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Characterization of chemical compaction aids for fine-grained soils

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Characterization of chemical compaction aids

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TABLE OF CONTENTS

CHAPTER I.

INTRODUCTION

Mechanical stabilization is the most common and important method of soil improvement techniques. In ancient times, it was customary to compact fills to be used as dams or levees. Paved roads existed in Egypt several thousand years before Christianity is a good evidence that ancient engineers used soil densification as a method for soil improvement (38).

Since R. Proctor discovered the important relationship between soil density, moisture content, and compactive effort, many research were directed toward improving the density characteristics of the soil by means of chemical stabilization to decrease the settlement and increase the strength of the soil (24).

Statement of the Problem

Nowadays, the growth of highway construction increases the demand for rapid development of the compaction technology to satisfy the requirements of both economy and efficiency. To meet this demand, various commercial chemical additives have appeared on market, which have been promoted as chemical compaction aids. The manufacturers claimed that these chemicals increase the densification and strength and improve the compactability of the soils at less water content and compacting effort than compaction without treatment. This approach became attractive to many soil engineers since it is an easy way to improve the soil engineering performance at lower cost. Unfortunately

the compaction aids were disappointing in many cases and frequently failed to give positive results.

An extensive laboratory study of chemical compaction aids has been carried out, with a variety of soils, in ISU soil laboratory to evaluate the effectiveness of each product within the fine-grained soils. The project is entitled "Chemical Compaction Aids for Fine-Grained Soils" and sponsored by the Federal Highway Administration. In this research project, compaction tests were performed to study the effect of chemical additive on optimum moisture content and maximum dry density. Also, K-test was used to measure the change in strength parameters of the treated soils immediately following compaction and, for some soils, after 7 days moist-curing period. Several significant parameters were included in the compaction process and influenced the overall performance of any chemical treated soil. Besides, soils used in this research, which have different physical properties, react differently when treated with various chemical compaction aids.

Based on the compaction and strength tests data, it was indicated that none of the chemicals is approved to be effective for all soils. It was stated that some chemicals are effective with certain soils while there are ineffective with the rest of the soils. In other words, certain chemical-soil combinations have produced definite improvements. Otherwise, no clear correlation was found between the soil mineralogy and the chemicals effectiveness. The study has succeeded to provide us with a general evaluation for each chemical and its degree of effectiveness for each soil, and made some recommendations for users

to assist them in selecting the proper chemical compaction aid for each
soil. However, the above investigation did not explain the possible
chemical reactions between soils and chemicals which stands behind the
effectiveness or uselessness of each chemical. A critical question
still to be asked is "How do these chemicals react with fine-grained
soil to improve its compactability?" It is believed that this question
could be answered if the physical chemistry of the compaction process
had been studied.

Scope of Investigation

In recent years, emphasis has been placed on explaining the
mechanical behavior of soils by means of physico-chemistry or surface
chemistry phenomena. This is especially so with fine-grained soils
where the mechanical behavior may be demonstrated to depend on the
surface properties of the mineral particles which constitute the soil
mass. Compaction aids may act to alter these surface properties in a
way that increases compactability. Therefore, the most logical basis to
completely analyze the mechanistic behavior of soils and understand
the chemical-soil interaction is to study the problem in relation to its
physical chemistry.

The physico-chemical property of concern involves the energy and
force of intereaction between soil particles when mixed with a chemical-
water solution, and the effect of chemical on the surface charge and
potential of the soil particles, and consequently the degree of inter-
action between them. Zeta-potential determination of the treated and

untreated soil will assist in predicting of the effect of chemical on surface potential of the soil particles and accordingly, their interaction.

What extremely complicates the analysis of the process is the secrecy of the chemicals makeup, and the difficulty in identifying them; they are expected to contain a mixture of chemical compounds and waste materials. Complete chemical information for each chemical was not available from the producers.

The objective of this study is the characterization of the chemical compaction aids by means of infrared spectroscopy to identify, as possible, the main functional groups. Also, the Vapor Pressure Osmometer will be used to estimate the molecular weights of some of the chemicals. Infrared techniques will be utilized to study the changes of the surface-groups vibrations caused by chemical molecules adsorption on the surface of the clay particles. This adsorption, if it occurs, can be observed by IR, and provide vital information on the mechanism of the reaction. The effect of chemicals on the surface potential of the soil particles will be studied by means of Lazer Zee Meter device that measures Zeta Potential.

Hopefully, by determining Zeta potential, and using infrared spectroscopy, we can draw a conclusion that gives a sensible explanation of the reaction that takes place between chemical and soil and help to predict the effectiveness of chemicals. The most optimistic object of this research is to develop a certain technique to characterize these chemicals as well as any new chemicals produced later and assist, along with compaction and strength tests, to make a definite judgment on each product.

CHAPTER II.

LITERATURE REVIEW

During the past 50 years, soil compaction has been of increasing interest to soil engineers. Much research was directed toward improving the strength characteristics of the compacted soil by soil stabilization. Soil engineers have realized the importance of colloidal chemistry in understanding the electrical forces acting between soil particles especially when the specific surface is large enough to cause the electrical forces to dominate the mass forces (22), i.e. in fine-grained soils.

Many scientists have discussed the factors included in the compaction process and described the compaction stages from both engineering and physical chemistry point of view. Handy (13) and Lambe (22) explain the characteristic plot of compacted density versus molding water content as follows: (1) In the presence of small amounts of water, the diffuse double layer of soil colloids is not fully developed; the electrolyte concentration is high, which depresses the double layer. This depression reduces the interparticle repulsion, causing a tendency toward flocculation, which gives a low degree of particle orientation and low density. (2) Increasing the molding water content expands the double layers around the soil particles, dilutes the electrolyte concentration and relieves the negative pore pressure. This effect reduces intergranular friction or the degree of flocculation, which permits a more orderly arrangement of particles, and a higher density. The term

lubrication well describes the increased interparticle repulsion that
permits the particles to slide past each other into a more oriented and
denser bed. (3) A further increase of water above an optimum moisture
content where the maximum density is reached, tend to cause positive
pore pressures which weaken the soil; it causes a further expansion of
the double layer and continued reduction in the net attractive forces
between particles, resulting in a reduction in strength. Even though a
more orderly arrangement of particles exists at this stage, the density
is lower because the added water has diluted the concentration of soil
particles per volume.

Foster (11) pointed out that for certain given moisture contents,
an increase in density results in increases in strength up to a certain
density, after which further increases in density result in a decrease
in strength as measured by CBR. Confirmation of the decrease in strength
is presented as field observations of the behavior of a silty clay soil.
The author believes that the decrease in strength is the result of the
development of pressure in the void phase of the soil structure. The
maximum strength occurs at moisture content less than the optimum
moisture content.

Soil stabilization has received the attention of researchers over a
period of many years. Herrin and Mitchell (15), investigating lime
stabilization, stated that at 5 percent lime by weight of soil, a de-
crease in maximum density and an increase in optimum moisture content
and strength was observed. Beyond this amount of lime, the lime fixation
point of Hilt et al. as cited in (15), little or no change in optimum moisture

content was noticed. The previously mentioned change in physical prop-
erties of clays as a result of lime treatment is generally agreed upon
in literature as being valid. However, the soil chemistry properties
responsible for these changes are not agreed upon. There are usually at
least four mechanisms presented in the literature to explain the
phenomena of lime treatment. These four mechanisms are: cation exchange,
flocculation, carbonation, and pozzolanic reaction. Ho and Handy (16)
have showed that the amount of calcium retained by the clay particles of
bentonite from lime - bentonite slurries increased with increasing per-
centage of lime. The writers hypothesized that at a higher pH, more
cations are adsorbed because of increasing dissociation of weak acidic
S_i OH groups exposed on clay crystal edges. Below pH 5 the cation exchange
capacity is fairly constant, due to isomorphous substitution in the clay
mineral structure. Diamond and Kinter (9) suggest that the colloid
chemistry explanation is correct during the initial stage of floccula-
tion. But since flocculation is caused by the electrolyte, if the
electrolyte was removed, deflocculation would occur. They found out
that deflocculation resulting from the removal of lime from the pore
solution did not occur. Rather than deflocculate, the formed flocs
persisted and became more pronounced and stable with time. They postu-
lated that an immediate reaction takes place between the alumina-bearing
edges of the clay particles and the lime adsorbed on the clay surfaces.
After curing a calcium silicate hydrate is formed which stabilized the
flocs and knits the particles. Although the hypothesis of Diamond and
Kinter (9) has neither been confirmed nor disapproved, there is evidence

that a possible reaction does occur on the clay edges.

Sodium chloride, when first used, was considered primarily as a dust palliative for open-surfaced aggregate roads, and then has become widely used for road construction, as pointed out by Sheeler (36). Gow, Davidson and Sheeler (12) reported that there are several reasons sodium chloride has been used as a soil-aggregate stabilizer. One reason is that sodium chloride acts as a lubrication agent to increase compacted density. Another factor is moisture retention from reduced vapor pressure in the pore water. Increased soil strength and stability have been attributed to recrystallization of sodium chloride. The recrystallization acts both to cement the particles together and fill the voids. Although some researchers believe this phenomenon to be true, others indicate that further research is necessary.

Marks and Haliburton (26) found that small percentage of sodium chloride added to raw soil have negligible effects on soil plasticity while increasing the compacted density and decreasing the optimum moisture content. Workability and moisture-retention qualities of the raw soil also were enhanced. When small percentages of sodium chloride were added to lime-modified soil, similar results were obtained. The authors think that sodium chloride may be used as a compaction aid, and as a catalyst in increasing the strength of lime modified and stabilized soils.

Organic compounds have been used successfully in soil stabilization. Davidson and Glab (6) have indicated that certain organic compounds such as fatty acid amine acetate, furnish large organic cations when dissolved in water, have considerable promise as an admixtures to increase

the stability of soils. Hoover and Davidson (18) have tried several cationic chemicals, such as amines and quarternary amonium salts, as stabilizing agents for Iowa loess. They stated that these chemicals in amounts ranging from 0.08 to less than 1.0 percent dry weight of soil substantially improved the stability of the loess. The chemicals were applied as solutions in water added to the soil in the amount necessary for compaction to near standard proctor density. They hypothesized that these organic chemicals dissociate in water to produce organic cations which may have exceedingly complex structures. These large organic cations are adsorbed to clay surfaces of the soil in cation exchange re-actions, replacing smaller inorganic cations that are present. Hoover, Davidson, and Plunkett (19) performed tests on four Iowa soils stabilized with two organic cationic chemicals, a quaternary amonium chloride and fatty amine acetate in combination with lignin. The use of the soil-organic cationic chemical-lignin combinations indicated increased com-pressive strength of the soil with a reduction of moisture adsorption and expansion. The benefits gained with the combination of soil, chemical and lignin was more than with the soil and chemical only.

Phosphoric acid also has been used in soil stabilization. Michaels and Tausch (28) used phosphoric acid at 0.05 percent by weight of soil in compacting a low plasticity clayey silt. The phosphoric acid signif-icantly increased compacted density and produced a large increase in soaked strength. A heavy montmorillonitic soil was also treated with phosphoric acid, and exhibited major improvement in soaked strength by incorporation of relatively high (0.5 to 2.0 percent by weight)

concentrations of sodium fluosilicate in conjunction with phosphoric acid.

Rosauer, Handy, and Demirel (33) studied the effectiveness of a quaternary ammonium chloride containing long unsaturated hydrocarbon chains, in soil stabilization. They found that this chemical is effective in stabilizing soils primarily by waterproofing the clay fraction. The nature of interaction between the organic salts and Wyoming bentonite was studied by means of x-ray diffraction. There was no direct evidence for interlayer penetration by the organic cation, perhaps because of the unwidely tetrahedral arrangement of the organic molecule. They suspected that the lack of interlayer penetration may explain the unusual effectiveness of the dialkyl dimethyl ammonium compounds as waterproofers for montmorillonite soils. Demirel and Davidson (7) utilized the x-ray diffraction to study the progress of reactions between phosphoric acid and montmorillonite, vermiculite, illite, chlorite, and kaolinite in the presence of water. Chemical analyses of the treated soils were performed at certain intervals. The reduction in heights of major diffraction peaks of the clay minerals were used as an index of reactivity with phosphoric acid. Changes in the diffraction peak intensities of the treated soils were used for estimating the extent of the reaction. Demirel and Davidson (7) emphasized that this technique cannot be used to predict the chemical mechanism of the complex hetrogeneous clay mineral-phosphoric acid reaction or its extent in a thermodynamics sense. Comparison between the peaks of the x-ray diffraction patterns was the only way to study the relative extent of reaction.

In the recent decades, improvement of soil properties with dispersants has received the attention of some investigators. Lambe (23) investigated the effect of addition of trace dispersants to soils in compaction early in 1954. He added sodium chloride tetraphosphate to fine grained soils. He found out that such dispersant increases the density and reduces the optimum moisture content of the compacted soil, and sometimes reduces the cohesion. He attributed the interaction between soil and dispersant to the reduction of interparticle attractive forces, or the increase of repulsive forces which tends to separate particles at points of contact and permits the particles to align themselves in more orderly orientation. A high degree of particle orientation leads to the decrease in volume. He stated that the dispersant-treated soils pick up considerably less water than the untreated soil. As strength is inversely related to water content, a higher strength of treated soil is expected. On the other hand, since the degree of compaction is inversely related to the resistance of soil to compaction, which is related to its strength, and the dispersive agent increases the degree of compaction, the added density obtained by dispersion would be expected to produce essentially no added strength. Lambe (23) has mentioned that the reaction between soil and dispersant increases the negative potential of the soil surface. Since the particle potential constitutes the repulsion between particles, the net effect of a dispersant - soil reaction is an increase of repulsion between particles. He concluded from this study that the most effective dispersant with one soil may be one of the least effective with another soil.

Chu and Davidson (4) compared the effectiveness of several defloc-
culating agents for the dispersion of soils, and studied their effect
on specific gravity of soil particles and the viscosity of suspending
medium. Among three chemicals compared, sodium metaphosphate was the
most promising deflocculating agent. The authors emphasized the
necessity of using a fresh prepared agent because a possible decrease in
its dispersive action may take place with time.

A number of studies have established the importance of colloid
chemistry in understanding the fundamental behavior of fine grained
soils. Van Olphen (41), Lambe (22), and Mitchell (30) describe the
electrical forces acting between the clay particles using the principles
of colloid chemistry and crystal chemistry. Lambe (22) stated that
a tendency toward flocculation is usually caused by increasing electro-
lyte concentration, ion valence, and temperature; and decreasing
dielectric constant, size of hydrated ion, pH, and anion adsorption.
The influence of the first four variables follows the Goy-Chapman theory
of the diffuse double layer; a decrease in the double-layer thickness
reduces the electrical repulsion, which in turn causes a tendency toward
flocculation. Van Olphen(41) studied in detail the theory of
stability of hydrophobic sols and its technological applications,
especially in drilling fluids. He discussed the interaction of clay
and inorganic salts as well as organic compounds, and the electrokinetic
and electrochemical properties of clay-water systems, and described the
mechanism of peptization of clay suspensions. He emphasized that the
chemisorption of anions of the peptizer on the clay crystal edges is

responsible for the reversal of the charge on these sites, which in turn eleminates the face-to-edge attraction. This results in the breakdown of the links between particles. The reversal of the edge charge is reflected as an increase in the electrophoretic mobility of the clay particles.

Lambe (23) and Mitchell (29, 30) supported the concept that clay peptization is staged at the edges of the clay particle, and results in an increase of the electrokinetic potential, while the flat surface of clay particle plays the major role in flocculation, which is reflected as a decrease in the electrokinetic potential. Ho and Handy (17) have studied the electrokinetic properties of lime-treated bentonites. Their investigation indicated that zeta potential generally decreases when Na- and Ca-bentonites were treated with varying amounts of $Ca(OH)_2$. This decrease in zeta potential was accompanied with a distinct flocculation of soils. Zeta potential almost ceased to decrease at the "lime retention point".

Senich (35) developed an apparatus and a procedure to study the double layer properties of clays. He used a flat electrophoretic cell and a microscope to measure the velocity of movement of colloid clay particles in suspension when an electric field is applied. He used Wyoming bentonite (< 1 μm) in his investigation. He calculated the electrophoretic velocity as follows:

$$\mu = \frac{D \, \xi \, E}{4 \, \pi \, \eta}$$

where

μ = electrophoretic velocity

D = dielectric constant

E = potential gradient, volts/cm

η = viscosity

ξ = zeta potential

He emphasized that the clay colloid fraction of soils has the most impor-
tance in the physical and chemical properties of fine grained soils, and
concluded that the effect of increasing soil concentrations in the
dilute concentrations investigated had little effect on increasing the
zeta potential of the system. Also, the polyvalent cations are more
effective in reducing the zeta potential than monovalent cations; both
having a deflocculating effect. Schofield (34), Wakatsuki et al. (43) and
Lambe (22) investigated the effect of pH on electric charge carried by
clay particles. Schofield (34) reported that a treated illitic clay
(< 2 μm) with acid ammonium oxalate carry a constant negative charge
between pH 2.5 and pH 5, due presumably to isomorphous substitution re-
placement. Additional negative charges develop with a rise in pH above
6. He explained that negative charges arise from isomorphous replace-
ments within the crystal lattice of the clay mineral, and such a re-
placement is a permanent feature of the crystals in as much as it
could not change reversily with changes in pH. The rise on the negative
charge of both treated and untreated soil between pH 6 and pH 7.5 proves
the existence of sites that are uncharged below pH 6, but become

negatively charged at higher pH values. No doubt some of these sites
are to be found along the edges of silicon-oxygen sheets of clay
minerals. His speculation agrees with the concept of edge adsorption
stated by many researchers.

Wakatsuki, Furukawa, and Kawaguchi (43) investigated the specific
and nonspecific adsorption of inorganic ions, particularly the specific
adsorption of cations on kaolinite. They include many kinds of
cationic species such as $Cr(ON_3)_3 \cdot 9 H_2O$, $Al(NO_3)_3 \cdot 9 H_2O$, $Fe(NO_3)_3 \cdot
6 H_2O$, $MgCl_2$, KCl, NH_4CL, etc. They used two kinds of kaolinites,
from Georgia kaolin, and from Japan. They found out that Mg^{2+} and Zn^{2+}
showed a high specific adsorbability on SiO_2 under neutral to alkaline
conditions. Electrophoretic mobility increased with increasing pH, and
decreased at higher ionic concentrations. The specifically adsorbed
cations showed a reverse in charge at higher concentrations when zeta
potential was measured. Cations classified into non-specifically ad-
sorbed showed a decrease in zeta potential with increasing cation con-
centration, but the reversal of charge was not observed. The zeta
potential results of some species in aqueous dispersion system was
correlated to their solubility. They stated that the solubility product
can be calculated from the reversal charge concentration, at which zeta
potential equals zero, and from pH data in the colloid dispersion system.
Lambe (22) also stated that the pH of the pore fluid affects the net
negative charge on a soil particle by altering the extent of dissocia-
tion of OH^- groups on the edges of the particles. High pH encourages
the dissociation and increases the net charge, thus expanding the double

layer; low pH does the reverse. The adsorption of anions, especially polyvalent anions, increases the charge on the particles and thereby causes dispersion.

Mitchell (29) explored a new area for studying the electrical properties of soils. He studied the mechanism of dielectric dispersion and conductivity dispersion to demonstrate that electrical response characteristics can be used to reflect differences in soil structure determining factors.

For the past three years, the Iowa State University Engineering Research Institute has been conducting the "Chemical Compaction Aids for Fine-Grained Soils" project to evaluate the effectiveness of chemicals in compaction process. More than twenty chemicals under different commercial names are included. Some of them are not marketed as compaction aids but as soil stabilizers, soil conditioners, soil penetrance, etc. For most, only manufactuers' and suppliers' trade literature is available. Approximately 25 fine-grained soils were selected from various locations to be representative of major soil types throughout the United States, having a variety of clay mineralogy. Whited (44) and Yang (45) investigated many chemicals, primarily from the engineering point of view. They performed strength tests and moisture-density tests for treated and untreated soils. The research succeeded in evaluating the potentialities of each chemical in compaction, but much remained to be learned about the interaction mechanism between soils and chemicals. Therefore, it appeared that a study of the physical-chemical relationships resulting from the chemical treatment of soil was needed in this

project to clarify these relationships and to achieve a better under-
standing of the effect of chemicals.

CHAPTER III.

INFRARED SPECTROMETRIC IDENTIFICATION

OF CHEMICAL COMPACTION AIDS

Introduction

In 1800, the existence of infrared rays (IR) was discovered by
William Herschel. The apparatus used by him consisted of some thermom-
eters and a prism producing a spectrum by exposing to the sun's rays.
He found that red rays not only gave a heat effect, but that this
phenomenon persisted also beyond that region and that its intensity
there even increased. This invisible heat radiation of 1-100 µm wave-
length, which followed the same laws of reflection and refraction as
visible light, was called infrared (32).

The subdivision of this extensive range of wavelengths into the
near infrared region from about 1 µm to 25 µm, and the far infrared be-
yond 25 µm, was initially made according to experimental difficulty. Such
a distinction, which is necessarily arbitrary, is now primarily defended
on grounds of theoretical significance. The near infrared is that region
in which molecular vibrations may be studied, where molecular rotation
and the vibration of crystalline lattices usually occur at longer wave-
lengths. These general comments are tabulated in Fig. 3-1.

Coblentz, in the first decade of the present century, confirmed that
infrared adsorption spectra are peculiar to the particular molecule
examined. By 1939, the behavior of a large number of simple molecular
systems had been investigated in detail and explained in terms of ac-
cepted molecular models (3). The type of information which studies in the
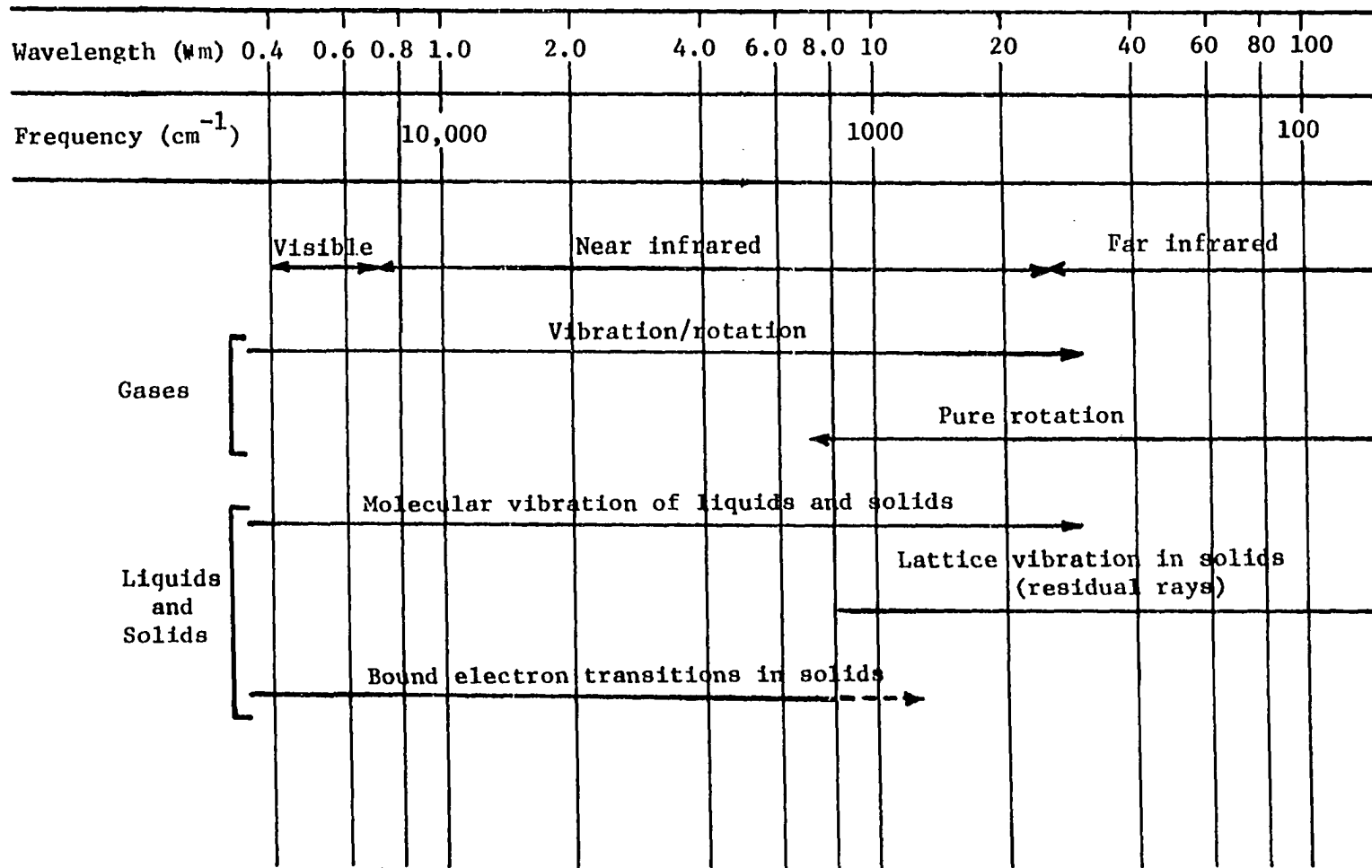
Figure 3-1. The infrared spectrum. Origin of spectra

"near infrared" region may be expected to assist can be classified under six headings: (1) The thermodynamic behavior of a molecular system can be calculated if its modes of vibration and rotation are known. (2) Information on chemical bonding may be obtained and discrimination made between rival structures. (3) Substances may be identified from their infrared spectra so that, by a process analogous to fingerprinting, the molecules may be identified. (4) Under certain conditions mixtures may be analyzed. (5) Reactions may be followed. (6) Valuable information on the energy configuration of electrons in solids may be obtained.

Not all of these goals can yet be pursued with complete freedom. In the brief theoretical discussion that follows, it is clear that even a fairly simple molecule can give an extremely complex pattern.

Infrared spectra interpretation is mainly on an empirical basis. The interpreter takes advantage of this complexity when he matches a spectrum of an unknown compound against that of an authentic sample. A Peak-by-peak correlation is excellent evidence for identity. On the other hand, it turns out that certain groups of atoms give rise to vibration bands at or near the same frequency regardless of the structure of the rest of the molecule. It is this feature which permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characteristic group frequencies.

In this research we attempted to use infrared spectroscopy to characterize and, if possible, identify the various chemical compaction aids. The complexity and the secrecy of the chemicals limited the re-

sults obtained. However, the method has been successful in revealing the main functional groups in some of the chemicals. We shall rely heavily on these characteristic group frequencies. Since we do not rely solely on infrared spectra for identification, a detailed analysis of the spectrum is not required.

Following our general plan, we shall present only sufficient theory to accomplish our purpose – utilization of infrared spectra in the characterization of chemical compaction aids.

Theory

Infrared radiation of wavelengths longer than about 100μ is absorbed and converted by an organic molecules into energy of molecular rotation. This adsorption is quantized; thus, a molecular rotation spectrum consists of discrete lines.

Infrared radiation in the range from about 1 to 100 μ is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is also quantized, but vibrational spectra appear as bands rather than lines because a single vibrational energy change is accompanied by a number of rotational energy changes. It is with these vibrational bands – particularly those occurring between 2.5 and 15 μ– that we shall be concerned.

Band positions in infrared spectra are presented either as wavelengths or frequencies. The common unit of wavelength in infrared spectrometry is the micro-meter (μ). Frequencies are usually expressed in terms of wave numbers (ν) whose unit is the reciprocal centimeter

(cm^{-1}). In terms of this unit, the wave number is the reciprocal of the wavelength in centimeters. Or, when the wavelength is in microns, the wave number is $\frac{1}{\mu} \times 10^4$.

Band intensities are expressed either as transmittance (T) or absorbance (A). Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. Absorbance is the logarithm to the base 10 of the reciprocal of the transmittance, $A = \log_{10} (\frac{1}{T})$.

There are two types of molecular vibrations: stretching and bending. A stretching vibration is the vibration along the bond axis such that the distance between the two atoms is increased or decreased. A bending vibration involves a change in bond angles. Only those stretching and bending vibrations which result in a rythmical change in the dipole moment of the molecule are observed in the infrared. It is the net change in charge distribution within the molecule produced by stretching and bending which makes interaction possible between the molecule and the oscillating field of the infrared radiation. The various stretching and bending modes for an AX_2 group as shown in Fig. 3-2.

A nonlinear molecule of n atoms has $3n - 6$ possible fundamental vibrations. The theoretical number of fundamental vibrations (absorption frequencies) will not be observed because overtones and combination tones can increase, and other phenomena can reduce the number of observed bands. The following can reduce the theoretical number of bands:
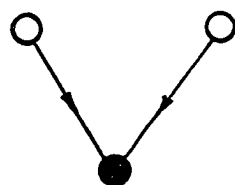
Symmetrical
stretching
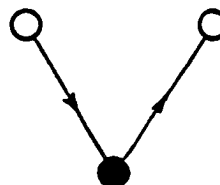
Asymmetrical
stretching

STRETCHING VIBRATIONS
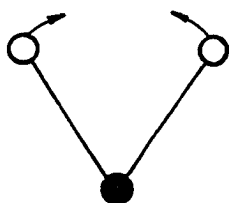
In-plane bending
or scissoring
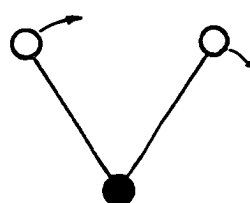
In-plane bending
or scissoring
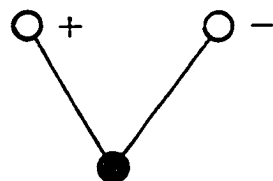
Out-of-plane bending
or twisting
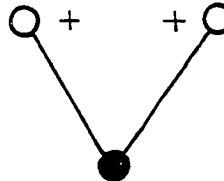
Out-of-plane bending
or wagging

BENDING VIBRATIONS

Fig. 3-2. Vibrational modes for AX_2 group. (+ and — represent relative movement at right angles to the surface of the page.)

1. Fundamental frequencies which fall outside of the $2.5 - 15\mu$ region.

2. Fundamental bands which are too weak to be observed.

3. Fundamental vibrations which are so close that the bands coalesce.

4. The occurence of a degenerate band from several absorptions of the same frequency in highly symmetrical molecules.

5. The failure of certain fundamental vibrations to appear in the infrared because of lack of required change in dipole character of the molecule.

General assignments for stretching frequencies can be derived by the application of Hooke's law. In the application of the law, two atoms and their connecting bond are treated as two masses joined by a spring. The following equation, derived from Hooke's law, states the relationship between frequency of oscillation, atomic masses, and the forces constant of the bond (10).

$$\nu = \frac{1}{2\pi c} \left[\frac{f}{\frac{M_x \cdot M_y}{M_x + M_y}} \right]^{1/2}$$

where

ν: the vibrational frequency (cm^{-1})

c: velocity of the electromagnetic radiation (cm/sec)

f: force constant of bond (dynes/cm)

M_x and M_y: mass of atom x and atom y, respectively (g).

The value of f is approximately 5×10^5 dynes per cm for single bonds and approximately two or three times this value for double bonds

and triple bonds, respectively.

Less energy is needed to produce bending than stretching vibrations of the same bond; bending vibrations are therefore, found at lower frequencies.

The effects of hydrogen bonding on stretching and bending vibrations should be noted: Hydrogen bonding decreases stretching frequencies and increase bending frequencies.

Sample Handling

Liquids may be examined neat (undiluted) or in solution. Neat liquids are examined between plates, with or without spacers (0.005 - 0.1 mm thick). Volatile liquids can be examined neat in sealed cells. The amount of material needed is between 1 mg and 10 mg. The solutions are handled in cells from 0.1 mm to 1 mm in thickness. Concentrations are usually between 0.05 and 10%; the amount of solute required is in the range of 1 to 15 mg. A compensating cell of either fixed or variable thickness and filled with solvent is placed in the reference beam to subtract the adsorption spectrum of the solvent. The spectrum thus obtained is that of the solute except in those regions in which the solvent absorbs strongly, such that no transmittance is obtained.

In our case, the solvent is water for the chemical compaction aids. It is known that salt cells are not suitable for samples containing water because the water will dissolve the sodium chloride cells or plates. For this reason, silver chloride cells (throwaway IR cells, no. TAC-1) and polyethelene cells were tried, but no spectrum was transmitted. Salt cells were tried and gave reasonable results, although

the water contained in the chemical compaction aids dissolved the cells to some extent. To reduce the cell damage as much as possible, salt plates, instead of the liquid cell, were used to minimize the contact time between the salt plates and the chemical by eliminating cell filling and emptying time. Circular and rectangular salt plates were used. A drop of the chemical was placed between two salt plates and squeezed to form a very thin film, then the cell was mounted in the IR spectrophotometer to be tested.

This method was rather successful with many chemicals. Some chemicals did not show any spectrum and reacted severly with the cell material. The cell plates were polished after every test to renew the smooth surfaces.

Instrumentation

The modern double-beam infrared spectrophotometer consists of five principal sections: radiation source, sampling area, photometer, monochromator, and detector. A Beckman spectrophotometer model IR4 was used in this study. The diagram of its optical system is shown in Figure 3-3.

Radiation Source. Infrared radiation is produced by electrically heating a source, usually a Nernst filament for a globar to 1000-1800 °c. The Nernst filament is fabricated from a binder and oxides of zirconium, thorium, and cerium. The globar is a small rod of silicon carbide. The image of the source must be wider than the maximum width of the slits. The globar has a negative temperature coefficient of resistance and at
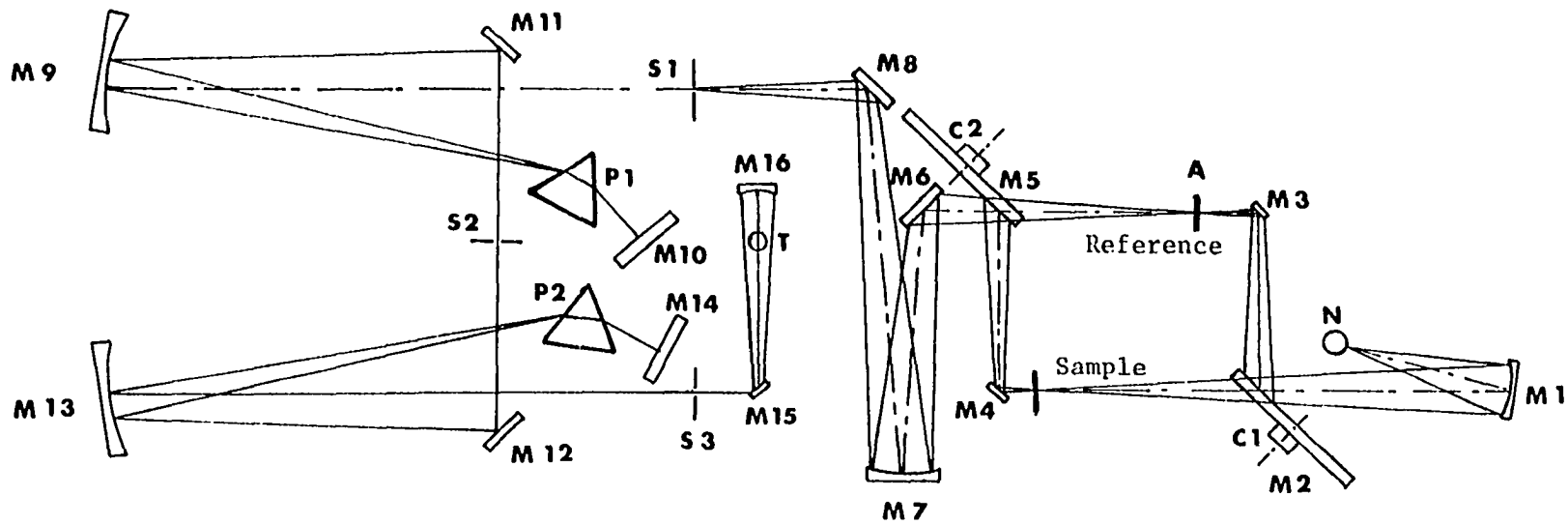
N :	Nernst Glower	T :	Thermocouple
C_1, C_2:	Half mirror chopper	A :	Optical attenuator
S_1, S_2:	Entrance slits	S_3:	Exit slit
P_1, P_2:	Prisms	$M_1, M_2, \ldots M_{16}$:	Mirrors

Figure 3-3. Optical diagram of beckman spectrophotometer model 1R4

ambient temperatures the glower resistance is too high to permit appreciable conduction. The source intensity level, after being established through use of the manual control, is automatically maintained by the glower regulator.

The radiation from the source is divided into two beams the sample beam and the reference beam.

Sampling Space. Reference and sample beams enter the sampling area and pass through the reference cell and sampling cell, respectively. The instrument sample space is located between the photometer and the monochromator sections. The sampling area accommodates a wide variety of sampling accessories, and is equipped with a variety of cell holders designed to hold liquid and gas cells and plates for KBr pellets and mulls.

Photometer. The photometer section of the IR4 is directly related to the measurement of infrared intensity. The principal components are the sychronous demodulator, chopper mirror, reference mirror, photometer diagonal mirror, reference comb, linear comb potentiommeter, comb servo motor, source housing, source light gate, monitor phototube, Nernst glower and heaters.

Monochromator. In IR4 double-prism, Littrow Monochromater disperses the instrument radiation. Maximum resolution is obtained by using prism materials only in their range of greatest dispersing effectiveness. Each material has only a rather narrow effective range. Sodium chloride prisms are widely accepted as a compromise material for the range

$4000-650 \text{ cm}^{-1}$ $(2.5 - 15.4 \text{ } \mu m)$, though they are somewhat deficient at the high frequency (short wave length) end.

The narrower the slit width, the greater is the resolution. Therefore the slit width is programmed to increase as the emitted source energy decreases, so that constant reference beam energy enters the monochromater.

Detector. The detector is a device which measures radiant energy by means of its heating effect. Two common types of detectors are the thermocouple and bolometer. In IR4 the detector is thermocouple detector (1.9 ohm rapid response vacuum type detects the 11 cycles chopped source radiation). The chopped radiation falling on the thermocouple KB5 lens is focused on the detector element where it generates a minute 11 cycle voltage. This alternating signal is supplied first to the preamplifier through an input transformer, and subsequently to the signal output amplifier. The amplified signal of the detector is used to position the optical attenuator so that the radiation from the reference and sample beam are kept at equal intensity. The amount of attenuation required is a direct measure of the adsorption by the sample. The movement of the attenuator is recorded by the recording chart pen.

Interpretation of the Spectra

Infrared spectra have been made for many chemical compaction aids to reveal any identical chemicals, and major components. The composition of chemical compaction aids in general is too complicated to be easily identified from the IR spectra, but at least the main functional groups of most of the chemical could be ascertained so that any future

changes can be detected and similar compaction aids under different commercial names can be recognized. The IR spectra of the chemicals are shown in Figure 3-4.

The following are the results of the infrared spectra interpretation:

SC-518. A transparent blue, viscous liquid, soluble in water, insoluble in benzene, carbon tetrachloride, or chloroform. Strong broad I.R. peaks at 2.9 and 6.1μ, weak peak at 4.7μ, and strong background at 8 to 15μ. Presence of water is indicated. A rather strong triplet occurs at 3.45μ, medium sharp peak at 6.95μ, medium triplet at 7.3μ, strong peak at 9.1μ, and additional weak peaks at 7.8, 8.1, and 10.7. The I.R. spectrum suggests an organic aliphatic alcohol.

Petro-S. A transparent reddish-brown viscous liquid, soluble in water, insoluble in benezene, carbon tetrachloride or chloroform. Strong broad peaks at 2.9 and 6.1μ, and a weak peak at 4.7μ, indicate the presence of water. A strong triplet occurs at 3.4μ, weak but sharp peaks at 6.6, 6.9 and 7.3μ, with a strong broad peak at 9.5μ. The strong triplet at 3.4μ suggests the presence of an aliphatic compound. However, the spectrum also indicates a high percentage of water which may obscure adsorption of other compounds. The producer, Petrochemical Co., Inc., refers to Petro-S as a sodium alkyl ethylene sulfonate in liquid form.

Coherex. A yellowish grey viscous liquid, soluble in water, insoluble in benzene, carbon tetrachloride or chloroform. The producer, Golden Bear Division, Witco Chemical, refers to Coherex as a concentrated highly stable emulsion of petroleum oils and resins consisting of about
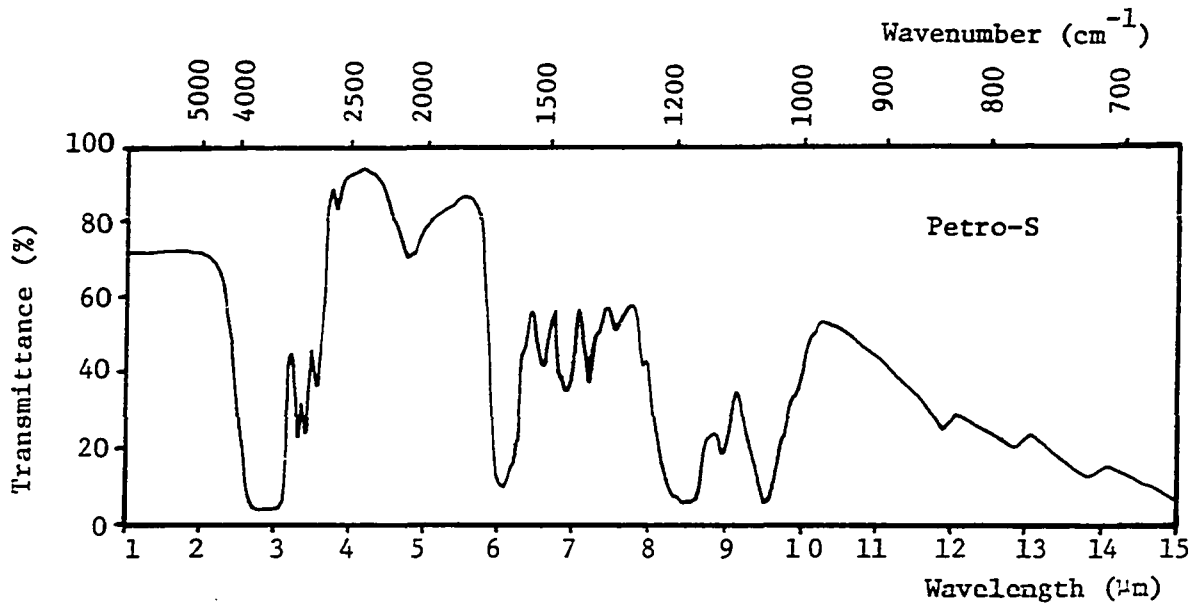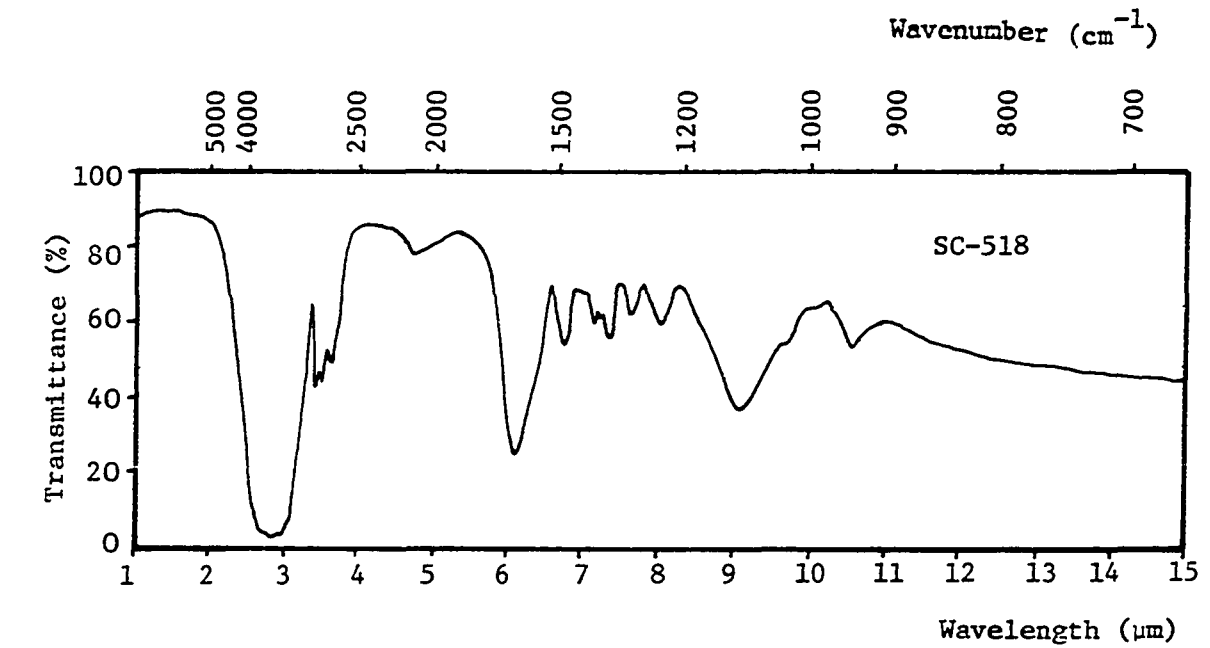
Figure 3-4. Infrared spectra of chemical compaction aids
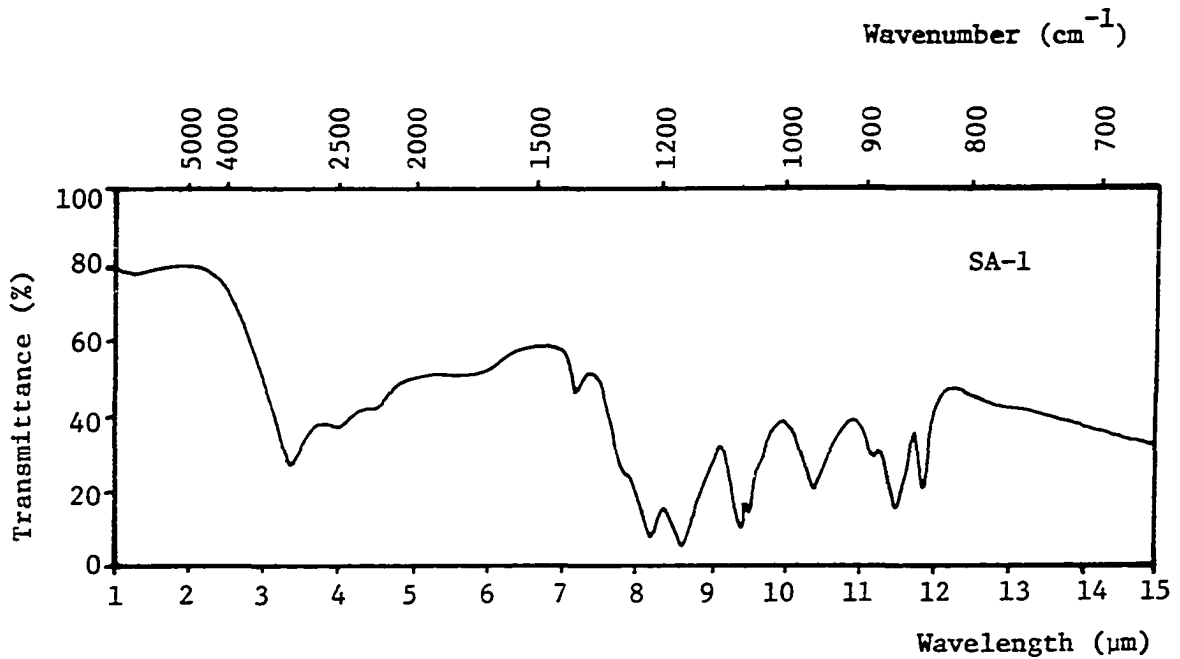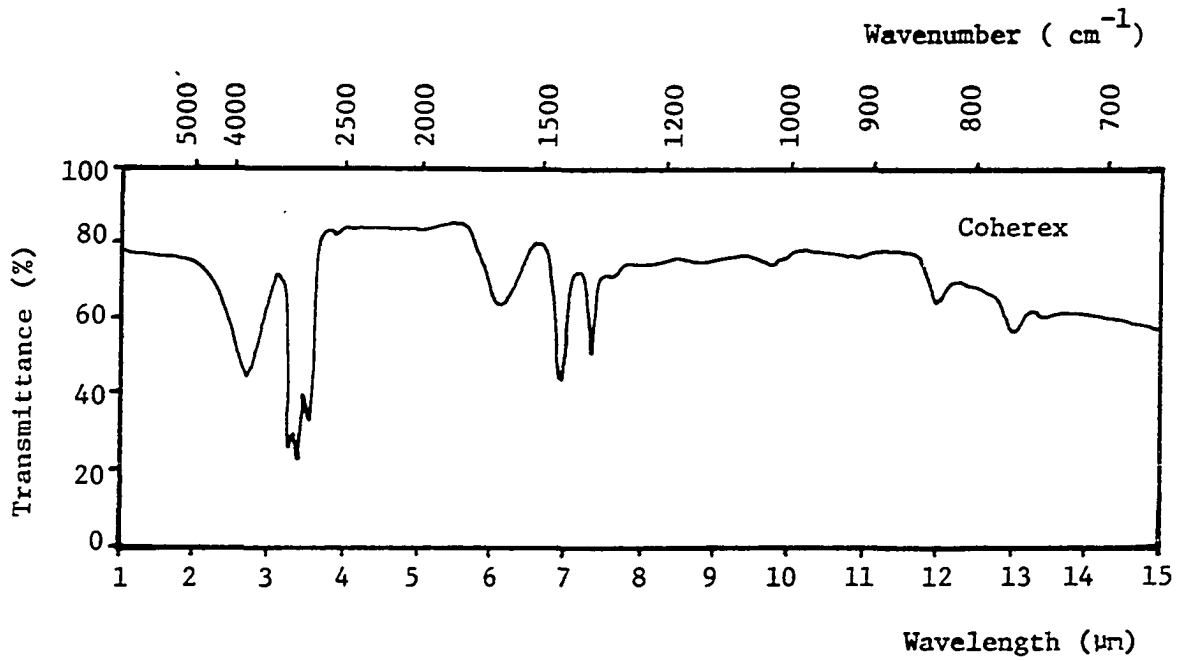
Figure 3-4. (Continued)

Figure 3-4. (Continued)

Figure 3-4. (Continued)

34

Figure 3-4. (Continued)

35

Wavenumber (cm^{-1})

Aerosol OT 75%

Wavelength (μm)

Wavenumber (cm^{-1})

Poly-Tergent

Wavelength (μm)
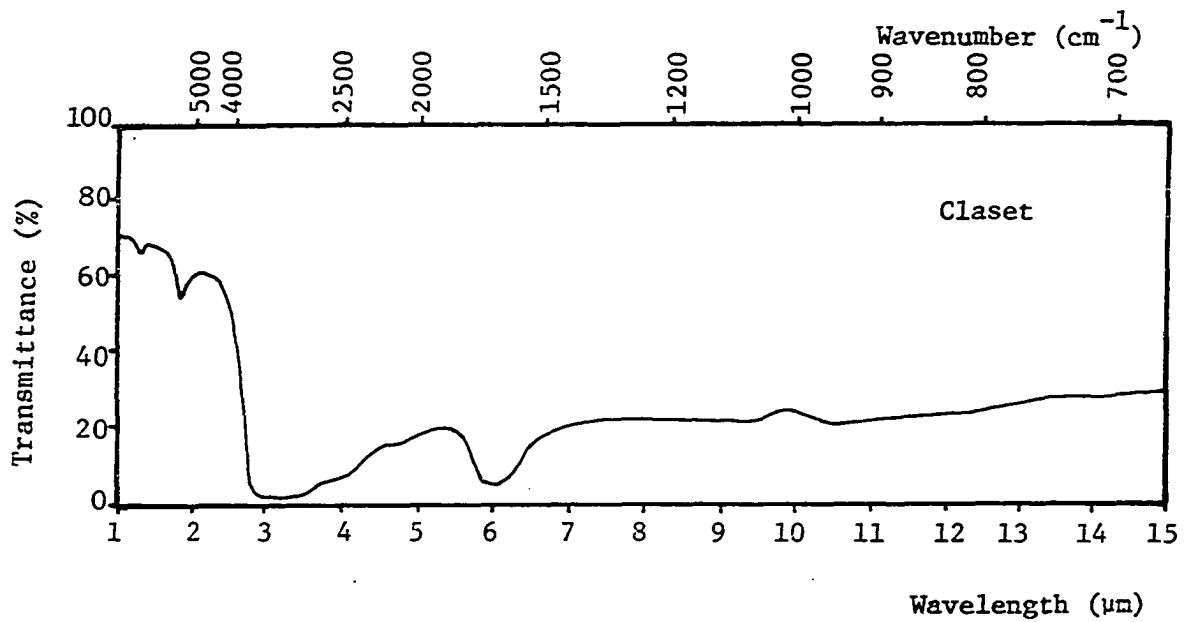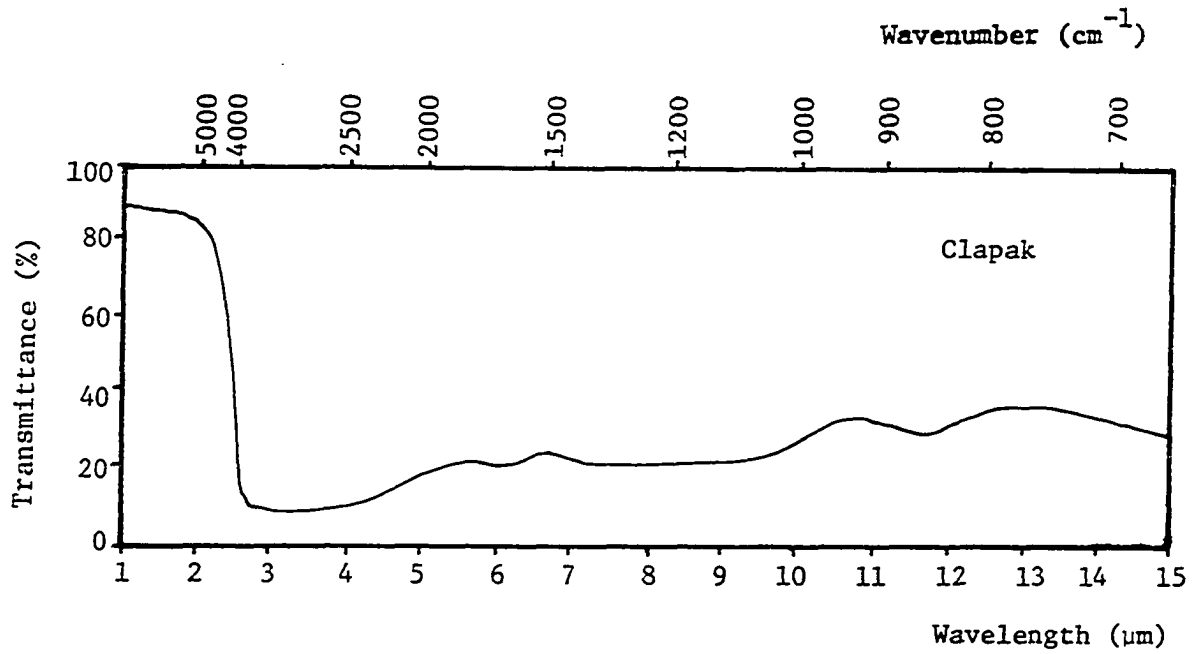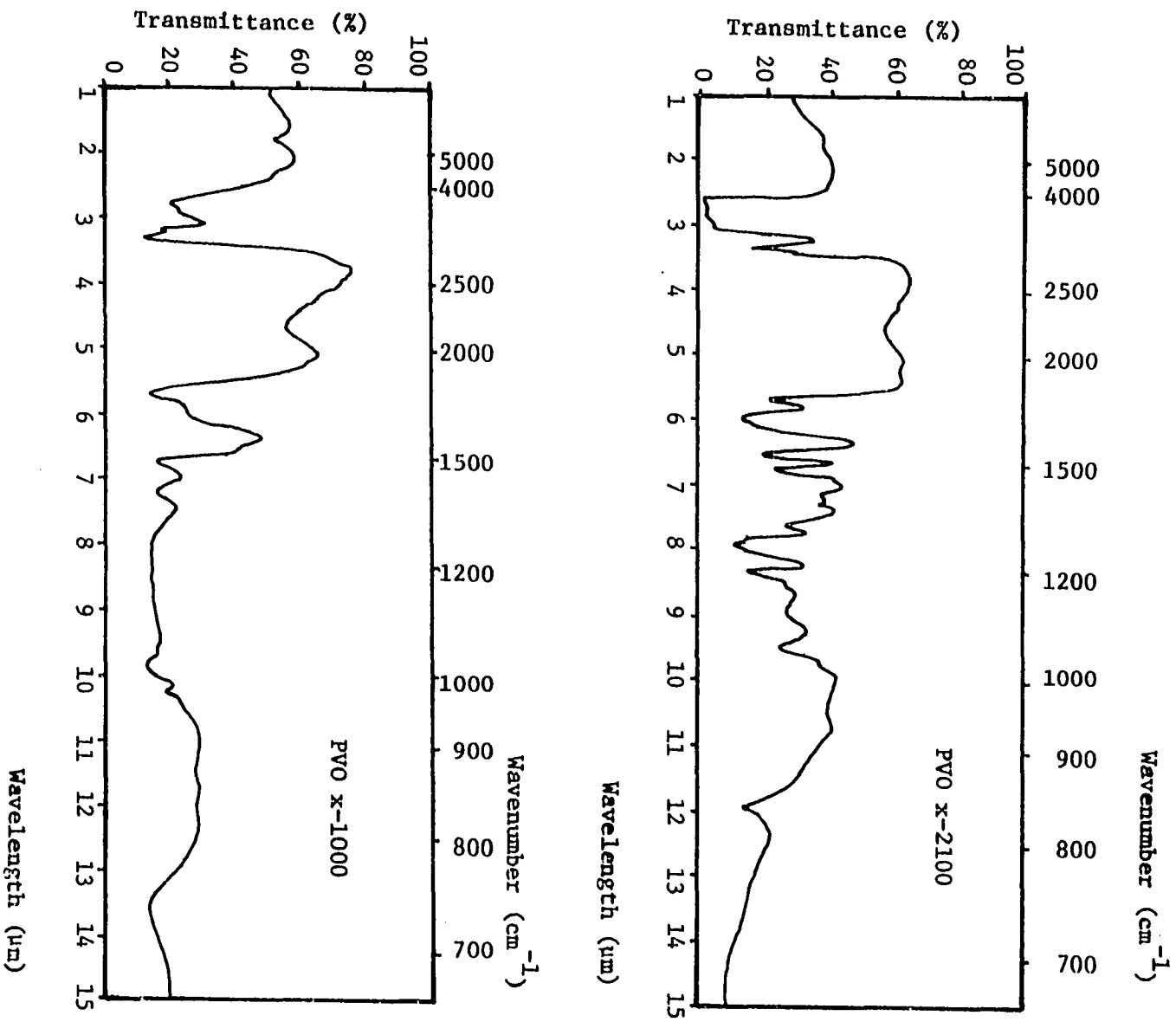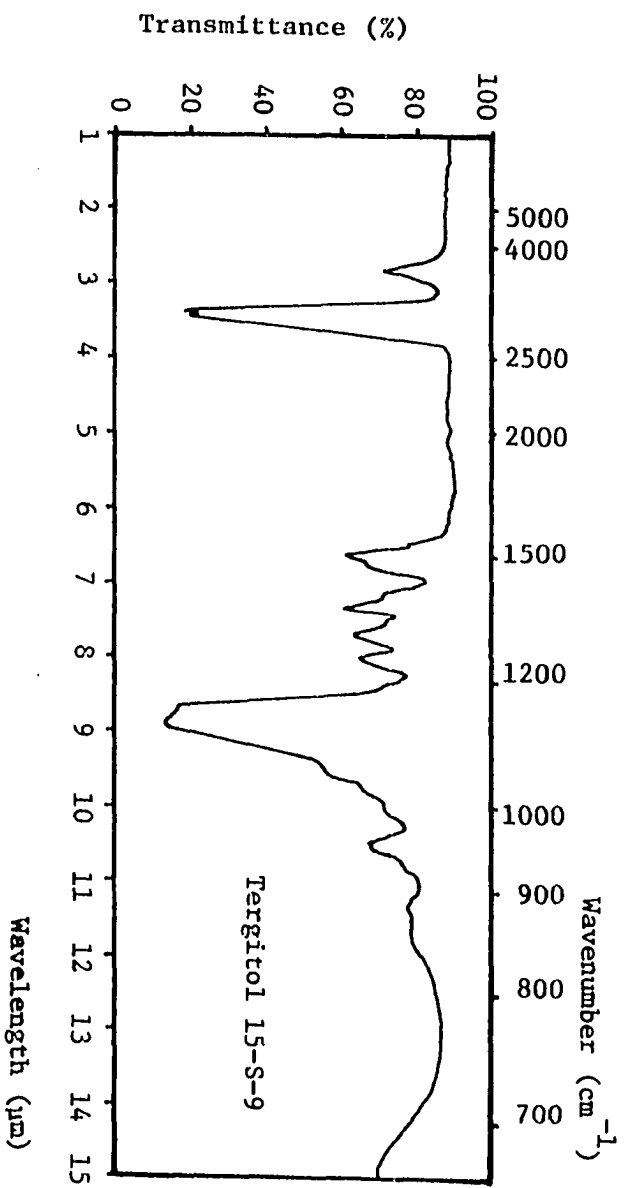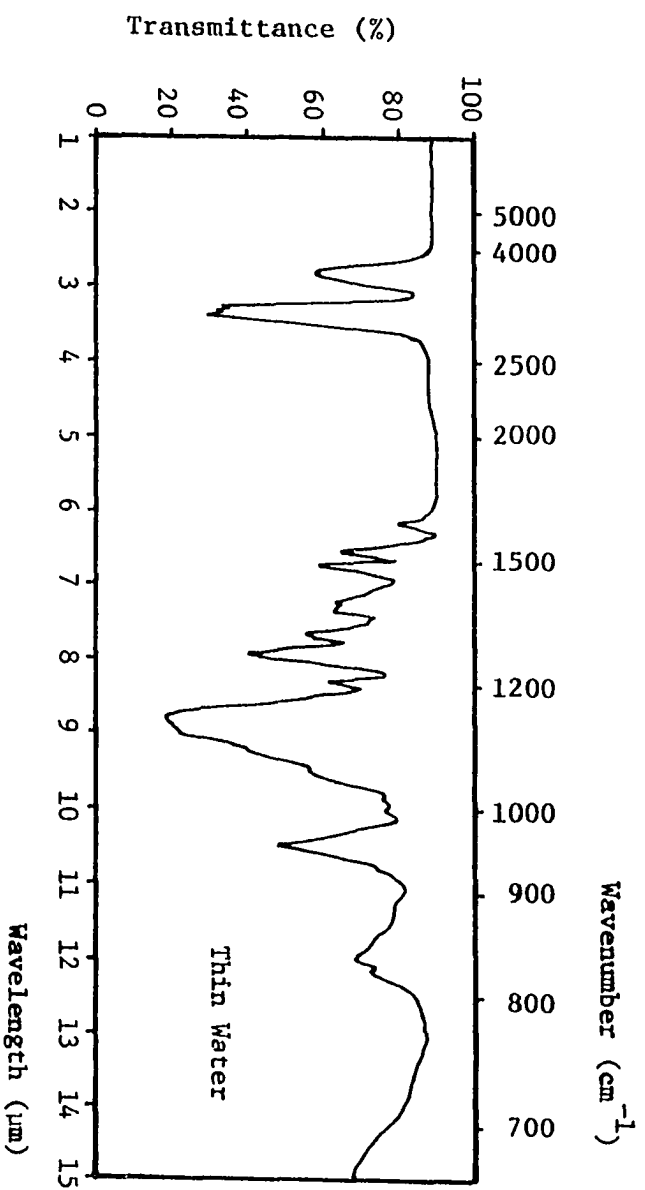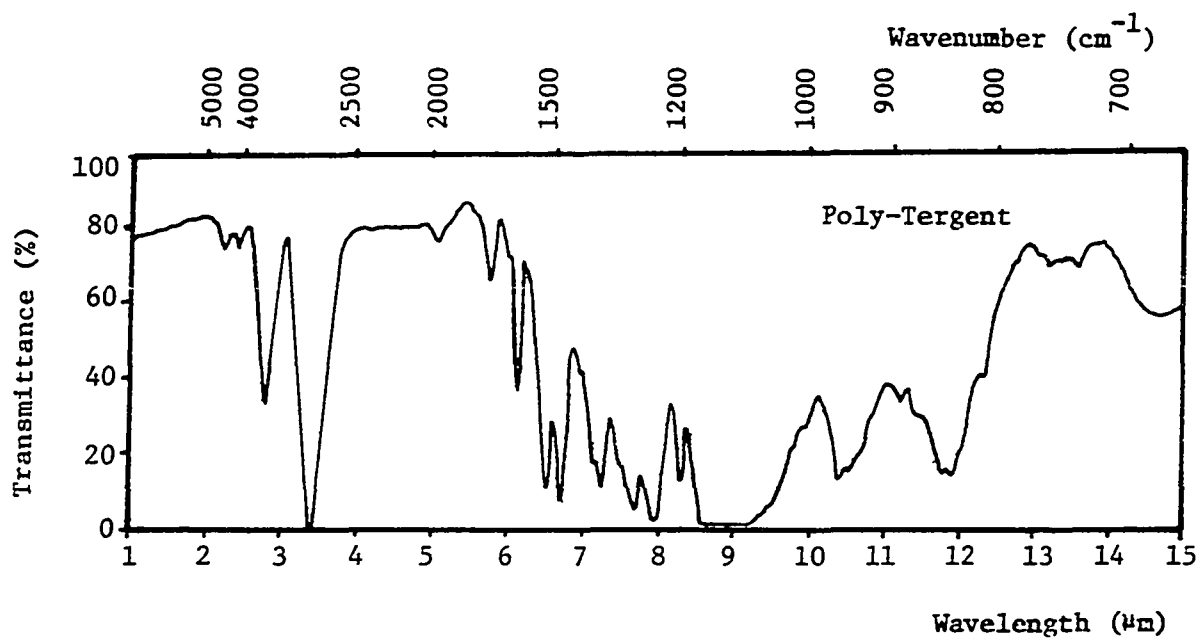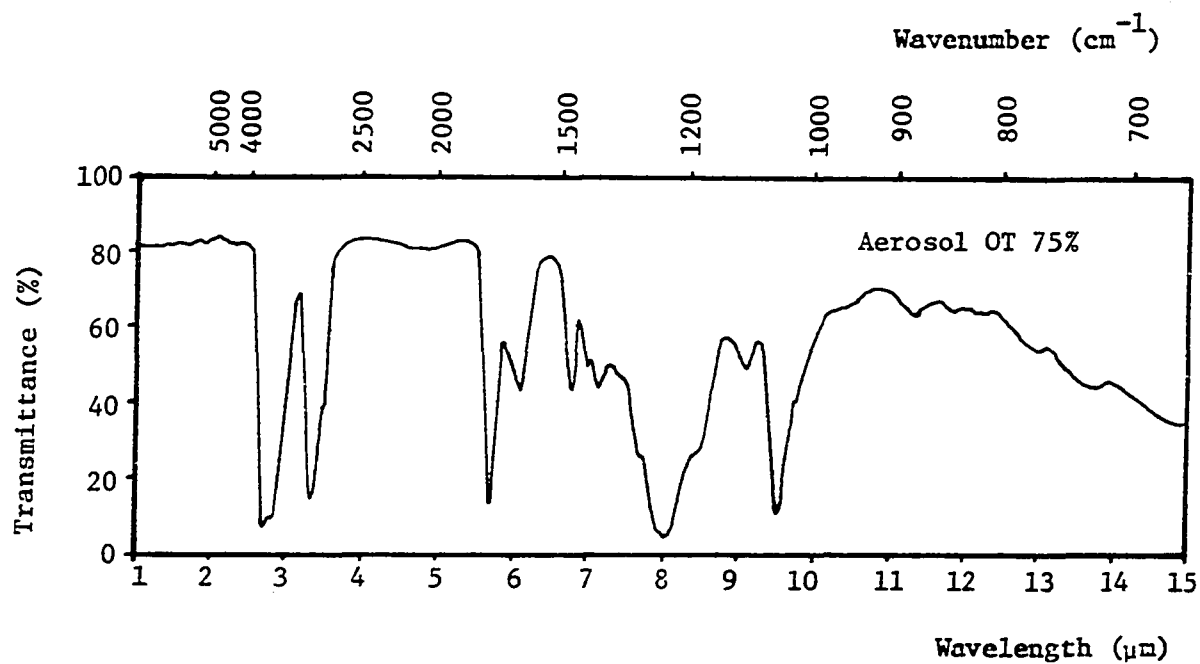
Figure 3-4. (Continued)

60% resins and 40% wetting solution. The I.R. spectrum did not produce
a great deal of information. Medium broad peaks at 2.9 and 6.1μ, and
a high background at 8 to 15μ indicate the presence of water. A
medium sharp peak at 6.9μ, may be due to a C-H stretch, while a
similar peak at 7.3μ, may indicate CH$_3$. The spectrum indicates the
possibility of an unsaturated aliphatic compound.

SA-1. A black viscous liquid, soluble in water, insoluble in ben-
zene, carbon tetrachloride or chloroform. Being highly acidic, the
SA-1 appeared to react with the sodium chloride I.R. cell plates and
did not produce any significant peaks.

Clapak. A black viscous liquid, soluble in water, insoluble in
benezene, carbon tetrachloride or chloroform. Being highly acidic,
Clapak appeared to react with the sodium chloride cell plates, pro-
ducing a meaningless smooth line spectrum.

Claset. A transparent orange liquid, soluble in water, insoluble
in benezene, carbon tetrachloride, or chloroform. Very strong broad
peaks at 2.9 and 6.1μ, and a strong background at 8 to 15μ, indicate
an abundance of water. Quantity of water may have obscured adsorptions
of other compounds.

PVO X-2100. A white viscous liquid, soluble in water, insoluble
in benezene, carbon tetrachloride or chloroform. Strong broad peaks
at 2.8 and 6.0μ, and a weak peak at 4.7μ, indicate presence of water.
Medium sharp peaks occur at 5.65, 6.5, 6.7, and 8.35μ, with a medium
broad peak at 7.9μ, a doublet at 3.85μ, and weak broad peaks at 7.6,

8.9, 9.4 and 11.9 . The spectrum suggests either an ester or an acetate.

PVO-X-1000. A yellowish white viscous liquid, soluble in water, insoluble in benzene, carbon tetrachloride or chloroform. Medium broad peaks at 2.8 and 6.0µ, weak peak at 4.7µ, and background at 8 to 15µ, indicate presence of water. Strong peaks occur at 3.3 and 5.65µ, with weak broad peaks at 6.8, 7.2 and 9.95µ. I.R. spectrum suggests the possibility of an ester.

PVO International, Inc., the producer of both X-2000 and X-1000 describe the products as liquid concentrates of polymers – in – water dispersion, with non-ionic surfactants, emulsifiers and plasticizers.

Thinwater. A transparent medium viscous liquid, soluble in water, insoluble in chloroform or carbon tetrachloride. This product reacts with benezene, producing a white solution. The spectrum indicates a strong sharp triplet at 3.4µ, strong broad peak at 8.8µ, probably due to C-O stretch, a medium peak at 2.9µ, possibly due to OH in an alcohol, medium sharp peaks at 6.55, 6.8, 7.65 and 10.5µ, a medium broad doublet at 12.0µ, and weak sharp peaks at 6.7 and 8.9µ. Thinwater may be an aliphatic alcohol but may also contain some ether.

Tergitol 15-S-9. A transparent viscous liquid, soluble in water, chloroform and carbon tetrachloride. Reaction with benzene produces a white solution. This product shows a strong broad peak at 8.8µ, strong sharp doublet at 3.4µ, and medium peaks at 2.9, 6.8, 7.35, 7.7, 8.0, and 10.5µ. The spectrum suggests presence of an aliphatic alcohol and possibly some ether, not unlike Thinwater. Both Tergitol and Thinwater appear to contain the same major compounds, though Thinwater also appears

to contain a small quantity of an unknown unsaturated material.

A nuclear magnetic resonance spectrometer test was conducted on a 50% solution of Tergitol, using carbon tetrachloride as the solvent. The NMR spectrum showed the product as nonaromatic, nonolefinic, but containing ether and alcohol. The 1967 North American edition of McCutcheon's Detergents and Emulsifiers lists similar Tergitol products as a nonylphenyl polyethylene glycol ether.

Aerosol OT-75%. A transparent viscous liquid, soluble in water, benzene, carbon tetrachloride and chloroform. Strong sharp I.R. peaks at 2.8, 5.8 and 9.5µ, medium peaks at 6.0 and 6.8µ, weak peaks at 7.15, 9.15, and 11.3µ, and a strong sharp triplet at 3.4µ. The spectrum suggests that it might contain some ester and alcohol. The manufacturer American Cyanamid Co., lists this product as a sodium dioctyl sulfosuccinate.

Polytergent B-300. A transparent viscous liquid, soluble in water and chloroform, but reacting with carbon tetrachloride and benzene forming a white solution. Strong sharp peaks at 2.8, 3.4, 6.1, 6.5, 6.7, 7.6, 7.7, 7.9 and 8.3µ, strong broad peaks at 9, 10.5, and 11.9µ, and weak peaks at 5, 5.7, 6.2, 11.2, and 13.6µ. The IR spectrum suggests a partially unsaturated alcohol and ester. McCutcheon's Detergents and Emulsifiers shows this product to be a nonylphenoxy polyethoxyethanol.

As noted from the preceding descriptions, infrared technique assisted in recognizing some of the chemical compounds found in these products.

CHAPTER IV.

VAPOR PRESSURE OSMOMETER

Introduction

There are several means for the determination of the molecular

weights. Membrane osmometry is a good means for the determination of

the number-average molecular weight ($\bar{M}n$) for polymers which cannot

diffuse through the semipermeable membrane. Because of this diffusion

restriction, polymers usually must have molecular weights in excess

of 20,000 in order to be considered as appropriate candidates for

membrane osmometry. Light scattering and viscometry also have minimum

molecular-weight restrictions. The ebullimometric and cryoscopic

techniques usually employed for micromolecular substances have been

used to determine $\bar{M}n$ for polymers whose molecular weight was below

30,000; however, these methods are both time-consuming and imprecise.

The determination of molecular weight by end-group analysis using either

physical or chemical means is applicable to polymers with a low degree

of polymerization. The best method for determining molecular weights

as low as 200 and in excess of 10^6 as well as providing the molecular-

weight distribution for the system appears to be gel permeation chroma-

tography. The vapor pressure osmometer (VPO) is a low cost, solvent-

independent instrument for determination of the molecular weight of

small macromolecules.

The name of "vapor-pressure osmometer" is perhaps, an unfortunate

choice since the device is designed to record a temperature difference

of the solvent and the solution. If VPO is considered as osmosis, and it can be the solvent rather than the solute is being transported, the instrument would be a vapor osmometer in contrast to the conventional membrane osmometer.

Theory

VPO is a variation of the isopiestic or of the isothermal distillation techniques, whereby a solvent and a solution in that solvent are placed side by side in a closed container; however, VPO measures the difference in temperature created by the condensation of solvent on a sensitive thermistor containing a solution of the solute whose molecular weight is to be determined. The iso-piestic method measures a difference in vapor pressures while the isothermal distillation techniques depend upon a difference in volume. Despite the specific changes being measured in the three techniques, each change is proportional to the colligative property of the solution – the lowering of the vapor pressure.

The acceptance of VPO over the other devices which seek to determine the molecular weight can be related to the sensitivity of the detector. For ideal solvents with low heat of vaporization – the differential thermistors of the VPO are capable of detecting differences in temperature of the order of $0.0001°$; this sensitivity should permit the determination of $\bar{M}_n$ for samples up to 20,000.

Since the solute-solvent interaction will vary with concentration molecular-weight measurements by VPO, as by other solution methods, must be conducted within controlled concentration ranges. If the concen-

tration is too high, significant condensation will occur on the solution droplet, thereby reducing the difference in vapor pressure between the solution and the solvent. In addition, the colligative property-concentration relationship will exhibit a sharp curvature. The sensitivity of the measurement is reduced at low concentrations.

The variation of a colligative property of the solution with concentration can be expressed by a virial expansion:

$$\frac{\Delta R}{K_c} = \frac{1}{\bar{M}_n} \; [1 + \Gamma_2 \, c + g \, \Gamma_2^2 \, c^2 \;] \qquad (4\text{-}1)$$

where ΔR is the difference in resistance caused by the difference in vapor pressure between the solvent and the solution, K is a calibration constant, Γ_2 is the second virial coefficient, and g is a solute-solvent interaction function. The last term of Eq. (4-1) is insignificant at low concentrations and can be neglected. If Eq. (4-1) is rewritten in the form

$$\frac{\Delta R}{c} = \frac{K}{\bar{M}_n} + \frac{K\Gamma^2}{\bar{M}_n} \, c \qquad (4\text{-}2)$$

One readily can see that the plot of $\Delta R/c$ versus c should be linear and that M_n will be equal to the quotient of K divided by the intercept of the line, provided that K is given the dimensions of ohms-liters/g and c the dimensions of g/liter.

Equation (4-1) becomes a perfect square if the ideal value for g (0.25) for a solute in a good solvent is used:

$$\frac{\Delta R}{c} = \frac{K}{M_n} \; [\; 1 + \frac{\Gamma_2}{2} \, c \;]^2 \qquad (4\text{-}3)$$

It is preferable to plot ($\Delta R/c$) versus c if $\Delta R/c$ is greater than twice

($\Delta R/c$)$_o$ ($\Delta R/c$ when c = 0). The use of the square root function will

keep the relation linear over a greater concentration range. None of

the previously presented equations holds if $\Delta R/c$ is greater than six

times ($\Delta R/c$)$_o$.

One additional correction must be made to account for the decrease

with time of the value of $\Delta R/c$ caused by the change in concentration of

the solution droplet resulting from the condensation of solvent on the

sample thermistor. If we assume that the concentration - time depend-

ency is a linear function, then

$$- \frac{dc}{dt} = kc \qquad (4-4)$$

by integrating Eq. (4-4) when c = c$_o$ at t = t$_o$, one obtains

$$c = c_o \exp - kt \qquad (4-5)$$

By substituting Eq. (4-5) into Eq. (4-4) but neglecting the second

term in the latter equation, one obtains

$$\Delta R = \frac{K}{\overline{M}_n} C_o \exp{-kt} \qquad (4-6)$$

Equation (4-6) has been shown to be valid at high kt values; however,

with solvents where the k value is relatively small, Eq. (4-6) can be

expressed in a linear form:

$$\Delta R = \frac{K}{\overline{M}_n} C_o - \frac{K}{\overline{M}_n} C_o kt$$

In any event, a plot either of ΔR versus t or log ΔR versus t should

give a straight line whose intercept (ΔR)$_o$ is the difference in resis-

tance for the solution concentration as prepared.

Instrumentation

The vapor pressure osmometer available is the Mechrolab Osometer model 301. It is composed of a sample chamber assembly illustrated in Fig. 4-1, and a control unit which houses a wheatstone bridge, a null indicator, and a heater-control circuit.

In the vapor pressure osmometer two bead thermositors (large change in resistance [ΔR] for a relatively small change in temperature) are suspended in a precisely thermostated chamber saturated with solvent vapor. The beads are two legs of the wheatstone bridge.

The sample chamber of the osmometer consists of a foam insulated thermal block containing the thermistor probe and six syringes suspended in a closed cup containing solvent. The chamber is designed such that the syringes can be lowered in order to apply a drop of solution to one thermistor and a drop of solvent to the other thermistor without requiring the system to be opened. The syringe tips and thermistors can be viewed through the mirrored viewing path located on the side of the sample chamber.

When a drop of solvent is placed on the reference thermistor and a drop of solution placed on the measuring thermistor, solvent condenses on the solution drop because of the lower vapor pressure of the solution (Fig. 4-2). This condensation warms the measuring thermistor, producing a bridge imbalance (ΔR). The corresponding ($T_2 - T_1$) is proportional to the number of solute molecules in the solution as predicted by the Clausius-Clapeyron equation:
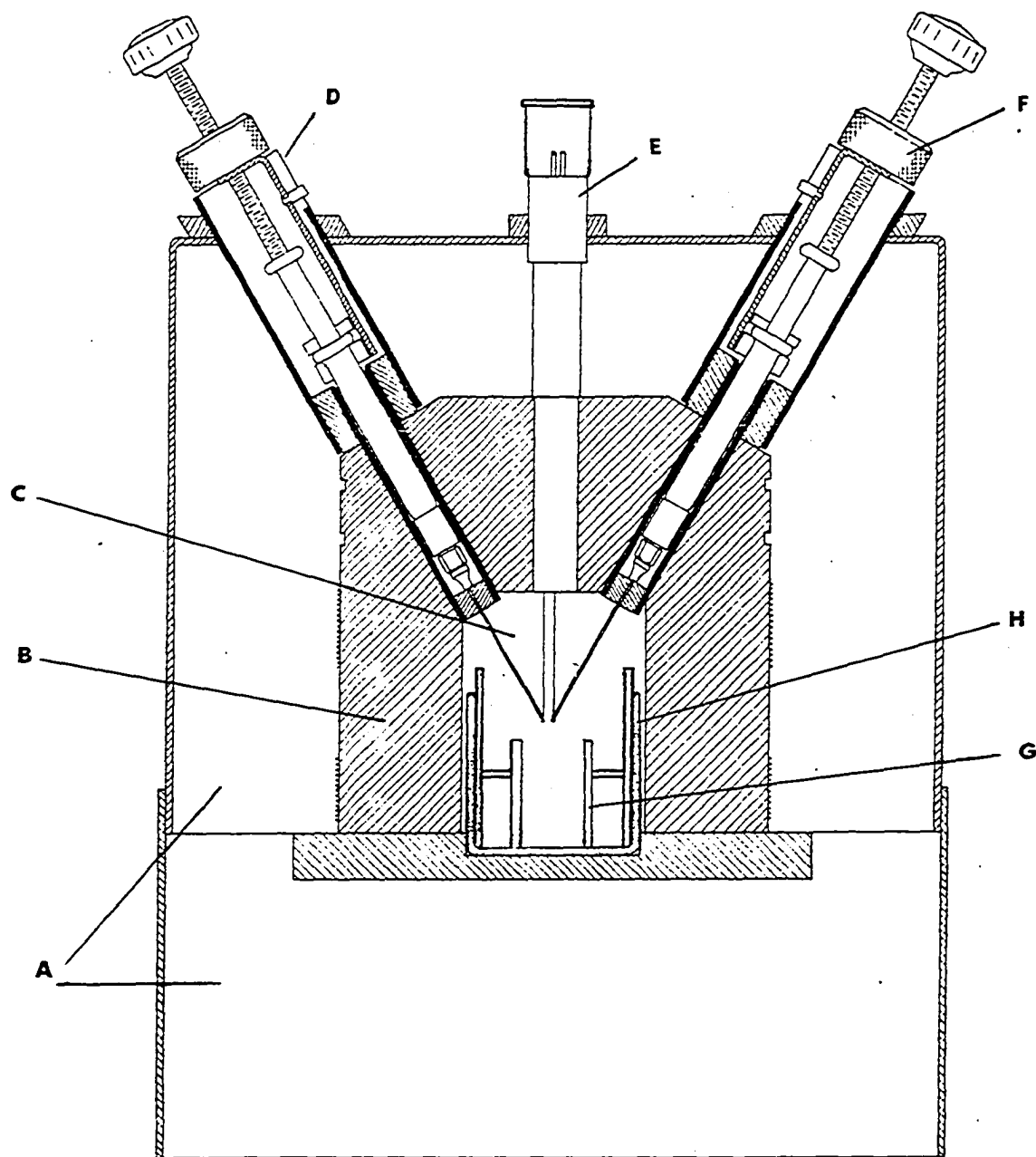
A: Foam   E: Thermistor probe
B: Thermal block   F: Syringe in down positoin
C: Chamber   G: Wick
D: Syringe guide   H: Solvent cup

Figure 4-1. The sample chamber assembly of the Osmometer
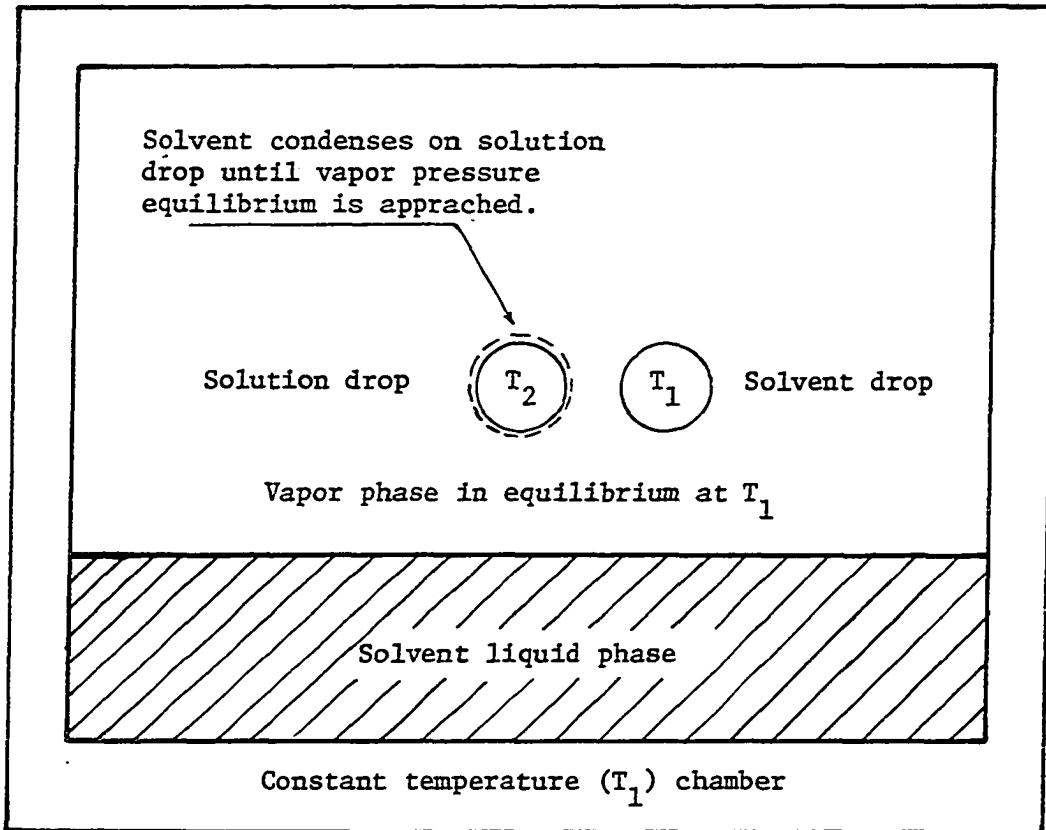
Figure 4-2. Solvent condensation on solution drop

$$T_2 - T_1 = \frac{R\ T^2}{\lambda \times 1000}\ m$$

where: m = molality of the solution

λ = heat of vaporization per gram of solvent

and $(T_2 - T_1) \propto \Delta R$

Since ΔR is a relative quantity dependent on both the solvent and the probe, the VPO must be calibrated with a known molecular weight solute for each solvent and probe used. Known concentrations of sucrose (M.W. = 342.30) dissolved in distilled water were used in this case to determine the molar constant (K). The calibration curve is shown in Fig. 4-3. The calibration curve is extrapolated to infinite dilution to determine K which found to be 34.937. Once K is established, it does not vary for the particular probe and solvent used and only a single calibration is needed. Similar curves are made with the unknown solutes - the chemical compaction aids - using weight concentrations and distilled water as a solvent. These weight concentrations varied from chemical to another. They were chosen after many trials to suit each chemical's physical properties, in order to give the best possible results. These curves are shown in Figures 4-4, 4-5, and 4-6. Each curve is extrapolated to infinite dilution to determine $(\Delta R/c)_{c \to 0}$

The molecular weight of the unknown is then:

$$M.W. = \frac{K}{(\Delta R/c)_{c \to 0}}$$

A computer program was written to assist in plotting the curves shown in Figures 4-4, 4-5, and 4-6, and to determine the intercept of each curve and the corresponding molecular weight.
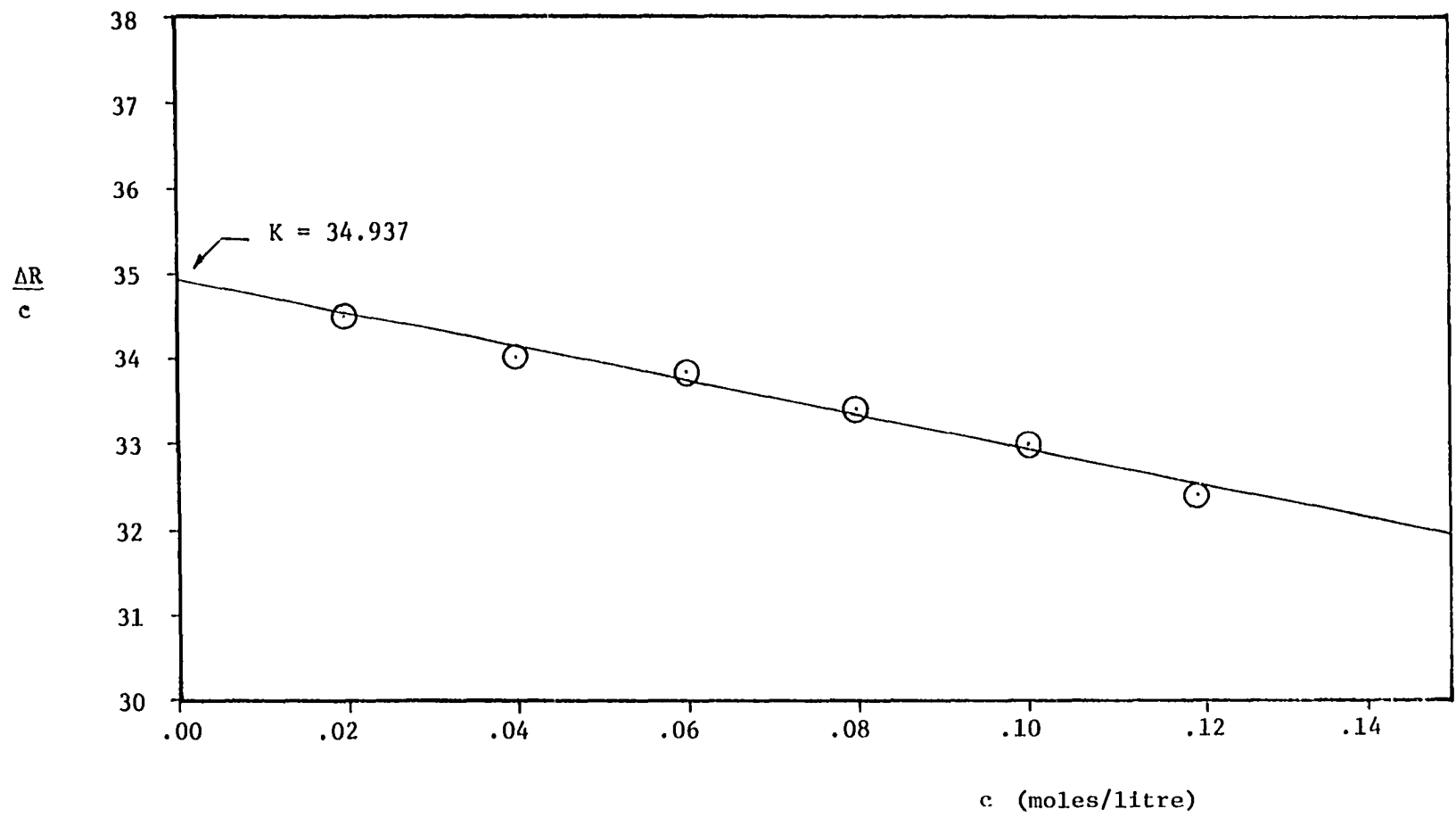
Fig. 4-3. Calibration curve (sucrose in H_2O)
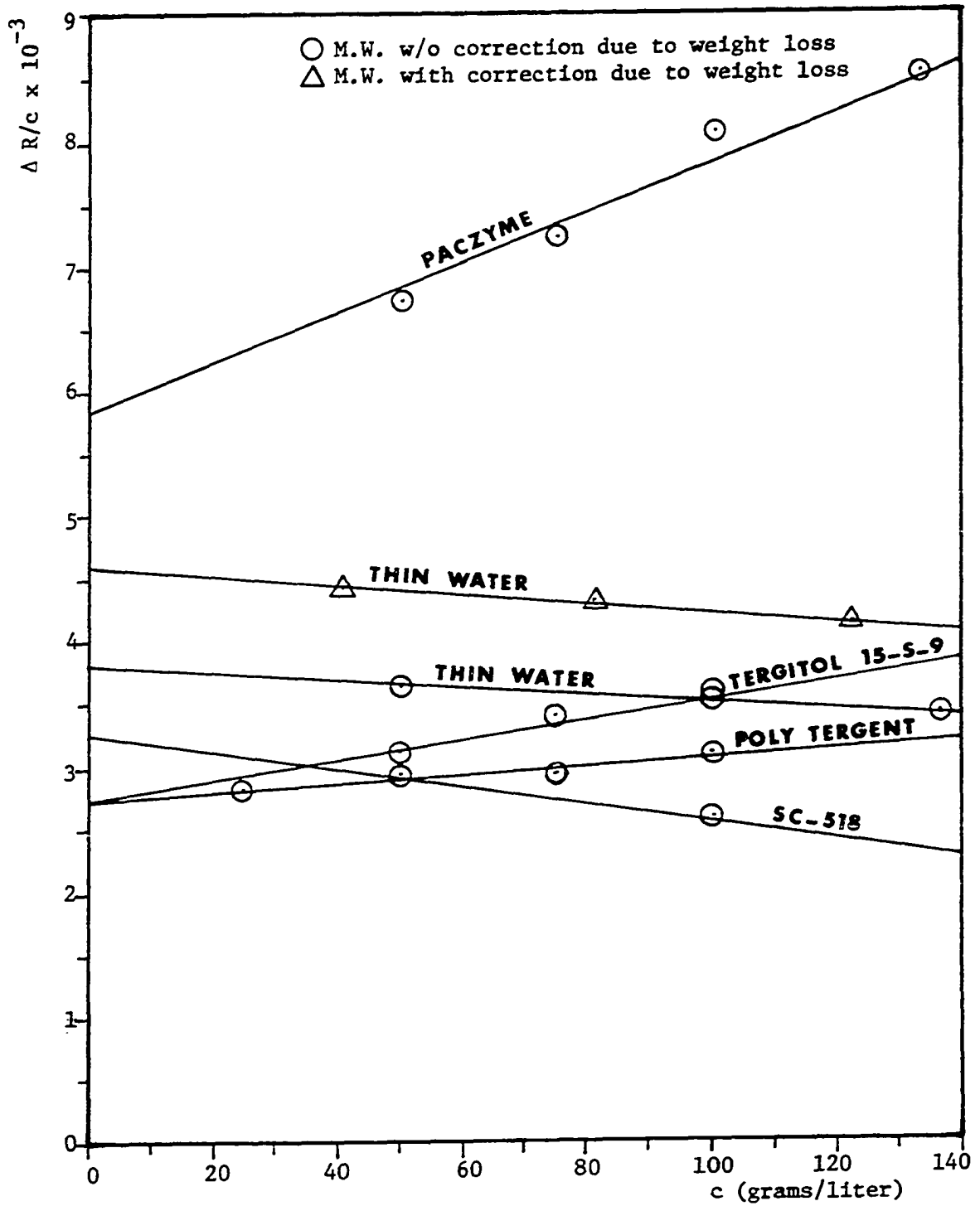
Figure 4-4. Δ R/c versus c of chemical compaction aids
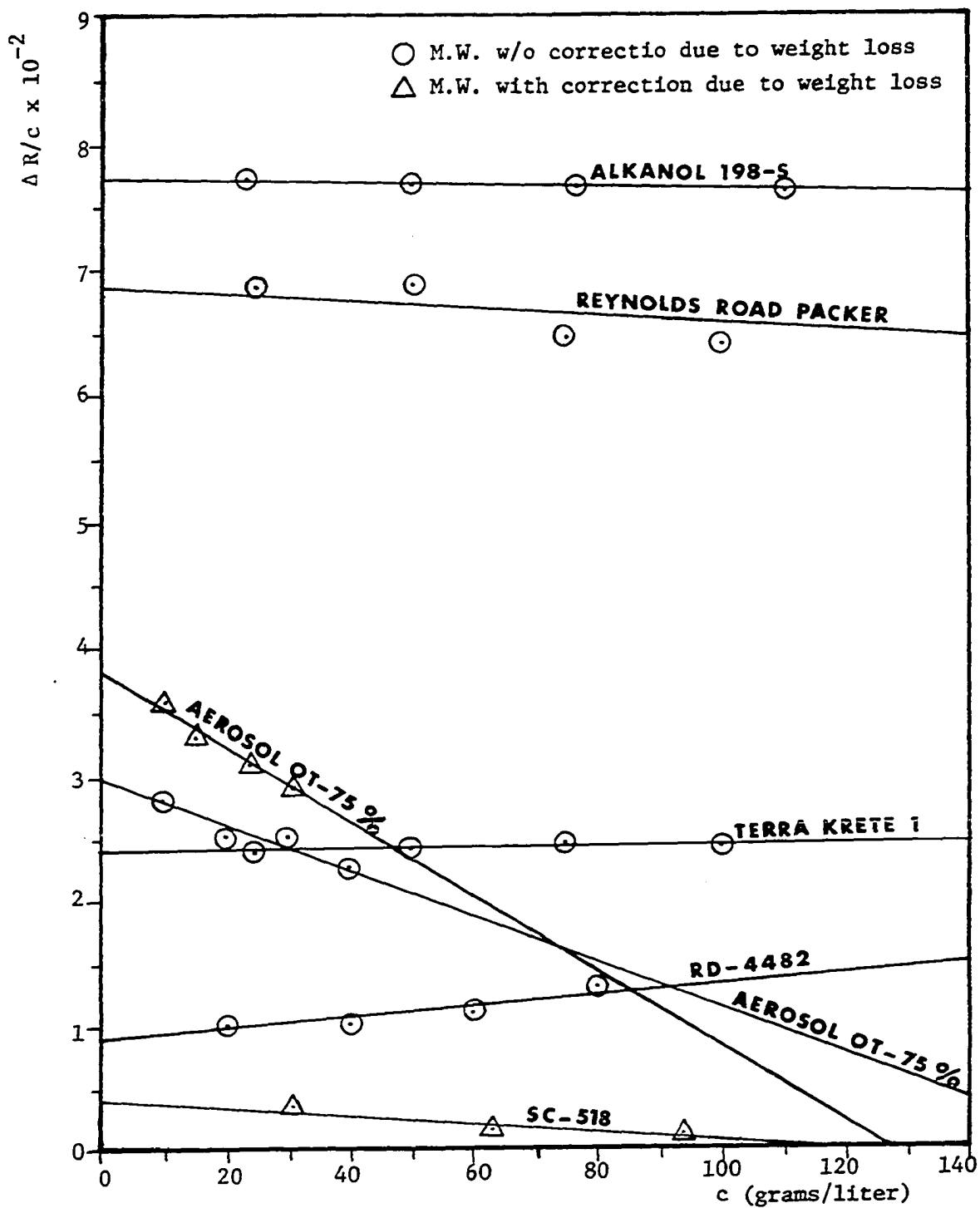
Figure 4-5. $\Delta R/c$ versus c of chemical compaction aids
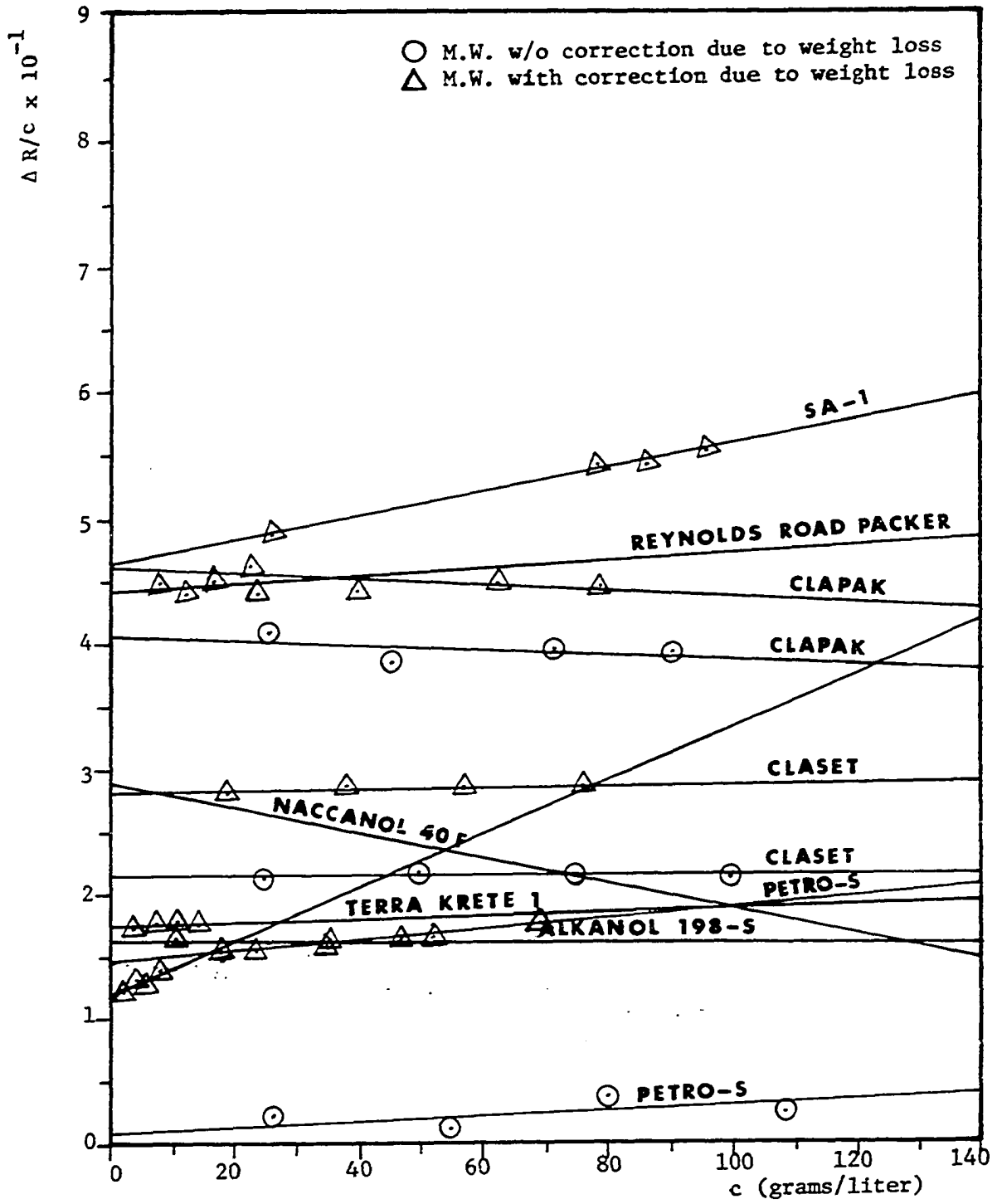
Figure 4-6. $\Delta R/c$ versus c of chemical compaction aids

Results

Sensitivity of the vapor pressure osmometer, when using water as a
solvent, is lower than its sensitivity when an organic solvent is used.
The reason is the high heat of vaporization of water. ΔR for water is
about 55 ohms per mole. A 3% weight concentration would give 1% precision
for molecular weights up to 700 and 4.3% precision up to 3500. The final
accuracy of a measurement is dependent on several factors unrelated to
instrument precision, such as the extrapolation, interactions, purity,
and concentration effects.

There were two main problems resulted in some errors in the molecular
weight determination of the chemical compaction aids. The first is the
impurity of the chemicals. The second is that some chemicals contain
undetermined amount of water. Manufacturers, literature, patents, etc.,
have indicated that many of the products studied in this project may
contain either water or other volatiles. Infrared spectra presented
in Chapter III indicated the presence of water in many chemical compaction
aids, and also the presence of alcohol and/or ether in some of them.
Some of the products may contain combinations of water, alcohol, etc.
For example, Aerosol OT-75% is described by the manufacturer, American
Cyanamid Company as containing "75% active ingredient, the remainder
being water and approximately 5% of a lower alcohol to provide fluidity."
Specifications and typical analysis by the manufacturer indicate a
solids content of 75 $\pm$ 2% by weight.

The percentage weight loss of each product after being subjected to
105°c temperature for 24 hours was calculated. Weight losses due to

volatilization of portions of each products ranged from 0 (polytergent B-300 and Tergitol 15-S-9) to 95.0% (Paczyme). Percent weight loss of Aerosol OT-75% was 21.5%, the bulk obviously thus being water, at the same time being within reasonable proximity of the manufacturer's limits of possible volatiles. One exception to a weight loss at 105°c was the 4.1% weight gain with SA-1. Several re-runs produced identical results. Either the SA-1 undergoes some form of chemical change or tends to absorb moisture after being at 105°c.

Water, at the first place, was used as a solvent in VPO tests because it is the only solvent that all the chemical compaction aids can be dissolved in. This is naturally because they have to be dissolved in the mixing water in the compaction process. Some organic chemicals were tried as solvents but none of them dissolves all the chemicals. As water was contained in some chemicals, and was used, at the same time, as a solvent, the real concentrations used to plot $\Delta R/C$ versus concentrations, for these chemicals, could not be determined precisely. Therefore, the molecular weights were calculated once as if the products contain no water, and then after the concentrations were corrected for the loss of volatiles at 105°c as if all the weight loss was water. Table 4-1 presents results of the vapor pressure osmometer tests. The molecular weights reported under column A represent the entire product, while those in column B represent a molecular weight corrected for loss of all volatiles at 105°c. Table 4-1 also presents the percentage weight loss of each product after being subjected to 105°c temperature for 24 hours. It is believed that the correct molecular weight of each chemical

Table 4-1. Composite molecular weights as determined by vapor pressure osometer

Chemical Product	Weight loss or gain at 105°c, %	Molecular Weight, g/mole	
		A[a]	B[b]
Clapak	-12.6	87	76
Claset	-24.2	166	125
Petro-S	-30.1	346	244
SA-1	+ 4.1	76	76
SC-518	-69.5	10,695	3359
Polytergent B-300	0	12,940	12,940
Thinwater	-18.8	9194	7650
Tergitol 15-S-9	0	12782	12782
Terra-Krete 1	-86.3	1480	202
Paczyme	-95.0	5994	293
Alkanol 189-S	-53.1	453	213
Road Packer	-84.2	512	79
Aerosol OT 75%	-21.5	1165	920
Naccanol 40F	-	120	-
RD-4482	-	3882	-

[a] A = Molecular weight without correction due to weight loss.
[b] B = Molecular weight with correction due to weight loss.

is somewhere in the range between the two estimated molecular weights A and B. There is one evidence that supports this result. Literature provided us by manufacturers/distributors gives the molecular weight of the active ingredient of only one product listed on Table 4-1, Alkanol 189-S. According to E.I. DuPont de Nemours & Co., Inc., this product contains 31.5% sodium alkyl sulfonate at a molecular weight of 354 as the "active ingredient." the manufacturers "Information Bulletin", contains no information on the inactive ingredient(s). Table 4-1 shows 53.1% volatile weight loss with molecular weights A and B of 453 and 213 respectively. Molecular weight of the active ingredient is about midway between A and B. If the inactive ingredient is an alcohol, molecular weight of common alcoholic solvents are in the range of 50 to well in excess of 100 and commonly have boiling points less than 100°c. Some form of alcohol could thus account for the difference between molecular weight of the active product and that determined under column A, Table 4-1. The disparity between the active ingredient and molecular weight corrected for percent volatile weight loss column B, Table 4-1, is possibly due to a volatility and/or chemical change of the active ingredient at 105°c.

It was noticed that the molecular weights corrected for percentage volatiles, changed in near direct proportion to measured percent weight loss, i.e., the higher the weight loss the lower the determined molecular weight. For example, Paczyme had 95.0% weight loss at 105°c, and initial and corrected molecular weights of 5994 and 293 grams/mole respectively. Polytergent B-300 had zero percent weight loss and thus produced both molecular weights 12,940 grams/mole.

Although the vapor pressure osmometer is used to determine the average molecular weight of the solute, the complexity of the chemicals composition decreases the accuracy of the results, because the purer the tested substance the accurate the determined molecular weight.

Inspite of the errors in the VPO results, it was the simplest, fastest and the only available method to determine the molecular weight. It might be important to mention that Mass Spectrometry was used to measure the molecular weights of five of the chemical compaction aids but it did not give any results because of the impurity of the chemicals. Therefore, at least, the vapor pressure osmometer provided us with data that gave an idea about the range of the molecular weight of these chemicals which serves in their characterization and help in identifying similar products having different commercial tradenames, and in comparing between them.

CHAPTER V.

ZETA POTENTIAL DETERMINATION OF

CHEMICALLY TREATED SOILS

Geotechnical engineers have come to realize the importance of physical chemistry in analyzing the mechanism of interaction between soil particles. Physico-chemistry and surface chemistry should be especially pertinent in analyzing the performance of soils treated with the chemical compaction aids.

In this chapter, some fundamentals will be reviewed to furnish a basis for the conducted tests and the analysis of the results.

Theory and Background

The electric double layer concept

A clay suspension is a dispersion of very small particles which is called a clay suspension or a colloidal solution (when particle size is less than 1 μm). A clay-water-electrolyte system is considered to be a hydrophobic colloid. It is a two-phase system: such liquid dispersions of small solid particles, with a large interfacial area, have a behavior dominated by surface forces.

Two forces exist between the particles in clay suspension: attractive and repulsive (41). The attractive force is attributed to the van der Waals attraction forces between all the atoms of one particle and all the atoms of another particle. The magnitude of the total attractive force depends basically on the size and shape of the particle. The particle attraction is counteracted by repulsive

force between the particles. This repulsive force is of an electric nature. Clay particles move when an electric field is applied indicating that the particles carry an electric charge; this phenomena is called "electrophoresis".

The charge on clay particles is attributed to two mechanisms: (1) lattice imperfections, resulting from isomorphous substitution in clay minerals, which may cause a net positive or negative lattice charge. (2) preferential adsorption of specific ions on the active adsorption sites where unsatisfied valence of surface atoms exists. Such ions are called peptizing ions, if they create the stabilizing or peptizing charge by chemisorption, or potential-determining ions if they are identical with the ions constituting the particle lattice.

The clay suspension does not have a net charge, therefore, the particle charge must be compensated in the suspension. The internal balance of charges in the suspension is incorporated in the concept of the "double layer". The double layer consists of the particle charge and an equivalent amount of ionic charge which is accumulated in the liquid near the particle surface. The accumulated ions of opposite sign are called "counter-ions".

The counter-ions are electrostatically attracted by the oppositely charged surface. At the same time, they diffuse away from the particle surface, because of their thermal motion, forming a "diffuse layer". Figure 5-1 is a sketch of the charged particle surface and the distribution of ions in the diffuse layer, assuming that the particle is negatively charged and the counter-ions, in this case, are cations.
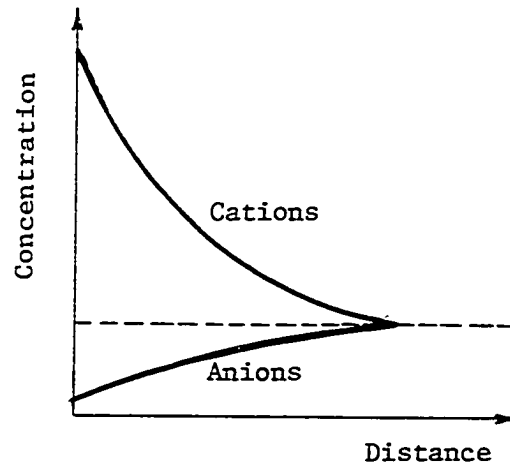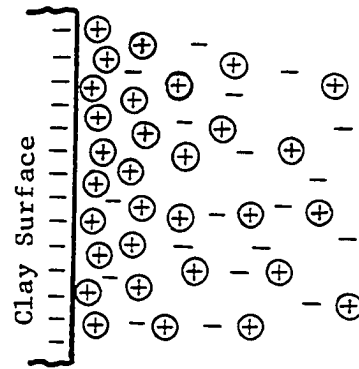
Figure 5-1. The charged particle surface and the distribution of ions in the difuse layer
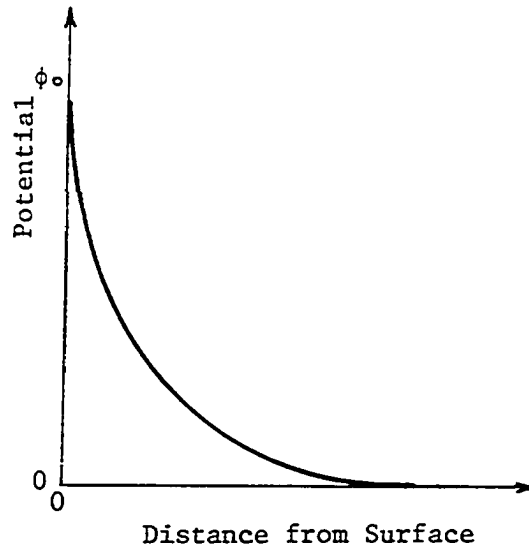
Figure 5-2. The electrical potential variation with distance from surface

The difference in ion concentration between the diffuse layer and the bulk solution outside the diffuse layer creates an electric potential which has a maximum value at the particle surface and decreases roughly exponentially with the distance from the surface. Figure 5-2 represents the electric potential plotted as a function of the distance from the particle surface.

When the double layer is created by adsorption of potential-determining ions, the electric potential at the particle surface is solely determined by the concentration of these ions in solution. In this case the potential is given by the Nernst equation:

$$\phi_o = \frac{kT}{ve} \ln \frac{c}{c_o} \tag{5-1}$$

where,

ϕ_o = the electric potential at the surface

k = Boltzmann constant

T = the absolute temperature

e = the electronic charge

v = the valance of the potential-determining ions

c = the concentration of the potential-determining ions in the solution

c_o = the concentration of the potential-determining ions at the zero point of charge (where the potential is zero).

The diffuse counter-ion layer is compressed toward the surface of the particle when the electrolyte concentration is increased. The effect

of electrolyte addition on the surface potential and the surface charge of the particle depends on the type of double layer.

If the surface potential of the particles is determined by the concentration of potential-determining ions, addition of kinds of ions other than the potential-determining ions into solution will not affect the surface potential, but the surface charge increases with increasing these indifferent ions concentration(41).

If the surface charge of the particle is determined by interior lattice imperfections, the surface charge does not change but the surface potential decreases, and the double layer is compressed,with increasing electrolyte concentration. The higher the valence of the counter-ions, the more the double layer is compressed (41).

The Goy model of electric double layer presented above is too ideal and unrealistic in some aspects. Stern tried to create a more realistic double-layer model by considering the distance of closest approach of a counter-ion to the charged surface is limited by the size of these ions, and the counter-ion charge is separated from the surface charge by a layer in which there is no charge. In this "Stern layer" the electric potential drops linearly with the distance, from the maximum potential at the surface to a certain value which is called Stern potential. For the Stern model, the addition of electrolyte to the solution results not only in a compression of the diffuse part of the double layer but also in a shift of the counter-ions from the diffuse layer to the Stern layer and hence in a decrease of the Stern layer potential.

Particle interaction

When two particles approach each other in suspension owing to their Brownian motion, their respective diffuse counter-ion layers interfere with each other, and develop a repulsive energy which competes with the attractive energy resulting from van der Waals attraction. Figure 5-3 shows the resultant of the attractive and repulsive energies at two electrolyte concentrations. If the particles approach each other at a distance beyond the distance where the resultant energy maximum (the energy barrier) is located, they will separate again because the repulsive energy is still higher than the attractive energy. Hence the distance to this energy barrier is the minimum distance required for kinetic stability. The energy barrier becomes shallower as the electrolyte concentration increases, and at a certain concentration the attractive energy will overcome the repulsive energy and the result will be particle agglomeration.

The double layer on the surface of clay particles

The clay lattice carries a net negative charge as a result of isomorphous substitutions. The net negative lattice charge is compensated by cations which diffuse away in the presence of water to form the counter-ion diffuse layer as mentioned before. These cations, like all counter-ions, are exchangeable for other cations. The negative double layer normally exists on the flat surfaces of the clay particles. The atomic structure of the edge surfaces is entirely different from that of the flat-layer surfaces in that at the edges of the plates, the tetrahedral silica sheets and the octahedral alumina sheets are disrupted,
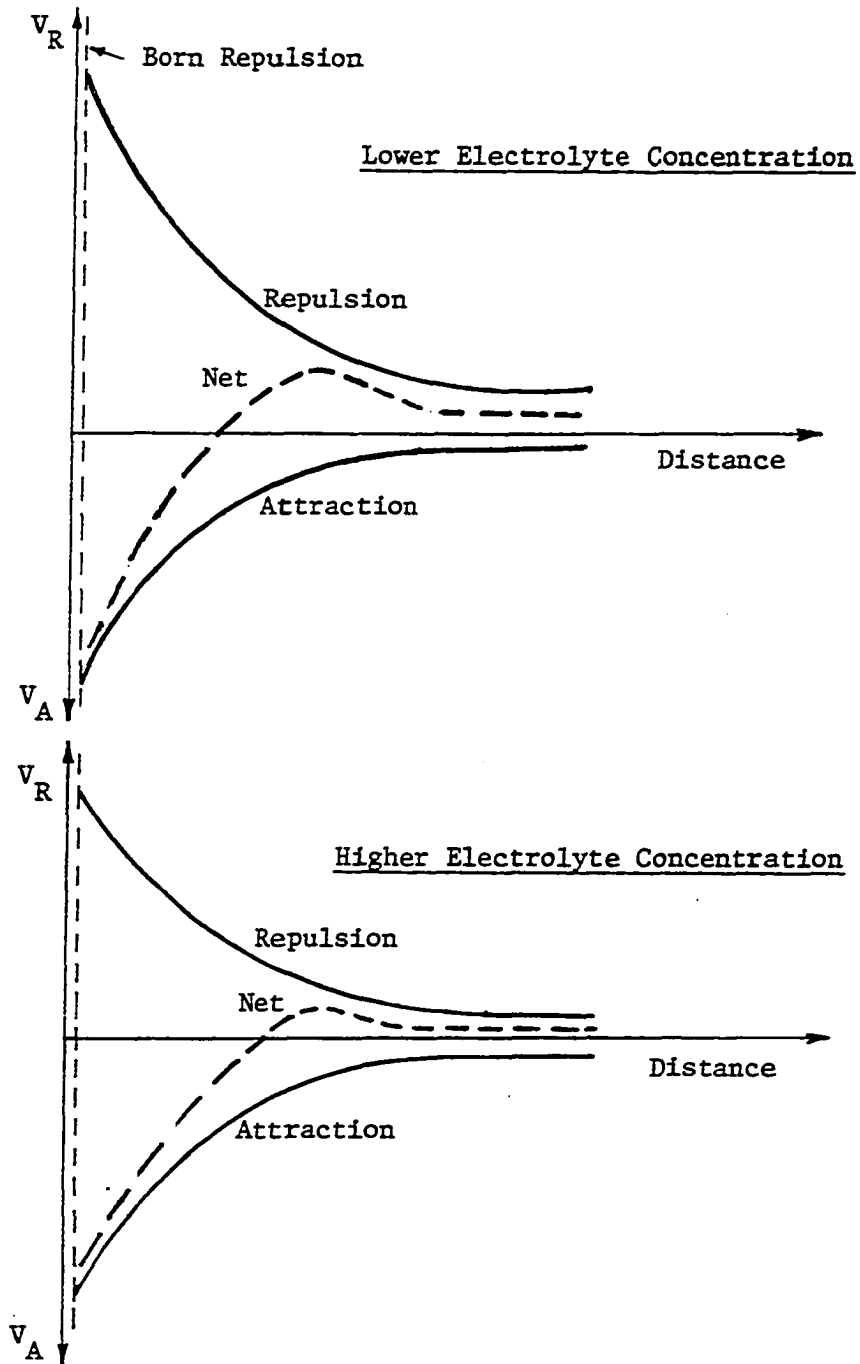
Figure 5-3. Energies of repulsion, attraction, and net curves of interaction for two colloidal particles at two electrolyte concentrations

and primary bonds are broken. On such surfaces an electric double-
layer is created by the adsorption of peptizing or potential-determining
ions. There is a definite possibility that in a neutral clay suspension
a positive double layer is created on the edge surfaces owing to the
exposed alumina sheet. Despite the fact that the net electrophoretic
charge of the clay particles is always negative, the existence of a
positive double layer can not be excluded, since the negative double
layer on the large flat surfaces may well predominate in the electro-
phoretic experiment (41).

Several observations support the concept of a positive edge charge.
For example, clays show a certain anion adsorption capacity under
certain conditions which is a result of the positive edge double layer.
Also, the positive edge double layer is responsible for the electro-
static attraction between the edges and the negatively charged flat
surfaces of the clay particles which results at the known edge-to-
face particles association forming a card-house structure.

Although the double layer of the clay particle may be more compli-
cated than that due to the difference in crystallography of the exposed
surfaces of the platelike particles, we have to accept the fact that the
clay particle may carry two different types of electric double layer on
its surface. This concept will play a significant part in the inter-
pretation of the mechanism of the effects of the various chemical com-
paction aids on clay soils, as it is discussed later.

·The "Zeta Potential"

The zeta potential is the electric potential in the double layer
at the interface between a particle which moves in an electric field
and the surrounding liquid. The zeta potential is computed from the
electrophoretic mobility of the suspension particles. Upon the
addition of an electrolyte, the zeta potential usually decreases, and
at the flocculation value of the electrolyte it was considered to have
reached a critical value below which the particle repulsion is no longer
strong enough to prevent flocculation.

Zeta potential represents the electric potential at a distance
from the surface in the double layer at the shearing or slipping plane
between the bulk liquid and an envelope of the counter-ions which moves
with the particle. Zeta potential is not equal to the surface potential,
but it is comparable with the Stern potential. Like the Stern
potential, the zeta potential may be expected to decrease with increas-
ing electrolyte concentration because of a shift of counter-ions toward
the Stern layer when the diffuse double layer is compressed. Therefore,
it is not surprising that a relation exists between colloidal stability
and the magnitude of zeta potential.

It should be pointed out that there is no experimental way of
determining the surface potential, but zeta potential can be measured by
conducting an electrophoresis experiment. Zeta potential in this
research was measured by a device called Laser Zee Meter. The main
features of the device and the experiment procedure are described in the
following paragraphs.

Instrumentation

A Laser Zee Meter Model 400 was used to measure zeta potential of colloid particles in soil-water suspension. It measures zeta potential by determining the rate at which these particles move in a known electric field. The particles are observed with a microscope (overall magnification is 270); therefore, this technique is called micro-electrophoresis.

The colloid to be measured is placed in an electrophoresis cell consisting of two electrode chambers and a connecting chamber with length = 10 cm, width = 15 mm, depth = 1.5 mm, for viewing the particles. A voltage is applied between two electrodes, one located in each chamber. The anode is made of molybdenum, and the cathode is platinum. The applied voltage produces a uniform electric field in the viewing chamber and the charged particles respond by moving toward one of the electrodes. The direction of movement is determined by the sign of the charge. The speed of the particles is directly proportional to the magnitude of zeta potential. However, there is one important complicating factor. When the voltage is applied to the cell not only do the particles move with respect to the fluid but the fluid moves with respect to the cell. This second effect is referred to as electroosmosis and is characterized by a movement of the fluid in one direction near the surface of the viewing chamber walls, accompanied by a return flow in the opposite direction. Therefore, all measurements must be made at the surface where the fluid is stationary or the stationary layer, or errors due to the fluid movement will occur. Lazer Zee Meter provides means for insuring that the

measurements are made at the stationary layer, which is at 212 μm from the top of the cell.

Once the microscope and laser are focused at the correct level a zeta potential measurement can be made by a unique patented technique. By adjusting the prism control until the apparent motion caused by the prism exactly cancels the particle velocity caused by the applied field, the particles appear stationary in the field of view, and the zeta potential is displayed on a digital readout. The zeta potential reading is independent of the applied cell voltage which can be varied from 0 - 400 volts; field strength is 0 - 40 volts/cm. 200 volts is commonly used as the applied cell voltage.

The range of zeta potential is -100 to + 100 mv with accuracy of ± 5%.

The Laser Zee Meter also measures the specific conductance of the colloid in the cell. Conductance is the reciprocal of the resistance, ohms, and its units are in mhos. The specific conductance is the conductance per unit length, i.e. mhos/cm. The measurement range varies from 100 k μ mhos to 1 μ mhos with accuracy ± 10%. The temperature of the sample solution can be measured before filling the cell by means of a special connection by the Lazer Zee Meter itself. It is customary to take all the data at same reference temperature such as 20°c. Therefore, temperature of each sample should be determined, and the measured zeta potential at this temperature should be corrected to a reference temperature 20°c. This correction can be made as follows:

$$\text{Z.P.}_{\text{(corrected)}} = \text{Z.P.}_{\text{(measured)}} \times (I - 0.02T)$$

where T = temperature in °c above 20°c.

The temperature correction arroused from the fact that the surface potential is proportional to the temperature of the suspension as shown in the equation (5-1).

Sample Preparation

In this research, twelve soils of the soils involved in the project were selected to be tested in the zeta potential experiments. The physical and chemical properties of these soils which were determined in Phase I of the project, are shown in Table 5-1. Besides the natural soils, montmorillonitic and kaolinitic clays which have a high degree of purity, were included. The montmorillonitic soil is Wyoming Bentonite which is essentially sodium montmorillonite with minor amounts of feldspar and quartz. The kaolinitic soil is collected from Mesa Alta, New Mexico, by Ward's Natural Science Establishment, Rochester, New York. It is listed under the commercial name kaolinite #9.

Seven chemicals were selected to treat the soils: Clapak, Claset, Petro-S, Thin Water, SA-1, Road Packer, SC-518.

The first step in sample preparation was a sedimentation process which was carried out as follows:

1. 100 gm of soil was mixed with distilled water by a mixer until the soil was broken down into its individual particles (approximately 10 minutes).

Table 5-1. Physical and chemical properties of the selected soils

Series or Name Location	Bearden North Dakota	Renohill Wyoming	Rimrock Arizona	Peavine Oregon	Marias Montana	Shelby Iowa
Horizon & Depth Sampled	C	B/C	C 3"–34"	B/C 12"–60"	A/C 4"–35"	B/C
Textural Composition:						
Gravel (>4.76mm)	0.0	0.1	3.1	0	0.1	0.0
Sand (4.76–0.074mm)	4.4	8.2	8.2	44.8	7.4	2.6
Silt (0.074–0.005mm)	39.6	24.7	41.2	21.2	34.3	57.4
Clay (0.005mm)	56.0	67.0	47.5	34.0	58.2	40.0
Colloids (<0.001mm)	35.0	53.0	40.2	20.4	46.4	34.1
Chemical Properties:						
Cation Exchange Capacity, m.e./100g	20.8	33.4	37.6	48.8	27.7	29.6
pH	7.9	7.1	7.99	3.28	5.54	6.5
Physical Properties:						
Liquid Limit, %	41.00	58.00	44.0	62.3	45.5	54.00
Plastic Limit, %	27.00	26.00	24.9	49.7	22.6	32.00
Plasticity Index, %	14.00	32.00	19.1	12.6	22.9	22.00
Specific Gravity	2.66	2.77	2.75	2.80	2.72	2.70
Classification:						
Engr.–AASHO	A-7-6(10)	A-7-6(20)	A-7-6(12)	A-7-5(7)	A-7-6(14)	A-7-5(15)
Predominant Clay Minerals	Montmorillonite	Montmorillonite	Montmorillonite	Montmorillonite	Montmorillonite	Montmorillonite
Other Minerals	Illite Dolomite Calcite Quartz	Illite Dolomite Calcite Quartz	Feldspar	–	Feldspar Calcite	Illite

69

Table 5-1. (Continued)

Series or Name Location	Frederick Virginia	Persanti South Carolina	Nappanee Michigan	Vergennes Vermont	Melbourne Washington	Grundite Illinois
Horizon & Depth Sampled	B/C	B/C	B/C 10"-36"	B/C 12"-62"	B 14"-56"	-
Textural Composition:						
Gravel (4.76mm)	1.9	2.5	0.2	0.2	0.1	0.6
Sand (4.76-0.074mm)	11.8	47.6	16.5	4.5	30.7	22.7
Silt (0.074-0.005mm)	24.3	11.9	23.3	31.1	36.7	37.7
Clay (0.005mm)	62.0	38.0	60.0	64.2	42.5	39.0
Colloids (0.001mm)	51.0	30.0	41.0	35.1	28.4	29.0
Chemical Properties:						
Cation Exchange Capacity, m.e./100g	15.4	16.4	22.2	12.9	48.8	23.6
pH	3.9	5.0	-	7.02	4.61	2.4
Physical Properties:						
Liquid Limit, %	49.00	44.00	43.9	33.2	36.8	50.00
Plastic Limit, %	33.00	29.00	25.0	22.3	26.2	29.00
Plasticity Index, %	16.00	15.00	18.9	10.9	10.2	21.00
Specific Gravity	2.73	2.80	2.74	2.77	2.72	2.77
Classification:						
Engr.-AASHO	A-7-5(12)	A-7-6(11)	A-7-6(15)	A-6(8)	A-6(8)	A-7-6(9)
Predominant Clay Minerals	Kaolinite Vermiculite	Kaolinite	Vermiculite Illite	Vermiculite Illite	Vermiculite	Illite
Other Minerals	Feldspar	Vermiculite Illite	Feldspar Kaolinite	Kaolinite Feldspar Calcite Dolomite	Feldspar Illite	disordered Kaolinite

70

2. After mixing, the specimen was washed into a graduated
   cylinder and distilled water was added to bring the level to
   the 1000-cc mark.

3. The soil and water were shaken in the graduated cylinder and
   left to settle for 20 hours.

4. After 20 hours, the upper part of the suspension, which con-
   tains the particles less than $2 \mu m$ in size (see the Appendix)
   was carefully poured into a large evaporating dish to be dried
   in the oven, at $105°c$.

The object of the sedimentation process was to prepare a sample
which included only the clay and colloidal part of each soil. Several
hundreds of grams of each soil, one hundred in each graduated cylinder,
were used to prepare enough sample to carry out zeta potential experi-
ments on untreated and chemically treated soils.

The treatment of the soil sample was done as follows:

1. A chemical-water solution was prepared at a concentration of 1%
   using each of the seven selected chemicals and distilled water.

2. For each soil, 10 cm^3 of the chemical-water solution were
   leached through a 1 gm of soil ($< 2 \mu m$), using millipore filter
   paper (type vc, opening $= 0.1 \mu m$). A partial vacuum
   accelerated the process.

3. After leaching, half of the sample was dried in the oven for
   two hours at $105°c$, and the other half was stored in the wet
   condition in a closed container to be tested after 7 days.

At this point the sample is ready to be used in the electropheretic experiment. The sample must exhibit a Tyndall effect to be tested in Laser Zee Meter and this is usually achieved by having a colloidal concentration in the range of 50-500 ppm. If the sample is too dilute, few particles can be seen in the field of view at one time, increasing the time needed to make a measurement. Conversely, too concentrated a slurry results in viewing hundreds of particles at once and causes excessively high light diffusion. Therefore, the colloidal concentration was chosen to be 200 ppm. The experiment proceeded as follows:

1. 0.1 gm of each sample was mixed with about 100 cm^3 distilled water in a 200 cm^3 beaker and agitated for 10 minutes by means of a magnetic stirrer, then transferred to a 500 cm^3 graduated cylinder. Distilled water was added up to the mark to form a clay suspension with the required concentration.

2. The suspension was shaken, and about 20 cm^3 was withdrawn by a syringe and placed into a beaker for measurement of pH. Additional suspension was withdrawn to fill the Laser Zee Meter cell.

3. After filling the cell and placing it in the proper place in the Laser Zee Meter, zeta potential and specific conductance could be measured by following the operating procedure of the device specified by the manufacturer.

4. The sample then was emptied from the cell into a beaker and temperature was measured using a special connection provided by the device.

The above procedure was used for each soil and for each chemical-soil combination to measure zeta potential for the treated soil and the untreated soil, immediately after preparation, and 7 days after treatment.

Results

Tables 5-2 to 5-15 present the results of the electrokinetic experiments of the selected soils and chemicals. Zeta potential results were compared with the data obtained from the compaction test conducted in Phase II of the project which included moisture-density tests to evaluate the compaction effectiveness. The latter is expressed as an increase in the maximum dry density and a decrease in the optimum moisture content. The Iowa Continuous K-Test was used to monitor the changes in the strength parameters such as k, ϕ, c, and E.

When the numerical value of the zeta potential of the chemical-treated soil was higher than the zeta potential of the untreated soil, in most cases, the chemical was previously found to be an effective aid to compaction, and when the numerical value of zeta potential of the chemically treated soil was less than zeta potential of the untreated soil, the chemical was ineffective as a compaction aid, although it sometimes improved the strength parameters.

Strength data were obtained from selected soil-chemical combinations prepared at 100% AASHO T-99 compaction, wrapped, sealed, and stored for 7 days in a moist-cure room at near 72° and 100% relative humidity. The K-Test was performed on each specimen. The results of those tests deserved a special attention because they throw light on

Table 5-2. Zeta potential, specific Conductance, pH of untreated and chemically treated Bearden series

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to Z.P.[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	7.65	7.65	-14.1	-14.1	12	12		
Clapak	6.05	6.44	-18.1	-15.8	15	13	+	Z
Claset	6.48	6.42	-15.1	- 9.2	10	7	+	Z
Petro-S	7.61	7.00	-14.8	-13.1	12	11	+	Z
Thin Water	7.00	6.90	-14.6	-13.7	10	8	0	Z
SA-1	6.20	6.13	-13.7	-14.4	26	17	-	X

[a] + = fully to partially effective, 0 = partially effective, - = not effective.

[b] Z = expected to be effective, X = expected to be ineffective.

74

Table 5-3 . Zeta potential, specific conductance, pH of untreated and chemically treated Renohill series

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to Z.P[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	5.80	5.80	-19.0	-19.0	8	8		
Clapak	5.02	4.64	-28.6	-25.9	7	9	-	Z
Claset	5.57	5.70	-18.6	-19.4	5	4	-	X
Petro-S	6.30	6.42	-26.5	-22.4	4	4	0	Z
SC-518	6.55	6.22	-18.8	-17.0	4	4	-	X

[a] 0 = partially effective, - = not effective.

[b] Z = expected to be effective, X = expected to be ineffective.

Table 5-4. Zeta potential, specific conductance, pH of untreated and chemically treated Rimrock series

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to Z.P.[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	7.00	7.00	-19.7	-19.7	7	7		
Clapak	5.20	5.13	-24.2	-25.9	7	10	+	Z
Claset	6.55	5.32	-22.6	-21.9	6	8	0	Z
Petro-S	5.35	7.00	-17.9	-20.2	8	8	-	X
Thin Water	6.04	7.00	-19.1	-19.2	5	7		X
SA-1	5.00	4.90	-22.9	-20.6	15	22	+	Z

[a] + = fully to partially effective, 0 = partially effective, - = not effective.

[b] Z = expected to be effective, X = expected to be ineffective.

Table 5-5 . Zeta potential, specific conductance, pH of untreated and chemically treated Peavine series

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to Z.P.[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	5.20	5.20	-33.0	-33.0	4	4		
Clapak	4.82	4.90	-22.8	-25.9	12	10	+	X
Claset	4.70	5.00	-18.6	-14.6	8	8	0	X
Petro-S	5.60	6.00	-38.2	-37.8	4	4	0	Z
Thin Water	5.78	5.60	-34.0	-31.3	2	2	++	Z
SA-1	4.75	4.75	-24.2	-21.4	12	12	+	X
SC-518	5.65	4.88	-34.2	-33.8	3	4	+	Z
Road Packer	5.20	4.82	-35.9	-29.4	4	5	+	Z

[a] ++ = fully effective, + = fully to partially effective, 0 = partially effective.

[b] Z = expected to be effective, X = expected to be ineffective.

77

Table 5-6 . Zeta potential, specific conductance, pH of untreated and chemically treated Marias series

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to $Z.P$[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	8.95	8.95	− 9.3	− 9.3	17	17		
Clapak	7.15	7.00	−11.8	−17.2	16	16	+	Z
Claset	7.00	7.60	−10.2	−13.0	12	12	+	Z
Petro-S	9.12	9.10	−12.3	−13.1	17	20	+	Z
Thin Water	8.80	9.00	− 9.3	−12.6	17	17		X
SA-1	6.00	6.20	−17.8	−14.5	21	21	++	Z

[a] ++ = fully effective, + = fully to partially effective.

[b] Z = expected to be effective, X = expected to be ineffective.

Table 5-7. Zeta potential, specific conductance, pH of untreated and chemically treated Frederick series

Chemical Compaction Aids	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC^a	Expected Compaction Effectiveness according to $Z.P.^b$
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	5.50	5.50	-21.8	-21.8	3	3		
Clapak	5.00	5.00	- 9.1	-14.2	8	6	-	X
Claset	5.10	5.00	-15.9	- 3.2	5	7	-	X
Petro-S	5.75	5.84	-31.9	-35.9	3	3	+	Z
Thin Water	5.00	5.65	-25.2	-30.3	3	3	+	Z
SA-1	4.85	5.05	-20.3	-21.4	6	5	-	X

[a] ++ = fully effective, + = fully to partially effective, - = not effective.

[b] Z = expected to be effective, X = expected to be ineffective.

Table 5-8. Zeta potential, specific conductance, pH of untreated and chemically treated Persanti series

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to Z.P[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	6.00	6.00	-19.2	-19.2	3	3		
Clapak	5.00	5.00	- 8.2	-12.6	9	6	0	X
Claset	4.48	5.20	- 2.0	- 4.2	5	6	-	X
Petro-S	5.85	5.95	-29.6	-26.7	3	3	+	Z
Thin Water	6.00	6.00	-20.4	-18.9	3	3	0	Z
SA-1	4.92	4.44	-13.8	-18.2	9	7	-	X
SC-518	6.00	6.00	-10.2	-10.8	3	3	-	X

[a] + = fully to partially effective, 0 = partially effective, - = not effective.
[b] Z = expected to be effective, X = expected to be ineffective.

Table 5-9. Zeta Potential, Specific Conductance, pH of untreated and chemically treated Nappanee series

Chemical Compaction Aid	pH		Zeta Potential m. V.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to Z.P[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	7.82	7.82	-19.4	-19.4	12	12		
Clapak	6.45	6.45	-19.2	-19.8	18	18	-	X
Claset	6.65	6.65	-10.9	-14.2	8	6	-	X
Petro-S	8.65	9.00	-19.0	-18.0	13	13	-	X
Thin Water	8.82	8.90	-17.0	-18.8	14	15		X
SA-1	6.00	6.80	-21.7	-20.8	25	20	+	Z

[a] + = fully to partially effective, - = not effective.

[b] Z = expected to be effective, X = expected to be ineffective.

81

Table 5-10. Zeta potential, specific conductance, pH of untreated and chemically treated Vergennes series

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to Z.P.[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	9.00	9.00	-12.9	-12.9	15	15		
Clapak	6.27	6.10	-20.8	-20.7	18	18	0	Z
Thin Water	9.00	9.00	-19.0	-12.4	15	19	+	Z
SC-518	9.00	9.00	-16.9	-10.5	15	15	0	Z
Road Packer	8.75	8.50	-12.4	-14.1	13	11	-	X
Petro-S	9.15	9.15	-17.9	-10.9	20	20	+	Z
SA-1	6.00	6.00	-19.0	-16.3	38	38	0	Z

[a] + = fully to partially effective, 0 = partially effective, - = not effective.

[b] Z = expected to be effective, X = expected to be ineffective.

Table 5-11. Zeta potential, specific conductance, pH of untreated and chemically treated Melbourne series

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to Z.P.[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	5.88	5.88	-19.6	-19.6	4	4		
Clapak	4.91	5.00	-13.8	-14.5	10	7	0	X
Claset	5.00	5.00	-14.7	- 9.0	4	5	+	X
Petro-S	5.86	5.15	-34.7	-23.3	4	3	+	Z
SC-518	5.10	5.76	-25.6	-19.6	4	2	0	Z
SA-1	4.85	4.42	-20.5	-20.0	10	12	+	Z

[a] + = fully to partially effective, 0 = partially effective.

[b] Z = expected to be effective, X = expected to be ineffective.

83

Table 5-12. Zeta potential, specific conductance, and pH of untreated and chemically treated Shelby series

	pH		Zeta Potential m. v.		Specific Conductance μ mhos/cm		Compaction Effectiveness at max. γ_d and OMC[a]	Expected Compaction Effectiveness according to z.P.[b]
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days		
(Untreated)	7.00	7.00	-19.9	-19.9	5	5		
Claset	5.43	5.79	-21.0	-27.3	5	7	+	Z
Thinwater	6.22	6.22	-20.5	-24.8	4	4	+	Z

[a] + = fully to partially effective.

[b] Z = expected to be effective.

84

the performance of the chemical with time, and thus help in a re-evaluation of each chemical including the time effect. These results were compared with zeta potential results of the treated soils when tested after 7 days. It was found that when the numerical value of zeta potential of the treated soil decreased with time, a gain in strength was found. When it decreased after 7 days to the extent that it dropped below the zeta potential of the untreated soil, a loss in density occurred. On the other hand, if the numerical value of zeta potential of the treated soil increased with time, a loss in strength was observed and frequently was combined with a further increase in density.

The analysis of the results lead to the above hypothesis which depended on the correlation between the compaction test and compaction growth study data, and zeta potential results. Despite some exceptions where the two tests did not correlate, in most cases the rules mentioned before seem to be correct.

The following is the comparison, in detail, between the results of zeta potential and compaction tests which shows the correlation between them and how far they support the above hypothesis.

Bearden Series

   a. Clapak. The numerical value of zeta potential increased initially after treatment comparing with the untreated soil, and then it decreased with time. The compaction test data showed that it is effective and the ultimate bearing capacity increased with time.

b. <u>Claset.</u> The numerical value of zeta potential of the treated soil increased slightly when tested right after sample preparation, however, it decreased with time to the extent that it became less than the zeta potential of the untreated soil after 7 days of treatment. Compaction tests showed that Claset is effective for Bearden Series, but a decrease in density was noticed after 7 days-moist cure.

c. <u>Petro-S.</u> It behaved as Claset and Clapak with Bearden Series. Zeta potential increased initially and then decreased with time. Compaction tests showed that it is effective. This chemical-soil combination was not included in the compaction growth study. Therefore, no information was available concerning the strength improvement after 7 days.

d. <u>Thin Water.</u> Zeta potential numerical value slightly increased after treatment and then decreased with time. The compaction test indicated that this chemical is partially effective in compaction. The density decreased and the ultimate bearing capacity was improved 7 days after treatment.

e. <u>SA-1.</u> Zeta potential numerical value was less than zeta potential of the untreated soil. It also tended to increase with time. Compaction test data indicated that this chemical is not effective for compaction. No information was available concerning the strength and density after 7 days.

Renohill Series

    a. __Clapak.__ Zeta potential numerical value increased right after treatment compared to the untreated soil. It decreased 7 days after treatment. Compaction tests showed no improvement, and both density and ultimate bearing capacity exhibited a reduction after 7 days moist-cure. This is the only case so far that the compaction test data did not agree with the hypothesis of zeta potential criteria of effectiveness.

    b. __Claset.__ The numerical value of zeta potential was less than zeta potential of the untreated soil. It increased slightly 7 days after treatment. Compaction test results indicated that Claset was not effective for compaction. On the contrary, it showed some improvements in strength parameters. After 7 day moist-cure, the compaction growth study showed a slight reduction in both density and ultimate bearing capacity.

    c. __Petro-S.__ The numerical value of zeta potential was higher than zeta potential of the untreated soil. After 7 days of treatment, zeta potential decreased but still higher than zeta potential of the untreated soil. Compaction tests indicated that Petro-S is effective compaction aid for Renohill series. No information was available about strength and density changes after 7 days moist-cure; this combination was not included in the compaction growth study.

    d. __SC-518.__ The numerical value of zeta potential decreased upon treatment. It also continued to decrease with time. Compaction

tests considered this chemical as ineffective for compaction. According to compaction growth study, the density decreased but the strength increased after 7 days moist cure.

Rimrock Series

a. Clapak. The numerical value of zeta potential was higher than zeta potential of the untreated soil. Seven days after treatment, it further increased. Compaction test data showed that Clapak is effective as a compaction aid for Rimrock Series. Compaction growth study did not include this chemical-soil combination.

b. Claset. The numerical value of zeta potential of the treated soil was higher than zeta potential of the untreated soil but it decreased slightly 7 days after treatment. Compaction test results considered this chemical as an effective compaction aid for Rimrock Series.

c. Petro-S. The numerical value of zeta potential decreased comparing with zeta potential of the untreated soil. However, it increased with time till it became higher than zeta potential of the untreated soil, after 7 days. Compaction tests showed that it is ineffective. Compaction growth study reported a reduction in the ultimate bearing capacity combined with a slight improvement in density after 7 days moist-cure.

d. SA-1. The numerical value of zeta potential increased comparing with the untreated soil. It decreased with time. Compaction tests indicated that SA-1 is effective for compaction. No information was available concerning the strength and density

changes with time.

e. <u>Thin Water.</u> The numerical value of zeta potential was less than zeta potential of the untreated soil. It almost did not change with time. Compaction tests reported no effectiveness in compaction. This chemical-soil combination was not included in the compaction growth study.

Peavine Series

a. <u>Clapak.</u> The numerical value of zeta potential decreased right after treatment but it increased with time. Compaction tests reported that it is effective. In this case compaction test results are not in agreement with zeta potential criteria. No information was available about strength and density after 7 days.

b. <u>Claset.</u> The numerical value of zeta potential decreased upon treatment and continued decreasing with time. Compaction tests indicated that it slightly improved compaction. No information was available about the density and strength after 7 days.

c. <u>Petro-S.</u> The numerical value of zeta potential increased after treatment. It decreased slightly after 7 days. Compaction tests showed that it is effective. This chemical-soil combination was not included in the compaction growth study.

d. <u>Thin Water.</u> The numerical value of zeta potential increased right after treatment and then decreased with time. Compaction tests indicated that it is effective. Compaction growth study reported some improvement in ultimate bearing capacity combined

with slight decrease in density.

e. <u>SA-1.</u> The numerical value of zeta potential of the treated soil was less than zeta potential of the untreated soil, when compared right after treatment. It continued to decrease with time. Compaction tests reported some improvement in compaction. An increase in ultimate bearing capacity and also in density was noticed after 7 days moist-cure. In this case, the compactability improvement could not be correlated with zeta potential criteria.

f. <u>SC-518.</u> The numerical value of zeta potential increased right after treatment comparing with zeta potential of the untreated soil. It decreased slightly 7 days after treatment. Compaction test results stated that SC-518 is effective. Compaction growth study reported an improvement in ultimate bearing capacity accompanied by a decrease in density after 7 days moist-cure.

g. <u>Road Packer.</u> The numerical value of zeta potential was higher than zeta potential of the untreated soil. It decreased 7 days after treatment till it became less than zeta potential of the untreated soil. Compaction test data indicated that it is effective. Compaction growth study reported an increase in ultimate bearing capacity combined with no change in density after 7 days moist-cure.

Marias Series

a. <u>Clapak.</u> The numerical value of zeta potential increased upon treatment. It continued to increase as noticed after 7 days. Compaction test results stated that it is effective. This chemical-soil combination was not included in the compaction growth study, therefore, no information available concerning the strength and density after 7 days.

b. <u>Claset.</u> The numerical value of zeta potential was higher than zeta potential of the untreated soil. It continued to increase as noticed 7 days after treatment. Compaction test data concluded that it is effective. This chemical-soil combination was not included in the compaction growth study.

c. <u>Petro-S.</u> The numerical value of zeta potential increased upon treatment. It continued to increase with time as noticed after 7 days. Compaction test results stated that Petro-S was effective. This combination was not included in the compaction growth study.

d. <u>SA-1.</u> The numerical value of zeta potential increased considerably after treatment. Then it decreased with time as indicated 7 days after treatment. Compaction test results stated that it is effective. After 7 day moisture-cure, a considerable improvement in ultimate bearing capacity was noticed, which was accompanied by some decrease in density.

e. <u>Thinwater.</u> The numerical value of zeta potential did not change right after treatment, but it increased 7 days after treatment.

No compaction test was conducted for this combination.

Frederick Series

   a. <u>Clapak.</u> The numerical value of zeta potential was considerably less than zeta potential of the untreated soil. It increased to some extent 7 days after treatment, however, it did not reach zeta potential of the untreated soil. Compaction tests showed that Clapak was ineffective in compaction but it caused minor improvement in strength parameters. After 7 days moist-cure, a reduction in the ultimate bearing capacity combined with an increase in density were observed.

   b. <u>Claset.</u> The numerical value of zeta potential decreased upon treatment and continued to decrease drastically as noticed 7 days after treatment. Compaction test data showed that it is ineffective in compaction but it caused a remarkable improvement in strength parameters. No information was available about the changes in the strength and density after 7 days.

   c. <u>Petro-S.</u> The numerical value of zeta potential increased right after treatment and continued to increase with time as noticed after 7 days. Compaction test results stated that Petro-S is effective in compaction. After 7 days moist-cure, the density increased while the ultimate bearing capacity was slightly reduced.

   d. <u>SA-1.</u> The numerical value of zeta potential decreased right after treatment and slightly increased after 7 days. Compaction test results showed that SA-1 is ineffective in case of

Frederick Series. After 7 days, the density increased and the ultimate bearing capacity decreased.

e. <u>Thinwater.</u> The numerical value of zeta potential increased after treatment and continued to increase with time as noticed 7 days after treatment. Compaction test results showed that it improved the density. This combination was not included in the compaction growth study.

Persanti Series

a. <u>Clapak.</u> The numerical value of zeta potential decreased right after treatment. Then it increased with time as noticed from its value 7 days after treatment. Compaction tests showed slight improvement in compactability. No information about strength or density was reported after 7 days.

b. <u>Claset.</u> The numerical value of zeta potential decreased drastically upon treatment. It increased slightly after 7 days. Compaction tests proved that it is ineffective in compaction but it caused some improvements in strength parameters. After 7 days, the strength decreased and the density slightly improved.

c. <u>Petro-S.</u> The numerical value of zeta potential decreased after treatment. It decreased with time as indicated after 7 days. Compaction test results stated that it is effective. This chemical-soil combination was not included in the compaction growth study, i.e. no information was available about the chemical performance concerning strength and density after 7 days.

d. <u>Thinwater.</u> The numerical value of zeta potential increased.

Then it decreased after 7 days. Compaction tests proved that this chemical is effective. When the treated soil was tested after 7 days moist-cure, the strength was higher and the density was slightly lower.

e. <u>SA-1.</u> The numerical value of zeta potential was higher than zeta potential of the untreated soil when tested right after treatment. After 7 days, it increased. Compaction test results indicated that it is ineffective. This chemical-soil combination was not presented in the compaction growth study.

f. <u>SC-518.</u> The numerical value of zeta potential was less than zeta potential of the untreated soil. After 7 days, it increased slightly. Compaction tests proved that it is not effective. This chemical-soil combination was not included in the compaction growth study.

Nappanee Series

a. <u>Clapak.</u> The numerical value of zeta potential decreased slightly upon treatment. Then it increased slightly 7 days after treatment. Compaction test results showed that it is ineffective. After 7 days moist-cure, the density increased, but the ultimate bearing capacity decreased.

b. <u>Claset.</u> The numerical value of zeta potential decreased considerably after treatment. It increased to some extent with time as indicated after 7 days. Compaction tests proved it is ineffective, some improvement in the strength parameters was noticed. After 7 days moist-cure, the ultimate bearing capacity

decreased while the density increased.

c. <u>Petro-S.</u> The numerical value of zeta potential decreased

slightly after treatment. After 7 days it decreased more.

Compaction tests showed that it is not effective in compaction

but it caused minor improvement in strength parameters. No

information was available concerning the change in strength

and density with time.

d. <u>Thinwater.</u> The numerical value of zeta potential decreased after

treatment. Then it increased with time as indicated after 7 days.

No compaction test or strength test was conducted for this

chemical-soil combination.

e. <u>SA-1.</u> The numerical value of zeta potential increased upon

treatment. It decreased slightly after 7 days. Compaction test

results proved that it is effective. This chemical-soil combina-

tion was not tested in the compaction growth study.

<u>Vergennes Series</u>

a. <u>Clapak.</u> The numerical value of zeta potential of the treated

soil was higher than zeta potential of the untreated. Its value

did not change with time and stayed higher than the untreated

soil. According to the compaction test results, it is

effective. After 7 days moist-cure, a reduction in the ultimate

bearing capacity was noticed. Also the density decreased

slightly.

b. <u>Thinwater.</u> The numerical value of zeta potential increased

upon treatment. But it decreased again with time till it be-

became slightly less than zeta potential of the untreated soil. According to compaction test results, it is effective. After 7 days moist-cure, the ultimate bearing capacity increased but the density decreased slightly.

c. Road Packer. The numerical value of zeta potential decreased slightly upon treatment. But it increased after 7 days. Compaction test results indicated that it is ineffective. After 7 days moist-cure, the strength dropped down and the density increased.

d. SC-518. The numerical value of zeta potential of the treated soil was higher than zeta potential of the untreated soil. But it decreased with time till it became less than zeta potential of the untreated soil, after 7 days. Compaction test results indicated that it is effective. After 7 days moist-cure, both the ultimate bearing capacity and density were higher than the untreated soil.

e. Petro-S. The numerical value of zeta potential increased upon treatment. It decreased with time to become less than zeta potential of the untreated soil after 7 days of treatment. Compaction tests proved that it is effective. No information was available about the change in strength and density after 7 days.

f. SA-1. The numerical value of zeta potential increased and stayed unchanged after 7 days and higher than zeta potential of the untreated soil. Compaction tests proved it is effective.

After 7 days moist-cure, both density and ultimate bearing

capacity was lower than these values of the untreated soil.

Melbourne series

a. Clapak. The numerical value of zeta potential of the treated

soil was lower than zeta potential of the untreated soil. It

increased further with time. However, the compaction test

showed a slight improvement in compaction as well as some im-

provement in strength parameters. No information about the

change in strength and density after 7 days was available.

b. Claset. The numerical value of zeta potential of the treated

soil was lower than zeta potential of the untreated soil. It

decreased more with time. Compaction tests showed that it is

effective in compaction, as well as it improved the strength

parameters. After 7 days moist-cure, an improvement in the

ultimate bearing capacity was noticed but no change occurred

to the density, comaring to the untreated soil.

c. Petro-S. The numerical value of zeta potential of the treated

soil increased considerably. It decreased with time. According

to compaction test results, it is effective. After 7 days

moist-cure, the ultimate bearing capacity of the treated soil

was higher than the untreated. Also, the density was slightly

higher.

d. SC-518. The numerical value of zeta potential was higher than

zeta potential of the untreated soil. It decreased with time.

Compaction tests showed that it is effective. This chemical-

soil combination was not tested after 7 days moist-cure to

detect the changes in density and strength with time.

e. <u>SA-1.</u> The numerical value of zeta potential of the treated
soil was higher than zeta potential of the untreated soil. It
decreased slightly with time. Compaction tests showed that this
chemical is effective for Melbourne soil. After 7 days moist-
cure, the ultimate bearing capacity of the treated soil was
higher than the untreated soil but the density was lower.

After presenting in detail, the results of zeta potential tests of
the treated versus untreated soils with different chemicals, and comparing
them with the compaction test data as well as the compaction growth data,
when available, we can see that zeta potential criteria mentioned earlier
holds true in the majority of the chemical-soil combinations. Among 52
combinations, the zeta potential results correlate very well with the
other results in 46 cases, i.e. it was successful 88% of the time. Since
there are fewer opportunities for experimental error in the zeta
potential test than in the laboratory compaction evaluations, it is
possible that zeta potential, in the cases of disagreement may be the
more accurate and reliable. For instance, it was found that the maxi-
mum dry density as well as the optimum moisture content in the compaction
test depends to a large extent on the initial moisture content of the
soil before compaction. The disagreement between the zeta potential
criteria and compaction test data was mainly in the case of Clapak treat-
ment of some soils such as Renohill, Peavine, Persanti, and Melbourne.
This chemical is marketed as a soil stabilizer for clays rather than a
chemical compaction aid. Zeta potential showed that it had flocculating

effect in most cases, expressed as a decrease in zeta potential, which means that this chemical should improve the strength parameters and the bearing capacity.

The other cases of disagreement were Claset with Peavine, SA-1 with Peavine, and Claset with Melbourne. Other than these few cases, zeta potential criteria was in full agreement with the compaction and compaction growth results and the strong correlation between the effectiveness of each chemical and zeta potential measurements of the treated soils was very clear. The theory that stands behind this correlation and the success of zeta potential as a criteria to predict the effectiveness of chemicals will be discussed in detail in Chapter VI.

Another strong support to zeta potential capability in predicting the effectiveness was the treatment of Shelby soil in the field with Claset and Thinwater. In both cases, an increase in density was noticed after treatment. When the treated soil was tested in the field after ten months, it was found that the density continued to increase while the strength was considerably reduced. Table 5-12 presents the results of zeta potential tests; in both cases, the numerical value of zeta potential increased slightly after treatment and continued to increase with time as indicated from the 7 day results. Therefore, the zeta potential criteria is very consistent with the field performance of these two chemicals when used in Shelby soil treatment.

The bentonite, kaolinite, and grundite soils were analyzed by the zeta potential test, x-ray diffraction, and infrared analysis to explore possible correlations which might throw some light on the mechanisms of

Table 5-13. Zeta Potential, specific conductance, and pH of Grundite

Chemical Compaction Aid	pH		Zeta Potential m.v.		Specific Conductance μmhos	
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days
–	4.85	4.85	–14.9	–14.9	18	18
Clapak	4.95	4.94	–28.0	–25.9	9	7
Claset	5.08	5.12	–31.9	–22.8	5	8
Petro-S	5.30	5.37	–27.2	–27.9	5	7
Thinwater	5.63	5.50	–21.7	–29.8	8	6
SA-1	4.70	4.82	–22.2	–26.3	17	14

Table 5-14. Zeta Potential, specific conductance and pH of Bentonite

Chemical Compaction Aid	pH		Zeta Potential m.v.		Specific Conductance μmhos	
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days
-	7.00	7.00	-41.2	-41.2	7	7
Clapak	4.70	4.65	-36.0	-27.9	25	24
Claset	6.00	5.23	-37.8	-33.6	8	8
Petro-S	6.88	6.70	-38.7	-34.0	12	9
Thinwater	6.90	6.75	-32.2	-37.4	8	5
SA-1	4.45	4.26	-29.5	-25.3	36	36

Table 5-15. Zeta Potential, specific conductance and pH of Kaolinite

Chemical Compaction Aid	pH		Zeta Potential m. v.		Specific Conductance μmhos	
	at 0 time	after 7 days	at 0 time	after 7 days	at 0 time	after 7 days
–	5.94	5.94	−24.4	−24.4	5	5
Clapak	4.51	5.23	− 3.2	−13.8	38	5
Claset	5.50	5.45	− 4.5	− 4.7	5	4
Petro-S	5.97	5.20	−19.2	−16.7	5	4
Thinwater	5.79	5.90	−23.6	−22.6	5	3
SA-1	5.16	5.09	−20.7	−17.5	8	8

chemical reaction with soils consisting essentially of single clay minerals.

Table 5-13 presents the results of zeta potential tests on the illitic Grundite soil. The zeta potential of the treated soil was higher than zeta potential of the untreated soil in all cases. In the case of Clapak and Claset, the zeta potential of the treated soil decreased to some extent after 7 days, but was still higher than the zeta potential of the untreated soil. In the case of Petro-S, Thinwater, and SA-1, the zeta potential of the treated soil continued to increase with time. There was not much information about the effectiveness of such chemicals with Grundite soil other than Petro-S, Claset, and SA-1 showed some improvement in compaction.

Table 5-14 presents the zeta potential results of Bentonite soil which is mainly sodium montmorillonite. The zeta potential of the treated soil was less than zeta potential of the untreated soil in all cases. In the case of Clapak, Claset, Petro-S, and SA-1, the zeta potential of the treated soil decreased with time as indicated from the 7-day results. In the case of Thinwater, the zeta potential of the treated soil increased with time. According to zeta potential criteria, none of these chemicals is expected to be effective in compaction of such soil.

Table 5-15 presents the results of Kaolinite soil. The zeta potential of the treated soil was lower than zeta potential of the untreated soil in all cases. In the case of Clapak and Claset, zeta potential of the

treated soil increased with time, but in case of Petro-S, Thinwater, and SA-1, it decreased with time. According to zeta potential criteria, all these chemicals are expected to be ineffective for compaction of kaolinite.

No correlation was found between the results with the pure clay mineral soils and the rest of the raw soils, even having the same predominant clay mineralogy. Also, pH values of the treated soils have no direct relation with the effectiveness of the chemical in compaction. Specific conductance values of the treated soil appeared to have no correlation with either the chemical effectiveness or zeta potential values. The role of pH and specific conductance will be discussed in the next chapter.

Infrared Observations

The infrared spectrum of a mineral is a characteristic feature which helps in the identification of mineral species. The adsorption bands arise from vibrations of the atoms or ions in the structure, and the frequencies of vibrations are dependent on the mass of the atoms, the restraining forces of the bonds, and the geometry of the structure. As a result, the spectrum of a mineral is sensitive to isomorphous replacements in its structure, as these affect both band strength and atom masses. The symmetry and regularity of a structure play an important part in determining the intensity and frequency of its vibrations, so that the infrared spectrum is often a sensitive indicator of the degree of order of a crystalline mineral.

Many applications of infrared spectroscopy are basically empirical, depending on comparison of the spectrum of the sample being investigated with those of more fully characterized samples. In soils, it was believed that the study of the changes in the surface-groups vibrations due to the adsorption of organic or inorganic molecules present in the chemical which might be adsorbed on the surface, can provide information on the mechanism of adsorption.

The soil samples had to be prepared by a special way to be used in infrared study, since the particle size should be smaller than the wavelength of the rays to eliminate scattering and reflection. Clay particles separated by sedimentation process for zeta potential experiment were already of suitable size for the infrared study. Among the four methods of sample preparation; the powder film method, the mull method, the pellet method, and the reflection method, the pellet method was selected to prepare the soil samples: 10 mg of soil -- either treated or untreated -- were mixed with an excess of K Br (1:500). After drying the mixture at 120°c, it was pressed in a die for 1 minute at about 10 ton/cm^2 into a transparent pellet of 10mm diameter and about 1 mm thickness. A reference pellet with only K Br was used in the reference beam.

Figure 5-4, 5-5, and 5-6 show the infrared spectra of grundite, kaolinite, and bentonite, respectively. These curves represent the spectra of the untreated soils, the soils treated with Clapak, Claset, Petro-S, Thinwater, and SA-1, and spectra of the treated soil after 7 days. It was noticed that there is not much difference between the
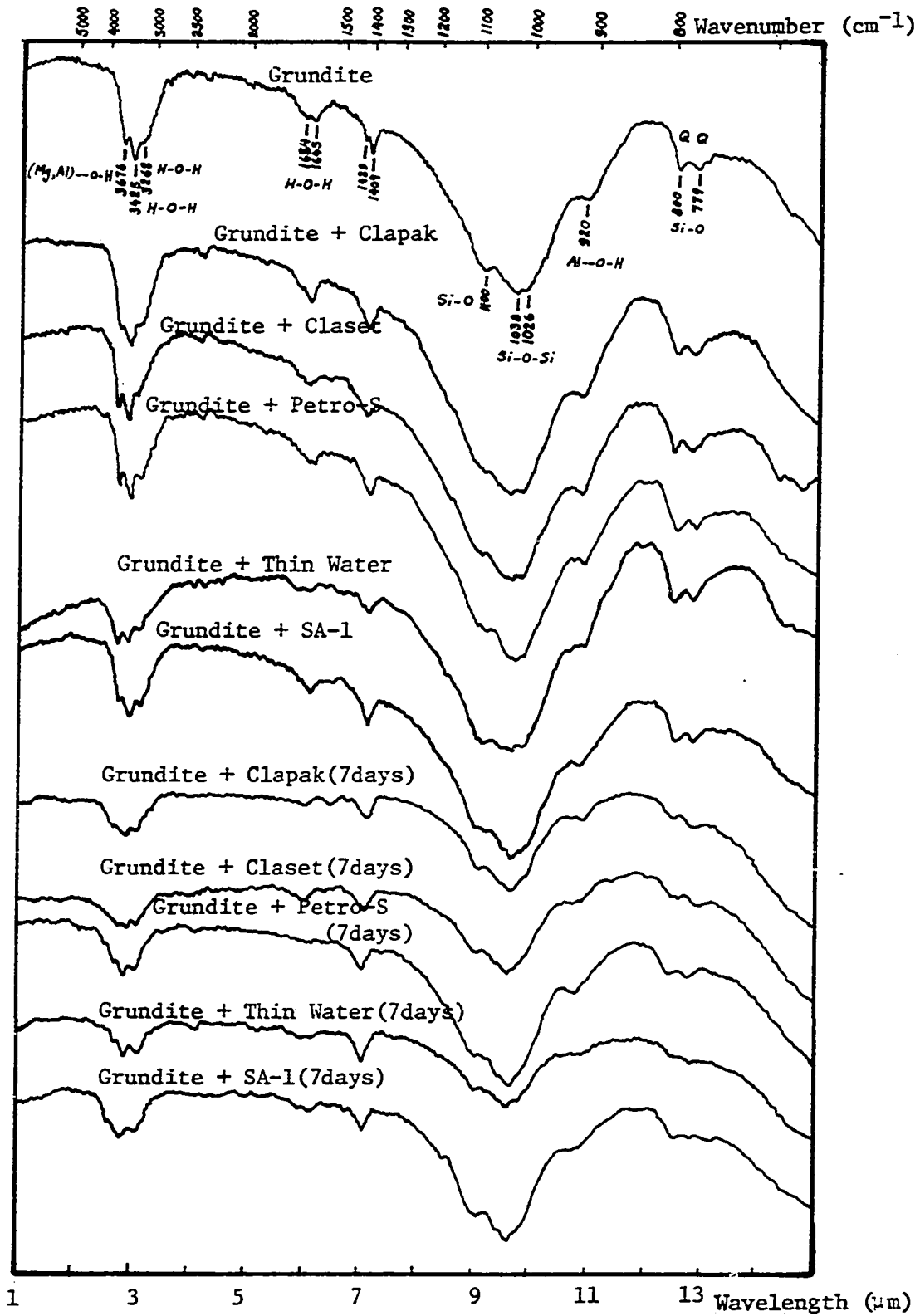
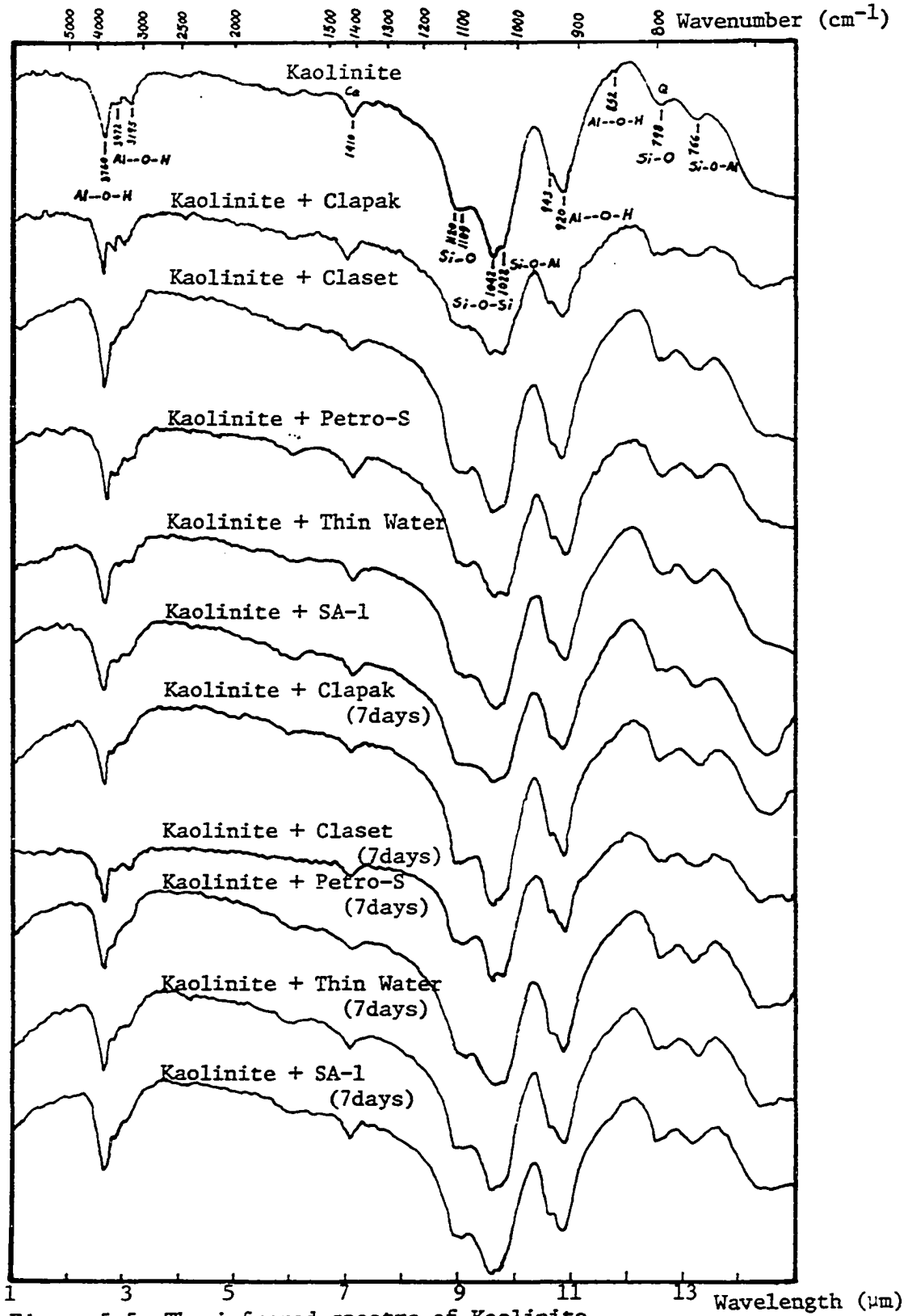Figure 5-4. The infrared spectra of Grundite
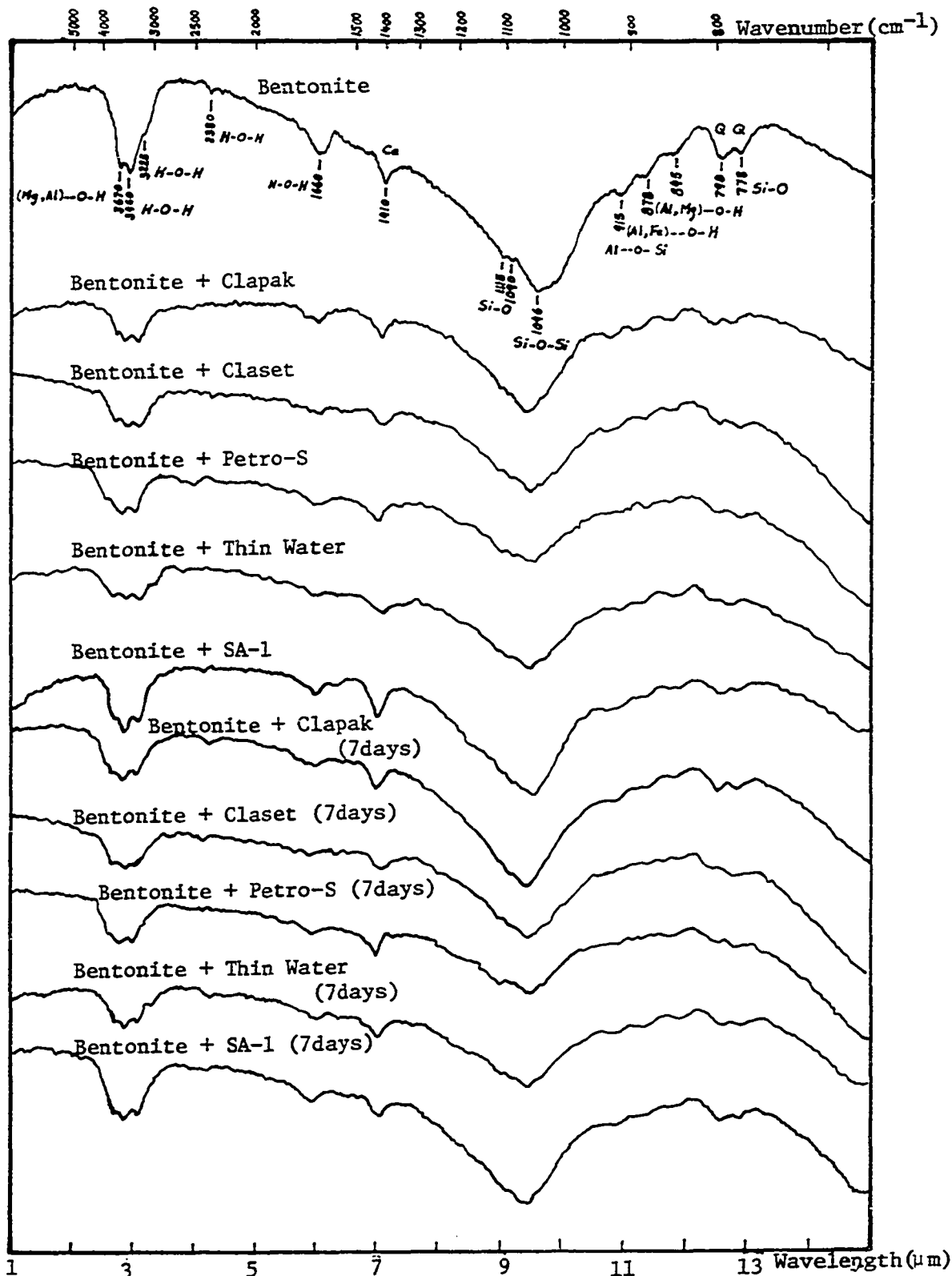
Figure 5-5. The infrared spectra of Kaolinite

Figure 5-6. The infrared spectra of Bentonite

treated and untreated soil spectra. The main functional groups were presented in every spectrum. There was no significant change that can be inferred to any isomorphous substitution caused by the chemical treatments. Only minute shifts in the frequencies of vibrations and minor differences in their intensities were observed when comparing with the untreated soil spectra.

Some of the natural soils also were tested by the infrared technique. These included the Bearden, Renohill, Rimrock, Peavine, Marias, Frederick, Nappannee, and Melbourne. In all of them no significant differences were noticed between the infrared spectra of the untreated soil and those of the chemically treated soils.

X-Ray Observations

Figure 5-7, 5-8, and 5-9 show the x-ray diffraction patterns of the untreated and chemically treated bentonite (sodium montmorillonite). Kaolinite, and Grundite soils, respectively. The selected chemicals for treatment were Clapak, Claset, Petro-S, Thinwater, and SA-1, the same chemicals used in infrared spectroscopy. In case of Grundite and Kaolinite, the x-ray diffraction patterns of the treated soils were almost identical as the untreated soil. That means the chemical did not affect the interior structure of the clay particles, and the interaction between the clay minerals and the chemicals was limited to the exterior surfaces of the unit layer, i.e., in the double layer. An exact analysis of the changes in the double layer upon the addition of chemicals which react with the constituents of the double layer cannot be detected by
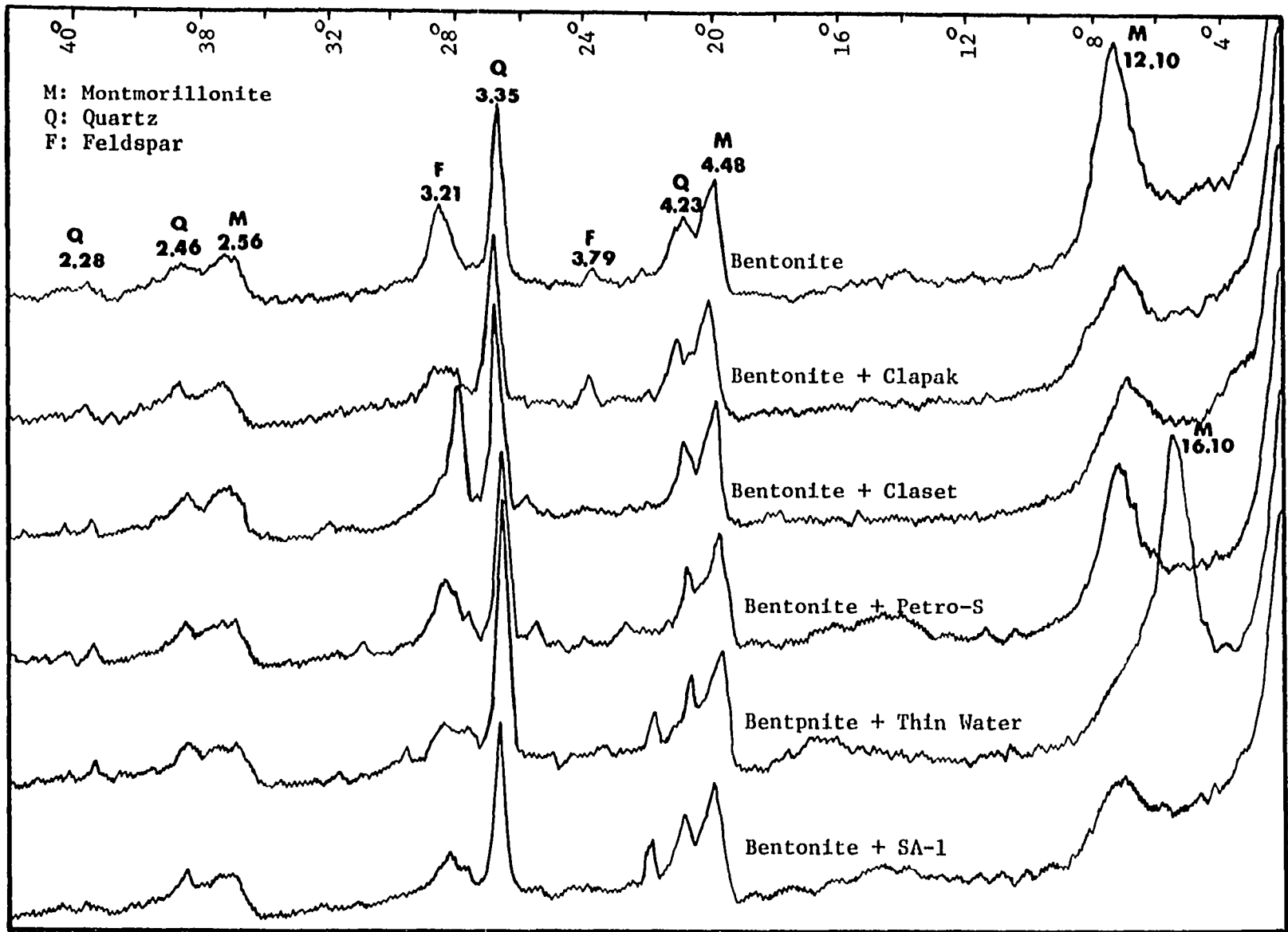
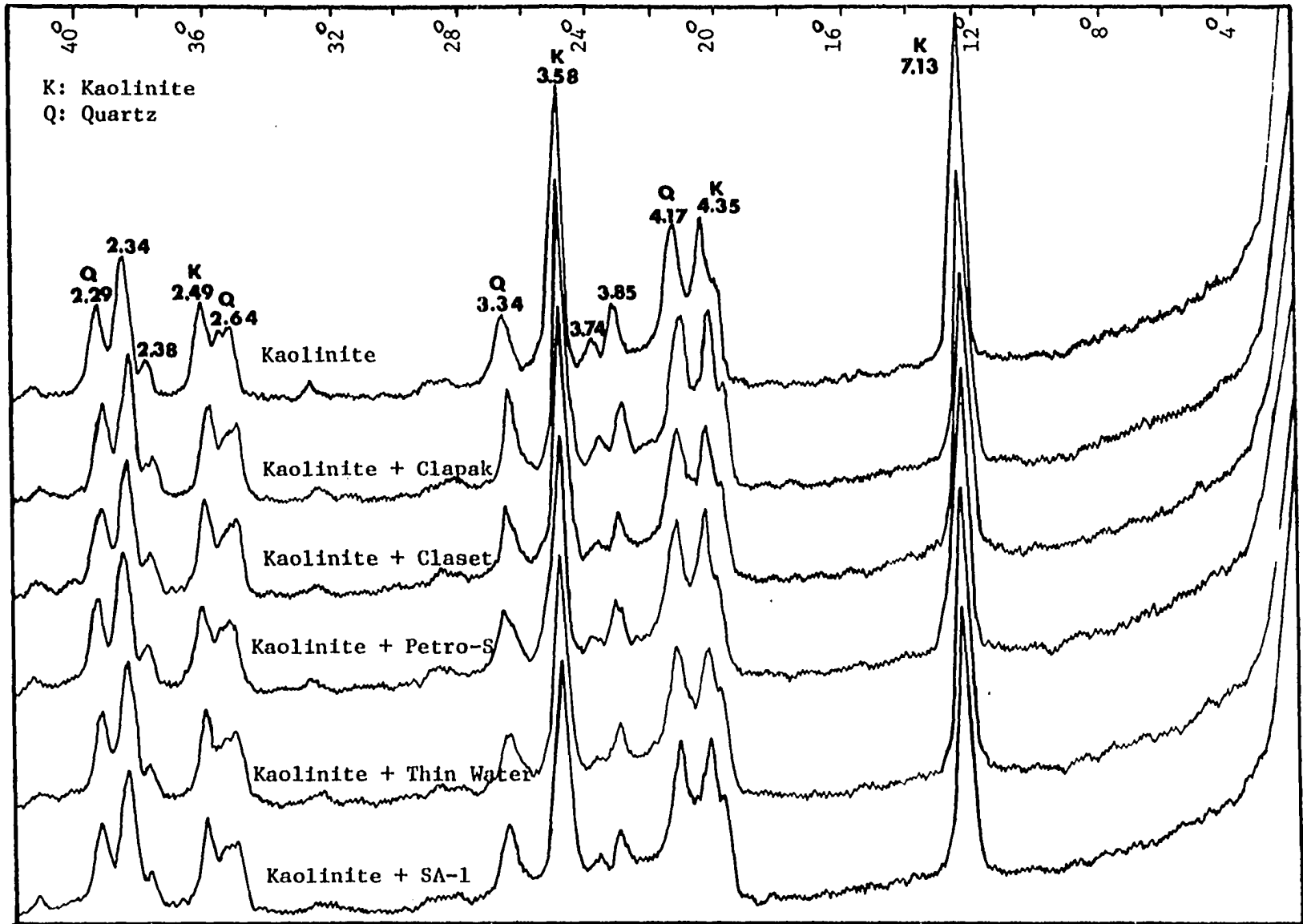Figure 5- 7. X-ray diffraction of untreated and chemically treated Bentonite

Figure 5-8. X-ray diffraction of untreated and chemically treated Kaolinite

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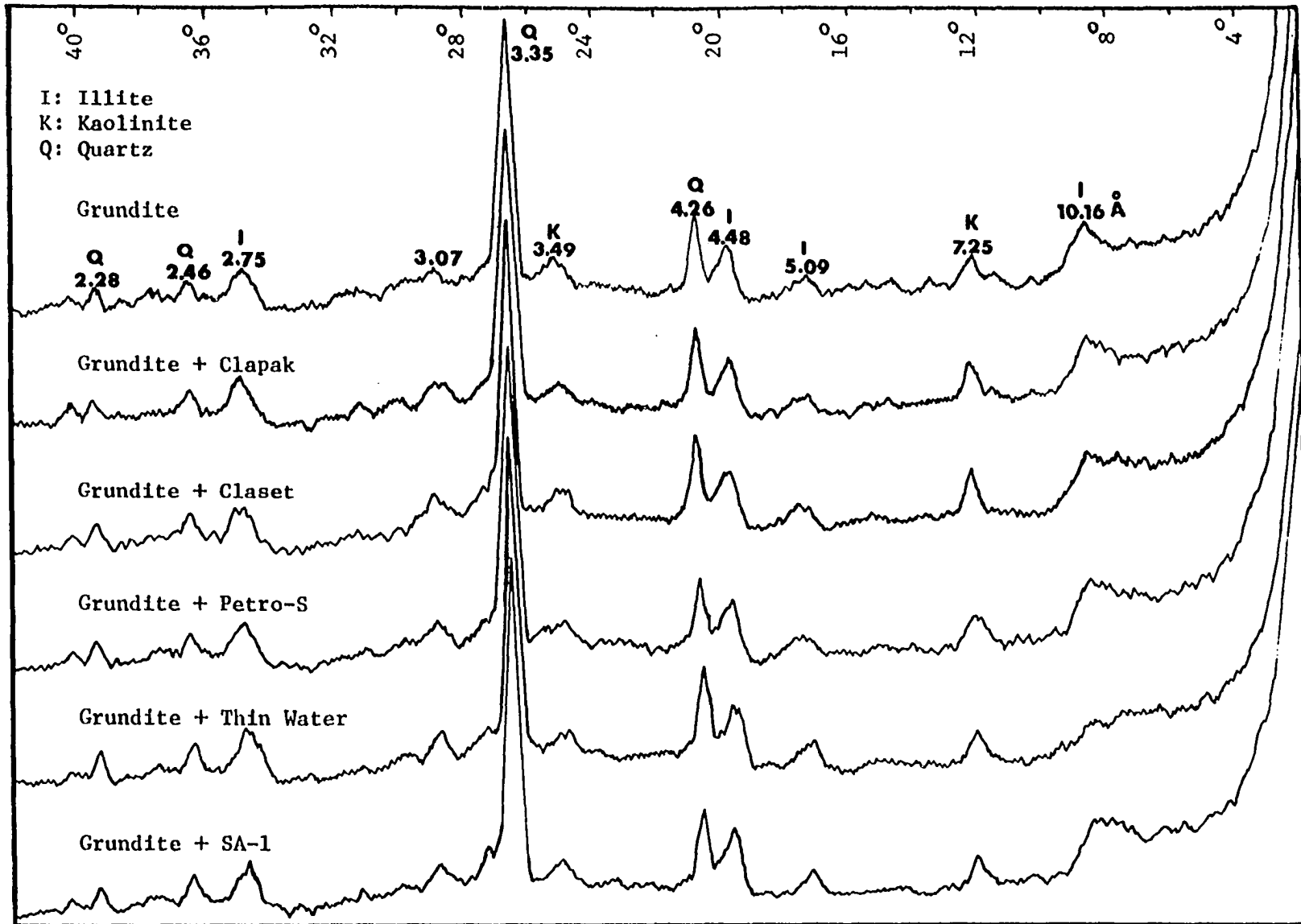
Figure 5-9. X-ray diffraction of untreated and chemically treated Grundite

x-ray diffraction because of the small quantities involved. Such changes
must be inferred on the basis of indirect evidence such as electro-
kinetic behavior, already discussed.

In the case of montmorillonite, the x-ray diffraction patterns did
not change much when the soil was treated with Clapak, Claset, Petro-S,
or SA-1. The most noticeable change was in Thinwater treatment. An
increase of 4Å was observed in the basal spacing, which went from 12 to
16 Å. This indicates that the adsorption of organic ions is not limited
to the exterior surfaces of the unit-layer packets of the expanding clay,
but that interlamellar adsorption also took place, causing an increase
of the basal spacing. These interlamellar adsorption complexes are
usually called "clay-organic complexes" (41). It might be important to
mention that Thinwater has the highest molecular weight of the five
selected chemicals. From a compaction standpoint interlamellar adsorp-
tion is believed to be deleterious since it removes the chemicals from
double layer system.

CHAPTER VI.

DISCUSSION

The analysis of clays as colloids can provide insight into the repulsive and attractive forces and their influence on the double layer interactions and particle arrangements. Also, it assists in understanding the flocculation and deflocculation phenomena which play an important part in the development of soil fabric and structure which in turn exert a major effect on physical and mechanical properties of compacted soil.

First, a review of some observations relative to soils plus chemical compaction aids should help to visualize the possible mechanisms of interaction between the soils and the chemicals.

1. A few tenths of percent of chemical compaction aids are often sufficient to affect the physical and mechanical properties of the compacted soil. Most chemical compaction aids contain a considerable amount of organic ions. The active concentration or "activity" of these ions is smaller than their actual concentration, and more so when the valency of the ions increases. That means, the effective concentration of chemical is even less than the amount added to the soil.

2. Ion exchange might contribute to the process of chemical treatment of soils, but the amount of chemical added to improve compaction is far below the amount which would be needed for complete ion exchange.

3. Different clays respond quite differently toward the same chemical compaction aid, even if they have the same predominant clay mineralogy.

4. The electrophoretic mobility of the clay particles usually changed upon the addition of small amounts of the chemicals, which proved that the chemical additive affects the electric double layer on the particle surfaces. This effect was reflected as a change in the electrokinetic potential or zeta potential.

5. It was concluded from the analysis of zeta potential test results that most chemicals proved to be effective in compaction when the numerical value of zeta potential increased (became more negative) compared with zeta potential of the untreated soil. On the contrary, when the numerical value of zeta potential of the treated soil was less than zeta potential of the untreated soil, the chemical was ineffective in compaction.

6. X-ray diffraction patterns of bentonite, kaolinite, and grundite soils did not show any significant changes between the untreated and chemically treated soils, except in case of bentonite plus Thinwater, where the basal spacing increased as a result of interlamellar adsorption of the chemical. These results emphasized that the effect of chemicals is primarily through surface interactions and not by altering the particle structure.

7. Infrared spectroscopy did not add much information; the spectra of the chemically treated bentonite, kaolinite, and Grundite,

were similar to the spectra of those of untreated clays. On the other hand, the similarity of the spectra of each soil regardless of treatment, indicated that no isomorphous replacement in the clay particle took place upon chemical treatment.

8. Surface tension experiments were conducted by other researchers in the project. Surface tension values varied significantly with the different chemical products, and there was no direct correlation between a product's ability to improve compaction and the surface tension of the additive concentration (Whited (44)).

Possible Mechanism

In the light of the above observations which were crystallized from this research, we can speculate on the possible mechanism of inter-action between soils and chemicals.

Electrical properties of clay-water systems are determined princip-ally by the structure of the electric double layers on the clay surfaces. Although the negative-face double layer probably plays the major part, possible contributions of the edge double layer should not be overlooked in the interpretation of electrochemical and electrokinetic behavior of the clay systems.

The clay lattice carries a net negative charge as a result of isomorphous substitution of certain positive elements by such elements of lower valence. The net negative lattice charge is compensated by cations located on the unit-layer surfaces, and form the diffuse

counter-ion layer in the presence of water. The atomic structure of the
edge surfaces of the plate like clay particles is entirely different
from that of the flat-layer surfaces. At the edges of the plates, the
tetrahedral silica sheets and the octahedral alumina sheets are dis-
rupted, and primary bonds are broken. Such surfaces may carry a positive
double layer in acid solution with hydrogen or aluminum ions acting as
potential-determining ions, and a negative double layer in alkaline
solution with hydroxyl ions acting as potential-determining ions. The
zero point of charge does not necessarily occur at neutral pH; it
actually varies with the crystal structure. Hence, there is a definite
possibility that in a neutral clay suspension a positive layer is
created on the edge surfaces owing to the exposed alumina sheet. This
double layer may become more positive with decreasing pH, or its sign
may be reversed with increasing pH. Despite the fact that the net
electrophoretic charge of the clay particles is always negative, the
existance of a positive edge double layer may not be excluded, since the
negative double layer on the large flat surfaces may well predominate in
the electrophoretic experiment.

Clays show a certain anion adsorption capacity under certain con-
ditions, although this capacity is rather small. It seems likely that a
positive double layer is responsible for the adsorption of anions acting
as counter-ions.

Flocculation phenomenon

The flocculation process is dominated by the negative double layer
on the flat surfaces of the clay particle. When the edge surfaces carry

a weak negative double layer or none at all, because of a low concentration or absence of potential-determining anions for these surfaces, the addition of a small amount of a flocculating chemical causes a compression of the existing edge double layers. When the double layers are compressed, a reduction in the surface potential will occur which is reflected as a decrease in the numerical value of zeta potential of the chemical treated soil compared to zeta potential of the untreated soil. With increasing chemical concentration both double layers, on the surfaces and on the edges, are further compressed. The van der Waals attraction between edges or between edges and faces will dominate. In the concentrated clay suspension, or in the case of compacted soil if we consider it as a highly concentrated clay suspension, edge-to-face and edge-to-edge association leads to formation of continuous linked, card-house structure which is rather stiff with large void spaces, low density, high strength, and low compactability.

If the edge surfaces carry a positive double layer, the presence of the positive edge leads to positive-edge-to-negative-face attractions. Upon the addition of chemical, both the double layers on surface and edge are compressed. The van der Waals attraction between the edges and faces enhances the opposite-charge attraction, and the edge-to-face attraction and the face-to-face repulsion becomes favorable for the formation of the card-house structure.

If the chemical concentration is high, face-to-face association is promoted and might lead to agglomeration.

The zeta potential results showed that the flocculating power of

each chemical varied from soil to another even if it caused flocculation in both. Apparently, different clays react differently on chemical addition because of differences in their initial double-layer structure.

Deflocculation phenomenon

When the chemical contains peptizing anions, these anions may react with cations are exposed at the particle edges, such as aluminum. These anions appear to have a specific reactivity with the exposed-edge cations. Consequently, they will be chemisorbed at the edges, forming complex anions or insoluble salts. Chemisorbed leading to the formation of complex anions creates a powerful negative edge double layer. When an insoluble, neutral salt is the reaction product, it seems likely that additional anions preferentially adsorbed on the salt surface will act as potential-determining ions. Alternatively, the spatial distribution of the positive charge sites on the edge surfaces may be such that the two or more valences of the peptizing anions cannot be satisfied simultaneously. Therefore, perhaps one valence may be neutralized by the attachment of the anion at one positive charge site, whereas the other negative groups of the anion may build up a negative charge. An anion with a rather high valence, such as organic anions, may become attached with a fraction of its ionic groups to a number of charge sites, depending on the geometrical fit between the ionized groups of anion and the location of the edge charges.

When a negative edge double layer is created, the positive-edge-to-negative-face attraction would be eliminated, and strong edge-to-edge

as well as edge-to-face repulsion could be created. Thus, the particle links are broken down, and the stiffness of clay is reduced. The repelling particles of a deflocculating structure should allow a higher degree of compaction than the attracting particles of a deflocculated structure. The deflocculated particles are able to slide and roll past each other because of mutual repulsion, thus they form a closely packed and dense structure when compacted.

The charge reversal of the edges of clay plates seems to be the basic mechanism underlying the chemical improvement of clay compaction. A reversal of the positive edge charge is also in agreement with the observation that the electrophoretic mobility of the clay particles increases upon the addition of small amounts of these peptizing chemicals. The electrophoretic experiment showed that the numerical value of zeta potential of the treated soil was higher than zeta potential of the untreated soil when the chemical proved to be effective in compaction.

In addition, the adsorption capacity of the clay for anions is usually rather small. Such a low adsorption capacity would be expected if the comparatively small edge surfaces were the site of adsorption. Only small amounts of peptizer are needed to build a negative double layer on the small edge surfaces; the consequent breakdown of the card house of clay plates must have a drastic effect on the rigidity of an initially flocculated structure.

Most of the chemical compaction aids contain a considerable amount of organic compounds as indicated from their infrared spectra and their

high molecular weights. The mechanism of peptization is essentially the same as for inorganic chemicals. Some organic compounds of long-chain macromolecules with ionized groups along the chain, when present in the chemical, they have a tremendous peptizing action. Many organic compounds containing polar groups are strongly adsorbed on the layer surfaces of a clay displacing the adsorbed water. Also, some organic ionic groups become attached to the surface of clay particles, and simultaneously the hydrocarbon chains displace the water from clay surface. Therefore, the presence of chemical in compaction process may decrease the amount of water needed to attain the optimum moisture content.

There is also an explanation of the fact that different clays respond quite differently toward the same chemical compaction aid, even if they have the same predominant mineralogy. Clay peptization is staged at the edges, where chemisorption of the anions of the peptizers with the exposed octahedral cations occurs. Clays often differ in the type of substituting ions in the octahedral sheet, therefore, in different clays, different cations will be exposed at the broken edges. Instead of, or in addition to aluminum, magnesium, ferric, other ions may be exposed. The anions in the chemical appear to have a specific reactivity with each kind of exposed cations which results in a noticeable difference in the behavior of the treated soils.

Specific conductance

Specific conductance data on soils was derived from the conductance of the clay suspension in the electrophoretic experiment. The specific conductance varied randomly for each soil-chemical combination. No

correlation was found between the specific conductance and the compaction effectiveness. Generally an increase in specific conductance with increasing chemical or suspension concentration was observed. The relations between the specific conductance and suspension concentration, and between the specific conductance and chemical concentration, were almost linear.

The specific electric conductivity is different than the surface conductance of clays. The surface conductance measures the product of the number of counter-ions per sq cm of the surface and the average mobility of these ions. For clay surfaces, usually the density of charge is independent of the electrolyte concentration; therefore, the specific surface conductance changes only if the average mobility of the ions changes. Possibly it becomes lower because of the compression of the double layer, which might result in a greater retarding effect by the oppositely charged surface on the counter-ions (41). The effect of chemicals on the surface conductance of clays cannot be evaluated from the specific conductance measurements of the clay suspension. Thus, the specific conductance measurements of the bulk solution has no significance.

Role of pH

Clay particles may have hydroxyl (OH) exposed on their surfaces and edges. The tendency for the hydroxyl to dissociate,

$$S_iOH \xrightarrow{H_2O} S_iO^- + H^+ \, ,$$
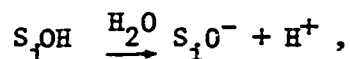
is strongly influenced by the pH, the higher the pH, the greater the

tendency for the H^+ to go into solution, and the greater the effective

negative charge of the particle.

In addition to this, alumina, which is exposed at the edges of

clay particles, is amphoteric and ionizes positively at low pH and

negatively at high pH. As a consequence, positive double layers may

develop at the edges of some clay particles in an acid environment.

Such double layers are of the constant surface potential type, as

opposed to constant surface charge, with H^+ serving as the potential

determining ion (30).

A low pH promotes a positive edge-to negative surface interaction,

often leading to flocculation of clay particles.

Stable suspensions or dispersions of clay particles often require

high pH conditions. Quantitative relationships between pH and compaction

effectiveness do not appear to be available at present.

When natural raw clays were treated with alkaline chemicals the

beneficial effects on stability are often higher than predicted from

their effect on sodium montmorillonite clay. This was particularly

true when the raw clay shows an acid reaction. In the acid form most

clays are less stable than in the sodium clay. In addition, organic

acids are often present in the raw clay. These will be neutralized by

the added alkali, and the organic salts which are thus formed frequently

and act as a peptizing chemical.

Time effect

The electrophoretic experiment has shown that the numerical value

of zeta potential of the treated soil is higher than zeta potential of

the untreated soil when tested right after treatment. After 7 days, the numerical value of zeta potential of the treated soil continued to increase in some cases, and tended to decrease in others. The increase of zeta potential with time suggests a continuing chemisorption of the peptizing ions from the chemicals on more edge surfaces, resulting in better deflocculation and higher density, usually accompanied by a reduction in strength. On the other hand, a decrease in the numerical value of zeta potential of the treated soil with time indicates a tendency to flocculation after being deflocculated. As we mentioned before, some chemicals contain organic compounds of long-chain macromolecules with ionized groups such as polyelectrolytes along the chains. These polyelectrolytes have a high viscosity as a consequence of the presence of the stretched molecules. They can be dissolved in water; their functional groups become more or less dissociated. Most of the chemical compaction aids have a noticeably high viscocity, and they are soluble in water. Thus, it is believed that they contain such polyelectrolytes. At low polyelectrolyte concentrations, the long-chain ions may be adsorbed on more than one clay particle simultaneously, thus providing a link between the particles, which promotes flocculation. This bridging effect will show up as the time passes after compaction which allows the particle to come closer together. Another factor might be involved, the presence of air in the compacted soil. The compacted soil does not reach 100% saturation, and it contains some air in the voids along with the pore solution. This air plus biological activity might cause some kind of oxidation of the chemical compounds, decreasing

the effectiveness of the peptizing anions, reflected as a decrease in zeta potential with time.

When the numerical value of zeta potential of the treated soil showed a decrease after treatment comparing to the untreated soil, that indicates flocculation. If it continued decreasing with time, that means the double layer is further compressed resulting in more flocculation with time. If zeta potential tended to increase with time, a little peptization is taking place and competes with the flocculating ions.

Summary

In summary, the most significant relationship to predict the influence of a chemical on compactability is that if the chemical increases the zeta potential of the soil, the ease of compaction generally increases. An illustration is Figure 6-1, in which the change in maximum dry density for the selected soils and chemical treatments is plotted versus the change in zeta potential measured at a single percentage chemical. A t-test of a linear regression indicates a 79% probability that the observed trend is not due to chance. It also will be noted that most points fall in the first and third quarters of the gragh, as predicted by this hypothesis.
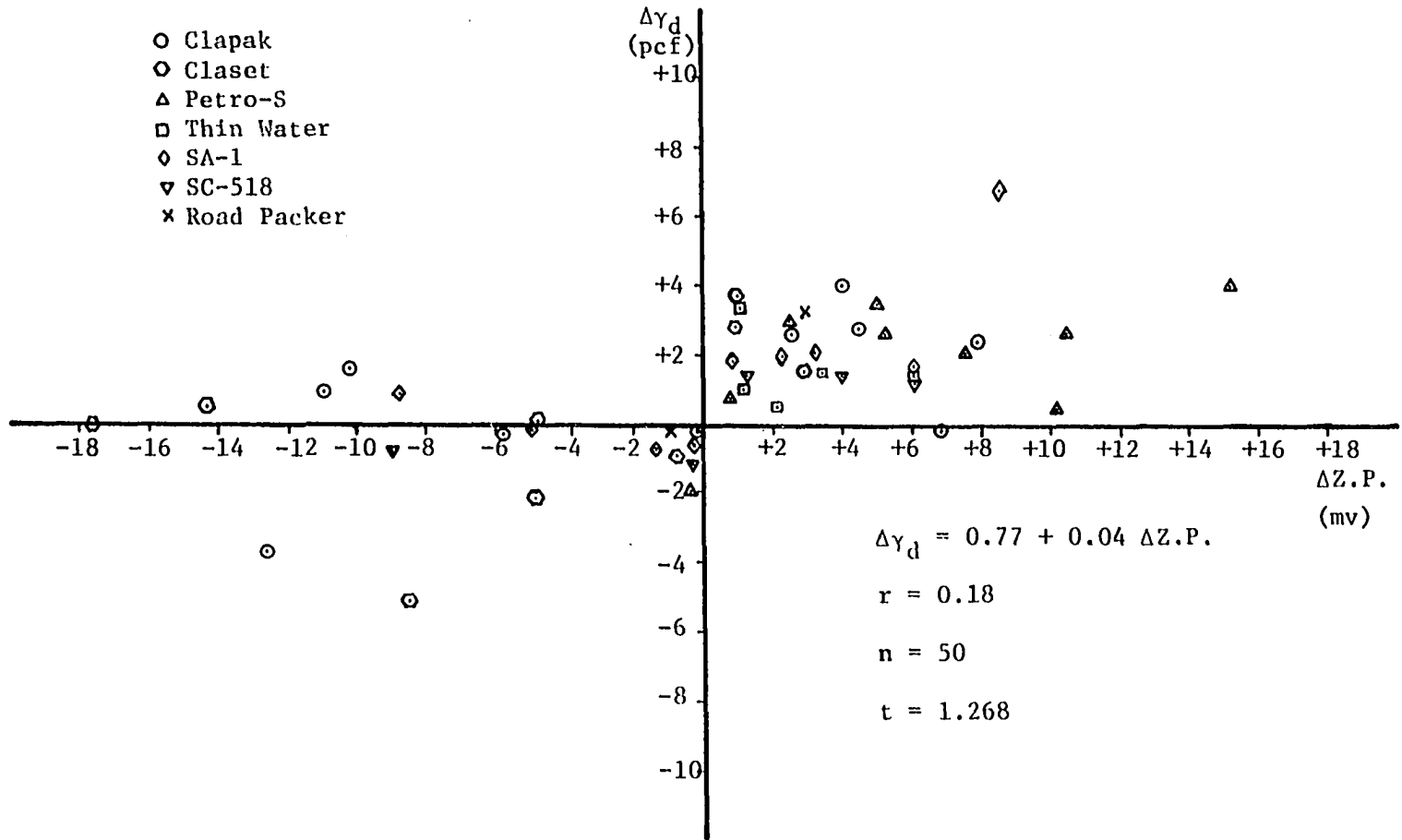
Figure 6-1. Change in maximum dry density versus change in zeta potential

CHAPTER VII.

CONCLUSIONS

Significance of Zeta Potential

The investigation has shown that zeta potential of chemically treated

soils is of primary significance in determining the effectiveness of the

chemicals as aids for soil compaction.

Zeta potential reflects the changes in double layer interactions

and ion exchange which alter interparticle forces and particle arrange-

ments which in turn may impart the soil structure with favorable proper-

ties for compaction such as higher density, lower optimum moisture content,

and sometimes, improvement in strength parameters. An interpretation

of soil behavior in terms of modes of particle association is helpful

in determining how chemicals change the soil system to obtain desired

properties.

The major effect of chemical compaction aids was interpreted in

terms of flocculation-deflocculation of the clay-water system of the

chemical is added, which was reflected in the zeta potential measurements.

Interaction Mechanisms

The possible mechanisms of interaction between soil particles when

the chemical is added, may be summarized as follows:

(1) When the chemical is added to the soil, some ions which are

     present in the chemical may replace the ions which are

     originally present on the clay particles surfaces, or some-

     times, replace the water molecules attached to the particle

     surfaces. In other words, ion exchange takes place. This

process depends on the preferential adsorption of the clay

particles and the availability of donor ions in the chemical.

Also, the chemical may contain ions that could be adsorbed on

surfaces of the clay particles as potential determining ions.

In both cases, upon the addition of chemical, the negative

double layers would be compressed and repulsive energy may

decrease to the extent that van der Waals attraction will

dominate. In this case flocculation is expected, and zeta

potential tends to decrease. As a result of the flocculated

structure, the compaction will be hindered and resisted, i.e.

This chemical is ineffective as a chemical compaction aid.

(2) If the chemical supplies the system with peptizing anions which

have a specific reactivity with the exposed ions of the edges

of clay layers, with which they form either a complex anions

or an insoluble salt, these anions will be chemisorbed at

the edges, and consequently, the edge charge is reversed. When

a negative double layer is created on the edge surfaces, the

edge-to-face association is prevented and deflocculation of

the system takes place, resulting in the ease of compaction

and a higher density. Zeta potential will increase as a result

of the edge-charge reversal.

These mechanisms are consistent with the observation that a few

tenths of one percent of the chemical can alter the system and has a

remarkable effect on compaction. This small amount is related to the

known small anion adsorption of clays. Also, different clays were found

to respond quite differently toward the same chemical, although sometimes they have the same predominant clay mineralogy; this may be because clays often differ in the type of the substituting ions in the octahedral sheet; hence in different clays, different cations will be exposed at the broken edges, and consequently the peptizing power and effectivity of each chemical should vary with the type of clay.

It is important to mention that the effectiveness of a chemical could be reversed if the percentage of the chemical additive is too high. When the chemical concentration increases, the double layer on both edge and surface of the clay particles is further compressed untill the repulsive energy is no longer able to counteract the van der Waals attraction. Then, flocculation may occur.

A combination of the above two mechanisms may occur if the chemical contains molecules that dissociate to cations which are preferentially adsorbed to face surface of the clay particle, and anions which act as peptizing ions at the edge surface. In this case, a conflict between flocculation and deflocculation may take place and result in some confusion and uncertainty as to the effectiveness of the chemical.

X-ray diffraction and infrared spectroscopy did not show any significant potentialities in this research. However, these negative results indicated that the effect of chemicals on fine-grained soils is basically surface interactions which might envolve minute shifts in infrared spectra and x-ray diffraction, i.e. the chemical effect is predominantly electrokinetic, not structural. Therefore, such

changes must be inferred on the basis of indirect evidence which was rep-

resented in the success of the electrokinetic experiment and its posi-

tive results that correlate very well with the compaction and strength

tests.

Zeta Potential Criteria

The criteria for characterization of chemical compaction aids can be

summarized as follows:

(1) When the numerical value of zeta potential of the chemical treated

soil is higher (zeta potential is more negative) than zeta poten-

tial of the untreated soil, when measured right after sample

preparation, and tends to decrease with time to some extent but

after 7 days is still higher than the zeta potential of the un-

treated soil; this chemical is expected to be effective for com-

paction as well as allowing improvement in strength with time.

(2) On the contrary, if the numerical value of zeta potential of

the chemical-treated soil is less than zeta potential of the

untreated soil when tested right after sample preparation, this

chemical is expected to be ineffective. It still may improve

the strength, but it will not improve the compaction.

(3) If the numerical value of zeta potential of the chemical-treated

soil is higher than zeta potential of the untreated soil, and

continues to increase with time, it is good for compaction and

the density will increase with time, but at the expense of the

strength which is expected to decrease with time. Therefore, if

the loss in strength with time is inacceptable, this chemical

should be avoided.

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APPENDIX: SEDIMENTATION PROCESS

100 gm of soil is mixed with distilled water by a blender until the soil is broken down into individual particles. The mixing time is approximately 10 minutes. After mixing, the specimen is washed into a 1000 cc graduated cylinder. Distilled water was added to bring the level to the 1000 - cc mark. The cylinder is provided with a measuring tape on its outer wall to measure the heights in cm starting from up, and increasing downward. The soil-water mixture is shaken into the cylinder and is left to settle for 20 hours. After 20 hours, the upper 29 cm of the suspension, which contains the clay colloidal part that has particle size less than 2 μm, is carefully poured into a large evaporating dish to be dried in the oven.

The time required to let the particles larger than 2 μm in diameter to settle down for 29 cm is calculated according to ASTM Designation: D422-63. The diameter of a particle shall be calculated according to Stokes' Law, on the basis that a particle of this diameter at the surface of the suspension at the beginning of sedimentation and has settled to the level at which the suspension will be poured. According to Stokes' Law:

$$D = \quad [30n/980 \ (G_1 - G_2] \ x \ L/T$$

where:

D = diameter of particle, mm,

n = coefficient of viscosity of the suspending medium (in this
case water) in poises (varies with changes in temperature of
the suspending medium),

L = distance from the surface to the level at which the density of the suspension is being measured, cm

T = interval of time from beginning of sedimentation to the taking of the reading, min.,

G = specific gravity of soil particles, and

G_1 = specific gravity of suspending medium

For convenience in calculations the above equation may be written as follows:

$$D = K \sqrt{L/T}$$

where:

K = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a temperature, 25°c, and average specific gravity of soil particles, 2.65, is 0.01286.

Thus, for T = 20 hours and D = 2 µm

$$D = K \sqrt{L/T}$$

$$.002 = 0.01286 \sqrt{L/(20 \times 60)}$$

$$L = 29.024 \text{ cm} \simeq 29 \text{ cm}$$