

MECHANISM OF STABILIZATION OF COHESIVE SOILS BY TREATMENT WITH ORGANIC CATIONS¹

by

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ABSTRACT

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

INTRODUCTION

The mechanical properties of a soil vary substantially as a function of the water content. Addition of chemicals to a soil markedly influences the amount of water and the manner in which it is associated with soil particles. Organic compounds, for example, can decrease the water permeability of a soil used for lining a reservoir or an irrigation canal (Davidson and Demirel, 1960). Some success has been obtained in improving soil structure by the addition of certain organic chemicals (Grossi and Woollen, 1955). Such additives also reduce the plasticity of a soil, partly by increasing the size of the soil aggregates (Davidson, 1949; Kardoush, Hoover and Davidson, 1957).

From an engineering standpoint the most important influence that large organic cationic compounds have on soils is that of strength retention. A soil that is compacted exhibits a certain amount of strength, or resistance to a load or force. If the compacted soil is immersed in water, the strength is greatly reduced and may become zero. However, if a soil is first treated with small additions of an organic cationic compound, then compacted and immersed in water, the strength is not reduced so drastically (Henderson, 1949; Kardoush, Hoover and Davidson, 1957). It becomes obvious then that the organic compound influences the water absorption of a soil.

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Two other interesting phenomena occur when organic cationic chemicals are added to soil. As the amount of chemical added to the soil is increased, the strength of the specimen after immersion in water is increased, but above a certain optimum amount of the chemical, the strength is rapidly reduced. And secondly, the strength of an air-dried treated soil is lower than that of an air-dried untreated soil; that is, if specimens are not immersed in water prior to testing (Davidson, 1949; Hoover and Davidson, 1956; Kardoush, Hoover and Davidson, 1957).

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

CHARACTERISTICS OF LARGE ORGANIC CATIONIC CHEMICALS

These chemicals fall under the general heading of amines and have large hydrocarbon radicals with 8 to 22 carbon atoms. As might be expected, not all of them are soluble in water. Frequently, the organic complex is treated so as to produce a soluble salt, such as an organic chloride, etc. (Hoover and Davidson, 1956). These are characterized by having a positively charged cationic end and a negatively charged anionic end. The resultant cations formed have both a hydrophilic nature due to the net positive charge of the amine group and a hydrophobic nature due to the large hydrocarbon radical.

Experiments have indicated that a very intimate mixing of chemical and soil provide for maximum effect (Henderson, 1949). Therefore, the amount of organic chemical added is dependent on cost, solubility, ease of mixing, and needed and obtained effectiveness. If the additive can be added in a water solution or dispersion, effectiveness is increased, and usually less than 1 percent by weight of the dry soil is required.

In laboratory experiments a concentrated stock solution or dispersion of the chemical is prepared and then added to the soil to give the desired ratio of chemical to dry soil. Then sufficient water is added to provide optimum moisture for compaction of the particular soil (Hoover and Davidson, 1956).

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

Regardless of field or laboratory conditions or the type of machinery available, the salient fact is that moisture serves the double purpose of

acting as a carrier for the organic cations and of providing the optimum moisture for maximum compaction. The latter is by nature interdependent on the soil type and mineralogy. The amount of compaction in turn is dependent on the engineering requirements of the soil.

Generally—and this by no means describes the limits—soils treated with organic cationic compounds are used for lower pavement components where stability requirements cannot be met by untreated soils. It was stated that soils treated with organic compounds exhibit lower dry strengths than those that are untreated. This strength is, however, still above the minimum desirable. It is under adverse but normal environmental conditions that the treated soil shows more strength retention than the untreated soil (Davidson, 1949; Kardoush, Hoover and Davidson, 1957).

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

THE INFLUENCE OF ORGANIC CATIONS ON SOIL MOISTURE

Orientation of Water Dipoles

Dry soils are generally hard because the moisture still present is oriented as a thin dipolar film linking soil particles. If water is added to the soil, the film thickens, dipoles are disorganized, and the hardness or strength disappears (Handy, 1957).

When organic cations are added to a soil, the cationic end of the chemical balances the negative surface charge of the clay particles by replacing the inorganic cations already present; the clay tends to flocculate and has less ability to take up water.

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

The importance of orientation of soil moisture to soil particles is clearly indicated in the following experiment: A set of treated soil specimens was compacted and then allowed to air dry. An identical set of treated specimens was compacted and then allowed to age or cure in a moist atmosphere. Both sets of specimens were immersed in water before testing. The moist-cured specimens had less strength than the air-dried specimens (Kardoush,

Hoover and Davidson, 1957). Drying, therefore, is instrumental in obtaining a better arrangement of water films on soil particles. And since immersed strengths of chemically treated soils are greater than those of untreated soils, it may be possible to assign to the organic cation chemical the ability to influence the arrangement of water films in such a manner as to stabilize the bonding action of these films.

Because of the strong electric field associated with inorganic cations, water dipoles are oriented with respect to the cation and the clay particle. The affinity for water in this system is relatively great; therefore, additional

TABLE 1.—EFFECT OF ARQUAD 2HT ON THE BASAL SPACINGS OF A SODIUM BENTONITE

Moisture Condition	Basal Spacings (Å)			
	Treated		Untreated	
Air dried	11.9		11.0	
Moisture Chamber for 24 hr	15.5	~59	15.5	~59
Re-wetted		~20 ~63	~20 v. weak	~68
Moisture Chamber for 5 days	18.0		18.8	
Re-wetted		19.6 —	19.6 v. weak	~88

water can enter and cause disorganization of the oriented dipoles. Organic cations, on the other hand, set up a weaker electric field thus inducing less orientation of water dipoles; the affinity for water is weak, and additional water is not pulled into the system. Therefore, organic cations stabilize the bonding action of the weakly oriented water dipoles already present.

Preliminary X-ray analyses of soils treated with organic cations indicate that the above conclusion is valid. A sample of a Wyoming bentonite (Na-bentonite) was treated with a dilute dispersion of an organic cation, Arquad 2HT. An untreated sample wetted with distilled water served as a control. The data are presented in Table 1 (Rosauer and Handy, 1960).

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

inhibit expansion of the treated clay. Therefore, the length of curing is an important factor in obtaining maximum effectiveness of the organic cation by supplying the necessary moisture for effective orientation of water dipoles.

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

Surface Tension

Organic cations also reduce the surface tension in a soil-water mix. This reduction has two pronounced effects on the soil: the cohesion is reduced and the surface free energy is reduced (Davidson and Demirel, 1960a). The lowered cohesion results in the observed decrease in dry strength of treated soils, as well as the lowered plasticity. From the observed slight increase in internal friction and the considerable decrease in cohesion it follows that the shearing strength decreases (Davidson, 1949).

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

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

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

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

Since organic chemicals have both polar hydrophilic groups and non-polar hydrophobic groups, their solvation energy is low and the chemical

potential at a certain activity (which is a function of concentration) may be considered low. If the negative of the free energy change is small compared to the increase in surface free energy, the system would defeat absorption of excess water, since this would cause an increase in the total free energy.

In applying these considerations to a soil specimen that has been treated with an organic cation the following conditions are indicated. As the specimen is cured or air dried, water leaves the system. The concentration of

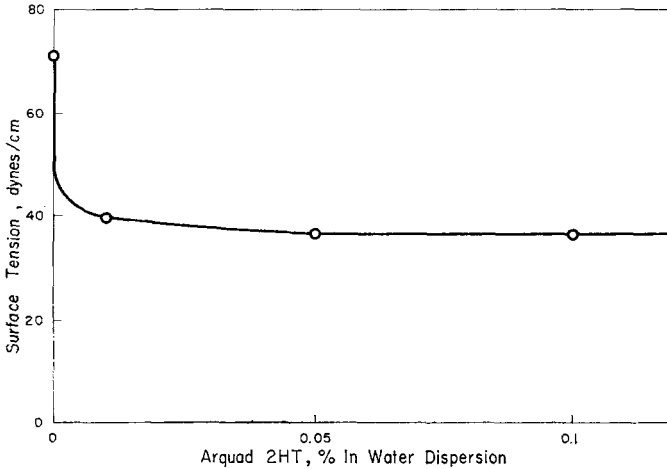


FIGURE 1.—Effect of Arquad 2HT on surface tension. Data by courtesy of the Armour Industrial Chemical Company. Arquad 2HT is a typical organic cationic chemical, specifically a quaternary ammonium chloride.

the cation increases, the concentration of water decreases, and, according to the data in Fig. 1, the surface tension increases. However, since the surface energy strives for a minimum, the increase in energy is slight and equilibrium is maintained. This is true only in the very low concentration range. If the concentration of chemical is greatly increased, by oven drying, for example, the change in surface tension upon addition of water is practically zero. If placed in a humid atmosphere, the system can readily take up moisture owing to the chemical potential and the absence of a great change in surface energy.

Excessively dried, treated soils should, therefore, readily take up moisture from the environment, whereas air-dried specimens should adsorb only a limited amount.

CONCLUSIONS

Organic cationic chemicals influence the amount of water adsorbed by a treated soil as well as the bonding action of water dipoles. X-ray diffraction analysis shows that this bonding action is stabilized by the pre-

sence of organic cations after proper curing. These chemicals also reduce the surface tension in a soil-water mix, thus resulting in a waterproofing condition. These two concepts explain why immersed strengths of treated soils are higher than those of untreated soils, and why treated soils require a period of curing before definite strength properties are exhibited.

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