INVESTIGATION OF BASE-EXCHANGE AND POLYMERIZATION FOR THE STABILIZATION OF CLAYS

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Signature of Author______________________________________

Department of Civil and Sanitary Engineering, January 8, 1949

Signature of Professor in
Charge of Research ________________________________

Signature of Professor in Charge
of Chemical Phases of Research ________________________
(Professor of Chemical Engineering)

Signature of Chairman of Department
Committee on Graduate Students ______________________

Cambridge, Massachusetts
January 8, 1949

Professor Joseph S. Newell
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts

Dear Sir:

In partial fulfilment of the requirements for the degree of Doctor of Science in Civil Engineering at the Massachusetts Institute of Technology, I submit herewith a thesis entitled, INVESTIGATION OF BASE-EXCHANGE AND POLYMERIZATION FOR THE STABILIZATION OF CLAYS.

Respectfully,

Victor F. B. de Mello

VFBdM:dd

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ACKNOWLEDGMENTS

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The author wishes to express his sincere gratitude, primarily to Professor E. A. Hauser for having inspired this investigation and for his encouragement and advice in the early stages when the author was a novice in a field that entailed colloid chemical work almost completely; to Professor D. W. Taylor for his advice and constant encouragement; and to Professor W. H. Stockmayer for his very helpful advice on some of the polymerization work.

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Finally, for critically reviewing the draft of this presentation special thanks go to Professor D. W. Taylor, Professor E. A. Hauser, Mrs. M. S. Pomeroy and Dr. T. W. Lambe.

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FOREWORD

The study of chemical soil solidification, or stabilization, involves a new branch of soil mechanis--namely, the study of modifications of the engineering properties of soils by chemical admixture. The proper understanding of such a study, therefore, clearly necessitates a fair knowledge of chemistry.

Further, this investigation was undertaken as specific for clays, the thesis study representing an attempt to apply colloid chemical knowledge to the chemical stabilization of clays. Civil Engineers are well acquainted with the physical concept of particle size according to which they readily concede the important fraction of most clays to lie in the colloidal range of dimensions. Special emphasis must, therefore, be laid to the fact that the proper understanding of such a study is dependent upon adequate familiarity with colloidal chemistry.

Since it is inevitable that Civil Engineers do not, in general, have the knowledge of chemistry and colloid chemistry needed for the thorough understanding of this thesis study, the presentation of this thesis to Civil Engineers poses a very difficult problem. The author considers it highly unsatisfactory to use in the presentation of the actual subject matter of the thesis definitions and explanations that will at best consist of extracts from standard elementary textbooks on inorganic, organic and colloid chemistry. In order to assist the readers in refreshing their memories on unfamiliar chemical terminology and some of the fundamental colloid chemical concepts involved, the author is appending 1) a glossary of chemical terms (Appendix II, page 213) and 2) a brief presentation of the clay mineral concept, upon which is based the understanding of the fundamentals of colloid chemistry that are applicable to the common clay minerals. (Appendix III, page 215)

INTRODUCTION

In October, 1946, the Civil Engineering Department of the Massachusetts Institute of Technology undertook a research project on the solidification of soils by chemical treatment, sponsored by the U.S. Engineer Corps.

Interest in solidification or stabilization of soils by chemical admixture has grown steadily in the past few years. With bare indications of success on hand, interested parties have extrapolated their aims to the point of miraculous treatments which could be sprayed from the air so as to solidify any soil, rapidly and fairly permanently. For military emergencies, it may well be imagined that the achievement of such spectacular solidifying treatments which could render any soil suitable for the landing of aircraft, would be a tantalizing objective.

In connection with this research project the author had the opportunity to conduct the extensive literature review on all work directly or indirectly related to soil solidification by chemical treatment. A brief review of this study would serve as an excellent spring-board for this thesis study, but it is felt that, since the Final Report of the first phase of the Soil Solidification Project has already presented that material, the introductory remarks may here be limited to the mention of a few of the salient points. The readers are requested to refer to the Report on the Literature Review(11)* if they wish to ascertain the details that are herein omitted.

Since this brief survey is merely attempted with a view to emphasizing the significance of this thesis study, it is thought advisable to subdivide the effect of the chemical admixture into two categories, namely an inherent strength increase, and an improvement of the water-stability of the soil. If we subdivide soils into the commonly employed nomenclature of sands, silts, and clays, and for the present restrict our attention to clays, a study of all work hitherto done on the chemical solidification of soils will make one fact glaring and inescapable - there is no treatment that inherently increases the shearing strength of a clay.**

The calcium chloride and sodium chloride admixtures do not presume to have any direct strengthening action. The use of Portland Cement, which is a very successful method of solidifying sands, drops in applicability very markedly as one moves down the scale of particle-size of soil: cement on hydration effects a rigid bond between particles, but since

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* Numbers in parentheses refer to numbers in the Bibliography found on page .

** This statement has to be modified a little. The fact is that treatments that do increase the shearing strength of a clay (e.g., Portland Cement) use excessive quantities of admixture because the first fraction of the treatment inactivates the clay, the rest of the treatment then acting on it as on a plain filler.

soil grains act merely as inert fillers that are "spot-welded" by the cement to neighboring soil grains, cement treatments on clays are very poor. Bituminous treatments are conceded to be of two types: in the case of cohesionless soils, the use of higher viscosity bitumens imparts the necessary cohesion, but in the case of clayey soils the bituminous treatment merely waterproofs. The sodium silicate solidification process is applicable only to sands; although a recent research project studied the possibility of using silicates of soda for the stabilization of clays, there is no clearly distinguishable data to indicate any promise. Finally, the recently opened field of natural and synthetic resins emphasizes the same point. All of the natural resin treatments merely serve as waterproofing treatments, with the exception of Stabinol which consists of a mixture of a natural resin and Portland Cement - and perhaps for that very reason is not reported as being very successful in the solidification of clays. The possibilities in the use of synthetic resins are so many and so varied, that the author is loth to make any statement concerning their applicability for solidification of clays, but research reports to date have reported success merely in the use of resins for the solidification of sandy or silty materials.*

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* As a matter of fact, this thesis study may well be considered to be within the broad field of application of synthetic resins to solidification of soils.

Thus one of the important deductions that arose out of the literature survey, was the fact that no chemical method is at present available for strengthening a clay. Some of the more effective chemical treatments may still be applicable to clayey soils, but in effect the clay fraction is a deteriorating component. The fatter the clay, the more active the clay, the greater is the decrease in effectiveness of the solidifying treatment. Of course, practically all chemical stabilization work has until now been carried out on surface soils in connection with highway and airport construction. Thus it may well be argued that the case of solidifying a saturated all-clay soil has never arisen in highway and runway construction - which merely touches off another point which the author deems worthy of mention as a prelude to this thesis study.

Practically all the research work done to date on chemical soil solidification has used so-called natural soils. Here it is Virginia Sandy Loam, there it is Clermont Silty Clay; and in all cases the reader is left utterly at a loss to analyze the results from the point of view of quantitative effects contributed by the various components. A few of the more recent investigations have shown a desirable trend towards initiating the research with simplified soil systems: in the case of some of the latest research on the use of synthetic resins for soil solidification, clean silica sand was used, and in the case of the investigation of "Silicate of Soda as A Soil Stabilizing Agent"(12) the action of the silicate of soda was first studied on samples of several pure clay minerals.

Finally, the review of literature made the author aware of a rather striking correlation between the "activity" of a clay as regards engineering characteristics and the chemical reactivity of the clay. And in general it seemed that the reason why solidifying treatments became less and less successful as they were applied to fatter and fatter clays, could be sought in the philosophy of the treatments. These treatments expected the clay component of the soil to remain merely as an inert filler, as the sand and silt grains appeared to do quite obligingly. It was conceded that the larger surface area of filler would require suitable increases in percentage treatments, and due arrangements were made to meet that demand. But the clay had a surprise in store: it refused to act as an inert filler. It often reacted with the admixed chemical, inactivating considerable fractions of it. Unwilling to relinquish the original treatments, and determined to achieve results in spite of the clay, investigators had to resort to using excessive amounts of the treatment, or in some way to anticipate the treatment by another chemical treatment that would satiate the clay. Consider the Portland Cement treatment, for example: in the case of many clays it was found that base-exchange might take place, depriving the Portland Cement of some of its calcium, and thus it was found that either an excess of

Portland Cement had to be used, or else a pretreatment of the clay with calcium chloride might prove advantageous.

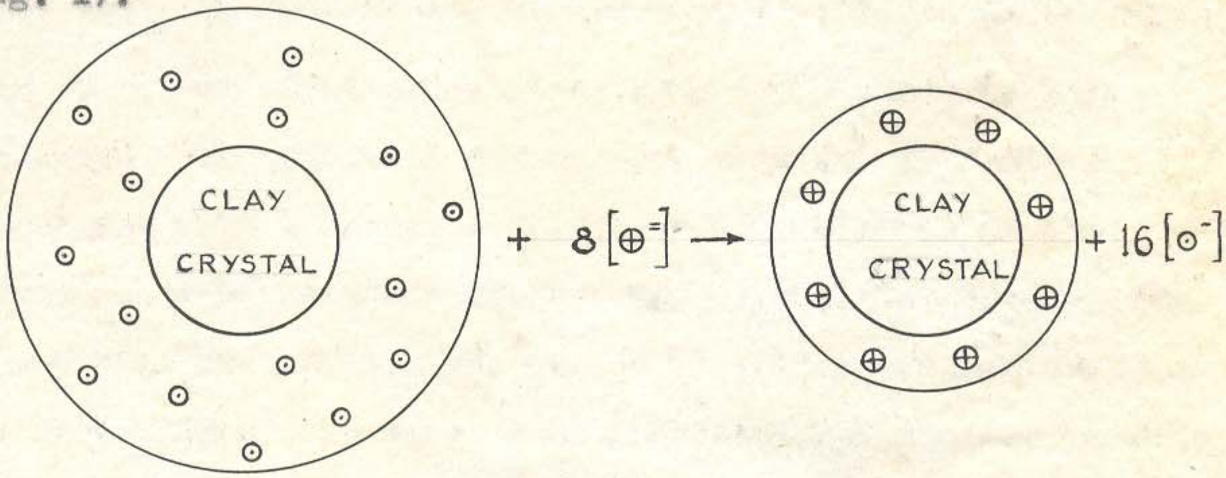
Thus it is that out of the literature review arose the three main points that led to this thesis investigation. First, the obvious need for some work on the chemical treatment primarily of clays; second, the firm decision to initiate the investigations with the use of a simplified soil system - namely, a pure clay mineral; and third, the interesting objective of attempting a solidifying treatment that might coax the clay into cooperation rather than hand-cuff it into submission.

BACKGROUND MATERIAL

It was cursorily stated in the Introduction that there appeared to be an unmistakable correlation between the engineering properties of clays and their chemical reactivity. The nature of the chemical reactivity must be promptly specified: the author has in mind the common base-exchange reaction that is so often mentioned in connection with clays. In the past few decades, since its discovery, the base-exchange reaction of clays has proved to be the one important reaction by means of which the properties of clayey soils may be radically changed.

For the sake of clarity, space will here be devoted to mention of some of the details intimately connected with the colloid chemistry of the clay minerals. It has long since been established that clay particles are crystalline platelets. The crystallographic structures of these crystalline platelets have been studied by careful X-ray diffraction work, and on the basis of these structures it may be asserted that the clays commonly encountered in Soil Mechanics work fall into one or more of the following groups: the montmorillonites, the illites, and the kaolinites. To a greater or smaller extent, the clay minerals exhibit the property of base-exchange, and a consideration of the crystal structure of the clay minerals will serve to explain this property. However, a discussion of the crystal structures of the clay minerals would here represent a lengthy digression. Appendix III of this thesis, taken from the Final Report on the first phase of the Soil Solidification Project(11) presents a summary of the clay mineral concept, and for further information the interested reader is requested to refer to the bibliography in the above reference.

The crystal units of the clay minerals as they occur in nature are usually negatively charged and, therefore, carry enough adsorbed cations (positively charged ions, such as Na^+, Ca^{++}) to establish the balance of charges dictated by the Law of Least Free Energy. In contact with water, however, these adsorbed cations dissociate from the minute clay crystals into the surrounding water. In the presence of water, therefore, the clay mineral units surrounded by their positive counterions form the colloidal micelle which participates in the base-exchange reaction as pictured below (Fig. 1).



⊙ Monovalent cation; e.g., Na^+ in the case of sodium-clay

⊕ Divalent cation; e.g., Ca^{++}

- Monovalent anion; e.g., Cl^-

The counterions of the clay particle can be exchanged with cations from the dispersion medium. Thus, for example, by adding calcium chloride, $CaCl_2$, to a dispersion of a sodium-clay, we will obtain a calcium-clay by base-exchange of calcium (Ca^{++}) ions for the sodium (Na^{+}) counterions. (Note: henceforth in this thesis the exchangeable base associated with a clay will always be specified when naming a clay - thus a sodium-montmorillonite, a calcium-kaolinite.)

The specific reaction in the case of the example given may be written:

$$\boxed{\text{clay}}\begin{matrix}-Na\\-Na\end{matrix} + CaCl_2 \longrightarrow \boxed{\text{clay}}\big\}Ca + 2\ NaCl$$

Such a base-exchange reaction will obviously be more pronounced, the greater the number of exchangeable ions that the clay particle carries. The clay particle in Fig. 1 is shown carrying sixteen sodium (Na^{+}) ions: it is, therefore, able to adsorb eight divalent calcium (Ca^{++}) ions by base-exchange. The number of sodium ions that are actually associated with a particle of sodium-clay depends on the structural configuration of the clay crystal, as is explained in Appendix III. Since the number of polyvalent cations that can be exchanged for the sodium ions of a sodium-clay depends on the number of sodium ions associated with the clay particle, it is evident that the number of polyvalent cations that can be exchanged will depend on the structural configuration of the clay crystal. It is difficult to determine the number of cations that can be adsorbed by each individual clay particle, and so the common measure used relates to the number of cations that are adsorbed per 100 grams of clay. This measure of the ability of a clay to adsorb cations is called the cation-exchange or base-exchange capacity, which is expressed in milliequivalents of cations per 100 grams of clay. Montmorillonites have the highest exchange capacity, ranging from 60 to 100 me., illites follow with exchange capacities ranging from 20 to 40, and kaolinites have the lowest exchange capacities, 3 to 15 me.

The comments on base-exchange will here be limited to the above two paragraphs, since more detailed consideration of its theoretical aspects will be given in a subsequent chapter. Two basic points have been made in connection with the chemical reactivity of clays: the important considerations are the base-exchange capacity, and the nature of the exchangeable base present. Intensive research on base-exchange of clays has been carried out in the fields of colloid chemistry and agriculture, and more recently the knowledge thereby accumulated has been utilized by soil mechanics investigators interested in opening the field of soil chemistry for its promise in soil stabilization. It is significant to note that almost invariably the nature of the effects of the clay minerals and their exchangeable bases on the engineering properties of soils were predictable in a qualitative manner on the basis of existing knowledge of the fundamentals of colloid chemistry.*

Let us consider very briefly the qualitative relationships between the engineering properties of clayey soils and 1) the magnitude of the exchange capacity, and 2) the nature of the exchangeable bases, associated with the clay component.

General Relationships Between Exchange Capacity of a Clay and Some Engineering Properties

It should first be noted that in order to eliminate the effects of exchangeable bases, the comparisons should be made with clays that are all saturated with the same base. It is true, however, that the preponderance of the effect of the clay mineral is often felt in spite of changes in saturating cations; for example, the behavior of montmorillonites is in a class quite distinct from that of kaolinites, regardless of the exchangeable base.

Originally almost all the research on correlations between engineering properties and "chemical" composition of clays employed the concept of the silica/sesquioxide ratio (SiO_2/R_2O_3, where R_2O_3 represents Al_2O_3, Fe_2O_3). Practicability favors the retention of that concept in most soil mechanics work, but fundamental research has found it necessary to revert to the specific determination of the clay-mineral

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* Serious deviations from this norm are possible and probable in soils of high organic content, etc.

component and the exchange capacity. Laboratory investigations have confirmed theoretical expectations that the exchange capacity is fairly directly related to the silica/sesquioxide ratio. In considering the three main types of clay minerals, it is easy to conclude by merely examining their crystallographic structures, that the montmorillonites have the highest SiO_2/R_2O_3 ratios, the illites follow, and kaolinite has the lowest SiO_2/R_2O_3 ratio. Simultaneously be it noted that the exchange capacities of these three principal clay mineral groups follow the same progression. Hence in defining general trends of the effects of exchange capacity on clay properties, it is sufficient to define the relative behavior of montmorillonites, illites and kaolinites.

The montmorillonites have a high water-holding capacity. They also have very low permeabilities; illites are intermediate, and kaolinites have relatively much greater permeabilities. The montmorillonites also absorb much more water than kaolinites, although at a much slower rate. As a result of the high water-holding capacity and swelling properties of montmorillonites, these clays tend to show the greatest amount but slowest rate of consolidation. Finally, because of the high water-holding capacity, montmorillonites have high liquid limits and plasticity indices.

All of these results can be explained qualitatively by consideration of the crystal structures of the minerals and the fundamentals of colloid chemistry.

A general conclusion that becomes apparent is that the montmorillonites are probably the most troublesome clays in soil engineering: their extreme sensitivity to change by contact with water makes them particularly annoying in soil stabilization work. Simultaneously, however, their high exchange capacity makes them the most suited for modification of properties by base-exchange.

General Relationships Between the Exchangeable Base of a Clay and Its Engineering Properties

The importance of the effect of exchangeable bases on the engineering properties of clays is obviously greatest in the case of montmorillonites, which have the highest exchange capacities.

A montmorillonitic clay containing sodium as the exchangeable base can take up two to three times as much water as a similar clay containing calcium: in general the montmorillonites saturated with trivalent cations (Al^{+++}, Fe^{+++}) have smaller water affinity than the montmorillonites saturated with divalent cations (Ca^{++}, Mg^{++}, Ba^{++}, Pb^{++}) and these again have much smaller water affinities than the montmorillonites saturated with monovalent cations (Li^{+}, Na^{+}). A sodium-montmorillonite will, therefore, have a lower permeability, a greater total amount of consolidation under a given load, and a slower rate of water absorption and shrinkage than a calcium-montmorillonite. At the same water content a sodium-montmorillonite has a much higher shearing strength than a calcium-montmorillonite; but since a calcium-montmorillonite is in turn more readily compacted, a comparison of shearing strengths at a fixed compactive effort will not show the calcium-montmorillonite at such a loss. No systematic quantitative results are, however, available on these comparisons; at best it may be assumed that the difference between the shearing strengths of sodium-montmorillonite and calcium-montmorillonite subjected to the same compactive effort is probably small.* Hence the advantage of water stability effected by exchange of calcium for the sodium is the determining factor favoring this exchange for soil stabilization, when compaction is used.

Complex Metal-Organic Ion Exchange

The above two paragraphs outline the general scope of base-exchange hitherto applied in soil engineering work. Recent developments in the field of colloid chemistry considerably broaden the promise in the use of base-exchange for the stabilization of clays. These advances have been based on the use of base-exchange with complex metal-organic ions, which will herein be briefly explained.

When calcium chloride, $CaCl_2$, is dissolved in water, it ionizes as represented by the equation:

$$CaCl_2 \rightleftharpoons Ca^{++} + 2(Cl^-)$$

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* A few tests run by the author checked this estimate quite well. See page .

Such a solution of calcium chloride will, by virtue of its calcium (Ca^{++}) ions, enter into a base-exchange reaction with a suspension of sodium-bentonite; this exchange reaction may be represented as follows:

$$\boxed{\text{clay}}\begin{matrix}-Na\\-Na\end{matrix} + Ca^{++} \longrightarrow \boxed{\text{clay}}\rangle Ca + 2(Na^{+})$$

The case above detailed represents base-exchange of a simple cation. Many polyvalent salts, however, are capable of ionizing to yield complex ions, and then the base-exchange reaction takes place with the supplied complex ion just as easily as it would with a simple cation. Lead acetate, $Pb(CH_3COO)_2$, for example, when dissolved in water ionizes to give either simple divalent lead ions (Pb^{++}) or complex monovalent lead acetate ($PbCH_3COO^{+}$) ions.

$$Pb\ (CH_3COO)_2 \rightleftharpoons (PbCH_3COO)^{+} + (CH_3COO)^{-}$$

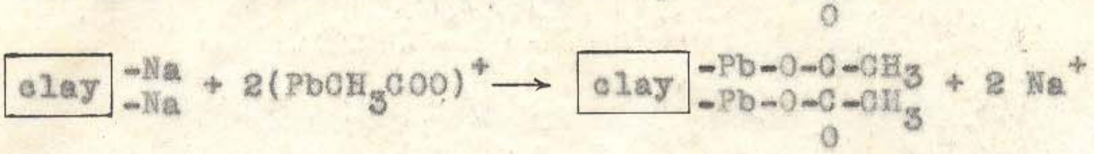
and also $$Pb\ (CH_3COO)_2 \rightleftharpoons Pb^{++} + 2(CH_3COO)^{-}$$

Such a salt as lead acetate, $Pb(CH_3COO)_2$, is called a difunctional salt, and its ionization behavior is represented by the following equation:

$$Pb(CH_3COO)_2 \rightleftharpoons (PbCH_3COO)^{+} + (CH_3COO)^{-} \rightleftharpoons Pb^{++} + 2(CH_3COO)^{-}$$

The nature of the ionization is controlled by the concentration of the solution, the complex monovalent ion being more abundant in concentrated solutions. It need hardly be pointed out that this phenomenon cannot occur with salts of monovalent cations.

Base-exchange of sodium-bentonite with lead acetate can now be seen to contain two possibilities:



$$\boxed{\text{clay}}\begin{matrix}-\text{Na}\\-\text{Na}\end{matrix} + 2(\text{PbCH}_3\text{COO})^+ \longrightarrow \boxed{\text{clay}}\begin{matrix}-\text{Pb}-\text{O}-\overset{\text{O}}{\text{C}}-\text{CH}_3\\-\text{Pb}-\text{O}-\underset{\text{O}}{\text{C}}-\text{CH}_3\end{matrix} + 2\ \text{Na}^+$$

and $$\boxed{\text{clay}}\begin{matrix}-\text{Na}\\-\text{Na}\end{matrix} + \text{Pb}^{++} \longrightarrow \boxed{\text{clay}} > \text{Pb} + 2\ \text{Na}^+$$

the exchange with the complex lead acetate ion prevailing in concentrated solutions.

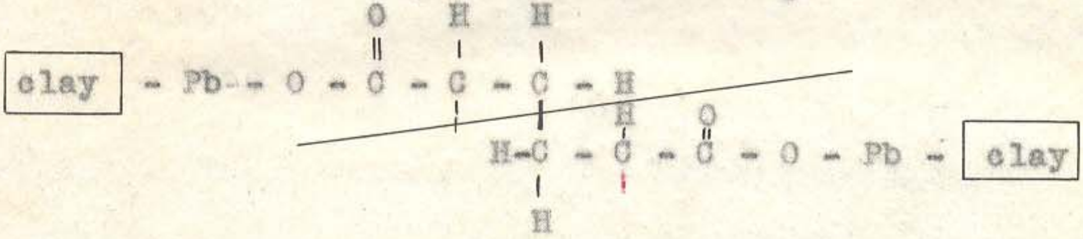
Research on the use of bentonite for the production of "synthetic mica", Alsifilm, yielded results of much interest in connection with base-exchange of simple and complex ions, but there is no knowledge of the possible effect of complex ion base-exchange on the engineering properties of clays.

<u>Base-Exchange With Polymerizable Complex Metal-Organic Ions</u>

The behavior described above in connection with lead acetate is not specific for lead acetate: a number of salts of divalent metals exhibit the same phenomenon. In general, it may be stated that salts of weak acids are capable of ionization into complex ions. A number of organic acids are relatively weak acids.

Of specific interest to this study are the unsaturated monobasic acids, such as acrylic and methacrylic acid, which are weak acids forming difunctional salts with divalent metals. It is thus possible to attach, by base-exchange, the complex lead acrylate ($CH_2CH\ COOPb^+$) or lead methacrylate ($CH_2C\ CH_3\ COOPb^+$) ion to a sodium-bentonite clay.

This fact is of special interest because, in view of the unsaturated nature of the acid radical employed, the organic component of the complex ion is capable of polymerization. The nature of polymerization will be explained in a subsequent chapter, but for the purposes of the present outline it may be considered a reaction which chemically bonds one such organic radical to another. Thus two clay particles with attached lead acrylate ions can by polymerization be chemically bonded to one another as shown by the following schematic drawing:



This fundamental invention, which has been termed the discovery of inorganic plastics, is described in U. S. Patent #2,401,348, "Molding Composition, Molded Product, and Method of Making" granted to Dr. E. A. Hauser and Mr. E. A. Dannenberg of M. I. T., June 4, 1946. The specific process described as an example in the patent is, in short, the following: bentonite saturated with base-exchanged lead acrylate is dried and powdered; this powder is then heat-and-pressure molded resulting in a hard resinous product. The polymerization of the acrylic radical, which is accomplished through the elevated temperature (with or without the use of a catalyst like benzoyl peroxide), effects a strong chemical bond between the clay particles. Furthermore, since the surface of the clay particles is thus rendered organic in nature and highly insoluble in water, the molded product is quite resistant to attack by water; this is especially true if the precaution has been taken to wash the clay free of exchanged sodium ions.

The specific process described above by an example serves to give a general idea of the invention in terms of a particular application. Of far greater importance, however, is the understanding of the significance of the new idea involved. It will be recalled that the tremendous and ever-growing plastics industry is fundamentally based on polymerization. Henceforth, base-exchangeable materials such as clays could in some measure share in the advances of the plastics industry. The degree to which this might be true would depend on the specific conditions dictated in any given circumstance.

The way has been opened, and wonderful possibilities arise.

Scope

The previous chapter had as its purpose the brief outlining of the ideas which originated this thesis investigation. In view of the fact that the base-exchange reaction is available for improvement of the engineering properties of clays, it was thought desirable to study the soil stabilizing effectiveness of the base-exchange treatment that seemed most promising, namely, base-exchange followed by polymerization. The aim of this investigation may accordingly be described as the following: to develop the conditions necessary for rendering the base-exchange and polymerization treatment for clays a practical possibility, and to investigate the effectiveness of such a treatment in the stabilization of clays. The investigations are fraught with the compromise between the desire to study the fundamental phenomena systematically and the objective of early arriving at an estimate of the effectiveness of the treatment under conditions approximating those of practical use.

It was decided to confine the bulk of the investigations to sodium-bentonite clay for at least three cogent reasons. Firstly, because the cornerstone of this study was the colloid chemical work on sodium-bentonite reported in the U. S. patent referred to in the previous chapter. Secondly, because thereby the objective was achieved of studying a simplified system of what might be considered a pure synthetic clay soil. Finally, because simultaneously the results obtained with sodium-bentonite would be highly significant as representing the order of magnitude of results to be expected at the extremity associated with very active clays of high base-exchange capacity.

A few tests were run on calcium-bentonite and hydrogen-kaolinite in order to assist in the interpretation of results.

All such tests were carried out in a manner approximating what might in field conditions represent the treatment of a clay at natural water content with a specific chemical admixture. The details of such conditions will be discussed later, but one important consideration must here be emphasized: the process of admixture obviously disregards the advisability of securing the optimum conditions of cooperation from a clay at natural conditions by not disturbing its "structure". Hence all the work herein reported must clearly be interpreted as connected with remolded clays, and the problem of optimum means of application of the treatment to clays is herewith understood not to have laid within the scope of this thesis. Actually, from the point of view of field practice admixing processes in clays are rather difficult, and therefore the incentive to develop suitable processes of application of this treatment is greatly multiplied.

Breaking down the work into fairly distinguishable sections, it may be summarized as follows:

1) Investigate the possibility of effecting polymerization of salts like calcium acrylate and calcium methacrylate in aqueous solutions at room temperatures. The application of the base-exchange and polymerization treatment to clays saturated with water obviously hinged on the achievement of positive results in this investigation.

2) Study the pertinent phases of the base-exchange reaction occurring on addition of calcium methacrylate to a sodium-bentonite clay gel at various water contents. The significance of this study was primarily connected with the evaluation of the effects of base-exchange alone, without subsequent polymerization, on the properties of clays.

3) Study base-exchanged and polymerized clay systems in comparison with the original untreated clays and with clays merely base-exchanged. The comparison with the original untreated clay was necessary for an overall evaluation of the effectiveness of the treatment; the comparison with the base-exchanged but unpolymerized clay was dictated by the academic interest in assessing the contribution of the polymerization to the properties of the clay.

The entire investigations were carried out on clay systems saturated with water at the start; even though the clay minerals were available in powder form, the author deemed it essential to begin by preparing clay gels at reasonable water contents, to simulate clay soils saturated with water. Clay soils occurring naturally are either wet and essentially saturated, or, if at all dry, form very hard clods and surfaces--they do not exist in powder form. Furthermore, dry clay particles may well be treated as discrete particles of cohesionless material, with the added advantage of much better surface adhesion. Clay particles are associated with troublesome behavior only when wet; in fact, the clay particle unit as usually considered has its hull of firmly adsorbed water around it. Hence the work was specifically aimed at the use of clay gels at natural water contents for the appropriate clay minerals.

RESUME OF SIGNIFICANT RESULTS

This thesis investigation can only be rightly viewed as a preliminary investigation. With the conclusion of the work herewith presented, the method of treatment studied cannot yet be properly evaluated in terms of applicability to practical problems. The only appropriate sequel to this work is the furtherance of the investigations, notably along lines suggested in Chapter XI. This thesis should, therefore, be carefully studied in every detail by those intending to further the investigations. For such readers, for whom every single item detailed in the following chapters should be significant, it is inadvisable and difficult to present a summary of "significant results".

However, the conclusion of the thesis does mark the conclusion of the preliminary investigations. The summary presentation of some of the more significant results is, therefore, appropriate. Obviously the reader must be well guarded against reading detailed information from the generalized statements that are made in this section.

The clays experimented with are sodium-bentonite, calcium-bentonite and hydrogen-kaolinite. In all three cases, the shear strength characteristics are of major interest; but only in the case of sodium-bentonite is the decrease of the water affinity of the clay by the treatment a factor of great importance. The discussion of water affinity is, therefore, limited to consideration of the sodium-bentonite case. In the following items it is implied, unless otherwise stated, that calcium acrylate is used for the base-exchange reaction which is capable of subsequent polymerization. For the polymerization, the catalysts employed are sodium thiosulfate and ammonium persulfate.

1) The base-exchange reaction achieves a very effective reduction of water affinity in the case of sodium-bentonite. In the case of such clays as calcium-bentonite and hydrogen-kaolinite, no noticeable decrease of the water affinity of the clay is effected. The base-exchange reaction alone controls the water affinity.

Unfortunately, as was expected, the base-exchange reaction involves a very sharp decrease of the shear strength of the clay. This decrease of strength is attributed partly to base-exchange and partly to the effect of the excess electrolyte in solution. The decrease of strength is particularly pronounced in the case of sodium-bentonite and hydrogen-kaolinite, but still is noticeable in the case of calcium-bentonite.

2) Polymerization of salts like calcium acrylate is effectively achieved, at low temperatures in the presence of water, by the use of appropriate redox catalysts. Several sets of redox catalysts were employed, a wide variation in their effectiveness being evident. For the treatment of clays it was found that among the sets of catalysts tried, sodium thiosulfate and ammonium persulfate in appropriate proportions gave results pronouncedly better than corresponding results obtained with other sets of catalysts.

It was found that complete polymerization and best strength results were obtained only when appreciable quantities of the catalysts were employed. The catalysts, therefore, affected the clay system in two ways: (a) through effecting the polymerization (b) through their presence in the system affecting other reactions, such as the base-exchange reaction. Hence the sodium thiosulfate and ammonium persulfate catalysts could be expected to modify the base-exchange reaction, especially by making ammonium ions available for exchange. Such exchange invariably thwarted to some extent the beneficial influence of the original base-exchange reaction on the water affinity: thus the samples of polymerized clay were quite often found to have slightly higher water affinities than those of the base-exchanged clay, prior to the addition of catalysts.

3) Discussing the effectiveness of the overall treatment in the stabilization of the three different clays, the following rough conclusions can be drawn.

(a) In the case of sodium-bentonite, the net effect of the polymerization is to achieve the recovery of the shearing strength of the untreated clay. The use of increasing amounts of treatment does not change the shearing strength, but improves the water affinity characteristics. Unfortunately it appears that the water affinity characteristics are "acceptable" only when appreciable amounts of calcium acrylate are used, resulting in treatments of at least 12% by weight of the wet clay.

(b) In the case of calcium-bentonite, moderate strength increases are obtained. Clay samples treated with admixtures totalling about 9% by weight of the wet clay, attain strengths about 2.5 times the strength of the untreated clay; correspondingly, treatments of about 4.5% by weight of the wet clay increase the strength of the clay to about 1.4 times the original strength.

(c) In the case of hydrogen-kaolin, quite pronounced strength increases are obtained. With a 5% treatment, the clay at 41% water content has its shearing strength increased from 10.3 psi to 34 psi; the clay at 52% water content has its strength increased from 1.5 psi to 19 psi; and the clay at 65% water content has its strength increased from 0.4 psi to 10 psi. Thus in the case of kaolinite, the ratio of the strength of the treated sample to the strength of the original clay varies, increasing with the water contents mentioned from 3.3 to 12.5 to 28.

(d) Analysis of shearing strength characteristics of the three clays indicates the existence of a definite relationship.between the ratio

$$\frac{\text{strength of polymerized sample}}{\text{strength of base-exchanged but unpolymerized sample}}$$

and the ratio $\frac{\text{gm. of calcium acrylate added}}{\text{gm. of dry clay}}$,

regardless of water content for each clay. Comparing these curves for the three clays it appears that the treatment is about equally effective when used with sodium-bentonite and calcium-bentonite. The results obtained on the kaolinite samples indicate that the treatment is much more effective with kaolinite than with bentonite, in fact, in the order of magnitude of 100 times as much.

4) The treatment should be viewed as being of interest only in cases where the clays cannot be subjected to consolidation subsequent to treatment. Consolidation of the samples to any appreciable pressure tends to wipe out the difference in shear strength of polymerized samples in comparison with samples merely base-exchanged.

5) The stress-strain characteristics of treated samples were studied only in the case of sodium-bentonite. The use of any appreciable percent treatment involved very distinct modifications of the stress-strain characteristics of the clay. Thus, for instance, the peak shear stress value

was obtained at much higher values of per cent strain in the case of treated samples.

Visual and tactual evidence support the statement that major changes in the stress-strain characteristics of the clays are also produced by the treatment in the case of calcium-bentonite and hydrogen-kaolinite.

MATERIALS AND CHEMICALS USED

The bulk of the investigation was conducted on a sodium-bentonite from Wyoming, for which the following analysis is given.(7)

Density of Dry Wyoming Bentonite 2.703

	%
Loss at 105°C	6.20
SiO_2	58.88
Fe_2O_3	2.86
Al_2O_3, Mn_3O_4, P_2O_5	26.16
CaO	0.80
MgO	2.67
Na_2O/K_2O as Na_2O	2.13
SO_3	0.00
	93.30

The powder was taken as commercially supplied, there being some impurities. No particular reason could be found for super centrifuging suspensions of the clay powder for the separation of the impurities and for the fractionation of the clay to a specific particle-size range. Consequently, the base-exchange capacity of the clay with its impurities is found to be only about 78 milli-equivalents per 100 grams of clay, (Fig. 2, p.) instead of the higher figures (about 100 me.) usually quoted for the same clay when purified.

Using the same sodium-bentonite clay, a calcium-bentonite clay powder was prepared in the following manner. A large batch of sodium-bentonite was stirred in water to form a homogeneous suspension of about 8% solids content.

To this suspension calcium chloride was added in a quantity calculated to be four times the exchange capacity of the clay. After stirring the batch to complete homogeneity and letting it stand a day, the clay was centrifuged to wash out the excess of calcium chloride and the sodium ions released by the base-exchange. The clay was washed several times until the supernatant liquid showed no presence of calcium ions, when tested with ammonium oxalate. The clay was then dried and ground in a ball-mill to a powder passing a #350 mesh sieve.

No details are available on the Florida kaolin clay that was used for a few tests. The clay was treated with hydrogen peroxide in order to digest the organic material, and was then electrodialyzed. The resulting hydrogen-kaolinite was dried and ground to a powder in the ball-mill.

In all the laboratory work distilled water was used. In all cases where commercially available chemicals could be obtained, C. P. grade materials were used. Hydrazine hydrate was obtained as an 85% aqueous solution from Eastman-Kodak and t-butyl-hydroperoxide as a 63% solution from Bay State Chemical Company.

The investigations were carried out entirely with calcium acrylate and calcium methacrylate. The preparation of these chemicals involves the simple reaction between the respective acid and calcium carbonate. Acrylic and methacrylic acid are supplied by Rohm and Haas Company, Philadelphia, in aqueous solutions. The acrylic acid was supplied in 60%

aqueous solution, containing 0.5% hydroquinone inhibitor; and the methacrylic acid was supplied in 20% aqueous solution with the same inhibitor. The preparation of the salts is chemically straightforward. To a given amount of acid was added the calcium carbonate powder in a quantity a little in excess of the calculated weight needed for completion of the reaction:

e.g., $CaCO_3 + 2(CH_2CHCOOH) \rightarrow Ca(CH_2CHCOO)_2 + H_2O + CO_2$

According to the solubility of the resulting salt, calcium acrylate or calcium methacrylate, the necessary amount of water was added so as to enable complete solution of all the salt produced. The batch was digested for several hours with continuous stirring at 60°C. Activated carbon powder, Norite, was added to remove the inhibitor, decolorizing the solution. On filtering off the excess calcium carbonate and the carbon black, a colorless solution of the desired salt, calcium acrylate or calcium methacrylate, was obtained. In some cases it was necessary to repeat the addition of carbon black a couple of times before complete removal of the inhibitor was achieved. The crystals of the desired salt, calcium acrylate or calcium methacrylate, were obtained partly by crystallizing from the saturated solution through cooling and evaporation on standing in an evaporating dish, and partly by evaporating under suction at 40°C. The dry crystals were ground to a fine white powder for use. The yield in such preparations was 90%.

In similar fashion small batches of lead acrylate, lead methacrylate, barium acrylate and barium methacrylate were also prepared with a view to furthering the investigations to include in some measure a study of the effect of the metallic ion involved in the treatment. However, time limitations precluded the possibility of conducting such further testing.

The use of the calcium salts for all the testing was decided upon by the following considerations: 1) more practical because of its availability and lower cost 2) solubility considerations 3) ease of finding catalysts. It may be mentioned, however, that Professor Hans F. Winterkorn expressed the opinion that the use of calcium invited bacterial activity which could destroy the stabilization. The size of ionic radius was one strong factor favoring the use of lead salts, but on other counts lead salts offer difficulties.

BASE-EXCHANGE STUDIES

Upon the addition of the calcium methacrylate or calcium acrylate to a sodium-bentonite gel at a specific water content, base-exchange takes place as has been mentioned in the introductory chapter of this thesis. Considering calcium methacrylate as an example, at a given concentration of its aqueous solution a dynamic equilibrium is established resulting in making available within the system the complex ions, $CH_2CCH_3COOCa^+$, and the simple ions Ca^{++} in specific proportions.

$$
\begin{array}{lrcl}
 & (CH_2CCH_3COO)_2\,Ca & \rightleftharpoons & CH_2CCH_3COOCa^+ + CH_2CCH_3COO^- \\
\text{and} & CH_2CCH_3COOCa^+ & \rightleftharpoons & Ca^{++} + CH_2CCH_3COO^- \\
\cline{2-4}
 & (CH_2CCH_3COO)_2\,Ca & \rightleftharpoons & 2(CH_2CCH_3COO)^- + Ca^{++}
\end{array}
$$

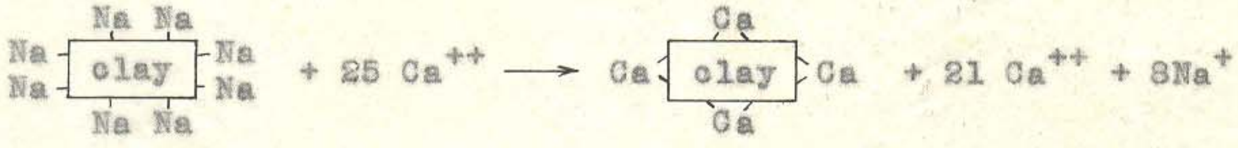
Accordingly, the existing sodium ions on the clay that are available for exchange may be exchanged either by the complex ions, $CH_2CCH_3COOCa^+$ or by the simple ions Ca^{++}. Actually, the sodium ions will be replaced partly by each. Further it may be that at certain low water contents not all the sodium ions are within easy reach for exchange. Hence it is probable that the clay gel after admixture of the calcium methacrylate will contain all three kinds of exchangeable ions attached to it in specific proportions.

The study of this base-exchange reaction was undertaken both for its own sake in providing a clearer understanding of the base-exchange taking place in clay soils upon the addition of salts like calcium chloride, and for the possible light that might be thrown on the relation between the amount of complex ion exchanged and the resulting product after polymerization.

Theory

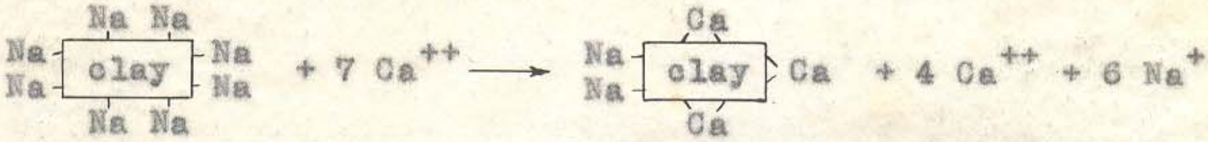
The study of the extent of base-exchange effected in sodium-bentonite sols in several colloid chemistry theses has employed the method of determination of the sodium set free, according to the following theory: every sodium ion set free by base-exchange is present in the liquid dispersion medium; the concentration of sodium ions in this liquid dispersion medium can be determined by appropriate gravimetric analysis, and hence by a simple computation the amount of sodium displaced from the clay may be determined. If we can be certain that the exchange was complete, such a procedure simultaneously gives us the exchange capacity of the clay.

In using clay sols of concentrations up to about 5% the procedure used was the following. After addition of the exchanging salt some of the liquid is extracted by centrifuging or super-centrifuging, and analyzed for the sodium content by the method of Barber and Koltoff.(2) It is known that for complete exchange, for the determination of the exchange capacity, the Law of Mass Action necessitates the use of an excess of the exchanging ion over the amount that may be computed to be necessary in view of the exchange capacity.



$$\begin{matrix}\text{Na}\\\text{Na}\end{matrix}\overset{\text{Na Na}}{\underset{\text{Na Na}}{\boxed{\text{clay}}}}\begin{matrix}\text{Na}\\\text{Na}\end{matrix} + 25\ \text{Ca}^{++} \longrightarrow \text{Ca}\overset{\text{Ca}}{\underset{\text{Ca}}{\boxed{\text{clay}}}}\text{Ca} + 21\ \text{Ca}^{++} + 8\text{Na}^{+}$$

Having determined the exchange capacity for the clay, is it possible to determine, for a specific case in consideration where the exchange is not complete and where the resulting clay contains all three kinds of exchangeable ions above mentioned (viz., Na^+, $CH_3CCH_3COOCa^+$ and Ca^{++}), how much of each of the ions is present? Obviously, a determination of the sodium exchanged will give us the amount of unexchanged sodium as the difference between the exchange capacity and the exchanged sodium.



Hence the problem is one of determining how much of the sodium is replaced by the Ca^{++} ion and how much by the $CH_3CCH_3COOCa^+$ ion. We may note that in the above schematic presentation one Ca^{++} ion occupied two Na^+ places. However, if the exchange were taking place both with Ca^{++} ions and with $CH_3CCH_3COOCa^+$ ions, which will henceforth be denoted as $CaMe^+$ ions for the sake of simplicity, it will be noted that one $CaMe^+$ ion replaces one Na^+ ion. On adding a given amount of calcium methacrylate, (henceforth will be denoted as $Ca(Me)_2$ for the sake of simplicity), to a clay gel we know just exactly how much calcium is being supplied to the system. For instance if we take the weight of calcium methacrylate, $Ca(Me)_2$, equivalent to six molecules, we know that the equivalent of six atomic weights of calcium have been supplied regardless of the manner in which the calcium methacrylate ionizes. But for every two sodium ions that are replaced by two $CaMe^+$ ions the equivalent of two atomic weights of calcium disappear from the liquid dispersion medium, whereas for every two sodium ions that are replaced by one Ca^{++} ion, the equivalent of only one atomic weight of calcium disappears from the liquid dispersion medium. Hence if the exchange is predominantly with $CaMe^+$ ions the liquid dispersion medium will be much poorer in calcium content than if the exchange is predominantly with Ca^{++} ions. In fact the actual amounts of each ion exchanged may be readily computed from two simple simultaneous equations if we not only determine the sodium content of the dispersion medium but also determine its calcium content after the exchange.

It is hoped that the following schematic presentation will aid in the understanding of this principle. Consider the case where the six molecules of calcium methacrylate ionize either as

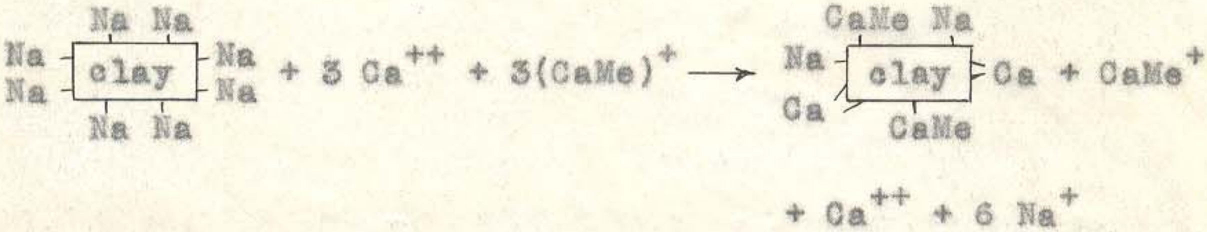
$$\text{(a)}\quad 6\,Ca(Me)_2 \rightleftharpoons 3\,Ca^{++} + 3(CaMe)^+ + 9(Me)^-$$

or as

$$\text{(b)}\quad 6\,Ca(Me)_2 \rightleftharpoons 2\,Ca^{++} + 4(CaMe)^+ + 8(Me)^-$$

In either case the equivalent of six atoms of calcium are supplied and the equivalent of six atoms exist after ionization. This may simply be checked by counting the number of Ca symbols on either side of the equation. For some of these Ca symbols to disappear on either side would represent a gross transgression of the Law of Conservation of Matter.

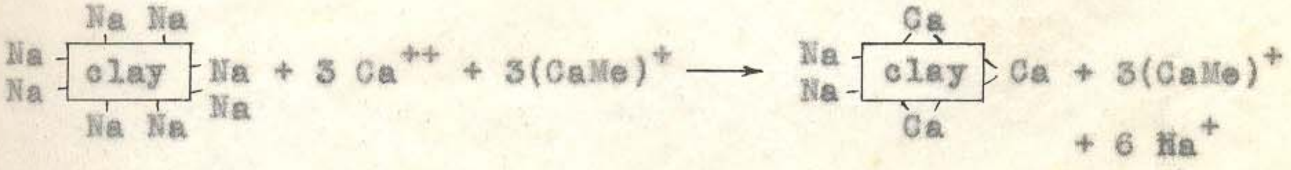
Now consider the same clay particle which has above been pictured as having a total of eight exchangeable sodium ions (a direct measure of the exchange capacity) and of which only six sodium ions are exchanged under the particular conditions imposed. Suppose that the exchange takes place in case (a) as follows:



$$\begin{array}{c}\mathrm{Na\ Na}\\ \begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\boxed{\text{clay}}\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\\ \mathrm{Na\ Na}\end{array} + 3\,\mathrm{Ca^{++}} + 3(\mathrm{CaMe})^{+} \longrightarrow \begin{array}{c}\mathrm{CaMe\ Na}\\ \begin{matrix}\mathrm{Na}\\ \mathrm{Ca}\end{matrix}\boxed{\text{clay}}\,\mathrm{Ca}\\ \mathrm{CaMe}\end{array} + \mathrm{CaMe^{+}} + \mathrm{Ca^{++}} + 6\,\mathrm{Na^{+}}$$

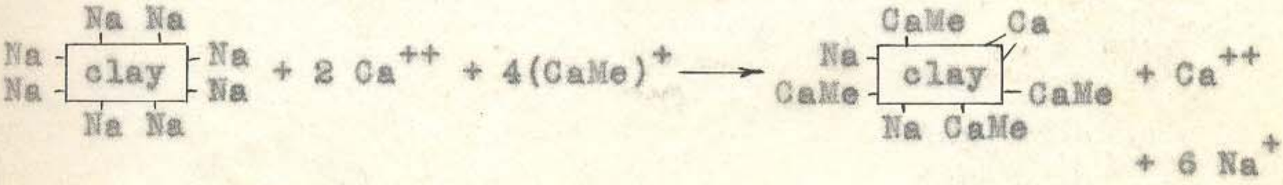
In this case, analysis of the dispersion medium for sodium and calcium would reveal that we have displaced the six sodium ions, and that we still have left the equivalent of two calcium atoms remaining in solution and hence that the equivalent of four of the six supplied calcium atoms have been taken up by the clay.

We cannot by any means change the proportions of $\mathrm{Ca^{++}}$, $\mathrm{CaMe^{+}}$ and $\mathrm{Na^{+}}$ ions associated with the clay particle without altering the analysis of the liquid dispersion medium. For instance, maintaining the exchanged sodium constant we may have



$$\begin{array}{c}\mathrm{Na\ Na}\\ \begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\boxed{\text{clay}}\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\\ \mathrm{Na\ Na}\end{array} + 3\,\mathrm{Ca^{++}} + 3(\mathrm{CaMe})^{+} \longrightarrow \begin{array}{c}\mathrm{Ca}\\ \begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\boxed{\text{clay}}\,\mathrm{Ca}\\ \mathrm{Ca}\end{array} + 3(\mathrm{CaMe})^{+} + 6\,\mathrm{Na^{+}}$$

or, as may happen in the case of ionization as in (b)



$$\begin{array}{c}\mathrm{Na\ Na}\\ \begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\boxed{\text{clay}}\begin{matrix}\mathrm{Na}\\ \mathrm{Na}\end{matrix}\\ \mathrm{Na\ Na}\end{array} + 2\,\mathrm{Ca^{++}} + 4(\mathrm{CaMe})^{+} \longrightarrow \begin{array}{c}\mathrm{CaMe\ \ Ca}\\ \begin{matrix}\mathrm{Na}\\ \mathrm{CaMe}\end{matrix}\boxed{\text{clay}}\,\mathrm{CaMe}\\ \mathrm{Na\ CaMe}\end{array} + \mathrm{Ca^{++}} + 6\,\mathrm{Na^{+}}$$

thus obtaining three or one equivalents of calcium in the analysis of the dispersion medium, rather than two as in the previous case.

The fact is that the relationship is controlled by two simultaneous equations, one relating to the charges associated with the ions, and the other relating to the weights: the ionic equation may be expressed as

$$\mathrm{CaMe} + 2\,\mathrm{Ca} = \Sigma\,\mathrm{Na}$$

since the number of sodium places occupied by the CaMe^+ and Ca^{++} ions is one per CaMe^+ ion and two per Ca^{++} ion. And the gravimetric equation, which merely represents the determination of the number of equivalent atomic weights of calcium adsorbed by the clay, can be represented by the equation

$$\mathrm{Ca} + \mathrm{CaMe} = \Sigma\,\mathrm{Ca} \text{ removed from solution}$$

because whether a Ca^{++} or a CaMe^+ ion is subtracted the resulting loss of calcium content of the solution is the same. Experimentally, the number of equivalent atomic weights of calcium removed from solution is obtained by subtracting the number remaining in solution from the number originally supplied.

Solving these simultaneous equations, we get the actual amount of each ion exchanged :-

$2\,Ca + CaMe = \Sigma\,Na = x$ (an experimentally determined value)

$\underline{Ca + CaMe = \Sigma\,Ca\ \text{disappeared}} = y$ (" " " " ")

Subtracting

$$Ca = x - y$$

Therefore,

$$CaMe = y - (x - y) = 2y - x$$

Development of Experimental Procedure

In attempting to study the base-exchange in sodium-bentonite clay gels at water contents below 500%, a difficulty encountered was that centrifuging the clay at 2000 rpm after treatment with the calcium methacrylate would not yield any supernatant solution for chemical analysis. Three possible solutions to this problem were considered: (1) to increase the speed of the centrifuge (2) to use an ultrafilter, by which the gels could be filtered by applying pressure from a nitrogen tank (3) to add an inert liquid which would in no way alter the ionic system under investigation but which, being completely miscible with water, would increase the volume of liquid in the system to any desired amount. The first two were rejected because there would always be a lower limit at which the method would no longer be feasible without further increasing the speed of the centrifuge or pressure from the nitrogen tank, and at lower water contents the desire to obtain reasonable amounts of solution to work with would probably require the use of larger and larger batches. The fact that calcium methacrylate had to prepared in the laboratory with considerable consumption of time, was a serious deterrent to the use of large batches in any of the testing.

A survey of common organic liquids showed that dioxane would probably meet the requirements. A check test was run with the following systems for comparison:

(a) 10.00 gm Na-bentonite + 100 cc H_2O + 10.00 gm $Ca(Me)_2$
(b) 10.00 gm Na-bentonite + 100 cc H_2O + 10.00 gm $Ca(Me)_2$
(c) 10.00 gm Na-bentonite + 100 cc H_2O + 50 cc dioxane + 10.00 gm $Ca(Me)_2$
(d) 10.00 gm Na-bentonite + 150 cc H_2O + 10.00 gm $Ca(Me)_2$
(e) 10.00 gm Na-bentonite + 200 cc H_2O + 10.00 gm $Ca(Me)_2$

After centrifuging, the supernatant liquid was analyzed for sodium, calcium, and methacrylate ions. The results of systems (a), (b) and (c) were exactly the same, within experimental accuracy, whereas systems (d) and (e) gave different results as would be expected. Thus it was established that dioxane could be used as an inert liquid for base-exchange analyses. Obviously such a check test could only be run with a case at high enough water content so that even without the addition of dioxane enough supernatant liquid could be obtained for the analyses by centrifuging. Further checks at lower water contents could be run, if desired, by centrifuging at higher speeds, but this was not thought necessary.

An attempt to rerun a few of the analyses after the liquid had been standing for a day proved the existence of some time effect which apparently threw calcium and methacrylic acid ions out of solution. It was discovered that this was due to the fact that the commercial dioxane used might contain peroxide: subsequent use of peroxide-free dioxane showed no evidence of this trouble. It is presumed that the peroxide initiated polymerization of the calcium methacrylate, throwing it out of solution. It was also noted that on heating above 80°C in order to boil down and concentrate the solutions for analysis, a white flocculent precipitate was obtained. The precaution was, therefore, observed of concentrating the solution by slight warming - or actually, since this was rather impractical, of not concentrating at all in most cases.

Testing Routine

Complete series of tests were run at different water contents and with different amounts of calcium methacrylate added. In order to simplify the description of the testing routine established, a particular case will here be outlined. Consider the following case: sodium-bentonite at about 200% water content, with the addition of calcium methacrylate equivalent to a solution of 14 grams in 100 cc of water.*

The procedure used was the following: 10 grams of dry sodium-bentonite powder were weighed out into a 250 ml. heavy-duty pyrex centrifuge bottle, the actual weight used being noted, 20 cc of distilled water were then introduced and the mass was thoroughly stirred into a homogeneous gel. The stirrer was carefully removed avoiding the removal of clay with it, and the centrifuge bottle was stoppered and allowed to stand for a day. Finally, 2.8 grams of calcium

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* It was found that 14 gms of calcium methacrylate dissolved in 100 cc of water resulted in a saturated solution at room temperatures.

methacrylate powder were introduced, the actual weight used being noted, and the mass was again thoroughly mixed until it was quite homogeneous and all the calcium methacrylate had dissolved. The stirrer was then carefully removed avoiding the removal of any of the clay with it.[*] The centrifuge bottle was stoppered and allowed to stand for a day before testing.

Finally, 50 cc of peroxide-free dioxane were introduced, the bottle was restoppered, and violently shaken. The batch was then centrifuged for 10 - 15 minutes at 2000 rpm. About 50 cc of clear supernatant solution were thus obtained. The absence of a Faraday cone when the solution was held to a beam of light proved the absence of small colloidal particles which would interfere with the delicate gravimetric sodium and calcium determinations.

The sodium determination was carried out with the use of zinc-uranyl acetate reagent developed by Barber and Koltoff. The reagent consists of:

A.	Uranyl acetate ($2H_2O$)	10 gm
	Acetic acid 30%	6 gm
	Water to make	65 gm

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[*] This stirring may best be done in the humid room to avoid evaporation of water. At the higher water contents the stirring could easily be achieved by inserting clean glass beads, stoppering the centrifuge bottle and shaking it vigorously.

B.	Zinc acetate (2H O)	30 gm
	Acetic acid 30%	3 gm
	Water to make	65 gm

Salts of A and B were dissolved by warming to 70°C. The two solutions were mixed and allowed to stand for 24 hours, after which time the precipitate formed by sodium in the reagents or in the glassware was filtered off. The reagent was stored in a pyrex bottle.

The sodium determination was carried out according to the Barber and Koltoff directions. For the gravimetric test, 2 cc of the supernatant liquid were pipetted out into a clean beaker and about 25 - 30 cc of the zinc-uranyl acetate reagent were added, and the mixture was allowed to stand for 30 minutes. The precipitate was filtered through a porcelain crucible with asbestos mat by suction, and then washed with 2 cc portions of the reagent five to ten times. After all the reagent was drawn off, washing was continued with 2 cc portions of absolute alcohol saturated with uranyl-zinc-sodium acetate precipitate, and several times with ether. After all the ether had been drawn off, the crucible was weighed, the gain in weight representing the weight of the precipitate. Since the precipitate has a composition $(UO_2)_3Zn\ Na(CH_3COO)_9 \times 6\ H_2O$, the weight of sodium is (0.01495 x wt. of ppt.).*

The precautions required in this gravimetric determination have been incorporated in the above description, and for

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* Ratio of atomic weight of Na to molecular weight of precipitate = 0.01495.

further details the original article may be consulted. It may be mentioned that Barber and Koltoff state that the presence of calcium does not affect this determination within the limits considered by the author. A check test was run proving that the dioxane also does not affect this sodium determination.

In all tests at least two sodium determinations were run, the results in all cases showing a deviation of less than 1%.

For the calcium determination 10 cc of the supernatant liquid were carefully pipetted off into a beaker, and an excess of ammonium oxalate was added whereupon a fine white precipitate of calcium oxalate was formed. Warming this solution and precipitate proved quite helpful in flocculating the precipitate and thus rendering its filtration simpler. After cooling, the precipitate was suction filtered in a porcelain crucible with asbestos mat: the precipitate was washed with distilled water and several times with ether, and then dried and weighed. The washing was then repeated and after redrying the new weight of the crucible plus the precipitate was checked against its previous value to ensure thorough washing. The weight of the calcium oxalate precipitate was thus obtained. In all tests at least two calcium determinations were made, the results again showing remarkable agreement.

Sample Test Data and Computation

Test #1. System 10 gm clay + 20 cc H_2O + 2.8 gm $Ca(Me)_2$

Weighed out	Clay	$Ca(Me)_2$	
	38.8620 gms	17.0500 gms	Added 20 cc H_2O
	-28.8670 gms	-14.2491 gms	Added 50 cc dioxane
	9.9950 gms	2.8009 gms	

Sodium Determination: Took 2 cc per test

1) Wt. of crucible (A)	18.1042 gm	Wt. of ppt. = 0.2460 gm
Wt. of crucible + ppt.	18.3502 gm	
2) Wt. of crucible (6)	16.6514 gm	Wt. of ppt. = 0.2470 gm
Wt. of crucible + ppt.	16.8984 gm	

Average weight of ppt. = 0.2465 gm

Therefore, weight of Na in 2 cc of liquid = 0.01495 x 0.2465 gm

Weight of Na in 70 cc of liquid = $0.01495 \times 0.2465 \times \frac{70}{2}$ gm

Weight of Na in 70 cc expressed in milliequivalents* =

$$\frac{0.01495 \times 0.2465}{0.023} \times \frac{70}{2} = 5.62 \text{ me.}$$

Hence base-exchanged sodium = 5.62 me. per 10 gms of clay

= 56.2 me/100 gms of clay

= 56.2 mm/100 gms of clay

Calcium Determination: Took 10 cc per test

1) Wt. of crucible (11)	17.0802 gm	Wt. of ppt. = 0.1663 gm
Wt. of crucible + ppt.	17.2465 gm	
2) Wt. of crucible (7)	16.4041 gm	Wt. of ppt. = 0.1680 gm
Wt. of crucible + ppt.	16.5721 gm	

Average weight of ppt. = 0.1671 gms

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* Atomic weight of Na = 23

Weight of Ca put into solution* = $\frac{40.1}{210.2}$ x 2.8 gms = 0.5342 gms

Weight of Ca in the solution after base-exchange**

$$\frac{40.1}{128.1} \times 0.1671 \times \frac{70}{10} \qquad = \underline{0.3662 \text{ gms}}$$

Weight of Ca absorbed by b.e. 0.1680 gms

Weight of Ca absorbed expressed in millimols = $\frac{0.1680}{0.0401}$ = 4.19

Therefore, Ca absorbed by b.e. = 4.19 mm. per 10 gms of clay

= 41.9 mm. per 100 gms of clay

Setting up the simultaneous equations, we have

$$\begin{aligned} CaMe + 2\,Ca &= 56.2 \\ \underline{CaMe + Ca} &\underline{= 41.9} \end{aligned}$$

Therefore, Ca^{++} = 14.3 mm. $CaMe^{+}$ = 27.6 mm.

Since the base-exchange capacity of the clay is 78 me/100 gms, we conclude that for the system studied, (78 - 56.2) i.e., 21.8 me. of Na per 100 gms of clay are unexchanged.

A batch of 100 gms of such a clay would, therefore, have associated with it 21.8 mm. of Na^{+}
14.3 mm. of Ca^{++}
27.6 mm. of $CaMe^{+}$

Sources of Error and Precautions

It must primarily be emphasized that the above computation is based on the assumption that there is no molecular adsorption superimposed on the base-exchange to deprive the solution of further calcium. In his S. M. thesis on "A Study of the Reactions of Lead Salts with Bentonite"(7), Mr. Geza E. Neuman discusses the possibility of coulombic

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* Atomic wt. of Ca = 40.1, Mol. wt. of $Ca(Me)_2$ = 210.2

** Mol. wt. of calcium oxalate = 128.1

attraction causing adsorption of some ions to the clay surface. It may be stated that such adsorption is concluded to be likely only in cases where the clay surface is saturated with the complex ions. In cases like the ones under investigation by the author, where the clay surface contains large proportions of Na^+ and Ca^{++} ions, such additional adsorption appears to be altogether unlikely. That no extra adsorption of $CaMe^+$ ions takes place was checked in one case by a determination of the concentration of methacrylate in the supernatant liquid.

Secondly, it may be pointed out that the greatest possible care in performing the gravimetric analyses is needed because of the nature of the computations. This observation is especially important in the case of the analysis for calcium. It may be noted that the computation of the weight of calcium absorbed by base-exchange involves the difference of two values which are of about the same magnitude resulting in a difference of much smaller magnitude. Hence even small per cent errors in the calcium determination are magnified into large per cent errors in relation to the important value of weight of calcium absorbed which determines the final computation of amounts of Ca^{++} and $CaMe^+$ ions absorbed.

Discussion of Results

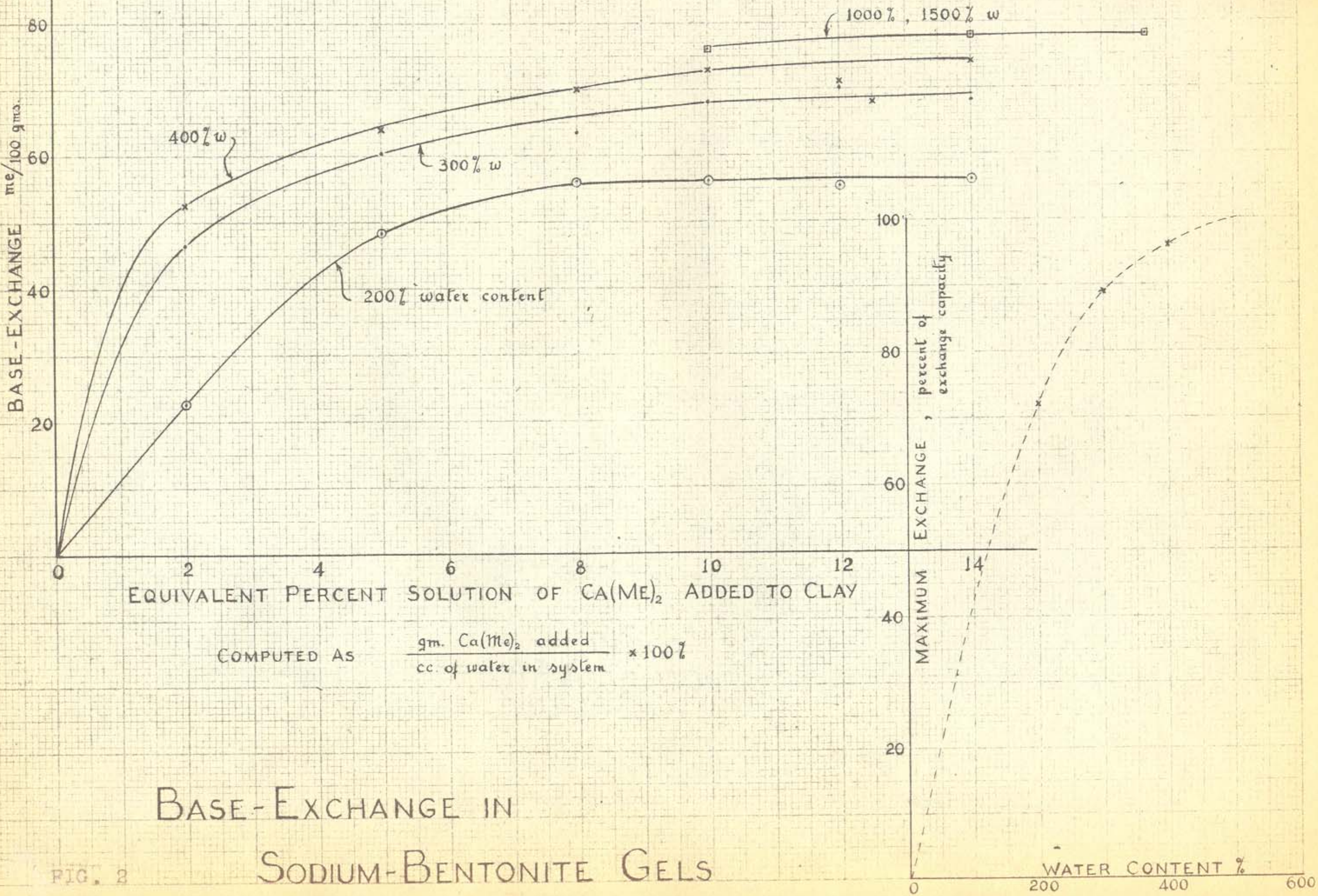
The results of these base-exchange tests are best presented in graphical form, as is undertaken in the following pages. The exchange capacity of the clay was established by a few tests at very high water contents (1000%, 1500%) and with high amounts of calcium methacrylate added.

Two facts are evidenced by the first graph (Fig. 2): (1) at each water content, the amount of sodium exchanged drops markedly as the amount of calcium methacrylate added is decreased, (2) but even with the addition of high amounts of calcium methacrylate, at water contents less than 500% there is a limiting value of sodium exchanged which is lower than the exchange capacity, this limiting value steadily decreasing with a decrease of the water content.

The next three graphs (Figs. 3, 4, 5) represent the details of the analyses of base-exchange for the three cases of sodium-bentonite at about 200%, 300% and 400% water content. Detailed discussion of these plots is unwarranted: they serve best in giving general ideas of how the exchange reaction varies. One inescapable fact is that the maximum amount of complex $CaMe^+$ ions are adsorbed under saturated conditions. Whether the other maxima and minima of $CaMe^+$ ions adsorbed can be correlated with any properties of the resulting clays will be discussed in its appropriate place.

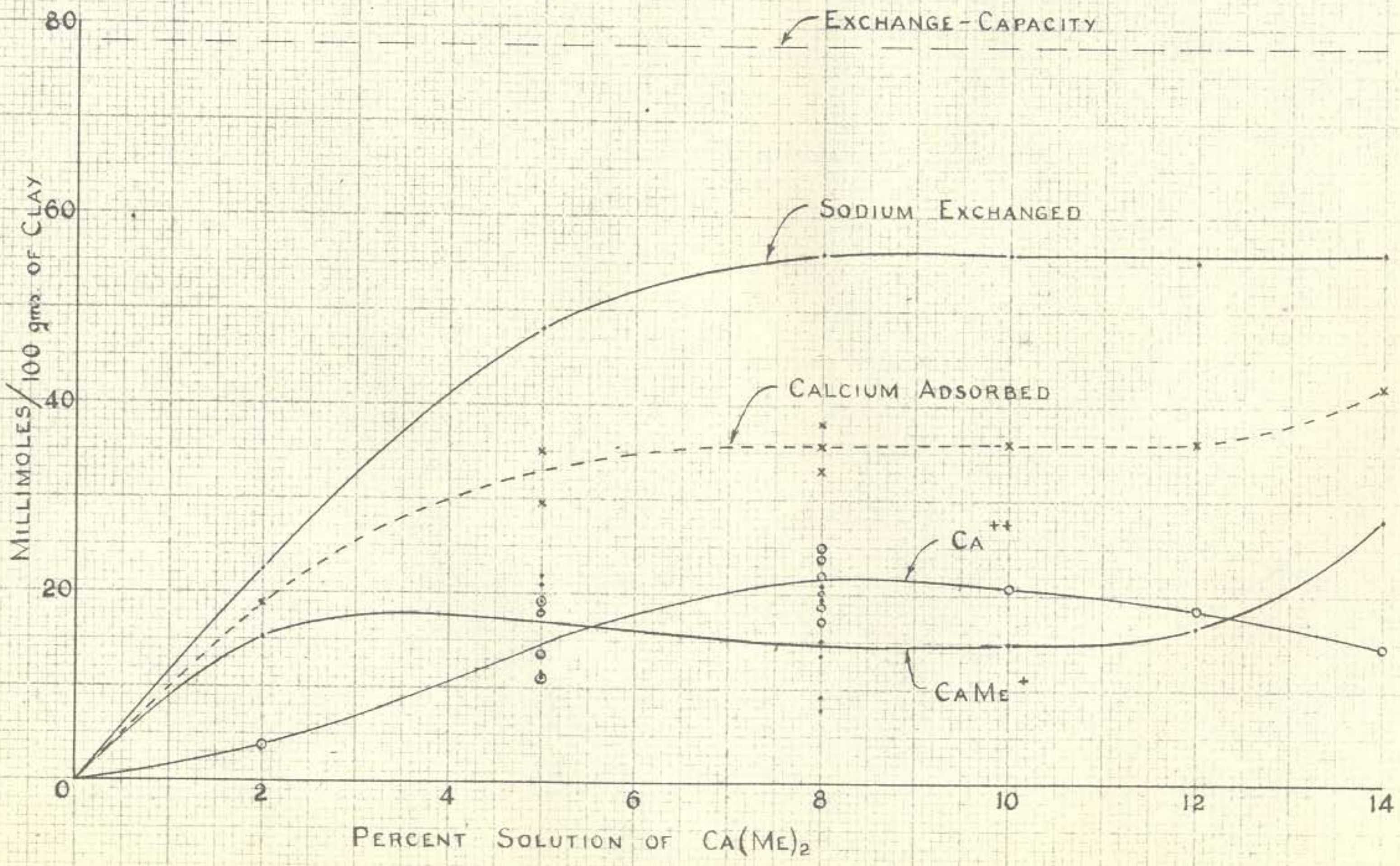
The graphical form adopted for presentation of the results requires some explanation.

(1) Figure 2 presents curves labeled as applying to 200% water content, 300% w, and 400% w. Correspondingly, Figures 3, 4 and 5 are described as representing conditions at 200%, 300% and 400% water contents. These water contents are meant to represent the water content of the original



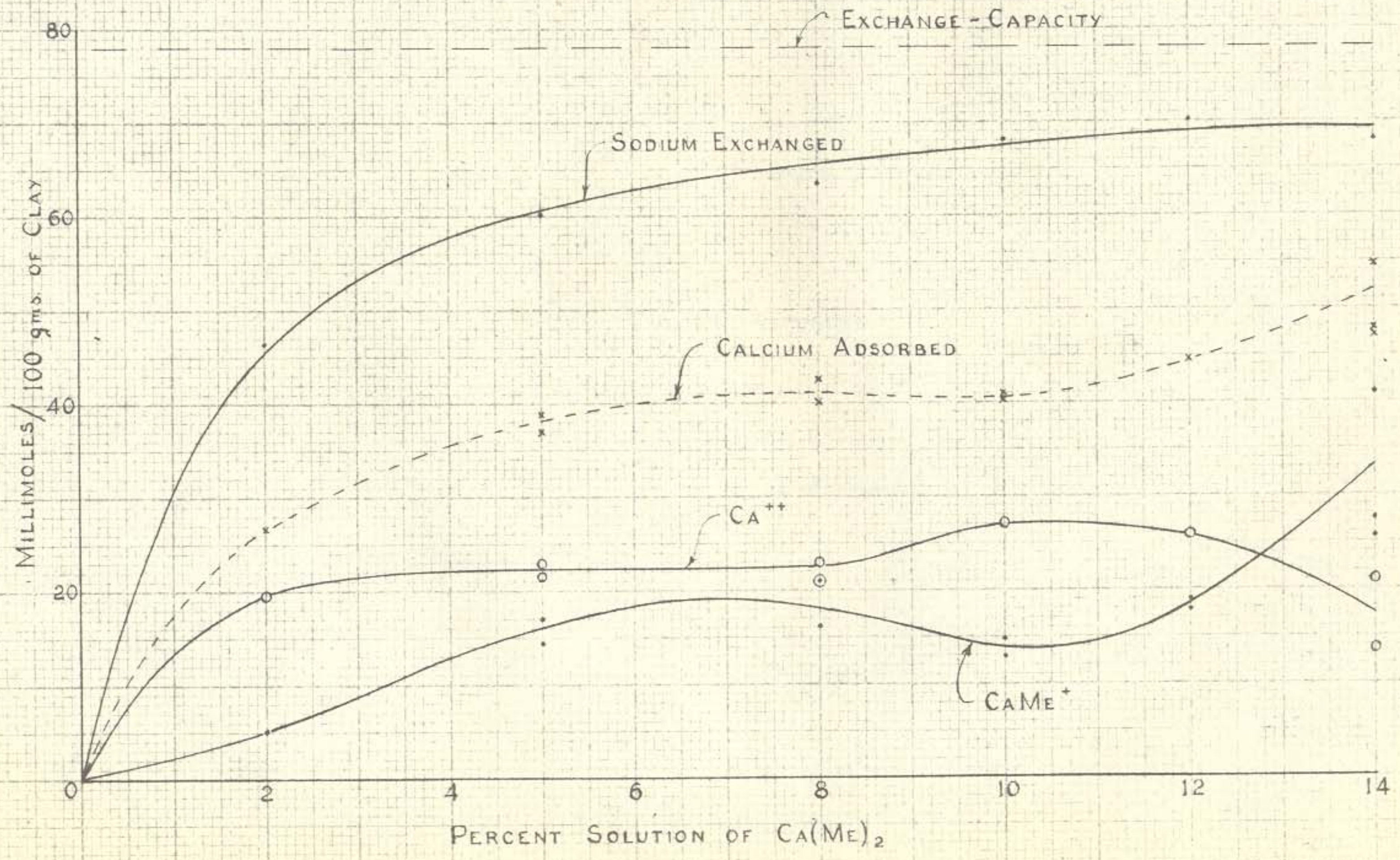
BASE-EXCHANGE IN SODIUM-BENTONITE GELS

FIG. 2



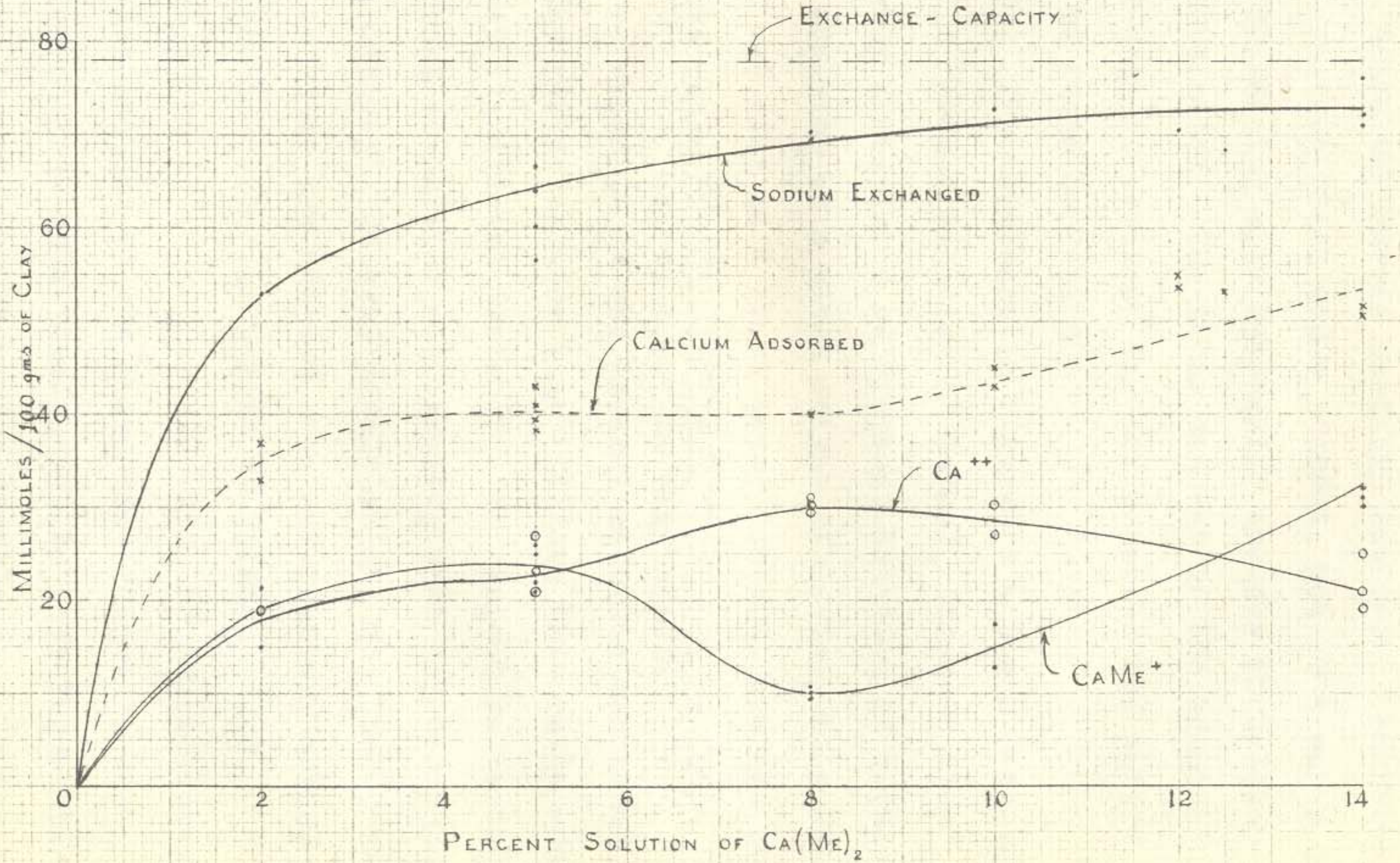
BASE-EXCHANGE IN SODIUM-BENTONITE
AT 200% WATER CONTENT

FIG. 3



Base - Exchange in Sodium - Bentonite
at 300% water content

FIG. 4



BASE - EXCHANGE IN SODIUM - BENTONITE
AT 400% WATER CONTENT

FIG. 5

untreated clay, which is obviously a very important variable to be considered. The addition of dry calcium methacrylate powder to the clay obviously causes a reduction of the water content. Hence the curves actually represent conditions not at a constant final water content, but at a water content steadily decreasing with increasing amounts of calcium methacrylate added. The water content of the original untreated clay is retained for reference to the entire curve in order to avoid confusion.

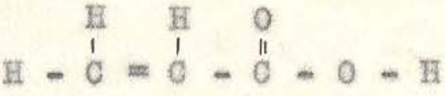
(2) The abscissae in Figures 2 - 5 are denoted as "Equivalent Percent Solution of $Ca(Me)_2$ Added to Clay", subsequently abbreviated to "Percent Solution of $Ca(Me)_2$". With the addition of a given weight of $Ca(Me)_2$ to a known weight of wet clay at a known water content, one can readily compute the ratio $\frac{\text{gm. of } Ca(Me)_2 \text{ added}}{\text{cc. of water in clay sample}} \times 100\%$. This ratio is referred to as the percent solution mentioned above. If the clay particles were inert fillers this ratio would be the most significant variable with respect to variations in the amount of calcium methacrylate used for treatment. Moreover, although the clay particles are not inert, the use of the same ratio was adopted as a satisfactory method of covering the variation of weight of $Ca(Me)_2$ added.

It is herewith emphasized that the nomenclature adopted with respect to the above two factors is kept standard throughout this thesis, and is very frequently employed in the graphs discussing results of polymerization studies on various clays. Further clarification on these points will, therefore, be considered unnecessary.

PRELIMINARY POLYMERIZATION STUDIES

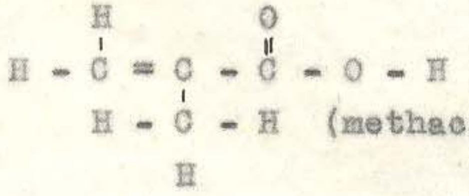
Polymers are substances, usually of high molecular weight, which contain recurring structural units. Polymerization is an intermolecular combination functionally capable of proceeding indefinitely: a simple molecule of the monomer, usually of low molecular weight, will chemically combine with another similar molecule forming a molecule consisting of two structural monomeric units firmly attached by chemical bond, and by the same process a third monomeric molecule will be chemically bonded to the dimer thus formed, a fourth molecule will be chemically bonded to the trimer, and so on indefinitely until the reaction is somehow blocked, or until all of the available monomer is used up. In addition polymerization, the intermolecular combination capable of proceeding indefinitely, is the combination of one unsaturated molecule with another. For example, carbon atoms linked by a double bond are converted to carbon atoms in a long chain. The reaction is characteristic of a great variety of unsaturated compounds and is one of the most important general reactions of organic chemistry.

In dealing with salts like calcium acrylate and calcium methacrylate we have to do with unsaturated compounds which are capable of addition polymerization. Since the unsaturation exists in the acrylic and methacrylic acid radical, we shall simplify the diagrammatic presentation of this polymerization reaction by studying merely the corresponding acid. The formulae for acrylic and methacrylic acids are $CH_2CHCOOH$ and CH_2CCH_3COOH: a look at the diagrammatic representation of their structures reveals that one of the carbon-carbon linkages is a double bond linkage, since the tetravalent carbon valency must be satisfied.



$$H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-H$$

(acrylic acid)



$$H-\overset{\overset{H}{|}}{C}=\underset{\substack{|\\ H-C-H\\ H}}{C}-\overset{\overset{O}{\|}}{C}-O-H$$

(methacrylic acid)

With suitable activation, addition polymerization will be instigated in an attempt to convert these double bonds into single carbon-carbon linkages.

It will be noticed that by the activation which tends to change a carbon-carbon double bond into a single valency linkage, e.g., $-\overset{|}{C}=\overset{|}{C}-$ to $-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-$, <u>two</u> single valence bonds are made available for condensation with another pair of valence bonds released in the same manner by another similar molecule. If a square carbon formation could be formed as shown on Fig. 6 (b), two molecules could mutually satisfy each other and thwart the development of the chain reaction. But the laws of organic chemistry do not permit such

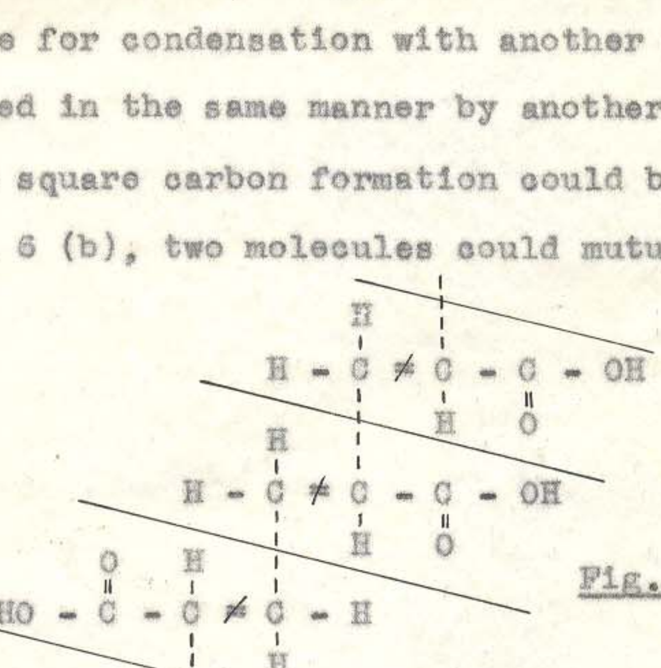
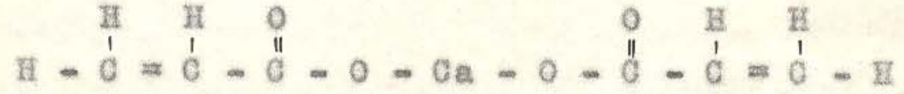


Fig. 6 (a)

Fig. 6 (b)

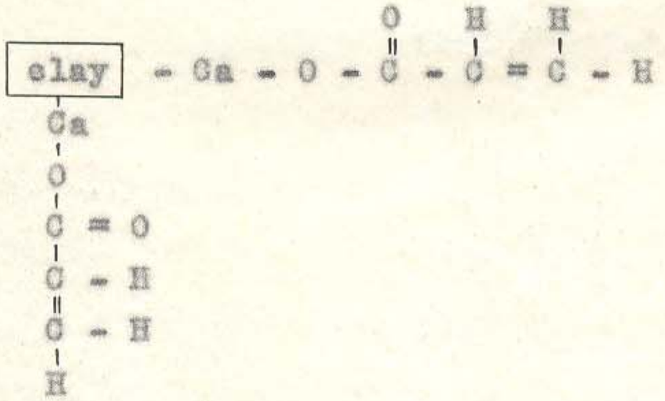
square carbon formations and so the reaction is bound to proceed indefinitely because "n" molecules bound to each other still have two arms outstretched. If the free arms are in some way occupied, the chain cannot be continued; thus a variety of impurities in the chemical system may block the reaction.

The calcium acrylate molecule may be diagrammatically pictured in quite the same manner.



$$H-\overset{H}{C}=\overset{H}{C}-\overset{O}{\overset{\|}{C}}-O-Ca-O-\overset{O}{\overset{\|}{C}}-\overset{H}{C}=\overset{H}{C}-H$$

and a clay particle with exchanged calcium acrylate ions may be presented as:



It may be noted further that in such systems since arms are stretched out in all three dimensions, the polymer will be cross-linked into a three-dimensional network.

The addition polymerization reaction is subject to initiation, surface effects, and inhibition as are other chain reactiors. The commonly used types of initiators are free radical generators, such as hydrogen peroxide, benzoyl peroxide, with heat being applied as may be necessary. In aqueous solutions at room temperatures the effective generation of free radicals must be attempted by other means.

The practical application of the base-exchange and polymerization treatment for the stabilization of clays hinged on the possibility of effecting polymerization at room temperatures in the presence of water. Polymerization of salts like calcium acrylate presents absolutely no problem, if one may resort to the application of heat. From the outset, the big problem that was faced in this thesis investigation was the necessity of achieving the same polymerization in aqueous solutions at temperatures equivalent to normal ground-water temperatures, or room temperatures.

Recent work on low-temperature aqueous polymerization of ethylenic monomers, such as acrylic acid and its derivatives, has evolved a new polymerization technique, described as reduction activation. "If M represents an ethylenic monomer, O an oxidising agent which catalyses its polymerization, and R a substance which is capable of reaction with O, and therefore normally a reducing agent, then it may be found that the rate of polymerization of M in the system M + O + R is much faster than in the system M + O"(1) and is effective at much lower temperatures.

The search for appropriate reduction-oxidation (redox) catalysts for activation of the aqueous room-temperature polymerization of the calcium methacrylate was conducted following the suggestions made in the article referred to above. The one major limitation that controlled the selection of ionic catalysts was that neither the calcium nor the methacrylic acid radical could be permitted to precipitate from solution by double decomposition. Fortunately, ammonium persulphate, which is mentioned as possessing remarkable efficiency as the oxidising agent, was available for use, since the persulphates of calcium, barium and lead are quite soluble. Silver nitrate, which has been reported to be a very efficient reduction activator for ammonium persulphate, could not be used because silver methacrylate was immediately precipitated.

A purely qualitative method was adopted for the search of suitable catalysts. To small batches of a saturated solution of calcium methacrylate, varying amounts and proportions of solutions of the reducing and oxidising agents under investigation were added in small drops; after stirring, the batches were allowed to stand and were observed for the formation of insoluble polymer. Samples were observed for as long a period as 24 hours, but it soon became apparent that any visible polymer almost invariably formed within the first half-hour. The formation of polymer was unmistakable, with the development of a rubbery or sticky mass of insoluble matter. There was absolutely no question in distinguishing such polymer from the precipitation of insoluble salts like silver methacrylate.

It is well-known that minute but varying quantities of impurities may seriously vitiate results because of their powerful effect on the rate of the oxidation-reduction reaction. Furthermore, the presence of oxygen is known to inhibit polymerization reactions in these systems. Hence, orthodox studies of such polymerization reactions should be conducted with materials of high purity, and in an atmosphere of nitrogen. Furthermore, since it is asserted that the effect of the activators is complicated by factors such as concentration and pH, such factors should be closely controlled and studied. However, in view of the civil engineering application of such polymerization data the author preferred to adapt the brief survey of the reaction to the less refined circumstances which would eventually have to be imposed upon it.

The use of ammonium persulfate and sodium bisulfite catalysts proved effective in polymerizing aqueous calcium methacrylate and calcium acrylate. The sodium bisulfite is not available for use with either barium or lead salts, because these metallic ions are precipitated by the bisulfite. Since the persulfate-bisulfite combination is reported as being particularly effective, and since it did prove effective for the purpose of this study, it was promptly used in the early tests on clay-calcium methacrylate systems.

Subsequently a wider search was conducted with a view to obtaining a few more sets of catalysts. The use of ammonium persulfate and sodium thiosulfate proved very effective, especially in the case of calcium acrylate. Further work indicated consistently that the acrylate was more readily polymerized than the methacrylate.*

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* This observation agreed with information supplied by Rohm and Haas Company, Philadelphia.

The use of the methacrylate had been recommended as giving less brittle a polymer, but since all the wet clay-acrylate or clay-methacrylate polymers obtained by the author were plastic, such brittleness of the dry polymer was concluded to be of no importance. Hence in subsequent work attention was centered on calcium acrylate.

The hydrogen peroxide-ferrous system of redox catalysts was tried but apparently iron acrylate is precipitated. Chromous, mercurous, cuprous, titanous and manganous metal ions are also suggested for use with hydrogen peroxide. However, data then available on polymerization of clay calcium methacrylate systems with persulfate-bisulfite catalysts had shown that comparatively large amounts of catalysts were required for complete polymerization. Anticipating the effect of such cations to be appreciable, the investigation of this group was not pursued. Hydrogen-peroxide and hydrazine hydrate very effectively polymerized a solution of calcium acrylate. However, in an attempt to polymerize the clay-acrylate system, difficulty was encountered in controlling the concentration of the peroxide; apparently the evolution of oxygen by the peroxide on contact with the clay inhibited the polymerization.

The further search for suitable oxidizing agents was directed mainly at trying out the remaining alkali persulfates, sodium hypochlorite, ceric nitrate, and t-butylhydroperoxide. Sodium persulfate, $Na_2S_2O_8$, is not available commercially. Potassium persulfate, $K_2S_2O_8$, was adopted as effective. Sodium hypochlorite, moderately recommended, was not found to be effective. Ceric sulfate which was well recommended, could not be used since calcium sulfate precipitated: an attempt to use ceric nitrate in its stead did not prove successful either, probably due to the precipitation of ceric acrylate. Tertiary-butyl-hydroperoxide was highly recommended because of its proven efficiency in the redox polymerization of styrene: it was found very effective. Cumene hydroperoxide was also tried in a sodium-dresinate emulsion, but was not found successful.

For the three oxidising catalysts (ammonium persulfate, potassium persulfate, and t-butyl-hydroperoxide) other suitable reducing agents were desired. A very wide qualitative search was conducted. Sodium sulfite, sodium nitrite, sodium oxalate, hydroquinone, hydroxylamine, hydrazine, quinone, catechol, phloroglucinol were tried.* This search was not intended to be exhaustive. It was merely hoped that enough different sets of catalysts could be discovered so as to evaluate the range of variation of properties of the polymer produced by various catalysts.

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* Many of the reagents recommended had to be omitted because they were not commercially available (e.g., metabisulphites); or because some of their properties made them particularly obnoxious (e.g., mercaptans and H_2S).

The sets of redox catalysts finally used were:

Monomer	Oxidizing Agent	Reduction Activator
Calcium Methacrylate	Ammonium Persulfate	Sodium Bisulfite
	" "	Sodium Thiosulfate
Calcium Acrylate	Ammonium Persulfate	Sodium Bisulfite
	" "	Sodium Thiosulfate
These may also be used with lead and barium salts	Ammonium Persulfate	Hydrazine Hydrate
	" "	Hydroxylamine Hydrochloride
	Potassium Persulfate	Sodium Bisulfite
	" "	Sodium Thiosulfate
	" "	Hydrazine Hydrate
	" "	Hydroxylamine Hydrochloride
	t-butyl-hydroperoxide	Sodium Bisulfite
	" " "	Sodium Thiosulfate
	" " "	Hydrazine Hydrate
	" " "	Hydroxylamine Hydrochloride

DEVELOPMENT OF APPARATUS AND TESTING TECHNIQUES

The primary concern in a study of the characteristics of the treated and untreated clays was to measure the shearing strength and to obtain some measure of the water affinity. It was also of interest to obtain a relative measure of the extent of polymerization achieved. In view of the anticipation of the running of scores or hundreds of tests in pursuing the analysis of the numerous variables involved, special consideration was given to two factors; namely, simplicity of testing technique and procedure, and economy of material.

Shearing Strength

The requirement of economy of material put out of consideration the standard direct shear, unconfined compression, and triaxial compression tests. One other point that had to be borne in mind was that the samples would have to be placed in the testing units immediately upon mixing and then allowed to polymerize "in situ" for the proposed curing time; reworking the material after polymerization, in order to mold it or to place it in the testing unit, might either not be possible at all or might conceivably destroy some of the strength gained by polymerization. If the direct shear machine were to be used, for instance, the requirement of 24 hours of curing time per sample would make it impossible to test more than one sample in every 36 hours or more, unless additional shear boxes were available. The use of small cylindrical samples to be tested in unconfined compression by a very sensitive proving ring was considered. But another trouble that was faced was the following: the base-exchange decreases the strength of the sodium-bentonite so markedly that a stiff sodium-bentonite gel at 200% water content would after base-exchange with the calcium methacrylate become so soft as to make it impossible to mold cylindrical samples that could stand up without sloughing off. The application of some form of ring shear was, therefore, suggested: the sample is suitably confined, and without the use of too much material an appreciable area of the clay is subjected to shear, thus resulting in a more measurable shearing force.

Thus was evolved a simple ring shear testing machine which is pictured in several views in the photographs, Figs. 7 - 11, on pages 66 - 69. No detailed written description of the apparatus will be given since the photographs are almost self-explanatory and well demonstrate the simplicity of the apparatus.

Fig. 7 shows the various parts of a single test unit. Ten such test units were made, in order to maintain a steady and rapid testing program. Since the treated clay was allowed to polymerize and cure "in situ" (i.e., in such testing units) for 24 hours before testing it was necessary to have many testing units. Fig. 8 shows a clay sample being placed in the testing unit. Fig. 9 shows the testing unit fitted with the top cover and aluminum cap which made it

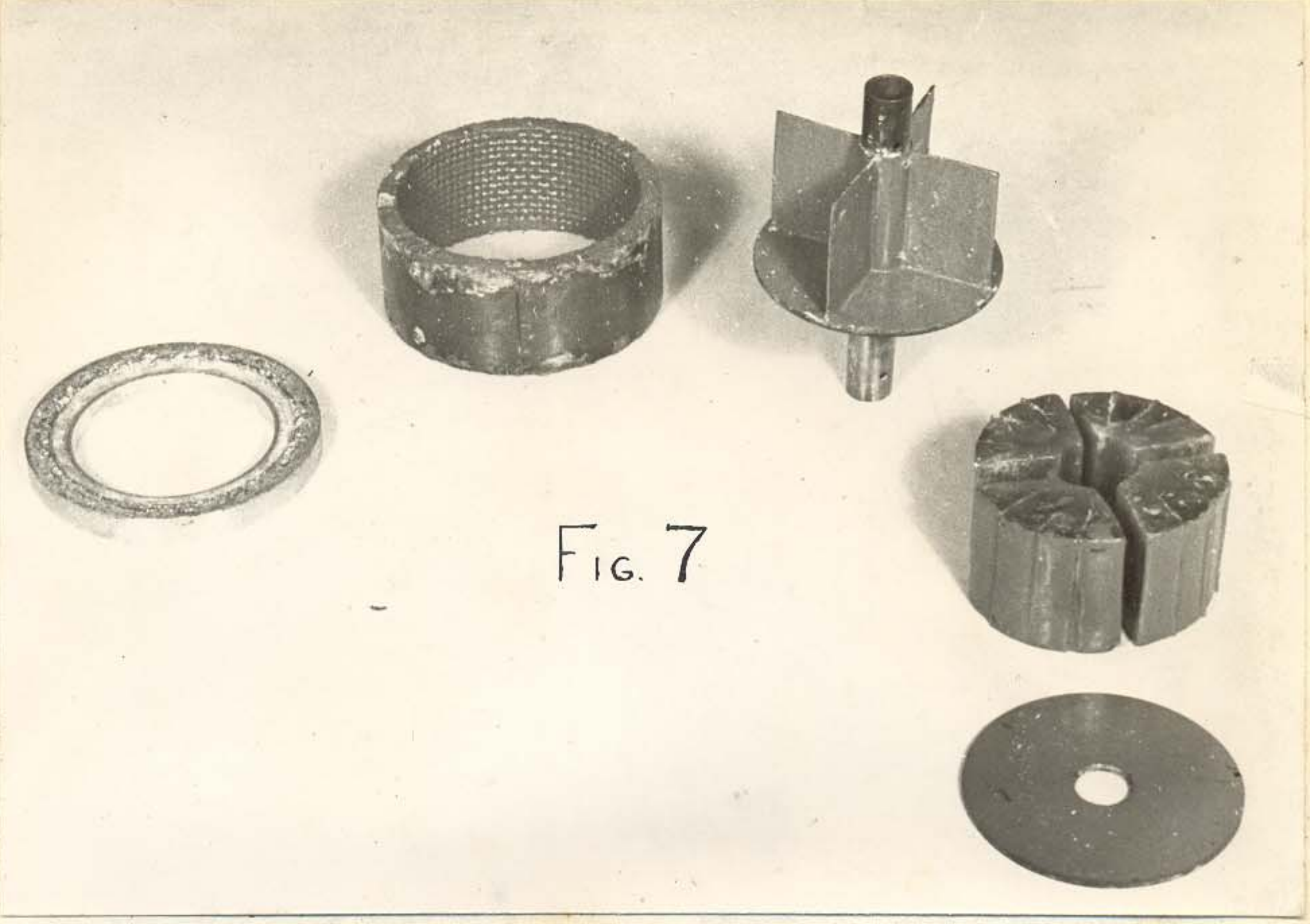


Fig. 7

Fig. 8

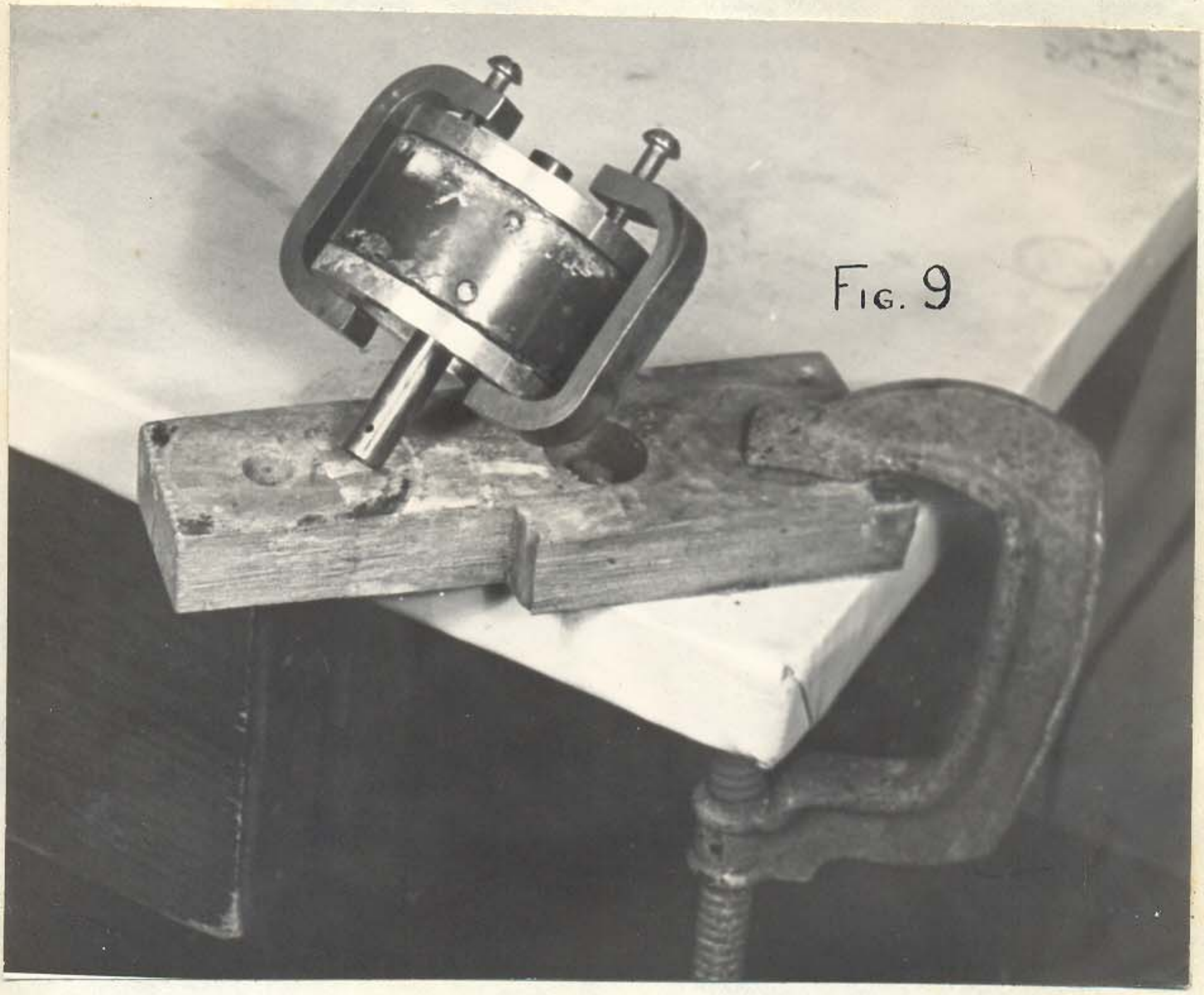
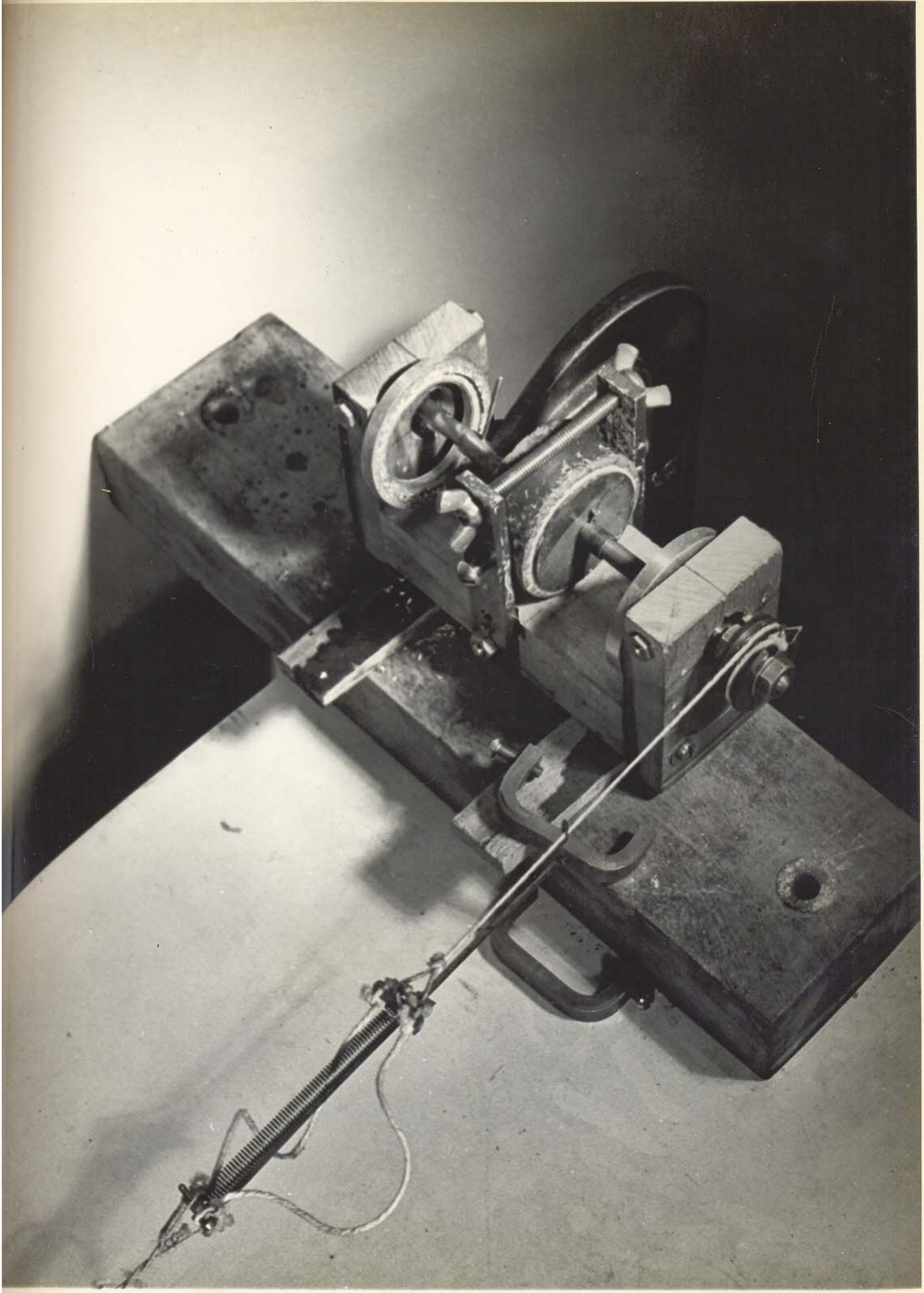
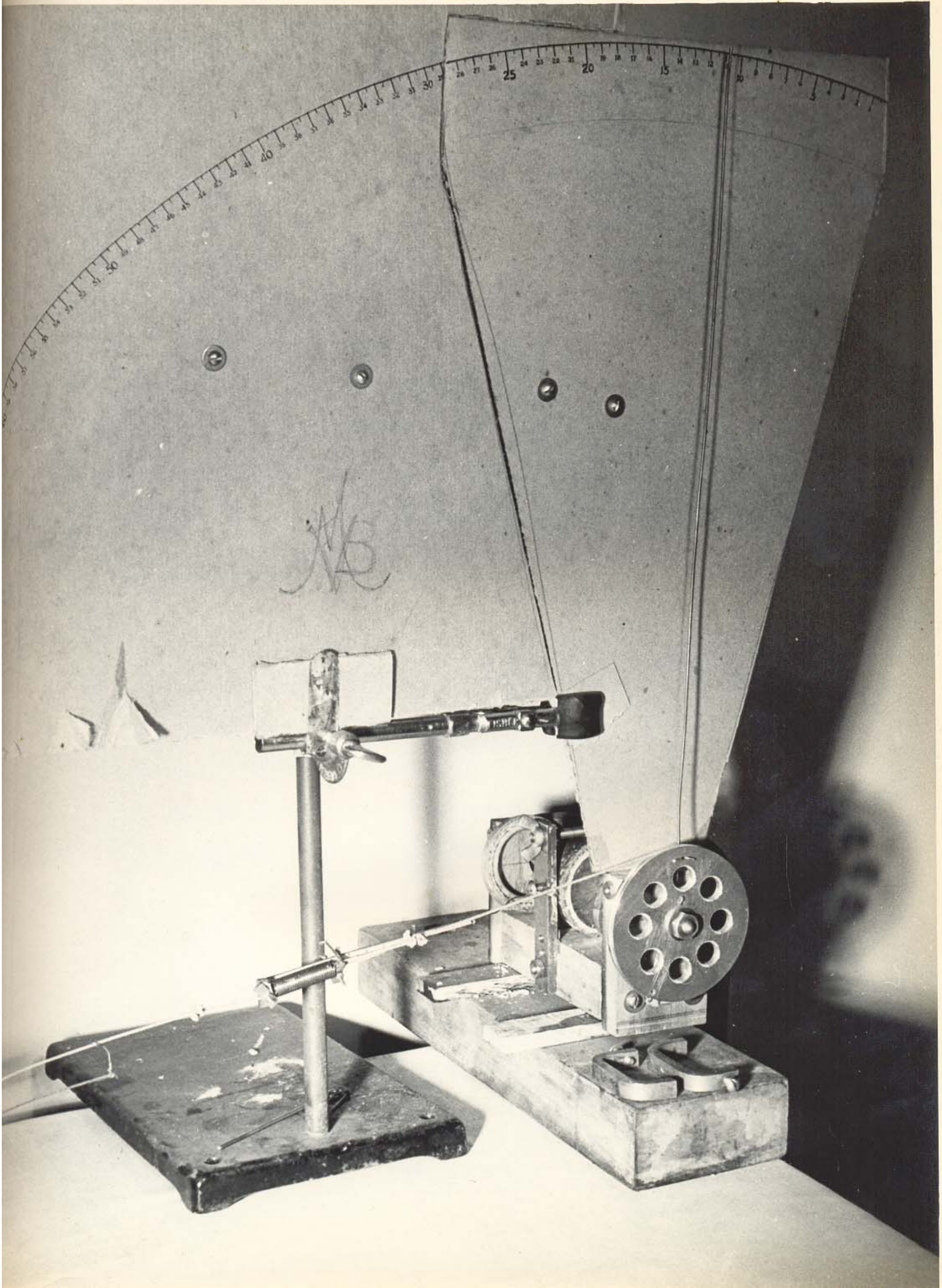


Fig. 9

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possible to clamp the testing unit, so as to avoid any disturbance of the clay. This clamping procedure was adopted for transferring the unit to the testing apparatus in view of the fact that the testing unit would be changed from a position in which its axis was vertical to one in which the axis was horizontal. Fig. 10 shows that unit in place in the testing apparatus. The top and bottom aluminum caps have been removed.

The tests were run by motor, the torque applied being steadily increased by allowing the string which transmitted the tension to wind on a shaft slowly rotated by the motor. The tension was measured by springs which were calibrated. Fig. 11 shows the same equipment adapted with a bigger pulley for the sake of samples with higher shearing strengths, and adapted with a pointer and a dial for the sake of obtaining approximate stress- strain diagrams.

All the important details concerning this shear testing equipment are given in Figs. 41, 42, 43, page This information includes the dimensions of the testing units, the calibrations of the springs with the computed factor for converting readings into results in pounds per square inch, and a plot which may be used for the determination of the rate of stress increase under the assumption of negligible strain. All the tests were run at the same speed.

With respect to the stress-strain diagrams it must be mentioned that they can at best represent close approximations to the actual stress-strain relationship. The main difficulty lay in establishing the zero stress-zero strain point. The springs all have a certain initial tension and thus the real zero-stress point cannot be easily obtained; the condition corresponding to a complete slack in the tension string cannot establish the zero point either, because of inevitable friction in the apparatus. The procedure adopted was to plot the curve of stress vs displacement of the pointer on the dial, and then to produce the initial straight line (approximate) backwards to intersect the zero-stress axis. This approach was reasonably effective.

Most of the shearing strength data was obtained by use of the simple ring-shear apparatus above described. Further, a few tests were run in the direct-shear machine, and finally also a few of the stronger samples, such as, for instance, the samples of treated kaolinite, were molded in cylinders of 0.72" diameter and about 1.5" in height, and were tested in unconfined compression using a sensitive proving ring.

Water Affinity

The desire to acquire adequate water affinity data in a relatively short period of time, with the use of a small amount of the clay, pointed to the idea of spreading a thin layer of clay on a porous plate maintained at water level, and noting the difference in water content of the clay after thus absorbing water for an arbitrary length of time. The amount of water that a clay absorbs is directly related to its swelling tendency; thus to some extent the preliminary selection of the better samples of treated clay could be based purely on a measure of the swelling at zero applied pressure. It is true that the more significant relation sought in connection with this research should be the loss of strength of the sample after water absorption; quite probably some samples would be able to absorb more water than others without showing as much of a decrease of strength. But the requirement of a strength test after water absorption as well as before would almost double the amount of material required per run; this was considered unwise for the preliminary selection.

The first attempts at developing the technique for such a water-absorption test were conducted as follows. Sodium-bentonite clay at about 200% water content was carefully spread to an even thickness* of 1.5 mm. on a porous stone of the type used in the consolidation apparatus. The porous stone was laid on the perforated plate of a clean desiccator partly filled with water: the water level was carefully adjusted to coincide with the top of the porous stone. It was believed that the probable source of error consisting of a variation of the type of contact between the clay gel and the porous stone would be essentially eliminated by establishing a free water surface at this level.

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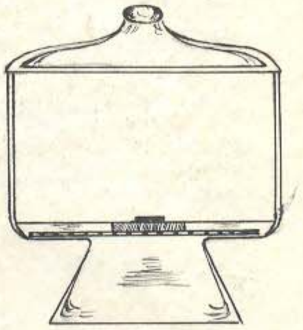
* A simple scraper was made for the purpose.

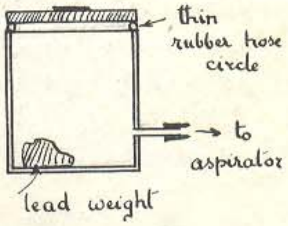


It was found that almost absolute elimination of evaporation of the water from the clay could be effected in such desiccators filled up to a certain level with water. The humidity in the humid room never was satisfactory enough to prevent such evaporation. Naturally, however, the desiccator had to be kept in the humid room because otherwise, on opening the lid to place the porous stone in it, the volume of air enclosed within the desiccator would drop to a relative humidity far below 100%.

Exactly twenty-four hours later the porous stone was carefully removed and some of the clay scraped off for a water content determination. The same procedure was followed with ten such porous stones and the water pick-up of the clay as established by the ten determinations was compared. Unfortunately, the results showed rather large differences. The tests were repeated to determine if the different results could be associated with particular porous stones. The lack of consistency was alarming.

For some time attention was, therefore, shifted to other possible methods. The two methods investigated were (1) a method separately developed by Winterkorn and Baver, and Freundlich(10, 5); and (2) a method consisting of centrifuging a suspension of the clay at a fixed speed and for a fixed length of time, and then finding the water content of the sediment. The details of this work will not be discussed, since many objections to the two methods arose during their attempted application. It was observed, however, that the Winterkorn-Baver (or Freundlich) method was basically no different from the porous stone method earlier attempted, except insofar as powdered colloids were placed on the porous stone, and the water pick-up was measured by the decrease in volume of water in a micropipette attached to the porous stone container. From many points of view, the necessity of drying and powdering the clay for this test was highly objectionable. It also became evident that despite the relatively elaborate apparatus and cumbersome testing procedure, involving even a constant temperature bath, the results were not very closely reproducible unless the greatest care was observed.

However, the use of the Winterkorn-Baver apparatus suggested the possible source of error in the simple porous plate procedure previously used, and encouraged renewed experimentation with it. It was indicated, in fact, that the source of error lay in the method of obtaining the measure of the water pick-up. Indeed, on close observation it was noticed that the top of the porous plate had quite an appreciable amount of free water which could easily be scraped up with the clay for the water content determination. The remedy seemed simple: to apply a little suction to the bottom of the porous plate just before scraping up the clay for the water content determination. Accordingly, a can was fitted, as shown, and connected to an aspirator nozzle; a circle of thin rubber hose was glued to the rim of the can in order to approximate an airtight contact with the bottom of the porous plate. On applying the suction to the porous plate the free water at its surface could be seen withdrawing; when the surface of the porous plate thus lost its shiny wet appearance, the clay was scraped up for the water content determination.



Evidently the trouble was precisely what had been suspected. Numerous check tests subsequently run showed consistent results within an accuracy of about 3%, which was considered amply satisfactory.

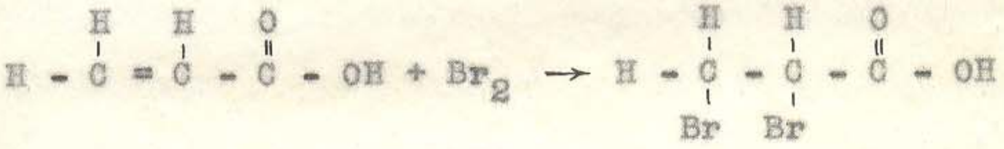
The simple procedure adopted for determining the relative water-affinity of the clay samples was the following: (1) find the water content of the sample (2) spread the clay on a porous stone as described above (3) place the porous stone in water in a desiccator, observing the precautions detailed above (4) at the end of 24 hours carefully remove the porous stone and obtain a water content determination of the clay, observing the precautions outlined above. The difference in water content, expressed also as a water content, is henceforth given as the measure of water-affinity; e.g., if a sample increased from a water content of 212% to a water content of 565%, its water pick-up is 353%.

The selection of the 24-hour period is to be explained primarily by the following two considerations: (1) The two factors of importance with respect to water-affinity of soils are the rate of water absorption and the magnitude of the total water absorption. Completion of water absorption is probably not reached before several days, but the measure of the rate of absorption is even more important than the determination of the total absorption. The selection of an arbitrary period of water absorption was directed at the hope of obtaining the maximum of information from a single test. Scattered tests indicated that the curve of water pick-up vs time effectively flattened after 24 hours of water absorption; hence relative values of total water absorption could reasonably be estimated from knowledge of the 24-hour water pick-up. Further, although the rate of water absorption was observed to be steadily decreasing even within the 24-hour period, it was relatively quite appreciable during a large part of that period. Thus the use of the 24-hour period permitted also the relative estimation of rates of water absorption; (2) The 24-hour period was the most practical period to use from the point of view of planning an efficient testing program involving scores of samples.

"Degree of Polymerization"

To obtain some measure of the extent of polymerization was considered essential. Actually, it was realized that molecular weight determinations constitute the only completely satisfactory criterion for evaluation of polymerization; but, how could molecular weight determinations be made on a polymerized calcium acrylate system?

Measuring the degree of unsaturation of the system was the most feasible solution. The usual procedure suggested is the bromine saturation test. The chemical phenomenon involved here is, in short, the following: double bonds or unsaturated linkages which have not been saturated with other atoms during the addition polymerization reaction, will readily absorb bromine atoms. This bromine absorption may be demonstrated graphically in the case of acrylic acid:



$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-OH+Br_2\rightarrow H-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OH$$

Hence, since two atoms of bromine are used up for the saturation of each double bond, a measure of the bromine absorbed by the system is a measure of the number of double bonds existing in the system. Since in addition polymerization the unsaturated linkages of one molecule become cross-linked (or saturated) with the double-bond linkages of another similar molecule, only those molecules which have not become cross-linked in the polymer system will ordinarily absorb bromine atoms.

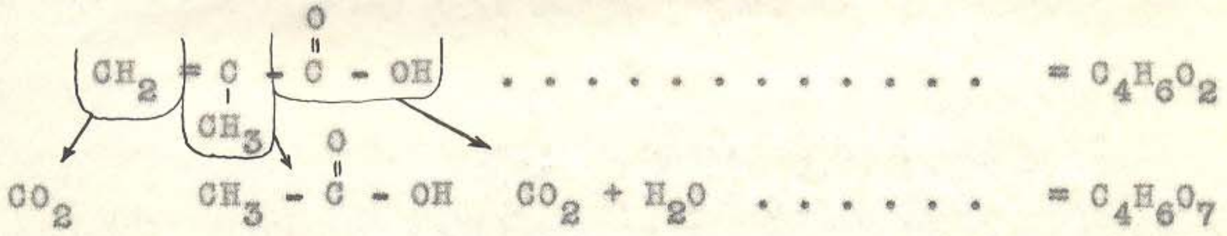
It must be noted that although ability to absorb bromine as above described indicates absence of polymerization, it cannot generally be said that the lack of such ability indicates presence of polymerization. The double bond may be saturated by other means thus prohibiting the entrance of bromine. However, thorough knowledge of the system being dealt with will permit the evaluation of the possibility of other substances saturating the double bond; and if no such substances exist, polymerization is demonstrated by the lack of absorption of bromine.

Many blank runs were made to determine if the bromine saturation test could be used for estimation of calcium methacrylate monomer. Many variations were attempted, such as using either a water solution or a methanol solution of bromine, and running the blanks on calcium methacrylate alone or in the presence of clay. It was thus learned that clay absorbed bromine. The really important conclusions were obtained from the blanks run on calcium methacrylate alone. Immediately upon addition of bromine, the calcium methacrylate absorbed considerably more bromine than could be needed for saturation of the double bond, and subsequently more and more bromine kept disappearing from the solution. This suggested that perhaps a substitution reaction was going on, removing bromine from the solution. At any rate it was quite evident that the bromine saturation test could not be used for estimation of the calcium methacrylate monomer -- at least, not without much greater refinement.

At this point the possibility of using potassium permanganate suggested itself. The decolorization of acidic potassium permanganate solutions is used as a qualitative test for unsaturation: could not this idea be used for a quantitative test? A trial run was made by titrating a solution of calcium methacrylate against a potassium permanganate solution. The procedure used in the standard sodium oxalate-potassium permanganate titration was followed in every detail; and fortunately, reproducible results were obtained.

The next step was that of determining the actual reaction involved. Theoretically, the following development was undertaken.

Assuming complete oxidation, in view of the elevated temperatures employed in the titration, methacrylic acid can be expected to break down as pictured below.



$$CH_2 = \underset{\underset{CH_3}{|}}{C} - \overset{\overset{O}{\|}}{C} - OH \quad \ldots\ldots\ldots\ldots\ldots \quad = C_4H_6O_2$$

$$CO_2 \qquad CH_3 - \overset{\overset{O}{\|}}{C} - OH \quad CO_2 + H_2O \quad \ldots\ldots \quad = C_4H_6O_7$$

This complete oxidation requires 5 (0) per molecule of methacrylic acid.

The reaction by which oxygen is supplied:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + 3H_2O + K_2SO_4 + 5\ (0)$$

or otherwise $2(MnO_4)^- + 6H \longrightarrow 2(Mn)^{++} + 5(0) + 3H_2O$

The reaction by which methacrylic acid is obtained from calcium methacrylate,

$$2H^+ + Ca(C_4H_5O_2)_2 \longrightarrow Ca^{++} + 2C_4H_6O_2$$

We combine the three equations as shown below

$$\begin{array}{lll}
 & 2H^{+} + Ca(C_4H_5O_2)_2 & \rightarrow Ca^{++} + 2C_4H_6O_2 \\
2 & C_4H_6O_2 + 5(O) & \rightarrow 2CO_2 + CH_3COOH + H_2O \\
2 & 2(MnO_4)^{-} + 6H^{+} & \rightarrow 2(Mn)^{++} + 5(O) + 3H_2O \\
\hline
\end{array}$$

$$4(MnO_4)^{-} + Ca(C_4H_5O_2)_2 + 14H^{+} \rightarrow Ca^{++} + 4CO_2 + 2CH_3COOH + 4Mn^{++} + 8H_2O$$

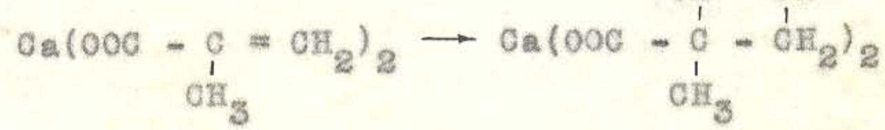
It is evident that for complete oxidation of calcium methacrylate, as pictured above, four molecular weights of potassium permanganate would be used up by one molecular weight of calcium methacrylate. Hence it is indicated that

$\frac{158 \times 4}{210.2} = 3.005$ gm $KMnO_4$ are consumed by 1 gm $Ca(Me)_2$.

Experimental data showed, however, that about 2.030 gm $KMnO_4$ were used up by 1 gm $Ca(Me)_2$. It was indicated, therefore, that under the conditions of test employed, a fairly distinct and reproducible end-point in the titration was obtained at an intermediate stage of the oxidation.

In order to inquire into the possible nature of this intermediate stage of the oxidation, the following step-wise development was undertaken.

(a) The first possibility of oxidation is the addition of two (OH) groups



$$Ca(OOC - \underset{CH_3}{\underset{|}{C}} = CH_2)_2 \rightarrow Ca(OOC - \underset{CH_3}{\underset{|}{\overset{\overset{OH}{|}}{C}}} - \overset{\overset{OH}{|}}{CH_2})_2$$

In this oxidation $2H_2O + 2(O)$ are required.

Combining this equation with the equation by which oxygen is supplied, we get

$$10H_2O + 5Ca(O_2C_4H_5)_2 + 4(MnO_4)^- + 12H^+ \rightarrow$$
$$5Ca(O_4C_4H_7)_2 + 4(Mn)^{++} + 6H_2O$$

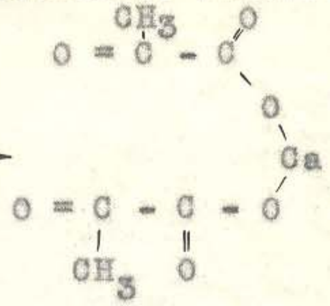
i.e.,

$$5Ca(Me)_2 + 4KMnO_4 + 6H_2SO_4 + 4H_2O \rightarrow$$
$$5Ca(O_4C_4H_7)_2 + 4MnSO_4 + 2K_2SO_4$$

It is obvious that the reaction proceeds beyond this initial step.

(b) The next possibility involves two reactions: first, the oxidation to calcium pyruvate and formic acid, and next, the inevitable oxidation of formic acid.

$$Ca(O_4C_4H_7)_2 + 4(O) \rightarrow$$



$$+ 2H_2CO_2 + 2H_2O$$

and $2H_2CO_2 + 2(O) \rightarrow 2CO_2 + 2H_2O$.

For these two oxidation reactions, we can write

$$5Ca(O_4C_4H_7)_2 + 8KMnO_4 + 12H_2SO_4 \rightarrow$$
$$5Ca(O_3C_3H_3)_2 + 10H_2CO_2 + 22\ H_2O + 8\ MnSO_4 + 4K_2SO_4$$

and $10H_2CO_2 + 4KMnO_4 + 6H_2SO_4 \rightarrow 4MnSO_4 + 2K_2SO_4 + 16H_2O + 10CO_2$

Combining the two, we get

$$5Ca(O_4C_4H_7)_2 + 12KMnO_4 + 18H_2SO_4 \rightarrow$$
$$5Ca(O_3C_3H_3)_2 + 38H_2O + 12MnSO_4 + 6K_2SO_4 + 10CO_2$$

Thus for the completion of oxidation to step (b), we find that a total of 16 molecular weights of potassium permanganate would be used up by 5 molecular weights of calcium methacrylate. Hence it is indicated that with oxidation proceeding to this stage, $\frac{158 \times 16}{5 \times 210.2} = 2.405$ gm $KMnO_4$ are consumed by 1 gm $Ca(Me)_2$.

It is thus indicated that, in the titration procedure followed, the oxidation is not even carried to completion of this second step. Moreover, the assumption that the oxidation would stop at the calcium pyruvate state is difficult to justify since pyruvic acid would normally be expected to oxidize to acetic acid, carbon dioxide and water. It must, therefore, be concluded that the consistent reproducibility of results obtained in the titration of calcium methacrylate with potassium permanganate was due to the personal standardization of the titration procedure employed, rather than to the achievement of a distinct theoretical end-point in the oxidation. However, in spite of the lack of theoretical support, the titration was adopted for the volumetric determination of calcium methacrylate.

How could this titration with potassium permanganate be used for determination of polymerization of clay-methacrylate systems? Direct titration against a clay-methacrylate suspension was impossible because of the difficulty of establishing the color end-point. The procedure finally developed was the following. To the clay-methacrylate system a known amount of sulphuric acid was added; the suspension was centrifuged, and the supernatant solution was titrated against a standard potassium permanganate solution. The sulfuric acid, which was necessary for acidification of the potassium permanganate titration would simultaneously serve to extract into solution all the methacrylate ions associated with the clay. This would be done partly by base-exchange and partly by the precipitation of $CaSO_4$ which by removing the calcium, Ca^{++}, ions from solution would tend to push the ionization of calcium methacrylate to the right.

$$Ca(Me)_2 \rightleftharpoons (CaMe)^+ + (Me)^- \rightleftharpoons Ca^{++} + 2(Me)^-$$

Finally, since the titration was performed with the supernatant liquid, it follows that only soluble material could affect the titration--a further separation between the polymerized and unpolymerized material.

The tests run to determine the properties of sodium-bentonite upon admixture with calcium methacrylate and calcium acrylate (i.e., base-exchange but no polymerization) furnished the blank titration results that were used for subsequent computations of degree of polymerization. A vast number of such blanks were available, as tabulated on page From the experimental results obtained for titration of calcium methacrylate, a weighted average ratio of 0.500 gm $Ca(Me)_2$ for 1 gm $KMnO_4$ was used. The blanks run at later dates showed higher ratios, averaging around 0.530 and 0.560.

It is conjectured that these higher ratios are explained by the incidence of a little polymerization in the calcium methacrylate, on standing at room temperature during the summer months. The results with calcium acrylate were much more closely reproducible. The average figure adopted for use was 0.405 gm $Ca(Ak)_2$ for 1 gm $KMnO_4$. It may be noted that in the case of calcium acrylate, the disagreement between the experimentally determined ratio and the ratio computed theoretically on the basis of complete oxidation, is of the same nature as above discussed in connection with calcium methacrylate.

The only conceivable impediment to the use of this simple procedure was the possible effect of the oxidation-reduction catalysts on this oxidation-reduction titration. Indeed, a check test corroborated expectations that any excess of the sodium bisulfite would naturally vitiate results because of its reducing action. The possibility of precipitating this excess of sodium bisulfite was investigated. It was found that a saturated lead acetate solution would effectively precipitate the bisulfite so as to leave the titration results unaffected. In using the sodium bisulfite catalyst, the use of lead acetate was, therefore, resorted to. Slight excesses of ammonium persulfate did not affect the titration: when present in large excesses there was a slight effect, increasing a little with time, reducing the amount of potassium permanganate used in the titration. This effect was not disconcerting as it was considered suggestive of polymerization.

With other sets of catalysts unfortunately no simple procedure was found for inactivating them. The procedure adopted, therefore, was of running blanks to find the effect of such sets of catalysts on the titration.

Final Testing Routine

The final procedure may best be outlined in relation to a specific case; generalized descriptions will be added where necessary.

Consider the case in which it is desired to test a sodium-bentonite clay gel at about 200% water content after base-exchange with the equivalent of a 10% solution of calcium methacrylate (according to the nomenclature used in the chapter on base-exchange studies); and to test also the same clay-methacrylate system after polymerization with appropriate amounts of ammonium persulfate-sodium bisulfite catalysts.

The amount of clay to be used was computed from a knowledge that about 18 cc. of the sample would be needed for the shear strength determination.

First, 7.5 grams of dry sodium-bentonite were carefully weighed out into a porcelain dish. Then, in the humid room, 15 cc. of distilled water were added, and the mass was thoroughly mixed with a spatula into a homogeneous clay gel. Next, 1.5 grams of dry calcium methacrylate were weighed out and added to the gel, the mass being thoroughly reworked into homogeneity. The base-exchanged clay was then ready for placing in one of the shear-testing units. It was found advisable to allow this testing unit to stand for a few hours before testing: the testing unit was, therefore, carefully placed on a plate in a desiccator partly filled with water, in order to avoid water-content changes by evaporation.

When the sample was ready to be tested, the testing unit was capped by the aluminum disc, clamped, and brought to the testing machine, where it was clamped in its proper position for shear testing. The clamps and aluminum disc caps of the testing unit were then removed and the motor was switched on. The maximum reading on the appropriate spring was recorded for use in computing the shearing strength. The shear test now being over, the testing unit was quickly removed and taken into the humid room. There the testing unit was opened and some of the clay was scraped off for a water content determination. A second sample of the clay was then scraped onto the end of a nickel spatula; the spatula and clay were quickly weighed and the clay was shaken off the spatula into a clean centrifuge bottle provided with clean glass beads and a rubber stopper. The centrifuge bottle was quickly stoppered and meanwhile the spatula with the remaining clay was reweighed; thus by difference the weight of wet clay in the centrifuge bottle was known. The rest of the clay from the testing unit was then spread onto a porous stone for a water pick-up determination, the initial time of water absorption being recorded. An appropriate volume of about 5 N sulfuric acid, approximately

100 cc., was then pipetted into the centrifuge bottle. The centrifuge bottle was restoppered and shaken vigorously, causing the clay to disperse. Subsequently the clay dispersion was centrifuged at 2000 rpm. and the clear supernatant solution titrated against a standard solution of potassium permanganate for concentration of methacrylate ion. The results of such a titration would represent a blank, since no polymerization was instigated.

The laboratory data for the above representative case were taken as follows:

Sample 7.5 Na-bent. + 15 cc. H_2O + 1.5 gm. $Ca(Me)_2$

Shearing Strength; Springs A $S_1 \rightarrow$ 9.9 cm.

Weight of clay taken for analysis

$$\begin{array}{r} 17.813 \\ -\underline{14.438} \\ 3.375 \text{ gm.} \end{array}$$

Added 3 cc. lead acetate soln. + 100 cc. H_2SO_4

Titration: 8.90 cc. of (0.1253 N) $KMnO_4$ vs 10 cc. supernatant solution

Water Content 0

$$\begin{array}{r} 25.635 \\ 23.697 \\ 22.631 \end{array} \quad \frac{1.938}{1.066} = 181.5\%$$

Spread the clay on porous plate #2 at 2:30 p.m.

At 24 hours, water content 0

$$\begin{array}{r} 27.289 \\ 24.023 \\ 22.631 \end{array} \quad \frac{3.266}{1.392} = 235\%$$

The computations may be outlined as follows:

Water pick-up in 24 hours = 235 - 181.5 = 53.5%

Shearing strength (from calibration) = $(390)(5.445 \times 10^{-4})$

$= 0.212 \text{ lbs/in}^2$

Titration blank:

In 2.815 gm. of wet clay there are 1.0 gm. of solids and 1.815 gm. of water.

In 2.815 gm. of wet clay there are $\frac{1.5}{1.5 + 7.5}$ gm., or $\frac{1.5}{9.0}$ gms., of $Ca(Me)_2$ and 1.815 gm. of water

Therefore, in 3.375 gm. of wet clay there are 0.2000 gm. of $Ca(Me)_2$ and 2.17 gm. water. Hence, 0.2000 gm. $Ca(Me)_2$ are dissolved in 100 + 3 + 2.17 = 105.2 cc. of solution. Hence, in 10 cc. of supernatant solution there is the equivalent of 0.0190 gm. $Ca(Me)_2$. In 8.90 cc. of (0.1253 N) $KMnO_4$ there are $\frac{8.90}{1000} \times 0.1253 \times 31.606 = 0.03522$ gm. $KMnO_4$.

Hence, in the titration 0.03522 gm. $KMnO_4$ is equivalent to 0.0190 gm. $Ca(Me)_2$; or 1 gm. $KMnO_4$ is equivalent to 0.539* gm. $Ca(Me)_2$.

Now the same system will be considered with the further addition of the catalysts to instigate polymerization. Take the case in which 0.2 gm. of sodium bisulfite and 0.7 gm. of ammonium persulfate were added as catalysts.

The base-exchanged clay was prepared as before. Further, 0.2 gm. of $NaHSO_3$ were added and the mass was thoroughly mixed; and finally 0.7 gm. of $(NH_4)_2S_2O_8$ were added and rapidly mixed into a homogeneous state. The resulting clay system was then quickly pressed into one of

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* This particular test gave a rather high value: an average figure that was used was 0.500 gm. (See page

the shear-testing units. The importance of speed must be emphasized in this step, and especially so in some cases where the clay begins to set by polymerization after as short a period of induction as one minute. The shear test was run 24 hours later. The rest of the testing routine was as above described, with only the following exception. To the wet clay in the centrifuge bottle was added first a known volume of concentrated lead acetate solution (say 2 cc.) and the clay and glass beads were well shaken to ensure complete mixing with this solution: this procedure was adopted as a simple method of getting rid of any excess $NaHSO_3$ (reducing agent) which would vitiate the results of the titration.[*] The sulfuric acid was then added, and the rest of the testing routine remained the same.

The laboratory data for this case are here given as as example:

Sample: 7.5 gm. Na-bent. + 15 cc. H_2O + 1.5 gm. $Ca(Me)_2$
+ 0.2 gm. $NaHSO_3$ + 0.7 gm. $(NH_4)_2S_2O_8$

At 24 hours, shear test

Springs A $S_1 \rightarrow S_2 \rightarrow S_3 \rightarrow$ 9.2 cm.[**]

Weight of clay taken for analysis

$$\begin{array}{r} 17.840 \\ \underline{-14.686} \\ 3.154 \text{ gm.} \end{array}$$

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[*] With all other reducing agents no such procedure was available and suitable blanks had to be run.

[**] Springs S_1 and S_2 were pulled to capacity, and the reading was obtained on Spring S_3.

Added 2 cc. lead acetate soln. + 75 cc. H_2SO_4

Titration: 0.50 cc. of (0.1253 N) $KMnO_4$ vs 10 cc. of supernatant solution.

Water content R 22.399 / 20.859 / 19.882 $\frac{1.540}{0.977} = 157.5\%$

Spread the clay on porous plate #5 at 10:15 p.m.

At 24 hours, water content R 24.927 / 20.922 / 19.882 $\frac{4.005}{1.040} = 385\%$

Additional data: at 36 hours,

Water content M 21.790 / 18.671 / 17.911 $\frac{3.119}{0.760} = 410\%$

The computations follow exactly the same pattern as before

$$2.575 \text{ gm. wet clay} \rightarrow \frac{1.5}{9.9} \text{ gm. } Ca(Me)_2 + 1.575 \text{ gm. } H_2O$$

$$\therefore 3.154 \text{ gm. wet clay} \rightarrow 0.1856 \text{ gm. } Ca(Me)_2 + 1.92 \text{ gm. } H_2O$$

$\therefore$ 0.1856 gm. $Ca(Me)_2$ was distributed in 78.92 cc. of solution

$\therefore$ in 10 cc. of solution we should have the equivalent of 0.02351 gm. $Ca(Me)_2$.

In 0.50 cc. of (0.1253 N) $KMnO_4$ we have 0.00198 gm. $KMnO_4$. But 1 gm. $KMnO_4$ is equivalent to 0.500 gm. $Ca(Me)_2$ as determined by the blank; therefore, we actually have in solution the equivalent of 0.00099 gm. $Ca(Me)_2$ per 10 cc.

Hence, $Ca(Me)_2$ rendered insoluble

$$\begin{array}{r} 0.02351 \text{ gm.} \\ \underline{-0.00099 \text{ gm.}} \\ 0.02252 \text{ gm.} \end{array}$$

$$\text{Extent of polymerization} = \frac{0.02252}{0.02351} = 95.8\%$$

$$\text{Shear strength (from calibration)} = (1135)(5.445 \times 10^{-4})$$

$$= 0.619 \text{ lbs/in}^2$$

Water pick-up in 24 hours = 227.5%

Water pick-up in 36 hours = 252.5%

It may be noted from the nature of the computations that slight errors in determining the water content or the weight of wet clay taken for the analysis of polymerization are hardly reflected in the computed result; so also minor errors in the titration will not significantly alter the computed result.

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE

General

The majority of the tests were run on sodium-bentonite at about 200% water content, obtained by mixing dry sodium-bentonite powder with distilled water, maintaining a ratio of $\frac{\text{gm. of clay powder}}{\text{cc. of distilled water}} - 0.5$. All the preliminary testing for investigation of the several variables was conducted on sodium-bentonite at about 200% water content. Finally, in order to investigate the applicability of the treatment with sodium-bentonite, further tests were included on this clay at about 300% water content and 100% water content.

In the investigation of the effectiveness of the treatment with the different clays at different water contents, the following three basic steps must be recognized in every case: (a) a study of the shear strength and water affinity properties of the original untreated clay (b) investigation of the shear strength and water affinity properties of the clay after addition of varying amounts of the reagent which supplies the base-exchanging and polymerizeable complex ions (calcium methacrylate, and calcium acrylate) (c) investigation of the shear strength and water affinity properties of the clay samples of case (b) after further addition of catalysts. Assuming, in the ideal case of admixture of insignificant amounts of catalysts, that the catalysts are not responsible for any action other than that of effecting polymerization, it is clear that a comparison of corresponding cases (c) and (b) would supply a direct measure of the effectiveness of the polymerization. The comparison between cases (c) and corresponding cases (b) with respect to shear strength is undertaken in two ways: first by a ratio $\frac{\text{strength of sample in case (c)}}{\text{strength of sample in corresponding case (b)}}$ which is denoted $\frac{\text{strength of polymerized sample}}{\text{strength of unpolymerized sample}}$ %; and secondly, by the difference of shear strengths, which is denoted as the "increase of strength psi". Although it is recognized that the catalyst addition is responsible for significant effects other than the polymerizing effect, the above idealized method of analyzing the results of polymerization is retained throughout this text.

I. Properties of the Sodium-Bentonite

Many ring-shear tests were run on samples of sodium-bentonite at different water contents and only the maximum values of shear stress were recorded in the first series of tests. At lower water contents, three direct-shear tests were run with the observation of complete stress-strain data. (Fig. 44, p.) Subsequently, five more ring-shear tests were run, an attempt being made to obtain approximate stress-strain data from the ring-shear apparatus. (Fig. 45, p. tabulated results, p.) The shearing strength of all these tests are plotted on page , to give the shearing strength vs water content relationship for the sodium-bentonite. (Fig. 12, p. 94) It must be emphasized that this plot is

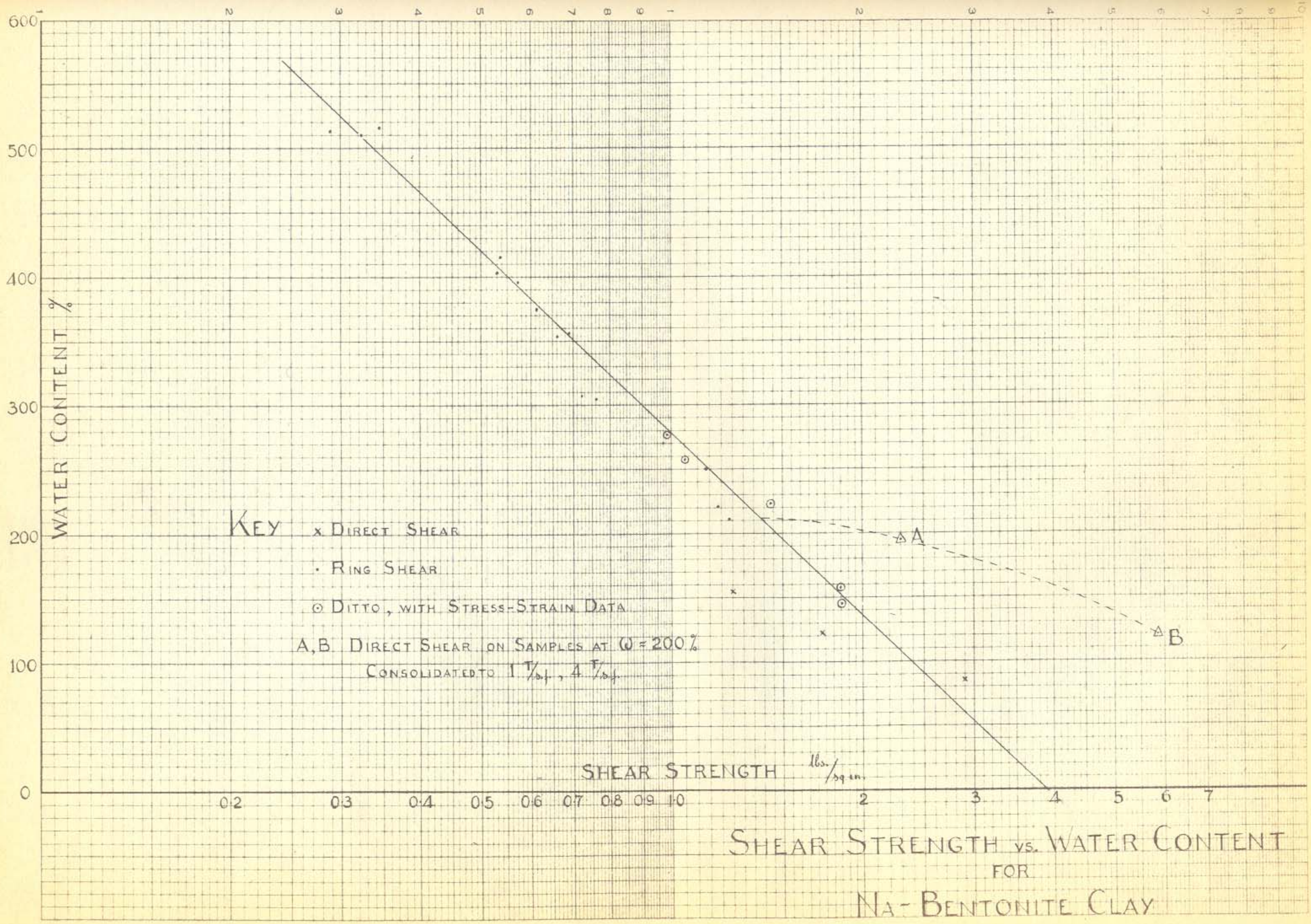

SHEAR STRENGTH vs. WATER CONTENT
FOR
NA - BENTONITE CLAY
WATER CONTENT %
600
500
400
300
200
100
0
SHEAR STRENGTH lbs./sq in.
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
2
3
4
5
6
7
KEY
x DIRECT SHEAR
· RING SHEAR
⊙ DITTO, WITH STRESS-STRAIN DATA
A, B DIRECT SHEAR ON SAMPLES AT ω = 200%
CONSOLIDATED TO 1 T/s.f., 4 T/s.f.
A
B

FIG. 12

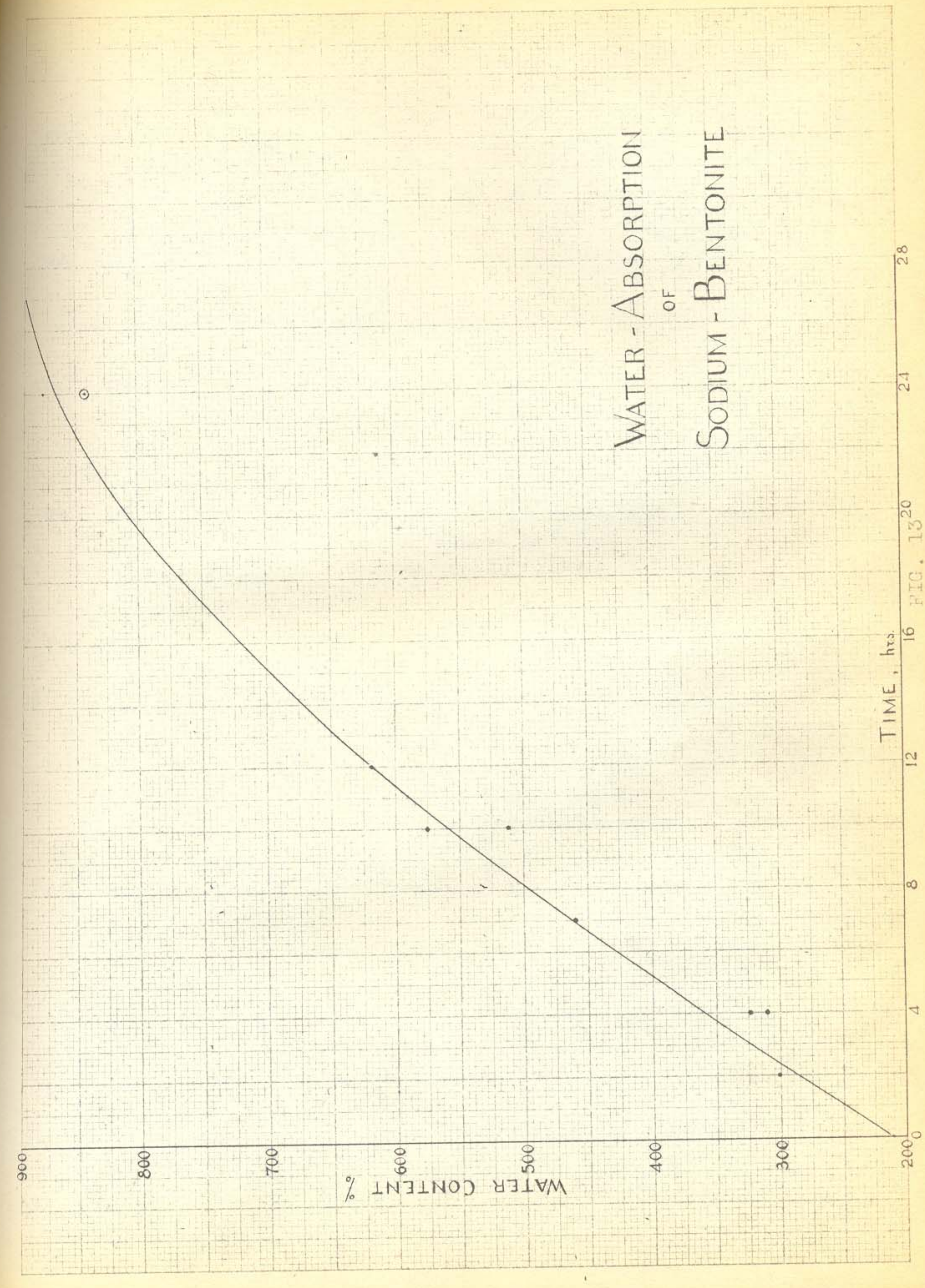
valid only for samples prepared at the respective water contents appearing as ordinates of the curve. Two more direct shear tests were obtained on samples of sodium-bentonite prepared at about 200% water content and then consolidated to 1 T/sf. and 4 T/sf. These tests and their purpose will be mentioned later, but it is of interest to note here the remarkably higher shearing strength obtained with these samples. The difference in strength at any given water content is quite clearly in large part due to a difference of the number of sodium ions active. Considering points on the two curves at 120% water content, it is presumed that for the sample that is consolidated from 200% water content, 56 me., which is 72% of the total exchange capacity, of sodium are active and the shear strength is about 6 psi. On the other hand for samples prepared at 120% water content only 48% of the total exchange capacity, or 37.5 me. of sodium, are active and the strength is about 2.2 psi. (Fig. 2, p. 49)

It may be noted, moreover, that the stress-strain curves of these consolidated samples indicate the development of a little "structure" in comparison with the stress-strain curves of the non-consolidated samples. (Fig. 46, The added shearing strength due to the development of "structure" is in part responsible for the large difference in strength at a given water content between consolidated and unconsolidated samples.

The other property of interest was the water absorption of the bentonite. A sample of sodium-bentonite increased in water-content from 208% to 842% in 24 hours, giving a water pick-up of 634% in the 24 hour period. It may be noted from the shear strength vs. water content plot that with such water absorption at the end of 24 hours the sodium-bentonite has no measurable shearing strength. One time-test was run, obtaining values of water absorption at 2, 4, 7, 10 and 12 hours. The plot of the results is presented herewith. (Fig. 13, p. 97) Finally a few tests were run on the water-absorption of a sample of sodium-bentonite prepared at about 300% water content; in 24 hours the water content increased to 860%.

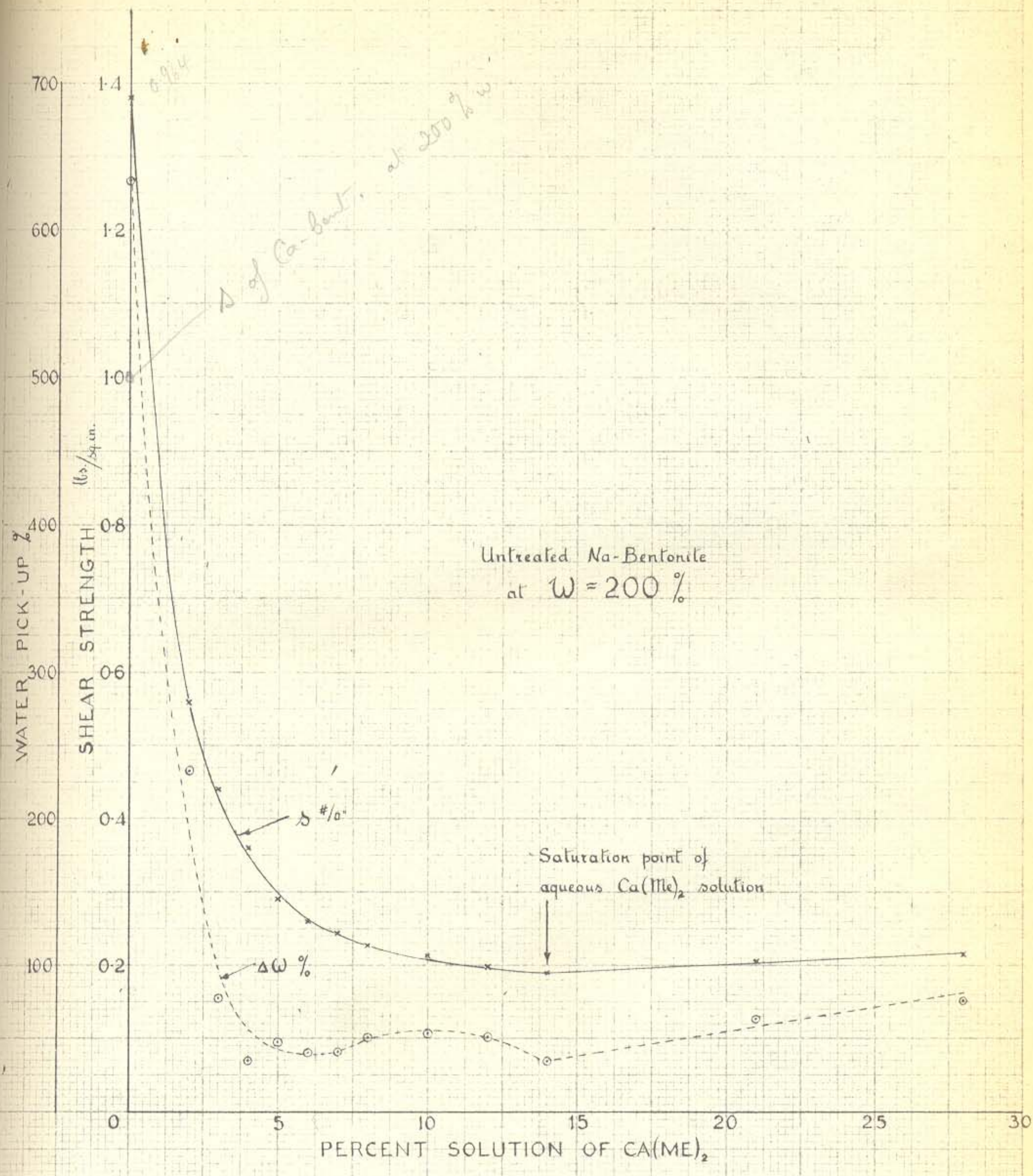
II. Properties of Sodium-Bentonite at 200% Water Content Upon Admixture with Calcium Methacrylate

The curves of Fig. 14, p. 98, present the results of tests carried out on sodium-bentonite clay to which various amounts of calcium methacrylate were added. The loss of strength with increasing addition of $Ca(Me)_2$ is very pronounced: it may be noted, however, that beyond the point of saturation of the solution, addition of the $Ca(Me)_2$ does not decrease the strength. It is evident by comparison with the shearing strength of calcium-bentonite (Fig. 31, p. at the same water contents that the loss of strength of sodium-bentonite on addition of calcium methacrylate is only partly explained by actual base-exchange: the effect of the



WATER - ABSORPTION OF SODIUM - BENTONITE

FIG. 13



STRENGTH AND WATER PICK-UP
OF
NA-BENTONITE
WITH CA(ME)₂ ADMIXTURES

FIG. 14

excess electrolyte in solution on the shearing strength seems to be very marked.

One further remark will here be made with respect to shearing strengths. It is clear that the addition of chemicals to a clay-water system so radically alters the shearing strength vs. water content relationship of the clay that it is quite pointless to refer to the shearing strengths in relation to the actual water contents. For example, a sodium-bentonite clay gel upon addition of calcium methacrylate rapidly loses its shearing strength although actually its water content is decreasing with the addition of the dry calcium methacrylate powder. However, the water content of the untreated clay is obviously a very important variable to be considered. The method is, therefore, adopted of referring to the water content of the untreated clay, regardless of the nature and extent of chemical admixture which subsequently alters the water content.

The water absorption curve shows relatively minor maxima and minima which may have academic significance in relation to the base-exchange data.

III. Polymerization Studies with Calcium Methacrylate, Sodium Bisulfite, Ammonium Persulfate

a) Preliminary tests: Na-bentonite at 200% w., $Ca(Me)_2$ admixture equivalent to 14% solution.

A number of runs were made on the same system, namely a sodium-bentonite clay gel at 200% water content with calcium methacrylate addition constituting a 14% solution, with wide variations in the amounts and proportions of the two catalysts. The samples were tested at 24 hours. The chart on page presents the results of these preliminary tests undertaken with a view to studying the variation of the degree of polymerization and the characteristics of the final product with variations in the amounts of the catalysts used.

Then, two time tests were run, one of long duration (over five days, testing samples at the end of each day) and one of short duration (over 24 hours, testing samples at 2, 6, 11 1/2 and 24 hours). The results definitely indicate that polymerization is rapid and either goes to completion rapidly or else is blocked. Fairly high concentrations of catalysts are necessary for complete polymerization. There is no definite indication, however, that a high degree of polymerization (as the term is used in this study) reflects on any of the strength characteristics of the product; in fact the effect of polymerization on the strength is not major in comparison with the probable purely ionic (base-exchange) effect of the catalysts. It does become apparent, however, that it is advisable to use concentrations of the ammonium persulfate at least as high as those of the sodium bisulfite, and preferably higher, for otherwise a thinly tacky product results.

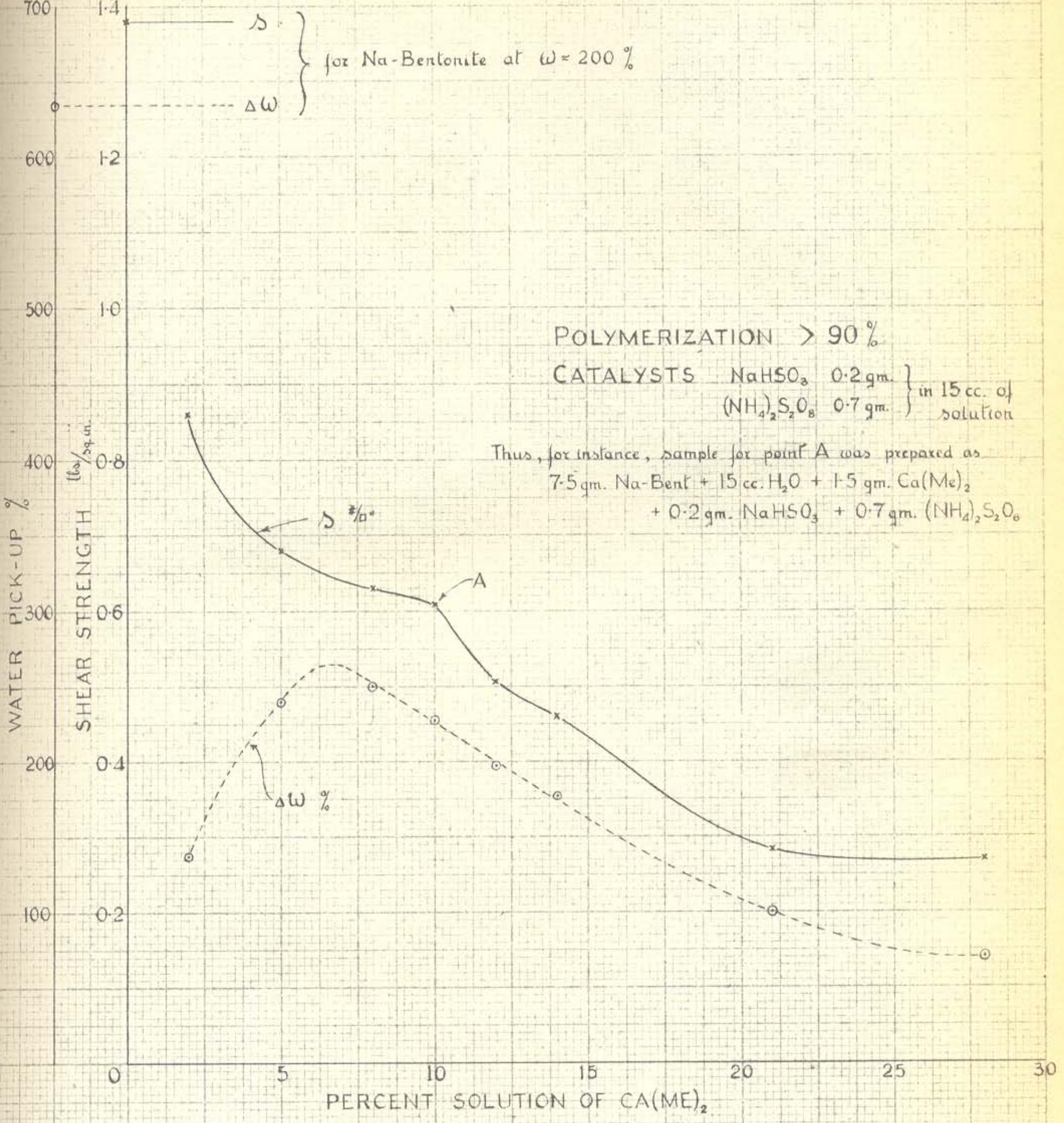
Finally, four separate samples were prepared at exactly similar conditions, to determine the reproducibility of results. Cases, like those tested, that go to complete polymerization are fairly reproducible, although there is still a noticeable strength variation that makes it particularly difficult to evaluate the relatively minor effects of strength increase that are attributable purely to polymerization.

b) Variation of Concentration of $Ca(Me)_2$ in the System

A complete series of tests was run keeping the catalysts constant and varying the amount of calcium methacrylate added. The results of this series of tests are tabulated in detail on page . The strength and water pick-up characteristics of the various samples are plotted on Fig. 15, page 102: in all the cases the polymerization was complete.

The two major observations that can be made are:

(1) By consulting the chart on page , it may be seen that the effect of increase of strength purely by polymerization is about constant (using the $NaHSO_3$ - $(NH_4)_2S_2O_8$ catalysts) regardless of the concentration of calcium methacrylate in solution, and this effect is small enough so that the controlling factor in determining the strength of the product is the base-exchange factor. Thus, the polymerization of calcium methacrylate with the bisulfite-persulfate catalysts is of such a nature that the calcium methacrylate/clay ratio has no influence on the strength of the polymerized product.



POLYMERIZATION > 90 %

CATALYSTS $NaHSO_3$ 0·2 gm. } in 15 cc. of solution
$(NH_4)_2S_2O_8$ 0·7 gm.

Thus, for instance, sample for point A was prepared as
7·5 gm. Na-Bent + 15 cc. H_2O + 1·5 gm. $Ca(Me)_2$
+ 0·2 gm. $NaHSO_3$ + 0·7 gm. $(NH_4)_2S_2O_8$

BENTONITE - CA(ME)$_2$

POLYMERIZED WITH

$NaHSO_3$, $(NH_4)_2S_2O_8$ CATALYSTS

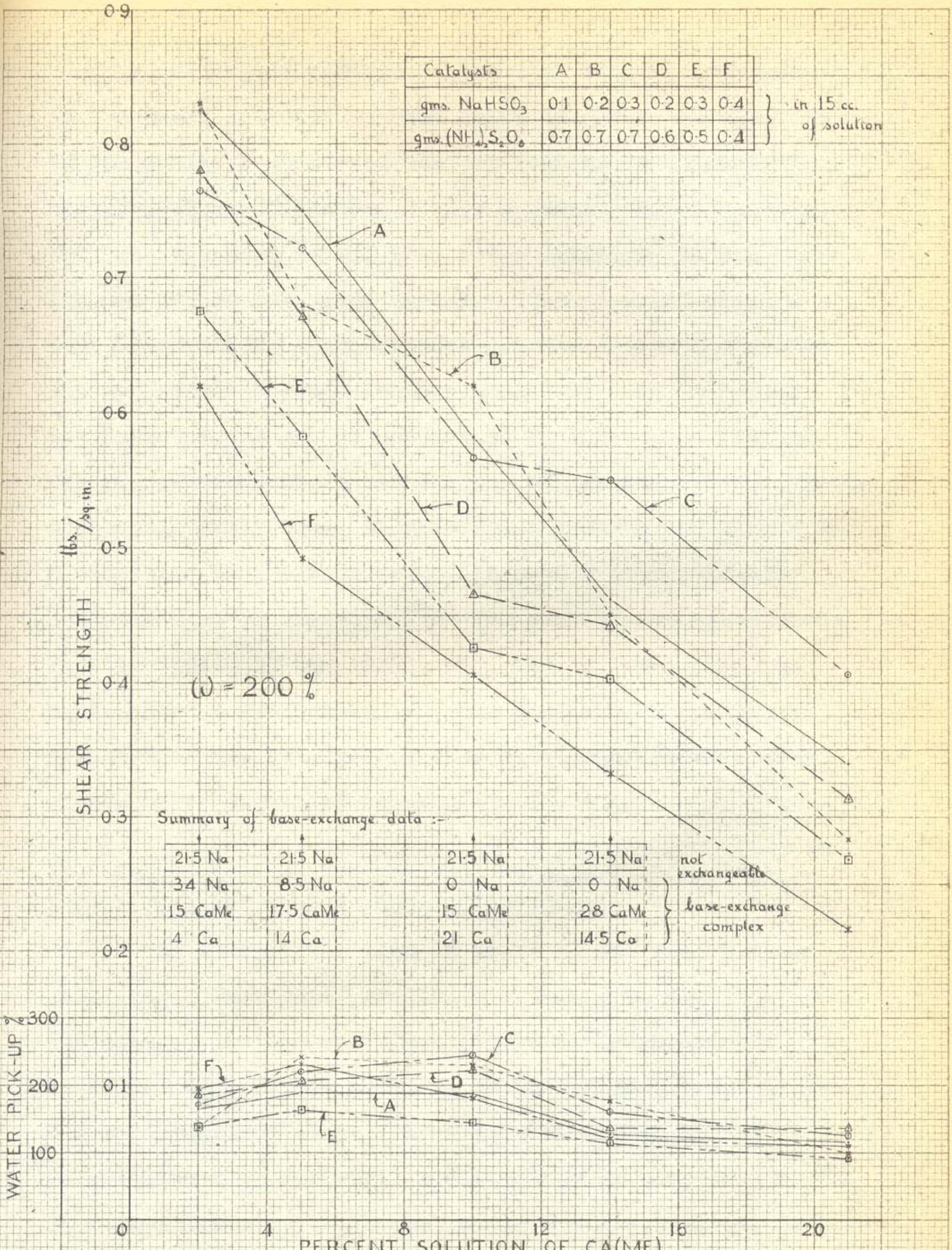
FIG. 15

(2) It may be readily noticed in Fig. 15, page 102, that the water pick-up characteristics show a very pronounced maximum. By comparison with Fig. 14, page 98, it may be noted that the water pick-up of all polymerized samples is considerably higher than the water pick-up of corresponding unpolymerized samples, except when the treatment is excessive (constituting what would be a 28% solution of $Ca(Me)_2$) or very slight (constituting a 2% solution of $Ca(Me)_2$).

These results were obviously somewhat alarming. In order to check on possible anomalous data, five more series of tests were run, not attempting, however, to obtain so many points on each curve. The results of these five series are ploted, together with the results of the previous series, on page 104, (Fig. 16). Thus on page are plotted strength and water pick-up characteristics of sodium-bentonite-calcium methacrylate systems polymerized with the following six sets of amounts of catalysts.

$NaHSO_3$	0.1 gm	0.2 gm	0.3 gm	0.2 gm	0.3 gm	0.4 gm
$(NH_4)_2S_2O_8$	0.7 gm	0.7 gm	0.7 gm	0.6 gm	0.5 gm	0.4 gm

All of these series show the same trends: the same steady decrease of strength of the sample with increasing amounts of $Ca(Me)_2$ added, in spite of polymerization; and in the water pick-up curve the same hump previously observed. Furthermore, it may be noted that the relative position of the "curves" for the various series strongly suggests that the highest strengths are obtained with the higher amounts of ammonium persulfate added. Unfortunately,



Catalysts	A	B	C	D	E	F
gms. $NaHSO_3$	0·1	0·2	0·3	0·2	0·3	0·4
gms. $(NH_4)_2S_2O_8$	0·7	0·7	0·7	0·6	0·5	0·4

} in 15 cc. of solution

Summary of base-exchange data :-

21·5 Na	21·5 Na	21·5 Na	21·5 Na	not exchangeable
34 Na	8·5 Na	0 Na	0 Na	base-exchange complex
15 CaMe	17·5 CaMe	15 CaMe	28 CaMe	
4 Ca	14 Ca	21 Ca	14·5 Ca	

POLYMERIZATION OF BENTONITE - $CA(ME)_2$ WITH $NAHSO_3$, $(NH_4)_2S_2O_8$ CATALYSTS

FIG. 16

however, the water pick-up of the clay samples increases in the same direction. Could it be that the ionic effect of the catalyst additions was pre-eminent in determining the properties of the final clay product? Practically all the data appeared to fit this interpretation, if the introduction of ammonium ions by base-exchange would yield a clay intermediate in properties between a sodium-clay and a clay saturated predominantly with $CaMe^+$ and Ca^{++} ions. For instance, it may be noted that in the case of the 2% $Ca(Me)_2$ samples, the water pick-up of the polymerized sample was consistently lower than in the corresponding case prior to addition of the catalysts: in such a case evidently much exchange of ammonium ions for sodium ions takes place. (At the bottom of the graph, Fig. 16, is summarized the base-exchange data obtained from samples prior to the addition of the catalysts.) The details of these series of tests are tabulated on page

IV. Polymerization Studies with Calcium Methacrylate, Sodium Thiosulfate and Ammonium Persulfate

An attempt was made to shift to the use of other catalysts. Very brief preliminary tests run with the catalysts hydrazine hydrate and t-butyl-hydroperoxide indicated no strength increase of the polymerized clay over the unpolymerized clay: the water absorption of the polymerized clay was still a little higher than that of the unpolymerized clay, although not as noticeably so as in the cases employing bisulfite-persulfate catalysts. The very effective use of sodium thiosulfate and ammonium persulfate for polymerization of calcium acrylate solutions (Chapter 7) suggested the advisability of running a series of tests with these catalysts as applied to clay-methacrylate systems.

Accordingly, a series of eight tests was run on clay-methacrylate systems at 200% water content comprising a 10% solution of admixed calcium methacrylate; the amounts and proportions of the catalysts were varied much in the same way as was done in a similar series with bisulfite-persulfate catalysts. The results are tabulated on page It is noted that the strength characteristics of the polymerized product are quite similar to those of the corresponding bisulfite-persulfate systems; again the evidence is that the effect of the polymerization on the strength increase is slight. The water affinity is quite noticeably lower than the water affinity of corresponding bisulfite-persulfate systems. No apparent ionic explanation occurs to the author since the amount of sodium supplied into the system is about equivalent in the two cases, and the concentration of ammonium persulfate is the same.

V. Base-Exchange Effect of the Added Catalysts on the Properties of the Final Product

In the last few sections the discussion has frequently attempted to separate the ionic effect of the catalysts from their polymerizing effect. That the catalysts above used were participating in base-exchange was distinctly evidenced by most of the data. In view of the possibility that such base-exchange might play an important role in determining the properties of the final product a series of tests was run with appropriate blanks, in order to attempt to evaluate such an effect. Unfortunately, time limitations forced the reduction of this investigation to an insufficient number of tests. In order to arrive at sound conclusions with regard to a separation of the base-exchange and the polymerization factors an especially extensive series of tests is required since, in every case, the blank must necessarily be a simulated blank.

A true blank would be considered to be a blank in which the actual reagents (e.g., calcium methacrylate, sodium bisulfite, and ammonium persulfate) were added, but the polymerization was completely inhibited by some method which simultaneously left the system otherwise completely undisturbed. If, instead, the approach used consists of substituting one or more of the actual reagents by reagents which are not capable of, or do not cause, polymerization, but are ionically similar, the blank is referred to as a simulated blank.

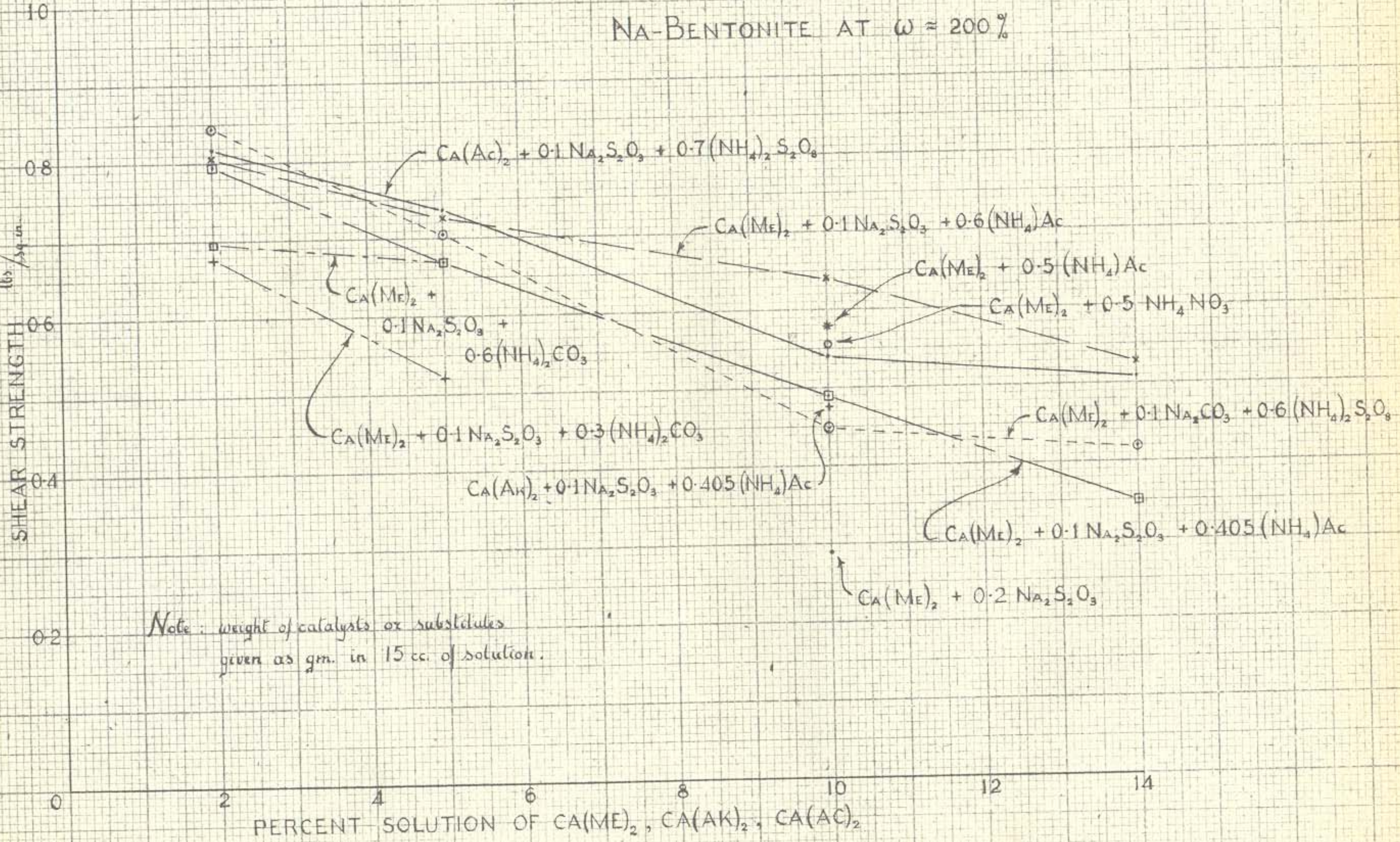
A first attempt was made by using sodium carbonate and ammonium persulfate in the clay-calcium methacrylate system. Tests were run by adding 0.1 gm. Na_2CO_3 and 0.6 gm. $(NH_4)_2S_2O_8$; computing purely on a basis of the amount of sodium introduced, this is about equivalent to the system 0.168 gm. $NaHSO_3$ + 0.6 gm. $(NH_4)_2S_2O_8$ and

0.20 gm. $Na_2S_2O_3 \cdot 5\ H_2O$ + 0.6 gm. $(NH_4)_2S_2O_8$. Unfortunately, it became evident that from two points of view the use of sodium carbonate and ammonium persulfate could be questioned: (1) the carbonate would tend to precipitate calcium (2) the persulfate causes polymerization even without the addition of reducing agent.

A few tests were run using 0.1 gm. sodium thiosulfate plus 0.3 gm. ammonium carbonate and 0.1 gm. sodium thiosulfate plus 0.6 gm. ammonium carbonate. The above objection to the use of the carbonate suggested the discontinuance of this series.

Finally two brief series of tests were run using sodium thiosulfate and ammonium acetate. 0.1 gm. of sodium thiosulfate was used in both series. The first series employed 0.405 gm. of ammonium acetate which was calculated to supply as much ammonium as is supplied by 0.6 gm. of ammonium persulfate. The second series employed 0.6 gm. of ammonium acetate which was calculated to supply as much ammonium as is supplied by 0.89 gm. of ammonium persulfate.

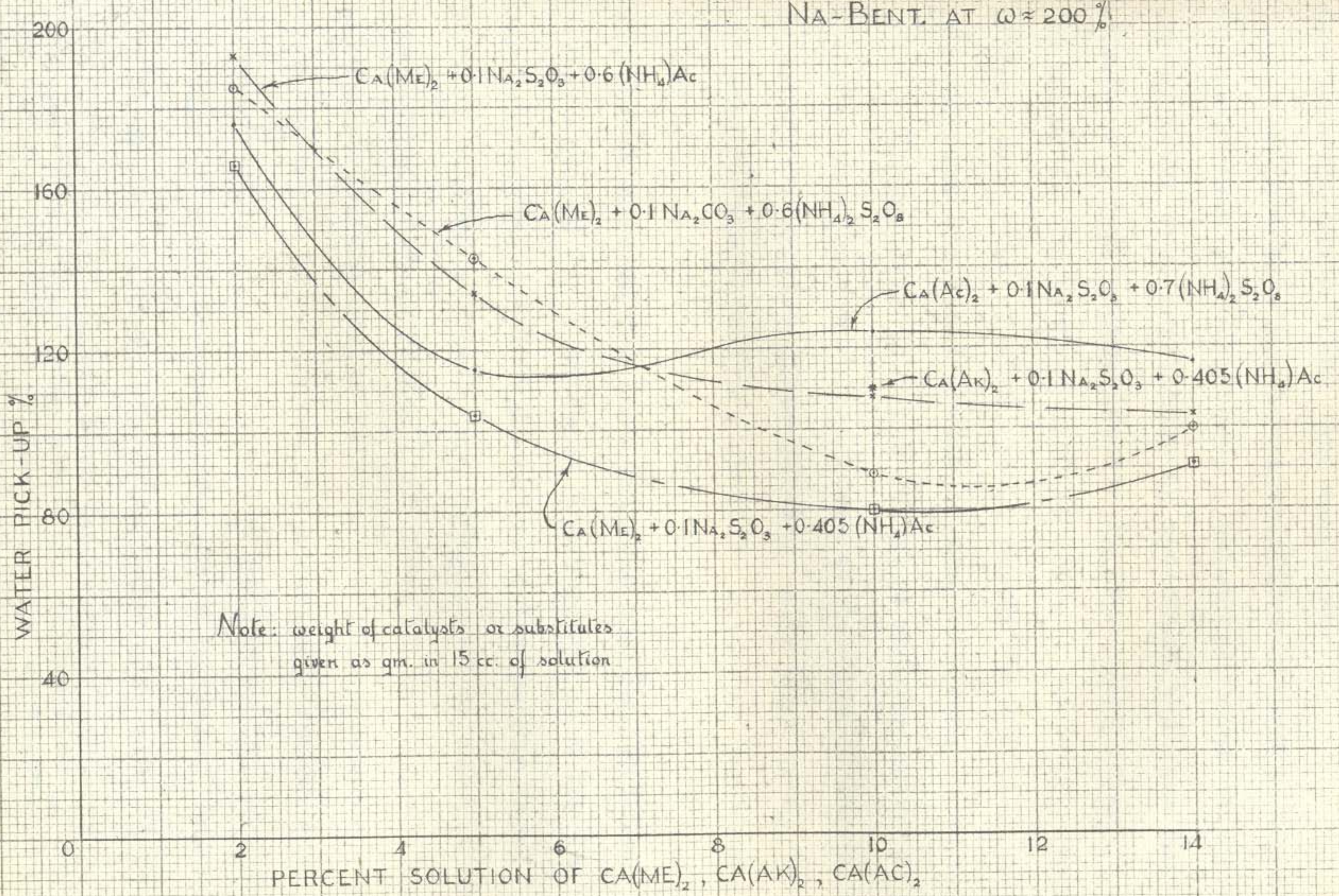
All of these results are plotted in Figs. 17 and 18, pages 109 and 110. These two plots were used in order to estimate the base-exchange effects of the catalysts. It is evident that with such scant data, the interpolation involves the possibility of major errors. Actually such data, in order to be of any real scientific value would have to be closely associated with thorough analyses of the exchangeable bases introduced. The procedure used in the base-exchange studies could be very simply adapted for this



Note: weight of catalysts or substitutes given as gm. in 15 cc. of solution.

(ME) = methacrylate
(AK) = acrylate
(Ac) = acetate

SIMULATED BLANKS
FOR
IONIC EFFECTS OF CATALYSTS



SIMULATED BLANKS
FOR
IONIC EFFECTS OF CATALYSTS

FIG. 18

purpose, by merely including data on the amount of ammonium supplied to the system and the amount of it present in the supernatant liquid after base-exchange.

Unfortunately, time limitations prevented the undertaking of such testing. From a practical point of view the above blanks were sufficient to establish the fact that the effect of actual polymerization in increasing strength is not major in the systems studied above. Moreover, from a practical point of view, it is purely of academic interest to subdivide the total effect of the catalysts.

In the same plot are included results obtained by a different approach. If instead of calcium methacrylate or calcium acrylate, other calcium salts were used, then the actual redox catalysts could be used for the blanks: if suitable calcium salts could be found, such an approach might even furnish the best possible blanks. Calcium acetate seemed to be the most appropriate salt for the purpose, having a molecular weight quite nearly equal to that of calcium acrylate, and being about as soluble as the methacrylate and acrylate.* In order to check how close an approximation the use of calcium acetate represented, a few tests were run to determine the shearing strength and water-affinity characteristics of sodium-bentonite with the addition of varying amounts of calcium acetate. The results are presented in Figs. 19, 20 on pages 112, 113; closer

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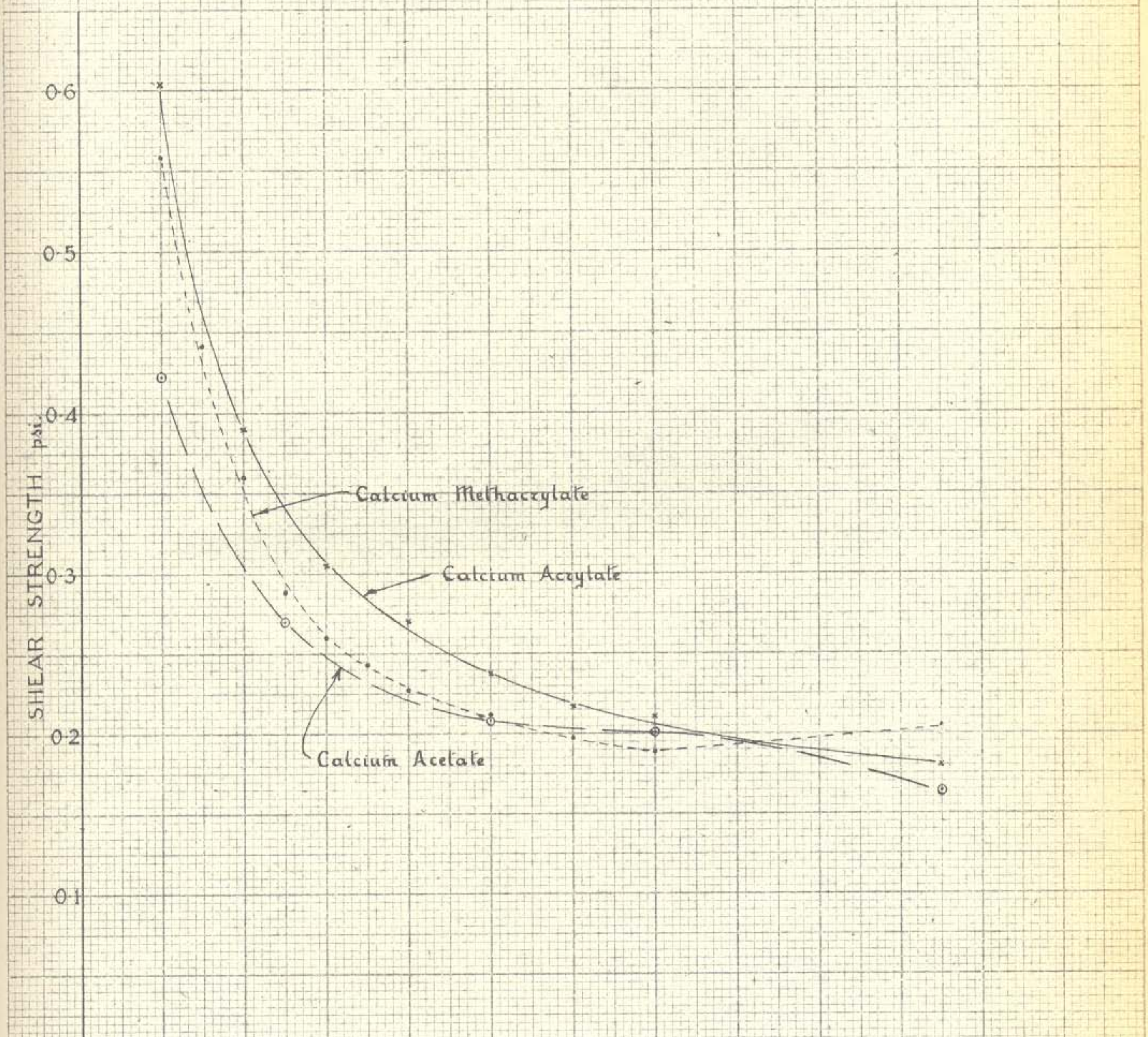
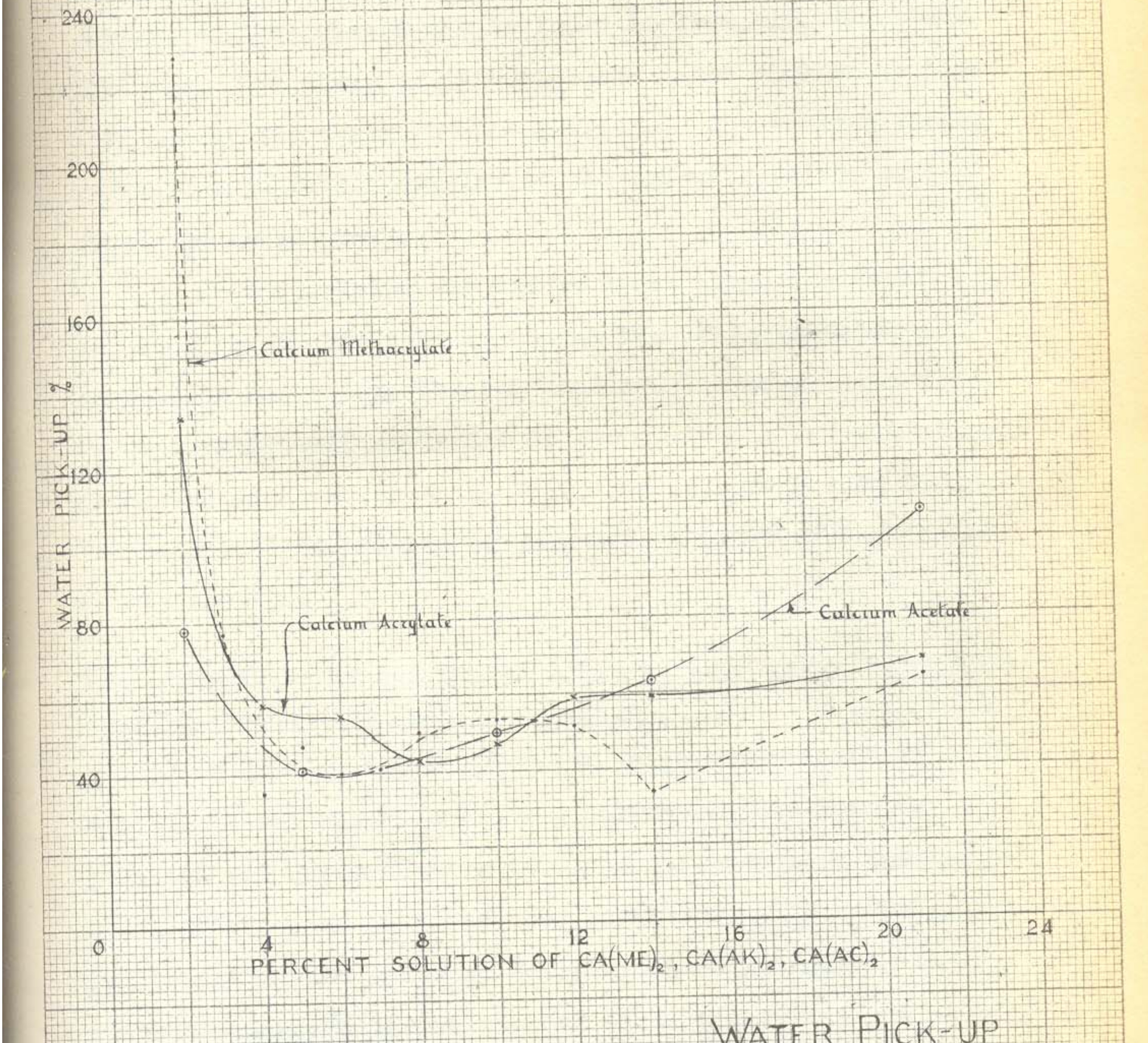
* It must be emphasized that these simple criteria do not presume to establish completely the suitability of the salt for the use intended. Ionization plays an important role; and the effect of the anion cannot be totally neglected. Hence, at best such a simulated blank represents an approximation.



SHEAR STRENGTH
OF
NA-BENTONITE AT $\omega = 200\%$
WITH
ADMIXTURES OF $CA(ME)_2$, $CA(AK)_2$, $CA(AC)_2$

FIG. 19



WATER PICK-UP
OF
NA-BENTONITE AT ω = 200%
WITH
ADMIXTURES OF $Ca(Me)_2$, $Ca(Ak)_2$, $Ca(Ac)_2$

FIG. 20

similarity would almost be too much to hope for. A series of tests was then run, using calcium acetate, to evaluate the ionic effect of addition of sodium thiosulfate-ammonium persulfate catalysts; a combination of 0.1 gm. sodium thiosulfate and 0.7 gm. ammonium persulfate was used. The results of these tests are included in Figs. 17, 18, pages 109, 110. The shearing strengths are quite similar to those obtained by the other simulated blanks. The water-affinity curve also is fairly similar to the curves obtained by the other simulated blanks.

As a conclusion it may be stated that the ionic effect of such catalysts as sodium bisulfite-ammonium persulfate and sodium thiosulfate-ammonium persulfate may be reasonably well estimated by appropriately and selectively using the data presented in Figs. 17, 18, pages 109, 110. The numerical estimation of this effect is attempted in the charts on pages

VI. Properties of Sodium-Bentonite at 200% Water Content Upon Admixture with Calcium Acrylate

A similar series of tests to that mentioned in section II was run with calcium acrylate. The results obtained are quite similar to those obtained with calcium methacrylate (see Figs. 19, 20, pages 112, 113). The only point that may be noted as being somewhat strange is the fact that for similar weights of calcium acrylate and calcium methacrylate added, the latter gives consistently lower strength results although actually the molar concentration of the solution is greater in the case of addition of calcium acrylate. (Molecular weight of $Ca(Me)_2$ = 210.2, molecular weight of $Ca(Ak)_2$ = 182.1)

Mention is here also made of a single test that was run with calcium acrylate, sodium thiosulfate and ammonium acetate, to determine the probable ionic effect of the catalysts. (Figs. 17, 18, pages 109, 110) More tests would have been run were it not for a fear of running short of calcium acrylate towards the end of the investigations; subsequently time limitations imposed difficulties on attempts to obtain complete data. Fortunately the indications are that the differences between the systems containing $Ca(Me)_2$ and those prepared with $Ca(Ak)_2$ are but slight as regards ionic effects.

VII. Polymerization Studies with Calcium Acrylate, Sodium Bisulfite and Ammonium Persulfate

Since the search for redox catalysts had proved much more fruitful with respect to calcium acrylate solutions than with calcium methacrylate solutions, it was decided to revert to the use of calcium acrylate for treatment of the clay-water systems. Accordingly the following few sections report results of brief series of tests conducted on bentonite-acrylate systems with various sets of catalysts. Since the purpose of these tests was to evaluate the effectiveness of the catalysts in instigating polymerization suitable for increasing the shearing strength of the clay and decreasing its water-affinity, variations in proportions and amounts of the two catalysts in each set had to be investigated. For the sake of brevity all other variables were maintained constant and thus the series of tests were run on a sodium-bentonite gel at 200% water content treated with calcium acrylate to make up the equivalent of a 10% solution of calcium acrylate in the system, e.g., 7.5 gms. Na-bentonite + 15 cc. H_2O + 1.5 gms. calcium acrylate. It was felt that the catalysts could be expected to rank in about the same order of merit if tested under any other conditions.

The first set of catalysts thus investigated was one of the sets that had previously been used with calcium methacrylate-clay, namely, sodium bisulfite and ammonium persulfate. The results are presented in the chart on page It may be noted that these results are quite similar to the corresponding results obtained with calcium methacrylate.

It was noticed that in general the samples that showed higher shearing strengths simultaneously showed higher water-absorption. In the case of such catalysts as sodium bisulfite and ammonium persulfate, these samples with higher strength and higher water absorption were usually produced by using high concentrations of ammonium persulfate and moderate concentrations of sodium bisulfite; it is quite likely that the results are to be explained in large part by the participation of the catalysts in base-exchange. However, roughly linear relationships between strength and water-affinity were also obtained by the use of all other catalysts, including such sets as hydrazine hydrate and t-butyl-hydroperoxide. For comparison of the effectiveness of the various catalysts the procedure was, therefore, adopted of plotting shearing strength vs. water absorption and thus establishing the various straight lines representing conditions produced by the several sets of catalysts. (Fig. 21 on pages 118, 119)

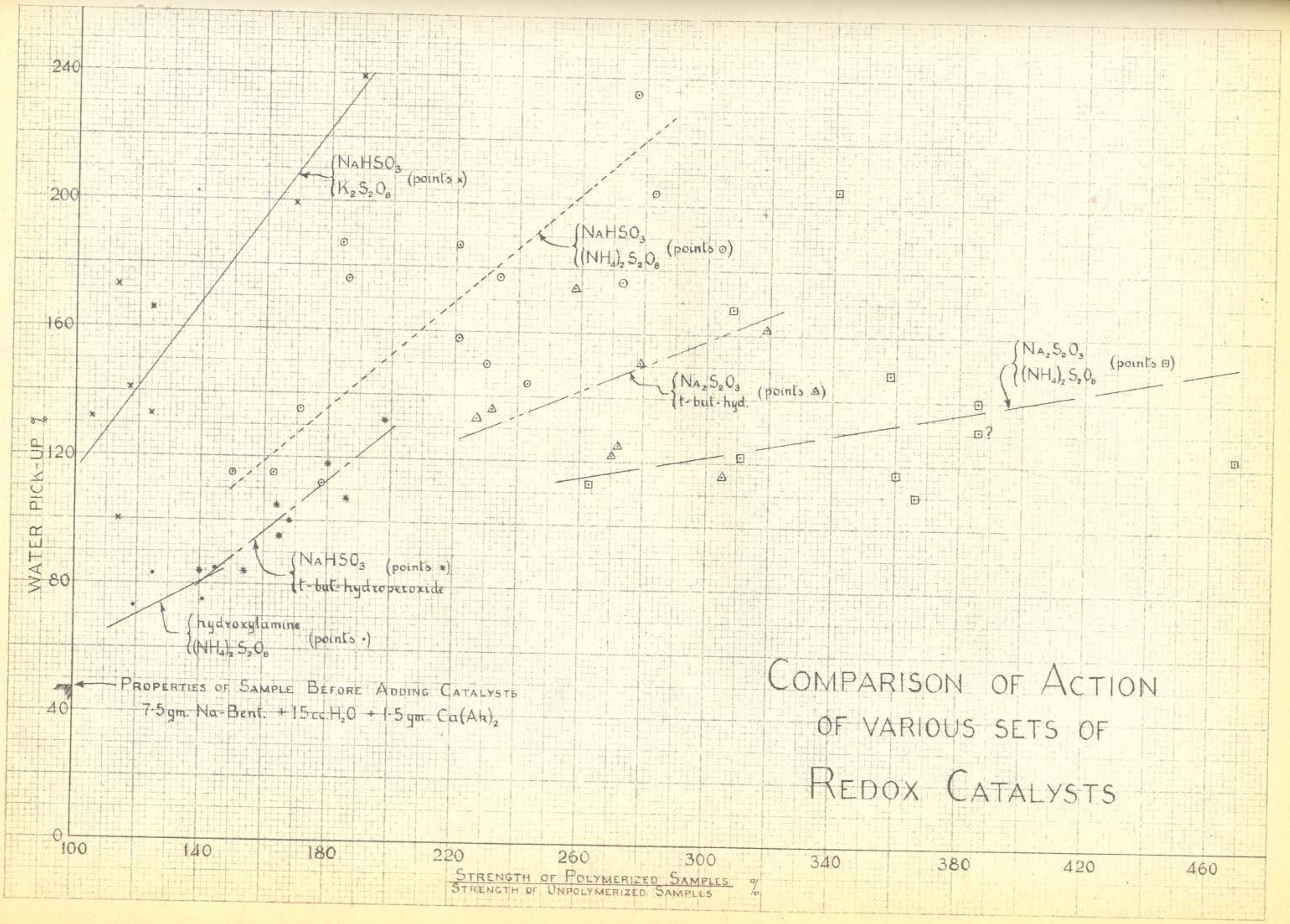
VIII. Polymerization Studies with Various Other Sets of Catalysts

A series of tests, similar to that mentioned above, was run for each of the remaining eleven sets of catalysts mentioned on page 63.

sodium bisulfite + t-butyl-hydroperoxide
" " + potassium persulfate
hydrazine hydrate + t-butyl-hydroperoxide
" " + ammonium persulfate
" " + potassium persulfate
hydroxylamine hydrochloride + t-butyl-hydroperoxide
" " " + ammonium persulfate
" " " + potassium persulfate
sodium thiosulfate + t-butyl-hydroperoxide
" " + ammonium persulfate
" " + potassium persulfate

The results are plotted in Fig. 21, pages 118, 119 and are presented in greater detail in charts on pages

With each set of catalysts one simulated blank was run with calcium acetate in order to delineate between the polymerizing and non-polymerizing effects of the catalyst addition. The results are somewhat too scant and erratic to permit drawing any but the most general conclusions. The contribution of polymerization to the shearing strength is in all cases small (except with the use of sodium thiosulfate



WATER PICK-UP %
240
200
160
120
80
40
0
100
140
180
220
260
300
340
380
420
460
STRENGTH OF POLYMERIZED SAMPLES / STRENGTH OF UNPOLYMERIZED SAMPLES %
NaHSO$_3$ K$_2$S$_2$O$_8$ (points ×)
NaHSO$_3$ (NH$_4$)$_2$S$_2$O$_8$ (points ⊙)
Na$_2$S$_2$O$_3$ t-but-hyd. (points ◬)
Na$_2$S$_2$O$_3$ (NH$_4$)$_2$S$_2$O$_8$ (points ⊡)
NaHSO$_3$ t-but-hydroperoxide (points *)
hydroxylamine (NH$_4$)$_2$S$_2$O$_8$ (points ·)
?
PROPERTIES OF SAMPLE BEFORE ADDING CATALYSTS
7·5gm. Na-Bent. + 15cc.H$_2$O + 1·5gm. Ca(Ak)$_2$
COMPARISON OF ACTION OF VARIOUS SETS OF REDOX CATALYSTS

FIG. 21

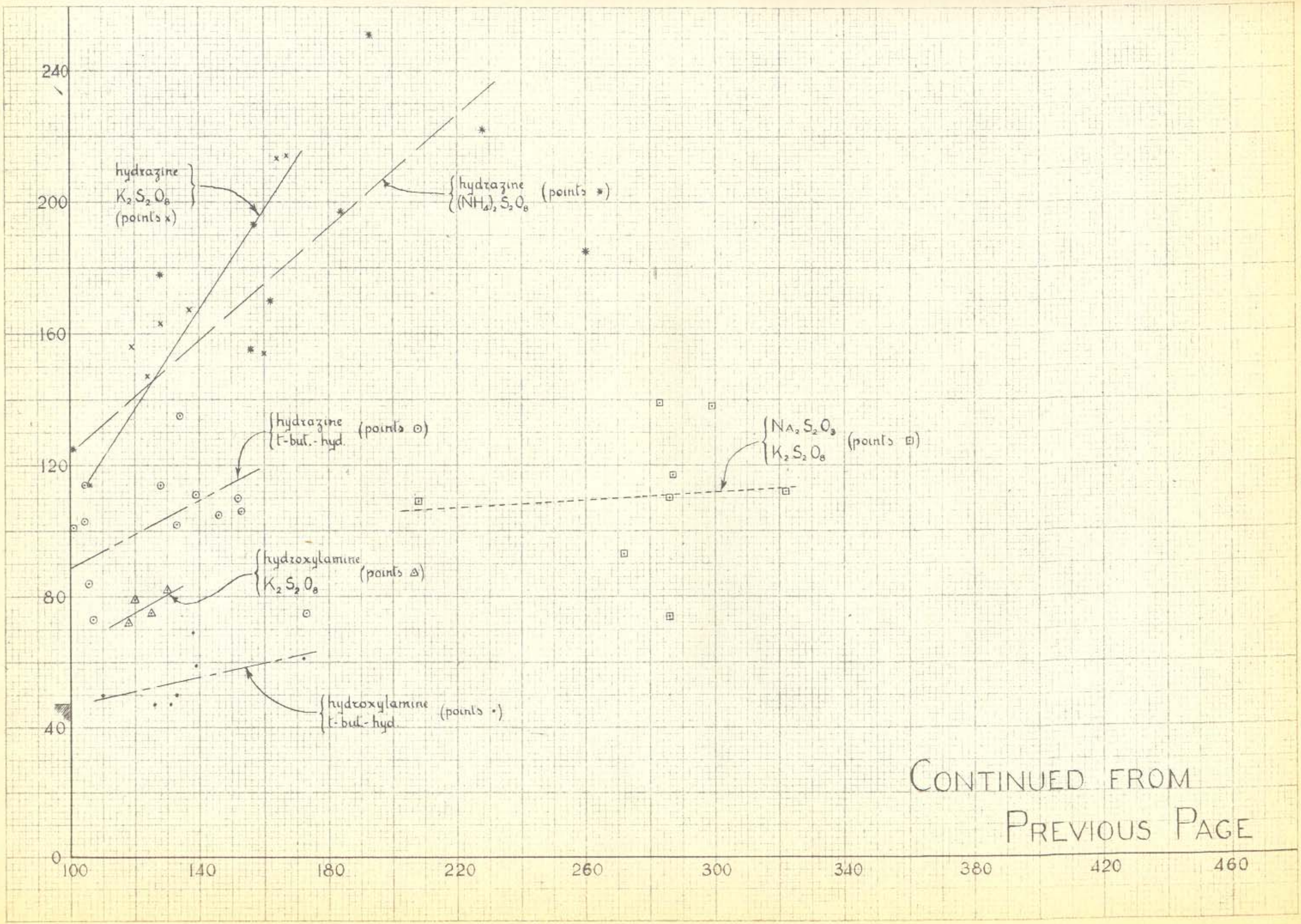

240
200
160
120
80
40
0
100
140
180
220
260
300
340
380
420
460
hydrazine $K_2S_2O_8$ (points x)
{hydrazine $(NH_4)_2S_2O_8$ (points *)
{hydrazine t-but.-hyd. (points ⊙)
{hydroxylamine $K_2S_2O_8$ (points △)
{hydroxylamine t-but.-hyd. (points ·)
{$Na_2S_2O_3$ $K_2S_2O_8$ (points ⊡)
CONTINUED FROM PREVIOUS PAGE

FIG. 21 (con't)

and ammonium persulfate). The previously noted curious trend indicating an increase of water affinity to be caused by the polymerization, is still supported by most of this data; but such scant data cannot accredit such an amazing statement. There is a possibility that the polymerization reaction in itself may cause a change in the exchangeable ions associated with the clay, by throwing calcium acrylate out of solution. Such an effect might explain the otherwise incomprehensible data.

All the catalysts tended to increase the water affinity of the treated clay in comparison with the base-exchanged but unpolymerized samples. The use of hydroxylamine hydrochloride achieved the retention of almost as low a water pick-up as that of the unpolymerized samples, especially when used in combination with t-butyl-hydroperoxide. Unfortunately, however, the strength increases due to polymerization in this case were not particularly encouraging. Among all the catalysts, indeed, the only set that gave strength results that approached the shearing strength of the original sodium-bentonite clay at 200% water content, was sodium thiosulfate-ammonium persulfate. A glance at the plot on pages 118 and 119 (Fig. 21) will establish beyond argument the remarkable superiority of sodium thiosulfate-ammonium persulfate for catalysation of this clay-calcium acrylate system. Unfortunately, it must be emphatically stated that in this matter of polymerization catalysis there cannot be the final assertion of absolute superiority of one catalyst over others. Under the conditions investigated, the sodium thiosulfate-ammonium persulfate catalysts are the best among the twelve sets tried. But the data obtained prove that the properties of the polymerized clay-acrylate system depend very much on the catalysts used. Is there any assurance that other catalysts not yet investigated in this study will not give vastly better results? The answer is no, with further research and luck better catalysts may be found: therein lies unsmothered the further hope of this process of stabilizing clays.

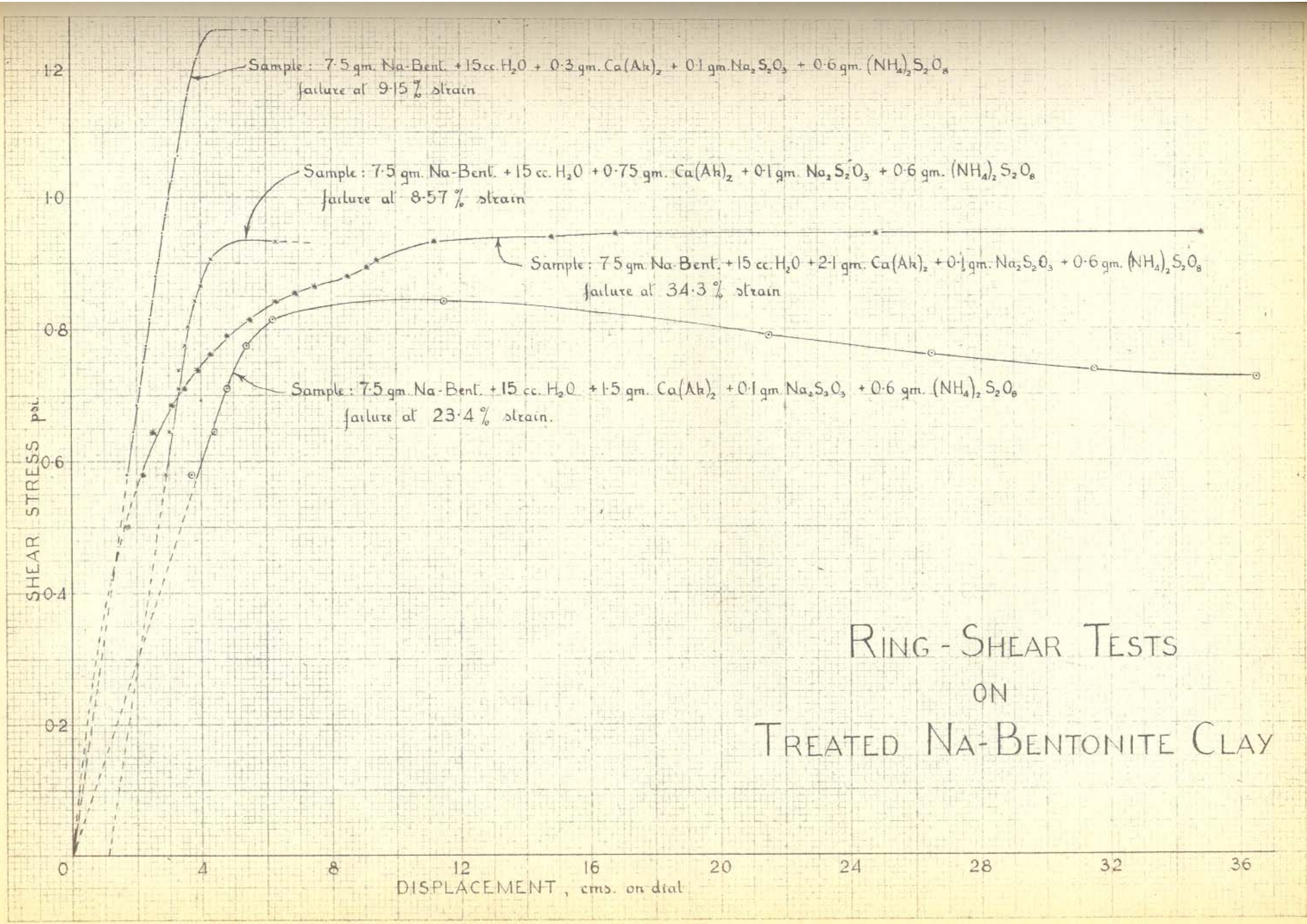
IX. Polymerization Studies with Calcium Acrylate, Sodium Thiosulfate, Ammonium Persulfate

Although the eventual discovery of any set of catalysts uperior to sodium thiosulfate and ammonium persulfate is likely to shadow the knowledge gained from a systematic study of clay-acrylate systems polymerized with these thiosulfate-persulfate catalysts, a brief series of tests was undertaken for such a study that might serve as a suitable conclusion for this thesis investigation. Here, at last, was obtained a polymerized bentonite-acrylate system that exhibited a shearing strength about equal to the strength of the original sodium-bentonite. Here, at last, was obtained a set of catalysts that so effectively polymerized the calcium acrylate that the strength increase due purely to polymerization was appreciable. Here, at last, was obtained a set of catalysts that made investigation of other variables in the system seem worthwhile.

Accordingly, a series of tests was run on sodium-bentonite at 200% water content with admixture of calcium acrylate equivalent to a 14% solution of the acrylate. The purpose was primarily to establish the optimum amounts and proportions of the two catalysts to be used. Once again, as had been the case in a similar study with the bisulfite-persulfate catalysts, it was found that best results were obtained with the use of relatively high concentrations of the ammonium persulfate and moderate or low concentrations of the sodium thiosulfate.

The four best sets of concentrations of the two catalysts to be used were then employed in completing a series of tests to investigate the effect of variation of the amount of calcium acrylate added to the sodium-bentonite. Accordingly, as had been previously done in the case of calcium methacrylate, sodium bisulfite and persulfate (Section III, page 99) the amount of calcium acrylate was varied to correspond to 2%, 5%, 10%, 14% and 21% aqueous solutions of the acrylate in the clay-water system. The results are presented in the charts on pages
Approximate stress-strain data were secured for most of these shearing strength tests: four sample stress-strain curves are plotted in Fig. 22 on page 123. (Tabulated results, pages

Discussing the results of the stress-strain curves briefly we may observe the following point. It will be noted that in the cases of the 2% and 5% treatment of calcium



RING - SHEAR TESTS
ON
TREATED NA-BENTONITE CLAY

FIG. 22

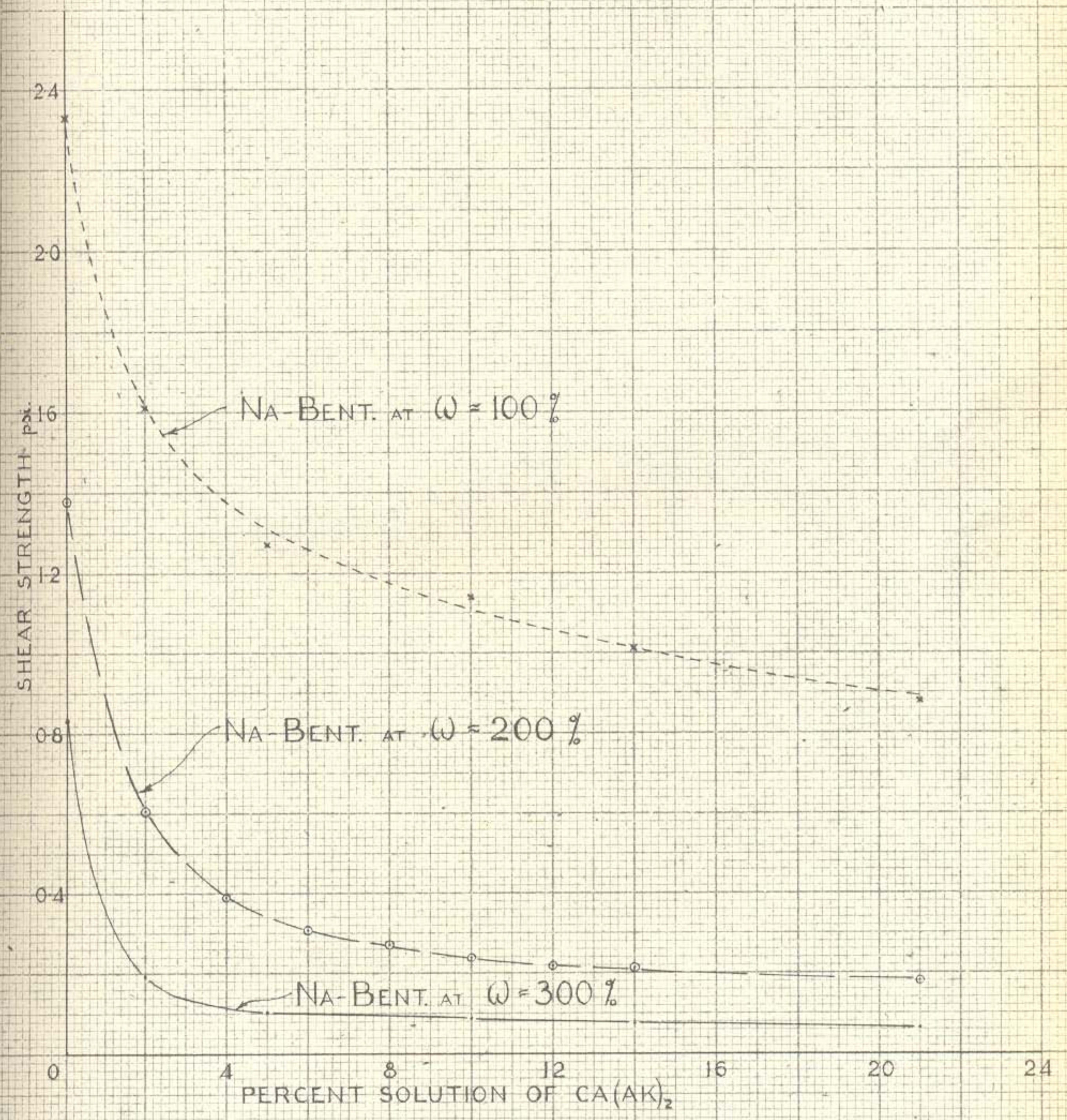
acrylate, the peak of the stress-strain curve is reached at about 9% strain, as had been previously obtained with untreated clay samples. However, in the case of the 10% treatment of calcium acrylate, the peak is reached at about 23% strain; and in the case of the 14% treatment, the peak is reached at about 34% strain. Indeed, with the 2% and 5% treatments the polymerized clay had the appearance of a stiff clay; whereas, with the 10% and 14% treatments the rubbery mass of polymerized clay could hardly be taken for a clay.

The strength and water-affinity results will be discussed in the following pages.

X. Properties of Sodium-Bentonite at 100% and 300% Water Content Upon Admixture with Calcium Acrylate

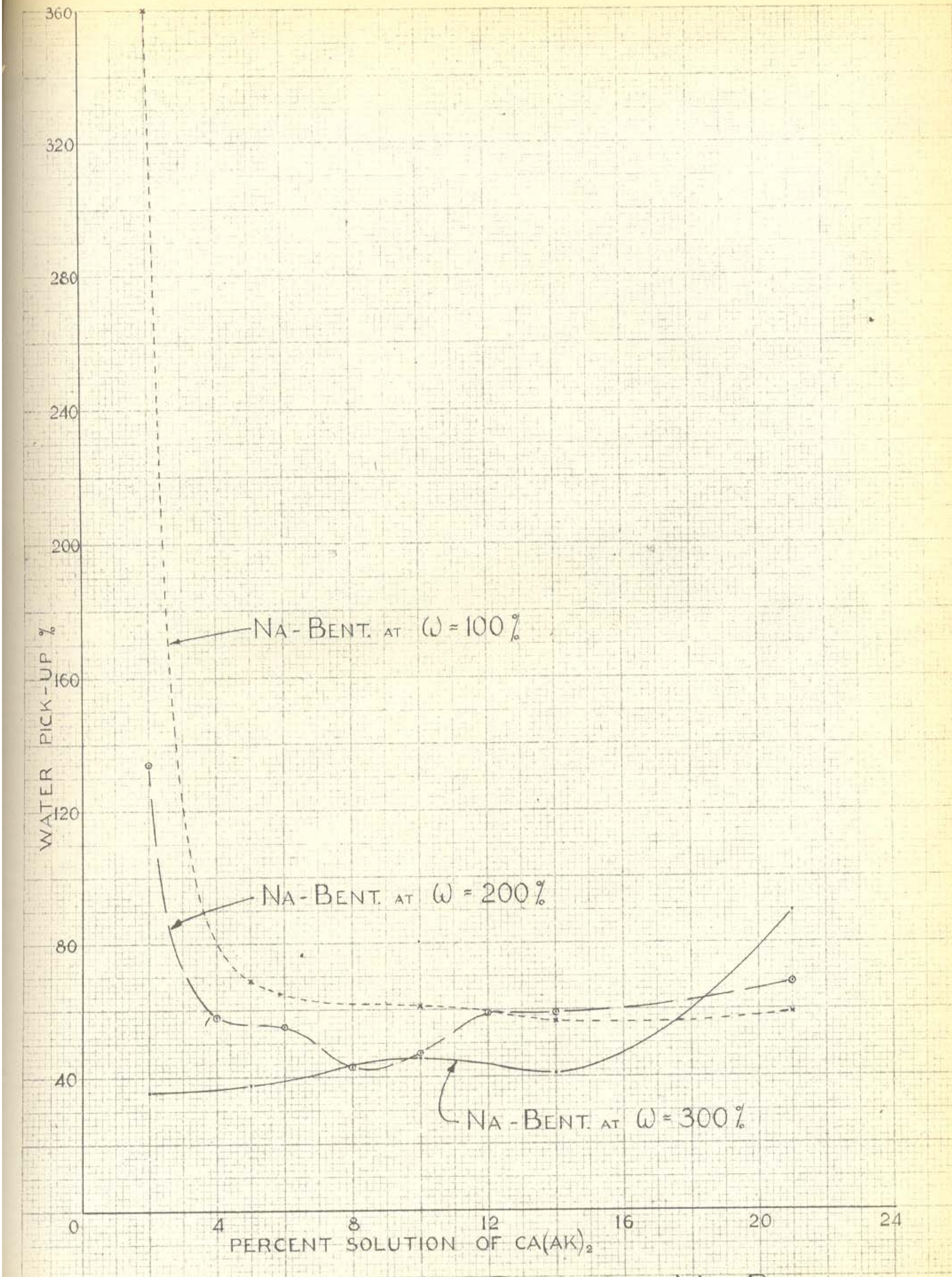
It appeared quite likely that the properties of the polymerized clay would depend to a considerable extent on the water content of the sodium-bentonite treated. At equivalent concentrations of acrylate solution in the clay-water system, variation of the water content of the system involves direct variations in the amount of calcium acrylate added per gram of clay. For example, in the preparation of samples for testing, the weights in the table on page 127 are used.

Consequently, in anticipation of testing polymerized samples at 100% and 300% water contents brief series of tests were carried out to determine the properties of the base-exchanged but unpolymerized clay-calcium acrylate samples.



SHEAR STRENGTH
OF
SODIUM - BENTONITE
WITH $CA(AK)_2$ ADMIXTURE

FIG. 23



WATER PICK-UP OF NA-BENTONITE
WITH $CA(AK)_2$ ADMIXTURES

FIG. 24

	Na-bent gms	Water cc.	$Ca(Ak)_2$ for 5% soln.
100% water content	15	15	0.75
200% " "	7.5	15	0.75
300% " "	6	18	0.90

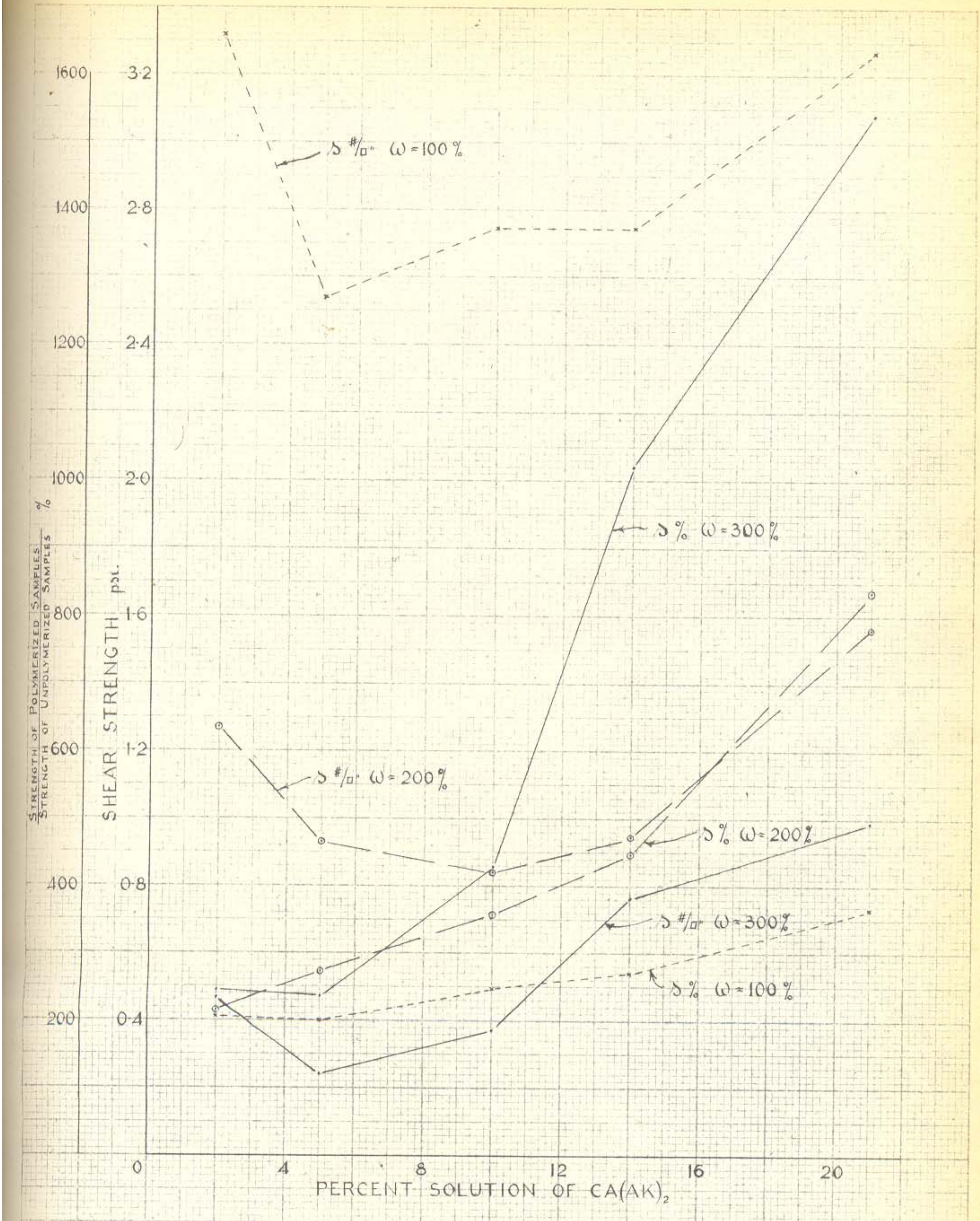
100% water content	$\frac{\text{gm } Ca(Ak)_2}{\text{gm dry clay}}$	$\frac{\text{gm } Ca(Ak)_2}{\text{gm wet clay}}$
100% water content	0.05	0.0250
200% " "	0.10	0.0333
300% " "	0.15	0.0375

The results are plotted in Figs. 23, 24, pages 125, 126; the corresponding results obtained on the sodium-bentonite at 200% water content are included in the same plots.

XI. Brief Polymerization Studies with Sodium-Bentonite at 100% and 300% Water Content, Using Calcium Acrylate, Sodium Thiosulfate and Ammonium Persulfate

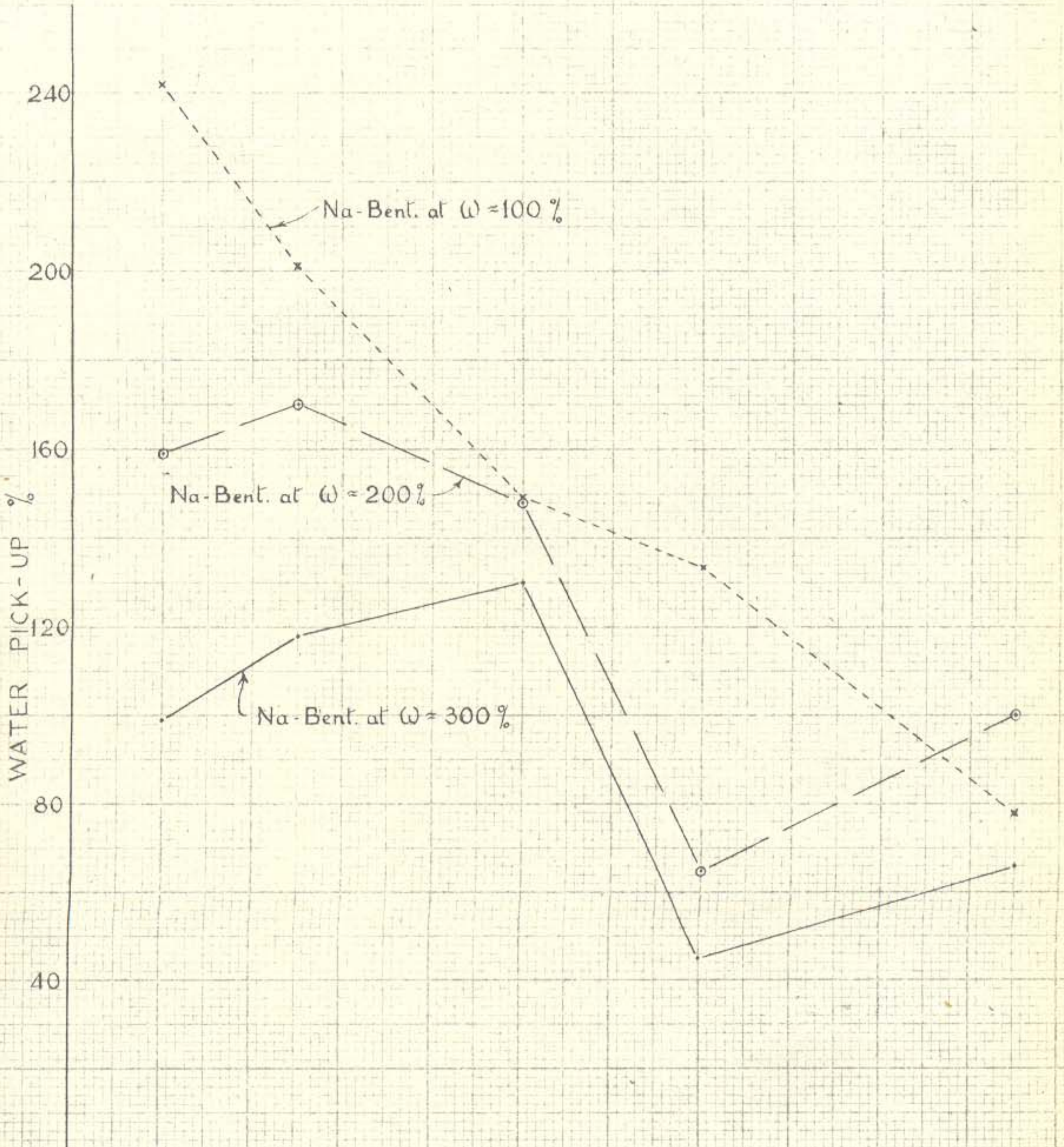
These two series of tests were indeed very brief, and, therefore, predict only general trends. Variations in amounts of catalysts were not investigated. Using fixed concentrations of the catalysts, a variation of the amount of calcium acrylate in the system was studied with reference to the properties of strength and water-affinity of the polymerized product.

The results are presented in graphical form in Figs. 25, 26 on pages 128, 129, and in greater detail in the chart on page   . Corresponding results of tests on sodium-bentonite at 200% water content are incorporated in these graphs for ease of comparison.



1600
1400
1200
1000
800
600
400
200
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
STRENGTH OF POLYMERIZED SAMPLES / STRENGTH OF UNPOLYMERIZED SAMPLES %
SHEAR STRENGTH psi.
0
4
8
12
16
20
PERCENT SOLUTION OF $CA(AK)_2$
S #/□" ω = 100%
S % ω = 300%
S #/□" ω = 200%
S % ω = 200%
S #/□" ω = 300%
S % ω = 100%
Catalysts $Na_2S_2O_3$, $(NH_4)_2S_2O_8$
SHEAR STRENGTH
OF TREATED
NA-BENTONITE CLAY

FIG. 25



WATER PICK-UP
OF TREATED
NA-BENTONITE CLAY

FIG. 26

It is evident that both base-exchange and polymerization play eminent roles in determining the properties of the treated clay. In every case the strength of the treated clay decreases in the intermediate range of calcium acrylate treatments: with 2% treatments of the calcium acrylate a fairly high strength is retained primarily because of the small amount of base-exchange taking place, whereas with 21% treatments of calcium-acrylate the strength of the treated clay is high primarily because of the polymerization which very effectively counteracts the weakening effect of the base-exchange. Hence, it is observed that the ratio

$$\frac{\text{strength of the polymerized sample}}{\text{strength of sample base-exchanged but unpolymerized}}$$

which is a rough measure of the effectiveness of polymerization, shows a steady increase with increase of per cent treatment of calcium acrylate. This ratio has been plotted in per cents in Fig. 25, page 128. It will thus be noted that with the 2% calcium acrylate treatments, the ratio of strength of polymerized sample to strength of sample merely base-exchanged is about 200% in all three cases (at water contents of 100%, 200% and 300%); whereas with the 21% calcium acrylate treatments the efficiency of polymerization as above measured shows a distinct increase with the increase of water content of the sample treated. This suggests a clear proportional relationship between the $\frac{\text{gm Ca(Ak)}_2}{\text{gm of dry clay}}$

and the $\frac{\text{strength of polymerized sample}}{\text{strength of unpolymerized sample}}$ under conditions of treatment where the polymerization plays the prominent role in determining the strength. Indeed, the relation is not simple and direct proportionality as may be seen in the plot on page 132, (Fig. 27); in this plot it will be observed that as the base-exchange factor increases in relative importance the slope of the curve decreases.

The significance of the ratio $\frac{\text{strength of polymerized sample}}{\text{strength of unpolymerized sampde}}$ may be questioned. Indeed, if the effectiveness of polymerization in strengthening a clay were dependent on simple cementation, the quest for a measure of the effectiveness of cementation would obviously lead to the use of the difference (strength of polymerized sample - strength of unpolymerized sample) lbs/in^2. In Fig. 28, page 133, are plotted the results of increase of strength (in lbs/in^2) vs. the ratio of $\frac{\text{gm } Ca(Ak)_2}{\text{gm dry clay}}$. At first thought, one is alarmed to find that the results obtained from the three series (at 100%, 200%, and 300% water content) do not plot on the same curve, in spite of the fact that we have seemingly taken care of the variation of water content by using $\frac{\text{gm } Ca(Ak)_2}{\text{gm dry clay}}$ for the abscissa.

However, let us look at the case a little more carefully. Let us first consider merely the formation of

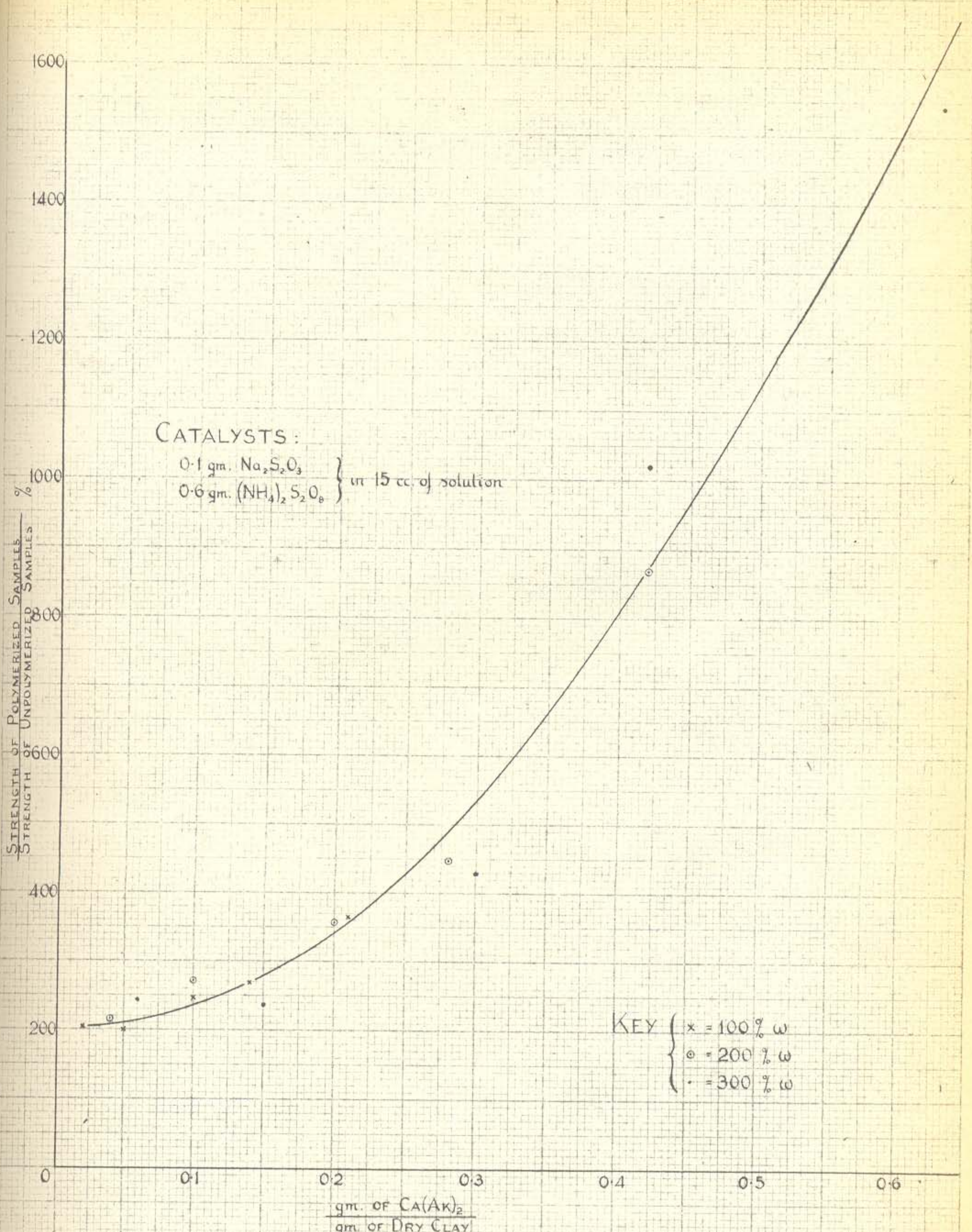
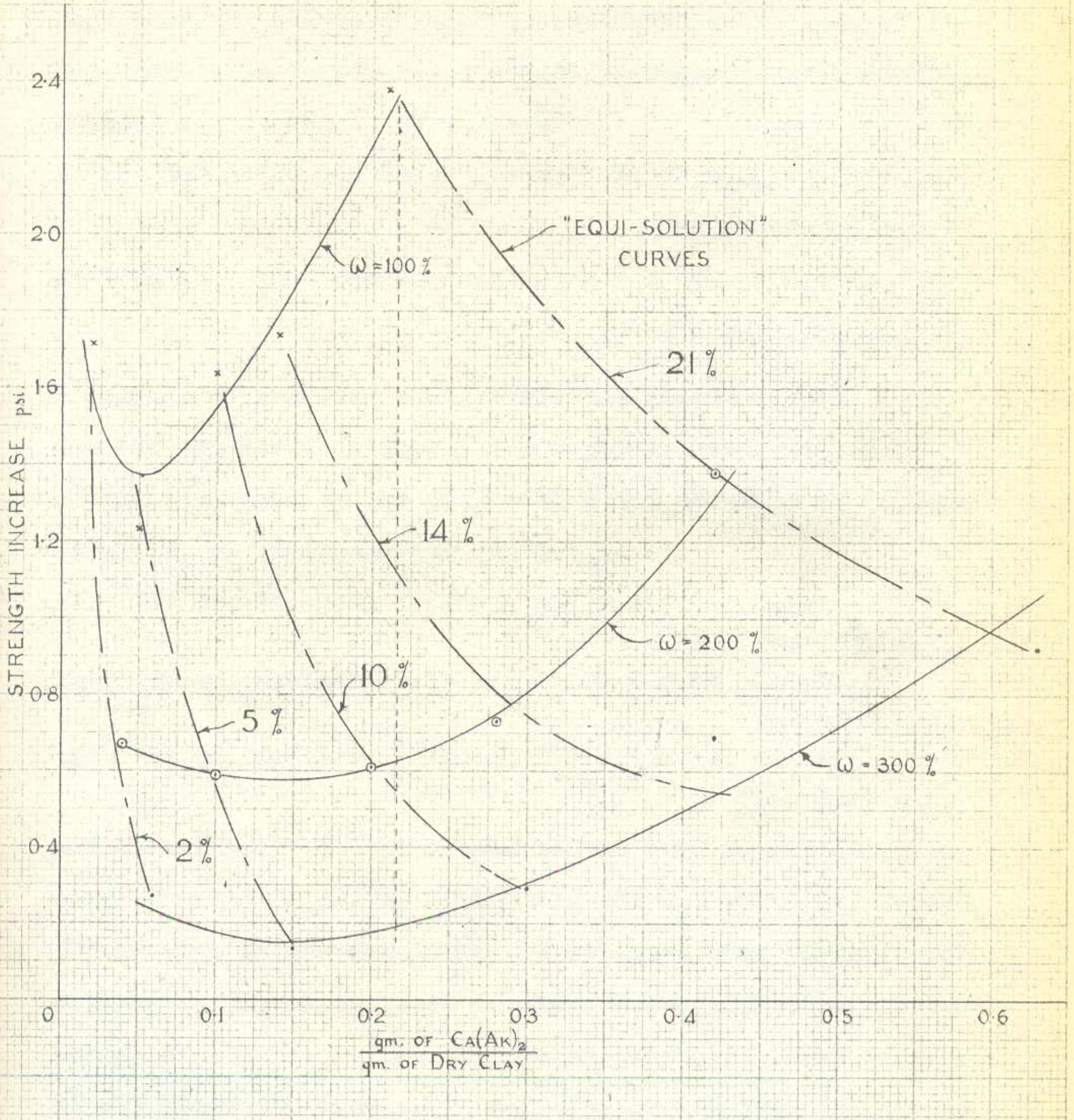

1600
1400
1200
1000
800
600
400
200
0
0·1
0·2
0·3
0·4
0·5
0·6
$\frac{\text{Strength of Polymerized Samples}}{\text{Strength of Unpolymerized Samples}}$ %
$\frac{\text{gm. of } Ca(Ak)_2}{\text{gm. of Dry Clay}}$
CATALYSTS:
0·1 gm. $Na_2S_2O_3$
0·6 gm. $(NH_4)_2S_2O_8$
in 15 cc. of solution
KEY
× = 100 % ω
⊙ = 200 % ω
· = 300 % ω
EFFECTIVENESS OF POLYMERIZATION
IN STRENGTHENING
NA-BENTONITE CLAY

FIG. 27



EFFECTIVENESS OF TREATMENT IN STRENGTHENING NA-BENTONITE CLAY

FIG. 28

the polymer, assuming for the moment that the clay is inert. In studying the formation of the polymer it can be assumed here that the polymerization is essentially the same if the concentrations involved are constant, regardless of actual amounts used. Hence, if we have

10 cc. H_2O + 0.3 gm. $Ca(Ak)_2$ + 0.1 gm. $Na_2S_2O_3$
+ 0.5 gm. $(NH_4)_2S_2O_8$

or 20 cc. H_2O + 0.6 gm. $Ca(Ak)_2$ + 0.2 gm. $Na_2S_2O_3$
+ 1.0 gm. $(NH_4)_2S_2O_8$

a polymer of the same characteristics should result. Considering for this discussion a particular case, such as the treatment of the clay with a 10% solution of calcium acrylate, we study samples consisting of

(1) 15 gm. Na-bent. + 15 cc. H_2O + 1.5 gm. $Ca(Ak)_2$ for 100% wat. cont.
(2) 7.5 gm. Na-bent. + 15 cc. H_2O + 1.5 gm. $Ca(Ak)_2$ for 200% wat. cont.
(3) 6 gm. Na-bent. + 18 cc. H_2O + 1.8 gm. $Ca(Ak)_2$ for 300% wat. cont.

and transposing the third case to the same volume of water we get (3a) 5 gm. Na-bent. + 15 cc. H_2O + 1.5 gm. $Ca(Ak)_2$

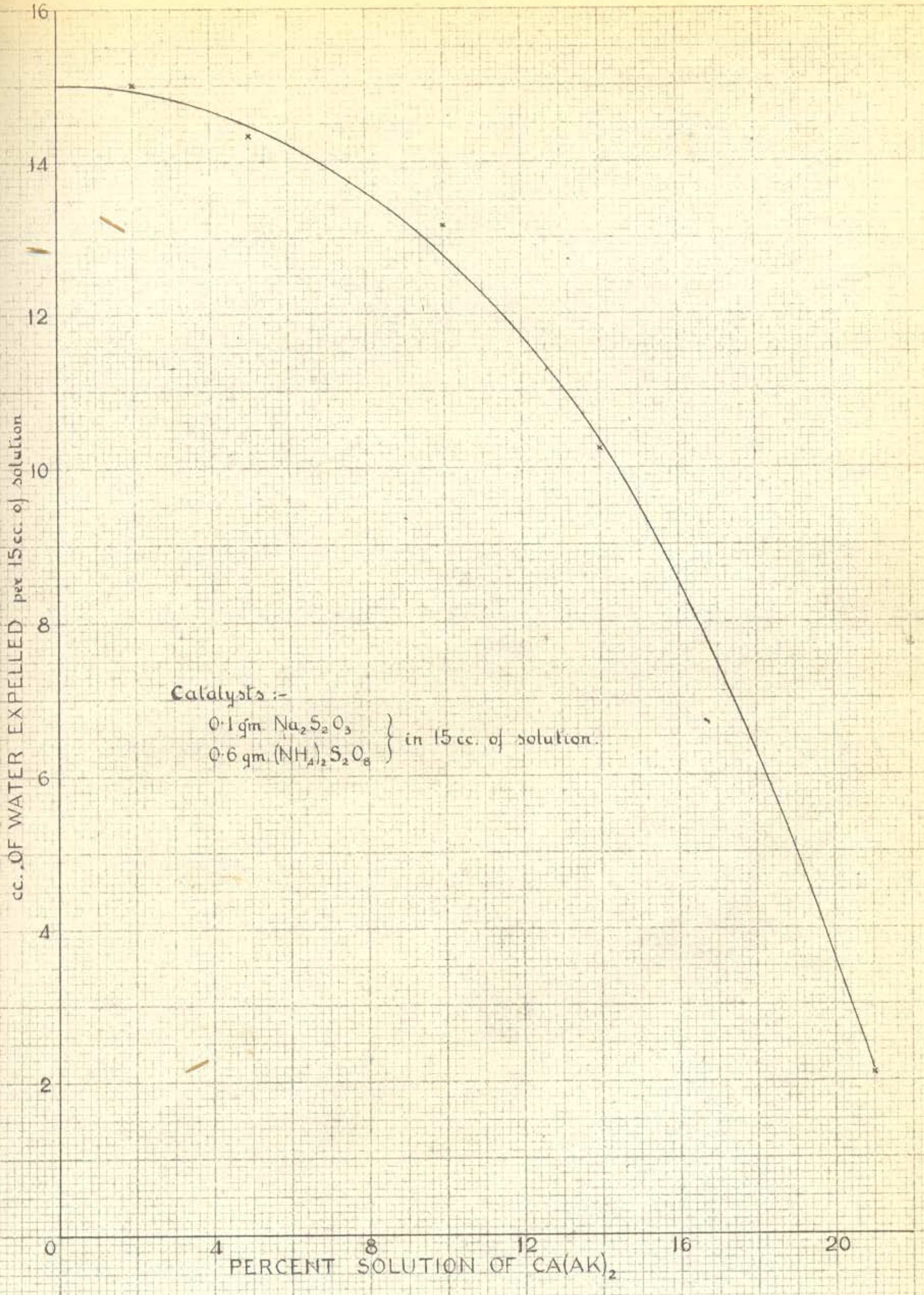
If the clay is now considered to be inert, the formation of polymer in all three cases involves essentially the polymerization of a 10% solution of calcium acrylate. What happens to all the water when a 10% solution of calcium acrylate is polymerized? In retrospect of the earlier search for catalysts, it was recalled that the polymer usually settled, occluding an appreciable amount of water in its structure, but leaving some clear supernatant liquid. Let us call this supernatant liquid the water that is squeezed out of the polymer by "syneresis". Would this syneresis account for the results noted on Fig. ? Assume, for example, that on polymerizing the above 15 cc. of a 10% solution of calcium acrylate we obtain 2 cc. of water by syneresis. This water is obviously taken up by the clay, and in case (1) the 2 cc. of water are taken up by 15 gm. of clay, in case (2) the 2 cc. of water are taken up by 7.5 gms of clay, and in case (3) the 2 cc. of water are taken up by 6 gm. of clay. Is it not obvious, now, why the water content of the sample does have a major significance in the plot of Fig. 28?

In order to check this hypothesis a brief series of tests was summarily undertaken. Each of five centrifuge tubes was filled with 15 cc. of a different concentration of calcium acrylate solution -- 2%, 5%, 10%, 14%, and 21%. With the addition of appropriate amounts of sodium thiosulfate and ammonium persulfate catalysts, polymerization was instigated in all solutions, and the centrifuge tubes were stoppered. After sufficient curing, the polymers were centrifuged* at a constant arbitrary speed and for a

---

* The analogy between centrifuging the polymers and the effect of water affinity of the clay in absorbing the water that is not occluded by the polymer may indeed be quite proximate. If relationships can be established of centrifuging speed and time vs. the water affinity of the clay such an approach may be used quite reliably in a roughly quantitative manner.

constant arbitrary length of time. The clear supernatant liquid was poured off into a graduated flask and measured. The values are plotted in Fig. 29, page 137. These results may, in fact, be used for a roughly quantitative check of the order of magnitude of the effects considered. In Fig. 28 a vertical line is drawn through the intersection of the 21% "equi-solution" line and the 100% water-content line. This line intersects the 200% and 300% lines at about the 11% and 7.5% equi-solution lines. By reference to Fig. 29, we find that 15 cc. of a 21% solution of calcium acrylate on polymerization expel about 2.2 cc. of water; 15 cc. of an 11% solution of calcium acrylate expel about 12.5 cc. of water; and 15 cc. of a 7.5% solution of calcium acrylate expel about 13.5 cc. of water. Hence 2.2 cc. of water are absorbed by 15 gm. of clay, 12.5 cc. of water are absorbed by 7.5 gm. of clay, and 13.5 cc. of water are absorbed by 5 gm. of clay. Reducing them all to a unit basis we find that in the case of 100% water content, 0.14 cc. of water are absorbed per gram of clay, in the case of 200% water content 1.67 cc. of water are absorbed per gram of clay, and in the case of 300% water content 2.70 cc. of water are absorbed per gram of clay. These three cases are all at the same ratio of $\frac{\text{gm Ca(Ak)}_2}{\text{gm dry clay}}$. Is it not quite apparent now why for the same ratio of $\frac{\text{gm Ca(Ak)}_2}{\text{gm dry clay}}$, the increase of strength due to polymerization is greatest at 100% water content and least at 300% water content?



SYNERESIS IN POLYMERIZATION
OF
AQUEOUS CA(AK)$_2$ SOLUTIONS

FIG. 29.

One question that still comes to mind is the following: how then do the results of tests at all water contents plot on the same curve in Fig. 27? One plausible explanation is as follows: in the actual polymerized clay-acrylate systems the "excess water" is shared by both the polymer and the clay; hence, by expressing the effectiveness of polymerization as a ratio of

$$\frac{\text{strength of polymerized sample}}{\text{strength of unpolymerized sample}}$$

the effect of such excess water is well accounted for.

In the above discussion the base-exchange factor has been neglected entirely. Obviously, this simplification reduces the discussion to the point of retaining merit only qualitatively. Actually it may be justifiably remarked that Fig. 27, page 132, should have been drawn with due attention to the ionic effect of the catalyst addition, if the necessary data were available. The base-exchange effect is especially important in explaining the high strengths at low per cent treatments of calcium acrylate.

Unfortunately, samples that owe their high strengths in large part to the base-exchange factor, retain a relatively high water-affinity. Exchange of sodium by calcium or calcium-acrylate ions is necessary for decreasing water-affinity: such exchange is inefficient at low water contents and with low amounts of calcium acrylate added. So although at low water contents and with low amounts of $Ca(Ak)_2$ treatment, the strength values are relatively very high this strength may be called an apparent strength, because it is accompanied by relatively high water-affinity. Indeed, as will be shown in the following section, the loss of such apparent strength per increment of water content increase is relatively very great.

One factor that has not been considered in the above discussions of shearing strength is the non-polymerizing, or ionic, effect of the catalyst addition. In the case of sodium-bentonite at 200% water content an attempt was made to estimate the influence of this factor. The analysis of the results is presented in chart form on page . It is again emphasized that this analysis merely represents an adequate estimate, in view of the nature of the simulated blanks that have to be employed. The interesting point to observe is that the estimated strengthening effect of polymerization is no smaller with 5% and 2% treatments of calcium acrylate than it is with 10% treatments--beyond that point there is a sharp increase in the strengthening effect. Allowing the aid of visual observation to steer the interpretation of such results, it is postulated that up to less than 10% treatments of calcium acrylate the polymerization establishes a lot of short links to strengthen the clay structure: the possible lengthening of such links does not further increase the strength of the clay structure. However, beyond 10% treatments the polymer itself forms a complete network which is capable of disregarding the clay structure and building up a structure of its own, which becomes stronger with an increase in the number of polymer links and cross-links. The stress-strain data indicated the establishment of an essentially different plastic material beyond 10% treatments of calcium acrylate. (Page 124)

XII. Effect of Water-Absorption on Shearing Strength of Polymerized Clay

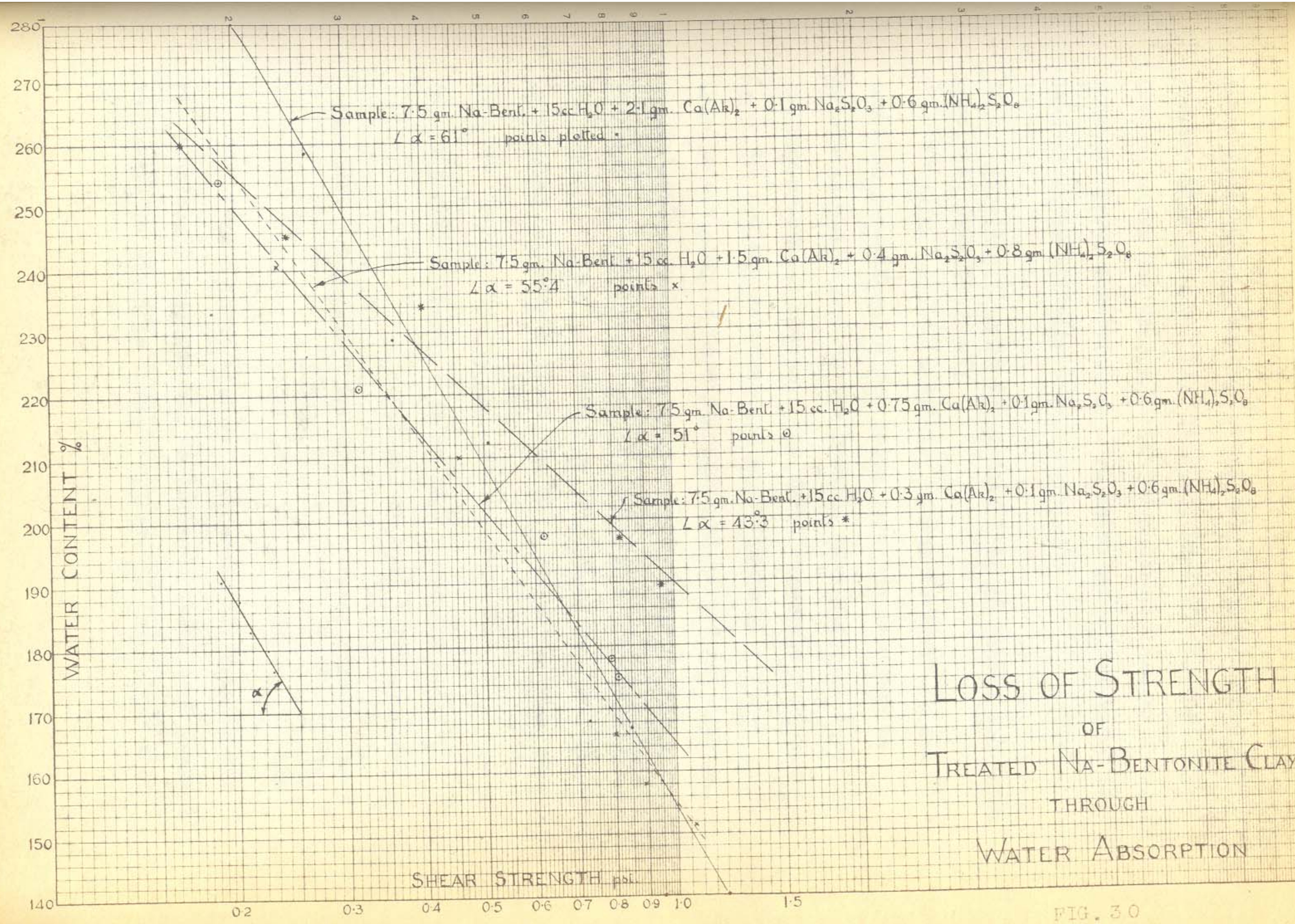
The selection of the samples that were considered best was based purely on a determination of the shearing strength and the amount of water absorbed in the 24-hour water-absorption test. However, as has been pointed out earlier, the information of greatest interest with respect to the water stability of the treated clay should be its shearing strength after water-absorption. Is it possible that some of the samples rejected for having higher water-affinity might have still retained higher shearing strengths after water-absorption than some of the samples that had smaller water-affinity? Yes, among the various samples produced with the various sets of catalysts it is quite possible that such cases may have arisen--especially since the shearing strengths of practically all samples after water-absorption were quite negligible, as could be estimated by sight and feel. But one thing is certain, in spite of its assertion depending on visual and tactual assessment; no sample of treated clay had a shearing strength after water-absorption that could be compared with the shearing strength (after water-absorption) of samples polymerized with thiosulfate-persulfate catalysts.

Before concluding the investigations, some attention had to be devoted to the study of the effect of water-absorption on the shearing strength of polymerized clay. Naturally, in view of the comments made above, the study of this factor was limited to clay treated with calcium acrylate, sodium thiosulfate and ammonium persulfate. The following systems were studied.

	Na-bent. gm.	H_2O cc.	$Ca(Ak)_2$ gm.	$Na_2S_2O_3$ gm.	$(NH_4)_2S_2O_8$ gm.	Water Content Change %
1	7.5	15	2.1	0.1	0.6	140 to 205
2	7.5	15	1.5	0.4	0.8	160.5 to 283.5
3	7.5	15	0.75	0.1	0.6	170 to 340
4	7.5	15	0.3	0.1	0.6	184 to 343

The procedure followed was simple: a fairly large batch of the clay was prepared and cured for the predetermined 24 hours; to several fractions of the polymerized clay different amounts of water were added; the shearing strength and water content of each of these small batches was determined. The results are plotted on page 142, (Fig. 30).

The following observations will be made from analysis of Fig. 30. (1) The polymerized clay retains the characteristic behavior of clays, with a linear relationship between water content and the logarithm of the shearing strength. (2) Plotting the test results of the above four samples to the same scale it is observed that the slope of the straight lines with respect to the shearing strength axis decreases steadily with a decrease of amount of calcium acrylate in the system. Hence, for a constant increment of



LOSS OF STRENGTH

OF

TREATED NA-BENTONITE CLAY

THROUGH

WATER ABSORPTION

FIG. 30

water content, the loss of strength in case (4) is much greater than in case (1). In fact, case (1) is the only case in which the sample retains a moderate shearing strength after absorbing as much water as indicated by the 24-hour water-affinity test.

XIII. Investigation of the Possibility of Mixing All Three Chemicals Simultaneously

Using calcium acrylate, sodium thiosulfate and ammonium persulfate, a few tests were run in order to determine the nature of the results that might be expected if, for practical reasons, the three chemicals were mixed into the sodium-bentonite gel simultaneously. Three independent samples were prepared and tested for each of the following systems:

(a) 7.5 gms. Na-bent. + 15 cc. H_2O + 2.1 gms. $Ca(Ak)_2$ + 0.1 gm. $Na_2S_2O_3$ + 0.6 gm. $(NH_4)_2S_2O_8$

Results:	Strength	Water Pick-up
	1.407 lbs/in^2	85.5%
	1.469 " "	111
	1.085 " "	89.5

(b) 7.5 gms. Na-bent. + 15 cc. H_2O + 0.3 gms $Ca(Ak)_2$ + 0.1 gm. $Na_2S_2O_3$ + 0.6 gm. $(NH_4)_2S_2O_8$

Results:	Strength	Water Pick-up
	1.250 lbs/in^2	219%
	1.611 " "	194
	1.080 " "	259

It is evident that in such cases the results are not as closely reproducible as in cases where each reagent is carefully mixed in turn. Further, it is evident that both the strength and the water pick-up values obtained for these samples are somewhat greater than corresponding values obtained for samples prepared by mixing the chemicals consecutively. The reason for the above observations seems obvious: with the rapid polymerization reaction setting in, the base-exchange reaction is hampered, and the presence of more exchangeable sodium ions associated with the clay increases both the shearing strength and the water pick-up.

XIV. Consolidated Samples

The investigations had hitherto been limited to testing the clay samples as prepared, without any consolidation. A program of testing that might be designed to consider consolidation as a new variable under investigation could reasonably occupy several months of intensive research. However, without undertaking an extensive investigation of this factor, it was still considered of major interest to run a few tests to compare the behavior of treated and untreated samples consolidated to the same pressure. Accordingly, six tests were run as follows: A sample of sodium-bentonite clay prepared at about 200% water content was consolidated in the direct shear machine to 1 T/sf and a quick shear test was run. Another sample of sodium-bentonite prepared at 212% water content was consolidated to 4 T/sf and similarly tested in quick-shear. Then, similar samples of sodium-bentonite base-exchanged with 10% treatment of calcium acrylate were similarly tested after consolidation to 1 T/sf and 4 T/sf. Indidentally, the remarkable rapidity of consolidation of these base-exchanged samples in comparison with the sodium-bentonite samples could not fail to be visually noticed. Finally, similar samples, base-exchanged and polymerized, were tested in the same fashion after consolidation to 1 T/sf and 4 T/sf respectively.

The results plotted in Fig. 46, page 209, are further tabulated as follows:

	Consolidation T/sf	Shearing Strength lbs/in^2	Water Content %	lbs/in^2 S as Prepared	W as Prepared %
Na-bentonite	1	2.30	195	1.38	212
Na-bentonite	4	5.83	120	1.38	212
Na-bentonite + 10% $Ca(Ak)_2$	1	1.81	90	0.235	180
Na-bentonite + 10% $Ca(Ak)_2$	4	4.72	63.7	0.235	180
Na-bentonite Polymerized	1	2.20	123.5	0.842	156
Na-bentonite Polymerized	4	3.86	103.5	0.842	156

Several rough conclusions may be made from this brief series of tests. (1) The clay modifications that are stiffer as prepared do not compress as much, under a fixed consolidation pressure, as those that are weak. (2) Consequently, as was approximately predicted, consolidation of various base-exchanged modifications of a clay to a constant pressure greatly reduces the differences of strength exhibited by the respective samples if tested without being subjected to consolidation. (3) For relatively small consolidation pressures the polymerized sample fits well in line with the above noted general trends. However, for the relatively large consolidation pressure of 4 T/sf, the polymerized sample no longer compresses as much as it should in order to fall in line with those trends. It seems quite likely that beyond a certain degree of compression the polymer structure may well hinder further compression.

APPLICATION OF THE TREATMENT TO OTHER CLAYS

Obviously it was of interest to investigate the range of applicability of this chemical treatment, which was originally expected to be effective with all clays. Any chemical treatment that is effective only for a particular soil of specific mineral content is quite naturally rather unwelcome in practice, because variations of soil type are too great and alarmingly rapid even in bodies of soil that appear to be homogeneous, and because seldom is it practical to analyse a soil prior to treatment. Time limitations made it impossible to test a variety of natural clays as had originally been planned. However, by testing merely two simplified clay systems it was hoped that sufficient grounds could be established for the rough prediction of the applicability of this soil stabilizing treatment. The clays tested were (1) a calcium-bentonite and (2) a hydrogen-kaolin. These clays are described on page

I. Application of the Treatment to Calcium-Bentonite

(a) Shearing Strength and Water-Absorption of Calcium-Bentonite

A few tests roughly established the straight line of water content vs. log shearing strength of the calcium-bentonite. It apparently was quite difficult to disperse the calcium-bentonite in water, prolonged working of the clay-water gel tending to give a stiffer clay: The noticeable scatter evidenced by the points plotted in Fig. 31, page 148,

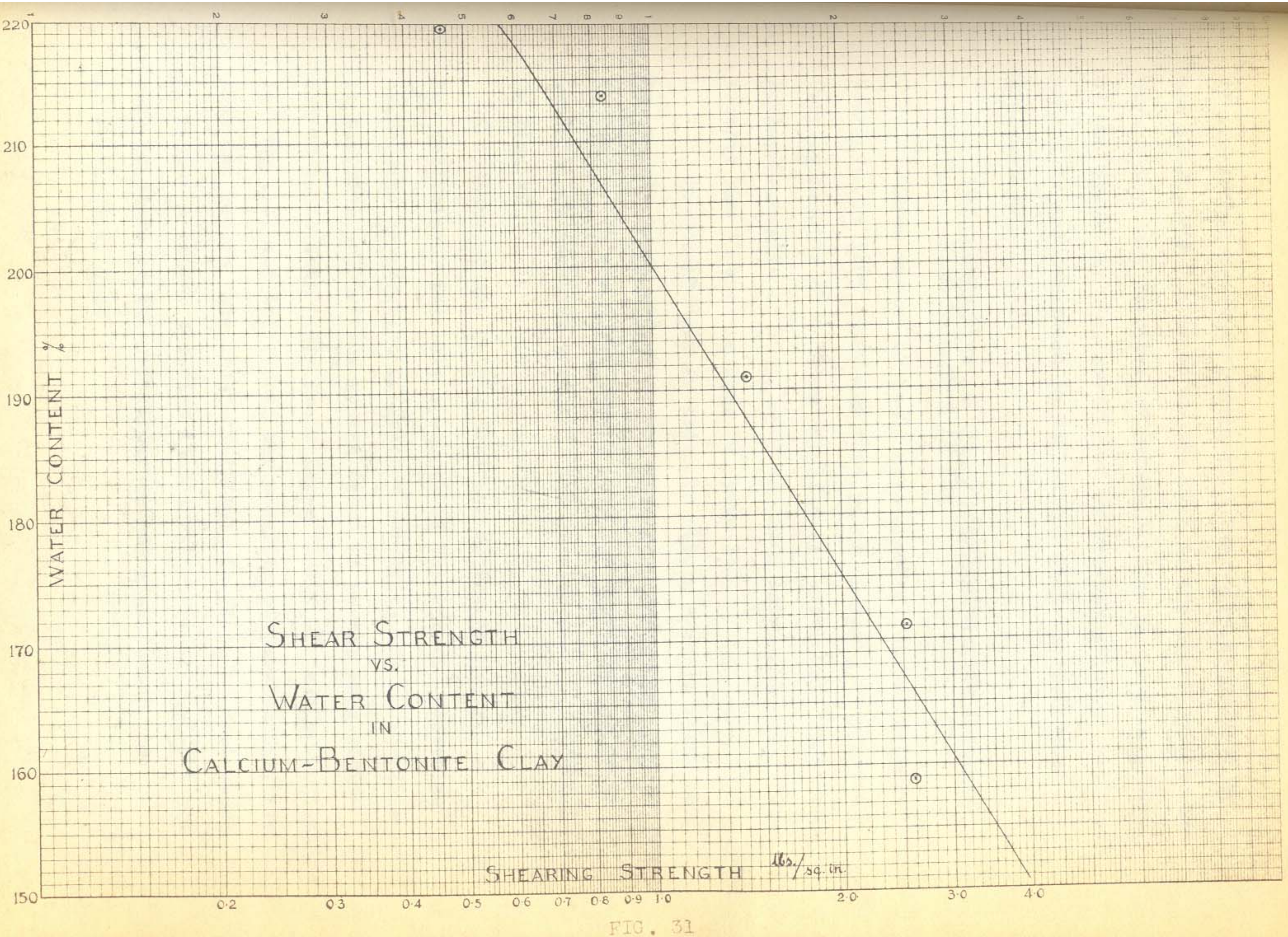

SHEAR STRENGTH
VS.
WATER CONTENT
IN
CALCIUM-BENTONITE CLAY
WATER CONTENT %
SHEARING STRENGTH lbs./sq. in.
220
210
200
190
180
170
160
150
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
2·0
3·0
4·0

FIG. 31

is attributed to this difficulty. The water-absorption of the calcium-bentonite is so low that in the stabilization of such a clay the decrease of water-affinity is obviously out of the question. The results of water-absorption of calcium-bentonite are presented in connection with the following sub-section.

(b) Properties of Calcium-Bentonite Upon Admixture with Calcium Acrylate

Three series of tests were carried out on calcium-bentonite at 140%, 170% and 200% water content, by admixing varying amounts of calcium acrylate (as previously done with sodium-bentonite at 100%, 200% and 300% water content). The results are plotted on Fig. 32, page 150.

Simultaneously in order to obtain a rough check on the purely ionic effect of the catalysts added for polymerization, a few simulated blanks were run using sodium thiosulfate and ammonium acetate. The results are also plotted on Fig. 32.

Some of the points that are worthy of mention are the following. (1) The strength of the calcium-bentonite is reduced by addition of calcium acrylate, but by no means in alarming proportions as was found to be the case with sodium-bentonite. (2) The water-affinity of calcium-bentonite is very low, and in general the addition of calcium acrylate does not reduce this water-affinity: in fact, in most cases it causes a slight increase in the water affinity. Although this increase of water-affinity is not significant, it is quite clear that

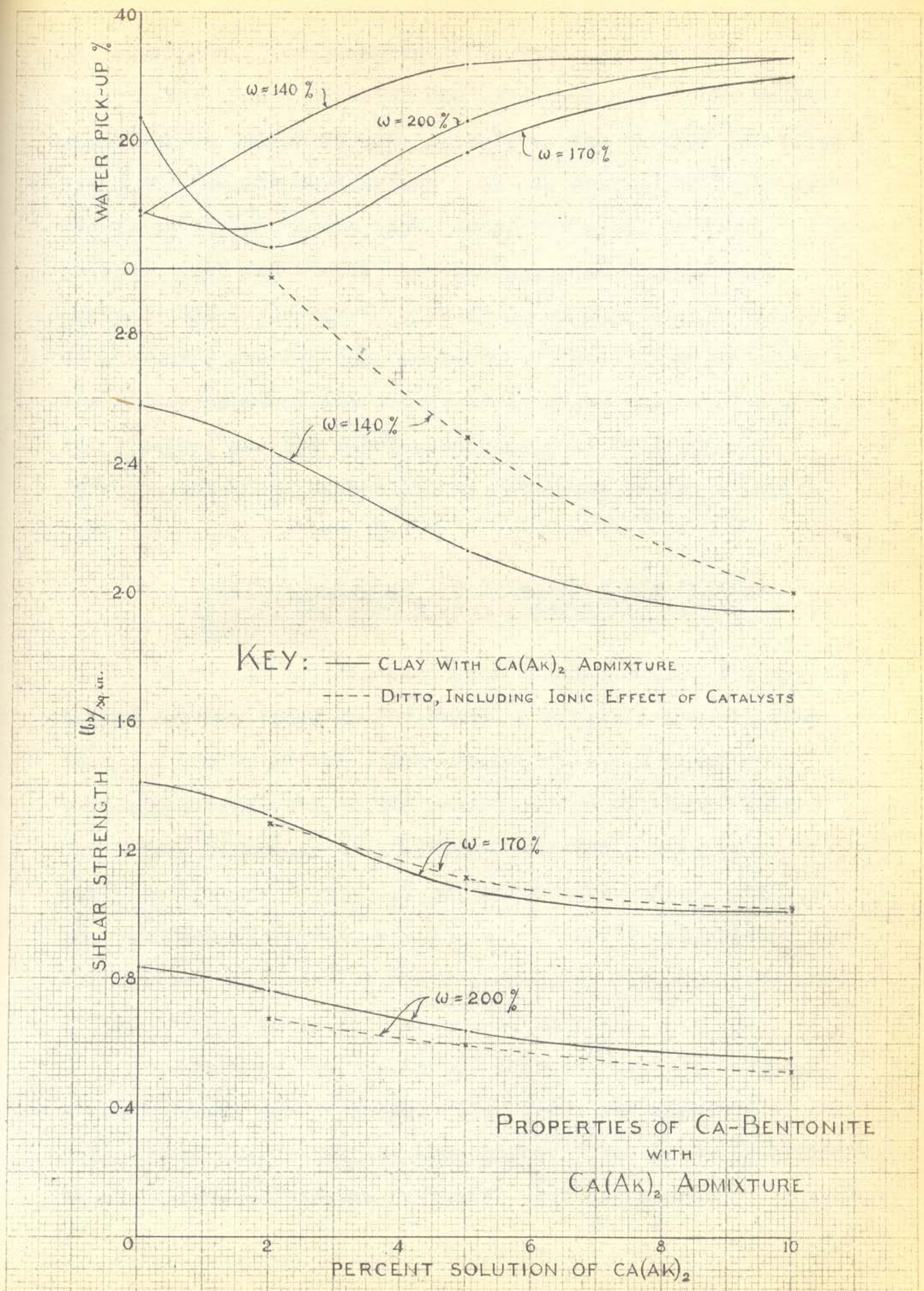

WATER PICK-UP %
40
20
0
ω = 140 %
ω = 200 %
ω = 170 %
SHEAR STRENGTH lbs/sq. in.
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0
ω = 140 %
ω = 170 %
ω = 200 %
KEY: —— CLAY WITH CA(AK)₂ ADMIXTURE
- - - - DITTO, INCLUDING IONIC EFFECT OF CATALYSTS
PROPERTIES OF CA-BENTONITE
WITH
CA(AK)₂ ADMIXTURE
0
2
4
6
8
10
PERCENT SOLUTION OF CA(AK)₂

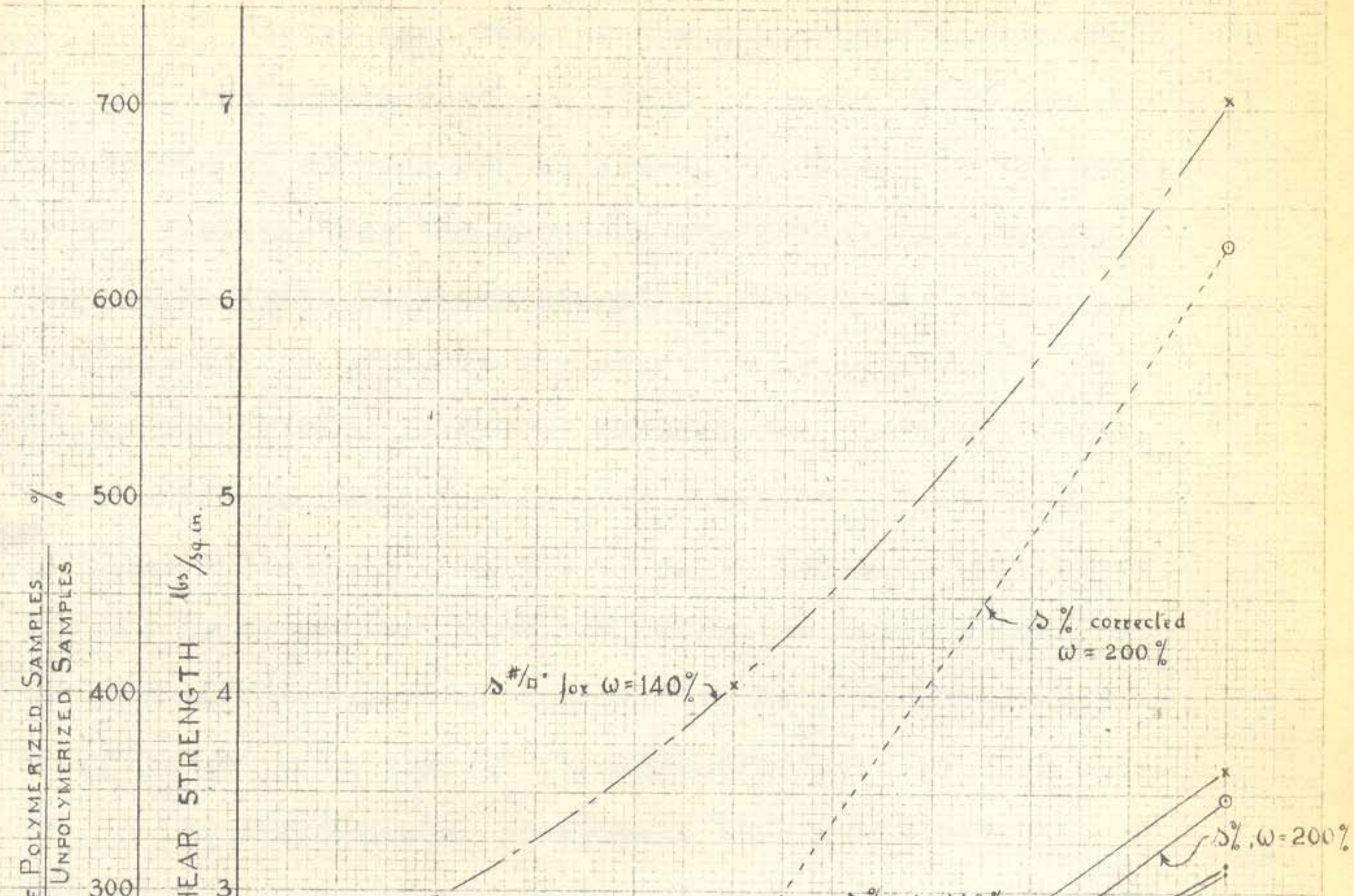
FIG. 32

the treatment of calcium-bentonite with calcium acrylate constitutes a case in which the effectiveness of the treatment will be judged almost entirely by the strength increase caused by the polymerization. (3) In noting the ionic effect of the catalysts on the strength of the clay, it is observed that for the calcium-bentonite at 140% water content this ionic effect results in an appreciable increase of strength; for the calcium-bentonite at 170% water content, the ionic effect of the catalysts is quite negligible; and finally, for the calcium-bentonite at 200% water content, the ionic effect of the catalysts causes a noticeable decrease of strength.

(c) Calcium-Bentonite - Calcium Acrylate Systems Polymerized with Sodium Thiosulfate, Ammonium Persulfate

For each calcium-bentonite - calcium acrylate system tested (as mentioned in (b) above) a single polymerization test was run by adding sodium thiosulfate and ammonium persulfate catalysts in the concentration which had been found most effective with sodium-bentonite - calcium acrylate systems; viz., 0.1 gm. sodium thiosulfate and 0.6 gm. ammonium persulfate per 15 cc. of liquid available in the system. The results are presented in Fig. 33, page 152, and are tabulated in further detail on page

Observing the results of these tests, the following general trends may be noted. (1) The water-affinity of the polymerized samples is somewhat higher than the water-affinity of the untreated calcium-bentonite, but not much so. In fact,



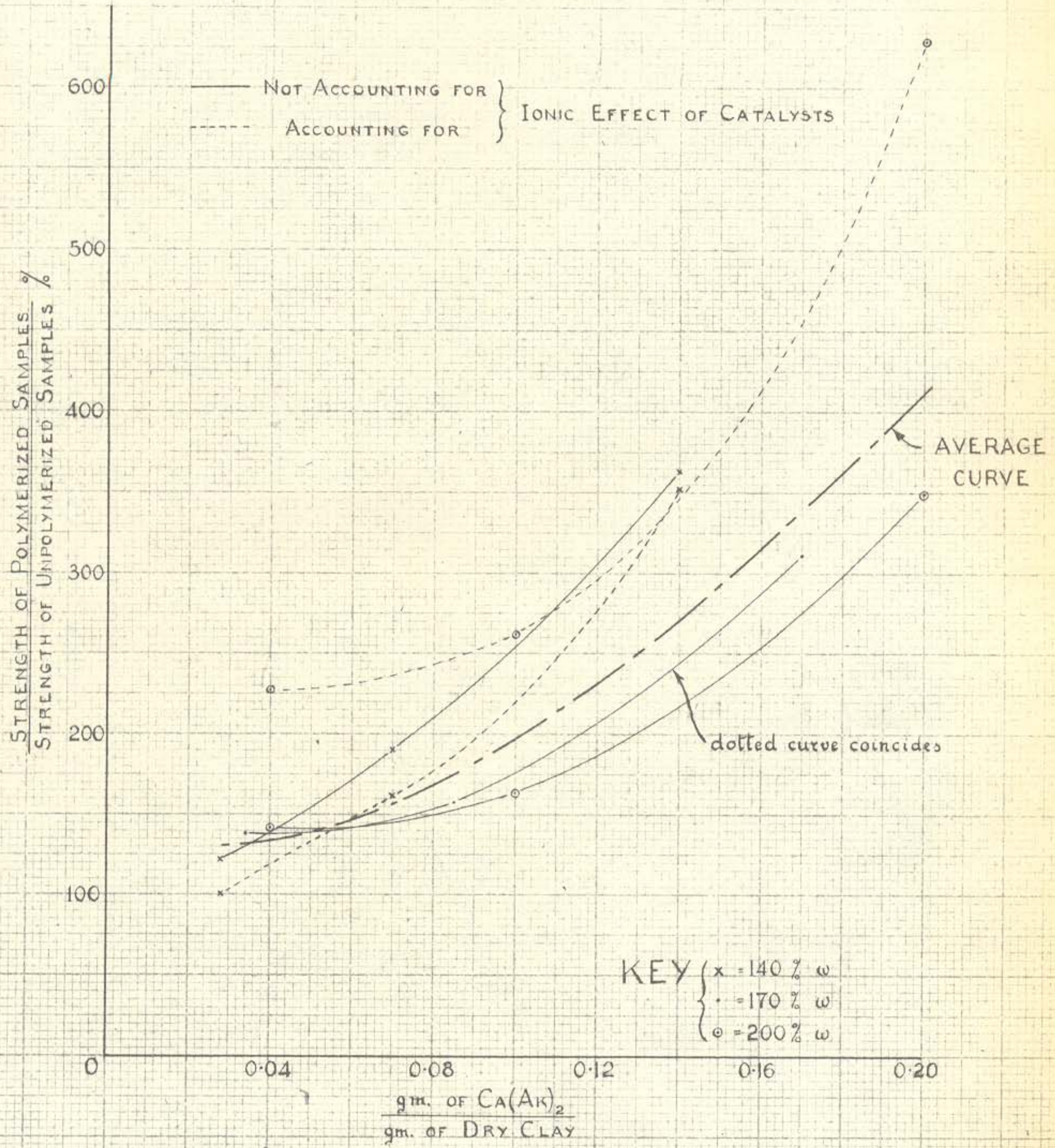
Catalysts $\begin{cases} Na_2S_2O_3 \\ (NH_4)_2S_2O_8 \end{cases}$

SHEAR STRENGTH
OF TREATED
CA-BENTONITE CLAY

FIG. 33

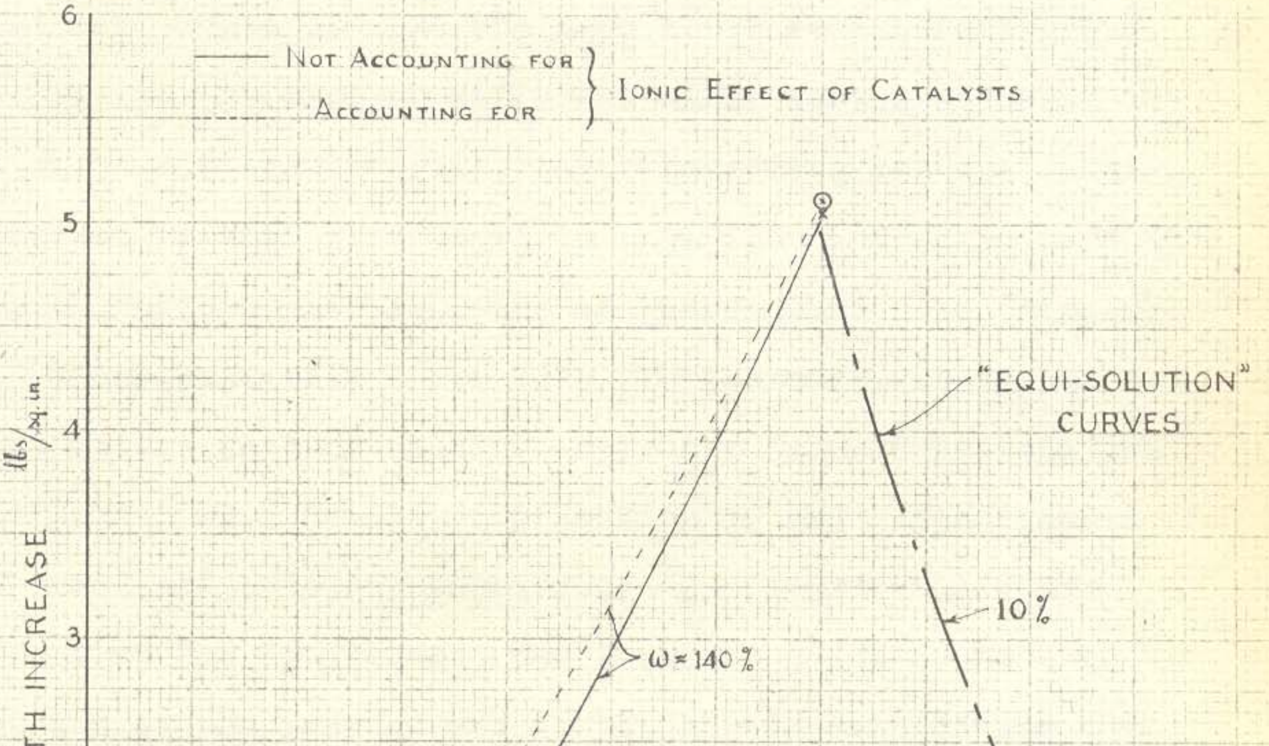
the water-affinity of these polymerized samples is even a little bit higher than that of the corresponding systems prior to the addition of catalysts in cases of 2% and 5% treatments of the calcium acrylate. However, in the cases of 10% treatment of the acrylate the polymerized sample shows a definite decrease of water-affinity in comparison with the sample prior to the addition of catalysts. (2) The water-affinity is not of much import, however, as has been mentioned above. Even a 2% treatment of calcium acrylate achieves a moderate strength increase by polymerization, in comparison with the untreated calcium-bentonite, and the effectiveness of the calcium acrylate treatment is being judged primarily by strength increases in this case.

At first glance it appears that doubtless the increase of strength caused by polymerization is greatest at the lowest water content. However, the trends are not at all well defined, and thus an analysis of the effectiveness of polymerization with relation to the ratio of $\frac{\text{gm Ca(Ak)}_2}{\text{gm dry clay}}$ yields a plot that represents an average trend only if some major scatter if overlooked. (Fig. 34, page 154) Further tests may be necessary in order to establish definite trends. The calcium acrylate polymerization does appreciably increase the shearing strength of calcium-bentonite clay, and there is a very rough trend of increase of per cent strengthening effect of polymerization with an increase of the ratio of $\frac{\text{gm Ca(Ak)}_2}{\text{gm dry clay}}$. However, consequently, in actual pounds per square inch the treatment is most



EFFECTIVENESS OF POLYMERIZATION
IN STRENGTHENING
CA-BENTONITE CLAY
USING $Ca(Ak)_2$, $Na_2S_2O_3$, $(NH_4)_2S_2O_8$

FIG. 34



EFFECTIVENESS OF TREATMENT
WITH
CA-BENTONITE CLAY

FIG. 35

effective at low water contents. This point has been discussed in detail in connection with sodium-bentonite: the trends exhibited with calcium-bentonite are roughly the same as those with sodium-bentonite, with only one noticeable exception. The expectation that all the points on Fig. 34 page 154, would plot on the same curve is not fulfilled: the values obtained at different water contents result in slightly different curves, notwithstanding the qualitative conclusions that were drawn on page 135, and which were well corroborated by the behavior of sodium-bentonite (Fig. 27) and hydrogen-kaolin (Fig. 39). Furthermore, it may be noted that in the case of calcium-bentonite laboratory data are available for a complete evaluation of the effectiveness of polymerization taking cognizance of the probable ionic effect of the catalysts. The curves tend to shift somewhat, but are of the same nature as the curves established for the per cent strengthening effect of polymerization neglecting the ionic effect of the catalysts. It is thus noted that the relationship between the per cent strengthening effect of polymerization and the ratio $\frac{\text{gm of Ca(Ak)}_2}{\text{gm dry clay}}$ is not as simple as to admit of an explanation that neglects base-exchange factors and that considers water-content a completely dependent variable. However, pending the acquisition of further data for the proper evaluation of such factors, approximate "average curve" can be established (Fig. 34) for use in comparison of results with those obtained with other clays.

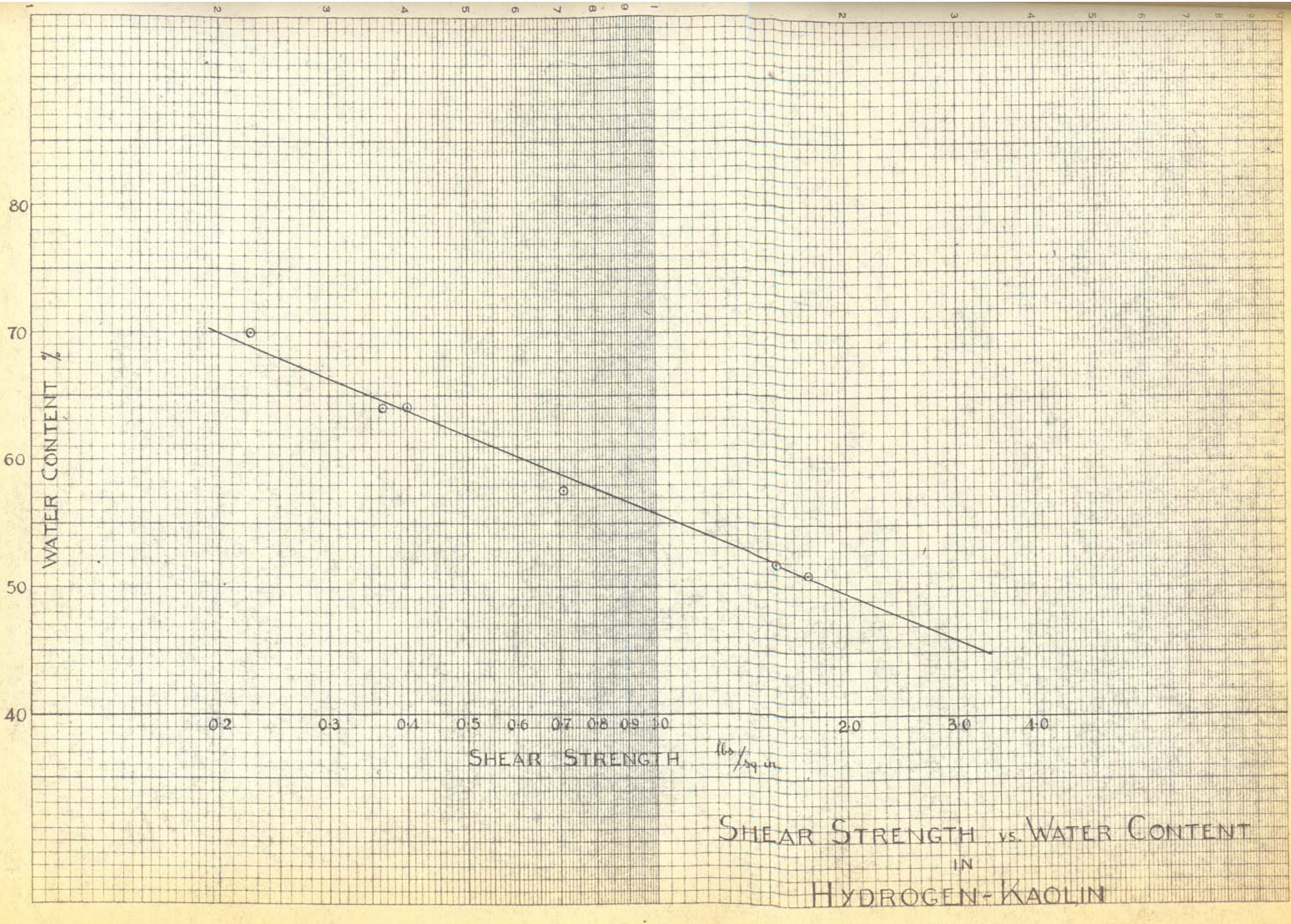
II. Application of the Treatment to Hydrogen-Kaolin

Exactly similar series of tests were run on hydrogen-kaolin clay as had been run with calcium-bentonite, except that the water contents of the kaolin clay samples had to be considerably lower. A few shear tests established the shearing strength vs. water content relationship for the untreated clay, as shown in Fig. 36, page 158; stress-strain data are available on a couple of the samples tested. The water-affinity of the kaolin clay is very low, indeed. Treatment of this clay might be considered to constitute the extreme case where the decrease of water-affinity is unfeasible and the effectiveness of the treatment is to be adjudged entirely on the basis of strength increases.

The properties of the hydrogen-kaolin at 41.5%, 52% and 65% water contents were studied after admixture of varying amounts of calcium acrylate to constitute 2%, 5% and 10% aqueous solutions of the acrylate in the system. The results are presented in Fig. 37, page 159. The trends are quite similar to those observed with the sodium and calcium-bentonites.

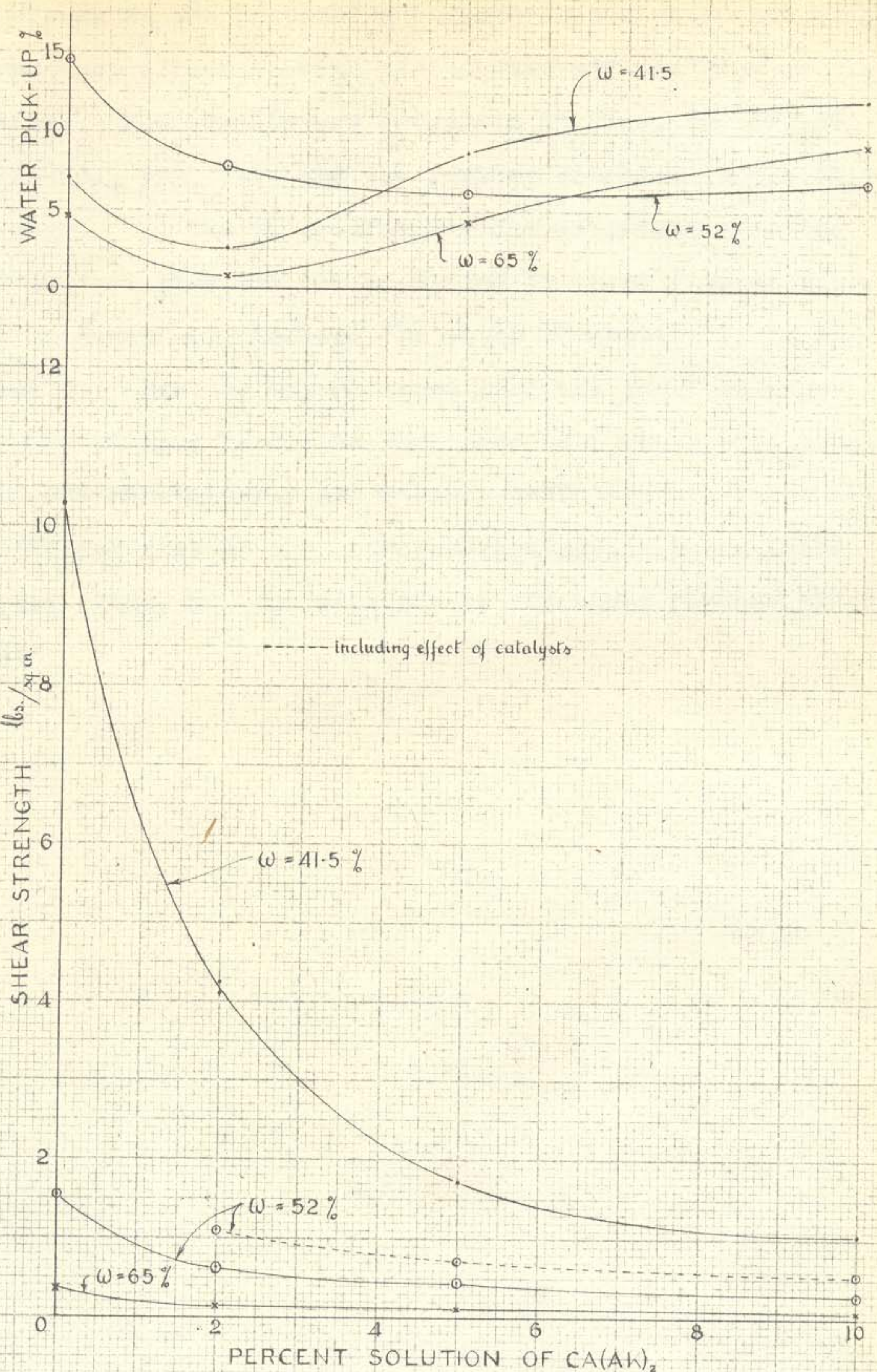
Simultaneously, in order to obtain a rough check on the magnitude of the ionic effect of the catalysts, simulated blanks were run for the series of tests at 52% water content, using sodium thiosulfate and ammonium acetate. These results are included in the plot on Fig. 37.

Finally, the three series of samples tested above were tested after polymerization using the thiosulfate-persulfate



SHEAR STRENGTH vs. WATER CONTENT
IN
HYDROGEN-KAOLIN

FIG. 36

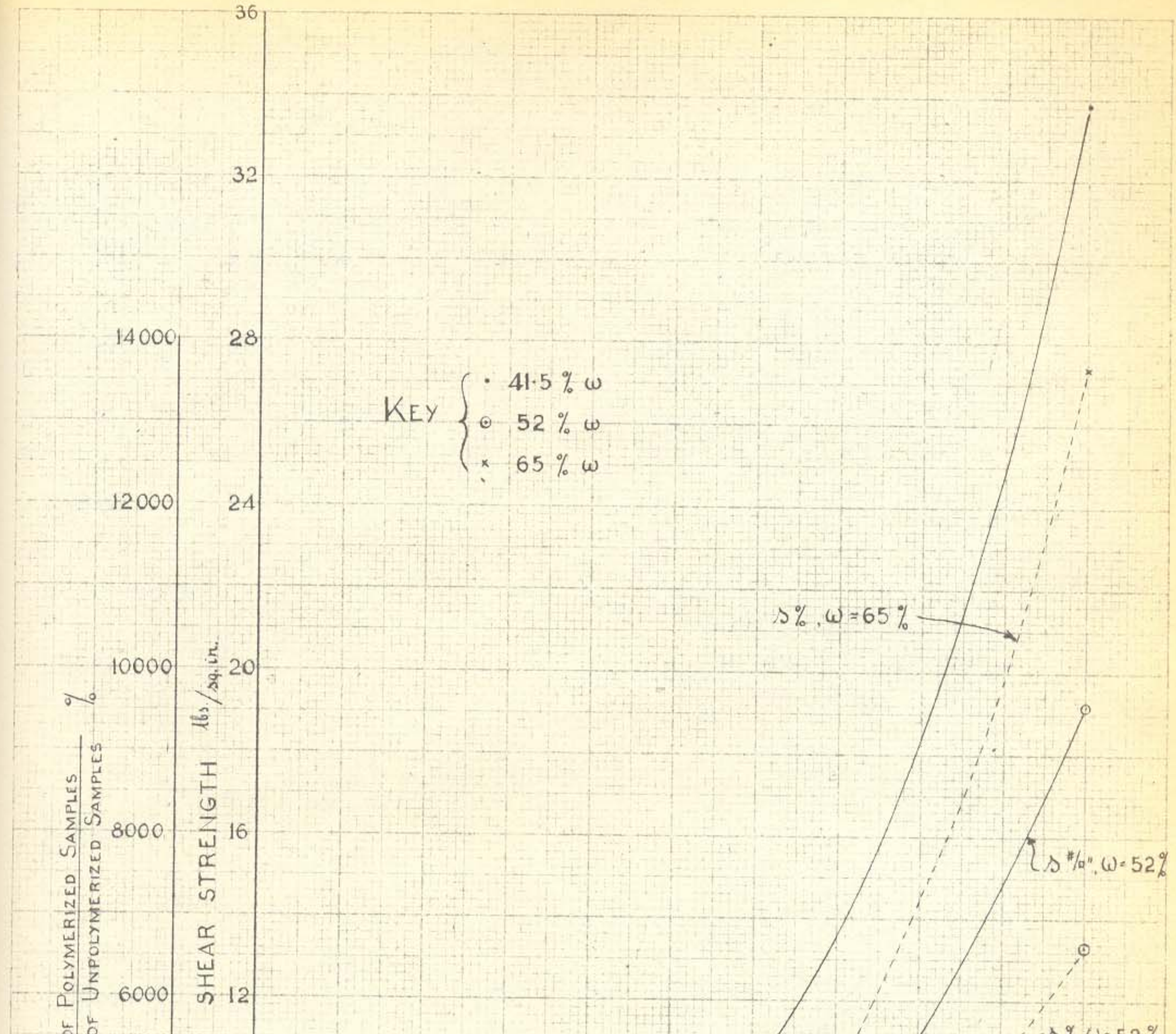


PROPERTIES OF H-KAOLIN
WITH
CA(AK)₂ ADMIXTURE

FIG. 37

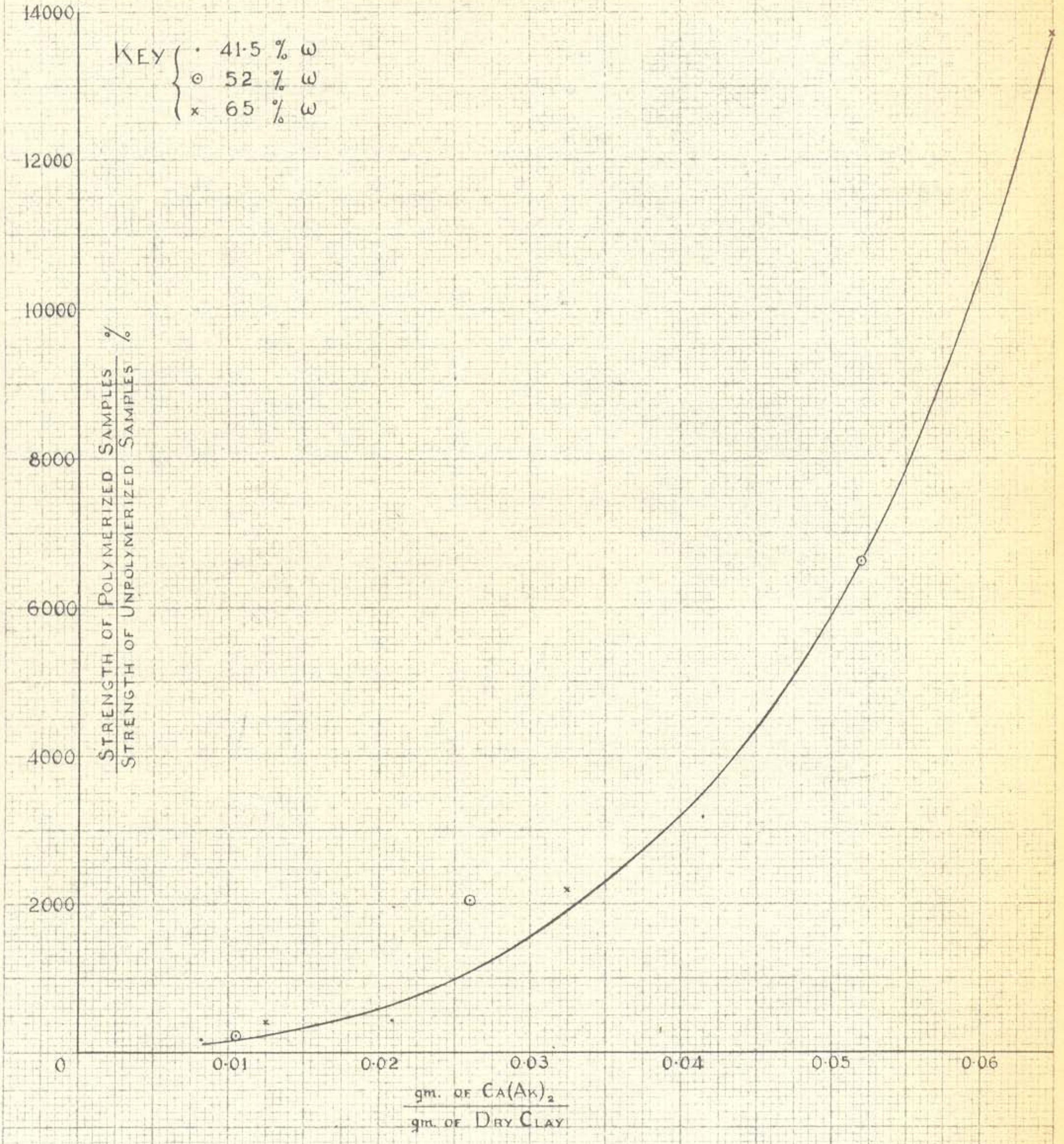
catalysts in the respective concentrations which had been found most effective with sodium-bentonite-calcium acrylate systems. The results are presented in Figs. 38, 39, 40, on pages 161, 162, 163, and are further detailed in the chart on page . The water-affinity characteristics of the polymerized clay are not presented in these figures and will not be discussed, because the water absorption is in all cases very low, as may be noted from the chart on page

It need hardly be mentioned that the trends observed with sodium-bentonite and calcium-bentonite are distinctly maintained also by the hydrogen-kaolinite. Hence these curves (Figs. 39, 40) will not be discussed further at this point.



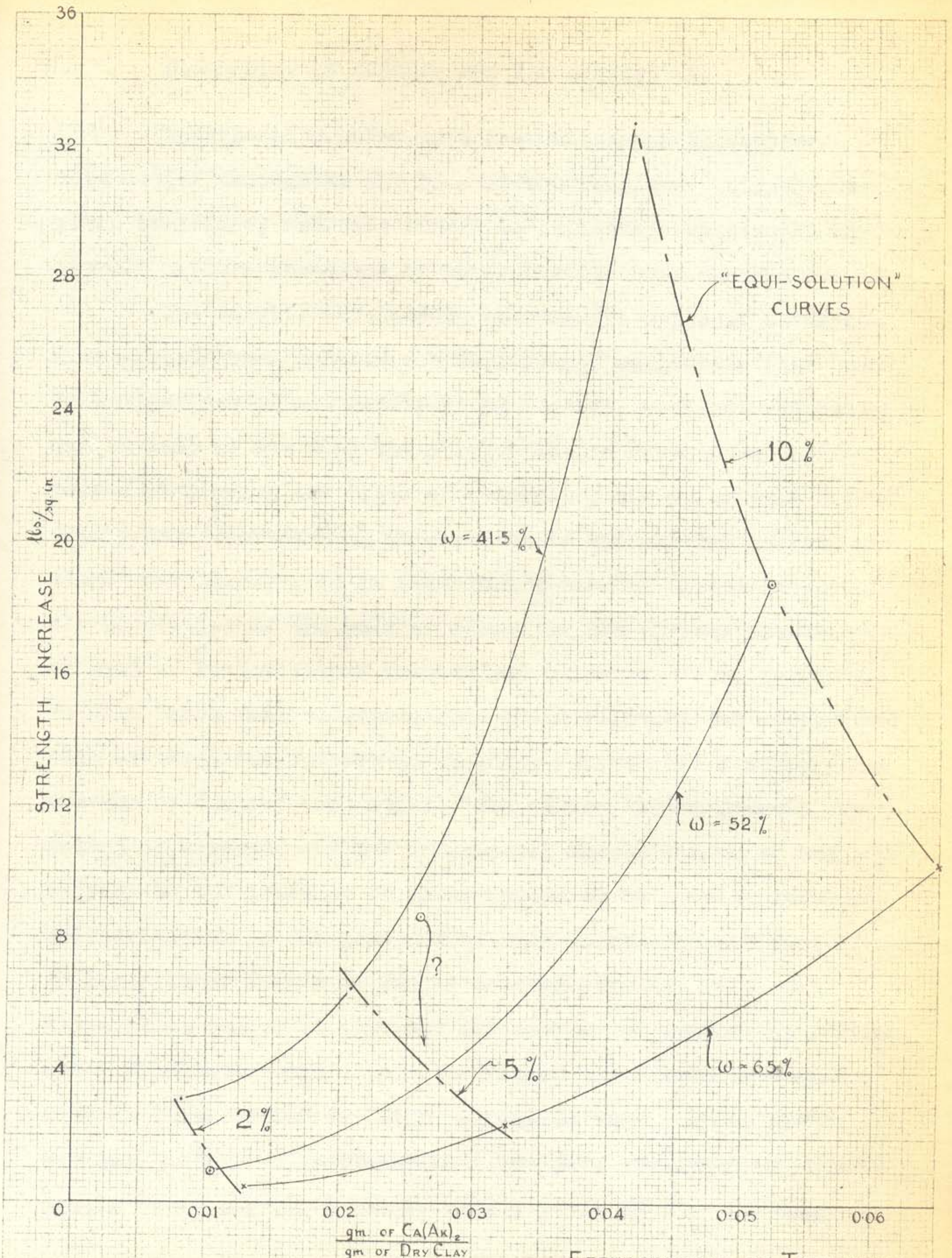
SHEAR STRENGTH OF TREATED H-KAOLINITE

FIG. 38



EFFECTIVENESS OF TREATMENT
APPLIED TO
HYDROGEN-KAOLINITE

FIG. 39



EFFECTIVENESS OF TREATMENT
WITH
H-KAOLIN

FIG. 40

DISCUSSION OF RESULTS AND RECOMMENDATIONS

Individual results have been discussed in considerable detail throughout the body of this thesis. This chapter will, therefore, restrict itself to an attempt to discuss the overall picture presented by these limited investigations.

The results obtained by varying the types of catalysts have already been pointed out as strongly suggesting that the investigations of new catalysts be doggedly pursued. No estimate can be made of how much the polymerization results may be improved by varying the types of catalysts, but it is felt that this point deserves much more extensive and careful investigation. Furthermore, it is felt that a careful investigation of the properties of the polymer formed by the various catalysts, as well as by variations in catalyst concentrations, may lead to data which will be significant in correlating the effectiveness of these two factors in yielding polymerized clay-acrylate systems of desired properties. The author cannot suggest any method of carrying out the fundamental investigation of the polymer in the presence of clay, unless it be assumed that the polymerization in the presence of clay is essentially similar to the polymerization of simple calcium acrylate solutions. Hence it is suggested that the polymerization studies be carried out with aqueous solutions, determining the molecular weight distributions achieved. With respect to such polymerization studies, it may be mentioned that the data presented in this thesis suggest quite strongly that a study of the phenomenon of "syneresis" during polymerization be included. In fact, it may prove most interesting to compare these results with other investigations attempting to correlate speeds and periods of centrifuging with the water affinity of a clay, and the volume of water expelled during polymerization with increases of water content and consequent decreases of strength.

All the polymerized samples obtained in the course of this study could in general be classified into one of the following three types. (1) Samples to all intents and purposes having the exact appearance of a wet clay, almost as if merely base-exchanged, though considerably stiffer. Practically all samples treated with less than the equivalent of 5% calcium acrylate or calcium methacrylate solutions were in this group. A few systems fell into this category even though treated with more of the acrylate and methacrylate: e.g., clay methacrylate systems with high persulfate concentrations and low bisulfite or thiosulfate concentrations, and even clay-acrylate systems with high persulfate and low bisulfite concentrations. (2) Samples that were extremely tacky and sticky could be drawn out into very long threads and could be torn apart and reworked together over and over again without evincing any distress. Such samples were invariably obtained with greater than 5% aqueous solution treatments of the acrylate and methacrylate. In the case of clay-methacrylate systems the use of moderate concentrations of bisulfite and persulfate catalysts yielded such samples; in the case of clay-acrylate systems the use of hydrazine hydrate and t-butyl-hydroperoxide catalysts resulted in similar samples.

(3) Samples resembling a stiff rubbery mass, apparently well cross-linked, with no adhesion. Such samples were only obtained in the case of systems with calcium acrylate, sodium thiosulfate and ammonium persulfate; they appeared to require the presence of more than the equivalent of 5% aqueous solution of calcium acrylate, and preferably low concentrations of the thiosulfate and high concentrations of the persulfate catalyst. If torn apart and reworked together, some joining was apparent, but these partially reknit surfaces tended to be weak.

It is evident that the latter two cases basically represent differences in the type of polymer, and the investigations suggested in the final paragraph should bring to light any pertinent information on this point. Base-exchange is the other major factor controlling the properties of these clay-acrylate systems, and it is the predominant influence in samples classified in group (1) above. The most important base-exchange investigation that is believed necessary in connection with this research has been mentioned earlier: the analysis of the exchangeable bases associated with the clay after addition of the catalysts--an analysis that can only be obtained by the use of simulated blanks. Whether or not the association of complex ions with the clay has much to do with the effectiveness of the treatment is not clear at present. A study of the exchangeable bases associated with the clay after the addition of catalysts would yield the most significant data for a conclusive answer to that question. But the study of base-exchange is of prime importance because of the effect on the water-affinity of the clay. It is evident from the data that unless excessive amounts of the acrylate are used, polymerization does not effectively decrease the water-affinity of the clay, which is mainly dependent on the exchangeable bases associated with the clay. The search for catalysts should, therefore, keep this factor in mind: the ideal catalysts would be those that polymerized very effectively but did not introduce undesirable cations, such as sodium or ammonium into the system.

Furthering the discussion of base-exchange somewhat, it may be helpful to consult again the curves shown on pages (Figs. 2 - 5). Primarily it should be noted that those base-exchange curves were obtained for sodium-bentonite clay gels prepared at the given water contents. Indications are that by preparing the sodium bentonite clay gels at higher water contents and homogeneously reducing the water content (by consolidation or drying) more (or all) of the sodium may be induced to participate in the reaction. The base exchange reaction itself may be carried out either prior to consolidation or just after it: obviously the results in each of these cases will be quite different from the results obtained in the course of the present study. If all the sodium ions could be induced to participate in the base-exchange reaction, doubtless the water-affinity characteristics of the clay would be improved considerably. However, the general nature of the curves indicating a decrease of total sodium exchanged with a decrease of the calcium methacrylate added will not change; and hence the author believes that there is little hope of decreasing the water-affinity of samples treated with less than the equivalent of 5% aqueous solutions of the methacrylate. This will constitute the greatest difficulty with respect to using small precent treatments of this type for stabilization of clays which need a considerable reduction of their water-affinity. Further testing on base-exchange should also include detailed analysis of the base-exchange reaction occurring in the calcium-bentonite and hydrogen-kaolinite. For instance, theoretical considerations make it seem unlikely that kaolinite would suffer from such a factor as a decrease in the number of active ions at lower water contents.

The question of consolidation has been brought up. It would be of interest to compare the properties of systems polymerized at higher water contents and consolidated to a lower water content, with the properties of systems prepared at the lower water content to represent similar final products. Such investigations could profitably be conducted both with simple acrylate polymers and with clay-acrylate polymers. Vice versa, similar tests should be conducted on "negative consolidation", i.e., on samples that have absorbed given amounts of water. Such information would probably throw much light on the variation of effectiveness of the treatment at different water contents, etc.

Another avenue of investigation that may justify some testing is the study of variations of the ions involved in the monomer of the treatment. For instance, lead acrylate and barium acrylate may be used; and variation of the anion may be investigated by using methacrylates, acrylates, crotonates. However, it is not believed that the ionic effect will be of major importance; the major effect will still result from the effectiveness of the polymerization. Hence, if for some unknown reason a particular salt polymerizes much more effectively than others, it might thus stake a strong claim for itself. Very rough indications lead the author to the suspicion that barium acrylate might be such a salt: three consecutive attempts were made to prepare it in the laboratory, and in all three cases it polymerized as crystallization was attempted.

Finally, a factor that deserves careful study is the length of the induction period and the speed of polymerization. In the use of thiosulfate-persulfate catalysts for the polymerization of calcium-acrylate solutions the author observed that the induction period was roughly one and one-half minutes (measuring it as the time between the addition of the catalysts and the start of the tremendously rapid clouding up of the solution: the gel-like polymer appeared to have attained maximum stiffness within five minutes). Such small induction periods may barely offer time enough for the adequate preparation of samples on a laboratory scale: but under conditions of field application, what can be done in one and one-half minutes? Is it possible to increase the period of induction, say, to a half-hour? Unfortunately, present indications are that in systems as impure as those under consideration, the polymerization either has a small induction period and is rapid, or else never takes place at all effectively. The importance of this factor cannot be overemphasized. If the induction period cannot be increased, the only hope seems to be in the development of a very rapid and efficient technique of application of the treatment to soils -- a consideration which was not within the scope of this thesis study, and which, incidentally, the author views with unfortunate scepticism insofar as one might be dealing with 100% clay bodies.

Turning to a comparison of the overall results obtained with the sodium-bentonite, calcium-bentonite, and hydrogen-kaolinite, only the strength results will herein be discussed since it has already been pointed out that the water-affinity characteristics seem to be predominantly dependent on base-exchange factors. The water contents of the systems studied were radically different, but the discussion on page has fairly well established that the plots on pages (Figs. 27, 34, 39) represent conditions that are essentially independent of water content. Therefore, if any comparisons are to be made on the three clays, they have to be based on Figs. 27, 34, 39. Overall comparisons should not be risked on so little data, but they will be attempted, nonetheless, in order to help steer further research. It appears that the curves for both calcium-bentonite and sodium-bentonite are fairly similar. For instance, at $\frac{0.2 \text{ gm of } Ca(Ak)_2}{\text{gm dry clay}}$ the curve for sodium-bentonite indicates a 340% effectiveness of polymerization, and the curve for calcium-bentonite indicates a 410% effectiveness of polymerization (approximately); at $\frac{0.12 \text{ gm } Ca(Ak)_2}{\text{gm dry clay}}$ the sodium-bentonite gives a value of 250% and the calcium-bentonite gives a value of 233%. Below this point it is not very fair to compare conditions because base-exchange begins to play the predominant role. On the other hand, there is absolutely no doubt that the kaolin clay behaves in a completely different manner. Even at $\frac{0.065 \text{ gm } Ca(Ak)_2}{\text{gm dry clay}}$, the highest value available, the kaolin clay gives as astounding a value of effectiveness of polymerization as 13,700%!

It may be just a coincidence that the ionic effect is indicated as being unimportant insofar as a calcium and a sodium-bentonite yield strength improvements in the same ratio by polymerization. However, if it is not a coincidence, then the intriguing question that arises is: Why is the treatment so very much more effective in the case of kaolin clay than in the case of bentonite clay? Is clay-mineral structure the factor that explains approximately 100:1 ratios of effectiveness of the strengthening effect in kaolin as compared to bentonite? Prolonged and serious thought has been given to this matter, but the author does not find any completely satisfactory hypothesis to explain those differences. Much more extensive laboratory investigations appear to be necessary. The research that is suggested along this line may be summarized as follows:

(1) Investigate further homoionic varieties of clay systems, as for example, hydrogen-bentonite, lead-bentonite, aluminum-bentonite, sodium-kaolinite, calcium-kaolinite and so on. Include tests on homoionic varieties of illitic clays.

(2) With each homoionic variety tested attempt to establish the limits for the trends discovered. For instance, all three curves on pages 132, 154, 162, (Figs. 27, 34, 39) are increasingly steep with an increase of $\frac{\text{gm } Ca(Ak)_2}{\text{gm dry clay}}$; but it is altogether improbable that such trends would be maintained ad infinitum. It is inevitable that both at the high and at the low range of $\frac{\text{gm } Ca(Ak)_2}{\text{gm dry clay}}$ there will be an apparent discontinuity. The study and interpretation of such discontinuities may throw much light on the problem. It is of special interest to pursue the studies of the various clays into conditions that overlap to some extent the range of conditions investigated with other clays. For instance, the studies conducted by the author cover the variation of water content of hydrogen-kaolin from 41.5% to 65%, of calcium-bentonite from 140% to 200%, of sodium-bentonite from 100% to 300%. It has been concluded that for the general conditions discussed on pages 112 - 115, the water content is not an independent

variable in the figures 27, 34, 39. However, if between 65% and 100% water content for kaolin there appears a discontinuous or gradual reversal of the trend, kaolin clay may even possibly line itself up with the bentonite between 100% and 300% water contents. Hence the importance of furthering the tests on kaolin to include 100% water content, and the tests on sodium-bentonite to include, say, 65% water content.

(3) To check on the possible influence of particle size and such factors as the number of me. of exchange capacity associated with each "particle", it may be of interest to use clay samples fractionated to various uniform sizes. Although in some cases effective sizes of clay particles vary with water content, some valuable qualitative trends may be detected through such work.

In conclusion, it may be stated that although these preliminary investigations could not establish the applicability of the base-exchange and polymerization treatment to the practical stabilization of clays, they certainly serve to open the road and spur the interest to the pursuit of investigations that should lead to the acquisition of very valuable knowledge. It is even possible to foresee that, at least in limited directions, this acquisition of knowledge will directly culminate in the achievement of an effective method of stabilizing clays.

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APPENDED BIBLIOGRAPHY

In view of the fact that Reference 11, page 174 is not available in published form, a few of the most important references listed in the bibliography of that report are herewith listed.

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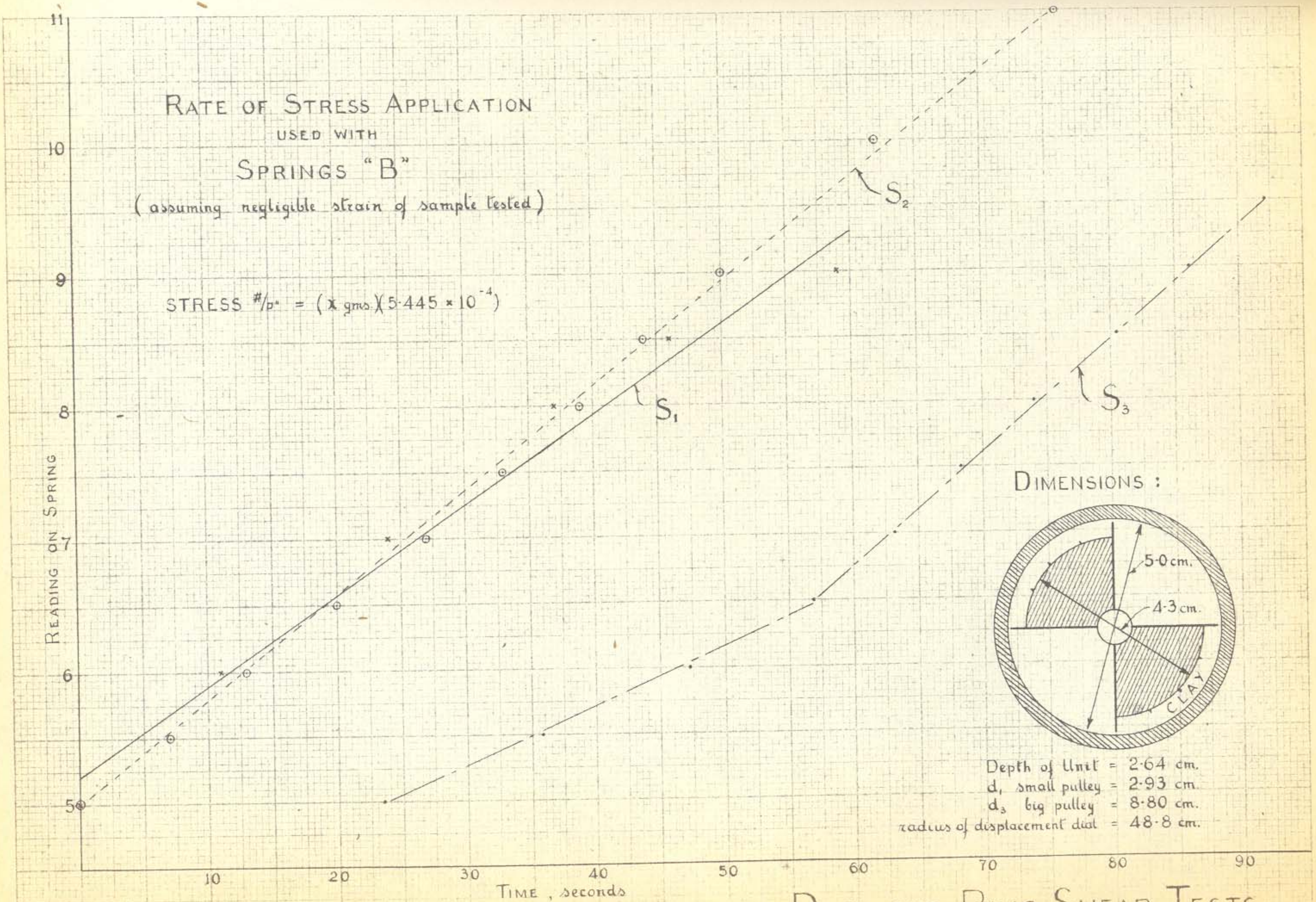
SUMMARIZED LABORATORY

DATA



DATA FOR RING-SHEAR TESTS

FIG. 41

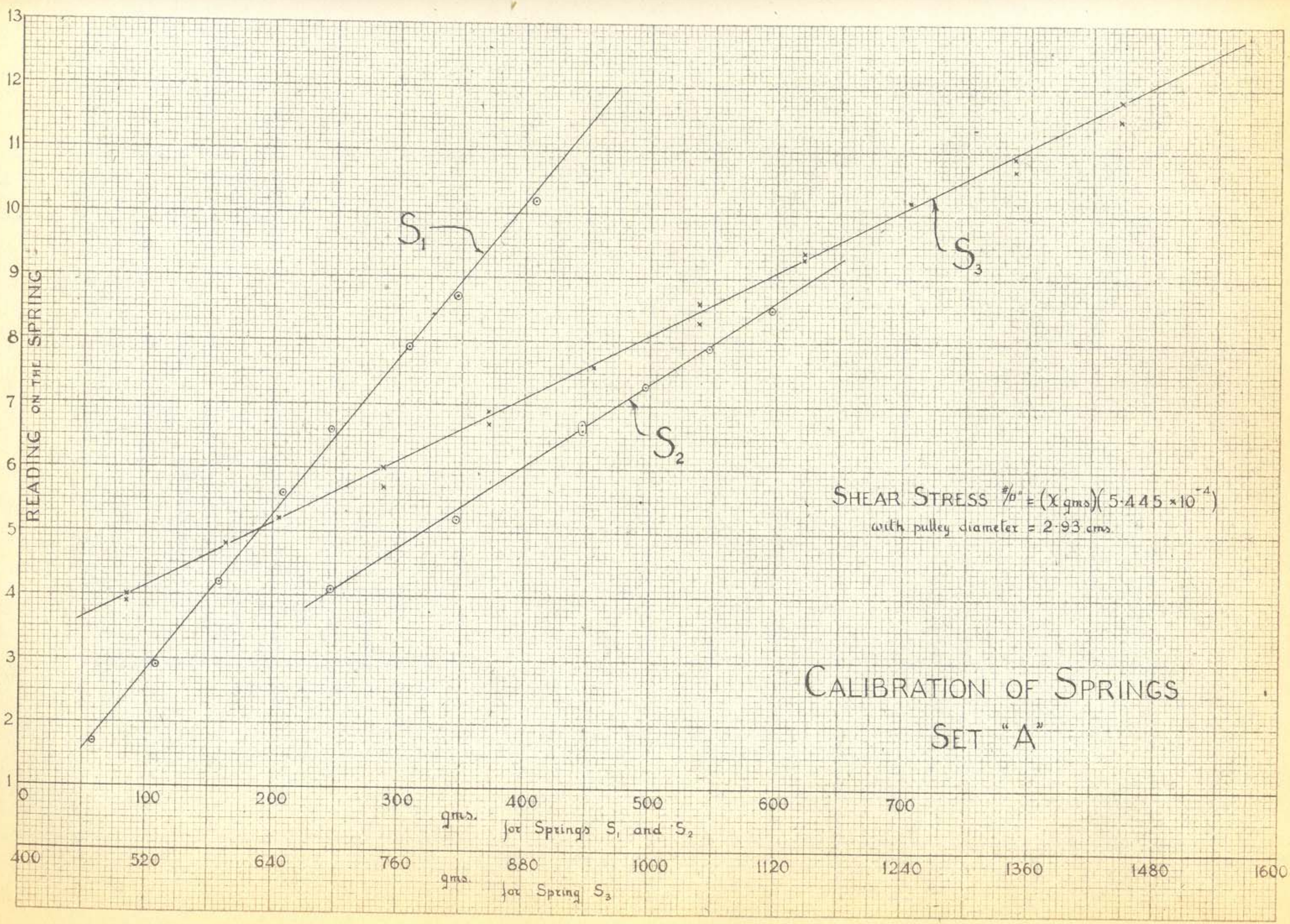

CALIBRATION OF SPRINGS
SET "A"
SHEAR STRESS #/□" = (X gms)(5·445 × 10⁻⁴)
with pulley diameter = 2·93 cms
READING ON THE SPRING
S₁
S₂
S₃
gms. for Springs S₁ and S₂
gms. for Spring S₃
0
100
200
300
400
500
600
700
400
520
640
760
880
1000
1120
1240
1360
1480
1600
1
2
3
4
5
6
7
8
9
10
11
12
13

FIG. 42

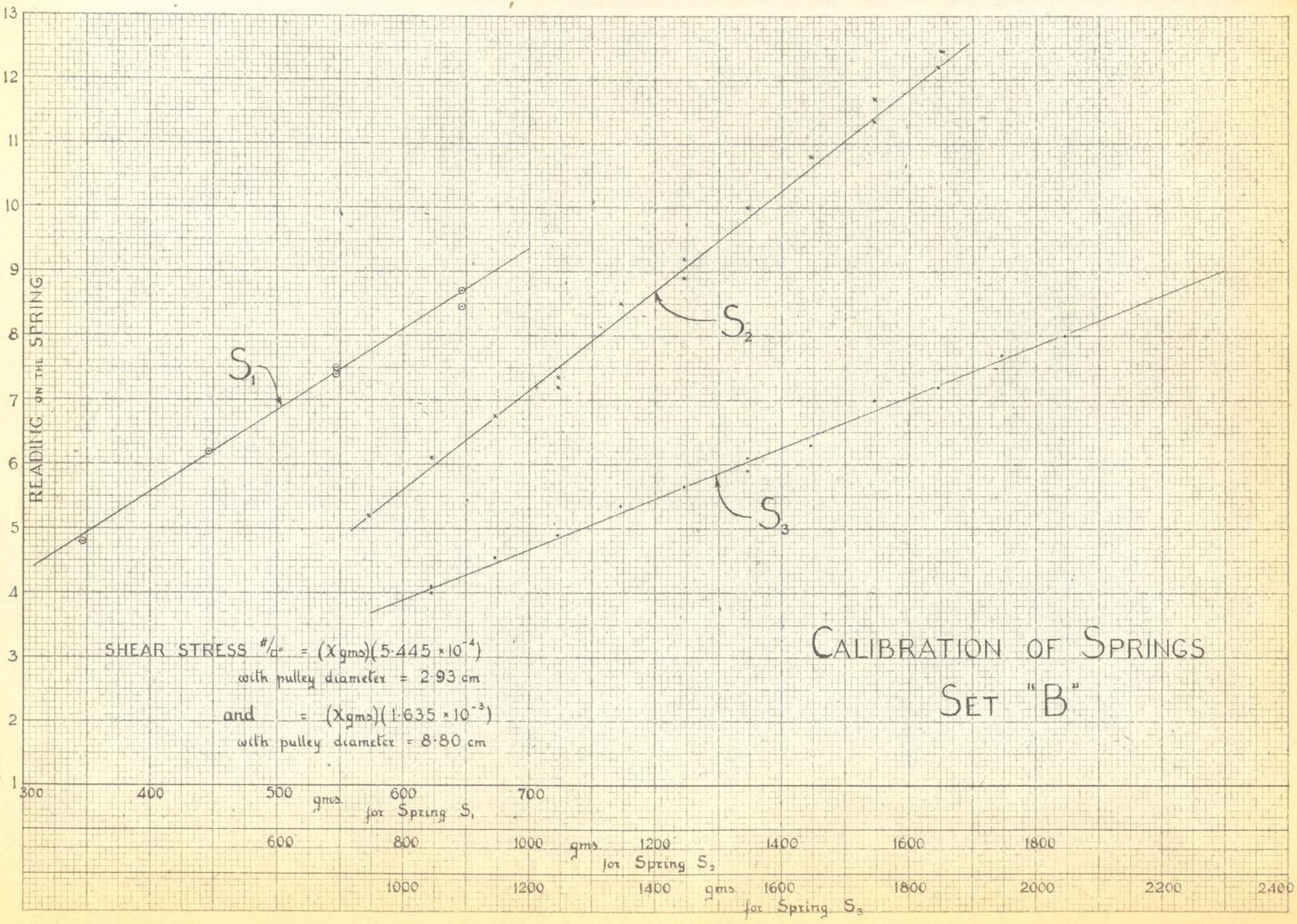

CALIBRATION OF SPRINGS
SET "B"
READING ON THE SPRING
SHEAR STRESS #/□" = (X gms)(5·445 × 10⁻⁴)
with pulley diameter = 2·93 cm
and = (X gms)(1·635 × 10⁻³)
with pulley diameter = 8·80 cm
S1
S2
S3
1
2
3
4
5
6
7
8
9
10
11
12
13
300
400
500
600
700
gms. for Spring S1
600
800
1000
1200
1400
1600
1800
gms. for Spring S2
1000
1200
1400
1600
1800
2000
2200
2400
gms. for Spring S3

FIG. 43

RESULTS OF BLANK TITRATIONS FOR DETERMINATION OF PERCENT POLYMERIZATION

1) Calcium Methacrylate

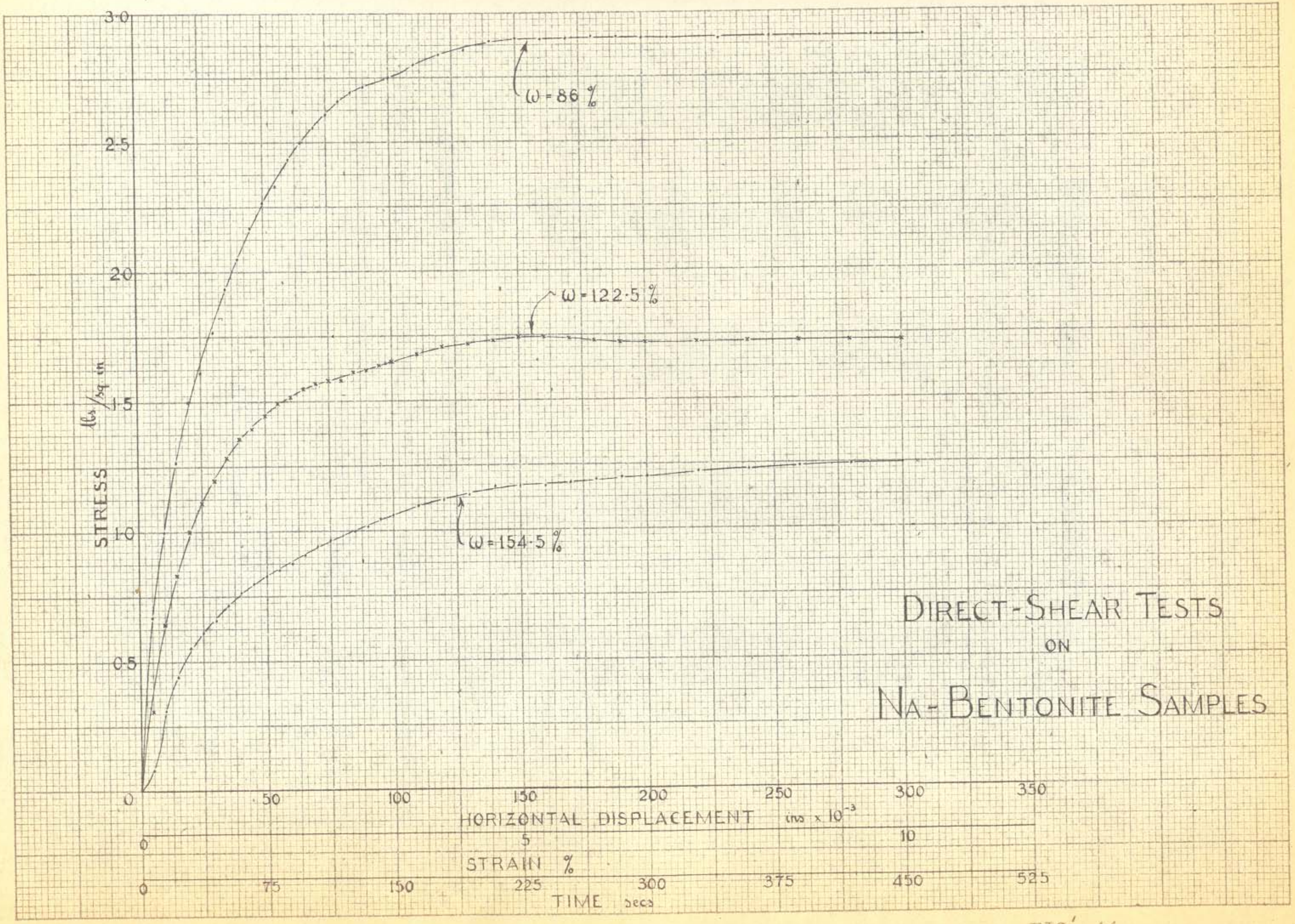
Samples tested: sodium-bentonite at 200% water content with admixture equivalent to

% soln. of $Ca(Me)_2$	1 gm. $KMnO_4$ equiv. to gm. of $Ca(Me)_2$
14	0.517
14	0.497
12	0.524
10	0.539
8	0.534
7	0.571
6	0.565
5	0.533
4	0.450
3	0.562
2	0.539

2) Calcium Acrylate

Samples tested: sodium-bentonite at 200% water content with admixture equivalent to

% soln. of $Ca(Ak)_2$	1 gm. $KMnO_4$ equiv. to gm. of $Ca(Ak)_2$
14	0.398
12	0.401
10	0.403
6	0.405
4	0.412
2	0.425



DIRECT-SHEAR TESTS
ON
NA-BENTONITE SAMPLES

FIG. 44

RING-SHEAR TESTS ON SODIUM-BENTONITE

A

Time mins.	Springs $S_B . S_1$	Dial, cms.	Stress lbs/in^2	Displacement cms.
0	0	3.25	0	0
1:55	2	6.4	---	3.15
2:25	3	7.0	---	3.75
2:50	4	7.3	---	4.05
3:12	5	7.7	0.580	4.45
3:45	6	8.0	0.711	4.75
4:05	6.5	8.2	0.777	4.95
4:20	7.0	8.4	0.842	5.15
4:40	7.5	8.6	0.908	5.35
5:00	8.0	8.75	0.973	5.50
5:25	8.5	9.05	1.039	5.80
5:50	S_2 4.9	9.35	1.179	6.10
6:04	5.2	9.60	1.241	6.35
5:16	5.5	9.90	1.303	6.65
5:28	5.8	10.4	1.367	7.15
5:40	6.1	11.0	1.425	7.75
6:00	6.15	12.0	1.435	8.75
6:01	5.8	17.0	1.367	13.75

Displacement = 8.3 - 3.4 = 4.9 cm. at failure

Displacement of shearing surface = 0.0512 x 4.9 = 0.251 cm.

Displacement of bottom of shear surface = 0.251 x $\frac{4.3}{5.0}$ = <u>0.216</u> cm.

Relative displacement . . . . = 0.035 cm.

$$\text{Strain} = \frac{0.035}{0.35} = 10\%$$

RING-SHEAR TESTS ON SODIUM-BENTONITE

B

Time	Springs $S_B.S_1$	Dial, cms.	Stress lbs/in^2	Displacement cms.
0	0	8.1	0	---
0	0	8.5	---	---
1:15	0	13.4	---	---
1:50	2.0	13.6	---	---
2:05	2.5	13.7	---	---
2:18	3.0	13.9	---	---
2:30	3.5	14.0	---	---
2:45	4.0	14.2	---	---
2:55	4.3	14.3	---	---
3:00	4.5	14.4	0.517	6.3
3:05	4.8	14.4	0.556	6.3
3:10	5.0	14.5	0.580	6.4
3:17	5.3	14.5	0.620	6.4
	5.5	14.6	0.645	6.5
	5.7	14.7	0.670	6.6
3:42	6.0	14.8	0.712	6.7
3:52	6.3	14.9	0.751	6.8
4:00	6.5	14.9	0.777	6.8
	6.7	15.0	0.803	6.9
4:17	7.0	15.1	0.842	7.0
	7.2	15.2	0.867	7.1
4:37	7.5	15.3	0.908	7.2
4:50	7.8	15.5	0.946	7.4
5:00	8.0	15.8	0.972	7.7
	8.1	16.1	0.985	8.0

Displacement = 8.0 - 5.5 = 3.5 cm. at failure

Displacement of shearing surface = 0.0512 x 3.5 = 0.179 cm.

Displacement of bottom of shear surface = $0.179 \times \frac{4.3}{5.0} = \underline{0.154}$ cm.

Relative displacement . . . . = 0.025 cm.

$$\text{Strain} = \frac{0.025}{0.35} = 7.15\%$$

RING-SHEAR TESTS ON SODIUM-BENTONITE

C

Time	Springs $S_B.S_1$	Dial, cms.	Stress lbs/in^2	Displacement cms.
0	0	3.9	0	0
2:00	2.0	5.9	?	---
2:27	3.0	6.4	?	---
2:52	4.0	6.6	?	---
3:00	4.3	6.7	?	---
3:07	4.5	6.8	0.517	2.9
3:13	4.8	6.8	0.556	2.9
3:17	5.0	6.9	0.580	3.0
3:25	5.3	7.0	0.620	3.1
3:35	5.55	7.0	0.650	3.1
3:50	6.00	7.1	0.712	3.2
4:00	6.3	7.3	0.751	3.4
4:12	6.6	7.4	0.790	3.5
4:25	7.0	7.5	0.842	3.6
4:47	7.5	7.6	0.908	3.7
5:04	8.0	7.8	0.972	3.9
5:20	$S_2$4.3	7.9	---	4.0
5:30	4.5	7.9	---	4.0
5:45	4.8	8.0	1.159	4.1
5:55	5.0	8.2	1.200	4.3
6:05	5.2	8.3	1.241	4.4
6:15	5.5	8.4	1.303	4.5
6:28	5.8	8.6	1.365	4.7
6:36	6.0	8.7	1.407	4.8
6:47	6.3	8.9	1.468	5.0
6:55	6.5	9.0	1.509	5.1
7:06	6.8	9.2	1.570	5.3
7:15	7.0	9.4	1.611	5.5
7:24	7.3	9.7	1.675	5.8
7:33	7.5	9.9	1.716	6.0
7:44	7.8	10.3	1.780	6.4
7:52	8.0	10.7	1.820	6.8
	8.15	13.0	1.850	9.1
	7.8	21.0	1.780	17.1

Displacement = 7 - 2.2 = 4.8 cm. at failure

Displacement of shearing surface = 0.0512 x 4.8 = 0.246 cm.

Displacement of bottom of clay layer $= 0.246 \times \frac{4.3}{5.0} = \underline{0.212}$ cm.

Relative displacement . . . . = 0.034 cm.

$$\text{Strain} = \frac{0.034}{0.35} = 9.71\%$$

RING-SHEAR TESTS ON SODIUM-BENTONITE

D

Time	Springs $S_B . S_1$	Dial, cms.	Stress lbs/in^2	Displacement cms.
	0	4.5	0	0
	2.0	7.1	?	2.6
0	3.0	7.6	?	3.1
	4.0	8.0	?	3.5
0:51	5.0	8.4	0.580	3.9
1:05	5.5	8.6	0.645	4.1
1:23	6.0	8.8	0.712	4.3
1:38	6.4	9.0	0.764	4.5
	6.7	9.2	0.803	4.7
2:00	7.0	9.3	0.842	4.8
2:10	7.3	9.5	0.880	5.0
2:22	7.6	9.6	0.919	5.1
2:37	8.0	9.8	0.972	5.3
2:49	8.2	10.0	0.998	5.5
3:05	8.5	10.7	1.039	6.2
	8.6	20.0	1.050	15.5
	8.2	36.0	0.998	31.5
	7.6	56.0	0.919	51.5
3:08	6.7	61.0	0.803	56.5

Displacement = 6.1 - 2.1 = 4.0 at failure

Displacement of shearing surface = 0.0512 x 4.0 = 0.205 cm.

Displacement of bottom of shearing surface $= 0.205 \times \frac{4.3}{5.0} = \underline{0.176}$ cm.

Relative displacement . . . . = 0.029 cm.

$$\text{Strain} = \frac{0.029}{0.35} = 8.29\%$$

RING-SHEAR TESTS ON SODIUM-BENTONITE

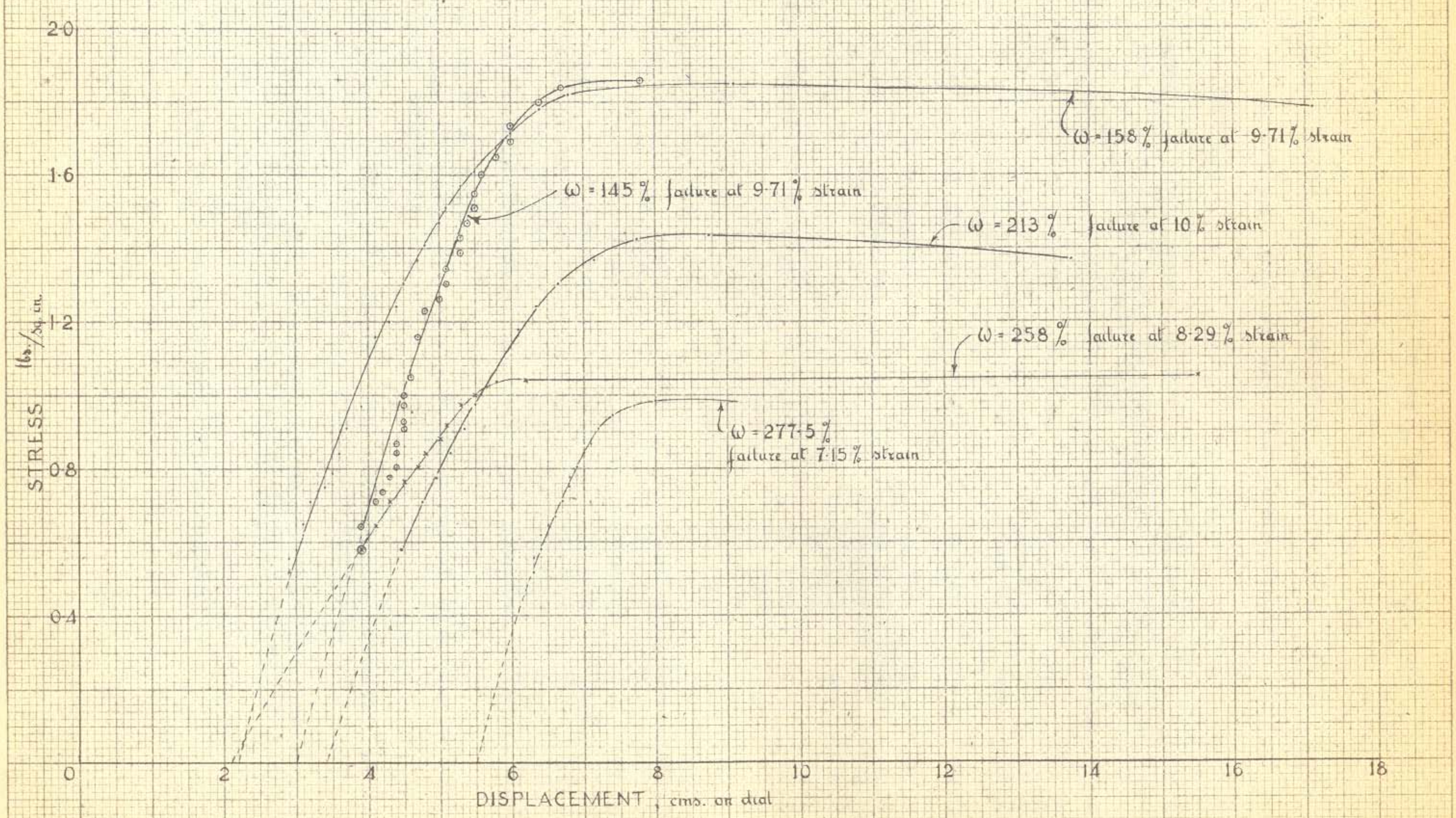
E

Time	Springs $S_B.S_1$	Dial, cms.	Stress lbs/in^2	Displacement cms.
0	0	2.0	0	0
1:30	2.0	4.7	?	2.7
1:57	3.0	4.9	?	2.9
2:24	4.0	5.2	?	3.2
2:50	5.0	5.9	0.580	3.9
3:04	5.5	5.9	0.645	3.9
3:20	6.0	6.1	0.712	4.1
3:29	6.2	6.2	0.737	4.2
3:39	6.5	6.3	0.777	4.3
3:47	6.7	6.4	0.803	4.4
3:58	7.0	6.4	0.842	4.4
4:07	7.2	6.4	0.867	4.4
4:16	7.5	6.5	0.908	4.5
4:24	7.7	6.5	0.932	4.5
4:33	8.0	6.5	0.972	4.5
4:44	8.2	6.5	0.998	4.5
4:59	8.6	6.6	1.050	4.6
5:19	S_2 4.8	6.7	1.159	4.7
5:32	5.15	6.8	1.231	4.8
5:43	5.3	7.0	1.262	5.0
5:50	5.5	7.1	1.303	5.1
5:58	5.7	7.1	1.344	5.1
6:06	5.9	7.3	1.387	5.3
6:14	6.1	7.3	1.427	5.3
6:21	6.3	7.4	1.468	5.4
6:27	6.5	7.5	1.509	5.5
6:36	6.7	7.5	1.550	5.5
6:44	6.95	7.6	1.602	5.6
6:54	7.2	7.8	1.651	5.8
7:03	7.4	8.0	1.693	6.0
7:09	7.6	8.0	1.735	6.0
7:20	7.9	8.4	1.797	6.4
7:27	8.1	8.7	1.839	6.7
7:29	8.2	9.8	1.860	7.8
7:30	6.1	60	1.427	58

Displacement = 7.8 - 3 = 4.8 at failure

Hence, as in C,

Strain = 9.71%



RING - SHEAR TESTS
ON
NA - BENTONITE SAMPLES

FIG. 45

Preliminary Polymerization Studies with Sodium-Bentonite

Using $Ca(Me)_2$ equivalent to a 14% solution: i.e. equiv. to a soln. contg. 0.666 moles of $Ca(me)_2$ per 1000 cc.

$NaHSO_3$, and $(NH_4)_2S_2O_8$ in varying concentrations as noted.

Original Na-bentonite clay at about 200% water content: shearing strength = 1.380 psi., water pickup = 634%

Except as noted, polymerized samples tested 24 hours after start of polymerization; water pickup values are for 24-hour test.

SAMPLE: 7.5 gms. Na-bent. + 15 cc. H_2O + 2.1 gm. $Ca(Me)_2$ + x gm. $NaHSO_3$ + Y gm. $(NH_4)_2 S_2O_8$

N°	$NaHSO_3$ gms.	$NaHSO_3$ moles per 1000 cc.	$(NH_4)_2S_2O_8$ gms.	$(NH_4)_2S_2O_8$ moles per 1000 cc.	Shear Strength psi.	Water pickup %	Comparison with base-exchanged, unpolymerized samples.			Estimated ionic effects of catalysts		Effect of Polymerization		Poly-merization %	Remarks
							Strength %	ΔS psi.	ΔW%	Strength psi	water pickup %	ΔS psi.	ΔW%		
1	0.3	0.192	0.7	0.2045	0.553	---	285	0.364	---	0.470	---	0.083	---	93.8	Stiff gel
2	0	0	0.7	0.2045	0.474	---	245	0.285	---	0.360	---	0.114	---	15.2	Stiff gel
3	0.3	0.192	0.3	0.0876	0.240	---	124	0.051	---	0.200	---	0.040	---	59.2	Slightly tacky
4	0.4	0.256	0.4	0.1168	0.308	---	159	0.119	---	0.260	---	0.048	---	65.0	Slightly tacky
5	0.3	0.192	0.5	0.1460	0.393	---	203	0.204	---	0.340	---	0.053	---	62.7	
6.	0.2	0.128	0.6	0.1752	0.440	---	227	0.251	---	0.370	---	0.070	---	68.9	
7	0.1	0.064	0.7	0.2045	0.507	---	261	0.318	---	0.370	---	0.137	---	62.3**	
2(a)					0.482	---	248	0.293	---	0.360	---	0.122	---	39.2	At 48 hrs
2(b)	Long duration time test for case #2				0.572	---	295	0.383	---	0.360	---	0.212	---	45.8	At 72 hrs
2(c)					0.530	---	274	0.341	---	0.360	---	0.170	---	42.3	At 96 hrs
2(d)					0.565	---	292	0.376	---	0.360	---	0.205	---	45.8	At 120 hrs
7(a)					0.385	---	198	0.196	---	0.370	---	0.015	---	63.3	At 2 hrs
7(b)					0.441	---	227	0.252	---	0.370	---	0.071	---	72.6)	At 6 hrs
7(b)*	Short duration time test for case #7				0.441	---	227	0.252	---	0.370	---	0.071	---	82.0)	
7(c)					0.441	---	227	0.252	---	0.370	---	0.071	---	75.0	At 11.5 hrs
7(d)					0.455	---	234	0.266	---	0.370	---	0.085	---	77.1)	At 24 hrs
7(d)*					0.434	---	224	0.245	---	0.370	---	0.064	---	85.3)	
8(a)	0.2	0.128	0.7	0.2045	0.471	182.5	243	0.282	148.5	0.420	110	0.051	72.5	91.2	
8(b)	Ditto: four separate samples prepared to investigate reproducibility of results				0.434	175	224	0.245	141	0.420	110	0.014	65	95.9	
8(c)					0.438	174	226	0.249	140	0.420	110	0.018	64	95.8	
8(d)					0.501	174	259	0.312	140	0.420	110	0.081	64	94.3	

* Shear testing unit filled with polymerized sample just before testing

** Titrations in cases 1-7 were checked 36 hours later, showing that polymerization time effects are negligible after dispersion of the sample in dilute sulphuric acid.

Conclusions: (1) The long duration time test (N°2) apparently indicates that polymerization proceeds beyond 24 hours, but not beyond 48 hrs. It is more likely, however, that the results reflect merely the irreproducibility of results in separately prepared samples.

(2) The short duration time test (N°7) indicates that results are not very closely reproducible. Most of the polymerization takes place before 2 hrs., and is then blocked. A little more polymerization takes place in a sample in a porcelain dish than in samples confined in testing units.

(3) The reproducibility test, #8, shows that in cases where polymerization goes to completion, results are reproducible.

Polymerization Studies with Sodium-Bentonite at 200% Water Content

Using Ca(Me)$_2$, NaHSO$_3$, (NH$_4$)$_2$S$_2$O$_8$

Investigating variation of calcium methacrylate concentration

Catalyst concentrations : NaHSO$_3$ 0.2 gm) (NH$_4$)$_2$S$_2$O$_8$ 0.7 gm) in 15 cc. of solution

Sample : 7.5 gm. Na-bent. + 15 cc. H$_2$O + 0.2 gm. NaHSO$_3$ + 0.7 gm. (NH$_4$)$_2$S$_2$O$_8$ + x gm. (Ca(Me)$_2$

Ca(Me)$_2$ gms.	% soln. of Ca(Me)$_2$	Without catalysts		Polymerized Sample		Comparison with Base-exchanged			Estimated ionic effects of catalysts		Effect of Polymerization		Polymerization %	Remarks
		Strength psi	Water pickup %	Strength psi	Water pickup %	Strength $\frac{(5)}{(3)}$ %	ΔS psi	ΔW%	Strength psi. (7)	Water Pickup % (8)	ΔS psi	ΔW%		
(1)	(2)	(3)	(4)	(5)	(6)		(5)-(3)	(6)-(4)			(5)-(7)	(6)-(8)		
0	0	1.380	634	---	---	---	---	---	---	---	---	---	---	---
0.3	2	0.558	228	0.830	138	149	0.272	-90	0.800	178	0.030	-40	98.5	Stiff gel
0.75	5	0.288	47.5	0.679	241	243	0.391	193	0.700	136	-0.021	105	98.5	Stiff gel
1.2	8	0.227	50.5	0.631	250	281	0.404	199	0.600	110	0.031	140	97.6	Stiff gel
1.5	10	0.212	53.5	0.619	228	296	0.407	174	0.540	100	0.079	128	95.8	Stiff gel
1.8	12	0.197	51.5	0.507	197	254	0.310	145	0.480	105	0.027	92	95.7	Stiff gel
2.1	14			0.434	175	224					0.014		91.2	
2.1	14			0.438	174	226					0.018		95.9	
2.1	14			0.471	182.5	243					0.051		95.8	
2.1	14			0.501	174	259					0.081		94.3	
Average		0.189	34	0.450	176.4	238	0.261	142	0.420	110	0.030	66	94.3	Slightly tacky
3.15	21	0.205	63.7	0.283	99	138	0.078	35	0.233	125	0.050	-26	92.6	Slightly tacky
42	28	0.216	75.7	0.271	70	125	0.055	-5.7	0.221	140	0.050	-70	95.0	Extremely tacky

Remarks (1) Indications are that the effect of polymerization in increasing strength is rather slight; and that the strength increase due to polymerization is about constant regardless of the concentration of Ca(Me)$_2$ used.

(2) It is difficult to see how polymerization can increase the water pick-up. The drawing of important conclusions from these indications is unwarranted in view of the nature of the data employed. It is believed that such factors as variations of temperature (which were neglected) may affect the water pick-up values, tending to explain the discrepancy.

(3) The fact that polymerization goes to completion even in cases where the Ca(Me)$_2$ is not completely dissolved, indicates that as Ca(Me)$_2$ is thrown out of solution by polymerization, the undissolved Ca(Me)$_2$ goes into solution and in turn polymerizes.

Polymerization Studies with Sodium-Bentonite at 200% water content

Using $Ca(Me)_2$, $NaHSO_3$, $(NH_4)_2S_2O_8$

Sample: 7.5 gm. Na-bent. + 15 cc. H_2O + x gm. $Ca(Me)_2$ + Y gm. $NaHSO_3$ + z gm. $(NH_4)_2S_2O_8$

% soln. of $Ca(Me)_2$	$Ca(Me)_2$ gms x	$NaHSO_3$ gms y	$(NH_4)_2S_2O_8$ gms z	Polymerized Sample		Comparison with base-exchanged			Estimated ionic effects of catalysts		Effect of Polymerization		Polymerization %
				Strength psi	Water Pickup %	Strength %	ΔS psi	ΔW %	Strength psi	Water Pickup %	ΔS psi.	ΔW %	
2	0.3	0.1	0.7	0.825	165	148	0.267	-63	0.780	170	0.045	-5	97.1
5	0.75			0.750	190	260	0.462	142.5	0.650	120	0.100	70	98.2
10	1.50			0.582	188	275	0.370	134.5	0.500	90	0.062	98	81.6
14	2.1			0.443	128	229	0.254	94	0.370	100	0.073	28	75.0
				0.481	---	248	0.292	---			0.111		69.7
21	3.15			0.339	116	165	0.134	52	0.230	120	0.109	-4	89.1
2	0.3	0.2	0.7	0.830	138	149	0.272	-90	0.800	178	0.030	-40	98.5
5	0.75			0.679	241	243	0.391	193	0.700	116	-0.021	105	98.5
10	1.50			0.619	228	296	0.407	174	0.540	90	0.079	128	95.8
14	2.1			0.450	176.4	238	0.261	142	0.420	100	0.030	66	94.3
21	3.15			0.283	99	138	0.078	35	0.233	120	0.050	-26	92.6
2	0.3	0.3	0.7	0.765	171	130	0.207	-57	0.780	190	-0.015	-19	98.2
5	0.75			0.722	220	251	0.434	172.5	0.650	150	0.072	70	97.2
10	1.5			0.567	246	267	0.355	192.5	0.500	110	0.067	136	96.2
14	2.1			0.546	161	281	0.357	127	0.470	120	0.076	41	85.0
				0.553	---	285	0.364				0.083	---	93.8
21	3.15			0.406	125	198	0.201	61	0.270	130	0.136	-5	96.0
2	0.3	0.2	0.6	0.780	187	140	0.222	-41	0.770	180	0.010	7	99.0
5	0.75			0.671	208	233	0.383	160.5	0.640	130	0.031	78	97.0
10	1.5			0.466	224	220	0.254	170.5	0.420	100	0.046	124	88.8
14	2.1			0.446	137	230	0.257	103	0.370	110	0.076	27	77.0
				0.440	---	227	0.251	---			0.070	---	68.9
21	3.15			0.313	137	153	0.108	73	0.230	128	0.083	12	86.7
2	0.3	0.3	0.5	0.675	137	115	0.117	-91	0.650	170	0.025	-33	96.2
5	0.75			0.582	163	202	0.294	115.5	0.550	100	0.032	63	96.1
10	1.5			0.426	144	200	0.214	90.5	0.400	85	0.026	59	78.8
14	2.1			0.412	115	212	0.223	81	0.340	90	0.072	25	79.0
				0.393	---	203	0.204	---			0.063	---	62.7
21	3.15			0.268	91	131	0.063	27	0.220	100	0.048	-9	88.3
2	0.3	0.4	0.4	0.619	191	111	0.061	-37	0.600	200	0.019	-9	98.0
5	0.75			0.492	231	171	0.204	183.5	0.460	150	0.032	81	97.0
10	1.5			0.406	184	192	0.194	130.5	0.360	120	0.046	64	81.2
14	2.1			0.356	120	184	0.167	86	0.260	120	0.096	0	72.9
				0.308	---	159	0.119	---			0.048	---	65.0
21	3.15			0.216	111	105	0.011	47	0.210	130	0.006	-19	83.8

Polymerization Studies with Sodium-Bentonite at 200% Water Content

Using $Ca(Me)_2$ equivalent to a 10% solution = i.e. equiv. to a soln. contg. 0.476 moles of $Ca(Me)_2$ per 1000 cc.

$Na_2S_2O_3$, and $(NH_4)_2S_2O_8$ in varying concentrations as noted.

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gm. $Ca(Me)_2$ + x gm $Na_2S_2O_3.5H_2O$ + y gm. $(NH_4)_2S_2O_8$

No.	$Na_2S_2O_3.5H_2O$ x gms.	$Na_2S_2O_3.5H_2O$ moles per 1000 cc.	$(NH_4)_2S_2O_8$ y gms.	$(NH_4)_2S_2O_8$ moles per 1000 cc.	Shear Strength psi	Water pickup %	Comparison with base-exchanged unpolymerized samples			Effect of Polymerization subtracting effect of catalysts		Polymerization %
							Strength %	ΔS psi	ΔW %	ΔS psi	ΔW %	
1	0.1	0.0278	0.7	0.2045	0.564	110	266	0.352	56	0.044	20	69.2
2	0.2	0.0537	0.7	0.2045	0.564	117	266	0.352	63	0.034	1	72.8
3	0.3	0.0805	0.7	0.2045	0.580	152	274	0.368	98	0.050	42	75.0
4	0.4	0.1074	0.8	0.2335	0.537	162	253	0.325	108	0.017	32	78.3
5	0.2	0.0537	0.6	0.1752	0.544	112	257	0.332	58	0.034	12	68.7
6	0.2	0.0537	0.5	0.1460	0.406	112	192	0.194	58	0.016	12	66.7
7	0.1	0.0278	0.6	0.1752	0.455	108	215	0.243	54	0.015	13	77.8
8	0.3	0.0805	0.5	0.1460	0.468	141	221	0.256	87	0.048	56	73.8

Remarks (1) The strength results are comparable to those obtained with the use of sodium bisulfite - ammonium persulfate catalysts

(2) The water pick-up is noticeably lower than corresponding values for bisulfite - persulfate catalysts.

(3) In other respects trends previously noted are maintained.

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with $Ca(Ak)_2$, $NaHSO_3$, $(NH_4)_2S_2O_8$

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gm. $Ca(Ak)_2$

$NaHSO_3$ gm.	$(NH_4)_2S_2O_8$ gm.	Shear Strength lbs/in^2	Water Pick-up %	Polymerization %	Strength Percent of Base-Exchanged but Unpolymerized
0.1	0.7	0.520	158	97.6	221
0.2	0.7	0.520	187	99.0	221
0.3	0.7	0.650	235	99.1	277
0.4	0.7	0.641	176	99.3	273
0.1	0.6	0.352	115	97.8	150
0.2	0.6	0.550	177	98.3	234
0.3	0.6	0.574	144	99.0	243
0.4	0.6	0.542	150	99.3	230
0.1	0.5	0.403	135	97.6	171
0.2	0.5	0.383	115	98.6	163
0.3	0.5	0.436	176	98.8	186
0.4	0.5	0.433	187	99.0	184
0.4	0.4	0.419	112	98.6	178
0.4	0.8	0.665	204	99.6	283

Blank with calcium acetate, to separate ionic effect of catalysts

0.1	0.7	0.658	120

Conclusion: effect of polymerization in increasing strength is but slight

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with $Ca(Ak)_2$, $NaHSO_3$, $K_2S_2O_8$

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gms. $Ca(Ak)_2$

$NaHSO_3$ gm.	$K_2S_2O_8$ gm.	Shear Strength lbs/in^2	Strength, percent of Base-Exchanged but Unpolymerized	Water Pick-up %
0.1	0.7	0.286	122	166
0.3	0.7	0.396	169	199
0.1	0.4	0.265	113	173
0.4	0.4	0.274	117	141
0.4	0.8	0.447	190	239
0.2	0.5	0.246	105	132
0.3	0.6	0.292	124	133
0.2	0.2	0.269	114	100

By inspection it may be seen that all cases are ≈ 95% polymerized.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.540		106

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with Ca(Ak)$_2$, NaHSO$_3$, t-butyl-hydroperoxide

Sample: 7.5 gms. Na-bent. + 15 cc. H$_2$O + 1.5 gms. Ca(Ak)$_2$

NaHSO$_3$ gm.	t-butyl-hydroperoxide cc.	Shear Strength lbs/in^2	Strength, percent of Base-Exchanged but Unpolymerized	Water Pick-up %
0.1	0.7	0.466	198	132
0.3	0.7	0.437	186	107
0.1	0.4	0.422	180	118
0.4	0.4	0.330	140	84
0.4	0.8	0.386	164	105
0.2	0.2	0.362	154	84
0.2	0.5	0.396	168	100
0.3	0.6	0.390	165	95

By inspection it may be seen that all cases are ≈ 95% polymerized.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.313		66

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with $Ca(Ak)_2$, hydrazine, t-butyl-hydroperoxide

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gms. $Ca(Ak)_2$

Hydrazine cc.	t-but-hyd. cc.	Shear Strength lbs/in^2	Shear Strength %	Water Pick-up %	Increase of Strength over Base-exchanged lbs/in^2	ΔW over Base-exchanged %
0.05	0.3	0.406	173	75	0.171	28
0.3	0.3	0.225	96	89	-0.010	42
0.1	0.4	0.313	133	102	0.078	55
0.2	0.4	0.252	107	73	0.017	26
0.1	0.5	0.357	152	110	0.022	63
0.2	0.5	0.327	139	111	0.092	64
0.3	0.5	0.245	104.5	114	0.010	67
0.4	0.5	0.245	104.5	103	0.010	56
0.1	0.6	0.280	105.5	84	0.045	37
0.2	0.6	0.315	134	135	0.080	88
0.3	0.6	0.238	101	101	0.003	54
0.25	0.75	0.343	146	105	0.108	58
0.3	0.8	0.301	128	114	0.066	67
0.4	0.8	0.359	153	106	0.124	59

Percent polymerization is omitted because all values are about 95%, by rough computation.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.217		134	

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with $Ca(Ak)_2$, hydrazine, $K_2S_2O_8$

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gms. $Ca(Ak)_2$

Hydrazine cc.	$K_2S_2O_8$ gm.	Shear Strength lbs/in^2	Shear Strength %	Water Pick-up %
0.1	0.7	0.393	167	214
0.3	0.7	0.386	164	213
0.1	0.4	0.301	128	163
0.4	0.4	0.377	160	154
0.7	0.9	0.292	124	147
0.2	0.2	0.250	106	114
0.2	0.5	0.280	119	156
0.3	0.6	0.312	137	167

By inspection it may be seen that all cases are ≈ 90% polymerized.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.691		129

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with $Ca(Ak)_2$, hydrazine, $(NH_4)_2S_2O_8$

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gms. $Ca(Ak)_2$

Hydrazine cc.	$(NH_4)_2S_2O_8$ gm.	Shear Strength lbs/in^2	Shear Strength %	Water Pick-up %
0.1	0.7	0.612	260	185
0.3	0.7	0.433	184	197
0.1	0.4	0.366	156	155
0.4	0.4	0.301	128	178
0.4	0.8	0.537	228	222
0.8	0.8	0.453	193	251
0.2	0.2	0.237	101	125
0.2	0.5	0.380	162	170
0.3	0.6	0.370	157	193

By inspection it may be seen that all cases are ≈ 95% polymerized.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.513		93

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with $Ca(Ak)_2$, sodium thiosulfate, t-butyl-hydroperoxide

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gms. $Ca(Ak)_2$

Na-thiosulfate gm.	t-but-hyd. cc.	Shear Strength lbs/in^2	Shear Strength %	Water Pick-up %
0.1	0.7	0.750	319	162
0.3	0.7	0.656	279	151
0.1	0.4	0.606	258	174
0.4	0.4	0.533	227	133
0.3	0.6	0.544	232	136
0.4	0.8	0.640	272	125
0.2	0.5	0.634	270	122
0.4	0.6	0.717	305	116

By inspection it may be seen that all cases are ≈ 95% polymerized.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.406		79

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with Ca(Ak)$_2$, sodium thiosulfate, $K_2S_2O_8$

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gms. Ca(Ak)$_2$

Na-thio. gm.	$K_2S_2O_8$ gm.	Shear Strength lbs/in^2	Shear Strength %	Water Pick-up %
0.1	0.7	0.676	287	117
0.3	0.7	0.703	299	138
0.1	0.4	0.672	286	74
0.4	0.4	0.488	208	109
0.3	0.6	0.640	272	93
0.4	0.8	0.758	322	112
0.2	0.5	0.672	286	110
0.4	0.6	0.666	283	139

By inspection and by comparison with the titration blanks run for sodium thiosulfate + $(NH_4)_2S_2O_8$ it may be seen that polymerization in these cases ≈ 95%.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.533		93

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with $Ca(Ak)_2$, hydroxylamine,
t-butyl-hydroperoxide

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gms. $Ca(Ak)_2$

Hydroxylamine gm.	t-but-hyd. cc.	Shear Strength lbs/in^2	Shear Strength %	Water Pick-up %
0.1	0.7	0.326	139	59
0.3	0.7	0.313	133	50
0.1	0.4	0.324	138	69
0.4	0.4	0.403	172	61
0.4	0.8	0.313	133	50
0.2	0.2	0.259	110	50
0.2	0.5	0.308	131	47
0.3	0.6	0.297	126	47

By inspection, with reference to the blank titrations, it may be seen that most cases are ≈ 90% polymerized.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.275		80

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Polymerization studies with Ca(Ak)$_2$, hydroxylamine, $(NH_4)_2S_2O_8$

Sample: 7.5 gms. Na-bent. + 15 cc. H_2O + 1.5 gms. Ca (Ak)$_2$

Hydroxylamine gm.	$(NH_4)_2S_2O_8$ gm.	Shear Strength lbs/in^2	Shear Strength %	Water Pick-up %
0.1	0.7	0.332	141	75
0.3	0.7	0.340	145	85
0.1	0.4	0.280	119	73
0.4	0.4	0.295	125	83

By inspection, with reference to the blank titrations, it may be seen that most cases are ≈ 90% polymerized.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.790		150

Polymerization studies with Ca(Ak)$_2$, hydroxylamine, $K_2S_2O_8$

Hydroxylamine gm.	$K_2S_2O_8$ gm.	Shear Strength lbs/in^2	Shear Strength %	Water Pick-up %
0.1	0.7	0.294	125	75
0.3	0.7	0.306	130	82
0.1	0.4	0.278	118	72
0.4	0.4	0.282	120	79

By inspection, with reference to the blank titrations, it may be seen that most cases are ≈ 90% polymerized.

Blank with calcium acetate, for determination of ionic effect of catalysts

0.1	0.7	0.474		112

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE

AT 200% WATER CONTENT

Using: Calcium acrylate in varying proportions as noted
Sodium thiosulfate and ammonium persulfate in
varying weights as noted, per 15 cc. of solution

Percent Solution of $Ca(Ak)_2$	$Na_2S_2O_3$ gms.	$(NH_4)_2S_2O_8$ gms.	Shear Strength lbs/in^2	Strength, Percent of Base-Exchanged, Unpolymerized	Water Pick-up %
21	0.1	0.6	1.561	869	100
14	0.1	0.7	0.894	423	87
	0.2	0.7	0.886	420	97
	0.3	0.7	0.880	417	108
	0.4	0.8	0.866	410	86
	0.2	0.6	0.880	417	75
	0.2	0.5	0.842	399	80
	0.1	0.6	0.946	448	65
	0.3	0.5	0.802	380	66
10	0.1	0.7	0.907	386	140
	0.3	0.7	0.802	341	205
	0.1	0.6	0.842	358	148
	0.2	0.6	0.725	308	168
	0.1	0.7	?	534?	131
	0.2	0.7	1.200?	511?	128
	0.1	0.4	0.846	360	117
	0.4	0.4	0.619	263	113
	0.3	0.6	0.730	311	122
	0.4	0.8	1.100?	468?	123
	0.2	0.5	0.861	366	110
5	0.1	0.7	0.907	265	185
	0.3	0.7	0.790	230	217
	0.1	0.6	0.933	272	170
	0.2	0.6	0.698	203	183
2	0.1	0.7	0.985	167	164
	0.3	0.7	1.026	174	158
	0.1	0.6	1.272	216	159
	0.2	0.6	1.038	176	147

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 200% WATER CONTENT

Using: Calcium acrylate, in varying proportions as noted
Sodium thiosulfate, 0.1 gm. in 15 cc. of solution
Ammonium persulfate, 0.6 gm. in 15 cc. of solution

Polymerization in all cases ≠ 95%

Analysis of Results

Percent Solution of $Ca(Ak)_2$	Shear Strength lbs/in^2	Water Pick-up %	Strength, Percent of Base-Exchanged	Increase Over Base-Exchanged Samples		Estimated Ionic Effect of Catalysts		Estimated Effect of Polymerization In Increasing		
				Strength lbs/in^2	Water Pick-up	Strength lbs/in^2	Water Pick-up	Strength lbs/in^2	Water Pick-up	Strength %
21	1.561	100	869	+1.381	+ 32	0.370	73	+1.191	+27	422
14	0.946	65	448	+0.735	+ 6	0.460	100	+0.486	-35	206
10	0.842	148	358	+0.607	+101	0.530	120	+0.312	+28	159
5	0.933	170	272	+0.590	+115	0.700	120	+0.233	+50	133
2	1.272	159	216	+0.668	+ 25	0.810	120	+0.462	+39	157
	1.080	157	180	+0.476	+ 23			+0.270	+37*	133

* It is difficult to see how the polymerization can increase the water affinity.

RING-SHEAR TESTS ON TREATED SAMPLE OF SODIUM-BENTONITE

Sample: 7.5 gm. Na-bent. + 15 cc. H_2O + 0.3 gm. $Ca(Ak)_2$
+ 0.1 gm. $Na_2S_2O_3$ + 0.6 gm. $(NH_4)_2S_2O_8$

A

Springs $S_B . S_1$	Dial, cms.	Stress lbs/in^2	Displacement cms.
0	15.5	0	0
2.0	16.1	---	0.6
3.0	16.5	---	1.0
4.0	16.8	---	1.3
5.0	17.2	0.580	1.7
5.5	17.4	0.645	1.9
5.8	17.5	0.685	2.0
6.0	17.6	0.711	2.1
6.3	17.7	0.750	2.2
6.5	17.8	0.776	2.3
6.8	17.9	0.816	2.4
7.0	18.0	0.842	2.5
7.3	18.1	0.880	2.6
7.5	18.2	0.907	2.7
7.8	18.3	0.946	2.8
8.0	18.4	0.973	2.9
8.2	18.5	0.997	3.0
8.4	18.6	1.025	3.1
8.7	18.8	1.062	3.3
S_2 4.8	19.1	1.160	3.6
5.1	19.4	1.220	3.9
5.35	20.0	1.272	4.5

Displacement = 4.5 - 0 = 4.5 cms. at failure

Displacement of shearing surface = 0.0512 x 4.5 = 0.230 cms.

Displacement of bottom of clay layer $= 0.230 \times \frac{4.3}{5.0} = \underline{0.198}$ cms.

Relative displacement of top vs. bottom of clay rim . . . . = 0.032 cms.

$$\text{Strain at failure} = \frac{0.032}{0.35} = 9.15\%$$

RING-SHEAR TESTS ON TREATED SAMPLE OF SODIUM-BENTONITE

Sample: 7.5 gm.Na-bent.+ 15 cc.H_2O + 0.75 gm.$Ca(Ak)_2$
+ 0.1 gm.$Na_2S_2O_5$ + 0.6 gm.$(NH_4)_2S_2O_8$

B

Springs $S_B.S_1$	Dial, cms.	Stress, lbs/in^2	Displacement cms.
0	3.5	0	0
2.0	4.8	---	1.3
3.0	5.7	---	2.2
4.0	6.3	---	2.8
5.0	6.4	0.580	2.9
5.5	6.5	0.645	3.0
6.0	6.8	0.711	3.3
6.2	6.8	0.738	3.3
6.5	7.0	0.776	3.5
6.7	7.1	0.803	3.6
7.0	7.3	0.842	3.8
7.2	7.5	0.866	4.0
7.5	7.8	0.907	4.3
7.7	9.8	0.933	6.3

Displacement = 5.2 - 1.1 = 4.1 cms. at failure

Displacement of shearing surface = 0.0512 x 4.1 = 0.210 cms.

Displacement of bottom of clay layer $= 0.210 \times \frac{4.3}{5.0} = \underline{0.180}$ cms.

Relative displacement of top vs. bottom of clay rim . . . . = 0.030 cms.

$$\text{Strain at failure} = \frac{0.030}{0.35} = 8.57\%$$

RING-SHEAR TESTS ON TREATED SAMPLE OF SODIUM-BENTONITE

Sample: 7.5 gm. Na-bent. + 15 cc. H_2O + 1.5 gm. $Ca(Ak)_2$
+ 0.1 gm. $Na_2S_2O_3$ + 0.6 gm. $(NH_4)_2S_2O_8$

C

Time mins.	Springs $S_B.S_1$	Dial, cms.	Stress lbs/in^2	Displacement cms.
0	2.0	0	---	0
0:25	3.0	0.6	---	0.6
0:53	4.0	1.4	---	1.4
1:17	5.0	2.2	0.580	2.2
1:32	5.5	2.9	0.645	2.9
1:50	6.0	3.3	0.711	3.3
2:10	6.5	3.9	0.776	3.9
2:20	6.8	4.7	0.816	4.7
2:32	7.0	10.0	0.842	10.0
	6.6	20	0.790	20
	6.4	25	0.762	25
	6.2	30	0.738	30
	6.1	35	0.725	35
	5.95	40	0.705	40
	5.75	45	0.679	45
	5.5	50	0.645	50
	5.3	55	0.620	55
3:20	5.1	60	0.594	60

It is very difficult to obtain the zero point on this stress-strain curve.

Displacement = 10 - (-1.5) = 11.5 cms. at failure

Displacement of shearing surface = 0.0512 x 11.5 = 0.589 cms.

Displacement of bottom of clay layer = 0.589 x $\frac{4.3}{5.0}$ = $\underline{0.507}$ cms.

Relative displacement of top vs. bottom of clay rim . . . . = 0.082 cms.

$$\text{Strain at failure} = \frac{0.082}{0.35} = 23.4\%$$

RING-SHEAR TESTS ON TREATED SAMPLE OF SODIUM-BENTONITE

Sample: 7.5 gm. Na-bent. + 15 cc. H_2O + 2.1 gm. $Ca(Ak)_2$
+ 0.1 gm. $Na_2S_2O_3$ + 0.6 gm. $(NH_4)_2S_2O_8$

D

Springs $S_B . S_1$	Dial, cms.	Stress lbs/in^2	Displacement cms.
4.0	7.9	---	0
5.0	8.4	0.580	0.5
5.5	8.7	0.645	0.8
5.8	9.3	0.685	1.4
6.0	9.7	0.711	1.8
6.2	10.1	0.738	2.2
6.4	10.5	0.762	2.6
6.6	11.0	0.790	3.1
6.8	11.7	0.816	3.8
7.0	12.5	0.842	4.6
7.1	13.1	0.854	5.2
7.2	13.7	0.866	5.8
7.3	14.7	0.880	6.8
7.4	16.3	0.894	7.4
7.5	16.6	0.907	7.7
7.7	18.4	0.932	9.5
7.75	21.0	0.940	13.1
7.8	23.0	0.946	15.1
7.8	31.0	0.946	23.1
7.8	41	0.946	33.1
7.7	44	0.932	36.1
7.7	47	0.932	39.1
7.6	53	0.920	45.1
7.5	59	0.907	51.1

It is very difficult to obtain the zero point on this stress-strain curve. Estimating roughly -1.7

Displacement = 15.1 - (-1.7) = 16.8 cms. at failure

Displacement of shearing surface = 0.0512 x 16.8 = 0.860 cms.

Displacement of bottom of clay layer = 0.860 x $\frac{4.3}{5.0}$ = 0.740 cms.

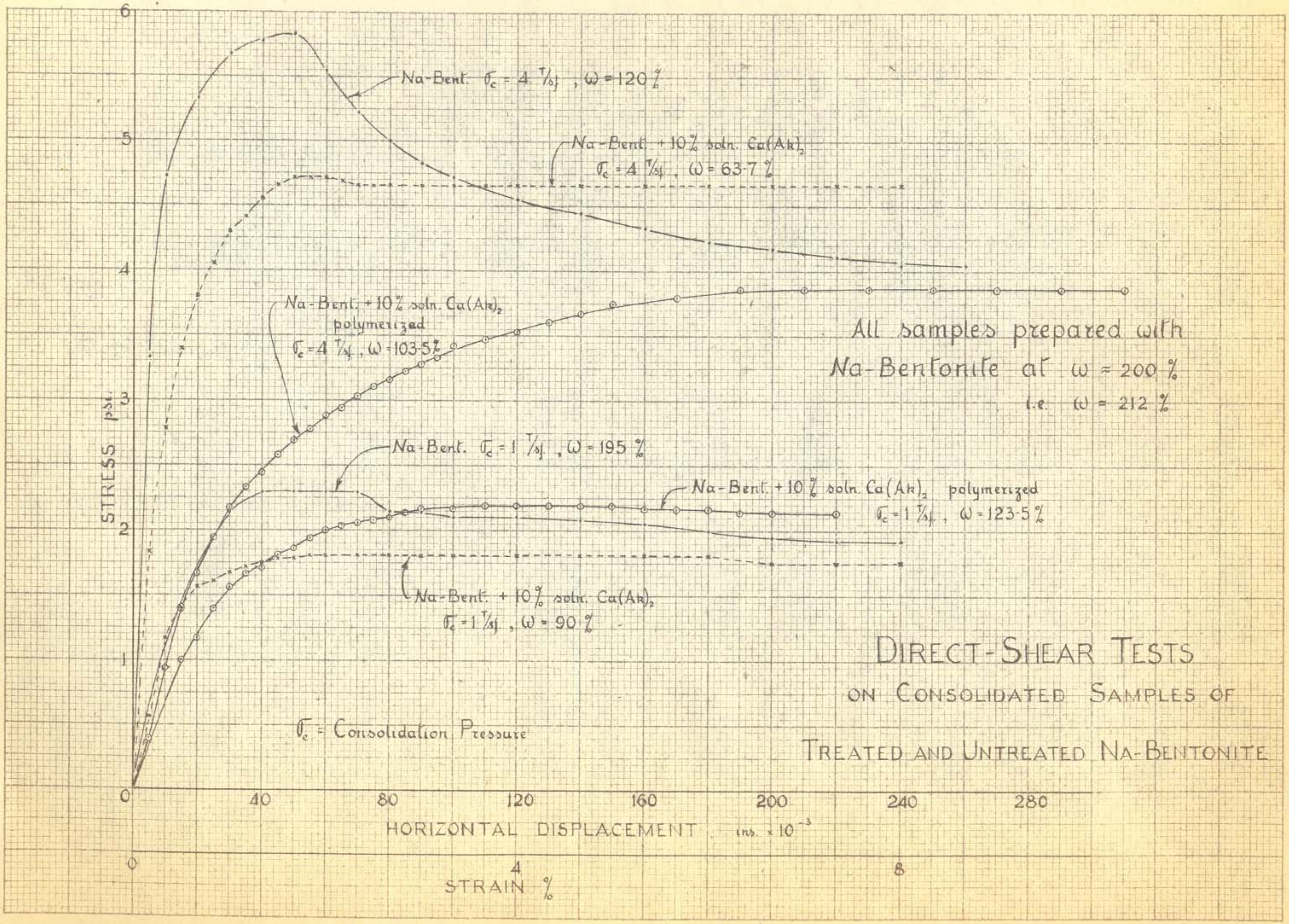
Relative displacement of top vs. bottom of clay rim . . . . = 0.120 cms.

$$\text{Strain at failure} = \frac{0.120}{0.035} = 34.3\%$$

APPLICATION OF THE TREATMENT TO SODIUM-BENTONITE AT 100% AND 300% WATER CONTENTS

Using: Calcium acrylate in varying proportions as noted
Sodium thiosulfate, 0.1 gm. in 15 cc. of solution
Ammonium persulfate, 0.6 gm. in 15 cc. of solution

Percent Solution of $Ca(Ak)_2$	Shear Strength lbs/in^2	Strength, percent of Base-Exchanged But Unpolymerized	Water Pick-up %
A. Sodium-bentonite at 100% water content			
21	3.27	365	78
14	2.745	270	133.5
10	2.745	248	148.5
5	2.54	200	210
2	3.32	206	242
B. Sodium-bentonite at 300% water content			
21	0.986	1540	66
14	0.765	1020	45
10	0.373	429	130
5	0.242	237	118
2	0.467	243	99



DIRECT-SHEAR TESTS
ON CONSOLIDATED SAMPLES OF
TREATED AND UNTREATED NA-BENTONITE

FIG. 46

APPLICATION OF THE TREATMENT TO CALCIUM-BENTONITE CLAY

Using: Calcium acrylate, in varying proportions as noted
Sodium thiosulfate, 0.1 gm. in 15 cc. of solution
Ammonium persulfate, 0.6 gm. in 15 cc. of solution

Percent Solution of $Ca(Ak)_2$ (1)	Base-exchanged, unpolymerized		Unpolymerized including Ionic Effect of Catalysts Shear Strength lbs/in^2 (4)	Polymerized					
	Shear Strength lbs/in^2 (2)	Water Pick-up % (3)		Shear Strength lbs/in^2 (5)	Water Pick-up % (6)	Increase of Strength lbs/in^2 (5)-(2)	Increase of Strength lbs/in^2 (5)-(4)	Ratio % $\frac{(5)}{(2)}$	Ratio % $\frac{(5)}{(4)}$
A. Calcium-bentonite at w = 140%									
0	2.58	38.3	—	—	—	—	—	—	—
2	2.44	20.5	2.975	2.95	31	0.37	—	121	100
5	2.13	32	2.48	4.05	42	1.92	1.57	190	163
10	1.945	33	1.995	7.05	21.8	5.105	5.055	362	353
B. Calcium-bentonite at w = 170%									
0	1.407	23.5	—	—	—	—	—	—	—
2	1.306	3.5	1.292	1.809	23	0.503	0.517	138.5	140
5	1.080	18.1	1.118	1.745	32.4	0.685	0.627	161.5	151
10	1.006	30	1.012	3.145	23.8	2.139	2.133	313	311
C. Calcium-bentonite at w = 200%									
0	0.836	9	—	—	—	—	—	—	—
2	0.761	7	0.474	1.080	20	0.319	0.606	142	228
5	0.638	23	0.397	1.039	37	0.401	0.642	163	262
10	0.558	33	0.309	1.946	23	1.388	1.637	349	630

APPLICATION OF THE TREATMENT TO HYDROGEN-KAOLIN CLAY

Using: Calcium acrylate, in varying proportions as noted
Sodium thiosulfate, 0.1 gm. in 15 cc. of solution
Ammonium persulfate, 0.6 gm. in 15 cc. of solution

Percent Solution of $Ca(Ak)_2$ (1)	Base-exchanged, unpolymerized		Unpolymerized including Ionic Effect of Catalysts	Polymerized					
	Shear Strength lbs/in^2 (2)	Water Pick-up % (3)	Shear Strength lbs/in^2 (4)	Shear Strength lbs/in^2 (5)	Water Pick-up % (6)	Increase of Strength lbs/in^2 (5)-(2)	Increase of Strength lbs/in^2 (5)-(4)	Ratio % $\frac{(5)}{(2)}$	Ratio % $\frac{(5)}{(4)}$
A. Hydrogen-kaolin at w = 41.5%									
0	10.3	7.1	—	—	—	—	—	—	—
2	4.11	2.6	—	7.27	3.8	3.16	—	177	—
	4.26					3.01		171	
5	1.716	8.7	—	8.16	5.0	6.44	—	475	—
10	0.062	12.1	—	33.85	13.2	32.79	—	3182	—
B. Hydrogen-kaolin at w = 52%									
0	1.530	14.5	—	—	—	—	—	—	—
2	0.633	7.8	1.104	1.562	1.6	0.929	0.558	247	141
5	0.440	6.1	0.712	9.13	5.2	8.69	8.42	2075	1280
					4.7				
10	0.289	6.9	0.530	19.17	9.0	18.88	18.64	6640	3620
C. Hydrogen-kaolin at w = 65%									
0	0.366	4.6	—	—	—	—	—	—	—
2	0.145	0.8	—	0.624	—	0.479	—	430	—
5	0.111	4.2	—	2.825	4.2	2.714	—	2545	—
				2.12		2.01		1911	
10	0.076	9.2	—	10.4	7.0	10.32	—	13690	—

APPENDIX I

Autobiographical Note

Education

June, 1946, S. B. in Civil Engineering, Massachusetts Institute of Technology

September, 1946, S. M. in Civil Engineering, Massachusetts Institute of Technology

Societies

Professional

Junior, American Society of Civil Engineers

Honorary

Member, Tau Beta Pi, Beta of Massachusetts

Member, The Society of the Sigma Xi

Professional Experience

1946 - Date, Research Associate in Civil Engineering, working on the Soil Solidification Project, Massachusetts Institute of Technology

APPENDIX II

Glossary of Chemical Terms Used

Atomic Weight: Weight of an atom referred to the oxygen atom as 16.000.

Base: A substance which gives hydroxide ion in solution, or which neutralizes acids, yielding water. The word base used in the compound word base-exchange is much better replaced by the word cation. (Cation-exchange)

Equivalent: Acid or base: the amount (weight) of substance necessary to give one mole of hydrogen or hydroxyl, respectively, in a neutralization reaction. A thousand milliequivalents = 1 equivalent. Usually the gram unit is assigned to these values: hence, if speaking of an exchange capacity of 100 me. of sodium per 100 gms. of clay, we mean that 100 x 0.001 x 23 gms. of sodium are exchanged. The atomic weight of sodium = 23 = equivalent weight of sodium.

Free Radical: A molecular fragment caused by the breaking of a chemical bond in such a manner that a single electron is left at the rupture point. This single electron confers extraordinary chemical reactivity upon the fragment. For example, when ferrous ion is added to a solution of hydrogen peroxide, it donates an electron to the latter which then splits, forming one hydroxyl ion and one hydroxyl radical:

$$H_2O_2 + Fe^{++} \qquad Fe^{+++} + H\ O \quad O\ H \qquad HO^- + HO + Fe^{+++}$$

Note that the oxygen in the hydroxyl <u>ion</u>, HO^-, possesses a full shell of 8 electrons, whereas the hydroxyl radical, HO , only possesses 7 electrons. The great reactivity of the radical results from its ability to withdraw an electron from nearly any molecule with which it comes in contact.

Ions, Ionization, Cations, Anions: Acids, bases and salts (electrolytes) dissociate to a certain extent in aqueous solution into two components, one positively charged and one negatively charged. The dissociation is called ionization, and the charged atoms or chemical radicals are called ions. A positively charged ion is called a cation, and a negatively charged ion is called an anion.

Micelle: The entire body of a colloidal dispersed particle, surrounded by its firmly adsorbed water hull and diffuse double layer of ions and counterions is called the colloidal micelle.

Molecular Weight, Mole, Millimole: The sum of the atomic weights of all the atoms of a molecule is the molecular weight. A mole is the weight of a substance in grams, numerically equal to its molecular weight; a "gram-molecule". A thousand millimoles make one mole.

Oxidation: The loss of electrons by an atom or group of atoms. As a special case, it may be associated with an increase of the oxygen associated with a group of atoms.

Reduction: The opposite of oxidation; gain in number of electrons by an atom or group of atoms.

Syneresis: Colloidal particles dispersed in liquid media sometimes refuse to occlude all of the liquid when they are caused to gel: some of the liquid is, therefore, squeezed out. This phenomenon is called syneresis.

Unsaturated Monobasic Acids: Organic acids which contain only one carboxyl group are called monobasic acids: they have but one hydrogen atom which undergoes ionization and which can be replaced by metals. If such organic acids contain a carbon to carbon linkage with a double bond instead of the single bond, they are unsaturated. Since ethylene C_2H_4, $H_2C = CH_2$, may be considered the parent of such unsaturated compounds, they may in places be referred to as ethylenic compounds.

Valence: The number of electron pair bonds which an atom shares with other atoms. Crudely speaking, it is the reciprocal of the number of atoms of the element which combines with one atom of hydrogen or one atom of chlorine, etc.

HCl: valence of chlorine = 1
H_2O: valence of oxygen = 2
$NaCl$: valence of sodium = 1
$CaCl_2$: valence of calcium = 2

THE CLAY MINERALS

An understanding of the lattice structure of the main clay minerals is very useful towards an understanding of the behavior of clays.

In making this presentation* the writer wishes to emphasize that although some of the points still seem to be contradictory, he has felt that it is best to present a unified and clear picture that will serve as a rational basis for the explanation of the fundamental properties of clays. The lattice structures of the main clay minerals are presented as actual facts that have been fully ascertained. The points of controversy are not major: they merely involve little rearrangements. For the sake of clarity it may be better to present merely one consistent theory, fully realizing that it may in parts only be a working hypothesis, than to attempt to follow all the arguments for and against the various theories.

The most widely accepted theory is hereby presented.

For many years before the advent of the X-ray, diffraction technique of studying the actual structural arrangement of the atoms comprising a crystal, chemical analysis was used in extensive studies to explain the differences in behavior of various clays. But the efforts were not successful, and it came to be realized that knowledge of the chemical composition of clays alone affords no sound basis for the prediction of the properties of a given clay. Besides the chemical composition, the spatial arrangement of the constituent atoms in relation to one another is of major importance in determining the properties of clays. Further investigation into the nature of the clay minerals has since proceeded on a basis of lattice structure.

The easiest way to understand the clay minerals, their similarities and their differences, is to visualize them as being built up from the same basic building units, the differences being, at least in part, accounted for by differences in the combinations of the building units. It is

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* The material for this presentation was acquired in large part from a study of the articles: 1) "Colloid Chemistry of Clays" by E. A. Hauser, Chemical Reviews, <u>37</u>, (1945); 2) "Modern Concepts of Clay Materials" by R. E. Grim, Journal of Geology, <u>50</u>, (1942); 3) "Colloid Chemistry in Ceramics" by E. A. Hauser, American Ceramic Society Journal, <u>24</u>, (1941), the figures are all taken from this article; 4) "Plasticity of Clays" by Hauser and Johnson, American Ceramic Society Journal, <u>25</u>, (1942).

far from the purpose of this presentation to discuss the actual genesis of the various clay-mineral crystals; and it is not contended that at some early geologic time these building units occurred as such in nature, and that they subsequently got together to form the clay minerals.

Discussions of the lattice structures of clay minerals usually are initiated with the concept of the silicon tetrahedron, the aluminum octahedron, and the magnesium octahedron as being the three main basic building units. These three primary building units are shown schematically as Figures 1, 2, and 3, page 120. The silicon tetrahedron is highly unbalanced electrically, since the silicon atom shares a total of four electrons with neighboring atoms and the four attached oxygen atoms require a total of eight electrons for saturation. Similarly the aluminum and magnesium octahedra are highly unbalanced. This unbalance corresponds to chemical valences, which act to combine the building units into more complex, but electrically balanced, structural units. The primary structural unit thus formed by the silicon tetrahedron is the hydrated silica sheet. Similarly the aluminum and magnesium octahedra form the gibbsite and brucite sheets. These are schematically shown as Figures 4, 5, and 6, page 120. The silicon tetrahedron, magnesium octahedron, and aluminum octahedron, being highly unbalanced, do not exist as isolated materials in nature. The hydrated silica sheet and the minerals brucite and gibbsite are electrically balanced structures, existing in nature in isolated form. The formation of the brucite, gibbsite and hydrated silica sheets from the magnesium and aluminum octahedra and the silicon tetrahedron will not be discussed herein. The brucite, gibbsite and hydrated silica sheets will for purposes of this report be considered as the primary structural units which combine to form the main clay minerals, namely the kaolinitic, illitic, and montmorillonitic clay minerals.

The gibbsite and brucite sheets will not be discussed in detail in this report. It is apparent from Figures 5 and 6 (page 120) that the layer lattices are saturated except for the edge and corner points of the sheets. In the gibbsite sheet trivalent aluminum atoms are sandwiched between two hydroxyl sheets, whereas in the brucite sheet divalent magnesium atoms occupy the positions between the two hydroxyl sheets. Because of the fact that aluminum shares three electrons while magnesium shares only two, the neutral sheet of aluminum octahedra can only be obtained if one third of the places occupied by magnesium in the octahedra sheet remain vacant. This results in the gibbsite sheets being somewhat more open-textured than the brucite. A study of Figure 14, page 121, in conjunction with Figures 5 and 6, page 120, will make the above point clear.

The hydrated silica sheet will be given somewhat more detailed consideration because the relationship of the size of ion in connection with the base-exchange properties of certain clays is dependent on the geometric configuration of this sheet, as is mentioned on page 109. In a hydrated silica sheet several silicon-oxygen tetrahedra are combined by sharing the appropriate oxygen atoms. This sharing of oxygen atoms may be considered as the result of a condensation reaction; as the name implies, this reaction involves the splitting off of a molecule of water when two hydroxyl groups are combined. For example, two compounds R(OH) and R'(OH) may condense to form a compound R-O-R' as shown: $R\text{-}O\boxed{H + HO}\text{-}R' \rightarrow R\text{-}O\text{-}R' \quad H_2O$. Thus the combination of silicon-oxygen tetrahedra may be considered as a condensation of tetrahedra which have the vertex oxygens replaced by hydroxyl groups. If silicon tetrahedra are combined so that two always share one oxygen, a zig-zagging chainlike structure results. Two such chains may further combine by condensation to form a hexogonal network structure. Figure 15 shows such a symmetrical network structure; to avoid confusion only one plane is shown, namely, that marked A in Figure 4, page 121. It will be seen that the oxygen atoms in this plane form a hexagonal network. An enlarged drawing of one such hexagon, drawn more truly to scale, is shown in Figure 16, page 121. It can be seen from this figure that the hole formed by each hexagon of oxygen atoms in this plane has a diameter of 2.64 Ångstrom units, which is the diameter of the oxygen atom.

It has been stated earlier that the common clay minerals can be considered as built up from the hydrated silica, brucite, and gibbsite sheets. The reaction by which these structural units may be considered to have combined to form the clay minerals, is the condensation reaction discussed above. The discussion of the complicated lattice structures of the clay minerals, therefore, can now be undertaken with great simplicity. This discussion will be limited to the clay minerals which are of greatest interest to the civil engineer engaged in soil mechanics work; namely the kaolinitic, illitic, and montmorillonitic clay minerals.

In the kaolin group the mineral halloysite deserves mention, although it is of somewhat rare occurrence because of its relative instability toward elevated temperatures. This clay mineral consists of a complete gibbsite layer lying on a complete hydrated silica sheet as shown in Figure 7, page 120. The gibbsite and hydrated silica layers are held together by secondary forces which effect the weak bond of cohesion between the OH-OH groups facing each other. At elevated temperatures condensation takes place, and a lattice identical with that of kaolinite results. A comparison of Figures 7 and 8 will show that the kaolinite lattice can be obtained from the halloysite lattice by splitting off a molecule of water from each pair of hydroxyl groups that are shown connected on Figure 7. The gibbsite and hydrated silica sheets in kaolinite are rigidly connected by shared oxygen links. Consideration of the lattice of halloysite is of marked interest; the progression of steps, starting with the stacking of a gibbsite sheet over the hydrated silica sheet, leading through the formation of halloysite to the eventual production of kaolinite by condensation, epitomizes the idea of the building up of the clay minerals from a few basic structural units.

Kaolinite is composed of a hydrated silica sheet combined, by shared oxygen bonds, with a lightly distorted gibbsite layer. The structure is electrically neutral, or balanced, from the point of view of electron distribution, except for spots of unsaturation along the edges of the sheets. Since the kaolinite crystals are electrically balanced, any increase in the size of parcels in a direction perpendicular to the plane of the sheets must be the result of a stacking up of crystals held together by secondary forces. Since these secondary forces are very weak in comparison with primary forces, cleavage will be easy between planes joined only by secondary forces whereas fracture across primary bonds is difficult. This ease of cleavage along planes parallel to the sheets of the layer lattice accounts for the fact that kaolinite clay particles are plate-shaped. The same is true of montmorillonite and illite. Further, it follows that the ease of cleavage depends on the strength of the secondary bond holding the individual parcels together. The secondary forces holding together parcels of kaolinite are relatively strong forces acting between the hydroxyl groups of one sheet and the basal oxygens of the silica sheet in the parcel stacked above. As will be seen later, the secondary forces holding individual parcels of montmorillonite together are relatively weak attraction forces between opposing oxygen sheets. This fact offers one explanation of the fact that montmorillonite is capable of a higher degree of dispersion in water than is kaolinite. The importance of adsorbed, hydratable cations in providing means to overcome the secondary bonds between particles by dissociation on contact with water, must also be recognized.

The kaolinite particle is electrically balanced except for unsaturation along broken edges, and the charge on particles of colloidal dimensions is acquired by adsorption of ions. Kaolinite dispersed in absolutely pure water will not form a stable colloidal suspension, because the colloidal particles do not acquire a charge. This fact is worth emphasizing because it sharply differentiates kaolinite from montmorillonite, which acquires its charge by surface dissociation of adsorbed cations and, therefore, disperses in absolutely pure water. (Refer to page 117) It was pointed out in the previous chapter, in connection with the acquisition of charge by colloidal crystals of silver bromide, that adsorption of ions must be preferential. In the case of kaolinite, hydroxyl (OH) ions are preferentially adsorbed, and the kaolinite particle thus acquires a net negative charge of a magnitude depending on the number of adsorbed (OH) ions. These adsorbed (OH) ions form the charge that is considered embedded in the particle, and cations from the dispersion medium will immediately form the counterions of the diffuse double layer. These counterions, cations, are exchangeable, and the number of them available for base-exchange (as well as their valency) determines the base-exchange capacity of the kaolinite.

The base-exchange capacity of kaolinite is known to be very low, being about 3-15 milliequivalents per 100 grams of clay. Further, the base-exchange capacity of kaolinite has been shown to increase with decreasing particle size, whereas the exchange capacity of montmorillonite does not vary with particle size. These findings are fully in accord with the differences in structure of kaolinite and montmorillonite. Thus from one point of view, in comparison with montmorillonite, the exchange capacity of kaolinite is low because there are no replacements within the lattice to set up unbalanced charges (see page 116). From another point of view, the base-exchange capacity of natural kaolinites is low because of the comparatively large particles that result from the strong OH-O secondary bond between individual crystals stacked over each other. It thus seems logical to assume that the broken bonds of the silicon and aluminum layers explain the adsorption of negative charges, and specifically of (OH) ions. The adsorptive capacity of kaolinite seems to be limited to broken oxygen bonds and/or the hydrogen of hydroxyls at flake edges. However, further thought indicates that only a limited number of negative charges are adsorbed on these broken edges, because the silicon and aluminum atoms are embedded in cavities formed by the much larger oxygen and hydroxyl atoms. It is very probable that the adsorption of hydroxyl ions, if they are present in the dispersion medium, will take place on the basal oxygen sheet of the individual particle. This adsorption is preferential because of the dipolar configuration of the hydroxyl ion.*

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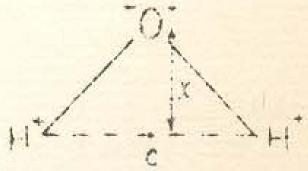
* A molecule in which the center of gravity of the negative charges does not coincide with the center of gravity of the positive charges has a dipolar configuration. Water, for instance, has a high dipole moment, $2ex$, where e is a unit charge. An ion like the hydroxyl ion, made up of two atoms, must of necessity have a dipolar configuration, besides having its unbalanced charge.



Summarizing, therefore, kaolinitic minerals are 1:1 lattice type minerals having low affinity for water and low surface activity. They have a very low base-exchange capacity, and show very little tendency toward swelling when wetted.

Montmorillonitic clay minerals have 2:1 type lattices inasmuch as their lattice is composed of two hydrated silica sheets with their vertex (OH) groups pointing toward each other and a gibbsite sheet sandwiched between them. The formation of the montmorillonite crystal may be considered as exactly similar to the formation of the kaolinite crystal, but with the condensation process that links a hydrated silica sheet to the gibbsite sheet taking place on both sides of the gibbsite sheet instead of merely on one side. The two hydrated silica sheets are, therefore, joined to the gibbsite sheet by shared oxygen bonds. Such a montmorillonitic crystal whose lattice structure consists of a pure gibbsite layer sandwiched between two pure hydrated silica layers is called an ideal montmorillonite. (See Figure 9, page 120) Only very rarely does a natural montmorillonite show evidence of possessing this ideal structure. By far the more common montmorillonites are the so-called "substituted montmorillonites". Before reverting to a consideration of the structure of substituted montmorillonites, however, it may be mentioned that, as in the case of kaolinite, the ideal montmorillonite structure is electrically neutral except for unsaturations along broken edges. However, even in the case of ideal montmorillonites two factors combine to make this mineral more active than kaolinite. The presence of one more silica layer per crystallite would tend to increase the edge adsorbability in comparison with that of the kaolinite structure, and the presence of two oxygen sheets per crystallite gives an increased chance of hydroxyl ion adsorption. Furthermore, unit crystals of ideal montmorillonite stacked over each other are held together only by very weak secondary forces acting between the opposing oxygens of the silicon-oxygen tetrahedra; it follows, therefore, that this type of clay mineral is more readily dispersed into smaller particles than kaolinite.

Accurate analysis of montmorillonites usually reveals the presence of varying amounts of magnesium and iron, which should not occur according to the ideal structure, and variations in the ratio of aluminum to silicon are frequently found. These discrepancies are explained by the theory that in nature certain substitutions have taken place within the lattice. If ferric atoms, which are trivalent, are substituted for the aluminum atoms of the gibbsite sheet, the lattice structure remains electrically balanced. However, if magnesium atoms, which are divalent, are substituted for the aluminum atoms of the gibbsite sheet the lattice takes on a net negative charge. In this case, the negative charge is located in the gibbsite sheet, that is, in the middle of the particle, and, therefore, the force of attraction for cations effective at the surface of the particle is relatively small. On the other hand, an increase in the ratio of aluminum to silicon over the theoretical ratio can only be explained by the assumption that some of the silicon atoms of the silica sheet have been replaced by aluminum atoms. This substitution also makes the particle acquire a net negative charge in view of the fact that tetravalent silicon has been replaced by trivalent aluminum; but in this case, the negative charge is located in the silica layer which is close to the surface of the particle, and, therefore, the resulting attraction for cations is relatively strong. Figure 13, page 120, shows a substituted montmorillonite in which one of the four aluminum atoms of the gibbsite layer has been replaced by a magnesium atom, resulting in a net unbalance of one negative charge. Substitutions in the layer of silicon atoms are somewhat less common but quite possible: such a substitution is shown in Figure 12 which is actually an illite (mica) -- a montmorillonite which owes most of its charge to substitutions in the silica layer approaches an illite.

Considering the substituted montmorillonites as they exist in nature, it is obvious that the particles possess adsorbed cations in a measure sufficient to balance the net negative charge: the law of least free energy requires it. Cations are primarily adsorbed on the surfaces of the silica sheets, about 80 per cent of the exchange positions of montmorillonite being on these surfaces. Broken oxygen bonds and the possibility of some replacement of hydrogen of hydroxyls at the edges of flakes account for the rest of the exchange capacity. In nature a cation very commonly found associated with montmorillonites by such adsorption, is sodium. A montmorillonite containing loosely adsorbed cations, if placed in pure water builds up a double layer without the need of electrolyte. The actual behavior of the clay will depend on the adsorbed cation, but in general it can be stated that the cations on hydration will dissociate to a certain distance from the surface of the particle and form the counterions of the diffuse double layer. Since most of the cations are adsorbed on the surfaces of the crystallites, they will tend, on hydration, to pry apart the units held together loosely by weak secondary O-O bonds. It has been pointed out before that such hydration of adsorbed cations helps to break up clay particles down to the ultimate particle size when dispersed in water. The effect of dispersing agents is, therefore, not as pronounced with montmorillonite as with kaolinite because the particle size of montmorillonite in a suspension is already at a minimum and the formation of the double layer does not depend on adsorption of ions from the dispersion medium.

The hydration of the adsorbed cations is also said to account for the high degree of swelling of montmorillonitic clays; a sodium montmorillonite has reached, by swelling, a c-dimension* (thickness) thrice the normal dimension. The amount of expansion of the montmorillonite lattice depends on the exchangeable cation carried by the particles. The amount of water between crystallites varies, within limits, depending on the amount of water available for the clay to absorb, and there is a corresponding variation in the c-dimension of the unit cell; the mineral is, therefore, said to have an expanding lattice.

In short, therefore, the montmorillonitic minerals have 2:1 type lattices which exhibit variation in one dimension with change of water content. They are characterized by very high surface activity and exchange power, base-exchange capacity being between 60 and 100 milliequivalents per 100 grams of clay. They have a high affinity for water and swell to a very marked degree.

Illites have a basic structure identical with that of ideal montmorillonite. Whereas montmorillonites usually show substitutions of magnesium for aluminum in the gibbsite sheet, resulting in net negative charges located in the center of the crystallite, illites exhibit a marked degree of substitution of aluminum for silicon in the silica sheets, resulting in negative charges close to the surface of the particle. Some montmorillonites show some such substitution of aluminum for silicon and thereby approach the illites, unless the effect of this substitution is partly balanced by adjustments in the gibbsite sheet. But illites do not show the variable spacing exhibited by the montmorillonitic minerals, and have little tendency to swell. How is this difference between illites and montmorillonites explained?

The fact that the negativity of the particle has its source very near the actual surface of the parcel causes the setting up of fairly strong attraction forces for positive charges. The cations that are adsorbed are held fairly strongly. In nature it is found that potassium ions are usually associated with illites. Considerations of size of exchangeable ions are used to explain this predominance of

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* The c-axis is perpendicular to the sheets in the clay mineral lattice. The height of the ultimate particle of montmorillonite, without water between units, is 9.6 Å. Maximum recorded expansion has given a c-dimension of 30 Å. It might be noted that pyrophillite (ideal montmorillonite) has a c-dimension of 9.2 Å. The increased height of the montmorillonite cell is explained by the presence of cations between the units.

potassium ions in illites. Of the common ions, the potassium ion is the only one which is of a size larger than the hole in the silica sheet, (see page 113) and, therefore, cannot penetrate into the structure. The potassium ions adsorbed on the surfaces of the crystallites act as bridges between adjacent particles, thus preventing a particle stack from being swelled by water entering between the parcels. Such adsorbed potassium ions are rather difficult to replace. In spite of substitutions in the illite lattice, the seat of much of the exchange capacity of illite is at flake edges. Many of the cations held between basal planes because of lattice replacements are not exchangeable, partly because illite does not break down readily into small parcels.

Extreme cases in which the replacement of silicon by aluminum in the silica sheets reaches a maximum and the adsorbed cations are entirely potassium ions, represent the practically inert mica. Illites take up positions intermediate between mica and highly plastic montmorillonites, depending on their structure. The greater the replacement of silicon by aluminum in the silica sheets, the closer the illite will resemble mica in its properties. Replacements of aluminum by magnesium in the gibbsite sheet are also found in illites, and the results of such changes in the ideal illite structure are similar to those occurring in altered montmorillonites. The lower the degree of replacement in the silica sheets and the greater the substitution of magnesium for aluminum in the gibbsite layer, the more closely will the illite resemble montmorillonite in behavior.

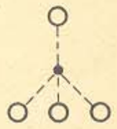
In short, therefore, illites are minerals of the 2:1 type lattice. Their properties are in most respects intermediate between those of kaolinites and those of montmorillonites. Their base-exchange capacity is about 30-50 milliequivalents per 100 grams of clay.

STRUCTURAL DATA OF CLAY MINERALS

The schematic drawings in the first columns represent the composition of the unit cell of the crystal lattice. All atoms are projected into one plane. The second column gives the number and type of atom or group in every lattice plane. The third column reveals the amount of available or needed electrons in every sheet. If the (+) and (-) in this column compensate each other, the crystal is electrically neutral. If they do not, the lattice carries either a positive or negative charge. As the plus and minus charges are listed for every layer, it is easy to determine where the unbalance actually occurs in the lattice.

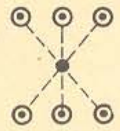
Taken from "Colloid Chemistry in Ceramics" by E. A. Hauser, Journal American Ceramic Society, 24, 179 (1941).

1 - SILICON TETRAHEDRON



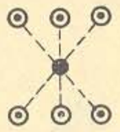
1 O	-2
1 Si	+4
3 O	-6

2 - ALUMINUM OCTAHEDRON



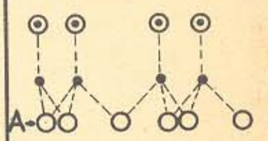
3 OH	-3
1 Al	+3
3 OH	-3

3 - MAGNESIUM OCTAHEDRON



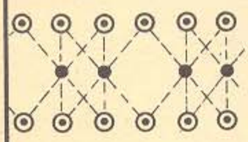
3 OH	-3
1 Mg	+2
3 OH	-3

4 - HYDRATED SILICA



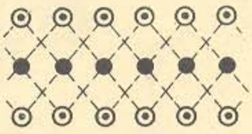
4 OH	-4
4 Si	+16
6 O	-12

5 - GIBBSITE



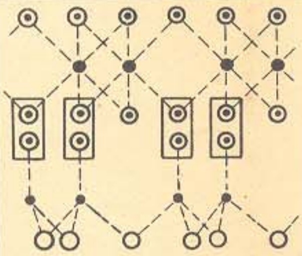
6 OH	-6
4 Al	+12
6 OH	-6

6 - BRUCITE



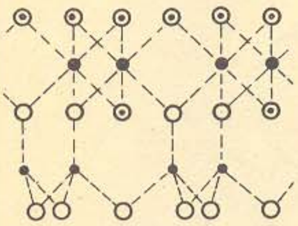
6 OH	-6
6 Mg	+12
6 OH	-6

7 - HALLOYSITE



6 OH	-6
4 Al	+12
6 OH 4 OH	-6 -4
4 Si	+16
6 O	-12

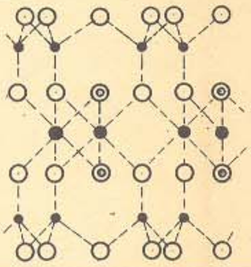
8 - KAOLINITE



6 OH	-6
4 Al	+12
4 O 2 OH	-10
4 Si	+16
6 O	-12

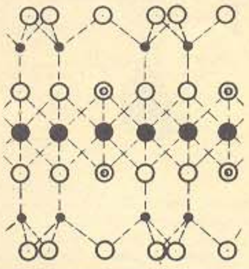
• - Si
• - Al
● - Mg
○ - O
◎ - OH

9 PYROPHYLLITE AND MONTMORILLONITE (IDEAL CASE)



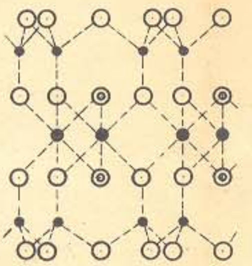
6 O	-12
4 Si	+16
4 O + 2 OH	-10
4 Al	+12
4 O + 2 OH	-10
4 Si	+16
6 O	-12

10 TALC



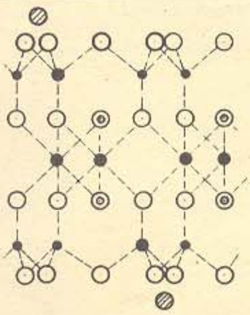
6 O	-12
4 Si	+16
4 O + 2 OH	-10
6 Mg	+12
4 O + 2 OH	-10
4 Si	+16
6 O	-12

11 NONTRONITE



6 O	-12
4 Si	+16
4 O + 2 OH	-10
4 Fe^{+++}	+12
4 O + 2 OH	-10
4 Si	+16
6 O	

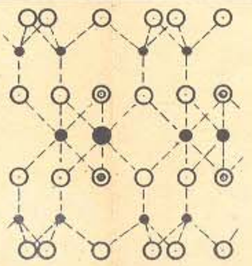
12 MICA (ILLITE)



1 K	+1
6 O	-12
3 Si + 1 Al	+15
4 O + 2 OH	-10
4 Al	+12
4 O + 2 OH	-10
3 Si + 1 Al	+15
6 O	-12
1 K	+1

+44
-44

13 MONTMORILLONITE (SUBSTITUTED)



6 O	-12
4 Si	+16
4 O + 2 OH	-10
3 Al + 1 Mg	+11
4 O + 2 OH	-10
4 Si	+16
6 O	-12

+43
-44

• - Si
• - Al, Fe^{+++}
● - Mg
○ - O
◎ - OH
▨ - K

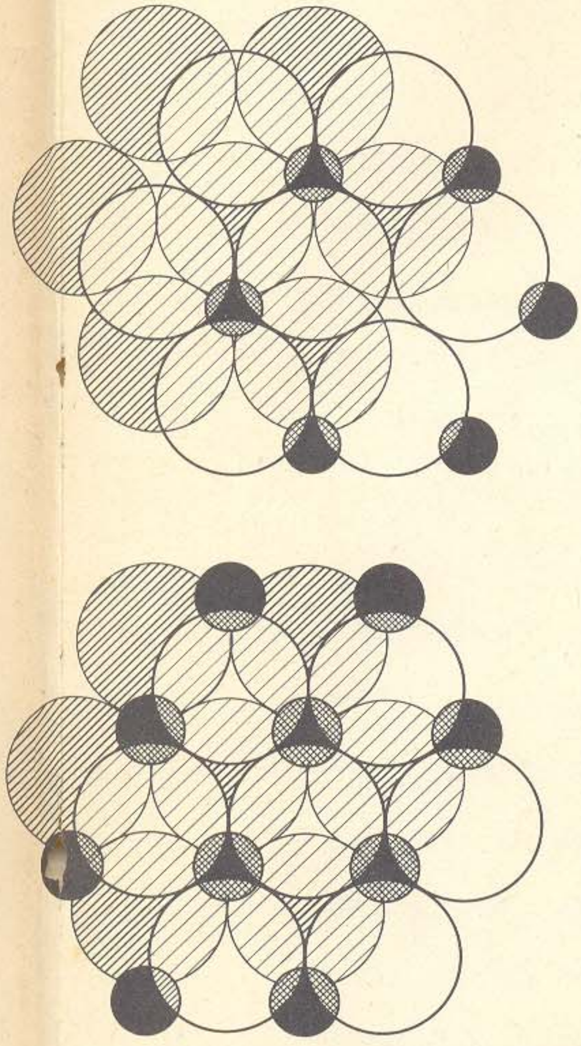


Fig. 14. (Bottom) Brucite $Mg(OH)_2$ (schematic); the hydroxyl groups constituting the upper layer have been drawn transparent so that the location of the magnesium atoms sandwiched between the two hydroxyl layers may be seen clearly. (Top) Gibbsite $Al(OH)_3$ (schematic); the hydroxyl groups in the top layer have been drawn transparent to show the location of the aluminum atoms sandwiched between the two staggered layers (compare positions of Al with those of Mg in bottom figure).

Taken from "Colloid Chemistry in Ceramics" by E. A. Hauser, Journal American Ceramic Society, 24, 179 (1941).

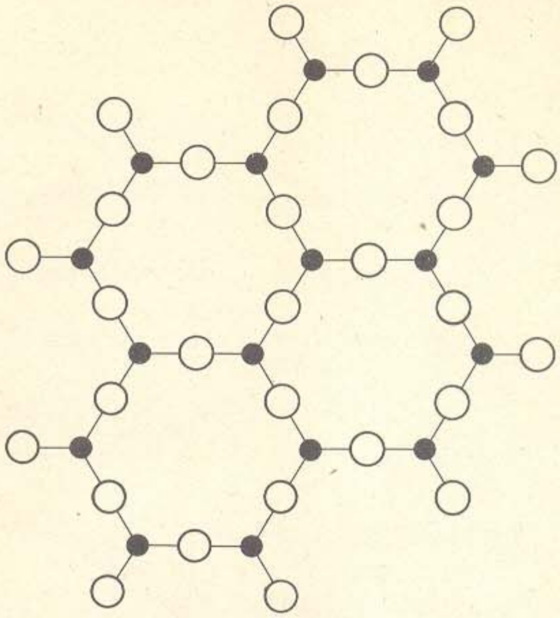


Fig. 15. Structure of a symmetrical silicon-oxygen sheet (schematic); only one plane shown.

Taken from "Colloid Chemistry in Ceramics" by E. A. Hauser, Journal American Ceramic Society, 24, 179 (1941).

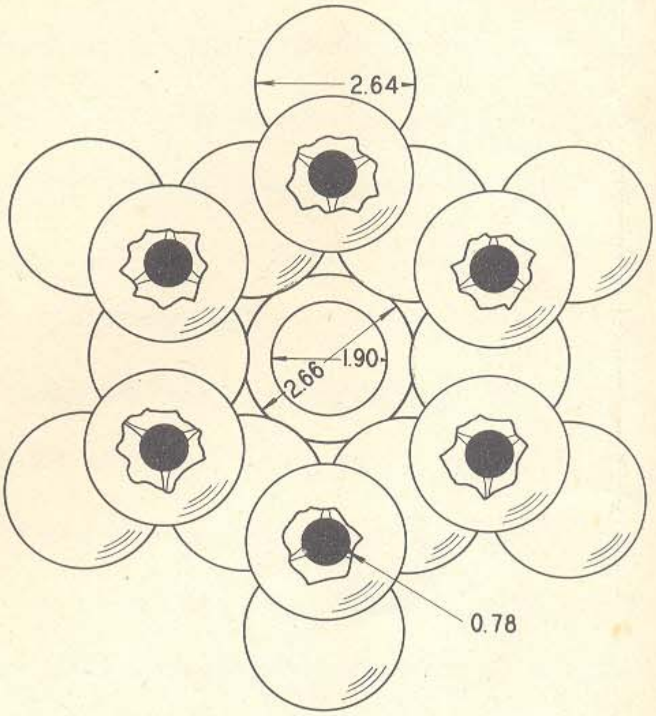


Fig. 16. Hexagonal arrangement of silicon-oxygen tetrahedra in a silica sheet (top view, schematic); the top oxygens have been cut open to show the location of the silicon atoms; into the center space two concentric circles have been drawn. The larger one corresponds in diameter to a potassium atom, the smaller one to a sodium atom; the actual dimensions in Angstrom units for the different atoms are indicated.

Taken from "Colloid Chemistry in Ceramics" by E. A. Hauser, Journal American Ceramic Society, 24, 179 (1941).

Abstract of Thesis Entitled

"INVESTIGATION OF BASE-EXCHANGE AND POLYMERIZATION FOR THE STABILIZATION OF CLAYS"

Thesis submitted by Victor F. B. de Mello to the Department of Civil and Sanitary Engineering, Massachusetts Institute of Technology, in partial fulfillment of requirements for the degree of Doctor of Science;

January 8, 1949

The purpose of this thesis was to investigate a general idea that seemed to offer great promise for the stabilization of clays: namely, the use of a treatment that would incorporate the advantages of both a base-exchange reaction and a subsequent polymerization reaction. For this purpose three clays were selected for study: sodium-bentonite, calcium-bentonite and hydrogen-kaolinite, the bulk of the work being done on the sodium-bentonite. And two representative salts were selected for use: namely, calcium methacrylate and calcium acrylate. Considerations of method of application of the treatment were not within the scope of this thesis: application of the treatment to the saturated clays was, therefore, undertaken in the laboratory by admixing the chemicals as dry powders and thoroughly working the clay into homogeneity.

The investigations involved in this study can be subdivided into three sections:

1) To investigate the possibility of polymerizing aqueous solutions of calcium acrylate and methacrylate at room temperatures

2) To study pertinent phases of the base-exchange reaction taking place on adding calcium methacrylate to sodium-bentonite

3) To investigate the effectiveness of the complete treatment, base-exchange and polymerization, when applied to the clays at water contents close to natural water contents. Shearing strength and water-affinity of the clay samples were used as the criteria of judgment for establishing relative merit of treated and untreated samples.

Redox catalysis proved effective in polymerizing the acrylate and methacrylate aqueous solutions. Several sets of redox catalysts were found to be applicable. The use of different sets of catalysts was found to result in treated clays of widely different properties. Sodium thiosulfate-ammonium persulfate catalysts gave very good results with calcium acrylate and were used for all subsequent work. It is pointed out that further relentless search for even better catalysts may well yield greatly improved polymers.

The study of the base-exchange reaction of sodium-bentonite gels proved that at low water contents and low per cent treatments of calcium methacrylate, much of the sodium associated with the clay is not exchanged. The water-affinity of the clay is appreciably lowered in proportion to the replacement of sodium ions. Unfortunately, because of detrimental secondary effects of the catalysts, the water-affinity of the polymerized samples was not quite as low as that of samples merely base-exchanged: but it still was very much lower than the water-affinity of the sodium-bentonite.

Comparing overall results obtained on the three clays tested it is evident that the water-affinity characteristics are determined by the base-exchange factors: in almost no case did the polymerization reaction by itself contribute to a decrease of water-affinity. In the case of sodium-bentonite, the treatment results in samples with shear strengths approximately equal to the shear strength of the untreated clay, but with greatly reduced water-affinities. In the case of calcium-bentonite a reduction of the already low water-affinity is hardly feasible: the net effect of the treatment is felt in moderate strength increases, treated samples having shear strengths about twice the strength of untreated samples. In the case of hydrogen-kaolinite also, reduction of the very low water-affinity of the clay is not feasible; the treatment results in marked strength increases even with but moderate per cent admixtures.

Analysis of the strength characteristics indicates the existence of a definite relationship between the ratio $\frac{\text{strength of polymerized sample}}{\text{strength of unpolymerized sample}}$ and the ratio

$\frac{\text{gm. of calcium acrylate added}}{\text{gm. of dry clay}}$ regardless of water content for each clay. Comparing these curves for the three clays, it appears that the treatment is about equally effective when used with sodium-bentonite and calcium-bentonite. The results obtained on the kaolinite samples indicate that the treatment is much more effective for kaolinite than for bentonite (in the order of magnitude of 100 times as much). No satisfactory explanation for this has been found; it is believed that further laboratory investigations are needed in order to clear this very interesting point. Recommendations for such further research are made.