin decreased the adsorption of gelatin by montmorillonite. The NH_2 groups of the gelatin were thought to react with the ketonic or aldehydic groups of the lignin, leaving fewer NH_2 groups for reaction with the clay.

In recent years, the use of waste lignin products, particularly sulfite waste liquor, has also been studied as a potential tanning agent for collagen (62).

b. Biological factors in ligno-protein-clay complexes

The resistance of clay-protein complexes and ligno-protein-clay complexes to biochemical decomposition has been studied by several investigators. Ensminger and Geiseking (63) observed that adsorption of albumen and hemoglobin by bentonite interfered with the enzymatic hydrolysis of these proteins in both acid and alkaline pancreatin suspensions. Kaolinite had no similar effect, indicating that biochemical resistance of the proteins apparently depends primarily upon their adsorption at the interlayers of expandable lattice type minerals.

A further reduction in the rate of protein decomposition can be obtained by the addition of lignin. Waksman and Iyer (48) found that a mere mechanical admixture of casein and lignin had a marked depressing effect on the decomposition of casein by soil cultures as determined by ammonia liberation. When the ligno-protein complex was prepared by mixing alkali solutions of the two materials and precipitating the complex by addition of an acid, decomposition of the casein was stopped almost completely.

Waksman and Iyer also studied the effect of various metal salts on the decomposition rates of ligno-casein complexes. When aqueous solutions of calcium chloride and magnesium chloride were added, the ligno-casein complex could be precipitated at much lower hydrogen ion concentrations and the decomposition by soil cultures was reduced practically to zero, indicating that metal-ligno-casein complexes having high resistance to biochemical attack had been formed.

Choice of protein

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

Zein has a molecular weight of about 40,000. Although it contains a relatively 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 inhibition of water (59, p. 153). Some investigators report that zein has no free basic groups (64) while others report a low acid exchange capacity of 10-20 m.e. per 100 grams (59, p. 143). This absence of free basic groups means that zein probably will not bond successfully to clay minerals by itself. On the other hand, the high proportion of amide groups may provide a good means of bonding to mineral surfaces through various metal ions.

Zein is soluble in water only within the narrow pH range of 11.3 to 12.7. Strong alkali metal hydroxides are the best dispersing agents although quaternary ammonium hydroxides have been found successful to a lesser degree. Zein is also dispersed in aqueous solution by a wide variety of soaplike compounds, including fatty acids and rosin (65).

The abundance of amide groups in zein allows crosslinking with formaldehyde to produce a product of improved toughness, mechanical strength and water-resistance. The reaction is slow compared with the same reactions with other proteins but may be catalyzed by acids. Small amounts of ammonia or primary amines act as promoters but are effective only in the presence of excess acid (64). Formaldehyde presumably forms methylene bridges between the nitrogen of a dicarboxylic acid amide group and that of a neighboring peptide linkage or a second amide group (66, p. 328). The reaction of formaldehyde with two amide groups is represented in Figure 40.

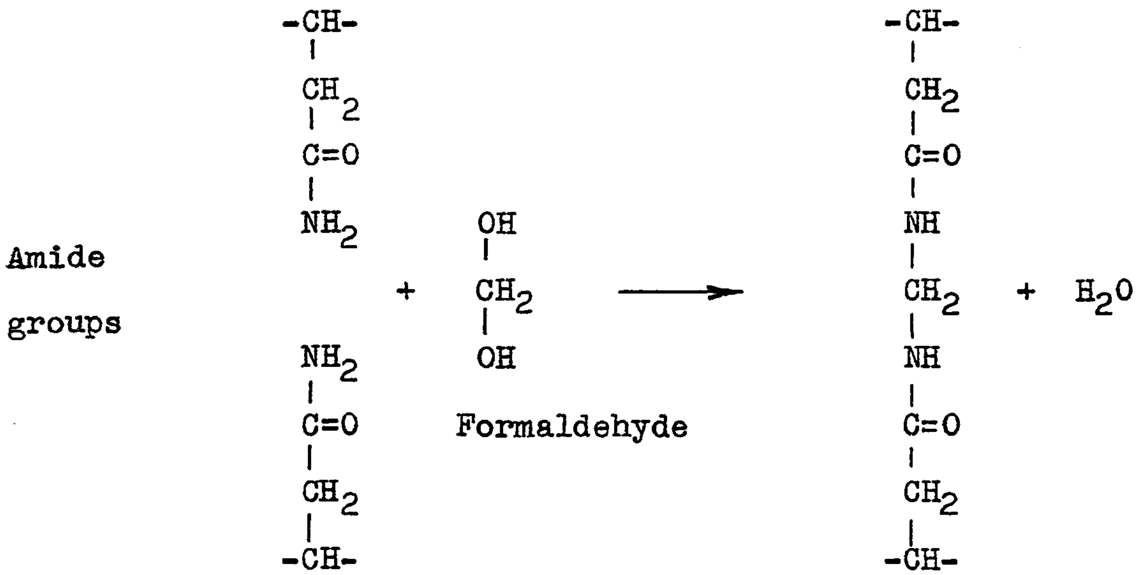


Fig. 40. Reaction of formaldehyde with amide groups.

Experimental Procedure and Results

The experimental work of this part was limited to a brief evaluation of the reactions represented in Figure 37 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 6, the addition of metal salts to the above 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 6 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 6 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.

Table 6. Unconfined compressive strengths of the silty loam treated with combinations of spent sulfite liquor and zein with organic cations and metal salts; percentages are based on weight of air-dry soil and solid content of additives. Strengths of 2 inch diameter by 2 inch high specimens measured after 7 day air drying plus 24 hour immersion

Organic cations and metal salts, 0.5%	No treatment	Spent sulfite liquor, 2%	Zein, 0.5%	2% spent sulfite liquor plus 0.5% zein
No treatment	slaked	slaked	slaked	slaked
$CaCl_2$	"	"	"	"
$MgCl_2$	"	"	"	"
$CuSO_4$	"	"	"	"
$FeCl_3$	"	"	"	"
$Co(NO_3)_2$	"	"	"	"
$Cr_2(SO_4)_3$	"	180 lbs.	130 lbs.	210 lbs.
$Hg(C_2H_3O_2)_2$	"	slaked	220	230
Armac T	300 lbs.	350 lbs.	290	260
Arquad 2HT hydroxide	330	370	340	270

The effect of spent sulfite liquor and zein on treatments with Armac T and Arquad 2HT are shown in Figures 41 and 42. The strength curves for samples containing Armac T generally lie somewhat higher than for samples containing Arquad 2HT. In each case the addition of 0.5% spent sulfite liquor increases the strength considerably, while the

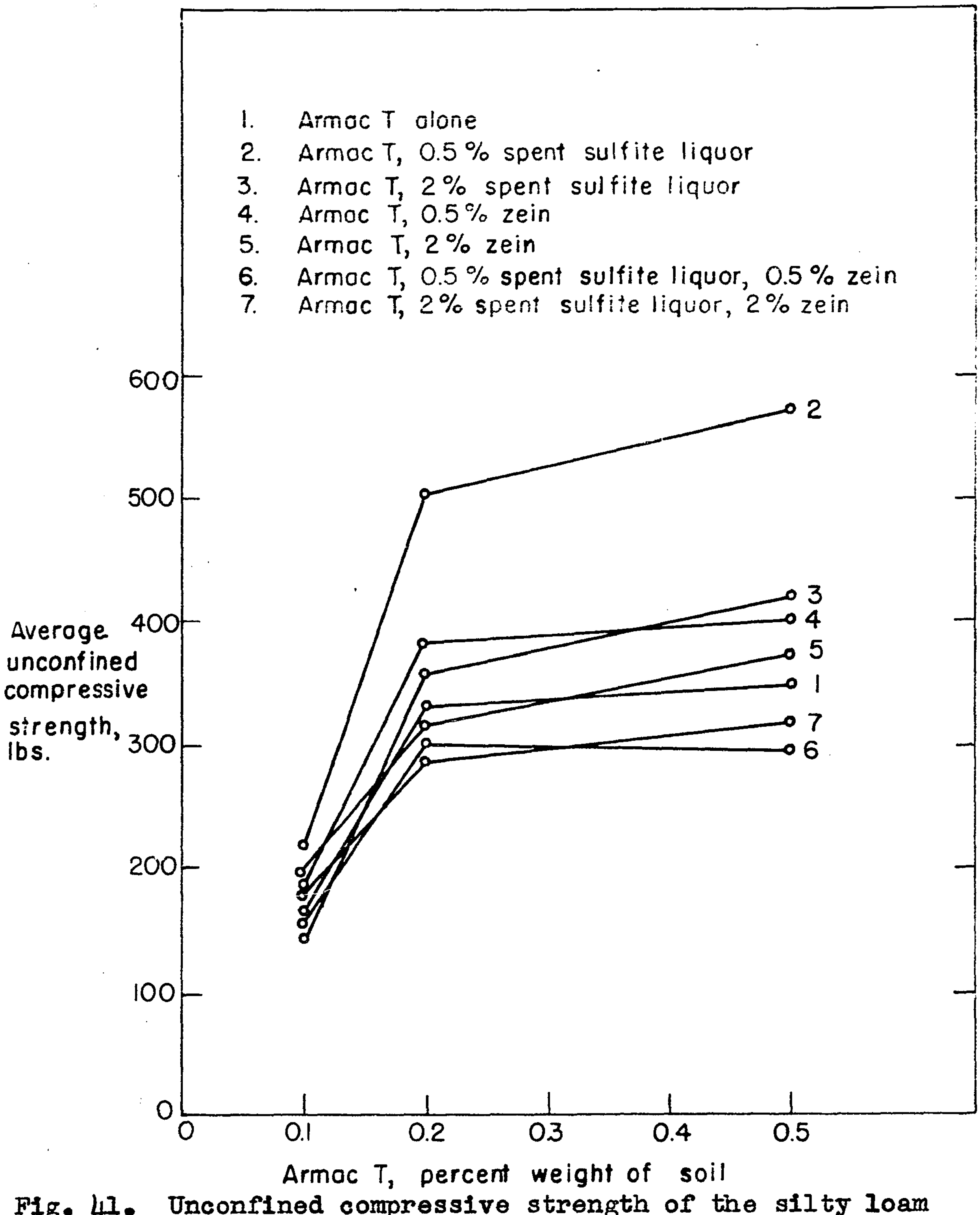


Fig. 41. Unconfined compressive strength of the silty loam treated with Armac T in combination with spent sulfite liquor and zein. Strengths of 2 inch high by 2 inch diameter specimens measured after 7 day air drying plus 24 hour immersion.

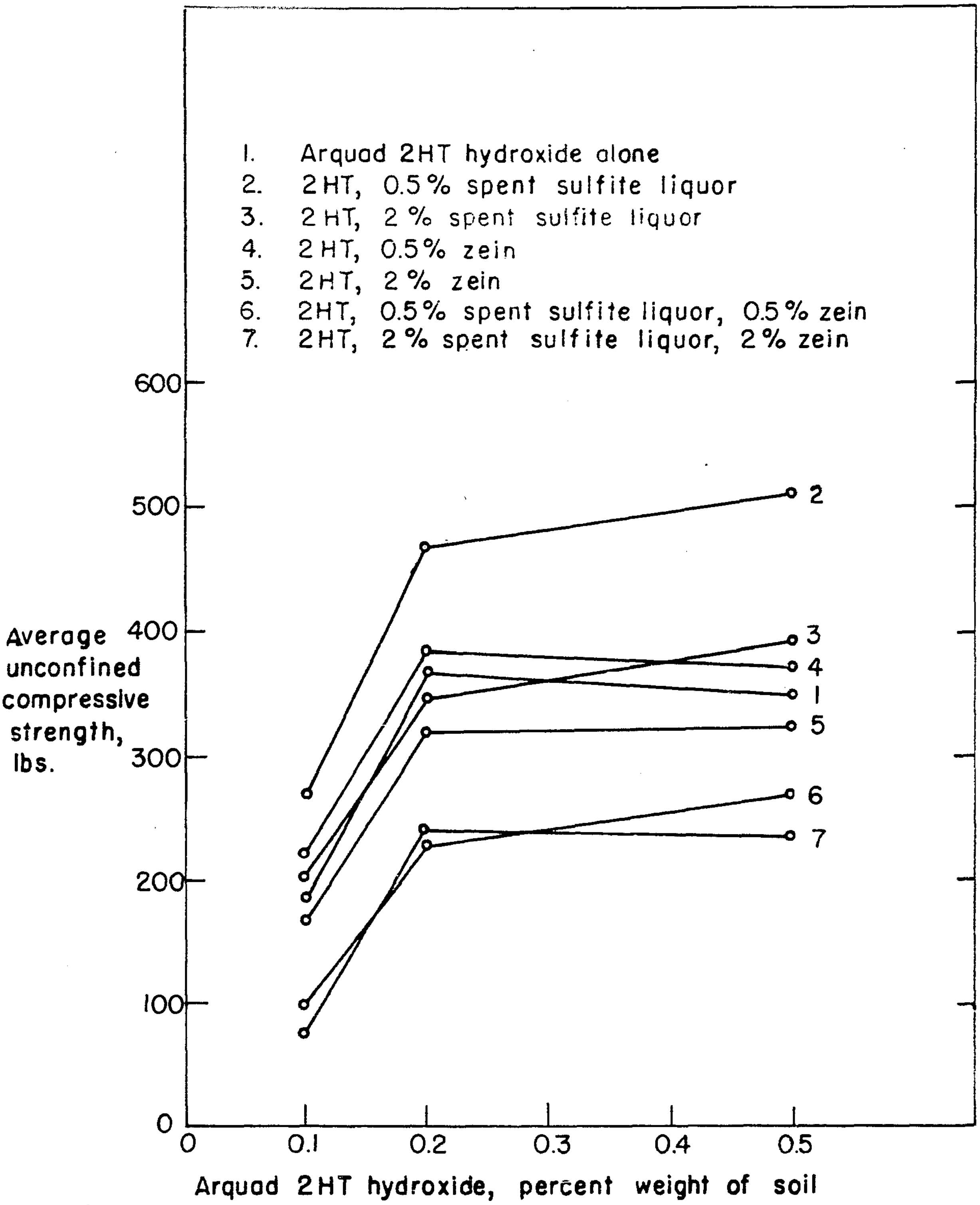


Fig. 42. Unconfined compressive strength of the silty loam treated with Arquad 2HT hydroxide in combination with spent sulfite liquor and zein. Strengths of 2 inch high by 2 inch diameter specimens measured after 7 day air drying plus 24 hour immersion.

addition of 2% 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%. 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 43a and 43b show the low strengths obtained for all treatments containing combinations of chromium and mercury salts with spent sulfite liquor and zein. Chromic sulfate with zein and spent sulfite liquor, curve 7 of Figure 43a, gave higher strengths than other combinations in this group.

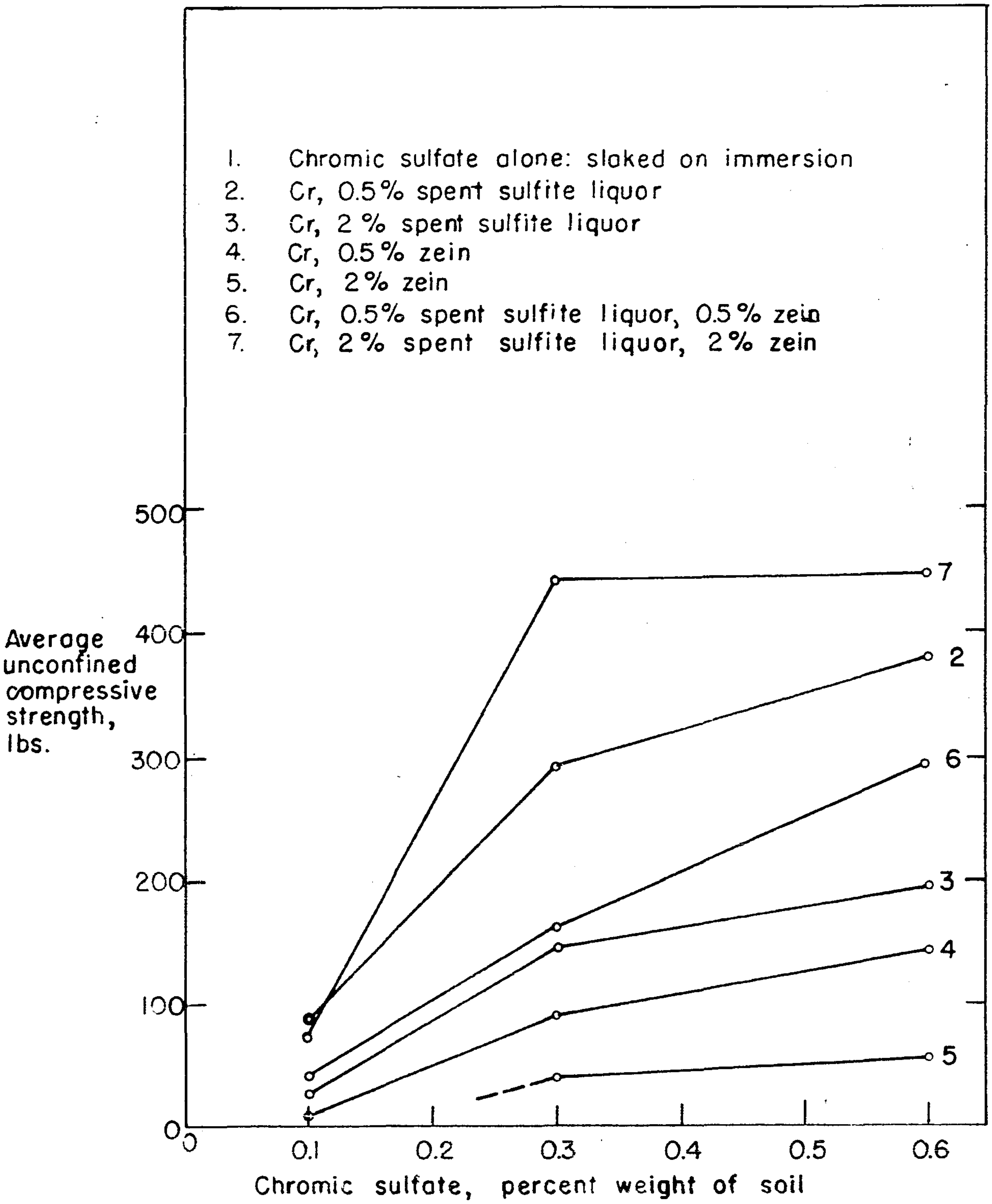


Fig. 43a. Unconfined compressive strength of the silty loam treated with chromic sulfate in combination with spent sulfite liquor and zein. Strengths of 2 inch high by 2 inch diameter specimens measured after 7 day air drying plus 24 hour immersion.

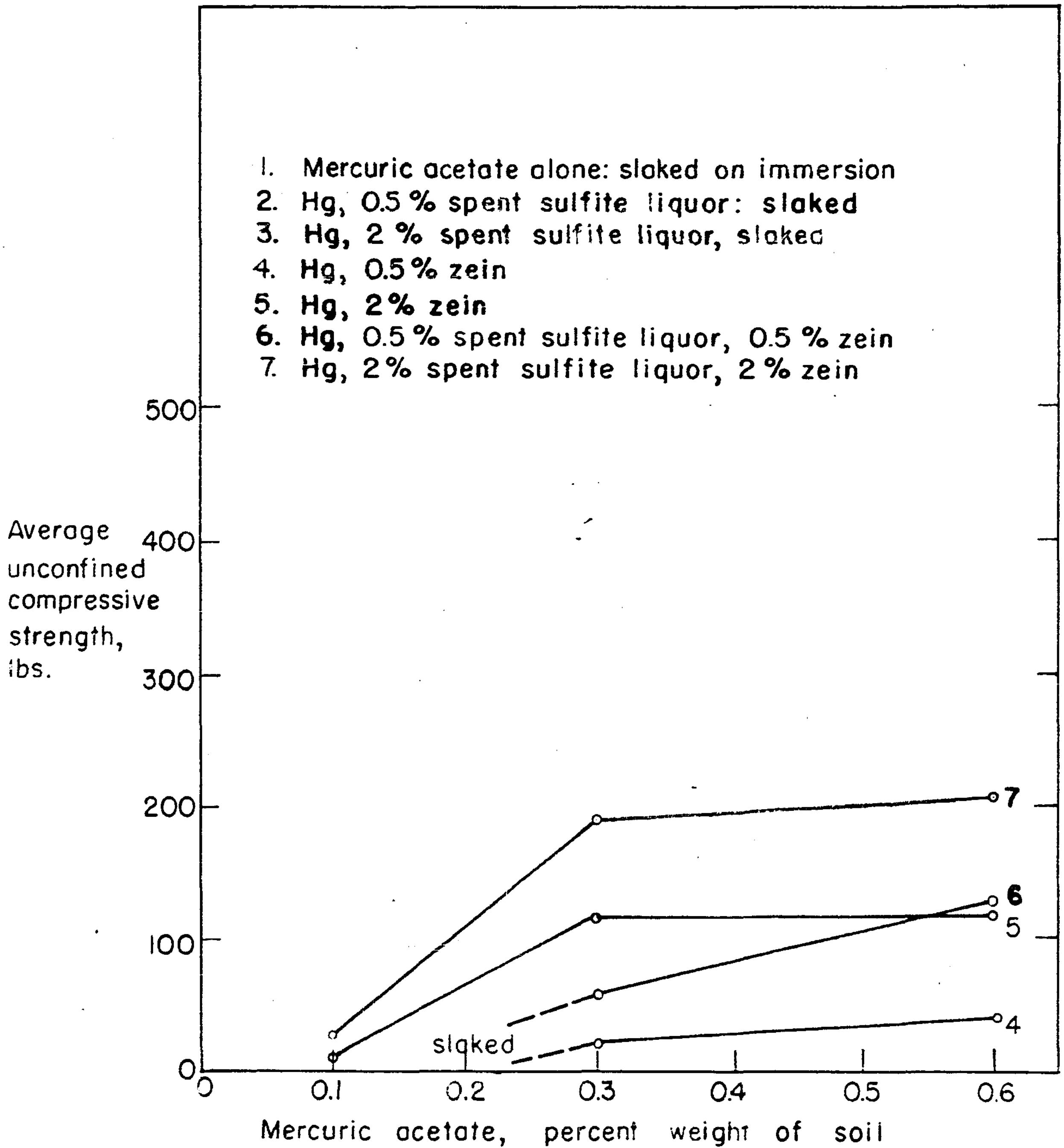


Fig. 43b. **Unconfined compressive strength of the silty loam treated with mercuric acetate in combination with spent sulfite liquor and zein. Strengths of 2 inch high by 2 inch diameter specimens measured after 7 day air drying plus 24 hour immersion.**

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.

Four methods were investigated for stabilizing soil by the use of large organic cations and polymers. Of these, highest strengths were obtained by combinations of polyacrylic acid and ferrous carbonate with two large organic cationic materials. 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 times. 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% of each of the two cationic materials with 0.6% 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. 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, however, may be worth some further study. Work has recently been done elsewhere on the use of a different polyacid-large organic cation combination for soil stabilization (67, see also 42).

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 effective only in quantities less than about 2%. The use of large organic cations with various waste products containing lignin definitely appears to merit further study.

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ACKNOWLEDGMENTS

This investigation constitutes a part of Project 283-S of the Iowa Engineering Experiment Station. The project, entitled "The Loess and Glacial Till Materials of Iowa; An Investigation of Their Physical and Chemical Properties and Techniques for Processing Them to Increase Their All-Weather Stability for Road Construction", is being conducted by contract with the Iowa State Highway Commission and under the sponsorship of the Iowa Highway Research Board. It is supported by funds provided by the Commission and the U. S. Bureau of Public Roads.

Gratitude is expressed to Armour Chemical Division, Monsanto Chemical Company and Rohm and Haas Company for samples of chemicals used in these investigations.

Sincere thanks go to Dr. D. T. Davidson, Project Director and Professor of Civil Engineering for his guidance and encouragement and to Drs. R. L. Handy and J. B. Sheeler, Assistant Professors of Civil Engineering, for instruction in the use of the X-ray equipment and for helpful suggestions during the research.

APPENDIX

Laboratory Apparatus

Oxidation apparatus

The oxidation apparatus (Figure 44) consisted of a 500 ml. 3-neck reaction flask into which oxygen was passed after being dried in a calcium chloride tube and heated in a flask supported on a heating mantly. A magnetic stirrer was used and constant temperature was maintained by a temperature bath and reflux condenser.

Polymerization apparatus

In designing a polymerization apparatus consideration was given to the following requirements:

1. Provision for running several polymerizations simultaneously
2. Temperature control within ±1° C.
3. Provision for agitating the polymer solutions
4. Provision for a gas inlet to each reaction chamber in order to determine inhibition or activation effects due to various atmospheres
5. Provision for removing and placing in operation any reaction chamber without disturbing the remaining reactions, and
6. A lamp behind the reaction chambers to facilitate visual observation of initiation periods (time of turbidity).

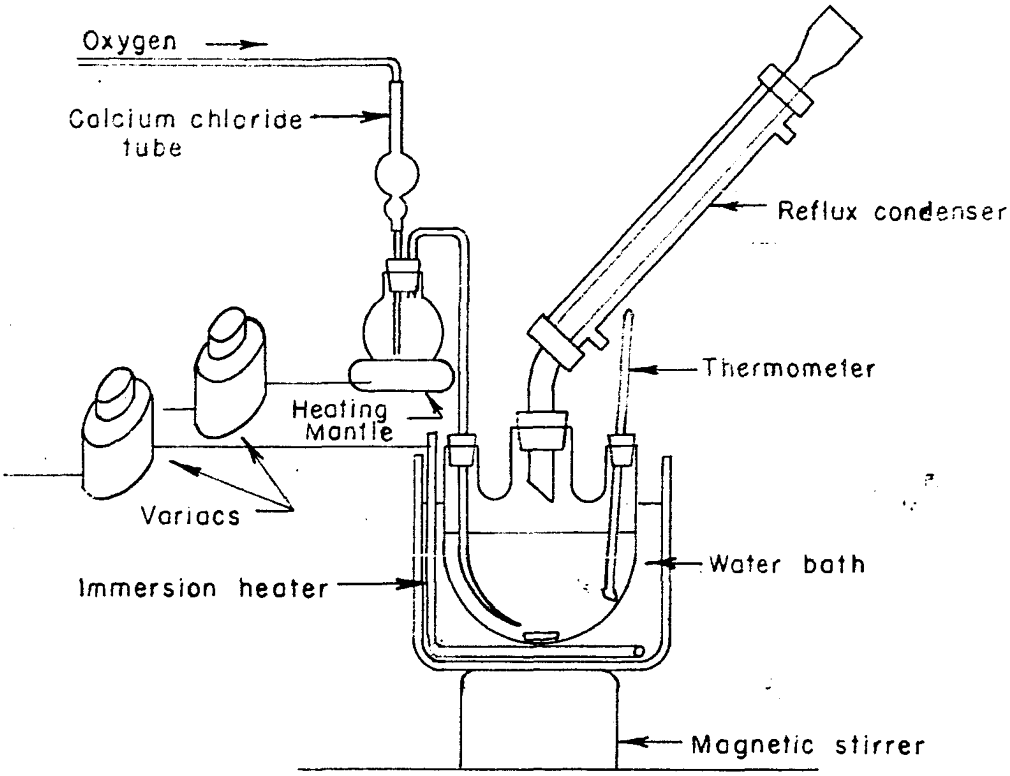


Fig. 44. Oxidation apparatus.

To fulfill these requirements an apparatus (Figure 45) was constructed in which eight 4-ounce screw cap glass bottles served as reaction flasks. Each bottle contained a glass rod stirrer and a capillary tube gas inlet. The bottles were supported in a temperature bath constructed of Plexiglass. Space was provided at the center of the bath for an electric lamp and a drive wheel which actuates the stirrer in each bottle. Gas could be passed into the bottles through a tygon plastic tubing manifold mounted around the outside of the temperature bath with branches leading to the capillary tube inlets of the individual bottles.

The capillary tubes were drawn to fine points in order to produce small gas bubbles of greater total surface area. Drawing the capillary tubes to fine points also insured even distribution of gas to all bottles by virtue of the large ratio of manifold cross section area to capillary cross section area.

Temperature control was provided by a circular immersion heater bent from 12 mm. Pyrex tubing and containing a #22 nichrome wire coil of sufficient length to reach a dull red heat at the maximum setting of a 120 volt variac.

The flow of gas to any reaction bottle could be stopped by placing a pinch cock on the tygon tubing leading to that bottle. By removing rubber band retainers the bottles could

Fig. 45. Polymerization apparatus, exploded view.

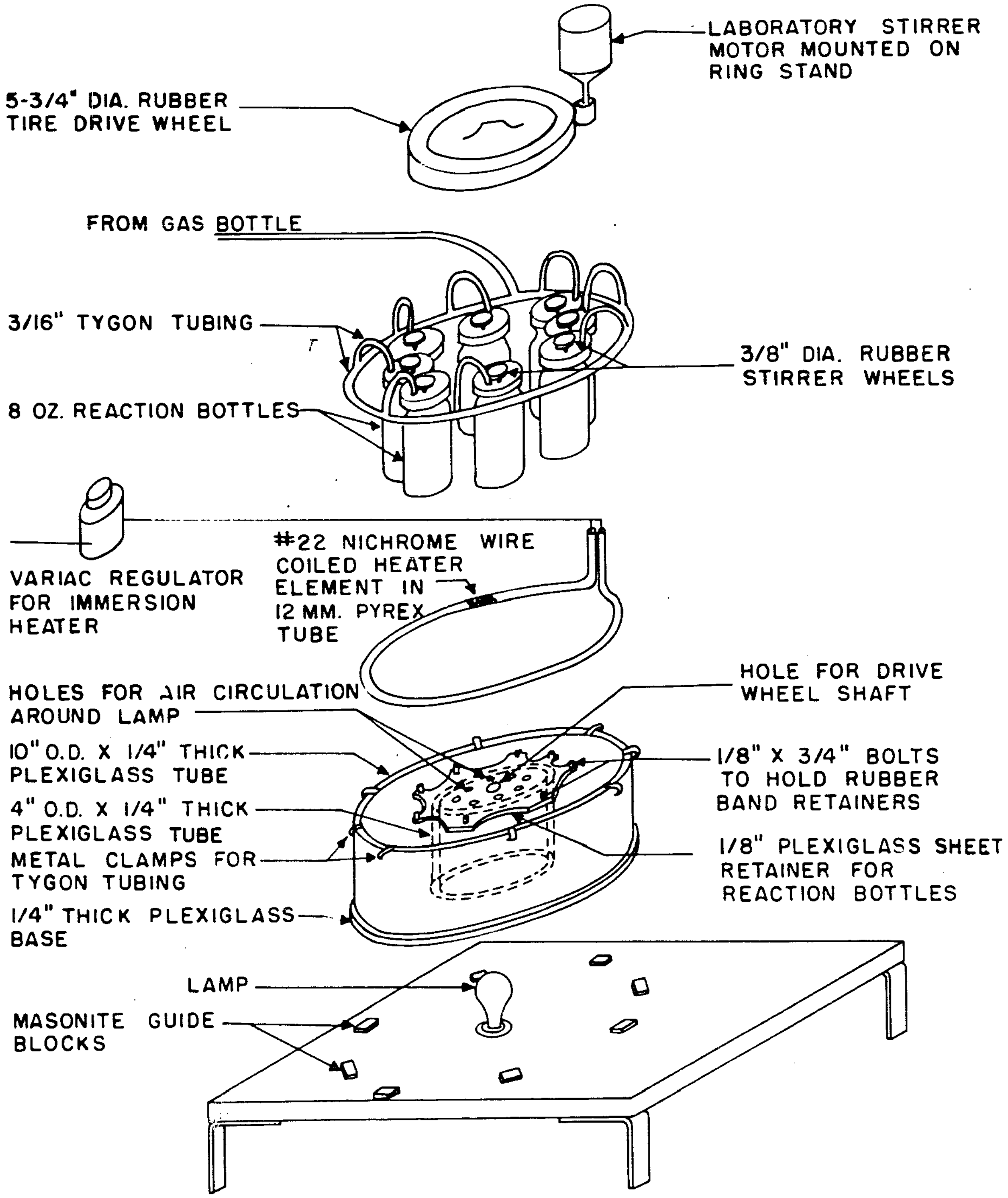
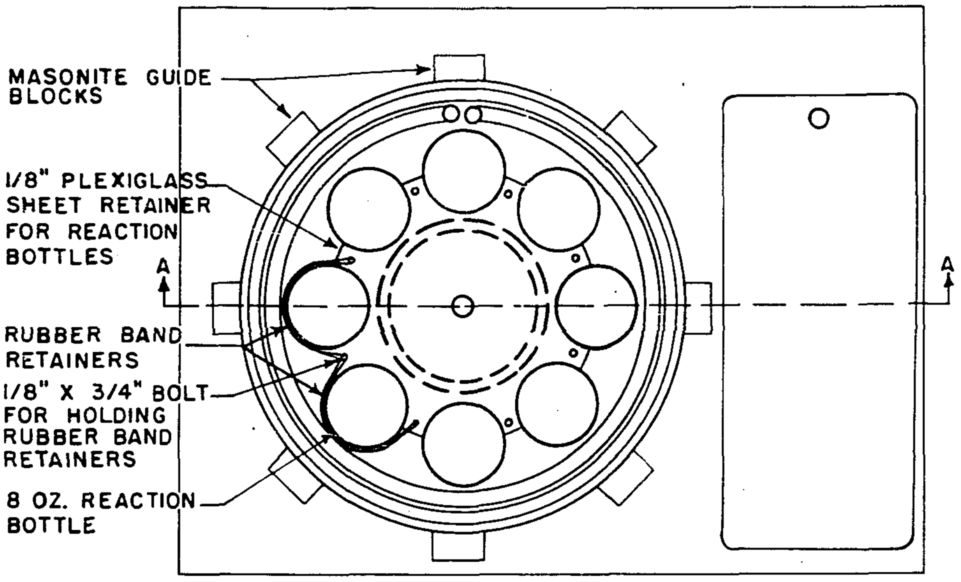
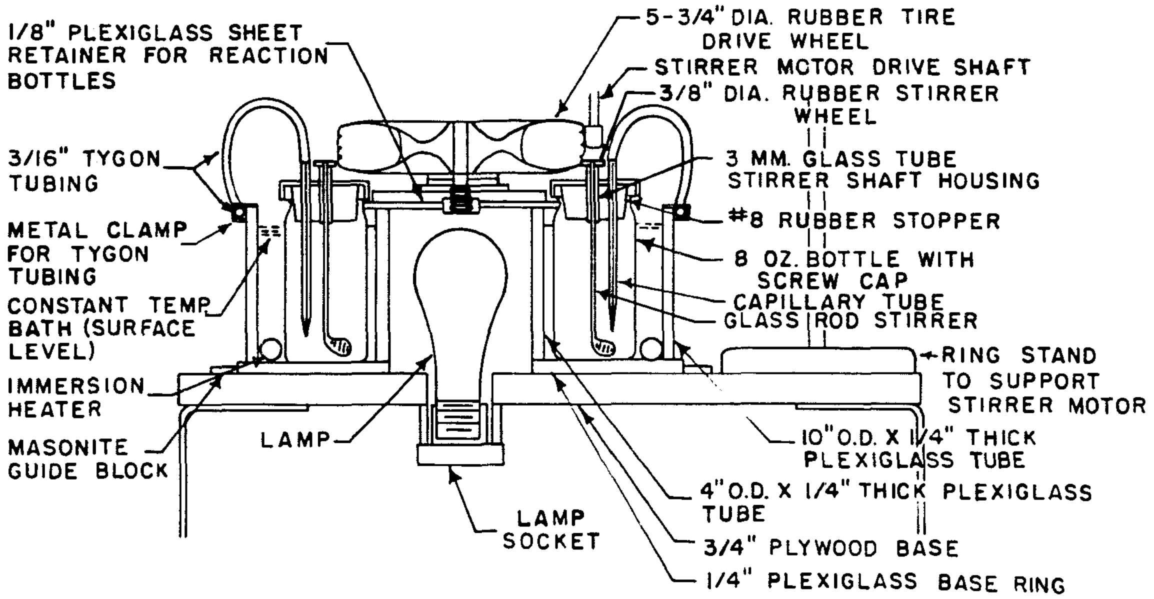

LABORATORY STIRRER MOTOR MOUNTED ON RING STAND
5-3/4" DIA. RUBBER TIRE DRIVE WHEEL
FROM GAS BOTTLE
3/16" TYGON TUBING
3/8" DIA. RUBBER STIRRER WHEELS
8 OZ. REACTION BOTTLES
VARIAC REGULATOR FOR IMMERSION HEATER
#22 NICHROME WIRE COILED HEATER ELEMENT IN 12 MM. PYREX TUBE
HOLE FOR DRIVE WHEEL SHAFT
HOLES FOR AIR CIRCULATION AROUND LAMP
10" O.D. X 1/4" THICK PLEXIGLASS TUBE
1/8" X 3/4" BOLTS TO HOLD RUBBER BAND RETAINERS
4" O.D. X 1/4" THICK PLEXIGLASS TUBE
1/8" PLEXIGLASS SHEET RETAINER FOR REACTION BOTTLES
METAL CLAMPS FOR TYGON TUBING
1/4" THICK PLEXIGLASS BASE
LAMP
MASONITE GUIDE BLOCKS

Fig. 46. Polymerization apparatus, orthagonal views.



TOP VIEW
(WITH DRIVE WHEEL REMOVED)



SECTION A-A

be taken from the bath individually for emptying and recharging without disturbing the operation of the remaining bottles. Masonite guides mounted on the plywood base allowed rotation of the entire apparatus during operation to facilitate handling the bottles.

A #8 rubber stopper was fastened inside the cap of each reaction bottle by means of small bolts. These stoppers supported the capillary inlet tubes and short lengths of glass tubing which served as housings for the stirrer shafts. Since these investigations did not require sampling during the course of polymerization no provision was made for removing samples without unscrewing the caps. If time-per cent conversion studies were to be made the apparatus could be easily modified by drilling a very small hole in the cap and rubber stopper through which a hypodermic syringe needle could be inserted in a manner similar to that employed with conventional polymerization apparatus having self-sealing crown caps.

Laboratory Procedures

Determination of peroxide number (a modification of Armour Chemical Division Method #122)

The peroxide number is the milli-equivalents of peroxide per kilogram of reactant. The oxidized products will reduce

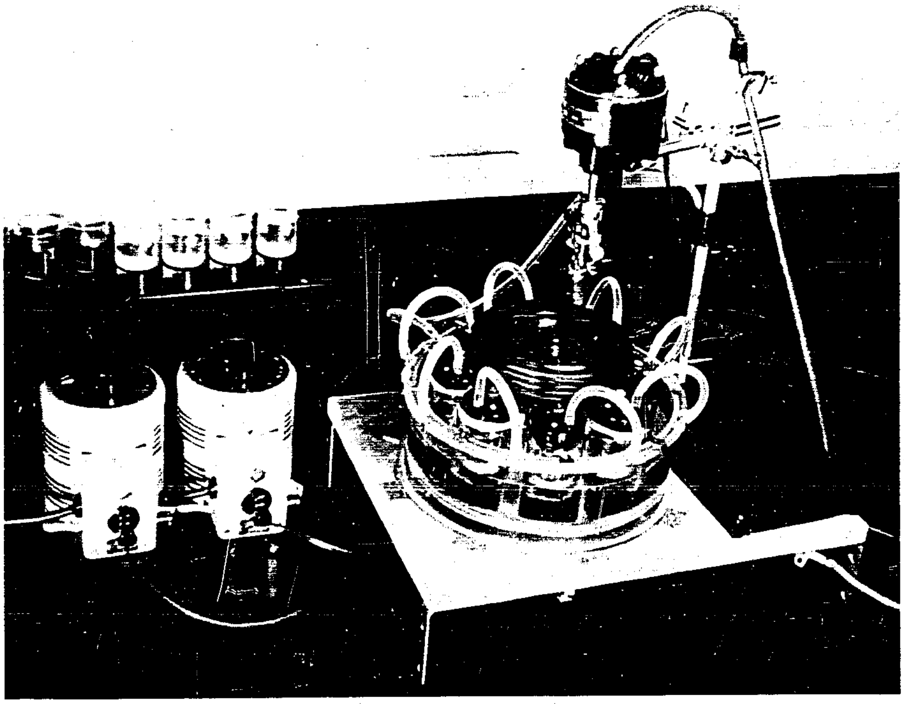


Fig. 47. Polymerization apparatus.

potassium iodide to liberate free iodine which is titrated with sodium thiosulfate.

Procedure:

1. Weigh 5 grams of sample (Arquad 2S weight) into a flask.

2. Add 25 ml. of a 1:1 by weight mixture of acetic acid and chloroform.

3. Add 1 ml. of potassium iodide-saturated aqueous solution and shake flask.

4. Add 100 ml. of distilled water and shake vigorously.

5. Titrate with N/100 sodium thiosulfate to a starch end point.

Peroxide number =

$$\frac{\text{ml. titration x normality of thiosulfate x 1000}}{\text{Sample weight}}$$

<u>Determination of iodine number</u> (a modification of Armour Chemical Division Method #113)

The iodine number is a measure of unsaturation and is expressed in centigrams of iodine absorbed per gram of sample.

Procedure:

1. Weigh 0.2 grams of sample (Arquad 2S weight) into a flask.

2. Add 20 cc. carbon tetrachloride.

3. Accurately add 20 cc. WiJS solution.[1]

4. Add 10 cc. of 2.5% aqueous mercuric acetate and allow to stand three minutes.

5. Add 50 cc. of 3% aqueous potassium iodide.

6. While shaking vigorously, titrate with 0.1N sodium thiosulfate to a starch endpoint.

7. Determine a blank in the same manner.

Iodine number =

$$\frac{(\text{ml. blank titration} - \text{ml. sample titration}) \times (\text{normality of thiosulfate}) \times 0.127}{\text{Sample weight}}$$

Removal of inhibitor from monomers

Hydroquinone was removed from methyl methacrylate by washing with 20 parts of a 5% sodium hydroxide 20% sodium chloride solution per 100 parts of monomer (68, p. 16).

Monomethyl ether of hydroquinone was removed from methyl acrylate by distilling at 44° C. under a vacuum of 210 mm. of mercury. The methyl acrylate distillate was collected in an ice bath after passing through cooling water kept at 16° C. (68, p. 16).

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[1] Preparation of the WiJS solution is lengthy and will not be described here. It is described in Armour Chemical Division's Method #108 and in most standard texts of organic analysis.

<u>Determination of cation exchange capacity</u> (from Davidson and Sheeler, reference 69)

Exchange of cations:

1. Weigh out about one gram (accurate to 1 mg) of soil passing the #10 sieve and place in a 300 ml centrifuge bottle. (A similar sample is weighed out for the hygroscopic moisture determination needed to convert air-dry weight to oven dry weight.)

2. Add 10 g of fine Ottawa sand to the clay in the centrifuge bottle. (Ottawa sand is inert and increases the permeability for the purpose of filtration in Step 7.)

3. Add 250 ml of neutral normal ammonium acetate to the contents of the centrifuge bottle and shake for three minutes.

4. Centrifuge at 2000 RPM for 10 minutes.

5. Decant the clear supernatant liquid.

6. Repeat Step 3.

7. Filter the contents of the centrifuge bottle with a Buchner funnel containing two fine filter papers.

8. Wash the material retained on the filter paper with 150 ml of neutral 70% (by volume) methyl alcohol to remove the excess ammonium acetate trapped in void spaces.

Distillation:

9. Transfer the filter paper and soil sample to a 500 ml Kjeldahl flask and cover with 150 ml of distilled water.

Soil clinging to the sides of the funnel may be transferred by wiping the funnel with a clean, wetted filter paper and placing in the flask.

10. Measure exactly 50 ml of 0.100 N hydrochloric acid into a 500 ml Erlenmeyer flask. Place the flask under a condenser with the receiving tube of the condenser extending well into the acid (Figure 48). Add 1 ml of 0.2% methyl red solution to the acid and a teaspoonful of magnesium oxide to the Kjeldahl flask.

11. Distill contents of Kjeldahl flask nearly to dryness.

Titration:

12. Remove Erlenmeyer flask and wash acid off receiving tube into the flask with distilled water.

13. Titrate the excess acid with 0.100 N sodium hydroxide. The end-point is evidenced by a yellow-orange color.

Calculations:

14. $c = \frac{A - B}{d} \times 100$

where c = cation exchange capacity, me per 100 g

A = (ml of HCl) (normality of HCl)

B = (ml of NaOH) (normality of NaOH)

d = weight of oven dry sample in grams

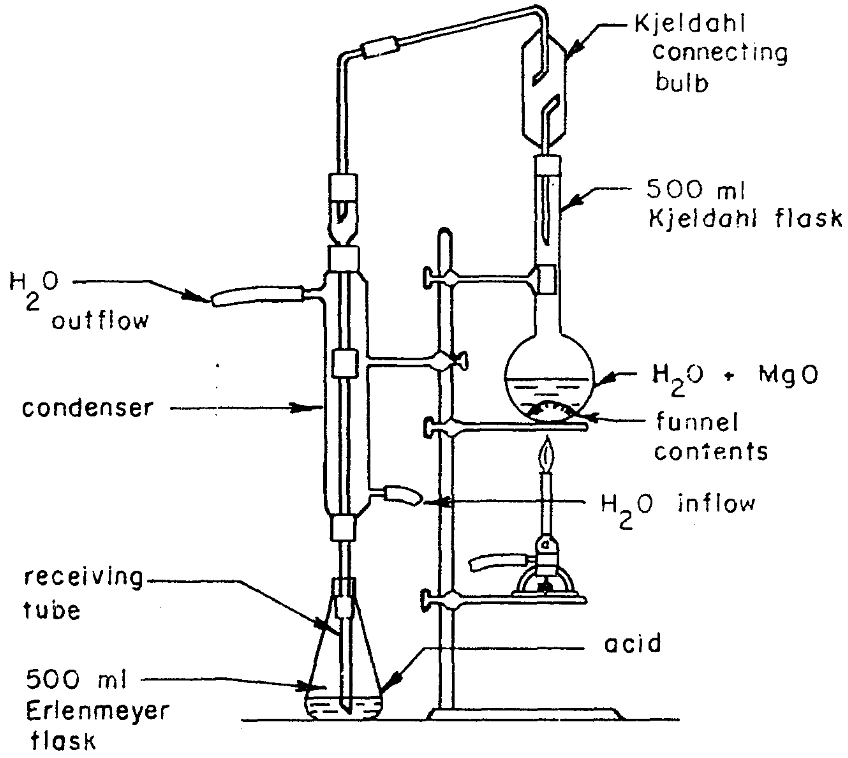

Fig. 48. Distillation apparatus for cation exchange capacity determination (taken from Davidson and Sheeler, reference 69).

Table 7. Properties and sources of chemicals used

Commercial name	Chemical description	Form	Per cent active fraction	Supplier	Price per lb. in drum lots
Part I					
	Acrylonitrile	Pure	100	Fisher Scientific Company	-
	Methyl acrylate	With 0.01% monomethyl ether of hydroquinone inhibitor		Rohm and Haas Company	0.40
	Methyl methacrylate	With 0.006% hydroquinone inhibitor		Rohm and Haas Company	0.31
Arquad 2S	Di-alkyl (soybean derived) di-methyl-ammonium chloride	Isoproponol solution	75	Armour Chemical Division	0.47
Part II					
Acrysol A-1	Polyacrylic acid	Aqueous solution	25	Rohm and Haas Company	0.30
Acrysol A-3	Polyacrylic acid	Aqueous solution	25	Rohm and Haas Company	0.30
Acrysol A-5	Polyacrylic acid	Aqueous solution	25	Rohm and Haas Company	0.30
Acrysol GS	Sodium salt of polyacrylic acid	Aqueous solution	$12\frac{1}{2}$	Rohm and Haas Company	0.12

Table 7. (Continued)

Commercial name	Chemical description	Form	Per cent active fraction	Supplier	Price per lb. in drum lots
Acrysol G-110	Ammonium salt of polyacrylic acid	Aqueous solution	22	Rohm and Haas Company	0.25
Acrysol ASE-75	A linear copolymer of acrylic ester with a carboxylic acid	Aqueous solution	40	Rohm and Haas Company	0.30
Acrysol ASE-60	A very slightly crosslinked copolymer of acrylic acid	Aqueous emulsion	28	Rohm and Haas Company	0.24
Rhoplex AC-33	An acrylic resin	Aqueous emulsion	46	Rohm and Haas Company	0.23
Krilium Loamaker	A hydrolyzed polyacrylonitrile	Powder		Monsanto Chemical Company	
Arquad 2HT	Di-hydrogenated tallow di-methylammonium chloride	Isoproponol solution	75	Armour Chemical Division	0.40
Armac T	Primary amine acetate derived from tallow fatty acids	Pure	100	Armour Chemical Division	0.32
Ethoduomene	N-octadecyl N, N', N'-tris-(2-hydroxyethyl) 1,3 trimethylene diamine	Pure	100	Armour Chemical Division	0.47

Table 7. (Continued)

Commercial name	Chemical description	Form	Per cent active fraction	Supplier	Price per lb. in drum lots
Arquad 12	Trimethyl dodecyl ammonium chloride	Isoproponol solution	50	Armour Chemical Division	0.56
Polyrad 1100 acetate	Reaction product of dehydroabietylamine and 11 moles of ethylene oxide	Pure	100	Hercules Powder Company	-
			Part III		
Acrysol CA	Salt of a polymeric tertiary amine	Aqueous solution	12½	Rohm and Haas Company	0.35 (pilot plant)
Acrysol CQ	Polymeric quaternary ammonium salt corresponding to Acrysol CA	Aqueous solution	12½	Rohm and Haas Company	0.35 (pilot plant)
			Part IV		
Spent sulfite liquor	71% lignins 24% sugars 5% resins and other substances	Aqueous solution	57% solids	Sulphite Pulp Manufacturers' Research League, Inc.	
Zein	Protein high in amide content, low in other functional groups	Powder	100	Nutritional Biochemicals Corporation	

Table 8. Properties of soils used

Laboratory sample number USBPR classification	20-2 silty loam	S-6-2 sand
Chemical properties		
Organic matter	0.17%	0.04%
Carbonates	10.17%	-
Iron	1.69%	-
Sulfate content	0.0%	-
Cation exchange capacity	8.7 me/100 gm	-
pH	8.7	6.7
Textural composition		
Sand	0.4%	94.4%
Silt	79.8%	4.1%
Clay	19.8%	3.0%
Colloidal clay	14.5%	1.4%

Mineralogical composition of clay fraction, both soils: Primarily montmorillonite with smaller quantities of illite and kaolinite.