AGENCY FOR INTERNATIONAL DEVELOPMENT
WASHINGTON, D. C. 20523
BIBLIOGRAPHIC INPUT SHEET

FOR AID USE ONLY
Batch 84 ARDA

1. SUBJECT CLASSIFICATION
A. PRIMARY: Science and technology — TC00-0000-0000
B. SECONDARY: Applications

2. TITLE AND SUBTITLE
Study of building materials from polymer stabilized soil

3. AUTHOR(S)
Zipf,K.A.

4. DOCUMENT DATE: 1978
5. NUMBER OF PAGES: 87p. 88p.
6. ARC NUMBER: ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS
Carnegie-Mellon

8. SUPPLEMENTARY NOTES (Sponsoring Organization, Publishers, Availability)
(Thesis M.S.--Carnegie-Mellon)

9. ABSTRACT

One of the main problems facing low-cost house construction is the availability of suitable building materials. Often they are not readily available and if procured the cost is often prohibitive. Of all materials common to any environment, the most universal is soil. The purpose of this study was to find admixtures to render sand or other soils suitable for construction. One such method is through the in-situ polymerization of water-soluble monomer. Calcium acrylate was the best of several monomers tested to stabilize soil. The report describes the history and characteristics of calcium acrylate. Several requirements must be met for the construction of a dwelling using chemically stabilized earth. The monomer system must be a water-soluble solid that can be polymerized in solution. It has to be non-toxic, inexpensive, and incorporated in small quantities. A literature survey indicated that the metal salts of acrylic or methacrylic acid would be the most likely candidates. Five monovalent salts were made and three divalent salts were produced. These were: potassium methacrylate, sodium methacrylate, potassium acrylate, socium acrylate, ammonium acrylate, barium acrylate, calcium acrylate and magnesium acrylate. A decision was reached to concentrate on the calcium acrylate because it would readily polymerize, needed no crosslinking compound and it would probably be the cheapest to manufacture. The experimental procedures used are outlined. The appendicies include building specifications, soil properties, and sample calculations.

10. CONTROL NUMBER: PN-AAF-615
11. PRICE OF DOCUMENT:

12. DESCRIPTORS
Brick industry
Construction materials
Housing
Low cost?
Soils

13. PROJECT NUMBER: 931022100
14. CONTRACT NUMBER: AID/ta-C-1345
15. TYPE OF DOCUMENT:

AID 590-1 (4-74)

AID/TA-C-1345
ARDA
PN-AAF-615

Carnegie-Mellon University

CARNEGIE INSTITUTE OF TECHNOLOGY

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF Master of Science

TITLE "Study of Building Material From Polymer Stabilized Soil"

PRESENTED BY Karl A. Zipf, Jr.

ACCEPTED BY THE DEPARTMENT OF Chemical Engineering

MAJOR PROFESSOR — 1/5/78 DATE

DEPARTMENT HEAD — 1/5/78 DATE

APPROVED BY THE COLLEGE COUNCIL

DEAN — 10 Jan 78 DATE

ABSTRACT

Calcium acrylate was the best of several monomers tested to stabilize soil as a construction material. A quarter of a century ago the monomer was investigated as a suitable road stabilizer or as a grout. For construction, an aqueous solution of the monomer was polymerized in the soil. Strength of the product increased with the amount of water removed reaching a maximum compressive strength of about 2000 psi for 3% calcium acrylate in soil. Rewetting caused the stabilized soil to revert to its soft state with little structural strength. Salts, soil composition and initiator concentration affect the product's final strength. The best building form for the monomer use would be bricks where two weeks drying for a two-inch-thick brick gives maximum hardness.

TABLE OF CONTENTS

	Page
ABSTRACT	i
CHAPTER 1 - INTRODUCTION	1
1.1 Preface	1
1.2 History of Calcium Acrylate	3
1.3 Characteristics of Calcium Acrylate	6
CHAPTER 2 - EXPERIMENTAL	13
CHAPTER 3 - EARLY RESEARCH	18
3.1 Acrylamide	18
3.2 Metal Acrylates	20
3.3 Methacrylates	21
3.4 Acrylates	21
3.5 Potassium Acrylate	22
3.6 Ammonium Acrylate	24
3.7 Sodium Acrylate	25
3.8 Divalent Acrylates	25
3.9 Barium Acrylate	26
CHAPTER 4 - CALCIUM ACRYLATE	28
4.1 Reasons for Choice	28
4.2 Monomer Manufacture	28
4.3 Gel Tests	31
4.4 Soil Stabilization	34
4.5 Calcium Acrylate Concentration	36

4.6 Drying Time of Stabilized Soil 41
4.7 Initiator Concentration 44
4.8 Effects Upon Compacting a Fresh Sample 47
4.9 Soaking Stabilized Soil in Water 50
4.10 Effects of Humidity Upon Stabilized Soil 55
4.11 Heating of Stabilized Soil 56
4.12 Effect of Sodium Chloride Upon Polymerization . . . 58
4.13 Soil Composition 60
4.14 Comparison of Calcium Acrylate to Acrylamide . . . 64

CHAPTER 5 - CONCLUSIONS 66

REFERENCES 68

APPENDICES 70
A.1 ABS Building Specifications 71
A.2 Soil Properties 72
A.3 Sample Calculations 74

1. INTRODUCTION

1.1 Preface

The Advanced Building Studies Program at Carnegie-Mellon University is a joint effort between the Departments of Architecture, Civil Engineering, and the School of Urban and Public Affairs. A portion of the research within the ABS program addresses the problem of ultra-low-cost housing for developing countries. Part of this research is funded by a contract with the Agency for International Development, proposal 08143-A. Under the co-principal investigators, Professor Volker H. Hartkopf (Architecture) and Professor Charles H. Goodspeed (Civil Engineering), the research has pursued topics in culture, economy, materials technology, and structural systems as they relate to housing.

One of the main problems facing low-cost house construction is the availability of suitable building materials. Often they are not readily available and if procured the cost is often prohibitive. Of all the materials readily available in any environment, the most universal is soil. Unless the soil is of a high clay content, suitable for adobe, it cannot readily be used for construction. Similarly, fired bricks are many times not feasible due t the high energy input. The most unsuitable naturally occurring soil is sand, being neither adequate for agriculture nor building.

The purpose of this study was to find admixtures to render sand, or other soils, suitable for construction. One such method is through the in-situ polymerization of a water-soluble monomer. Therefore, the aid of the Chemical Engineering Department was sought, under Dr. Stephen L. Rosen, to develop a functional chemical system for the stabilization of soils.

A monomer system is not the only means for stabilizin soil. Soil stabilization has been obtained using Portland cement, asphalt, oil, bitumen, lime and various resins(3). The purpose of this investigation is to gain a better understanding of a monomer system.

Several requirements, as outlined by the project coordinators, have to be met for the construction of a dwelling using chemically stabilized earth. The monomer system must be a water-soluble solid that can be polymerized in solution. It has to be non-toxic, inexpensive, and incorporated in small quantities. Initial experiments were conducted with an acrylamide system, which though it reacted nicely, was exceedingly toxic(11). Therefore, it was necessary to find another monomer. A literature survey indicated that the metal salts of acrylic or methacrylic acid would be the most likely candidates. Five monovalent salts were made and three divalent salts were produced. These were: potassium methacrylate, sodium methacrylate, potassium acrylate, sodium acrylate, ammonium acrylate, barium

acrylate, calcium acrylate and magnesium acrylate. Quickly a decision was reached to concentrate on the calcium acrylate. It was chosen because it would readily polymerize, needed no crosslinking compound and it would probably be the cheapest to manufacture.

History of Calcium Acrylate

The use of calcium acrylate for soil stabilization is not new. As part of the World War II-Korean War effort, the Massachusetts Institute of Technology applied calcium acrylate for the stabilization of unsuitable terrain for road or runway applications. The research was done for the Army and the project was headed by Professor John B. Wilbur of M.I.T. Further tests were done by the Engineer Research and Development Laboratories at Fort Belvoir, Virginia (8).

The system tested in 1950 consisted of calcium acrylate monomer in aqueous solution initiated by a free-radical system of sodium thiosulfate and ammonium persulfate. They mixed and reacted the system in situ and stablized Fort Belvoir's sandy clay soil to a depth of three inches. For each cubic yard of soil stabilized, 192 pounds of monomer was used, resulting in about 10% by dry weight (12). Tensile strengths after five hours were 5-10 psi and when dry were up to 500 psi (9).

William Lambe of M.I.T. initially suggested that the new-found calcium acrylate could be put to many uses

including as a building material (6). Within a few years of the Fort Belvoir tests, calcium acrylate was commercially available from Rohm and Haas Chemical Company and other concerns (4). The trend in published material indicated that calcium acrylate as a road stabilizer was abandoned in favor of applying it in chemical grouting. As a grout it did not have wide appeal since there were problems concerning erratic monomer reaction (10). In 1955, when American Cyanamid Company introduced their Am-955 (now Am-9) grout, an acrylamide-methylenebisacrylamide mixture, a direct comperitor for calcium acrylate was established (7).

The new water-soluble monomer system, AM-955, had neither the strength nor the resilience of the calcium acrylate and it was also far more toxic (4). Regardless of its characteristics and for reasons yet unfathomed, AM-955 quickly replaced calcium acrylate in the field of grouting. By 1960, calcium acrylate had dropped from use. Today calcium acrylate is only commercially available in small laboratory quantities from Haven Chemical Company or Polysciences, Inc. (1). Concluding from the library search no further work using calcium acrylate as a soil stabilizer has been done since the work was completed at the M.I.T. Soil Stabilization Laboratory in the mid-1950's.

Since the first chemical grouts appeared in 1939, with the advent of the Joosten process for sodium silicate (13), engineers have been more interested in their water

stopping properties than in anything else. Not until 1972 did anyone publish a strength comparative investigation of the available chemical grouts (14).

The work originally started in the late 1950's wtih the Warner Construction Corporation. In all, eight different grout systems were valuated. These are separated into four different categories.

1) Acrylamide - AM-9

2) Polyphenol Resin - Terranier

3) Resin Emulsions

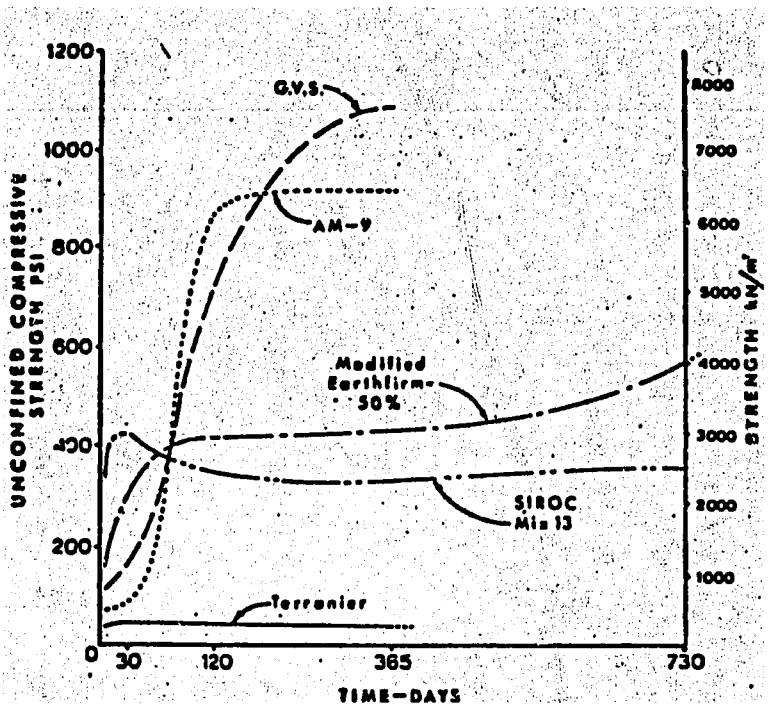
   a) ALREM Soil Binder
   b) Superstruct 22-0-2

4) Sodium Silicate base

   a) Earthfirm GVS
   b) Modified Earthform
   c) SIROC
   d) Silicate-Bicarbonate one-shot method (14)

Uniform samples were made, cured, and tested for compression. Sample preparation used in this research found its basis in this article. The conclusions were that for greatest strength one should have 1) a long gel time, 2) low moisture content, 3) slow drying rate, 4) well-gradated soil, and 5) freedom from wet and dry cycles (14).

Because calcium acrylate best fits these criteria, it may be useful to examine the system used by M.I.T.



Strength Development of Various Normal Cured Chemically Solidified Specimens

Figure 1.1 - Results of Warner's testing (14)

1.3 Characteristics of Calcium Acrylate

When calcium acrylate was discovered it was extensively characterized by Thomas William Lambe of M.I.T., one of the three patent holders. The other two are Victor F. B. de Mello and Ernst A. Hauser, patent number 2,651,6199, September 8, 1953 (2). The system that was employed in the

current research is sufficiently similar that an intact discussion of the results will be given and minor differences will be mentioned later in the discussion section.

Calcium acrylate is formed by the reaction of acrylic acid with either calcium carbonate or calcium hydroxide. The resulting monomer is a relatively non-toxic, white free-flowing powder (6). It is soluble in water to 44 parts/100 parts water at 75°F. Other solvents are glycerol, glycols, formamide, and diethanolamine. Aliphatics and aromatics are non-solvents. For a 30% aqueous solution the freezing point is 10°F, with a density of 1.130 gm/cm^3 at 75°F. The viscosity for the solution is about 6cp from a Brookfield viscometer (5).

The monomer forms a neutral solution (pH 6.5) and has a dispersing effect on clays and soils. Calcium acrylate exhibits analogous behavior to calcium acetate and calcium propionate. The major difference is that the acrylate has functional sites for polymerization (5).

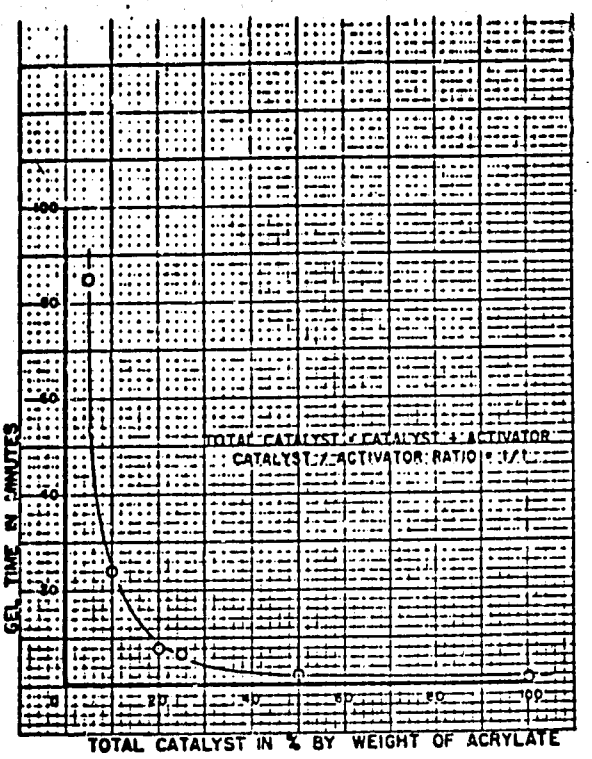
A crosslinked polymer from calcium acrylate can be formed in aqueous solution. Water is necessary for polymerization though the monomer need not be in solution. The monomer ionizes in water (6) and the double bonded carbons react and link together with a free radical catalyst. Chain crosslinking is ionic (5).

monomer	$CH_2=CH-COO-Ca-OOC-CH-CH_2$
cation	$+Ca-OOC-CH=CH_2$
anion	$-O-OC-CH=CH_2$ (6)

The most common catalyst is ammonium persulfate. An activator, sodium thiosulfate, speeds up the reaction by forming a redox system. It is suggested that these two chemicals be added to the monomer solution separately since together they may form an explosive mixture. The best ratio of persulfate:thiosulfate is 1:1 by weight (5).

The gel in solution forms in two stages. The first is a clouding of the solution followed by the forming of a milky, rubbery gel. Gel time is about 1.5 times longer than the turbidity time (5). Polymerization is an exothermic reaction with a 230°F exotherm being the highest attained. Upper gel temperature is about 110°F. Minimum monomer concentrations for a gel are about 5% and air is an inhibitor, regardless of the acrylate concentration (5).

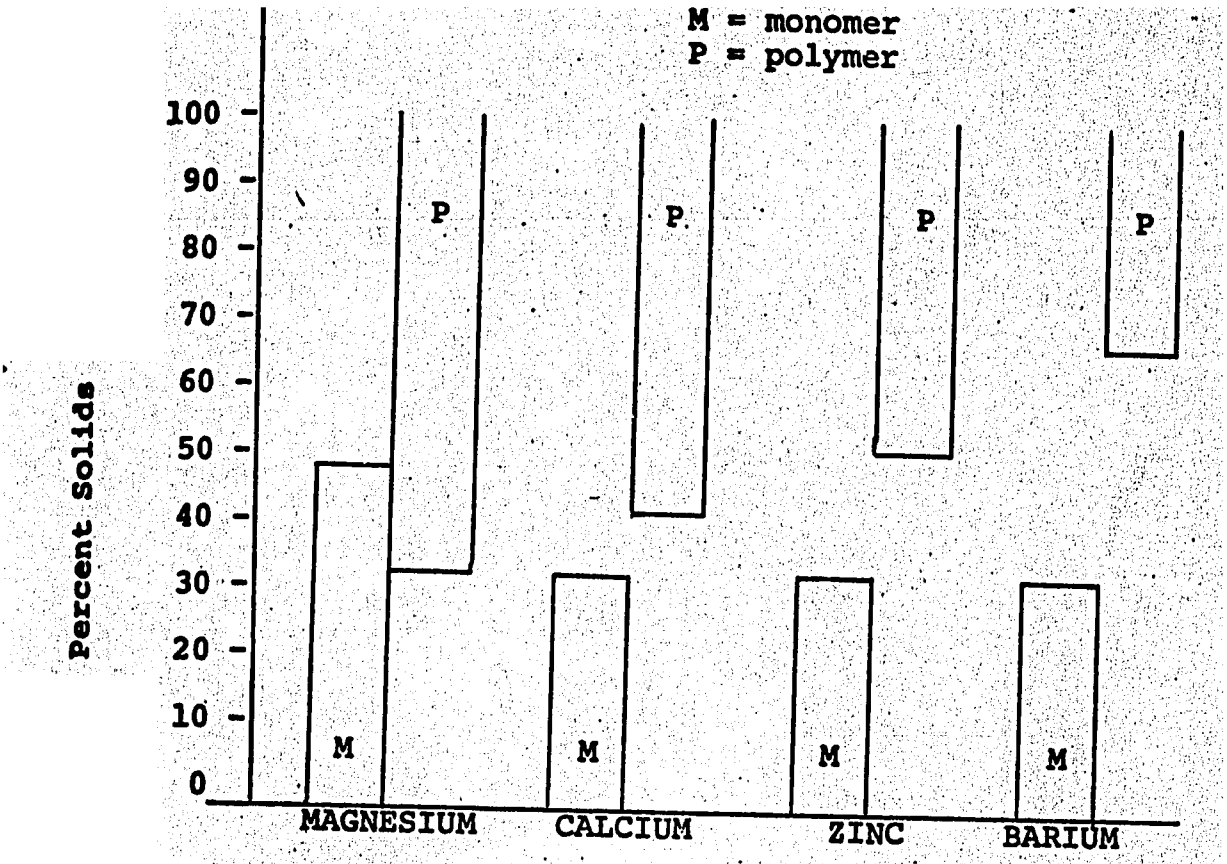
Reaction time is determined by two factors. The first is activator concentration (6). Second is the presence of certain metal ions, the most notable being copper followed by iron. Lead and aluminum have a lesser effect. These ions greatly accelerate reaction rate so that small amounts of these will give the same gel times with only 1/10 to 1/100 of the original activator. Rate of reaction also increases with temperature (5).



Effect of Catalyst Concentration
on Gel Time

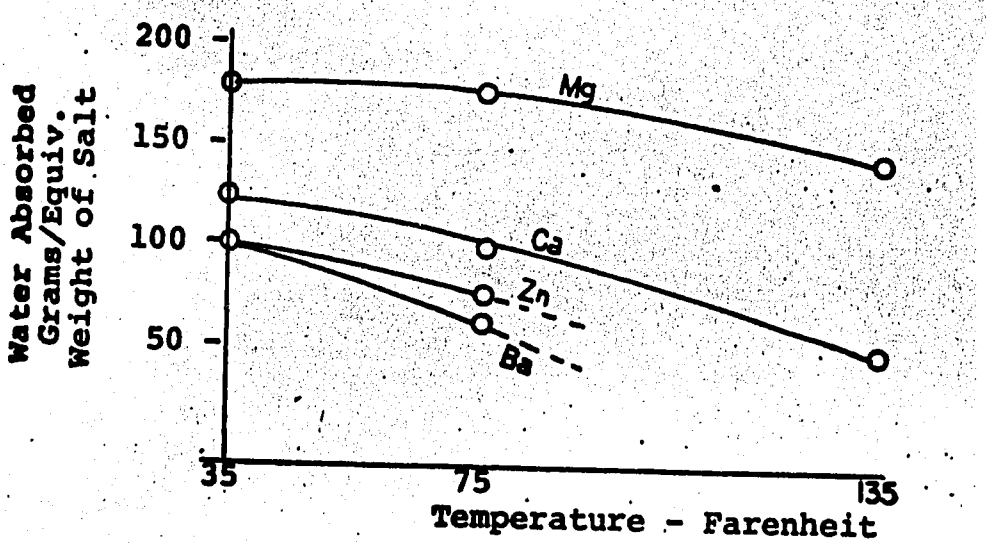
Figure 1.2 - Gel Time (6)

Poly-calcium acrylate is a true hydroplastic. The gel is water insoluble yet water is soluble in it. There is a maximum amount of water that can be dissolved in the polymer. Excess water in gelation will be sweated out (5). Water absorption by immersion can be dramatic but that by humidity is less, since calcium is hydrophobic (5). Increased temperature decreases water solubility. Too high a temperature will irreversibly degrade the polymer, but this occurs past the boiling point of water. Alcohol will



Monomer-water and polymer-water relationships for four acrylate salts
(After Hopkins)

Figure 1.3 - Monomer or Polymer Water Content (5)



Water Absorption Isotherms for Four Acrylate Salts

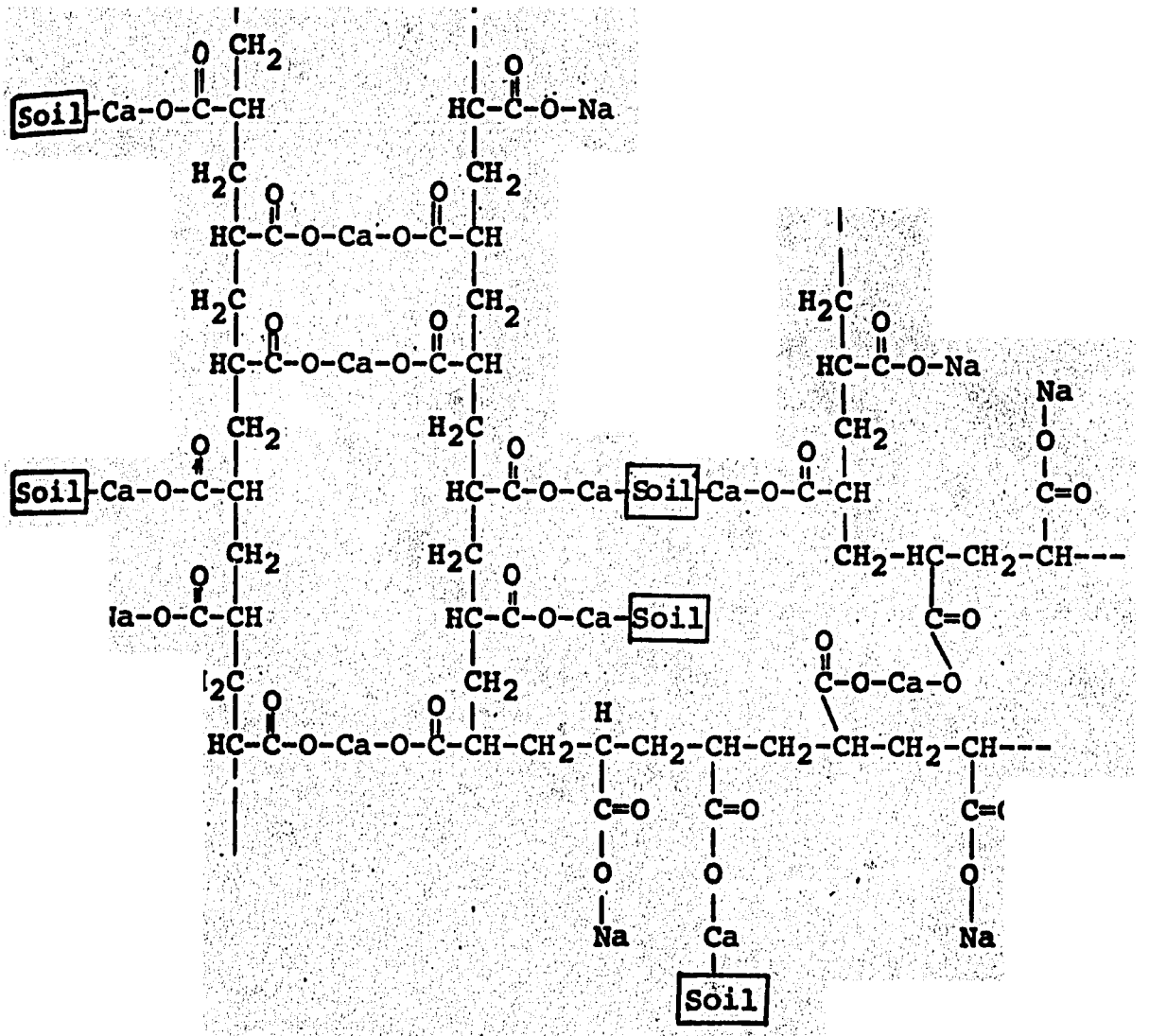
Figure 1.4 - Water Absorption (5)
(After Hopkins)

dehydrate the gel while organic solvents will have no effect upon it. The gel while wet will pick up heavy metal ions (5). Water is a true plasticizer of the polymer, and this greatly affects the strength of the gel. When dry, the polymer is hard and rigid, but upon plasticizing with water, it becomes a soft rubbery solid (5).

When stabilizing soil, water plays other roles besides that of a solvent for chemicals, and a medium for ionization and polymer propagation. It also determines the mixing effectiveness of the soil and monomer, compaction of the soil and shrinkage upon drying. These effects are due mostly to the added water with clays showing the greatest change (6).

In the soil an ion exchange takes place. The sodium present in the soil is exchanged for the calcium in the acrylate cation. This bonds the cation to the soil particle while the sodium ion that is released is attached to the acrylate anion. In polymerization the soil-bonded cations and sodium acrylates chain together to form a copolymer with the excess poly-calcium actylate present to act as an ionic crosslinker. Most of the strength comes from the polymer crosslinking, for the soil is held in a polymer net (6).

For soil stabilization it was advocated that less than 4% monomer by dry weight was ineffective, while greater than 10% was thought to be too costly (6).



Calcium Acrylate - Clay Polymer
(After Lambe)

Figure 1.5 - Soil-Polymer Binding (6)

The preceding summary of the background of the chemical system involved in the research will facilitate the understanding of the nature of the project. To complete the preliminary discussion the experimental procedures will be outlined.

2. EXPERIMENTAL

In performing the experiments, equipment and procedure were kept as simple as possible. This was done since the results would have to be duplicated in less than ideal conditions common to the field operations.

The chemical system consisted of the monomer, the two-part redox initiator system and at times ferrous sulfate which was used to accelerate the reaction. Throughout the experiment distilled water was used. This was done to lengthen the shelf life of the monomer solutions and to remove any items that might alter the reaction. Tap water was used for some of the later samples and no ill effects were noticed. All experiments were done at ambient temperature which was about 24°C.

Due to the small amounts used for some of the chemicals, it was decided that for greatest accuracy a water solution could be pipetted with the resulting minimum error of ± 0.05 ml. This in many cases gave an accuracy in weight of ± 0.005 gm. However, such accuracy was at times not reached and the error in chemical dose for the system could be as high as 2%.

Early experiments involved testing for the gelation of the polymer system. The procedure involved adding to a beaker the required amounts of water, monomer solution,

persulfate solution, and thiosulfate solution, respectively. The order as described was rigidly adhered to throughout the duration of the research. After it was briefly stirred the ferrous ion solution would be added, if needed.

Two systems were used to make the compression test samples. The first consisted of a one-inch-diameter cardboard tube, corked at one end. The premixed chemical system, as described above, was poured into the tube. Quickly it was followed by the predetermined amount of soil. Mixing speed is of the essence since one is allowed from 30 seconds to two minutes before the sample starts to set up. Stirring prevents air pockets from being formed in the saturated sand. The one-inch tubes were considered to be inadequate. The cardboard would soak up the solution, which would reduce the chemical concentration in the sand, giving a concentration gradient in the sample. The cardboard was removed before testing. Also, a larger block was desired for testing the calcium acrylate. Thus a different set-up was used.

The two-piece molds were made of cast brass with the mold faces machined smooth. They were open at the top and bottom and produced the standard 2x2x2-inch block for mortar testing. Since the chemical system was added first, all potential leaks had to be caulked. Plasticine filled the role admirably. Modeling clay was added to the clamped brass

mold so as to form a ridge on one surface. The mold was set, plasticine face down, to the system. Any clay that extruded into the sample cavities was trimmed away. The mold is water tight as long as it is not handled roughly. Occasionally, tetrafluoreothylene telomer lubricant was sprayed on the interior of the mold to facilitate an easy release of the soil samples. After the soil samples were stripped the whole process had to be repeated if another batch was desired.

The soil to be used was weighed out on a pan balance to ±0.5 gm, ±0.25%. Next the chemical components were mixed in a glass container in the order as described. Their amounts reflected the weight of the soil to be stabilized, and the water was dependent upon the void fraction of the soil. As soon as the chemical solution was complete it was dumped into the mold. Chemical mixing was not done in the mold because copper is a catalyst. The soil was then added to the mold, stirring as it was poured. For samples with greater than 80% sand, the correct amount of soil versus liquid could be determined when all the soil was set, and there was a thin film of water on the top, ensuring an even distribution of monomer. Soils consisting of clay or silt were a problem. The fine particles absorbed the water and it was determined that the best dispersion of the monomer could be achieved if enough liquid was added to give the soil a toothpaste consistency.

Most of the samples would react in one to two minutes after the sand was added. Complete gelation would be in about five minutes, but the sample would not be stripped from the mold for another ten to fifteen minutes. A few samples took longer to react, and some did not react at all. The change caused by polymerization is quite remarkable, and though the sample feels solid it is still fragile. Care must be taken in releasing it from the mold lest it be torn. The spray lubricant would prevent sticking, but sometimes a thin-bladed spatula was needed to release the samples from the mold walls. Soil containing less than 2% polymer is very weak when wet and caution must be taken that the sample is not fractured in handling. These cracks are irreparable and become a permanent source of weakness.

The fresh samples were then air dried, since maximum strength is a function of dryness. To ensure even dryness they were turned either twice daily for half a week, or the bottom was elevated to allow air circulation. After they were dry they were given to Civil Engineering to be tested for compression failure.

Stabilized soil samples were originally tested for compression on the Instron test machine. The results were graphically recorded. Since it had a maximum capacity of 8,000 pounds, its services were discontinued. The Tinius-Olsen test machine was then employed. This machine

did not produce a graph, but it had a capacity up to 150,000 pounds.

The samples were not capped and aluminum plates were placed between the machine's faces and the sample to prevent scarring the machine. For both machines the crosshead speed was 0.05 in/min., and force was applied until sample failure. The amount of force that was needed to cause failure was noted and this number was then divided by the sample's cross-sectional area perpendicular to the force. This gave the ultimate compressive strength for the sample in lb/in^2. It is this number that becomes the basis for discussion.

3. EARLY RESEARCH

Acrylamide

The earliest experimental work done was with an AM-9-type system in order to gain familiarity with a free-radical-initiated system. The AM-9-type system used consisted of ten parts by weight of acrylamide and one part by weight of methylenebisacrylamide. The initiator was ammonium persulfate and sodium bisulfite, while ferrous sulfate was used as a catalyst. Simple beaker tests for gelation produced a translucent rubbery gel from a 10% solution of monomers and 1% of the combined initiators in equal masses and a trace of ferrous ion. Gel time decreased with increased initiator concentration. Gels like the above which had initiator concentrations at about 10% of the monomer weight gave a 20-second gel time. Those with 2% initiator gave identical gels but with a time of about three minutes. If the initiator was reduced by a factor of ten, gel time was 20 minutes and the gel only reacted along the container walls. In all there was about 70% unreacted liquid left, which still contained monomer. If the other extreme is approached where the initiator was 30% of the solids then gelation was almost instantaneous and the result was a viscous liquid. In all cases except the last, the rigid crosslinked gel would only deform slightly under pressure before fracturing. Upon drying the gel would shrink to less than a fifth of its former volume and it would be hard and very strong. Its

flexibility would return after it had been soaked in water for several hours.

Soil samples were stabilized with this sytem. Here, knowledge was gained in sample preparation along with basic guidelines for producing a superior stabilized block. All the tests used the one-inch-diameter cardboard tubes. The average strength for samples containing 2.2% polymer by dry weight was 955.5 psi. These were made with plain white sand.

Table 3.1

Mixture for AM-9-Type Sand Samples

Components in grams	Sample Number C	Sample Number F
Monomer (10:1,AM:MBA)	1.0	1.0
Ammonium persulfate	0.1	0.05
Sodium bisulfite	0.1	0.05
Ferrous sulfate	trace	trace
Water	11.0	10.0
White sand	45.0	45.0
Compressive strength (psi)	790	1121
Drying time (days)	4	4

In making these samples it was learned that the addition of the sand slowed down the reaction by about a minute. This can be attributed to the large amount of air that gets stirred in when the sand is added, for oxygen is an inhibitor. Even though reduced initiator increased the strength a practical limit was reached. Samples that contained less initiator than F would contain pockets of unreacted material. The increased strength was probably due to increased chain length.

Thus it was concluded that a gel time of about two to three minutes as exhibited in sample F was the best and that about 2.5% polymer concentration in the soil would be adequate. Since acrylamide is extremely toxic it cannot be used for housing, even though the gel is safe. Consequently, a search was made for a suitable replacement with hopefully similar characteristics. The list of water-solubl monomers is short and after some thought the salts of acryli acid were considered the most promising.

Metal Acrylates

For study the acrylates were chosen. Two of these, sodium acrylate and calcium acrylate, were ordered from a commercial supplier, but these proved to be grossly impure and they would not polymerize under any known condition. Therefore, throughout the course of experimentation, all the salts of acrylic acid that were used were synthesized in the laboratory. Admittedly these were not the purest and the quality varied, but they were far more reliable than those supplied by the chemical supply house.

Preparation of the salts was easy. Stoichometric amounts of the metal hydroxide and acrylic acid, or methacrylic acid were weighed out. Enough water was added to make a 30-50% solution of the monomer and the hydroxide was dissolved in it. To this the acid was slowly added, stirring all the while. The reaction was almost instantaneous and it was exothermic, requiring occasional cooling.

Maximum temperature allowed was 40-45°C, since the monomer

$$MOH + H_2C{=}CH{-}COOH \qquad H_2C{=}CH{-}COO^-M^+ + H_2O$$

may polymerize if it gets too hot. Because this gave a monomer already in solution, it was used directly. Preparation of the salts of methacrylic acid was similar.

Methacrylates

Two salts of methacrylic acid were made. Potassium methacrylate, though it formed nice crystals, refused to polymerize under any condition that was employed. This was not true with its sister salt, sodium methacrylate. For a solution containing 20 gms of the salts and 0.5 gm each of potassium persulfate and sodium thiosulfate, and 20 gm water, reaction occurred in a few hours. This was noted by the thickening of the solution. The same result could be obtained if it was heated to 60-70°C for a half an hour. Being less than satisfactory as a monomer due to their slowness to react, the investigation into the salts of methacrylic acid was discontinued.

Acrylates

The metal acrylates can be distinguished by two main categories. The first is the monovalent group. The other is divalent, meaning that they can form ionic crosslinks. Each has only one carbon-carbon double bond in the carbon

chain that can undergo polymerization. The monovalent acrylates were first investigated.

Three salts were made in this category. They were the potassium, ammonium and sodium salts. To form a gel a copolymer with methylenebisacrylamide was used.

Potassium Acrylate

The potassium salt of acrylic acid was formed by the neutralization of the acid with an aqueous solution of potassium hydroxide. The reaction, like that of all the metal acrylates, was exothermic. If sufficiently strong solutions were used a temperature rise of 65°C could be obtained. Potassium acrylate monomer was extremely water soluble and the white crystals were hygroscopic.

Polymerization would occur at room temperature in solutions of 50% or greater if two to three days elapsed. This formed a gooey crumb. It would also polymerize with heat, and dilute solutions would polymerize with a free-radical initiator, either the persulfate-thiosulfate system, or the persulfate-bisulfite system. Heat would be evolved in polymerization, which at times would be dramatic (Figure 3.1, page 23). The resulting polymer would be a viscous solution, which was hydrophilic. Even after three months the polymer crumb that formed from a concentrated solution was still rubbery.

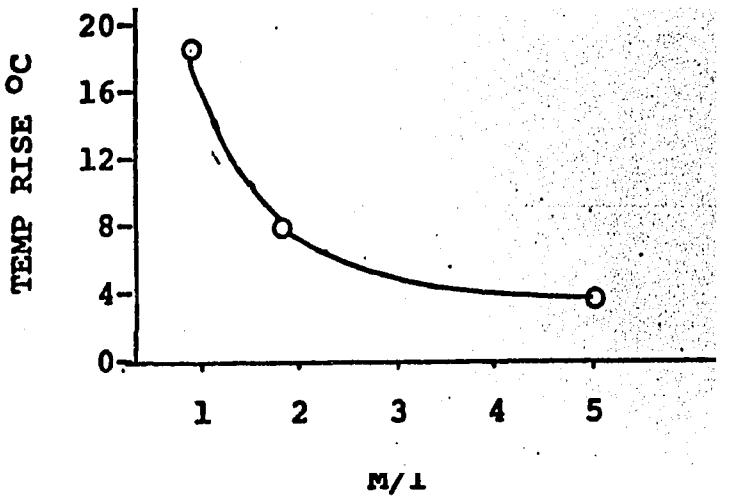


Figure 3.1 Heat rise in polymerization based on initiator concentration. M = weight of potassium acrylate monomer. I = combined weight of persulfate and bisulfite.
Water : Monomer = 5:1

A crosslinked gel (Table 3.2) was made from the monomer with the addition of methylenebisacrylamide. The gel was of a good quality, having shape, yet being flexible. Gel time was rather long for the system. A similar

Table 3.2

Chemical Composition of Crosslinked Gel of Potassium Acrylate

Potassium acrylate	2.0 grams
Methylenebisacrylamide	0.2
Ammonium persulfate	0.2
Sodium thiosulfate	0.2
Water	11.0
Ferrous sulfate	trace
Gel time	20 minutes

composition was used to try to stabilize brown sand, but reaction never occurred. Because of the polymer's

hydrophilic nature, poor reaction in sand, and need for a crosslinker, investigation was discontinued.

Ammonium Acrylate

Of all the monomers tested, ammonium acrylate was the only non-metallic salt. Monomer formation was by neutralizing acrylic acid with ammonia water. The monomer was very water soluble, and when monomer isolation was attempted, ammonia gas evolved, leaving behind acrylic acid.

Polymerization could be initiated with a free-radical system. A solution of water, monomer, $(NH_4)_2S_2O_8$, $NaHSO_3$, and Fe^{++} in the amounts of 25:6:1.5:1.5:trace had a reaction temperature rise of 24°C.

A crosslinked gel was formed, using methylenebis-acrylamide. For a similar solution, the gel formed from ammonium acrylate in about a third of the time as one did from potassium acrylate. Both gels were of equal quality. Ammonium acrylate was the only monofunctional salt that could form a stabilized soil.

Table 3.3

Composition of Sand Stabilized with Ammonium Acrylate

Ammonium acrylate	1.6 grams
Methylenebisacrylamide	0.16
Potassium persulfate	0.35
Sodium meta bisulfite	0.35
Water	21.0
Ferrous sulfate	trace
Brown sand	60
Gel time	10 minutes
Drying time (1" dia)	9 days
Compression strength	66 psi

The strength of the stabilized soil was deemed grossly inadequate and when compounded with the problems of separating a solid monomer all inquiry into ammonium acrylate ceased.

Sodium Acrylate

Results obtained from the previous acrylates were discouraging. Sodium acrylate was made by reacting the hydroxide with acrylic acid, but the monomer's solubility was limited to about 80gm/100gm water. The monomer could be easily isolated by evaporation and it gave a hard, white powder. Unfortunately polymerization was slow. For a solution containing water, monomer, persulfate, thiosulfate, and Fe^{++} in the ratio of 45:4:1:1 by weight, reaction time for polymerization was several hours, with a viscous liquid resulting. With this ended all experimentation with the monovalent salts.

Divalent Acrylates

From the monovalent acrylates it was learned that either the persulfate-bisulfite or the persulfate-thiosulfate initiator mix could be used. Since the thiosulfate was far more stable in solution than the bisulfite it was decided to use only the thiosulfate for the divalent monomers.

Three divale

calcium and magnesium. The magnesium acrylate was mad

from magnesium carbonate and acrylic acid. Gels were easily formed from this monomer using the above initiator system. However, the monomer solution was slow in evaporating and it finally took two months to air dry. Due to the difficulty in obtaining the solid and the probable higher cost than the calcium acrylate very little research was pursued.

Barium Acrylate

Barium acrylate was much like magnesium acrylate. The monomer, produced from barium hydroxide and acrylic acid, readily formed a water-insoluble polymer gel, via free-radical initiation. This gel is characteristic of all the divalent acrylates tested. The gel was opaque white and it was very soft, even when a third of it was polymer When pressure was applied, water could be squeezed out, and when soft, it can be torn. The tear is non-mending. Upon drying, the polymer is clear and colorless if free from impurities. It also becomes very strong and rigid like Plexiglas. Water does replasticize the polymer, but the rate is far slower than polymer made from acrylamide.

A one-inch diameter soil sample was made from barium acrylate. Composition is given in Table 3.4.

The system had a spotty gel and yielded a very poor sample. This was repeated with the same results and due to the poor reaction for sand, stabilization experiments with the barium system were terminated.

Table 3.4

Composition of Barium Acrylate Mixture for Stabilizing Sand

Barium acrylate	2.4 gm
Potassium persulfate	0.35 gm
Sodium thiosulfate	0.35 gm
Fe^{++}	trace
Water	17.0 gm
Brown sand	60 gm

4. CALCIUM ACRYLATE

1.1 Reasons for Choice

When calcium acrylate was chosen all research into other monomers ceased. Lead acrylate, zinc acrylate and aluminum acrylate were never investigated. Calcium acrylate seemed to be the best overall choice. The raw materials for manufacture are inexpensive and the monomer performed the best. It readily formed a gel and there was no problem in solidifying soil. Furthermore, its strength in sand exceeded the goal of 500 psi compressive strength by using 3% or less monomer by dry weight.

1.2 Monomer Manufacture

The manufacture of calcium acrylate can be carried out by two processes. The first is reacting acrylic acid with calcium carbonate and the second is by reacting the acid wtih calcium hydroxide.

$$2(CH_3{=}CHCOOH) + CaCO_3 \qquad Ca(CH_3{=}CHCOO)_2 + CO_2 + H_2O$$

$$2(CH_3{=}CHCOOH) + Ca(OH)_2 \qquad Ca(CH_3{=}CHCOO)_2 + 2H_2O$$

The first method evolves a gas which causes foaming. This was the method first used to obtain the monomer in the early part of the experiments. To produce the monomer, water and powdered calcium carbonate in excess were mixed

together to form a slurry. The proportions depend upon the monomer concentration desired, the upper limit being about 50 gm/100 gm water. Should an excess of monomer form, it will yield a paste of fine crystals which can be dissolved in water. Acrylic acid was slowly added to the carbonate slurry. The solution immediately starts to foam and ample space must be allowed for the foam. The rate of reaction was slow, so about an hour was allowed after the acid was added for the reaction to go to completion. When done, the excess carbonate was filtered off, leaving a clear, colorless solution that contained the monomer. If the highest quality of calcium carbonate was used there was no trace of color in the solution and the monomer was very reactive. This was used for the first half of the experiment until larger quantities of monomer were demanded.

The other method for producing the monomer is from the hydroxide. Here the reaction is almost instantaneous and a great deal of heat can be evolved, such that a 30% solution can be raised to 55°C. To keep it cool ice was used instead of water, and this was sufficient to keep the reaction below 30°C. To make the monomer, calcium hydroxide was added to water or ice and acrylic acid was stirred in until a neutral solution was obtained. Fischer's Laboratory Grade calcium hydroxide gave a clear monomer solution with a decided orange tint to it.

The reactivity of various hydroxide solutions would vary. Maximum reactivity would occur with a neutral or a slightly acidic solution. To insure this, a slight excess of acrylic acid was used in the manufacture of the monomer. This problem was never encountered with the monomer made from the carbonate since the carbonate was insoluble, and the carbon dioxide always gave an acidic solution. Poor reactivity of the monomer was noticed most in the sand. This would be manifest in the sample's strength which would be far lower than expected. Therefore, each test set was run with the same batch of monomer, but with careful monomer preparation the results from different solutions would be near constant.

In order to determine the solution concentration, a known quantity was pipetted and evaporated, leaving the monomer which is a dihydrate, $Ca(CH_3{=}CHCOO)_2 \cdot 2H_2O$. This is the form in which it is commercially sold (1). Obtaining the pure monomer was easy for either the solution could be air dried, or a concentrated crystal paste could be made by forming monomer in excess of the solubility limit. The latter method is most applicable to monomer formed from the hydroxide. Dry calcium acrylate monomer was a hard white solid. Crystals were opaque white and were in the form of

Gel Tests

Early experimentation with calcium acrylate involved simple gel tests. These were done to learn more about the system. Originally ammonium persulfate was used as the persulfate initiator since it readily went into solution. Later this was discarded in favor of potassium persulfate. The reasoning behind this will be dealt with later.

It was initially discovered that Fe^{++} concentration drastically affected reaction rate. Without it, gel time could be several hours, and with it, gelling could occur in a few seconds. Therefore, the ferrous sulfate amount was carefully regulated.

The first item of interest was how much initiator was needed to produce a gel in a reasonable amount of time. Tests 1-3 (Table 4.1, page 32) show that reaction for varying amounts of initiators produce gels equally fast. It should be noted that all gels filled the container and that number three was the most rigid.

To determine how grossly Fe^{++} altered the reaction rate, tests 4-7 were conducted. It showed that gel time was more dependent on the Fe^{++} concentration than the initiator concentration. The significance of this is that iron is a common compound in soils with the amount varying locally. Thus the initiator concentration has to be tailored to the specific soil used for the best results,

Test	Chemical - Grams: Calcium Acrylate	Ammonium Persulfate	Sodium Thio-sulfate	Ferrous Sulfate	Water	Gel Time: 5-10 sec.	1 min.	10 min.	1 hr.	1.5 hr.	6 hr.
1	1	0.15	0.15	0.005	11.5	cloudy	gel	complete			
2	1	0.1	0.01	0.005	11.5	cloudy	gel	complete			
3	1	0.05	0.05	0.005	11.5	cloudy	gel	complete			
4	.67	0.05	0.05	0.01	10	cloudy	gel	complete			
5	.67	0.05	0.05	0.001	10	---	---	cloudy	gel	complete	
6	.67	0.05	0.05	0.0001	10	---	---	---	---	cloudy	gel
7	.67	0.05	0.05	0.000	10	---	---	---	---	---	gel
8	.67	0.1	0.05	0.002	10.3	cloudy	cloudy	cloudy			
9	.67	0.05	0.05	0.002	10.3	cloudy	gel	complete			
10	.67	0.01	0.05	0.002	10.3	---	cloudy	gel			
11	0.67	0.0	0.005	0.004	6.5	---	---	---			
12	0.67	0.005	0.005	0.004	6.5	cloudy	goo	goo			
13	0.67	0.005	0.0	0.004	6.5	cloudy	---	goo			

Table 4.1

Various Gel Times
With Calcium Acrylate

but the general formulas used in this research have enough lattitude that they can be applied to most conditions. The exception is any soil system that is absolutely devoid of iron. Pure white sand is such an example.

Tests 8-10 and 11-13 were done to determine how the ratio of the two initiator components altered the results. Bes results occurred where they were equal in weight. Excess persu fate gave a poorer gel than excess thiosulfate. A total lack o persulfate causes no reaction, though a lack of thiosulfate doe not prevent reaction. Equal masses of the two are consequently the best since the proportions are simple and the results are excellent.

One of the ideas for the chemical system was that it could be all premixed and packaged dry, later being added to a given amount of water. This was done and it was discovered that ammonium persulfate prevented calcium acrylate from going into solution. Powdered monomer would not go into solution if it was placed in a beaker containing a 10% aqueous solution of the persulfate. If the monomer solution was mixed with persul- fate solution no precipitate was formed. The monomer dissolved in the 10% thiosulfate solution as readily as it dissolved in distilled water. Then it was thought that the initiator could be packaged separately, but upon mixing ammonium persulfate and sodium thiosulfate together in water sulfur was instantly precipitated out. The reaction was undesirable and it reduced the effectiveness of the initiator.

There are only two other persulfates readily available, lead persulfate and potassium persulfate. The latter was chosen as a replacement for the ammonium persulfate since it appeared to be the less toxic. The main disadvantage of this chemical is its poor solubility. A saturated solution occurs at about 5% at room temperature. However, this was justifiable since the potassium persulfate did not inhibit the calcium acrylate dissolution, and it did not form the sulfur precipitate when mixed with the thiosulfate. A few quick tests indicated that the monomer reacted as well with the potassium persulfate as with the ammonium persulfate. Thereafter, a potassium persulfate-sodium persulfate initiator system was used exclusively in a 1:1 ratio by weight.

Soil Stabilization

Soils are composed of three types of inorganic particles: sand, silt and clay. Organic soils were not considered. The sand used ranged from pea stone to a number 200 sieve, and a sieve analysis can be found in the Appendix. The color was a tan due to the iron, and it has been previously referred to as brown sand. Sand, when wet, has some cohesive strength due to the presence of water. When dry, it has no cohesive strength. Fine particles, the silts and the clays, increase the cohesive strength. Thus sand, by itself, is unsuited for building, and it was

desired to spend much of the time improving the cohesive properties of the material.

For making the 2x2x2-inch cubes of stabilized soil, 50 ml of liquid was needed for 225 gm (150 ml) of sand. The sand had enough iron in it so that ferrous sulfate was not needed. When the calcium acrylate made from the pure bicarbonate was used, the ratio was 16:1:1 of monomer, persulfate and thiosulfate respectively. This ratio was used throughout for all monomers. Normally, the system would start to gel two minutes after mixing had started, and polymerization would be complete after about ten minutes. Gel formation would occur first at the sides and bottom of the mold, due to the lesser amount of oxygen and the presence o copper. The last part to solidify would be the top center. Testing for gelation was simply done by noting how much resistance it took to insert a matchstick into the wet sand Before reaction, any amount of pressure would plunge the stick into the soupy sand, but after gelation, considerable resistance was met. To bury the stick in the sand would be foolish for a slight indentation on the surface constitutes a sufficient test. Polymerization was exothermic, but the effect could only be noticed for large monomer concentrations or large stabilized structures.

Fresh samples have all the voids filled with the polymer gel. After the stabilized soil has dried, the polymer shrinks, due to water loss, and the pores are

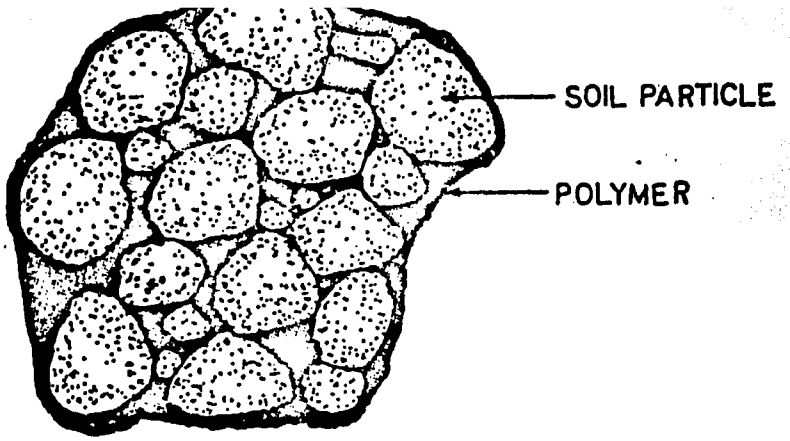
opened up again (Figure 4.1, page 37). The soil particles are surrounded by a polymer film. It is the thickness and the coverage of the film that determines the strength.

The strength of the polymer when dry was outstanding. It compares favorably with other plastics (Figure 4.2, page 38), but the strength is a function of moisture content.

When dry, the stabilized soil exhibits sudden failure (Figure 4.3, page 38). A wet sample not only being weaker gives a gradual failure.

Calcium Acrylate Concentration

The most costly component in stabilized soil construction is the monomer, which could probably comprise 80-90% of the chemical costs. Therefore, it is imperative to determine the amount of monomer necessary. Increased monomer does increase compressive strength, and after a sufficient drying time the effect is linear. This was also the case for relatively fresh samples still holding a large amount of water (Figure 4.4, page 39). For specimens in between a few hours and a few weeks the drying is erratic and thus strength is erratic.



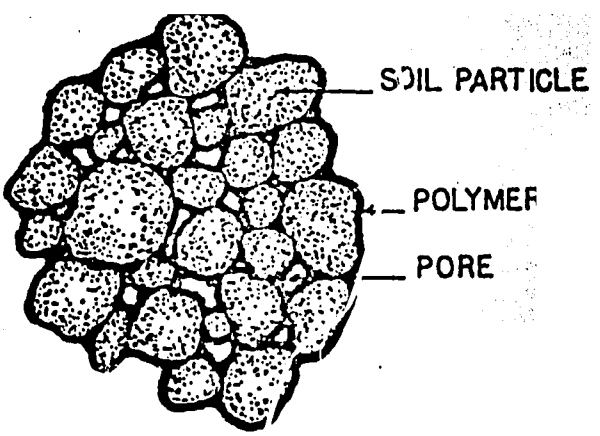


Figure 4.1. Magnified illustrations of stabilized soil.

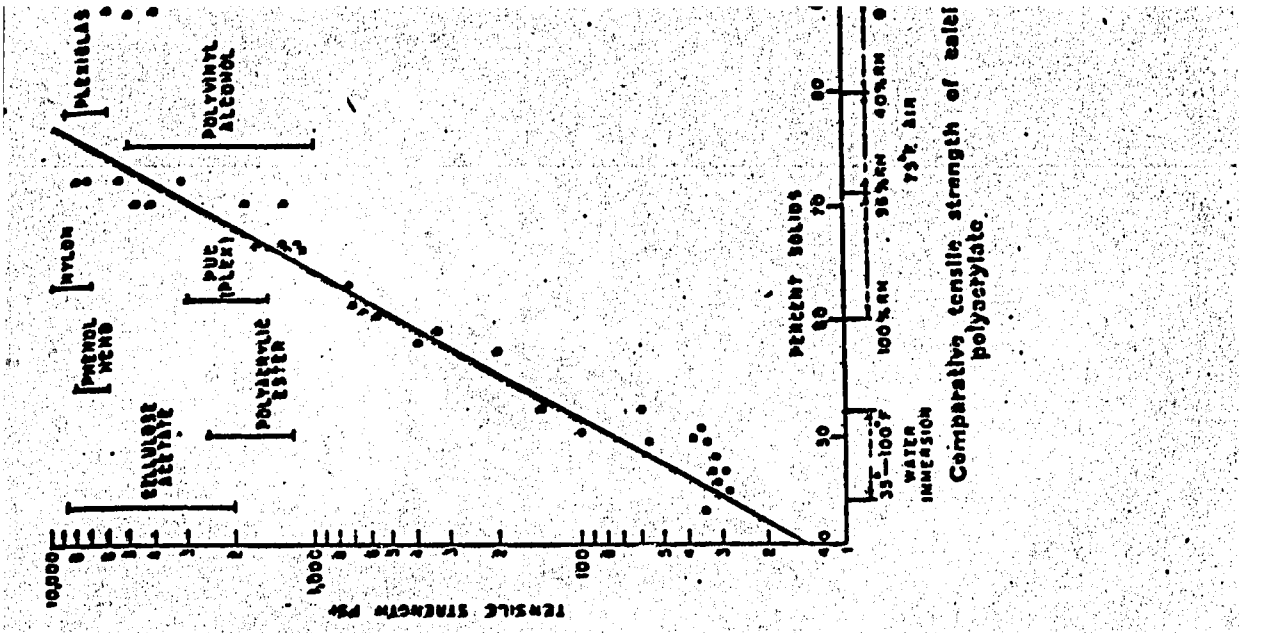


Figure 4.2. Strength of calcium acrylate polymer compared to other common polymers (5)

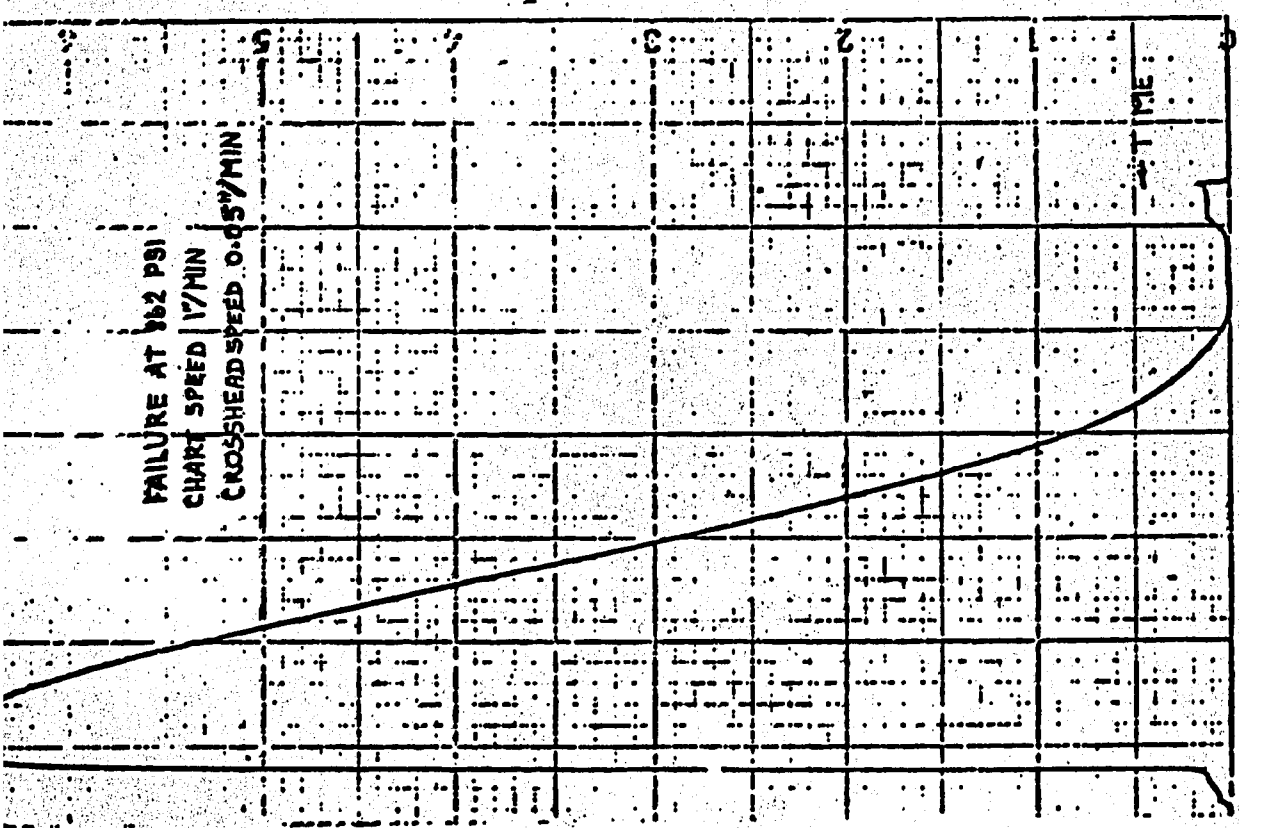


Figure 4.3. Failure of a 1" diameter sand sample stabilized with 2% calcium acrylate

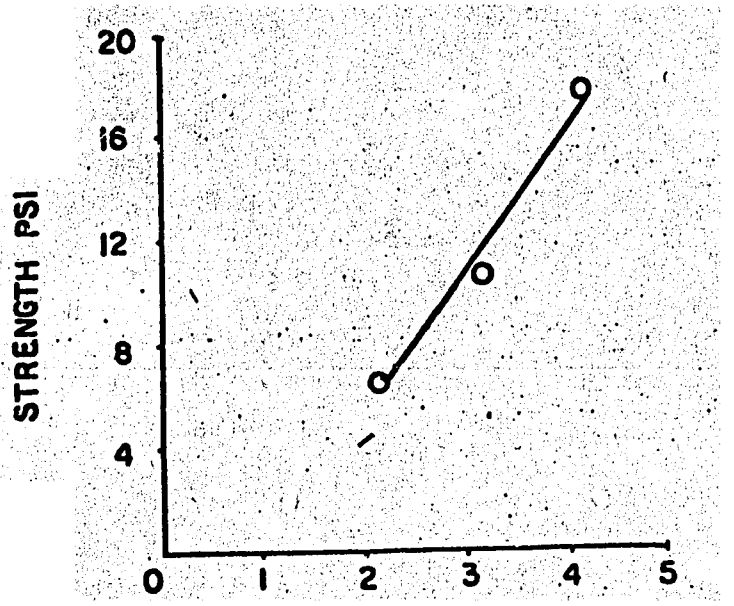


Figure 4.4. Compressive strengths of various concentrations of monomer in sand after 14 hours drying

Within a 1-6% monomer concentration range, based on dry weight, suitable guidelines can be established (Figure 4.5, page 40). Concentrations below 2% tend to be very fragile when wet, though they are quite strong when cured. A two-inch-thick block of sand was considered cured after a fortnight. Blocks in these low concentrations of 1-2% were plagued by other problems. The most notable of these was poor reaction. Low monomer concentrations gave slow gel times - on the order of 20 minutes often accompanied by incomplete reactions. Usually the surface exposed to air was the poorest. When dry these samples were prone to material loss by abrasion.

The other extreme was high acrylate concentrations from 4.5-6%. These are very stable when wet or dry and have great strength upon curing. The surfaces are quite

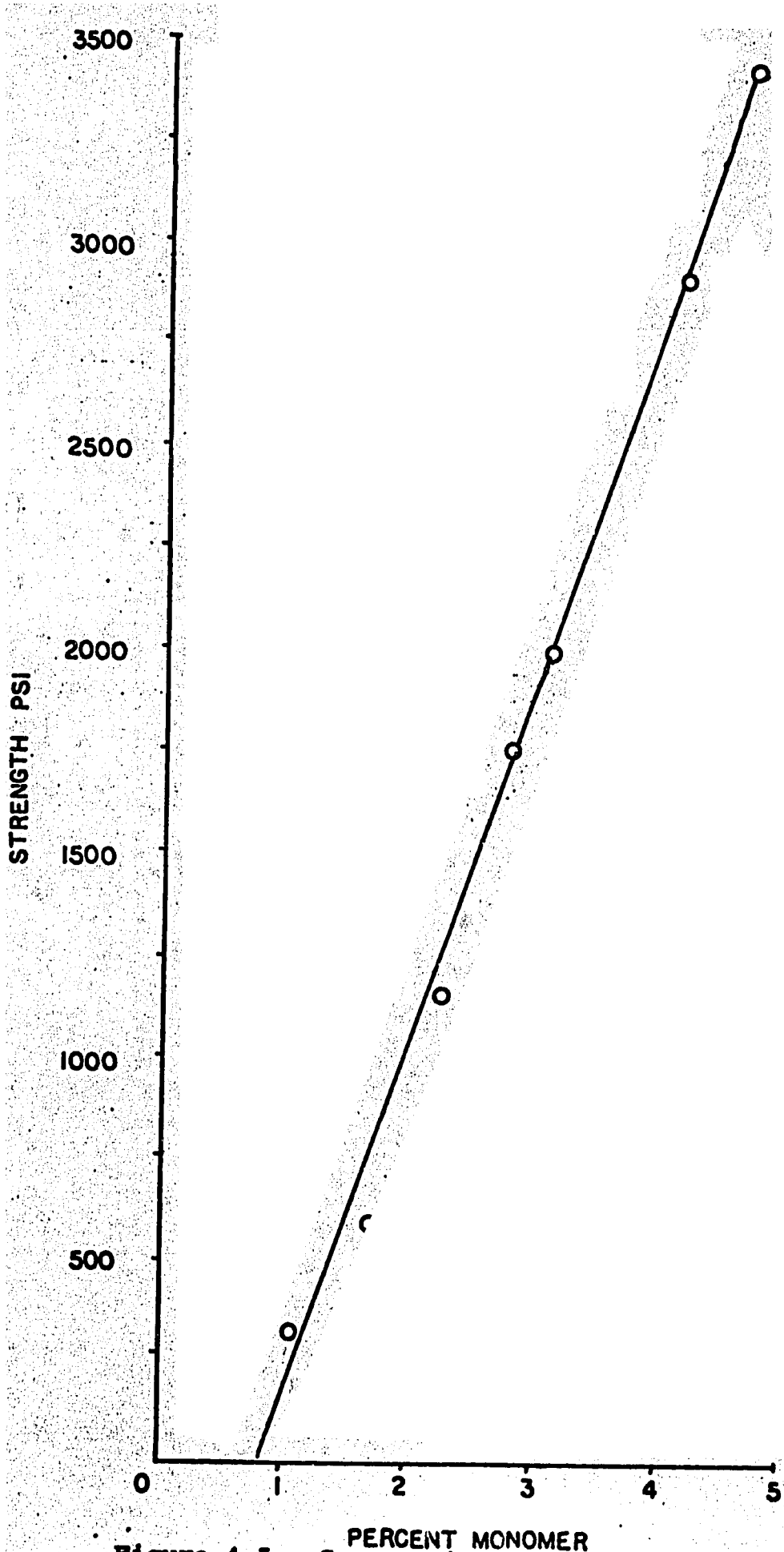


Figure 4.5. Compressive Strengths for sand stabilized with varying amounts of calcium scrylate. Drying time was 13 days.

well bonded and exhibited no loss of material with normal handling. Their main problem was that they react too fast in the mold for the 16:1:1 chemical mix. Mixing was sometimes incomplete when gelation set in and this led to a poor sample and irrecoverable loss of chemicals.

Optimum results came from sand stabilized with between 2.75-3.25% calcium acrylate by dry weight. Polymerization is very reliable giving a rather sturdy block of gelled sand. Curing gives a compressive strength of 1900-2000 psi for a two-inch-thick block with two weeks drying. To stabilize a cubic yard of sand it would take 75 pounds of monomer to give approximately a 3% concentration. This amount should give the best results both economically and structurally.

6 Drying Time of Stabilized Soil

Strength of stabilized soil depends on many parameters, including molecular size, polymer concentration and drying time. When fresh, and totally wet, the stabilized soil shows little compressive strength. For a 3% monomer sample the strength would be about 6 psi. Brief drying does not greatly improve this as depicted in Figure 4.4, (page 39). Maximum strength only comes with complete dryness from curing.

To test this, 2x2x2-inch cubes of sand were made and they were stabilized with 2%, 3% or 4% calcium acrylate.

They were air dried and their strengths with the time were noted (Figure 4.6, page 43). The resulting plot is an S curve. The first three days showed all the samples exhibiting about the same strengths. On the third day only the first quarter-inch of the sample was dry while the interior was still gummy.

The slope of the curve starts to increase after the third day and it was here that the effects of the monomer concentrations become evident. Even though there was no weight loss after the ninth day, sample compressive strength still increased with time. Maximum strength was obtained after 14 days. A test after two months yielded no change in strength.

An interesting observation was made concerning drying and the proximity of the sample's neighbors. The samples were set on one-fourth-inch glass rods in a rectangular arrangement, with an inch spacing between blocks. The blocks that had the fewest neighbors had a slightly quicker drying rate, being a fraction of a day faster. Because of this an average weight loss was plotted.

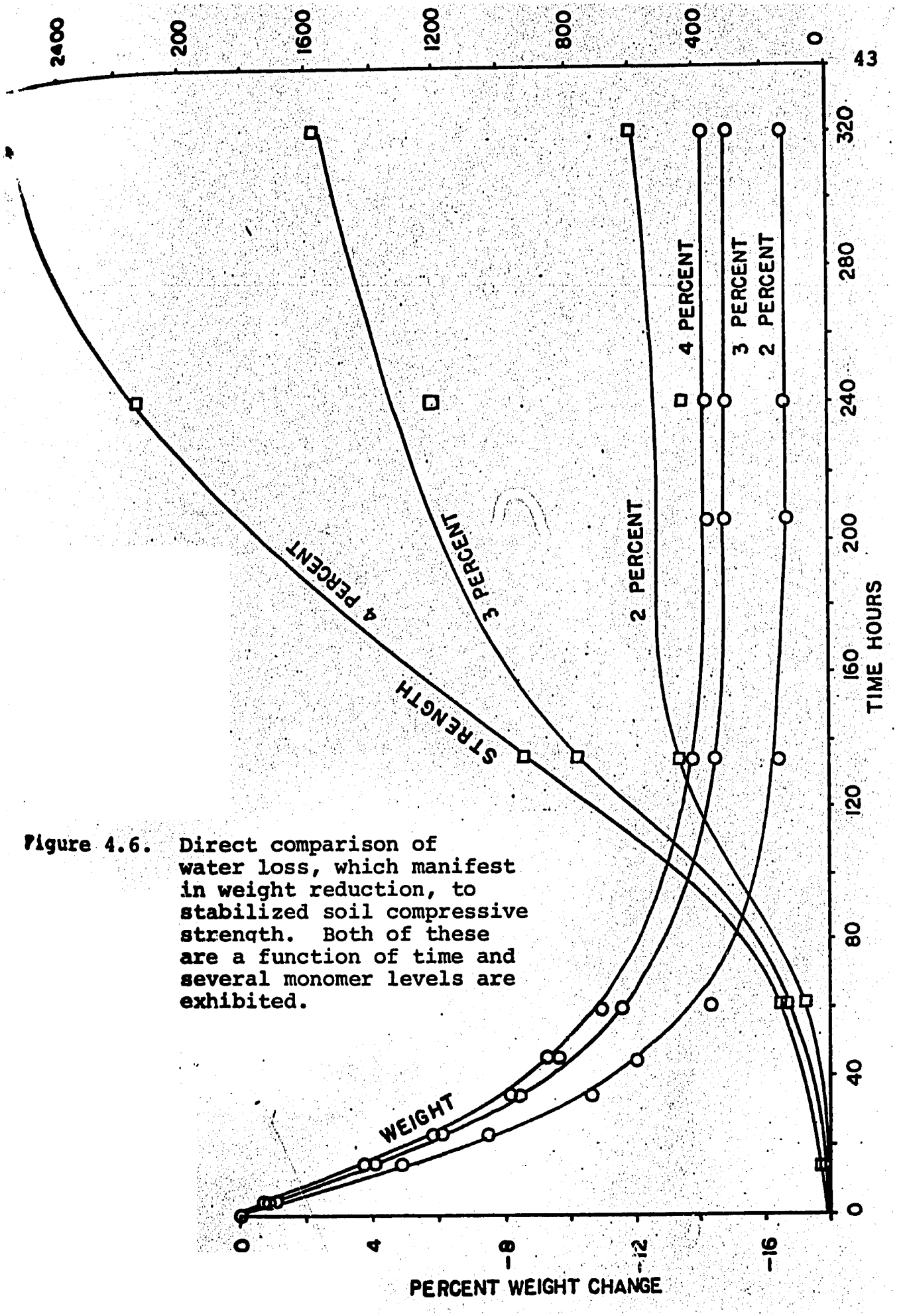


Figure 4.6. Direct comparison of water loss, which manifest in weight reduction, to stabilized soil compressive strength. Both of these are a function of time and several monomer levels are exhibited.

Initiator Concentration

Stabilized soil strength was also dependent upon initiator concentration. A series of tests was run for calcium acrylate, potassium persulfate and sodium thiosulfate concentrations. Four series were made at the chemical ratios of 8:1:1, 16:1:1, 32:1:1, and 64:1:1. The material stabilized was sand. Monomer concentrations were 2, 3, and 4%. For the samples with the least initiator, 64:1:1, reaction was very poor. The 2% sample never reacted and the 3-4% samples were too crumbly to derive any meaningful results. The rest of the samples in the other ratios gave good specimens. The exception was 2% for the 32:1:1 mix, which gave a marginal sample.

Gel times varied with the amount of initiator. The normally used mix of 16:1:1 gelled in 2-4 minutes, while the gel time for the 8:1:1 mixture was shorted by 1-2 minutes. Both of these gave a very sharp reaction time where in a 1-2-minute time span the soil would appear completely gelled. The high initiator levels held the danger of premature gellation before the soil was totally mixed with the chemical.

For the 32:1:1 and 64:1:1 chemical mixtures one did not get a sharp gel time where beginning and termination could be estimated. The change was gradual and it took place over a 20-40 minute period. This slower reaction allowed longer chains to be formed, which gave a stronger

polymer. The disadvantage was that there was increased time for chemical loss from the sample by leakage and that all the monomer might not have reacted. The poor reactivity of the 32:1:1 mix can be seen when comparing Figure 4.7 (page 46) with Figure 4.6 (page 43), which is a 16:1:1 mix.

It was determined that chemical concentrations in the ratio of 16:1:1 gave the best results for 3-4% monomer in sand (Figure 4.8, page 47). This was done because even though chain length was slightly sacrificed, it was compensated by a more complete polymerization, leading to uniform samples. Monomer concentrations below 3% in sand were very sensitive to initiator concentration. Even with the 16:1:1 ratio a 2% sample had an inferior polymerization. Increased initiator showed an increased strength due to a more complete reaction, which negated any losses from chain shortening. When an 8:1:1 ratio was used it removed all problems of reaction, and then the strength become dependent upon chain length.

Thus the role of initiator was most important in insuring a complete reaction which gave uniform and consistent results. Consideration of chain length should be secondary, and it should only be taken into account if large amounts of initiator are used. It is better to err with initiator excess than in the other direction.

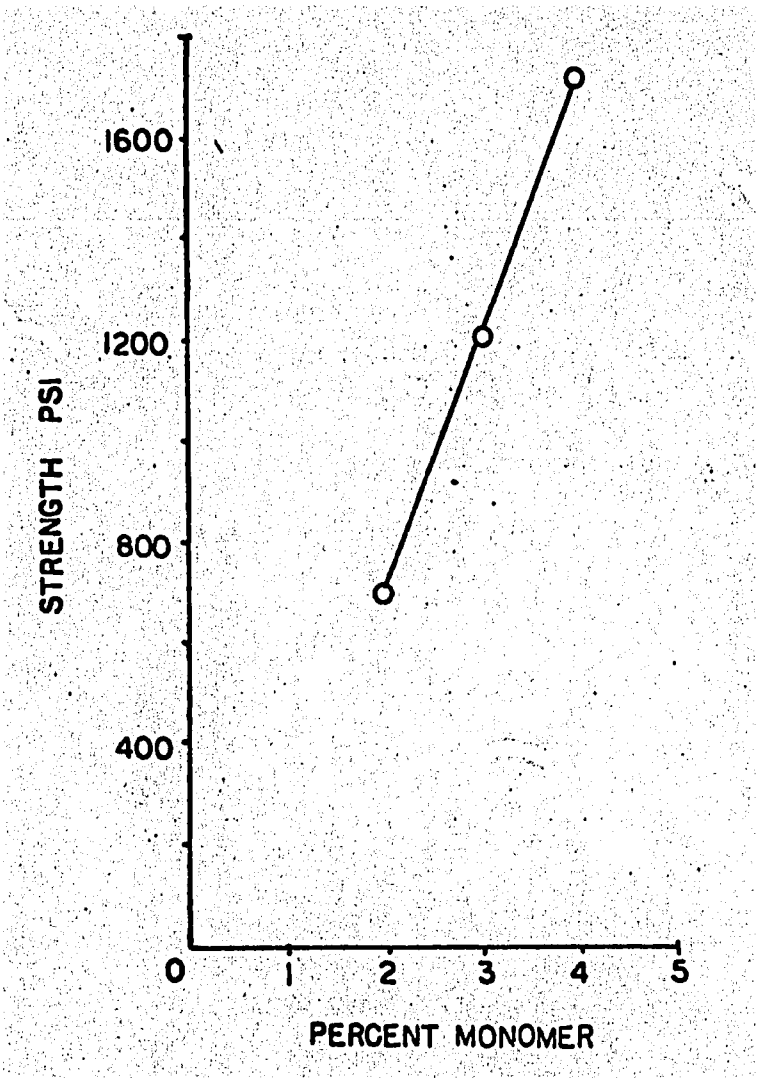


Figure 4.7. Compressive strength of stabilized sand with a chemical mix of 32:1:1. Drying time was 63 days.

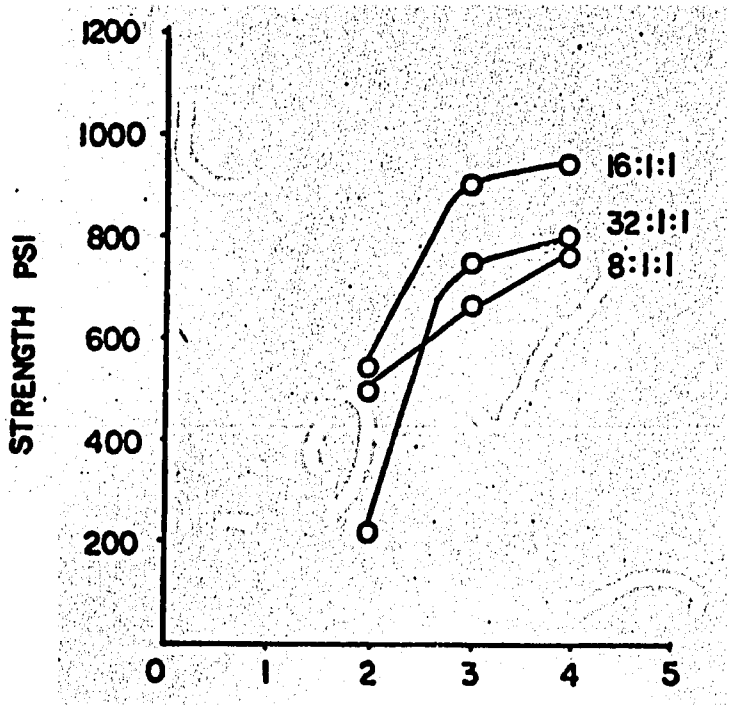


Figure 4.8. The effect of initiator concentration on soil strength. Samples tested for compression after 5 days drying.

1.8 Effects Upon Compacting a Fresh Sample

Because water content influenced the strength so greatly, an improved product could be had if the water could be quickly removed. An observation was made that, when fresh, water could be squeezed out of the gel. If this could be done, then a stronger block would be produced. To do this, a block of stabilized sand was made. As soon as it was removed from the mold it was weighed and measured, and placed in another clamped mold with an unsealed bottom. A block of poplar wood was used as a ram, and it was placed in a hydraulic press. Pressure was applied, and it took about a third of a minute to compress it. Maximum pressure was maintained for 15 seconds while the excess water was sponged up. The compressed block

was then removed from the mold, and it was allowed to air dry.

Three blocks were made containing 3.13% monomer by dry weight. The first was compressed to 938 psi and showed a 9% loss in height and a 2.9% loss in weight, i.e., 16% of the liquid. The second block was subjected to 1875 psi, and it showed a 12% reduction in height with a 4.4% loss in weight, losing 25% of the initial fluid (Figure 4.9, page 49). The last block was the control.

Drying of the blocks was rapid (Figure 4.10, page 49), and even the one with the greatest amount of water removed held only a 12-hour lead over the control. After ten days they were tested for compression and they all had virtually the same strength (Table 4.2, below). No apparent benefit can be had by compressing the fresh blocks, either in water reduction or in long-term strength. The only advantage was that it gave a slightly stronger block after compression with sharper corners and smoother surfaces, especially if a little clay is mixed with the sand. Should the compressed block be resaturated with water, it will expand to its former uncompressed volume.

Compaction Force psi	Dry Strength psi
0	1170 ± 35
938	1270 ± 38
1875	1170 ± 35

Table 4.2

Comparative Strengths of Compacted Sand
Stabilized with 3% Monomer
Drying time was 9 days.

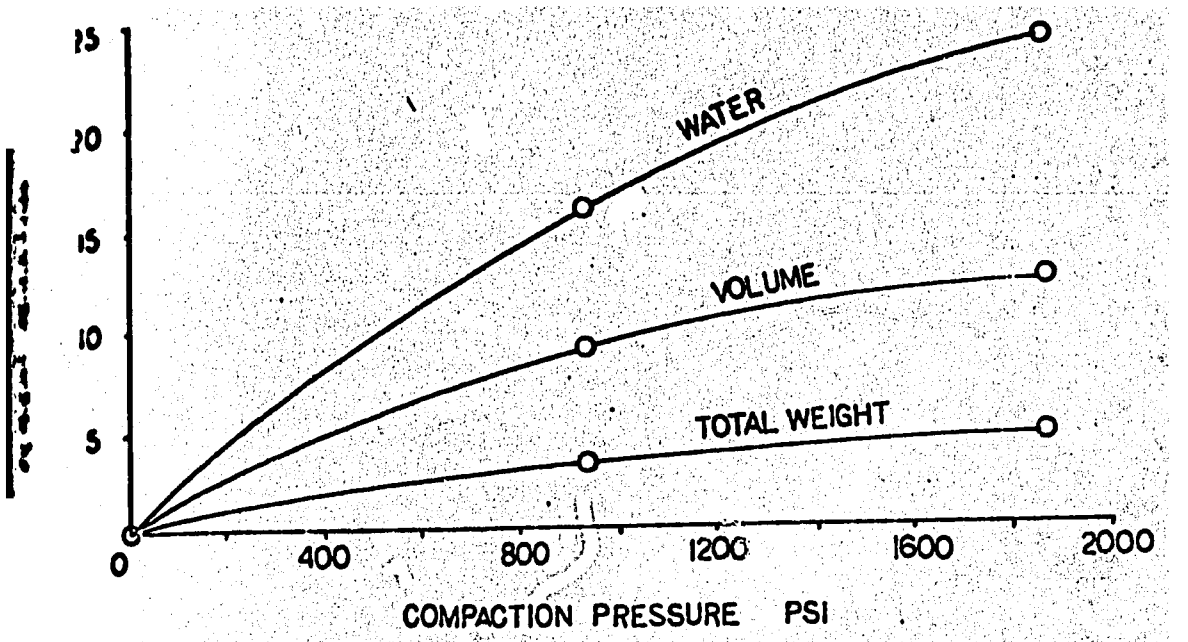


Figure 4.9. Change in various sample parameters when compacted.

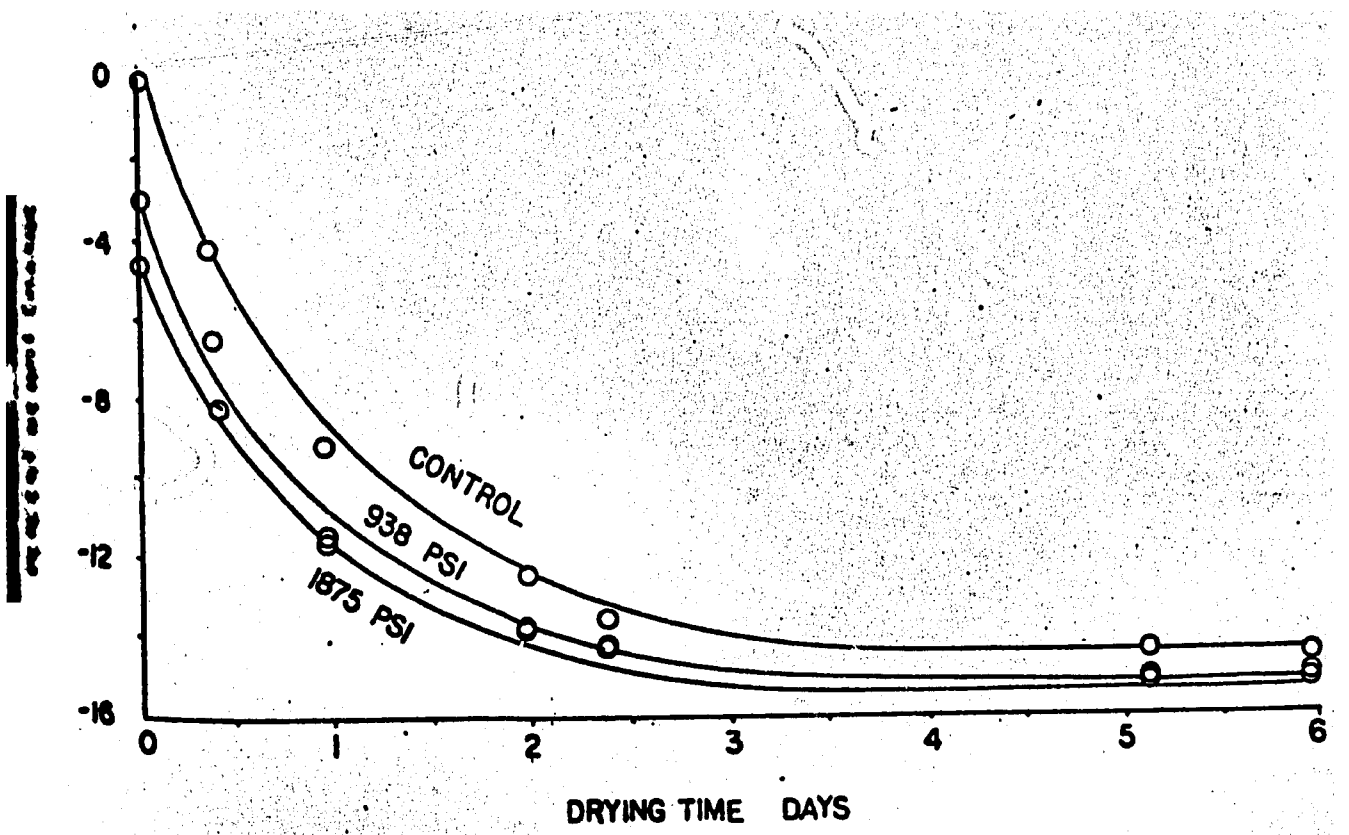


Figure 4.10. Water loss, as manifest by weight loss, of the samples.

.9 Soaking Stabilized Soil in Water

Water has a marked effect upon the strength of the stabilized soil. The reabsorption of water weakens the stabilized soil, though the soil will never dissolve. To maintain the strength of the stabilized soil, it is imperative to waterproof it. Absorption of water occurs in two steps. First, the water enters the soil through the pores and fills the voids. This is relatively quick and occurs in a matter of seconds. Second, the water plasticize and softens the polymer film. Since this is controlled by diffusion the rate is slower, taking many minutes.

Therefore, the best way to waterproof the stabilized soil is to prevent water from entering the structure. To do this one can either decrease the number and/or the size of the pores, or coat the outside to make an inpenetrable barrier to moisture. The worst possible case would be blocks made of coarse sand which has a large pore structure.

Two cured cubes of sand stabilized with 3% calcium acrylate were chosen. They had a volume of 7.9 cubic inches and a surface area of 23.9 square inches. It was suggested* that oil would be a good waterproofing agent, so one block weighing 225.8 grams was coated with 15.6 grams of 30-weight motor oil. The other block was the control. The blocks

---

*Dennis Mialki, undergraduate student, Department of Civil Engineering, Carnegie-Mellon University.

were immersed in water, removed and drained at various intervals, and weighed to determine how much weight was gained over the treated weight (Figure 4.11, page 52). The oil definitely retarded water absorption, for the untreated block gained 17.3% of its weight in water in the first 15 seconds. Within four minutes the block was noticeably softer The treated block absorbed water at a slower rate by displacing some of the oil. After about 30 minutes the top of the block, i.e., the only exposed surface in formation, started to slough off while the sides remained intact. This loss could not be prevented from continuing, and no explanation for this phenomenon could be given. After 30 minutes the block was forcibly broken in half and it was moist all the way through, though it was far stronger than the control.

Another solution to the water problem was to reduce the pore size to slow down water absorption. This was accomplished by mixing 5% silt and 5% clay with the sand. To further seal the blocks they were subjected to a pressure of 1000 psi to compact the block while fresh, giving it a smooth face very free from external pores. These blocks were made smaller in hopes of accelerating the process of water intake. Their volumes were 1.06 cubic inches with a total surface area of 7.2 square inches. They were stabilized with 3% calcium acrylate. Four samples were tested. The control, one coated with pump oil, which is a light oil, one coated with motor oil, and one coated with

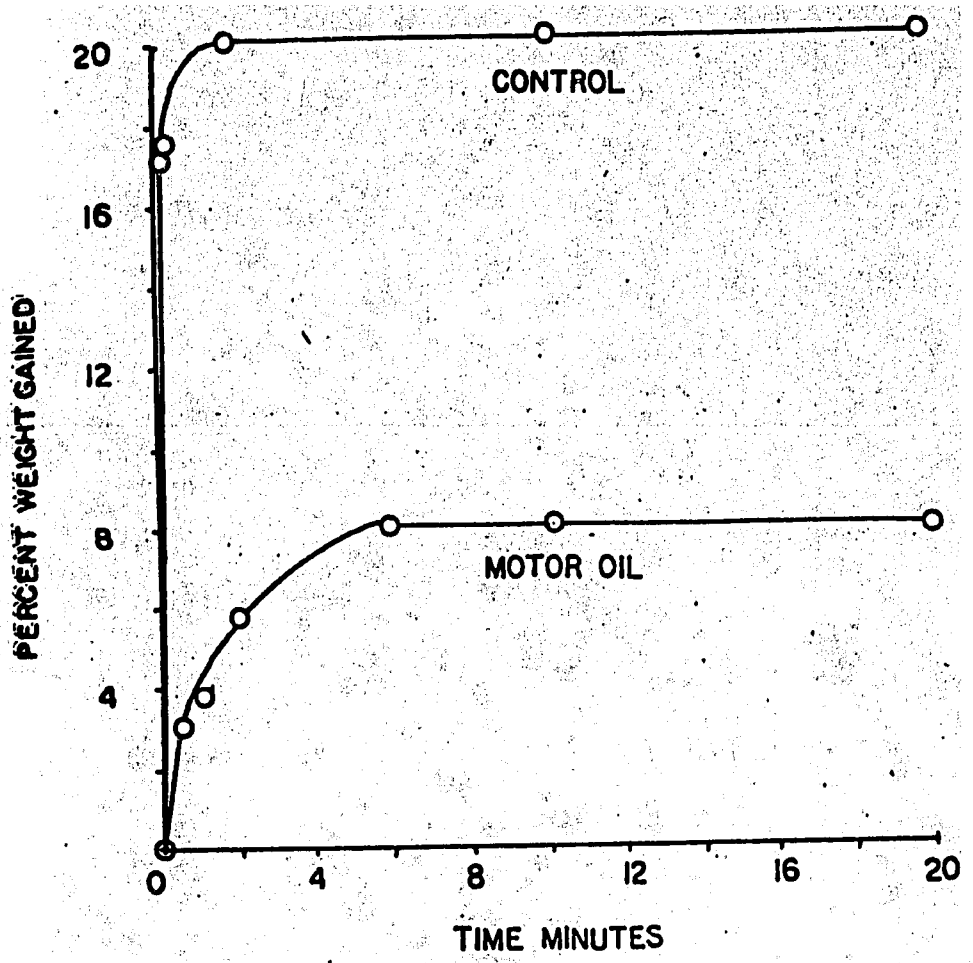


Figure 4.11. Water intake of large cubes of sand stabilized with 3% monomer

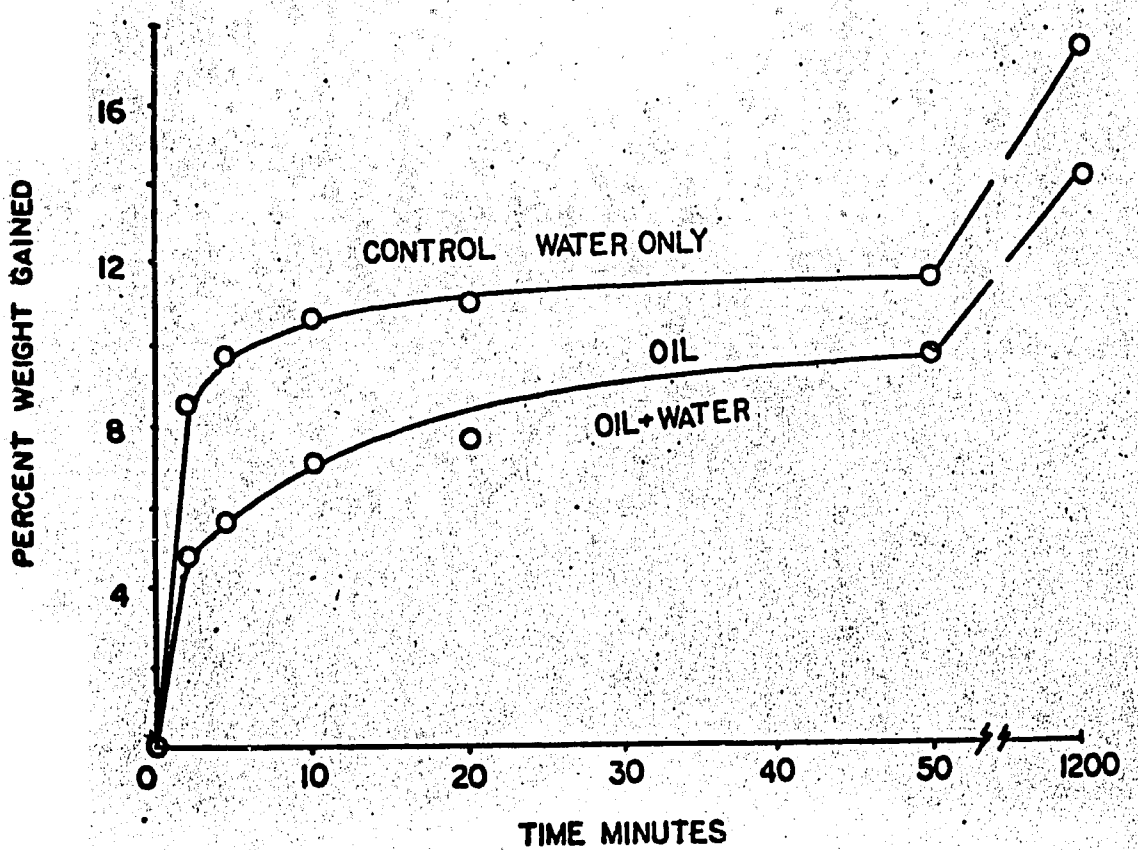


Figure 4.12. Weight gain in sample of just water and water and oil combined

Aliquat®. The Aliquat® was made in about a 10% solution and warmed to 50°C until it was about the consistency of paint. One coat was applied to the block surfaces and it was allowed to dry 24 hours. The coating was white and waxy. The motor oil block weighed 36.0 gm and gained 1.2 gm of oil.

Upon immersion in water the clayey control block had a slower absorption rate of water than the sand block (Figure 4.13, page 54). This contrasted with what was expected since the clay-silt-sand block had a greater area to volume ratio. As with the sand block, the clay-silt-sand block had the greatest intake in the first minute when it acquired almost half its total water intake. The Aliquat® slowed down the initial water intake, but since all the pores were evidently not sealed the total water absorbed became nearly that of the control. The only blocks that showed any slowing and stoppage of water absorption were the ones coated with oil. Not only was the initial water intake less, but total amount after a great time was less. The two types of oil behaved nearly the same. Plots of these tests go to 16 hours (Figure 4.14, page 54), but 36 hours indicated little if any change. After 16 hours the oil block was about as strong as a freshly made sample, while the Aliquat® and control were very soft. These latter two also swelled, giving a new volume of 1.28 cubic inches. Once dried they shrunk down to about 1.16 cubic inches, which was nearly their original volume before

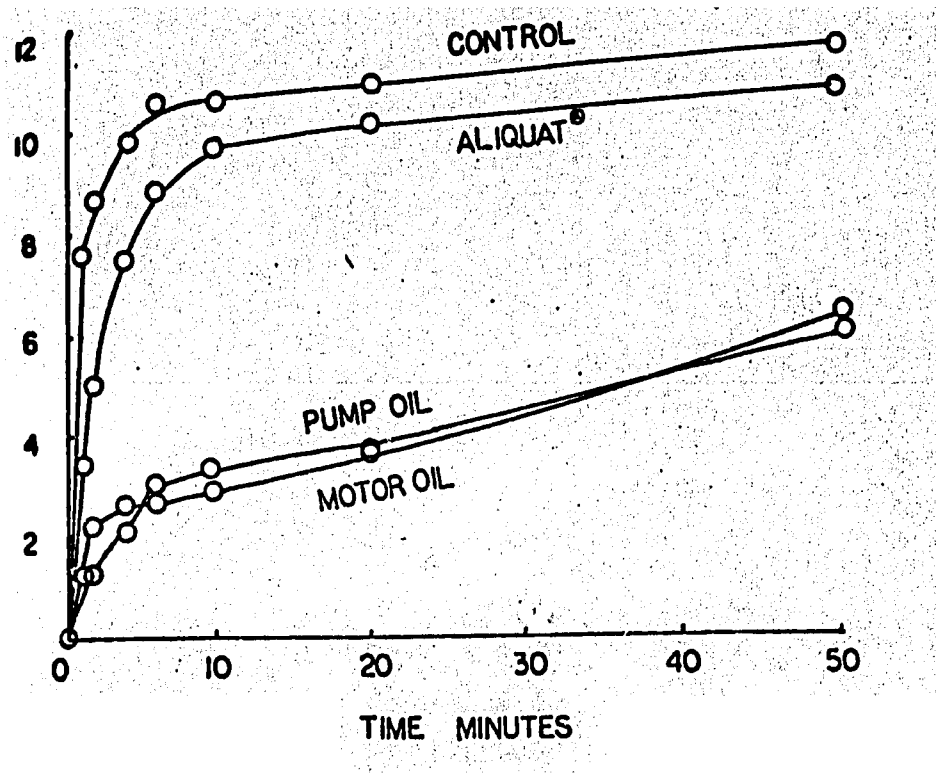


Figure 4.13. Water intake for small compacted samples after having been treated in several ways

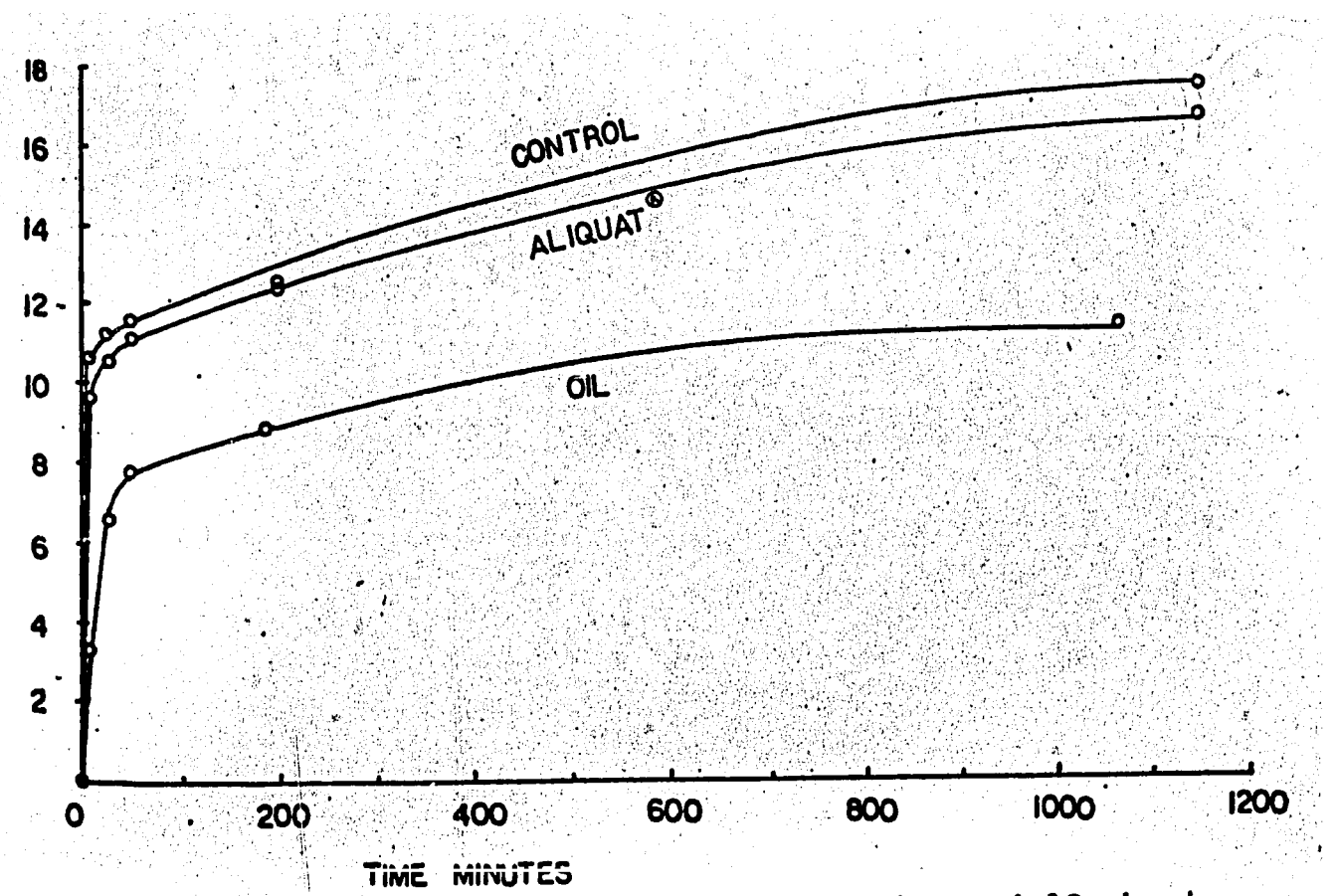


Figure 4.14. An extended graph of Figure 4.13 showing the two treatments and the control

compacting. The pump oil block showed no volume change after 36 hours nor any change after drying.

It may be argued that all the oil did was to fill up pores that would normally be occupied by water. A plot of the weight gain of the dry block with oil and water combined (Figure 4.12, page 52) was still less than the plot of a block with just water, indicating that the oil did reduce the water intake.

From the results it can be seen that water absorption can be reduced by either reducing the pore size of the soil or by coating the block with oil. A compacted block will swell when wet but oil inhibits this swelling. Even so, the oil treatment is not perfect, but it does dramatically reduce the initial water absorption. This is important since once water gets in it is harder to remove it and the polymer begins to soften.

Effects of Humidity Upon Stabilized Soil

Though water absorption upon immersion of stabilized soil may be spectacular, the acquisition of water from the atmosphere is almost negligible. Soil blocks were made from 5% clay, 5% silt and 90% sand bonded with 3% poly-calcium acrylate. These were cured for three weeks at about 50% humidity. One 2x2x2-inch block was subjected to drying at 87°C and another was placed in a closed environment of 100% humidi at 25°C. In both cases weight change was small (Figure 4.15, page 56), and there was no noticeable change in the sample appearance. It was evident that humidity had a small effect upon the

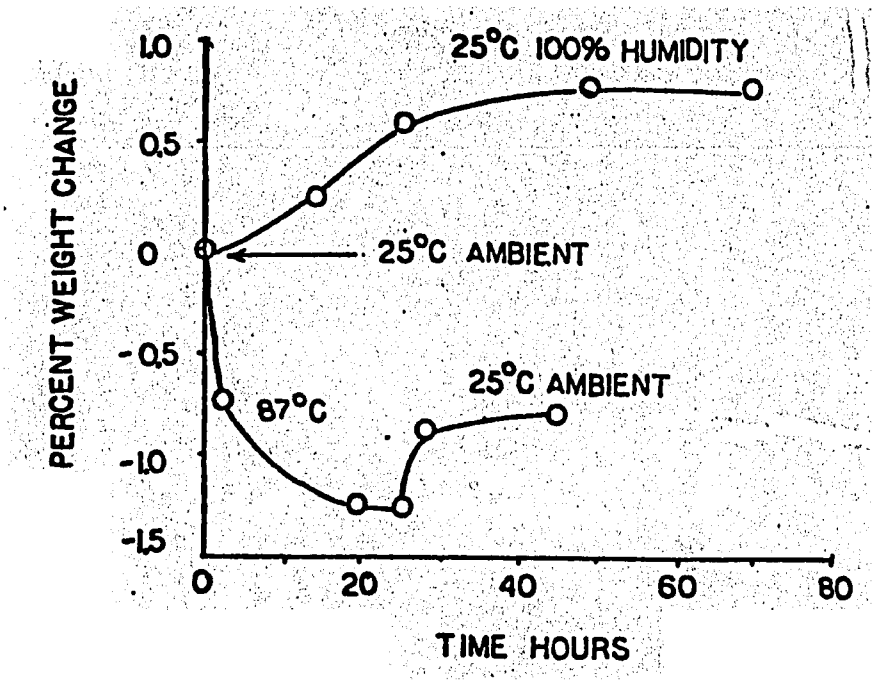


Figure 4.15. Weight change due to moisture from 0-100% humidity

Heating of Stabilized Soil

Due to the monomer's problems with water, the ideal locale for construction would be an area with low precipitation. These arid or semi-arid places are often subject to elevated temperatures. To test this, samples were placed in an oven and later they were examined.

The first test incorporated small samples identical to the ones used in the water immersion tests. These contained 3% monomer with a soil mix of 90% sand, 5% silt, and 5% clay. The small size permitted a rapid and complete heating of the sample. After 15 hours at 71°C, the stabilized

soil samples were removed and examined. No visible deterioration was evident since the edges were still sharp and there was no loss of soil with normal handling. A load of 375 psi could be supported by the samples.

Another test was run at a higher temperature, 87°C. Again small samples were used and also there was a 2x2x2-inch cube of the same mix. Another cube of sand with about 3% monomer was also tested. All samples were well cured before testing. They were placed in a closed oven and heated for 26 hours at 87°C. Once the baked samples had cooled they were examined and they appeared to be unaltered by the heat. It was noted that when struck, the soil blocks gave a sharper note than comparable unheated blocks. The cube of 90% sand, 5% silt, and 5% clay, stabilized with 3% calcium acrylate had a compressive strength of 558 $\pm$ 16 psi. This was about a third of the strength of the control which failed at 1505 $\pm$ 45 psi.

To examine what happens to the polymer, a one-inch-diameter piece of poly-calcium acrylate having a thickness of a quarter of an inch was heated. At 71 °C, there were a few internal fractures. When the temperature was increased to 87°C, the polymer was full of internal crazing. The exterior was unaltered and what was once a very hard object was now easily broken. Replastization would not repair the damage. Thus it appears that the damage from elevated temperatures is irreversible, causing a permanent structural

weakness in the stabilized soil.

Fortunately human habitation does not occur at temperatures that much exceed 50°C, so polymer weakening from heat can generally be ignored. The exception would be where stabilized soil was used to line a place containing fire. In this case the stabilized soil would weaken and the polymer could burn.

2 Effect of Sodium Chloride Upon Polymerization

One sometimes encounters in the field either saline water or saline soil. The polymer system is ionically cross linked and there should be some change associated if other ions are introduced. To investigate this possibility, various sand samples were made. These contained 225 gm sand and were 2.7% calcium acrylate by dry weight. Sodium chloride was added to the 50 ml calcium acrylate solution.

Ca-Acrylate	Initiator	Water	Sand	% CaAr	%NaCl/H_2O	%NaCl/Soil
6.16	1.0gm	50gm	225gm	2.7%	4%	0.85%
6.16	1.0gm	50	225	2.7	8	1.7
6.16	1.0gm	50	225	2.7	12	2.5

Table 4.3

Composition of Samples Containing NaCl

As usual the polymer was formed in the soil. For the highest concentrations of salt the reaction seemed faster.

This could be due to copper leached from the mold, since when the stabilized soil was removed from the mold a half an hour later the surface had a slight blue tinge. The specimens were dried for seven days and then tested for compression. The results for the sample with 4% salt in water gave a strength of 750 psi. This was about 75% of the strength of a salt-free sample. The decrease in strength was linear at seven days drying (Figure 4.16), so one must determine how much strength reduction can be acceptable. Since sea water is 3.5% salt, it would appear that this would be a suitable liquid to use in soil stabilization. Because only a small amount of salt in soil does decrease the strength it may make many soils unsuitable for building materials. The effect of other minerals was not tested since the combinations can be infinite, but sodium chloride being very common does alter the strength of the soil. Preliminary tests should be run with any dubious soil before construction.

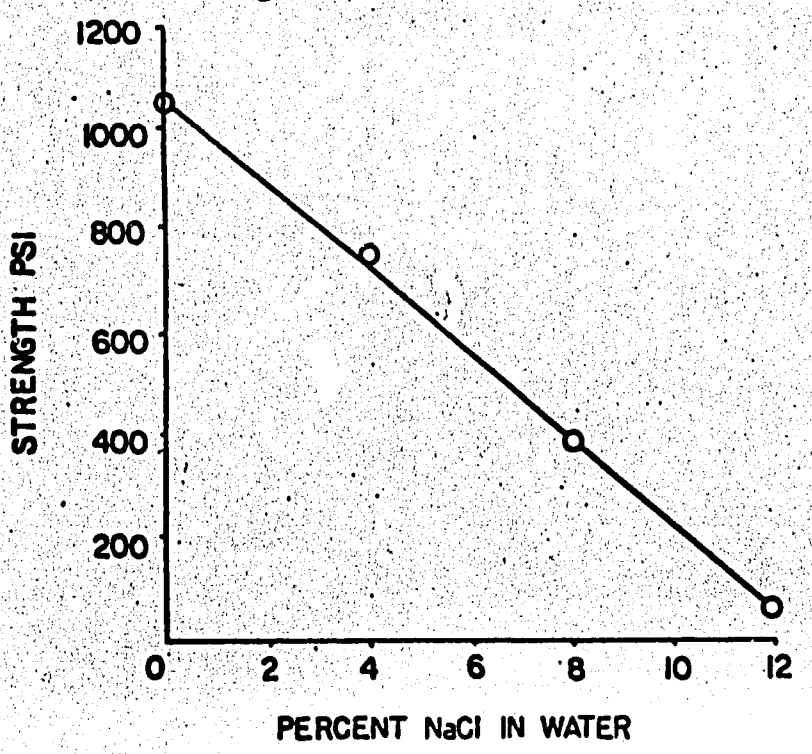


Figure 4.16. Reduction of compressive strength due to increased NaCl concentration. Drying time was 6 days for 2.7% monomer

Soil Composition

Most of the experiments have been run with pure sand or nearly pure sand. Therefore, tests were run to determine what effect sand, silt, and clay concentrations had upon the strength of the stabilized soil. Samples were made, being approximately two-inch cubes. Sand content was varied from 20% to 100%, with the calcium acrylate concentration being held at a constant 3%. It was felt that tests with less than 20% sand were useless, since in nature it is difficult to obtain either pure silt or clay.

In sample preparation the silts and clays were reduced to a fine dry powder and these were mixed in correct weights with the sand. Normal sample preparation was followed if attention was paid to the water content. Clays and silts demand more water than does sand, and for a given weight they occupy a greater volume than sand. Should too little water be used there is inadequate chemical mixture giving a permanently inferior sample. An excess of water gives a very soft sample and a longer drying time. By some experimentation an optimum amount of water was achieved based on the percent sand present (Figure 4.17, page 61).

By increasing the water content the volume of the sample also increases. Silt and clay, by their nature are rather fluffy and they can be packed, which also causes some mixing problems. The added water and

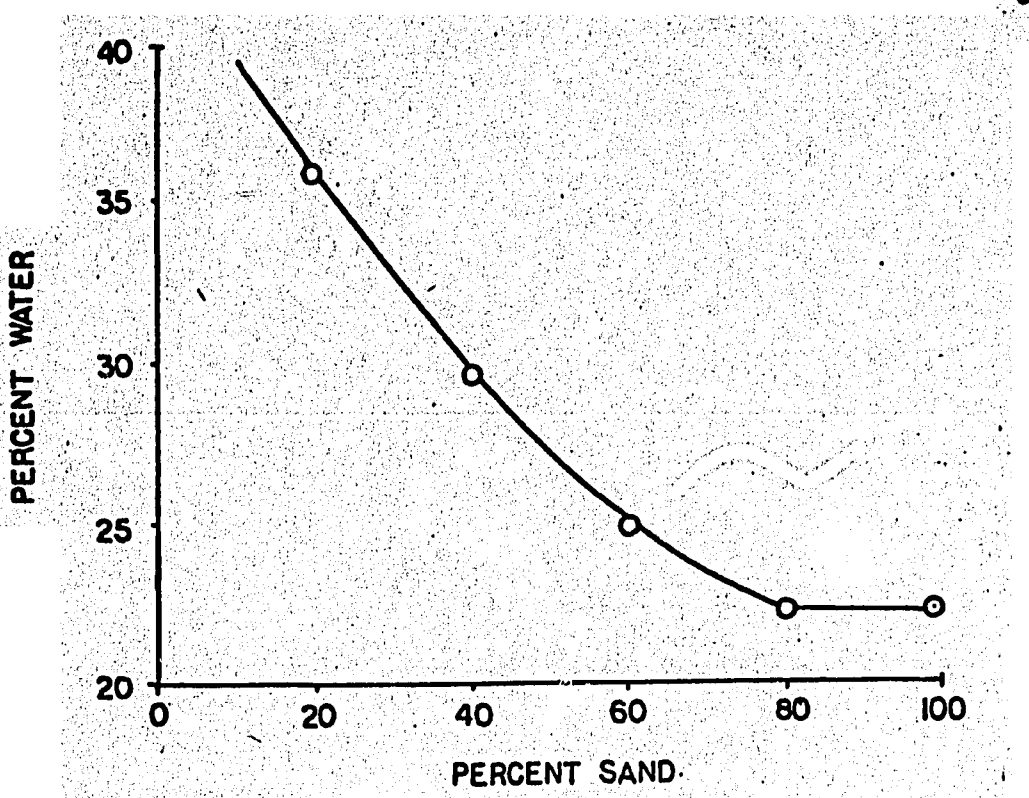


Figure 4.17. Amount of water needed to make a good soil mix. Water/dry soil x 100 = % water.
Sand/soil x 100 = % sand

packability of the soil caused the sample to shrink upon drying. Generally there was a greater volume change wit decreased sand (Table 4.4).

Table 4.4

Volume and Weight Changes in Various Soil Mixtures using 150 gm Soil and 3% Monomer

% Sand	Volume, in.^{3}		Weight, grams	
	Wet	Dry	Wet	Dry
80	4.88	4.88	179.2	154.5
60	5.34	4.84	185.2	154.4
40	5.69	5.04	189.7	153.6
20	6.1	5.20	194.4	150.9

Soil strength after curing was plotted on a triaxis diagram (Figure 4.18, page 63). There are two maxima. The small local maximum is a puzzle since it can be experimentally reproduced. Originally, it was thought the large maximum could be due to better soil reactivity because of the higher iron content of the fines. A sounder explanation would be the maximum was caused by soil packing. Volumetric measurements were made along a line of constant sand and the data as presented in Table 4.5 seem to support the packing theory. Regrettably, measurements were not taken at every point. One could question whether the packing was due to soil size or a mixing artifact. When broken open the samples contained air bubles about 1 mm in diameter. The air is probably a constant since it is not manifest in the wet volumes. Because the wet volumes were constant and the dry volumes were not, it can be argued that soil compaction due to shrinkage played the major role in the final strength. The smaller final volumes had the greater strengths.

Table 4.5

Volume Change and Associated Strength for Samples Made of 150 grams of Soil and 3% Monomer

Sand %	Silt %	Clay %	Volume in^3 ±5% Wet	Volume in^3 ±5% Dry	Strength psi ±3%
40	0	60	5.64	4.78	1668
40	30	30	5.79	4.92	1984
40	60	0	5.64	5.42	1245

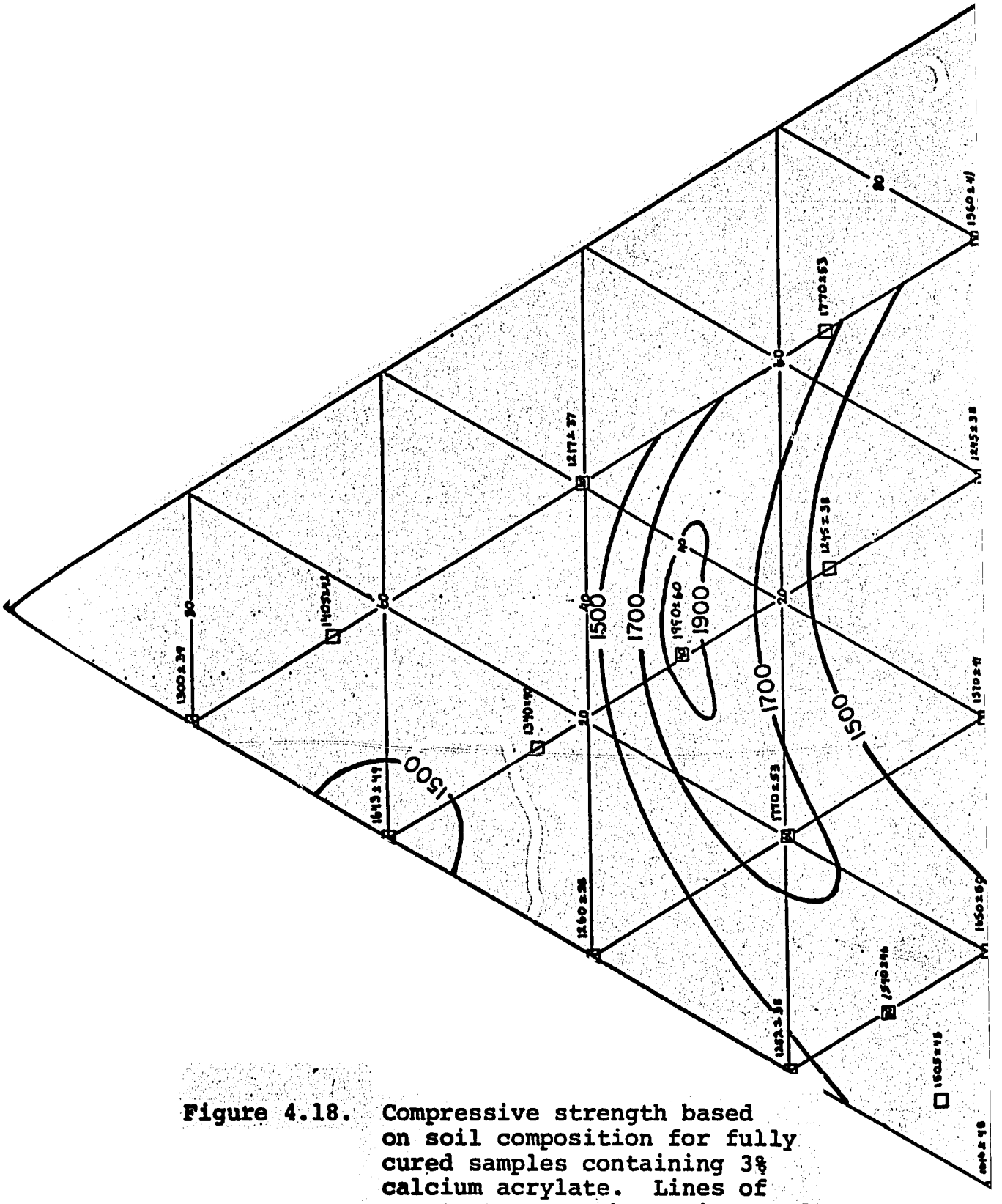


Figure 4.18. Compressive strength based on soil composition for fully cured samples containing 3% calcium acrylate. Lines of constant strength are in pounds per square inch.

It should be noted that when resoaked with water the samples will pick up 20% of their weight in water. They will also swell to their former volume or slightly beyond. However, they are, as a whole, slightly stronger when wet than a wet sand sample.

Comparison of Calcium Acrylate to Acrylamide

Most of the discussion has been about one monomer, calcium acrylate. Previously mentioned was another chemical system, the toxic AM-9. Being the only commercially available, water-soluble monomer system, it should be briefly tested as a comparison to the calcium acrylate. This was done in only one test situation, that of strength based on concentration. The system consisted of acrylamide, methylenebisacrylamide, potassium persulfate, and sodium thiosulfate in the ratios 14:6:1.6:1:1, respectively. This reflects the initiator concentrations used for the acrylate.

Sand was stabilized in the cubic molds and the blocks when fresh felt softer and tore easier than the corresponding acrylate block. When dry, the strength of the acrylamide was inferior (Figure 4.19, page 65). It should be noted that in Warner's article, AM-9 did not begin to show strength until after 30 days drying (Figure 1.1, page 6), for a 2.5-inch-diameter sand sample. Maximum strength was reached after four months, being 900 psi for 2.17% monomer. The previous test run in Section 3.1 gave the acrylamide

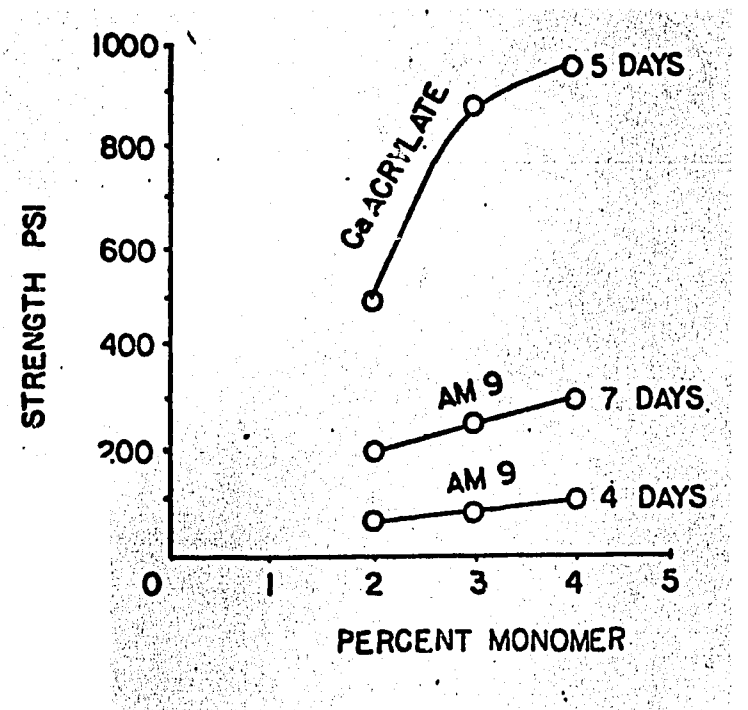


Figure 4.19. Acrylamide copolymer, AM-9, compared to calcium acrylate in sand stabilization

copolymer a strength of 1121 psi, which was comparable to cured calcium acrylate which failed at 1143 psi. For large samples it takes the AM-9 type longer to cure.

The last item of interest concerning the acrylamide copolymer was that a 4-mm-thick sample of dry polymer would totally plasticize to a rubbery gel after being immersed in water for a day. Dry calcium acrylate polymer being equally thick would only soften at the edges and after three days under water it would still be substantially unplasticized

5. CONCLUSIONS

1. Calcium acrylate was the best monomer tested for stabilizing soil. It was a water-soluble solid that was readily polymerized by a free-radical initiator.
2. Product strength met specifications. Soil containing 3% monomer had a maximum compressive strength of 2000 psi. However, a more common strength was in the range of 1300-1600 psi.
3. The effect of monomer concentration on strength was linear down to about 1% calcium acrylate. Below that reaction was very poor.
4. A monomer concentration of 3% was optimum. This gave a sufficiently reactive mixture that would gel in five to ten minutes and it was strong enough to handle when wet. The chemical mix used was 16 parts calcium acrylate and one part each of potassium persulfate and sodium thiosulfate.
5. Increasing the initiator concentration shortened reaction time. Salts of copper and iron also acted as accelerators
6. Sodium chloride reduced the stabilized soil strength. A concentration of 2.5% in the soil virtually destroyed all potential strength.
7. Soil composition had a bearing on the product strength. The best mixture tested was 40% sand, 40% silt and 20%

clay. For 3% calcium acrylate the strength was 2000 psi. Strength appears to be a function of soil packing. The denser the product the stronger it was.

8. Stabilized soil strengthens with water removal. A two inch-thick sample air dried at 25°C and normal humidity would reach maximum strength in a fortnight. Half strength was reached in about five days drying. Soil composition had no effect upon the ultimate drying time.

9. Water replasticizes the polymer, drastically reducing its strength. Stabilized soil would pick up 18-20% of its weight in water when immersed. Half of the weight gained occurred in the first five minutes. Soils containing a large amount of clay and/or silt would swell to their fresh volumes or slightly larger. When dry, these soils would shrink and the change in volume was up to 15%. Sand did not change size but it was the weakest when wet.

10. An oil coating on the dry stabilized soil retarded water penetration. The maximum amount of water acquired was about 12%.

11. Changes in humidity had little effect upon the cured samples.

12. Extreme temperatures in the range of 87°C caused permanent weakness in the stabilized soil. This reduced the strength by a third. The polymer, if heated high enough, will burn.

REFERENCES

1. Chemical Week Buyers Guide Issue. McGraw-Hill, Inc., New York, October 27, 1976, p. 392.

2. deMello, Victor F. B., et al. Stabilization of Soils, U. S. Patent 2,651,619, September 8, 1953.

3. Gallaway, Bob M., and Jon A. Epps. Soil Stabilization Course Notes. Department of Civil Engineering, Texas A&M University, 1975.

4. Gnaedinger, John P. "Soil Stabilization by Injection Techniques." Industrial and Engineering Chemistry, 47, 11, 2258-2265 (1955).

4. Hopkins, Robert P. "Acrylate Salts of Divalent Metals." Industrial and Engineering Chemistry, 47, 11, 2258-2265 (1955).

6. Lambe, T. William. "Stabilization of Soils with Calcium Acrylate." Boston Society of Civil Engineers, 138, 2, 127-154 (1951).

7. "Making Dirt Stick Together." Business Week, 1337, 76-78 (1955).

8. "Navy Process Makes Roads on Beaches." Engineering News Record, 144, 9, 26 (1950).

9. "New Soil Stabilization Method Developed Using Calcium Acrylate." Roads and Streets, 93, 4, 51 (1950).

0. Polivka, Milos, et al. "Field Experiences with Chemical Grouting." Proceedings of the American Society of Civil Engineers, 83, SM2, 1204-1 - 1204-31 (1957).

1. Scherer, Stephen. Emergency Shelter Project Soil Stabilization, Senior Project Report, Department of Chemical Engineering, Carnegie-Mellon University, May 8, 1974.

2. Smith, Vincent B. "Army, Navy Release New Data on Chemical Soil-Stabilization." Engineering News Record, 144, 11, 23-24 (1950).

13. "Stabilize with Chemicals?" Chemical Engineering, 59, 8, 228-233 (1952).

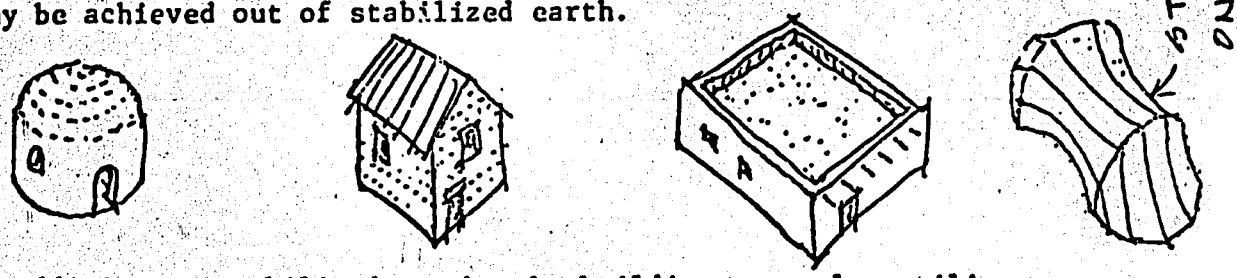
14. Warner, James. "Strength Properties of Chemically Stabilized Soils." Proceedings of the American Society of Civil Engineers, 98, SM11, 1163-1185 (1972).

APPENDICES

STABILIZED EARTH Advanced Building Studies

Applications:

Stabilized earth is to be used in the construction of buildings (primarily housing) whose height will not exceed two stories. It may be used in the floor, walls, and roof of the building. The sketches below indicate a few of the building forms which may be achieved out of stabilized earth.



In addition to stabilized earth, the buildings may also utilize wood, grasses, corrugated iron, and organic fibers for various components.

It may be necessary to use some type of reinforcement in conjunctic with the stabilized earth in locations where earthquake or high wind conditions prevail.

Construction techniques fall into two main categories: 1) block masonry, and 2) continuous forming, or "rammed earth". In the case of block masonry there are several ways to form the blocks (a complete description of conventional methods is given in the Handbook for Building Homes of Earth A.I.D., chapters 8-11).

In both construction methods the stabilizing compound is added to the soil before it is formed necessitating that it remain workable long enough to be loaded into the molds. However, consideration should be given to the possibility of using stabilizers or waterproofing compounds which could be applied after the material has been formed initially (possibly brushed onto selected surfaces).

A third construction possibility would be the continuous extrusion of a highly cohesive and quickly curing earth-based material from some sort of apparatus. This may not be feasible at the present time however.

Properties:

compressive strength: 600-1000 psi
tensile strength: 50 psi
(approx. same as low grade brick)

Stabilizer must not damage organic fibers.

Stabilized earth mixture must remain workable long enough to be formed.

Stabilizer must be nontoxic and nonpolluting.

A.2 Soil Properties

Three basic types of soils were used for the calcium acrylate experiments. These were sand, silt, and clay. Various mixtures of these three elements produced the soil for experimentation. The soil was devoid of organic matter.

The sand was mainly quartz, and had a tan color due to iron. There was a broad distribution of particle size. The largest particles were rounded. A sieve analysis using U. S. Standard Sieves can be found in Table A.1.

Silt came in large lumps and the color was yellow ochre. These lumps were ground and passed through a #60 sieve. About 5% of the silt consisted of fine angular gravel or sand, which was discarded. The powdered form allowed for superior mixing.

The clay was a powdered commercial product used for pottery. Its color was brick red.

Sand was the densest of the three, being 1.5 gm/cm^3. It had a void fraction of a third. The other two soil components were more difficult to get adcurate measurements due to soil packing. Their densities ranged from 1.1 gm/cm^3 to 1.4 gm/cm^3 depending upon how tightly packed the powder was. Void fraction was impossible to measure and mixing water amounts can be found in Figure 4.17.

When dry, sand had no compressive strength. Silt and clay do have structural strength and they were about equal.

For a sample of dry silt compressive failure occurred at 133 ± 4 psi. Clay failed at 125 ± 4 psi.

Sieve Analysis of Sand Used in Experiment
U.S. Standard Sieves Used

Sieve Size	Soil Percent
>20	19.2
30	9.9
40	17.9
50	21.2
60	9.5
70	5.8
80	6.6
100	4.1
140	2.9
200	1.3
∠200	1.6

A.3 Sample Calculations

3.1 For 4.2: Monomer manufacture

The production of all the monomers follow a similar set of calculations. Detailed analysis for the production of calcium acrylate from the hydroxide will be given.

Acrylic acid	$p = 1.05\ gm/cm^3$ $MW = 72.06$
Water	$p = 1\ gm/cm^3$ $MW = 18$
$Ca(OH)_2$	$MW = 74.09$
$Ca\ Ar_2$	$MW = 182$
$Ca\ Ar_2 \cdot 2H_2O$	$MW = 218$

Table A.2
Chemical Data

$$2(C_3O_2H_5) + CaOH_2 \qquad Ca(C_3O_2H_4)_2 + 2H_2O$$

Basis: 500 gm Acrylic acid

$$\frac{500gm\ Ar}{72.06\ gm/mol} = 6.94 \text{ moles acrylic acid}$$

Number of moles of $Ca(OH)_2$ needed is half of the acid.

6.94 moles/2 = 3.47 moles $Ca(OH)_2$

Mass of $Ca(OH)_2$:

3.49 mole x 74.09 gm/mole =

Since the purity of both the acid and hydroxide were uncertain, the hydroxide amount was reduced to give a

slightly acidic solution. Consequently a ratio of acid: hydroxide was 2:1.

Acrylic acid	500 gm	6.94 moles
$Ca(OH)_2$	250 gm	3.374 moles
Water	1300 gm	72.2 moles

Table A.3

Actual Chemical Amounts Used

Water in the solution is equal to the amount added plus the amount evolved.

Water evolved:

2 moles/mole of Ar x 6.94 moles Ar = 13.9 moles water
water

Total moles of water:

72.2 moles added
+13.9 moles evolved
87.1 moles total or 1568 gm

A.3.2 For 4.2: Monomer concentration

A fixed amount of calcium acrylate solution was weighed and the water evaporated. This took a week to produce a dry monomer.

Dish	1.3654 gm
3 ml soln & dish	4.7701 gm
3 ml soln	3.4047 gm
Dish & mono	2.5933 gm
Monomer	1.2229 gm

Table A.4

Data for Determining Monomer Concentration

Density of solution:

$$\frac{3.4047 \text{ gm}}{3.0 \text{ ml}} = 1.135 \text{ gm/cm}^3$$

Fractional weight of monomer in solution:

$$\frac{1.2229 \text{ gm mono}}{3.4047 \text{ gm soln}} = 0.359 \text{ mono/soln}$$

Amount of monomer per ml solution:

$$0.359 \text{ mono/soln} \times 1.135 \frac{\text{soln/cm}^3}{\text{gm}} = 0.408 \text{ gm mon/ml}$$

Because of the uncertainty of the volumetric measurement which gave varying amounts an average of 0.4 gm/ml was used. If this was compared with the theoretical yield from the reaction, one would get the following:

$$3.374 \text{ mole } Ca(OH)_2 \times 218 \text{ gm/mol mono} = 735.8 \text{ gm mono}$$

$$\frac{735.8 \text{ gm } CaAr_2 \cdot 2H_2O}{1300 \text{ gm } H_2O + 735.8 \text{ gm mono}} = 0.361 \text{ mon/soln}$$

This is close enough to 0.359 mol/soln which was determined experimentally.

A.3.3 For 4.3: Initiator Concentrations

To make a solution of sodium thiosulfate one dissolved 10 gm of thiosulfate in 100 gm of water. This gave a solution of approximately 0.1 gm/ml. Solutions of potassium persulfate were half the strength due to the low solubility of that salt.

A.3.4 For 4.3: Gel Tests

Test #1 from Table 4.1 will be calculated:

	Soln conc gm/ml	Amt. Used ml	Calc Mers gm
Calcium acrylate	0.33	3.0	1.0
Ammonium persulfate	0.1	1.5	0.15
Sodium thiosulfate	0.1	1.5	0.15
Ferrous sulfate	0.025	0.5	0.005
Water	1.0	5.0	11.5

Table A.5

Data for Test #1 in Table 4.1

mono mass = 3 ml x 0.33 gm/ml = 1.0 gm

Water = 3 + 1.5 + 1.5 + 0.5 + 5.0 = 11.5 gm

A.3.5 For 4.4: Chemical Dose in Soil

The molds took 150 ml of sand which weighed 225 $\pm$ 0.5 gm.

Monomer amount:

$$\frac{\text{Mono}}{\text{Mono + Soil}} \times 100 = \text{mono \%}$$

Therefore, for 3% calcium acrylate.

$$\frac{\text{mono}}{\text{mono} + 225} = 0.03$$

mono = 6.96 gm = 7.0 gm

The initiator amounts were not included due to their small amounts.

persulfate = 7.0 ÷ 16 = 0.44 gm

thiosulfate = 0.44 gm

Amount of monomer solution:

$$\frac{7.0 \text{ gm mono}}{0.4 \text{ gm/ml}} = 17.5 \text{ ml}$$

Water = 150 ml sand x 0.33 sand = 50

	Calculated			
	Mass gm	Soln conc gm/ml	Soln ml	Actual Soln ml
Calcium Acrylate	7.0	0.4	17.5	17.5±0.2
Persulfate	0.44	0.05	8.8	9.0±0.1
Thiosulfate	0.44	0.1	4.4	4.5±0.1
Water	50	1.0	19.3	20.0±0.2
Sand	225	1.5	150	150 ±0.5

Table A.6

Calculated and Actual Chemical Doses

The pipette had a 10 ml capacity and was calibrated in 0.1 ml increments. The sand was weighed to the nearest half gram. With leakage and/or spillage in sample preparation the monomer concentration in the soil would be accurate to about 2%.

3.6 For 4.5: Compression Strength

The Tinius-Olson test machine gave the total load on the sample to the nearest ten pounds. Measurement of the sample area was done with a ruler calibrated in 1/16-inch units.

$$\text{Area} = 2 \pm 1/32 \text{ inch} \times 2 \pm 1/32 \text{ inch}$$

$$\text{Area} = 4.0 \pm 0.126 \text{ in}^2 = 4 \pm 3\%$$

Total load at failure for a 3.13% calcium acrylate sample in Figure 4.5 was 7930 pounds.

$$\frac{7930 \text{ pounds}}{4 \text{ inch}^2} = 1983 \text{ psi} \pm 3\%$$

$$\text{Compressive failure} = 1983 \pm 59 \text{ psi}$$

3.7 For 4.6: Drying

Time hr.	Weight gm	% Weight Change
0	270.0	0.00
4	267.8	-0.81
15	260.7	-3.44
24	225.3	-5.44
38	248.5	-7.96
45	245.5	-9.07
62	239.0	-11.48
134	230.1	-14.78
206	229.6	-14.96
230	229.6	-14.96

Table A.7

Data for Drying a Single 3% Sample

At 24 hours:

$$\frac{(225.3 - 270)100}{270} = -5.44\%$$

These calculations are similar to the ones for compacting in Section 4.8.

For 4.8: Reduction of Various Parameters Upon Compression

$$\% \text{ reduction} = \frac{100\ (\text{Param}\ ((\text{Pres}=0)) - \text{Param}\ ((\text{Press}=P))}{\text{Param}\ (\text{Pres}=0)}$$

Weight (p = 0 psi) = 275 gm

Weight (p = 938 psi) = 267 gm

$$\frac{(267 - 275)100}{275} = 2.9\% \text{ reduction of wt.}$$

Weight H_2O (p = 0 psi) = 50 gm

Weight H_2O (p = 938 psi) = 50 - (275-267) = 42 gm

For 4.9: Water Immersion for Figure 4.13

	Oil	Control
Dry	36.0 gm	34.2 gm
Dry and Oil	37.2	34.2

	Oil		Control	
Time min.	Wt. gm	%	Wt. gm	%
0	37.2	0.00	34.2	0.00
1	37.7	1.34	36.8	7.60
2	37.7	1.34	37.1	8.48
4	38.0	2.15	37.5	9.65
6	38.3	2.96	37.8	10.53
10	38.4	3.23	37.8	10.53

Table A.8

Data for Stabilized Soil Immersed in Water as Presented in Figure 4.13

$$\% \text{ weight gained} = \frac{(wt\ (t=t) - Wt\ (t=o)\ 100}{Wt_{(t=o)}}$$

For oil at t = 4 min:

$$\frac{38.0 - 37.2}{37.2} = 2.15\% \text{ weight gained}$$

For Figure 4.12:

For Oil and Water:

Wt (t=o) = 36.0 gm
Wt oil = 1.2 gm
Wt (t=t) = Wt (t=t)

For 4.13: Amount of Mixing Water Needed as Seen in Figure 4.1

% Sand	Soil Wt gm	Water gm	% Water
100	150	33	22
80	150	33	22
60	150	39	26
40	150	43.5	29
20	150	52.6	35

Table A.9

Data for Soil Composition and Mixing Water

$$\% \text{ sand} = \frac{(Wt.\ sand)}{Wt.\ soil}\ 100$$

$$\% \text{ water} = \frac{(Wt.\ water)}{Wt.\ soil}\ 100$$

Soil mix: 60 gm sand, 45 gm silt, 45 gm clay

Soil = 60 + 45 + 45 = 150 gm

% Sand = $\frac{(60\ gm)}{150\ gm}$ 100 = 29%

% Water = $\frac{(43.5\ gm)}{150\ gm}$ 100 = 29%