

AN EVALUATION OF CONTINUOUS ULTRASONIC COAGULATION
EMPLOYING A BALL-CLAY HYDROSOL

by

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I. INTRODUCTION

Coagulation of colloidal particles in hydrosols is of considerable industrial concern. It is employed, for example, in industries that have occasion to handle slurries containing valuable solid matter of colloidal and near colloidal dimensions and where separation of the solids from the suspension medium is desired. Another important application is the treatment of domestic and industrial wastes in which separation of solids from the liquid suspension medium must be accomplished before discharge of the liquid into streams. Methods employed to accomplish coagulation include treatment of colloidal systems with chemical, mechanical, electrical, thermal, radiant, or ultrasonic energy.

Two factors that govern coagulation in hydrosols are (1) probability of collision and (2) adhesion of the colloidal particles. In order to coalesce, particles must first collide. The intensity of collision determines the degree to which the particles will adhere, provided they are at or near their isoelectric point.

It has been demonstrated previously that ultrasonic energy will increase the intensity as well as the number

of collisions of colloidal and near colloidal particles and consequently hasten their rate of coagulation. However, since this type of coagulation has only been reported in batchwise operations, it is believed that if ultrasonic energy is applied to a continuously flowing hydrosol, an evaluation may be made leading to its industrial utilization.

The purpose of this investigation was to design, construct, and evaluate a continuous-flow, ultrasonic coagulation unit, employing a ball-clay hydrosol for experimental tests.

II. LITERATURE REVIEW

Literature pertinent to the effects of ultrasonic insonation of a hydrosol was divided into the following spheres of interest: hydrosol coagulation, ultrasonics, generation of ultrasonic energy, effects produced by ultrasonic energy, mechanism of coagulation by ultrasonic energy, attenuation of ultrasonic energy in colloidal suspensions, and physical aspects of clay hydrosols.

Hydrosol Coagulation

Coagulation, as differentiated from precipitation (the formation of crystalline or amorphous solids from a supersaturated solution⁽¹⁶⁰⁾), is defined by Hauser⁽⁶⁷⁾ as the discontinuous decrease of the degree of dispersion which occurs when single particles of a sol agglomerate to form secondary particles, coagula, and finally a coarsely dispersed phase. Kruyt⁽⁸⁵⁾ more specifically states that coagulation proper is the grouping together of dispersed particles in a suspension; the ordinarily accompanying settling of the coagulum is only a secondary phenomenon, consequent upon the fact that, according to Stokes' law, larger particles settle more rapidly than smaller ones.

Assignment of Colloidal Systems. The colloidal state of matter is not, as one might be led to believe, a particular type of matter analogous to the solid, liquid, and gaseous states of matter. Rather, it represents a certain arbitrary range of subdivision of particles of one phase of matter dispersed in another phase. A fundamental requirement for such a condition is the mutual insolubility of the phases in question.

Size of Colloidal Particles. The arbitrary lines of demarcation for the field of colloidal dispersed particles have been taken as the limits of the dimensional range between about 1 and 500 millimicrons⁽⁶²⁾. The upper limit of 500 millimicrons is approximately the diameter of the smallest size particles that can be resolved in an optical microscope and corresponds to the wave length of visible light, from 4000 to 7600 angstrom units or 400 to 760 millimicrons. The lower limit of one millimicron corresponds to the diameter of molecular dispersed particles in systems in which heterogeneity is not detectable with either an optical microscope or an ultramicroscope. Figure 1 illustrates the entire range of disperse systems.

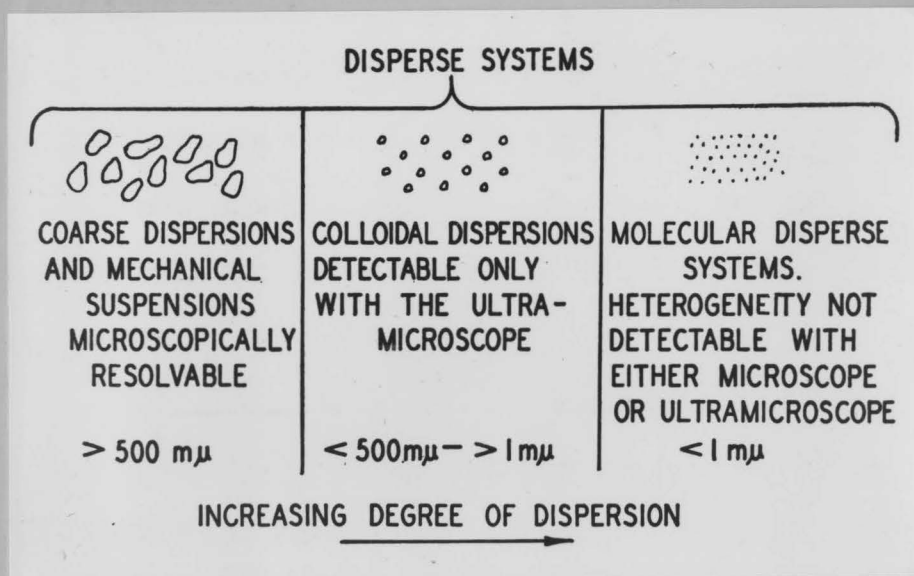


FIGURE 1. DISPERSE SYSTEMS.

HAUSER, E. A.: "COLLOID PHENOMENA," P. 25. MC GRAW-HILL BOOK CO., INC., NEW YORK, N. Y., 1939. 1 ED.

Types of Colloidal Systems. Classifying colloidal systems on the basis of combinations of the solid, liquid, and gaseous states of matter, eight types of systems have been recognized as shown in Table I.

Nomenclature. The term "sol" is generally applied to dispersions of solids in liquid, solid, or gaseous media⁽¹⁶⁸⁾. However, since dispersions of solid in liquid are the most common examples of this class, they are called "colloidal solutions" or "sols"⁽¹⁶⁸⁾. If the dispersion medium is water, the system is termed a "hydrosol"; if the dispersion medium is an organic liquid, the system is called an "organosol", or more specifically, an "alcosol" or "benzosol." Dispersions of solid in solid are termed "solid sols" and dispersions of either liquid or solid in gas are termed "aerosols." "Emulsion" is the general term for dispersions of liquid in either liquid or solid media⁽¹⁶⁸⁾.

Classification of Sols. There are two types of sols relative to the effect the dispersion medium has upon the dispersed phase. If the dispersion medium exerts a dissolving or attractive

TABLE I
Classification of Colloidal Systems

Dispersed Phase (Internal Phase)	Dispersion Medium (External Phase)	Name	Typical Examples
Solid	Liquid	Sol	Gold in water; nickel in benzene; arsenic trisulfide in water
Liquid	Liquid	Emulsion	Kerosene in water; water in benzene; mayonnaise
Gas	Liquid	Foam	Froth on beer; foam on soap solutions; meringues
Solid	Solid	Solid Sol	Gold ruby glass; certain gems; blue rock salt; black diamond
Liquid	Solid	Solid Emulsion	Certain minerals with liquid inclusions; milk quartz; opal; pearl
Gas	Solid	Solid Foam	Minerals with gaseous inclusions; pumice; lavas
Solid	Gas	Solid Aerosol	Smoke; volcanic dust; ammonium chloride fumes
Liquid	Gas	Liquid Aerosol	Fog; cloud; mist

Weiser, H. B.: "Colloid Chemistry," p. 3. John Wiley and Sons, Inc., New York, N. Y., 1949. 2 ed.

influence on the dispersed phase, resulting in lowered surface tension, increased viscosity, and the absence of any marked optical heterogeneity, the suspension is known as a lyophilic, or in the case of an aqueous dispersion medium, a hydrophilic sol⁽¹⁾. In contrast to this, if the dispersed phase exhibits very little, if any, affinity towards the dispersion medium, resulting in a surface tension and viscosity practically the same as the original dispersion medium and a marked optical heterogeneity, it is known as a lyophobic or hydrophobic sol⁽¹⁾. Examples of hydrophilic sols are dispersions of gelatin, glue, albumen, or bentonite in water. Examples of hydrophobic sols are colloidal metal, salts, or minerals in water.

Factors Controlling Coagulation. Kruyt⁽⁸⁵⁾ has recognized two factors controlling the coagulation of colloidal particles. They are, (1) the probability of collision and (2) the probability of adhesion of the colloidal particles as they collide.

Probability of Collision. In order that two particles coalesce⁽⁸⁵⁾ it is first necessary that the particles collide. The Brownian movement, which

is the random kinetic motion of colloidal particles due to bombardment by molecules of the suspension medium, can cause such collision. Therefore, collision is a necessary, but not controlling factor in the adhesion of colloidal particles.

Probability of Adhesion. Even though collision of colloidal particles may be present in a sol, the probability of adhesion of these particles depends upon the existence of a predominance of attractive forces between the particles⁽⁸⁵⁾. The major forces which are present between the particles are:

(1) gravitational forces of attraction, (2) surface or secondary valence forces which result in attraction, and (3) a like electric charge on the particles which results in a repulsive force.

Surface Forces. Kruyt⁽⁸⁵⁾ has pointed out that lyophobic colloid systems, free of electrolytes, are inherently unstable owing to an attraction of the particles which tends to decrease their surface energy. According to Lewis, Squires, and Broughton⁽⁸⁷⁾, when the surfaces of two solid particles come into contact, the surface fields of force would, in general, be of sufficient intensity

to require a considerable expenditure of energy to effect separation. These fields of force have been defined by Schmidt and Marlies⁽¹²²⁾ as secondary valence forces due to residual fields left about a molecule as a whole after two or more atoms have combined through primary bonds to form the molecule itself. Other names that have been applied to these fields of force are residual valence forces, van der Waals forces, intermolecular forces of attraction, and intermolecular cohesive forces⁽¹²²⁾. Hauser⁽⁶⁴⁾ elaborates on this subject, dividing the total energy "E" of a given body into inner energy "ei" and boundary energies "eb":

$$E = ei + eb \quad (1)$$

He⁽⁶⁴⁾ states also that the inner energy is proportional to the volume or mass of the body "v" and the boundary energies are proportional to the discontinuities or interfacial area between the particles and suspension medium designated as "w". If the energy of a volume unit in the interior is termed "i", and the intensity factor of the

discontinuity energies "f", then the total energy of the body can also be written:

$$E = vi + wf \quad (2)$$

and the total energy per unit volume would become:

$$E' = i + f(w/v) \quad (3)$$

If the value "w/v" is increased, i.e., the discontinuities of the system compared to the volume is increased, the boundary energies will predominate accordingly⁽⁶⁴⁾.

Stability of Colloids. According to Getman and Daniels⁽⁵¹⁾, the most important factors in the stability of colloids are zeta potential and solvation. Either the existence of a zeta potential which causes the particles to repel each other, or a film of adsorbed solvent which prevents the enclosed particles from touching each other, is sufficient to keep the dispersed particles in the colloidal state. The difference in factors causing stability, between lyophobic and lyophilic colloids, is illustrated in Figure 2. In the lyophobic colloids, where there is but

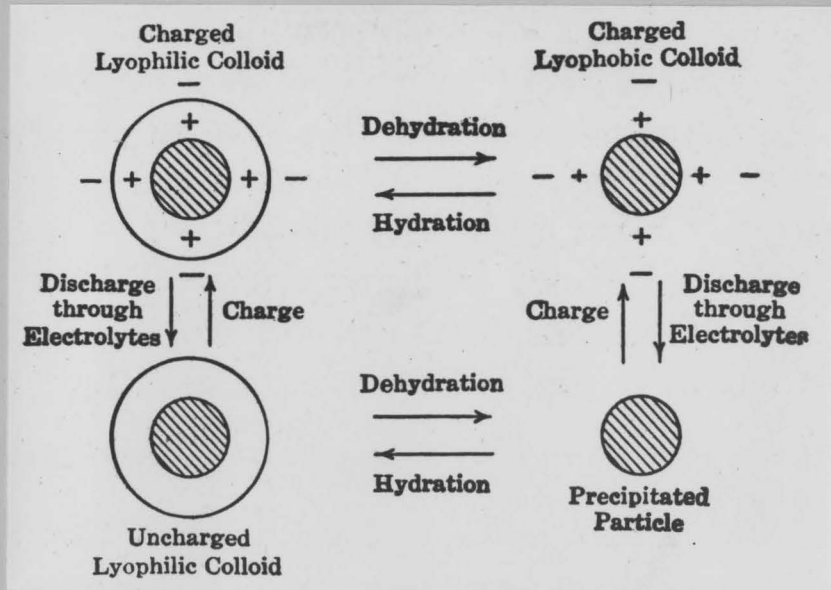


FIGURE 2. STABILITY OF COLLOIDS.

GETMAN, F. H. AND F. DANIELS: "OUTLINES OF PHYSICAL CHEMISTRY,"
P. 251. JOHN WILEY AND SONS, INC., NEW YORK, N. Y., 1947.
7 ED.

little attraction between dispersed particles and suspension medium, the solvation film does not enter in and the stability or instability of the colloid depends only on the presence or absence of a diffuse layer of ions about the particles. The lyophilic colloids, however, are solvated, i.e., they attract around themselves an atmosphere of the dispersion medium. Either the electrical double layer, or the hydrating atmosphere, or both together, is sufficient to keep the system in the colloidal state⁽⁵¹⁾. The particles become coagulated and the system loses its colloidal properties only when both the electrical double layer and the hydrating atmosphere are removed⁽⁵¹⁾. When the colloid has its minimum stability because of the absence of ions it is said to be at its isoelectric point. Under these conditions the zeta potential is practically zero and there is little or no tendency for the particles to migrate in an electric field.

Zeta Potential. The term "zeta potential" or electrokinetic potential, is used to designate the potential drop across the electric double layer of

ions, or more correctly across the diffuse double layer, which extends out from the interface between the colloidal particles and the suspension medium⁽⁵⁸⁾. The term, "diffuse double layer" is believed to be the most representative expression, according to Hartman⁽⁵⁸⁾, as it has been shown that the potential drop is not abrupt, but diffused over a short distance away from the colloidal particle.

In an explanation of the zeta potential and the diffuse double layer around colloidal particles, Hauser⁽⁶⁶⁾ has considered the precipitation of silver bromide from solutions of potassium bromide and silver nitrate. If these are exactly mixed in chemically equivalent proportions, a coarse precipitate results which settles rapidly. If the reaction is carried out in the presence of an excess of either one of the reagents, a large portion of the silver halide remains in suspension as a sol. If the reaction takes place in the presence of an excess of silver nitrate, it is found that the particles of this sol will migrate toward the cathode when placed in an electric field, which means that they carry a net positive charge.

On the other hand, if potassium bromide is used in excess, a negatively charged sol is obtained. The resulting charge on the colloidal particles is explained by the Fajans-Han law which postulates that such ions are preferentially attracted that can be incorporated into the crystal structure, i.e., ions of the same kind. Furthermore, there will always be a tendency to form the least soluble matter, and thus the formation of potassium bromide is less probable than the formation of a highly insoluble silver halide. This phenomenon is illustrated in Figure 3 which is a schematic arrangement of the diffuse double layer surrounding a silver bromide particle. Figure 3a represents a negatively charged particle and Figure 3b a positively charged particle. The designation "A" is the surface of the particle; "B" is the attached rigid ionic layer; "C" is the imaginary boundary between attached and movable liquid layer; and "D" is the diffuse ionic atmosphere in the movable part of the liquid⁽⁶⁶⁾.

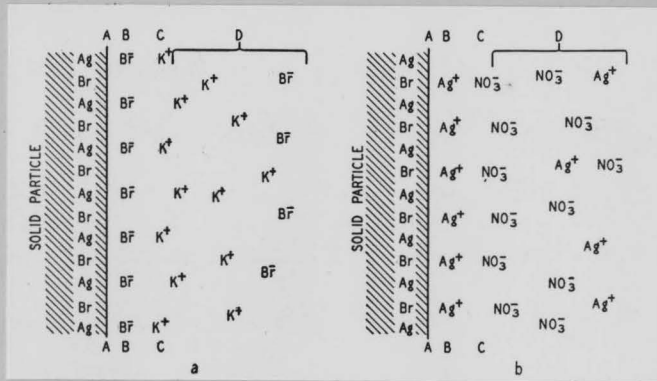


FIGURE 3. SCHEMATIC ARRANGEMENT OF THE DIFFUSE DOUBLE LAYER SURROUNDING A SILVER BROMIDE PARTICLE.

HAUSER, E. A.: "COLLOID PHENOMENA," P. 100. MC GRAW-HILL BOOK CO., INC., NEW YORK, N. Y., 1939. 1 ED.

Thermodynamic Potential. The zeta potential is not the only potential difference between a suspended particle and the medium of suspension. There is another potential, known as the thermodynamic or Nernst potential⁽⁶⁵⁾ between the solid surface of a particle and the interior of the liquid brought about by a reversible tendency for solution of the particle in the liquid. According to Glasstone⁽⁵²⁾, the establishment of a thermodynamic or Nernst potential is generally attributed to the rates of two opposing processes: (1) the passage of ions from a metal or nonmetal into solution, and (2) the discharge of the ions in the solution to form atoms of the metal or nonmetal. When equilibrium is established, the two processes occur at the same rate and a reversible potential is exhibited. If a system is considered having a given zeta potential⁽⁶⁶⁾, and the charge on the particles is decreased by the addition of an electrolyte, the diffuse double layer decreases. If the decrease reaches the point where the entire potential drop takes place within the limits of the diffuse double layer, the zeta potential

reaches a zero value and an unstable system from a colloidal point of view is produced, even though the " ψ " or thermodynamic potential exhibits a finite value. The above phenomenon is illustrated graphically in Figure 4 where the ordinate represents the wall of the particle and the abscissa, the distance from this wall. The line B-B represents the limit of the diffuse double layer. Figure 4a shows the zeta potential prior to the addition of an electrolyte and Figure 4b shows the zeta potential after the addition of an electrolyte.

Isoelectric Point. The isoelectric point of a colloiddally dispersed material is defined by Weiser⁽¹⁶⁹⁾ as the pH value of the dispersion medium at which the dispersed phase does not migrate in an electric field. At this point the zeta potential is zero⁽⁶⁰⁾ and there is a minimum amount of adsorbed ions on the colloidal particles.

Hartman⁽⁶⁰⁾ has distinguished between two phases of coagulation in connection with the isoelectric point: slow coagulation and rapid coagulation. Coagulation of sols begins at a rather

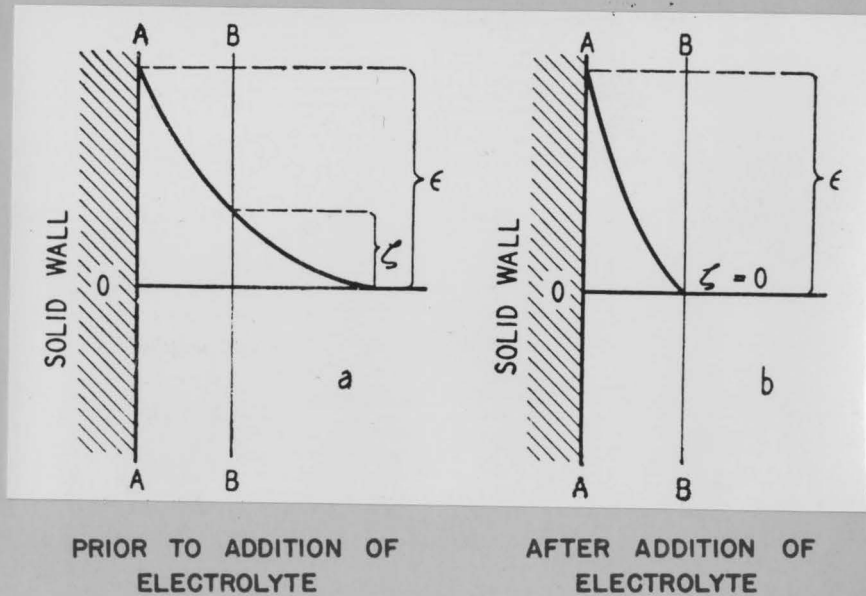


FIGURE 4. CHANGES IN ZETA POTENTIAL WITH ELECTROLYTE CONCENTRATION.

HAUSER, E. A.: "COLLOID PHENOMENA," P. 101. MC GRAW-HILL BOOK CO., INC., NEW YORK, N. Y., 1939. 1 ED.

definite critical zeta potential that is somewhat remote from the isoelectric point⁽⁶⁰⁾. The initiation of coagulation is brought about usually by the addition of relatively small quantities of electrolytes. Rapid coagulation, i.e., coagulation at the isoelectric point, is, on the other hand, usually brought about by the addition of relatively large amounts of suitable electrolytes⁽⁶⁰⁾.

Methods of Coagulation. Hauser⁽⁶⁷⁾ has distinguished five general methods of inducing coagulation in hydrosols. They are: (1) coagulation by the addition of electrolytes, (2) mechanical coagulation, (3) electrical coagulation, (d) thermal coagulation, and (5) coagulation by radiant energy.

Coagulation by the Addition of Electrolytes.

It has been pointed out by Hauser⁽⁶⁶⁾ that the stability of a colloidal dispersion is connected with the zeta potential of the dispersed particles. This is demonstrated not only by the fact that positively charged sols are preferentially coagulated by anions, whereas in the case of negatively charged particles the cations are mostly responsible

for coagulation, but also by what is known as the Hardy-Schulze valency rule which states that the coagulating power of the ion in question increases roughly in the proportion of 1:100:1000, for mono-, di-, and trivalent ions. If an electrolyte is added to a system having a given zeta potential, more ions of opposite charge are crowded into the liquid zone firmly attached to the particle thereby reducing the zeta potential. This results in increased neutralization of the net particle charge. The thickness of the complete diffuse electric double layer decreases; and if the decrease reaches the point where the entire potential drop takes place in the liquid zone firmly attached to the particle, the zeta potential reaches a zero value, resulting in a colloiddally unstable system⁽⁶⁶⁾.

Mechanical Coagulation. Coagulation occurs in many instances by the simple shaking of a sol. Hauser⁽⁶⁹⁾ states that the reason for this type of coagulation cannot be explained from a purely kinetic point of view, i.e., the particles simply

being driven together by the mechanical agitation, the probability of their collisions thus increased. Buzagh⁽²⁸⁾ believes that mechanical coagulation is the result of a surface effect, because an increased concentration of the disperse part always exists at an interface. Accordingly, coagulation will occur more easily in such a concentrated layer of dispersed particles, especially if the zeta potential of the system is low. If a sol is mechanically agitated, the interface is renewed constantly, thus causing more particles to coagulate. However, Hauser⁽⁷⁰⁾ states that there are certain cases of mechanical coagulation where surface effects fail to offer a satisfactory explanation and where a purely kinetic reasoning seems to give the best answer. For example, in producing dispersions of different substances in a ball mill, there is a maximum comminution obtainable for every given set of conditions, such as volume of charge, amount and size of pebbles, number of revolutions per minute. If milling is carried beyond this maximum,

a reagglomeration of the previously comminuted particles occurs.

Electrical Coagulation. Electrical coagulation⁽⁶⁹⁾ is illustrated in the case of the electrophoresis of lyophobic sols, whereby coagulation is affected by the discharge of colloidal particles on an appropriate electrode owing to the attraction of positively charged particles for a cathode and vice versa.

Thermal Coagulation. A large number of sols are materially influenced in their stability by radical changes in temperature⁽⁷⁰⁾. Many lyophobic sols will coagulate on being frozen. On the other hand, certain lyophilic colloids coagulate upon being heated. However, according to Lewis, Squires, and Broughton⁽⁸⁸⁾, the general influence of temperature on coagulation is small in comparison with other important influences, as the kinetic energy of the system, which would affect the probability of collision, increases very little with a rise in temperature.

Coagulation by Radiant Energy. Stability of colloidal systems can be materially decreased by

radiant energy⁽⁷¹⁾ in the form of radioactivity, x-rays, ultraviolet rays, and short wireless waves. Furthermore, in some cases, ultrasonic waves⁽⁷¹⁾ have been found to exercise a coagulating effect. It should be realized, however, that there is a fundamental distinction between radiant energy and ultrasonic energy. Radiant energy is composed of transverse vibrations, does not require a medium for propagation, and travels at about 186,000 miles per second. Ultrasonic energy, on the other hand, is composed of longitudinal or compressional waves which require a medium for propagation and travel at about one-millionth the velocity of radiant energy.

Ultrasonics

Existing literature on ultrasonics focuses attention on theoretical aspects as well as experimental observations, but practical industrial application of ultrasonic phenomena is lacking. In cases where ultrasonic waves have been demonstrated to accentuate certain physical and chemical phenomena, the experimental work has been on a batch scale, employing conventional, research-type generators. In order to give an adequate portrayal of the coagulation effect of ultrasonic waves, it is necessary to discuss investigations which have been made concerning the many physical and chemical effects of these waves.

Definition of Ultrasonic Waves. Ultrasonic waves are defined as high frequency, inaudible sound waves on the order of 15,000 cycles per second and upwards^(3,80). However, at these high frequencies, intensity factors become more pronounced. On many occasions, the term "supersonics" has been observed in the literature to be used synonymously with "ultrasonics," but the former term has now become associated with the velocity of projectiles and aircraft in air, relative to the

velocity of sound, while the latter term is more commonly associated with the frequency of sound waves.

Wave Motion. A wave is a temporary change in the shape or condition of a medium, which moves through the medium and transmits energy outward from the source⁽¹¹¹⁾. If the source of the waves is continuous, they follow one another at equal intervals of time in a procession which is known as a train of waves⁽¹¹¹⁾. If the source is discontinuous, the deformation of the transmitting medium may consist of a single pulse known as a wave pulse⁽¹⁴⁹⁾.

Types of Waves. Waves are classified on the basis of how the particles of the medium move with reference to the direction of propagation of the wave form⁽¹¹¹⁾.

Transverse Waves. A transverse wave is a wave in which the particles of the medium vibrate or the condition of the medium changes, at right angles to the direction of propagation of the wave⁽¹¹¹⁾. Light, radio waves, and x-rays are examples of transverse waves.

Longitudinal Waves. Longitudinal, or compressional, waves are those in which the particles of the medium vibrate, or the condition of the

medium changes, in the direction of propagation of the wave⁽¹¹¹⁾. Sound waves fall in this category.

Characteristics of Wave Motion. Waves, whether they are longitudinal or transverse, have three distinct characteristics. They are: (1) frequency, (2) wave length, and (3) amplitude. At a given frequency, the wave length is determined by the velocity which in turn is dependent upon the medium of transmission.

Frequency. The frequency of a wave is the number of complete vibrations which a particle of the transmitting medium makes in one second⁽¹¹¹⁾.

Wave Length. The wave length is the distance that the wave form advances while a particle makes one complete vibration⁽¹¹¹⁾. In a transverse wave, a wave length includes one crest and one trough; in a longitudinal wave, one compression and one rarefaction.

Amplitude. The amplitude of a wave is the maximum distance that a particle of the medium of transmission vibrates to either side of its equilibrium position⁽¹¹¹⁾.

Intensity of Waves. The intensity of a wave is the amount of energy conveyed by the wave per second through unit area taken at right angles to the direction of propagation⁽¹¹²⁾. It may be represented by the following equation⁽¹¹²⁾:

$$I = 2\pi^2 v D r^2 n^2 \quad (4)$$

where:

I = intensity, ergs/sq cm-sec

v = velocity of wave, cm/sec

d = density of medium, gm/cu cm

r = amplitude of vibration, cm

n = frequency, 1/sec

Consequently, it can be seen that, other factors being constant, wave intensity is proportional to the square of the amplitude and the square of the frequency.

Sonic Waves. The physiological definition of sound is that it consists of compressional waves which affect the auditory nerve and produce the sensation of hearing. However, the human ear is limited in its perception of vibrations, on the average, of about 20 cycles per second on the lower end, to 15,000 cycles per second on the

upper end⁽⁸⁰⁾. Whether sound is perceived or not, the media which transmits it must have two basic properties, elasticity and inertia⁽¹⁷⁶⁾. Equations 5 and 6 represent the forces required to overcome inertia and deform an elastic medium, respectively. Equations 7, 8, and 9 are derived from the two fundamental Equations, 5 and 6⁽¹⁸¹⁾:

$$\text{Inertia:} \quad f = ma \quad (5)$$

$$\text{Elasticity:} \quad f = -sx \quad (6)$$

$$ma = -sx \quad (7)$$

$$m \frac{d^2x}{dt^2} + sx = 0 \quad (8)$$

$$\frac{d^2x}{dt^2} + (s/m)x = 0 \quad (9)$$

where:

s = stiffness constant

m = mass

x = displacement

t = time

Equation 9 is the general second order differential equation for vibration, representing sinusoidal vibrations of simple harmonic motion, and neglecting

both damping and forced oscillations. Consequently, if a particle of a medium is displaced, it must be subject to a restoring force tending to counteract the displacement, and if the medium is to be capable of transmitting a train of waves, it must also possess inertia, so that when it is restored to its undisplaced position due to its elasticity, the momentum which it has acquired may carry it through that position to a displacement opposite to the original one⁽¹⁷⁶⁾. Accordingly, a vacuum will not transmit sound as it has no mass, of which inertia is a necessary property. Snow or a feather pillow will transmit sound very poorly; they have mass, but very little elasticity.

Ultrasonic Waves. The difference between ultrasonic and sonic waves is, from a human standpoint, purely accidental. The physical laws relating velocity, frequency, wave length, and intensity which are valid for audible sound are also valid for the ultrasonic range. However, the initiation and acceleration of certain chemical and physical processes by ultrasonic waves tend to demarcate them from sound of lower frequencies.

These phenomena are a direct result of the acceleration of the particles of the transmitting medium, which in turn depends upon the frequency⁽¹⁷⁵⁾.

Standing Waves. If two sound waves of the same frequency and amplitude, travelling in opposite directions, interfere with each other, a so-called stationary vibration results⁽¹⁷⁷⁾. At increments of one-half a wave length in this standing wave the displacement of the particles of the medium of transmission is always zero, either because the displacement of the particles due to each wave is zero, or because the displacement of the particles due to the two waves are equal and opposite. At other points, midway between these stationary points and also one-half wave length apart, the displacement is first a double displacement in one direction, then zero, then a double displacement in the opposite direction, then zero again and so on. The points of zero motion are known as nodes, and the points of maximum motion, antinodes⁽¹⁷⁷⁾. Consequently, the particles of the medium of transmission vibrate back and forth in such a manner as to cause a maximum pressure at a node at one instant in the cycle and a minimum pressure at

another instant, one-half phase later. If there is a difference in amplitude between two interfering waves travelling in opposite directions, e.g., a reflected wave having a lower amplitude than the incident wave from which it was derived, then the points at which particle displacements are equal and opposite will not coincide with those points at which the particle displacements due to each wave is zero⁽¹⁷⁷⁾. Therefore, a node will be composed of a fluctuation between the two points of zero displacement rather than being a definite point in itself. This will result in a distorted wave with assymetric particle oscillations⁽³⁶⁾.

Generation of Ultrasonic Waves

There are five essential types of generators⁽¹⁵⁰⁾ for producing both sonic and ultrasonic energy:

(1) mechanical, (2) thermal, (3) electromagnetic, (4) magnetostriction, and (5) piezoelectric. Of these, the siren generator, a subdivision of the mechanical type, and the piezoelectric generator have shown more promise of industrial application than the others. The siren type generator has already been employed in the

agglomeration of smoke, fog, and dust^(39,40,141). The piezoelectric generator will produce the highest frequencies obtainable and has been employed successfully in both solid and liquid systems. Its uses include: submarine communication and detection, testing and gaging of materials, and the production of numerous chemical, physical, thermal, and biological effects⁽¹⁵¹⁾. Investigators have claimed to have produced frequencies on the order of 5×10^5 kilocycles per second using this method of generation⁽¹¹⁾. Since a quartz piezoelectric type generator was employed in this investigation, it is the only one which will be considered. A recent development in piezoelectric transducers is the use of a ceramic barium titanate; of particular interest is the fact that it can be shaped into practically any desired form⁽⁷⁸⁾. This may well be an important step towards the industrial application of ultrasonic energy. Due to the high dielectric constant of barium titanate, electrical energy at a comparatively low voltage of from 50 to 100 volts may be used, thereby eliminating the necessity of an oil bath to prevent arcing across the electrodes and enabling the crystal to be coupled directly to its load.

Furthermore, due to the practically unlimited shape in which barium titanate crystals can be produced, they lend themselves readily to continuous process operation.

The Piezoelectric Effect. The brothers, Pierre and Jacques Curie^(12,129) discovered in the year 1880 that many crystals when subjected to pressure or tension developed electric charges on definite crystal surfaces. They called this phenomenon the piezoelectric effect. It has been observed in crystals of tourmaline, quartz, zinc blend, sodium chlorate, tartaric acid, silicious calamine, cane sugar and many other crystals of various systems⁽¹²⁾. This phenomenon is not confined to any particular class of crystals, but is present whenever one or more polar axes exist in a crystal^(4,12). A polar axis or direction in crystallography is defined as an imagined direction in a crystal, the two ends of which are not equivalent, i.e., if the crystal is rotated through 180 degrees about an axis at right angles to the polar axis, it cannot be made to coincide with its original position^(4,12). When pressure or tension is applied in the direction of a polar axis, the spacing of the ions out of which the crystal lattice is built up is not changed in the same relation, i.e., the centers of

positive and negative charges in the units of the crystal lattice do not occupy the same position. In consequence, free charges appear on the surfaces^(4,12).

Quartz Piezoelectric Generator. A piezoelectric generator makes use of the converse or reciprocal piezoelectric effect whereby the application of an alternating electric field applied to the surfaces of a piezoelectric crystal cause it to vibrate mechanically and emit sound waves of the same frequency as the alternating electric field; the amplitude being a maximum where there is resonance between the electric frequency and the natural mechanical frequency of the crystal^(5,13). Quartz has been preferred in piezoelectric ultrasonic generators because of the sharpness of its resonant frequency thereby enabling the procurement of a maximum energy output^(6,14). Physical ruggedness, lack of solubility, and resistance to corrosion are other favorable properties of quartz crystals. Since the amplitude of vibration of the quartz crystal is proportional to the voltage applied to it⁽⁷⁾, it is necessary for high power output requirements to have the crystal immersed in transformer oil to avoid arcing across the electrodes.

Effects Produced by Ultrasonic Waves

Numerous effects concerning the action of ultrasonic vibrations on solid, liquid, and gaseous systems have been reported in the literature. Only those effects believed to be closely associated with the ultrasonic coagulation of hydrosols have been presented here.

Cavitation. Sound energy, especially that at ultrasonic frequencies, has been observed to produce degassing of liquid media^(17,90,125,140,172,180). According to Weessler⁽¹⁷¹⁾, a one megacycle sound wave of about ten watts per square centimeter intensity, travelling through water, will cause an amplitude of motion of the water molecules of about 10^{-5} centimeters. But, the acceleration of these molecules attains very high values, about 250,000 times greater than the acceleration due to gravity. The maximum instantaneous velocity is about 40 centimeters per second. The pressure at a given point in the water changes from plus five atmospheres to minus five atmospheres, one million times each second. The negative portion of this sound wave tends to fracture the liquid and release any dissolved gas as minute bubbles. The cavities that are formed will collapse

with a violent hammering action which generates local pressures on an order of magnitude of 10^3 atmospheres. However, if the water is freed from dissolved gases and suspended particles, its cohesive strength is increased and no cavitation occurs unless negative pressures on the order of 100 atmospheres are applied.

Formation of Cavities. Measured values of the fracture pressure of water range from the positive vapor pressure to a negative pressure of about 350 atmospheres⁽⁴³⁾. However, the theoretical fracture pressure of water has been calculated to be 1320 negative atmospheres⁽⁴³⁾, assuming that the vapor bubble responsible for fracture took place in the interior of the liquid. Fisher⁽⁴³⁾ states that the low experimental values may result from the fact that the initial bubble forms instead at the interface between the liquid and the container, or between the liquid and a suspended particle, where, in the case of a paraffin-water interface, the fracture pressure is only 62 per cent of that for the fracture in the interior of the liquid.

Collapse of Cavities. Rayleigh⁽¹⁰⁵⁾ has calculated the pressure developed during the collapse of a spherical cavity, and found that thousands of atmospheres may be developed at the moment when the cavity collapses to a small fraction of its original diameter. Sollner⁽¹²⁵⁾ has stated that, if cavitation arises, it acts as a disruptive mechanical force, the collapsing cavities hammering at the material in the sound field, preferentially at the weaker spots which are the phase boundaries. He⁽¹²⁵⁾ states further, that the action of sound waves in producing emulsions and dispersions is fundamentally the same as mechanical agitation. However, besides the mechanical aspect of cavitation it is believed that there are three more probable phenomena which occur during cavitation: chemical, electrical, and thermal effects. Weyl and Marbae⁽¹⁷⁴⁾ have considered the chemical aspect as the fracture of molecules to form ions when a liquid is subjected to high negative pressure such as produced by an ultrasonic field. The electrical aspect has been considered from the standpoint of luminescence of liquids transversed by ultrasonic

waves (32,44,183), in that the luminescence is produced by electrical discharges associated with the surface of bubbles formed by cavitation. Finally, the thermal aspect, which is evidenced by considerable heat development in the course of sound treatment of a liquid, is considered by Wood and Loomis (180) to be particularly pronounced at phase boundaries where cavitation is most likely to occur.

Chemical Effects. Many investigators have reported effects produced in an ultrasonic field that appear to be correlated with chemical action. Such effects include: accelerated reaction rates, electrolytic effects, oxidation, luminescence, polymerization, decomposition, inversion of sucrose, increased crystallization, and the determination of molecular properties (152).

Chemical Reaction Rates. The effect of ultrasonics on heterogeneous reactions was studied by Moriguchi (91) who found that the formation of hydrogen in the reactions zinc plus hydrochloric acid, zinc plus sulfuric acid, and the formation of carbon dioxide in the reaction of calcium carbonate with hydrochloric acid was markedly promoted

by ultrasonic waves. Weissler⁽¹⁷³⁾ has reported the initiation and acceleration of chemical reactions by ultrasonic waves and presumed that the energy required to break chemical bonds becomes available through either: (1) friction between macromolecules and solvent, or (2) friction accompanying cavitation in the formation and collapse of small bubbles in the reaction medium.

Oxidation. Of the many chemical effects produced by ultrasonic insonation, the phenomenon of oxidation has attracted the most wide-spread interest.

Schmitt, Johnson, and Olson⁽¹²³⁾ have found that by treatment of water containing dissolved air and a little potassium iodide, free iodine results. The reason for this process is believed to be due to the production of hydrogen peroxide by insonation of water containing dissolved air or oxygen, which in turn oxidizes the potassium iodide to iodine^(83,117,123,138).

Weissler⁽¹⁷²⁾ has found that the rate of iodine liberation from an insonated aqueous potassium iodide solution was over 15 times greater when the

potassium iodide solution was kept fully saturated with carbon tetrachloride, and five times greater when the solution was half saturated with carbon tetrachloride at the start, than when none was present at all. The proposed theory for this "sonochemical" reaction⁽¹⁷²⁾ is that the carbon-to-chlorine bond is broken by the mechanical or possibly electrical forces generated at the collapse of cavitation bubbles which had been facilitated by the presence of air or some other dissolved gas. Once this chlorine is set free, it will react with the potassium iodide to produce free iodine.

It has been found by a number of investigators^(82,102,103,124,158) that ultrasonic insonation of water containing dissolved air not only activates the oxygen, but the nitrogen as well, forming nitrous and nitric acids.

Solov'eva⁽¹³⁸⁾ has demonstrated that ultrasonic waves will catalyze the oxidation of aqueous potassium iodide to potassium iodate and of aqueous ferrous sulfate to ferric sulfate by atmospheric oxygen. He⁽¹³⁸⁾ found that the rate of oxidation

increases with sound intensity, although the relation was not linear.

In the insonation of water by ultrasonic waves, Beuthe⁽¹⁶⁾ has shown that hydrogen peroxide is formed only in water saturated with oxygen or air, and the same might be concluded for all such chemical reactions observed. He⁽¹⁶⁾ states that the vibratory motion produced by the ultrasonic waves causes oxygen molecules to be ionized at the comparatively large boundary between liquid and gas, perhaps by the action of electric charges. The oxygen atoms thus formed are then absorbed by the water with the formation of hydrogen peroxide.

Ethyl alcohol has been shown by Gray⁽⁵⁴⁾ to be oxidized to acetic acid by 30 per cent hydrogen peroxide in minute quantities when subjected to 400, 700, 1000, and 1500 kilocycle insonation for one minute.

Electrolytic Effects. Moriguchi⁽⁹⁴⁾ has found that the overvoltage in the electrolysis of one normal solutions of potassium hydroxide, sodium hydroxide, and sulfuric acid is eliminated when ultrasonic waves are applied. The ultrasonic

waves are supposed to eliminate the diffusion layer between the electrode and the electrolyte. Moriguchi⁽⁹³⁾ also found that when ultrasonic waves are applied in the electrolysis of one-tenth normal copper sulfate solution, the voltage-current density curve becomes a straight line.

Polymerization. Demann and Asbach⁽⁴¹⁾ have expressed the belief that the rate of polymerization and condensation reactions can sometimes be accelerated considerably by ultrasonic waves. Acetic acid was polymerized with waves of changing frequency as conditions varied during the progress of the reaction. Yields which were stated to be impossible without insonation were obtained. Furthermore, the reaction could be directed in such a way that undesirable side reactions were either reduced or suppressed.

Depolymerization. Szalay^(144,145) has reported the splitting of highly polymeric molecules by means of ultrasonic waves. Using a frequency of 722 kilocycles, he⁽¹⁴⁴⁾ found that depolymerization of starch, gum arabic, and gelatin occurred.

This depolymerization was measured by a change in viscosity and also iodometrically in the case of the starch solution.

Decomposition. Lliboutry⁽⁸⁹⁾ has investigated the chemical action of ultrasonic waves having a frequency of 299 kilocycles in regards to decomposition reactions and found the decomposition of benzoyl oxide, diazobenzene chloride, and p-diazotoluene chloride were accelerated by these waves.

Porter and Young⁽¹⁰⁴⁾ have studied the Curtius rearrangement, wherein benzazide yields nitrogen and phenyl-isocyanate when heat is applied. Under the influence of ultrasonic waves the rate of decomposition was increased several fold although the frequency of the sound waves was far below the resonant frequency of the molecules.

Crystallization. Berlaga⁽¹⁵⁾ has observed an increase in the rate of crystallization and in the number of centers in the presence of ultrasonic waves. Cassady^(29,30) has studied the effects of 400 kilocycle insonation on the crystallization of aluminum trihydrate from a sodium aluminate solution. He found, (1) that the rate of

crystallization was inversely proportional to the number of insonations and to the seed charge,

(2) that crystallization was not initiated without a seed charge, and (3) that the number of centers was increased by insonation.

Determination of Molecular Properties.

Weissler⁽¹⁷³⁾ has considered that, since a sound wave is a mechanical impulse transmitted from molecule to molecule, one might expect the chemical structure to affect the speed of transmission. Among the molecular properties which he⁽¹⁷³⁾ has related to ultrasonic velocity are molecular weight, molecular volume, change of association with temperature, adiabatic compressibility, and the ratio of specific heats.

Thermal Effects. The attenuation of sound in liquid media is evidenced by a considerable thermal effect. According to Wood and Loomis⁽¹⁸¹⁾, a test tube filled with water and immersed in a beaker containing water and cracked ice heated rapidly when the beaker was placed in an ultrasonic field. This showed that the energy of the sound waves was converted into heat and absorbed by the system.

Freundlich, Sollner, and Rogowski⁽⁴⁸⁾ have shown that the heat developed by ultrasonic waves in a given oil mixture when the oil contained an equal weight of glass balls or small shot increases with decreasing ball radius, that is, with increasing solid-liquid interface. They⁽⁴⁸⁾ also observed that sound absorption in the liquid was strongly increased by the gas bubbles formed during cavitation and the heat generated by the sound in the liquid thus increased. This heating effect is a direct consequence of the area of interface of the substances traversed by ultrasonic waves.

Sollner⁽¹²⁵⁾ has stated that the thermal effect caused by sound treatment in liquid and solid systems is particularly pronounced in the presence of extended phase boundaries as they occur in heterogeneous systems.

Physical Effects. The physical phenomena initiated or accentuated by ultrasonic treatment are too numerous for complete consideration. However, the following effects, believed to be of interest in this investigation, have been included: (1) degassing of liquids; (2) formation of fogs; (3) viscosity, thixotropy, and rheopexy; (4) orientation of suspended particles; and (5) accumulation in liquid systems.

Degassing of Liquids. A sound wave travelling through a liquid compresses and stretches it periodically. If the stretch is moderate and the liquid is free of gas, nothing in particular happens, but if the liquid is saturated with gas, gas bubbles appear⁽¹²⁵⁾.

Boyle and Lehmann⁽²⁰⁾ were the first to observe that when ultrasonic waves are sent through liquids, gas bubbles are formed. Further investigations^(21,146) have shown that these bubbles are produced by the union of microscopically small bubbles already present in the liquid. The bubbles are driven towards the nodes of a stationary sound wave, and may be used as a means of detecting such waves. However, Bergmann⁽⁹⁾ states that the expansions of the liquid in the path of sound waves give rise to negative pressures in the liquid, leading to the emergence of any gas dissolved in it, and the formation of bubbles. Sorensen⁽¹³⁹⁾ has found that the driving out of one cubic centimeter of gas from water saturated with air required 51.2 kilowatts at 194 kilocycles, 72.6 kilowatts at 380 kilocycles, and 87.4

kilowatts at 530 kilocycles. Consequently, degassing is strongly dependent upon the frequency.

Formation of Fogs. The formation of fogs or the atomization of nonmetallic liquids was first demonstrated by Wood and Loomis⁽¹⁸⁰⁾ in which they treated a beaker containing a volatile liquid with sound waves of high frequency. They observed that the beaker filled rapidly with a white cloud.

Sollner⁽¹²⁷⁾ has investigated the ultrasonic formation of fogs and concluded that the process was due to cavitation, or more correctly to the vehement collapse of cavities. He⁽¹²⁷⁾ observed that no fogs were formed if the liquid was degassed and sealed in test tubes under vacuum. In this case, cavities may form, but lack of outside pressure prevents their collapse.

Viscosity, Thixotropy, and Rheopexy. Viscosity is that property of a fluid that determines its resistance to steady flow⁽¹¹⁰⁾. Sound waves do not affect the true viscosity of a flowing liquid⁽⁴⁵⁾. However, there is another type of

viscosity, known as anomalous or structural viscosity, to which the term thixotropy has been applied⁽⁵³⁾, that is affected by ultrasonic waves. This effect is the liquefaction of thixotropic gels due to the primary particles of these gels being loosened by cavitation^(48,50). Sollner⁽¹²⁵⁾ has given an example of gelatin and agar solutions whereby weak insonation is sufficient to reduce the viscosity only at low shear rates; more intense insonation effects an over-all reduction of viscosity at all shear rates. The solutions recover their structural properties rapidly on standing. The anomalous viscosity of gelatin solutions is much less affected if cavitation does not occur.

The time of solidification of certain types of thixotropic systems can be shortened by submitting them to a regular to and fro movement⁽¹²⁵⁾. This phenomena is called rheopecty⁽⁴⁷⁾. Rheopectic solidification can be brought about by treatment with sound in those rheopectic systems which are more paste-like than gel-like, and whose particles are big enough to be influenced individually, orientated, or translocated, by sound waves⁽²⁷⁾.

Orientation of Suspended Particles. Burger and Sollner⁽²⁷⁾ have shown that with ultrasonics, rod- or plate-like particles such as mica, mosaic gold, gypsum, selenite, steatite, quartz, and kaolin can be orientated with their longest axis normal to the flux of energy. These results were obtained as a rule with particles of microscopic size, but orientation was also found in truly colloidal solutions of vanadium oxide and ferric oxide.

Accumulation in Liquid Systems. Sollner⁽¹³⁴⁾, in his investigations of particles settling in a liquid in which a field of stationary sound waves is set up, has stated that the particles accumulate in planes of one-half wave length and may, as they settle, be collected in beautiful stationary wave patterns on a horizontal plate. He⁽¹³⁴⁾ credits Dorsing with being the first to observe that when a sound wave travels through a liquid containing some dissolved gas, a part of the gas is driven out and unites in small bubbles which accumulate in the nodal planes of stationary sound waves.

Sollner⁽¹³⁴⁾ also points out that in progressing waves, the bubbles are driven away from the source of sound.

Sollner and Bondy⁽¹³⁶⁾ have investigated accumulation and noted that it occurred at the nodes of the standing wave if the dispersed substance is less dense than the medium of dispersion, and at the antinodes if it is denser. They⁽¹³⁶⁾ point out that the decisive factor may not be simply the difference in densities between the medium of dispersion and the dispersed phase; it may be some closely related function which takes into account the difference in sound velocities. In an aqueous system containing particles both denser and less dense than water, ultrasonics can separate the two kinds of particles from each other.

Colloidal Effects of Ultrasonic Waves. Numerous investigators have reported diverse effects of ultrasonic waves on colloidal systems. In practically every case, a full and clear understanding of the complete mechanism involved has yet to be offered. Accounts of reported investigations thought to be of consequence to this investigation include: dispersion, peptization, emulsification,

coagulation of microscopic particles, demulsification, aerosol coagulation, and hydrosol coagulation.

Dispersion. The dispersion of solid substances such as glass, quartz, tin, lead, copper, and silver by means of ultrasonics has been studied by a number of investigators^(106,114,137), some^(114,137) of whom have claimed to have obtained colloidal systems. However, Sollner⁽¹²⁸⁾ has criticized their results on the basis that for a solid body to be truly dispersed by sound action, the surfaces must be clean, carefully freed from all adhering dust or foreign substances. He⁽¹²⁸⁾ states that all solid substances when initially insonated show some dispersion. However, he⁽¹²⁸⁾ points out the difference between substances which are really dispersed and those in which only adhering material is torn off. With the proper cleaning precautions of three or four insonations before testing, Sollner⁽¹²⁸⁾ found that silver, tin, glass, quartz, and marble are totally unaffected, even by prolonged, very intense insonation. Fibers of glass wool are broken, asbestos is split into fibers, and even tinfoil may be torn apart; but a true dispersion

yielding colloidal or semi-colloidal suspensions, is never observed under such conditions. Examples of substances comparatively easily dispersed in water, yielding colloidal or semi-colloidal suspensions, are: crystals of mica, gypsum, steatite, hematite, sulfur, and graphite⁽¹²⁸⁾. They are all substances of moderate cohesion which are easily split and broken⁽¹³³⁾.

The ultrasonic dispersion of liquid and molten metals has been studied by Bondy and Sollner⁽¹⁸⁾ and Richards⁽¹⁰⁶⁾, and they explain the mechanism as follows: when a test tube containing the metal and some water is brought into the oil fountain of an ultrasonic field, the violent transverse vibrations of the glass tube pump small quantities of water into the liquid metal; the water droplets rising in its interior reach the interface metal-water covered with a thin film of metal. When this film breaks, a cloud of minute metal droplets is thrown into the liquid. This mechanism of the formation of sols of liquid metals is the same as that of normal mechanical dispersion of mercury, which was studied by Nordlund⁽⁹⁵⁾.

Moriguchi⁽⁹²⁾ has found that when a plate of an electronegative metal was dipped into an aqueous solution of a less electronegative metallic salt and ultrasonic waves applied, the colloid of the depositing metal was obtained. For example, colloidal copper may be obtained by ultrasonic treatment of zinc in a copper sulfate solution.

Peptization. Sollner⁽¹³²⁾ has considered the peptizing action of ultrasonic waves on gels, gel-like substances, precipitates and sediments, and stated that all such systems contain pre-formed particles of colloidal or semi-colloidal size, and that it has been found that these particles may be separated from one another by the action of audible and inaudible sound waves.

Freundlich and Sollner⁽⁵⁰⁾ have demonstrated that the peptizing action of sound waves is due to cavitation. In the presence of high pressure or a vacuum, peptization is never observed.

Many investigators have reported the peptization or dispersion of precipitates, sediments, and gels, and among them may be mentioned: dye-stuffs and pigments^(156,157,182), metal

hydroxides^(48,49,50,116,120,121), starch^(98,99,100), carbon in aqueous alcohol⁽¹¹⁵⁾, reversible liquefaction of thixotropic systems, mostly of metal hydroxides^(48,49,50,118,119), and thixotropic silica gel⁽⁴⁶⁾.

The preparation of very fine grained photographic emulsions of great sensitivity was reported by Claus^(33,34,35) and Dangers⁽³⁸⁾ who ultrasonically insonated silver bromide emulsions during their preparation.

Emulsification. Richards⁽¹⁰⁶⁾ has emphasized the differences in the nature of the dispersion of mercury and the emulsification of organic liquids in water. The former phenomenon has been discussed under dispersion so an explanation of the latter is in order here.

Sollner⁽¹³⁰⁾ has concluded that a liquid disrupts under the stretch of ultrasonic waves. He and Bondy^(17,135) have concluded that emulsification is due substantially to cavitation. This explanation accounts for the fact that no emulsification occurs in a vacuum or when a high outside pressure is applied. In a vacuum, cavities

may be formed, but lack of sufficient outside pressure prevents their violent collapse. On the other hand, a sufficiently high outside pressure prevents the formation of cavities⁽¹³¹⁾. Disruption due to cavitation occurs preferentially at weak spots represented by phase boundaries such as an oil-water interface^(17,126). Thus, cavitation is favored where emulsification may occur⁽¹³¹⁾. Similarly, dissolved gases may act as weak spots as they are driven out by insonation, forming small bubbles and thus favoring cavitation⁽¹⁷⁾.

An industrial application of emulsification has been attempted by Chambers⁽³¹⁾, whereby, using a two kilowatt electromagnetic sound generator, he homogenized 250 gallons of milk per hour.

Aggregation of Microscopic Particles. Wood and Loomis⁽¹⁸⁰⁾ have discussed the phenomenon of flocculation in liquid systems with particles of a specific gravity not much greater than that of the liquid in which they are suspended. They⁽¹⁸⁰⁾ have observed that flocculation occurs the moment the liquid is traversed by the waves, the particles rushing together to form clusters which

gather into a single mass just under the surface. Examples of this phenomenon are the flocculation of the microorganism paramecium and waterlogged sawdust⁽¹⁸⁰⁾. Furthermore, Sollner and Bondy⁽¹³⁶⁾ have demonstrated coagulation of microscopic particles of quartz in an organic liquid as an example of inducing ultrasonic coagulation in an unstable suspension. They⁽¹³⁶⁾ state that if a test tube containing such a quartz suspension is insonated with low sound intensities, the particles accumulate and aggregate.

Demulsification. Sollner and Bondy⁽¹³⁶⁾ have studied the coagulation or demulsification of oil emulsions and concluded that, if cavitation does not occur, many stabilized emulsions may be broken by prolonged application of sound intensities too weak to cause emulsification.

Aerosol Coagulation. While intense ultrasonics have a strong dispersive effect on emulsions and liquid sols, their effect on aerosols is the opposite, namely strong coagulation of the particles⁽¹⁵³⁾. Bergmann⁽¹⁰⁾ has explained that

the difference in the action of ultrasonics on hydrosols and aerosols depends upon the fact that the first are much more stable. Ultrasonics produce disruptive forces in liquids through cavitation which does not take place in gases. Furthermore, aerosols are inherently more stable^(40,141,142,143).

Hydrosol Coagulation. The coagulation of colloidal particles in a liquid suspension has been studied by a number of investigators. Among them may be mentioned the work of Hermans⁽⁷⁶⁾ in which he investigated the influence of ultrasonic insonation on the rate of coagulation of negative silver iodide sols by electrolytes. He⁽⁷⁶⁾ found that coagulation is always accelerated by sound waves. This influence is negligible with high electrolytic concentration, but becomes more pronounced with low electrolytic concentration. Also investigated was the action of agitation and ultrasonic waves on the coagulation of unstable hydrophobic colloids by Boutaric and Bouchard⁽¹⁹⁾. It was found that when the flocculation of hydrophobic colloids by an electrolyte was studied

under ordinary conditions, the mixture may subsist for a long time without sedimentation even though it is at the isoelectric point. In submitting a very dilute agar-agar gel to ultrasonic insonation, it was observed that a regular system of stationary waves merely produced in the mass, cracks corresponding to inner planes, whereas a turbulent system caused complete disintegration of the gel.

More specific experimental evidence is cited in the work of Thompson⁽¹⁵⁵⁾ whereby he demonstrated, on a batch scale, that ultrasonic energy will increase the rate of coagulation and hindered settling of the solids in a five per cent phosphate tailing suspension when the system is near its isoelectric point. The distribution of solids in this suspension was approximately 95 per cent minus ten microns, 90 per cent minus five microns, 75 per cent minus two microns, 65 per cent minus one micron, and less than five per cent minus a tenth of a micron⁽¹⁴⁸⁾. Under optimum experimental conditions he obtained a 500 per cent increase in the rate of hindered settling over that of the control sample with a 10-minute period of insonation. He⁽¹⁵⁵⁾ stated that subjecting a five per

cent by weight phosphate tailing suspension to an ultrasonic field did not alter the inherent nature of the suspension nor impart to it any new property; but it did increase the rate at which the phenomenon of coagulation and hindered settling occurred.

Mechanism of Coagulation by Ultrasonic Energy

Although aerosols have been investigated quite thoroughly by a number of scientists^(22,40,127,141,179,180), information on the mechanism of hydrosol coagulation is considerably limited. In many instances, the theories on the mechanism of acoustic aerosol coagulation are comparable to acoustic hydrosol coagulation. Information on both aerosol and hydrosol coagulation by means of ultrasonic waves will be presented in this section.

Types of Coagulation. Before going further into the mechanism of acoustic coagulation, it may be well to mention the two types of coagulation which are recognized, perikinetic and orthokinetic coagulation.

Perikinetic Coagulation. Perikinetic coagulation⁽⁸⁴⁾ occurs in systems where essentially no sedimentation is taking place and where the probability

of collision is equally likely in any direction, being caused only by the chaotic Brownian movement.

Orthokinetic Coagulation. Orthokinetic coagulation⁽⁸⁴⁾ occurs in sedimenting systems where the probability of contact is greater in some directions than in others such as that due to the downward motion of the settling particles. Furthermore, large particles will drag along smaller ones and thus hasten the coagulation process.

Acoustic Aerosol Coagulation. In a study of acoustic aerosol coagulation, Brandt, Freund, and Hiedemann⁽²²⁾ have considered that (1) an increase in the probability of purely kinetic collisions between particles, and (2) the production of attractive forces between the particles, will cause coagulation. To these factors they⁽²²⁾ have attributed the orthokinetic collisions and the hydrodynamic forces which display themselves in an ultrasonic field.

Vibration of Particles and Induced Orthokinetic Coagulation. Two stages of acoustic coagulation have been considered⁽²³⁾. First, the particles take part in the vibration of the gas and its flow between the loops and nodes of the

vibration, whereby they are increased in size by collision. Second, the enlarged particles no longer take part in the sound vibrations, but describe irregular paths, during which they undergo new collisions with one another and the smaller particles, and are so further enlarged.

Brandt, Freund, and Hiedemann⁽²²⁾ have stated that corresponding to every particle size, there is a certain frequency up to which the particles will still follow the sound vibrations of the medium, while at higher frequencies their amplitudes are smaller. Consequently, there is for any anisotropic aerosol a certain favorable range of frequency, depending on the particle size, in which the amplitudes of the particles are variable, resulting in collisions and orthokinetic coagulation. The degree to which a particle in a stationary sound wave takes part in the acoustic vibration of the gas medium as depending on frequency and particle radius is given by the following equation⁽²²⁾:

$$\frac{X_p}{X_g} = \frac{1}{\frac{4\pi r^2 \gamma d}{9 \eta} + 1} \quad (10)$$

where:

X_p = vibration amplitude of particle, cm

X_g = vibration amplitude of gas, cm

r = particle radius, cm

γ = acoustic frequency, 1/sec

d = particle density, gm/cu cm

η = viscosity coefficient, gm/cm-sec

Figure 5 is a graphical representation of the above equation and shows that as the particle radius and frequency become greater, the amplitude ratio, X_p/X_g , becomes smaller. Therefore, the product $r^2\gamma$ determines the degree to which a particle will take part in the vibration of the gas. Furthermore, the lag of amplitude X_p of the particle behind amplitude X_g of the surrounding gas medium increases, on one hand, with increasing spherical radius and density of the particle, and on the other hand, with increasing frequency and decreasing viscosity.

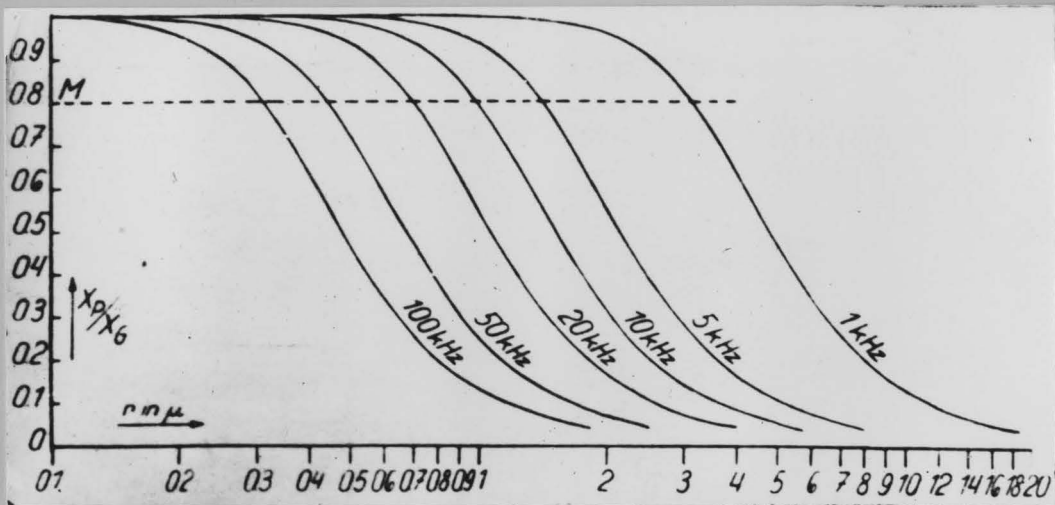


FIGURE 5. RATIO OF PARTICLE AMPLITUDE, X_p , TO GAS AMPLITUDE, X_g , AS A FUNCTION OF THE PARTICLE RADIUS AND ACOUSTIC FREQUENCY.

BRANDT, O., H. FREUND, AND E. HIEDEMANN: THE THEORY OF ACOUSTIC COAGULATION, KOLLOID-Z., 77, 106 (1936).

In applying Equation 10 to hydrosols, two criteria are necessary: (1) cavitation must be absent and (2) the hydrosol must be at its isoelectric point where there is an absence of electric charge on the dispersed particles. Furthermore, the viscosity of liquids is about two to three orders of magnitude greater than that of gases. This difference in viscosity would necessitate that a higher frequency be applied to hydrosols than to aerosols in order to maintain a constant particle-to-medium vibration amplitude ratio with other factors remaining constant.

Brandt, Freund, and Hiedemann⁽²²⁾ have considered a "critical particle size" or a "critical frequency" for a definite frequency or particle size, respectively, relative to which particles essentially covibrate with a gas vibration. They⁽²²⁾ define these critical values as lying along the line "M" (Figure 5) at which the curves begin to pass from their initial flat slope to the intermediate steeper slope; the particle size range being characteristic of aerosols.

Subsequently, coagulation of both aerosols and hydrosols in an acoustic field is aided by the fact that particles of various sizes have different vibrational amplitudes. Thus, the effect of orthokinetic coagulation in an acoustic field refers to coagulation which is produced by the increased probability of collision among suspended particles because of the different vibrational amplitudes of particles of various sizes.

Hydrodynamic Forces. The action of hydrodynamic forces between particles of an aerosol in an acoustic field, as investigated by Brandt, Freund, and Hiedemann⁽²²⁾, were found to be decisive at high ultrasonic frequencies, whereas at low frequencies, their effect decreases. They⁽²²⁾ concluded that when the acoustic frequency is increased over the range that is characterized by the different vibration amplitudes of the particles of an anisodisperse system, the effect of orthokinetic coagulation decreases, and when the critical value of " $r^2\gamma$ " for a given aerosol is exceeded appreciably, it disappears entirely, and an opposite reaction to frequency is found under the action of hydrodynamic forces.

Furthermore, they⁽²²⁾ state that, according to Konig, the attractive force between two spherical particles in a vibrating medium whose tie line is perpendicular to the direction of vibration, is inversely proportional to the fourth power of the distance between the centers. The hydrodynamic force between two particles whose tie line is at an acute angle to the direction of sound depends upon this angle, but Brandt, Freund, and Hiedemann⁽²²⁾ state that this cannot be calculated. The resulting effect is that the two particles are induced to aggregate by the attractive forces, even without kinetic collision, as soon as they approach a certain distance at which they are attracted to one another.

Concerning the above mentioned attraction between particles, Brandt, Freund, and Hiedemann⁽²²⁾ have stated that, for a given aerosol, the time of approach between the particles in an acoustic field, which determines the coagulation effect, depends markedly upon the frequency; the time being relatively short for high ultrasonic frequencies and increasing greatly as the frequency decreases. In general, the same effect may be considered

applicable to hydrosols, but on a different order of magnitude owing to the difference in viscosity between liquids and gases. For example⁽²²⁾, considering a given aerosol of particle concentration of 10^7 in one cubic centimeter and an average particle radius of 0.2 micron, the time of approach for one and ten kilocycles was found to be on the order of 1.5×10^{12} seconds; whereas, at 100 kilocycles it was 1.1×10^7 seconds; about 100,000 times smaller. Furthermore, for a given frequency, the time of approach decreases as the particle radius increases. At a particle radius of two microns and a frequency of 100 kilocycles, the time of approach was found to be 0.27 second. These values apply to relative high acoustic energies⁽²²⁾.

Consequently, it can be seen that even though in one frequency range the orthokinetic effect predominates and in another range the hydrodynamic effect is of greater consequence, they both act together in producing acoustic coagulation.

Comparison of Mechanical Agitation and Insonation.

In the experiments of Boutaric and Bouchard⁽¹⁹⁾, it is observed that when a colloidal solution plus an amount

of electrolyte sufficient to cause flocculation in about 45 minutes was subjected to insonation which contained a regular system of stationary waves, there did not appear to be any effect on coagulation. However, when the insonation did not cause a regular system of stationary waves, but rather formed a turbulent system, the convection currents contained in the liquid produced a sort of stirring action which was expressed by an acceleration of flocculation entirely similar to that caused by agitation with a glass rod.

Dipole Forces. The theory at present accepted⁽⁷⁶⁾ is that in which the charged colloidal particles are surrounded by an electric double layer which is partly distributed diffusely in the solution. As soon as the particles acquire a velocity with respect to the solvent, the double layer loses its spherical symmetry and a dipole is set up. These dipoles are all lying in the same direction, that is, the direction in which the sound is being propagated. The dipole forces between two particles which follow each other in the same line result in attraction, those between particles that are lying side by side result in repulsion. The former condition will occur more frequently than the latter, and the result will be a higher coagulation rate of the particles.

This would explain why the influence of the ultrasonic field is much more pronounced⁽⁷⁶⁾ in the case of low electrolytic concentrations than for high electrolytic concentrations. In the latter case the discharge of the particles is more complete, that is, the dipole is much smaller. Moreover, for a given charge on the particle, the dipole decreases with decreasing thickness of the diffuse double layer, that is, with increasing electrolytic concentration.

Attenuation of Ultrasonic Energy in Colloidal Suspensions

The attenuation of ultrasonic energy in a colloidal suspension is of considerable importance in coagulation studies using this type of energy. A knowledge of such is useful from both a theoretical and a control standpoint. Some general theoretical aspects of attenuation will be considered, followed by some experimental data which have been obtained for sound absorption in suspensions of irregular particles.

Theoretical Aspects. Apart from the purely geometric decrease in intensity due to spherical spread

of a beam of sound radiated from a small source, Vigoureux⁽¹⁶¹⁾ summarizes other causes, represented by viscosity, thermal conduction, scattering, and intramolecular forces, which all combine to produce an exponential decrease in intensity. The viscosity factor⁽¹⁶²⁾ involves the transformation of mechanical energy into heat waves due to the viscous forces which must be overcome as they oppose the relative motion of the layers of the medium of propagation. The thermal conduction factor⁽¹⁶³⁾ is concerned with the compression and rarefaction of the medium of propagation whereby the temperature is raised in the former condition and lowered in the latter. Thus, there is a tendency for heat to be conducted from the compression to the rarefaction, and this passage of heat down a temperature gradient means an increase of entropy and so a dissipation of energy. The scattering factor⁽¹⁶⁴⁾ is introduced when a wave impinges on obstacles more or less uniformly distributed throughout the medium of propagation resulting in diffraction and reflection of the sound wave. The fourth factor in the absorption and dissipation of sound energy is found in intramolecular exchanges of energy among the translational, rotational, and vibrational degrees of freedom of the medium of propagation⁽¹⁶⁵⁾.

Wood⁽¹⁷⁸⁾ gives the following equation relating the intensity after propagation through a distance "x" to the initial intensity at "x" equals zero:

$$I_x = I_0 e^{-2\alpha x} \quad (11)$$

where:

I_x = intensity at distance "x" from
"o", watts/sq cm

I_0 = initial intensity, watts/sq cm

α = absorption coefficient, l/cm

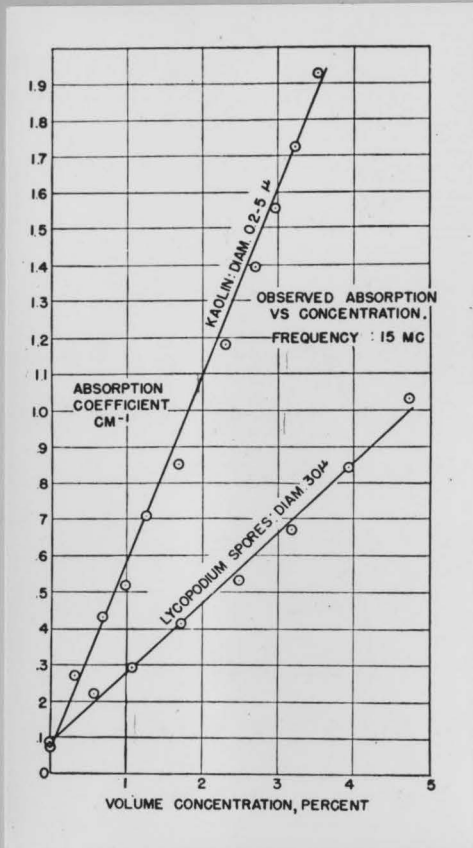
x = distance from initial intensity
level, cm

If the absolute intensity at "o" is known, the absolute intensity at "x" may be calculated from Equation 11. However, if the absolute intensity at "x" is not known, a value may be assumed, and a relative intensity at "x" calculated. The absorption coefficient, α , may be either calculated from theory⁽¹⁶¹⁾ or measured⁽¹⁵⁹⁾.

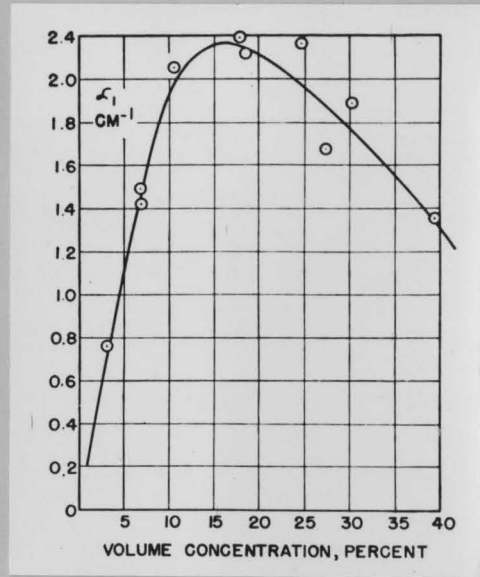
Experimental Data. Urick⁽¹⁵⁹⁾ has described the following method which he used in measurements of attenuation coefficients. A small quartz crystal, immersed in the suspension to be measured, was used to emit short

pulses of high frequency sound. These pulses were reflected by the plane at the bottom of the containing vessel, and, as in radar, were received by the same unit acting as a receiver. One-microsecond pulses of 15 megacycle sound were employed. After amplification and demodulation, the pulses were observed and measured on an oscilloscope screen. The successive reflections between crystal and reflector became weaker and farther apart as the distance of travel increased. By means of an input attenuator the first received pulse was adjusted to constant amplitude as the crystal-reflector distance varied, and the absorption coefficient obtained in terms of the rate of decrease of amplitude with distance. The coefficient so obtained will obviously be the sum of the absorption due to the pure suspension medium and that of the suspended particles themselves.

Figure 6a illustrates graphically the absorption coefficient plotted against volume concentration for kaolin and lycopodium spores having the particle sizes shown. The linearity of the absorption with concentration is in agreement with theory, and illustrates the



(A)



(B)

FREQUENCY: 1 MC

FIGURE 6. SOUND ABSORPTION COEFFICIENTS FOR KAOLIN HYDROSOLS.

URICK, R. J.: THE ABSORPTION OF SOUND IN SUSPENSIONS OF IRREGULAR PARTICLES, J. AM. ACOUSTICAL SOC., 20, 286 (1948).

additive nature of the absorption process⁽¹⁵⁹⁾. Figure 6b shows that this linearity holds good only at low concentrations where particle interactions can be neglected.

Physical Aspects of Clay Hydrosols

For the purposes of evaluating a continuous-flow, ultrasonic coagulation unit, a ball-clay hydrosol was considered satisfactory for reasons of its composition, settling rate, and hydrophobic nature. Consequently, it is desired to discuss the physical properties of clays and their behavior in aqueous suspension.

Composition of Clays. According to Grim⁽⁵⁵⁾, the term "clay" as used today carries with it three implications: (1) a natural material with plastic properties, (2) an essential composition of particles of very fine size grains, and (3) an essential composition of crystalline fragments of minerals that are essentially hydrous aluminum silicates or occasionally hydrous magnesium silicates. From the standpoint of physical chemistry, however, clays may be regarded as disperse systems of mineral fragments in which particles under two microns predominate⁽⁹⁷⁾.

Classification of Clays. Clays may be classified according to their origin, chemical and physical properties, or uses⁽¹⁰⁸⁾. However, extensive research in many laboratories has shown, beyond a reasonable doubt, that clay materials are composed essentially of crystalline particles which are members of any one or more of a few groups of minerals known as the "clay minerals"⁽⁵⁵⁾. The clay minerals are hydrous aluminum silicates, frequently with some replacement of the aluminum by iron and magnesium and with small amounts of alkalies and alkali earths⁽⁵⁵⁾. In addition to these components, variable, but usually small amounts of quartz, limonitic material, bohemite, hydrargillite, and organic material may be present in the clay⁽⁵⁵⁾. By far the most industrially important clays are those containing essentially the mineral kaolinite. A classification according to purity may be attempted by dividing these clays into kaolin, china-clay, and ball-clay. There are still other variations⁽¹⁰⁸⁾ but they are not considered relevant to this investigation.

Kaolin. Most kaolins as mined are rather siliceous, but in their washed condition approach closely the composition of kaolinite. They usually

contain less than five per cent impurities in the washed condition⁽¹⁰⁹⁾. However, the term kaolin is generally used in referring to unwashed clays of a high kaolinitic content and a white or nearly white burning character⁽¹⁰⁹⁾.

China-Clay. China-clay is a term commonly used in reference to washed kaolins that have had most of the siliceous impurities removed⁽¹⁰⁹⁾.

Ball-Clay. The term ball-clay is applied to those clays possessing good plasticity, usually strong bonding power, high refractoriness, and which burn white or creamy white⁽¹⁰⁹⁾. They represent the finest state of occurrence or hydrous aluminum silicate and usually contain more inorganic impurities than china-clay and also some organic impurities.

Physical Aspects of Clay Minerals. The clay minerals occur in most clays in particles less than about five microns in diameter⁽⁵⁵⁾. They possess excellent cleavages, and when mixed with water, the particles are frequently reduced in size, so that a wet determination of the particle size distribution will usually show most of the clay minerals in particles less than two microns,

even though they are coarser in the crude state⁽⁵⁵⁾. Recent studies with the electron microscope have indicated that certain of the clay minerals can exist in particles approaching their unit cell height, that is, about one millimicron⁽⁵⁵⁾. The clay minerals, except allophane, are crystalline, and much research indicates that almost all clays, including their smallest constituent particles, are made up of entirely crystalline material⁽⁵⁵⁾. The crystalline clay minerals are the dominant components of clay materials, and their properties must be accounted for on the basis of the crystalline components⁽⁵⁵⁾.

Classification of Clay Minerals. Three groups of major importance are recognized⁽⁵⁵⁾: illite, montmorillonite, and kaolinite groups; along with a number of groups of relatively minor importance⁽⁵⁵⁾. Since the application of X-ray diffraction analysis to the physical structure of clay minerals, a fairly conclusive amount of data has been accumulated on the lattice structure of these minerals. Figure 7 contains schematic drawings of the two basic structural units which are involved in the atomic lattices of the clay minerals⁽⁵⁵⁾. One is the alumina or gibbsite structure which consists of two sheets of closely packed oxygens and hydroxyls between

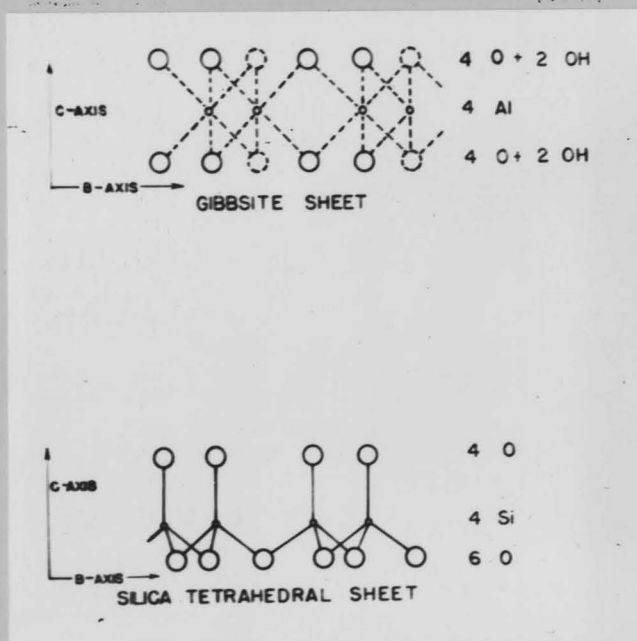


FIGURE 7. BASIC STRUCTURAL UNITS OF CLAYS.

GRIM, R. E.: MODERN CONCEPTS OF CLAY MINERALS, P. 238. ILLINOIS STATE GEOLOGICAL SURVEY, BULLETIN NO 80, URBANA, ILLINOIS, 1942.

which aluminum atoms are imbedded in such a position that they are equidistant from six oxygens. The second unit consists of a silica tetrahedral sheet linked to form a hexagonal network of the composition Si_4O_{10} when repeated indefinitely. This unit may be viewed as a sheet of loosely packed oxygen atoms with each oxygen atom linked to two silicon atoms directly above.

Illite Group. The name "illite" was suggested by Grim, Bray, and Bradley⁽⁵⁶⁾ as a group name, rather than a specific name of a clay mineral, for the constituents of clay minerals that are similar to, but not identical with, the white micas. They⁽⁵⁶⁾ have advanced the general formula $(\text{OH})_4\text{K}_y(\text{Al}_4\cdot\text{Fe}_4\cdot\text{Mg}_4\cdot\text{Mg}_6)(\text{Si}_{8-y}\cdot\text{Al}_y)\text{O}_{20}$, with "y" varying from 1 to 1.5. The illite structure is similar to that of montmorillonite except that about 15 per cent of the silicon positions are replaced by aluminum, and the resulting excess charges are chiefly satisfied by potassium ions between the silica sheets of two successive units⁽⁵⁵⁾. Figure 8 shows a schematic presentation of the structure of illite.

Montmorillonite Group. The montmorillonite group takes its name from the mineral montmorillonite,

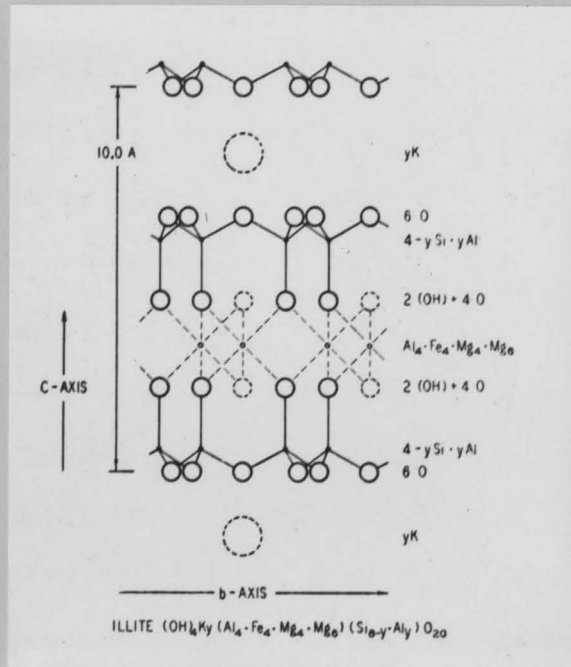


FIGURE 8. CRYSTAL STRUCTURE OF ILLITE.

GRIM, R. E.: MODERN CONCEPTS OF CLAY MINERALS, P. 244.
 ILLINOIS STATE GEOLOGICAL SURVEY, BULLETIN NO 80,
 URBANA, ILLINOIS, 1942.

the chief constituent of bentonite, with a probable composition of $(\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_{20}\cdot n\text{H}_2\text{O}$ ⁽⁵⁵⁾. The aluminum is usually partly replaced by magnesium and ferric iron. The structure of this mineral consists of one gibbsite sheet between two sheets of silica tetrahedral groups⁽⁵⁵⁾ as shown in Figure 9. The units are loosely held together in the direction of the c-axis with water present between them. The amount of water between the units varies, and therefore the mineral is said to have an expanding lattice. Without water between the structural units, the height of the cell is 9.6 angstrom units.

Kaolinite Group. Kaolinite, the chief member of this group, has the composition $(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$ ⁽⁵⁵⁾. Dickite and nacrite are other members of this group with the same composition but slightly different crystallographic forms⁽⁵⁵⁾. The kaolinite structure, as shown in Figure 10, is composed of a gibbsite sheet with a single tetrahedral silica sheet⁽⁵⁵⁾. The lattice structure does not expand with varying water content, probably because of the attraction of oxygen and hydroxyl layers which are adjacent

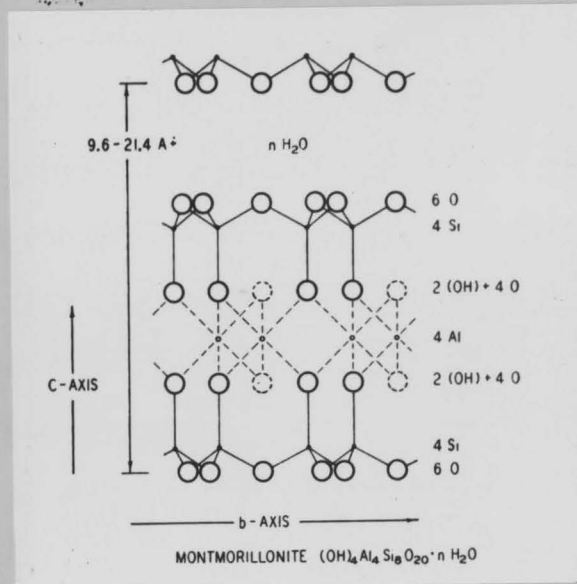


FIGURE 9. CRYSTAL STRUCTURE OF MONTMORILLONITE.

GRIM, R. E.: MODERN CONCEPTS OF CLAY MINERALS, P. 239.

ILLINOIS STATE GEOLOGICAL SURVEY, BULLETIN NO 80,
URBANA, ILLINOIS, 1942.

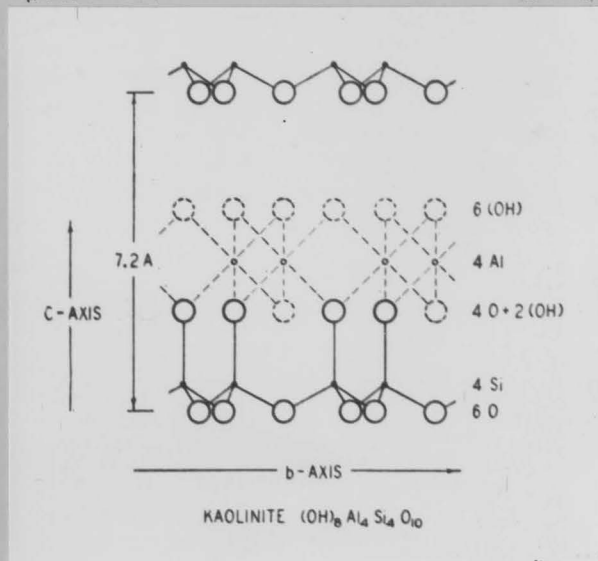


FIGURE 10. CRYSTAL STRUCTURE OF KAOLINITE.

GRIM, R. E.: MODERN CONCEPTS OF CLAY MINERALS, P. 246.
ILLINOIS STATE GEOLOGICAL SURVEY, BULLETIN NO 80,
URBANA, ILLINOIS, 1942.

when kaolinite units are stacked one above the other⁽⁵⁵⁾.

Clay-Water Suspensions. Since a ball-clay hydrosol was employed in this investigation, emphasis will be placed on the hydrosol properties of kaolinite, the chief constituent of kaolin, china-, and ball-clay.

Stability of Kaolinite-Water Suspensions. The only possibility for the development of a "net" electric charge in kaolinite lies in its fracture along the c-axis, that is, at the edges or corners of the individual plates or sheets⁽⁷⁵⁾. Accordingly, the most striking colloidal phenomenon exhibited by kaolinite is a direct consequence of the charge carried by the solid particle or nucleus⁽⁷⁵⁾. However, this charge may not be due only to the innate net charge due to fracture, but may also be due to the presence of electrolytes, the ions of which attach themselves to the particles. Consequently, the stability or instability of kaolinite hydrosols is largely governed by electrokinetic phenomena resulting from the presence or absence of charges on the surface of the clay particles, and the type, concentration, and arrangement

of the ions present in the dispersion medium⁽⁷⁵⁾. If the system under consideration consists of pure kaolinite and pure water, the only forces of consequence are those of molecular attraction and electrostatic repulsion due to fractured edges⁽⁷⁵⁾.

Effect of Active Areas Present on Kaolinite Crystals. The kaolinite crystal is built up of silicon and aluminum layers as shown in Figure 10. The crystal displays perfect basal cleavage⁽⁷⁹⁾, that is, cleavage between the individual unit cells, and along this cleavage plane no unsaturation can result from fracture, because no bonds are broken. An examination of the nature of the bonds in this crystal, according to the concepts of Pauling⁽¹⁰¹⁾, show that the weakest bonds are the Al-O, Al-OH, and the shared corners of the Si-O tetrahedra. Photographs of fine kaolinite particles taken with the electron microscope⁽⁴²⁾ show the particles to be roughly hexagonal. On this basis the formation of hexagonal plates of kaolinite particles may be expected with one fracture occurring along the cleavage plane, that is, between the Si-O tetrahedra and the OH layer, and the other fractures

occurring parallel to the c-axis in order to form thin hexagonal plates⁽⁷⁹⁾. The fracture along the cleavage plane causes no valence bonds to be broken and therefore no unsaturation of valence should result. This could not lead to the development of active spots⁽⁷⁹⁾. Fractures occurring parallel to the c-axis, however, will break valence bonds and such fractures will cause the formation of active areas on the surface of the crystal fragment⁽⁷⁹⁾.

According to Hauser⁽⁷³⁾, the ultimate clay crystal carries a net negative charge, the result of either anion adsorption onto its surface, or an unbalanced crystal lattice. Whatever the basic cause may be, the ultimate clay particle is believed to be a very complex anion⁽⁷³⁾. To balance its charge, the particle tends to adsorb the necessary number of cations available in its environment. When a clay particle is dispersed in water, these cations will hydrate, and depending on their valency and degree of hydratability, dissociate to a certain distance from the surface of the particle, thereby building up a diffuse electric double layer and forming a colloidal micelle⁽⁷³⁾.

Hofmann and Bilke⁽⁷⁷⁾ present a graphical illustration of the adsorption of cations onto a clay particle due to the unsaturated condition of the oxygen atoms in the Si-O tetrahedra along the edges. A redrawing of this illustration by Johnson and Norton⁽⁷⁹⁾ is shown in Figure 11.

pH and Isoelectric Point. According to Hall⁽⁵⁷⁾, the pH of water extracts from several clays by use of a hydrogen electrode were as follows:

South Carolina kaolin -----	4.40
Delaware kaolin -----	5.10
Virginia kaolin -----	5.05
Florida kaolin -----	6.80
Bentonite -----	9.72

The water-clay ratio for the kaolin extracts was four; for the bentonite extract it was seventy.

Clays do not have a sharp isoelectric point, probably due to the fact that they contain a mixture of colloids⁽⁵⁷⁾. However, for every clay-water-electrolyte mixture, there exists a certain pH, the isoelectric point, at which the rate of settling of the clay is a maximum and also another

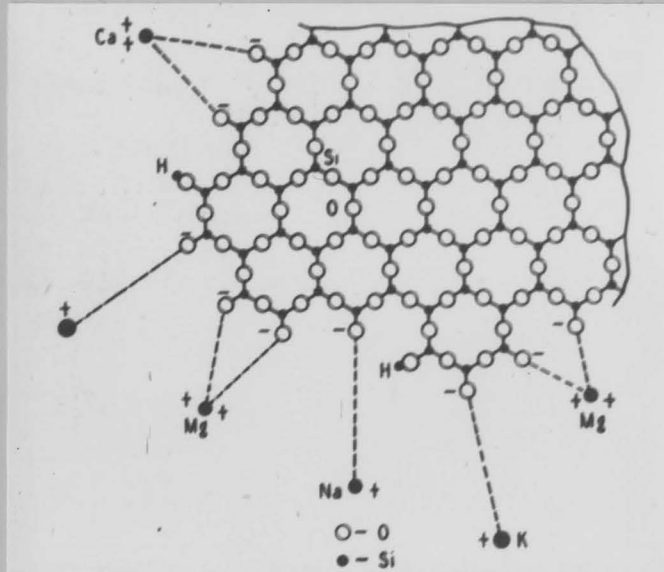


FIGURE 11. ADSORPTION OF CATIONS ON UNSATURATED OXYGEN ATOMS IN SI-O TETRAHEDRA.

HOFMANN, U. AND W. BILKE: UBER DIE INNERKRISTALLINE QUELLUNG UND DAS BASENAUSTAUSCHVERMOGEN DES MONTMORILLONITS, KOLLOID-Z., 77, 238-51 (1936).

pH at which there is a minimum rate of settling or a point of maximum deflocculation⁽⁵⁷⁾. Table II gives comparative values of pH of water extract, pH at isoelectric point, and pH at maximum deflocculation for a number of clays.

TABLE II

Characteristic pH Values for Some Clay-Water Suspensions

Clay	pH of Water Extract	pH at Isoelectric point	pH at Point of Maximum Deflocculation
Georgia kaolin	4.70	3.42	12.00
South Carolina kaolin	4.80	3.99	10.32
English china-clay	5.80	3.63	11.60

Hall, F.P.: Effect of Hydrogen Ion Concentration Upon Clay Suspensions, Am. Cer. Soc. J., 6, 994 (1923).

III. EXPERIMENTAL

The experimental section of this thesis includes the purpose of the investigation, the plan of experimentation, the materials and apparatus used, the method of procedure, the data and results obtained, and sample calculations.

Purpose of Investigation

The purpose of this investigation was to design, construct, and evaluate a continuous-flow, ultrasonic coagulation unit, employing a ball-clay hydrosol for experimental tests.

Plan of Experimentation

In general, the plan of experimentation was to subject a continuously flowing ball-clay hydrosol to an ultrasonic field and observe the effects produced on the hydrosol subsequent to insonation. Exploratory tests provided information which served to indicate that a four per cent by weight ball-clay hydrosol would serve as a suitable suspension.

Specifically, the plan of experimentation required: reviewing the literature; designing and constructing facilities for the preparation and continuous flow of a ball-clay hydrosol; designing and constructing a coagulating tube equipped with a crystal probe for measurement of relative pressure amplitudes of ultrasonic waves; devising techniques; devising methods of procedure; conducting exploratory investigations in regard to type of hydrosol to be used, electron microscopic observations of ball-clay particles, suspension flow rate, and crystal probe calibration; conducting experimental tests to determine the effect of frequency, intensity of insonation, flow rate, and recycle rate on coagulation and settling rate; conducting comparative tests to determine the effects of both continuous and batch mechanical agitation and batch ultrasonic treatment on coagulation and settling rate; and conducting control and reproducibility tests.

Materials

Following is a list of the materials used in this investigation:

Ball-Clay. Tennessee No 9, air-floated, analysis in Table III. Distributed by Kentucky-Tennessee Clay Co., Mayfield, Kentucky. Used in water suspension for coagulation tests.

Bentonite. Purified, air-floated. Distributed by American Colloid Co., Chicago, Ill. Used in exploratory settling tests.

Buffer Solution. Standard, pH of 4.00 ± 0.01 at 25°C , code No So-B-98. Distributed by Eimer and Amend, New York, N. Y. Used as a pH standard for pH meter.

Buffer Solution. Standard, pH of 10.00 ± 0.02 at 25°C , code No So-B-116. Distributed by Eimer and Amend, New York, N. Y. Used as a pH standard for pH meter.

Cement. Cellulose, crystal clear. Manufactured by Testor Chemical Co., Rockford, Ill.; distributed by Blacksburg Hardware Co., Inc., Blacksburg, Va. Used in bonding nickel electrodes to quartz crystal in crystal probe.

TABLE III

Analysis of Tennessee No 9 Ball-Clay

<u>Components</u>	<u>Percentages</u>
Silicon Dioxide, SiO ₂ -----	51.64
Aluminum Oxide, Al ₂ O ₃ -----	29.38
Ferric Oxide, Fe ₂ O ₃ -----	1.01
Titanium Dioxide, TiO ₂ -----	1.82
Calcium Oxide, CaO -----	0.65
Magnesium Oxide, MgO -----	0.77
Sodium Oxide, Na ₂ O -----	0.43
Potassium Oxide, K ₂ O -----	1.30
Ignition Loss -----	13.38

Kentucky-Tennessee Clay Co., Mayfield, Kentucky.

Ceramic Marking Ink. Black, code No 11-734.

Manufactured by Coors Porcelain Co., Golden, Colorado; distributed by Fisher Scientific Co., 7722 Woodbury Drive, Silver Spring, Md. Used in graduating settling tubes.

Chloroplatanic Acid. Technical, code No P-154.

Distributed by Fisher Scientific Co., 7722 Woodbury Drive, Silver Spring, Md. Used as a source of platinum for fusing same into pyrex glass tube.

Enamel. Black, code No 729. Manufactured by Sherwin-Williams Co., Cleveland, Ohio; distributed by Brown Stores Co., Inc., Blacksburg, Va. Used for painting panel board.

Ethylene Dichloride. Technical. Distributed by Thompson and Cooke, Inc., Washington, D. C. Used to fuse polystyrene pieces together in construction of transducer housing.

Flux. Liquid, "Tri-Flux", No 3 variety. Manufactured by Wolfe-Kote Co., Sheboygan, Wis.; distributed by Whitehead Metal Products Co., Inc., 303 West 10th St., New York, N. Y. Used as a flux for bonding tinned nickel disc to platinized pyrex glass.

Friction Tape. 3/4-inch width, code No 8. Manufactured by Appleton Rubber Co., Inc., Boston, Mass.; distributed by Brown Stores Co., Inc., Blacksburg, Va. Used for general purpose electrical insulation.

Kaolin. Kingsley variety, air-floated, analysis in Table IV. Distributed by United Clay Mines Corp., Trenton, N. J. Used in exploratory settling tests.

Mercury. Purified. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used as indicating fluid in flow rate and recycle rate manometers.

Paraffin Wax. Melting point range, 121-130 °F. Manufactured by Esso Standard Oil Co., Bayonne, N. J.; distributed by Blacksburg Hardware Co., Inc., Blacksburg, Va. Used for sealing wires into crystal probe tube.

Solder. Non-flux, 50-50 per cent lead-tin. Distributed by Noland Co., Roanoke, Va. Used for soldering nickel discs to platinized pyrex glass.

Solder. Rosin core, 50-50 per cent lead-tin. Manufactured by Davision Lead Co., Chicago, Ill.; distributed by Blacksburg Hardware Co., Inc., Blacksburg, Va. Used for general purpose soldering of experimental equipment.

TABLE IV

Analysis of Kingsley Kaolin

Components	Percentages
Silicon Dioxide, SiO ₂ -----	46.40
Aluminum Oxide, Al ₂ O ₃ -----	38.60
Ferric Oxide, Fe ₂ O ₃ -----	0.38
Titanium Dioxide, TiO ₂ -----	0.24
Calcium Oxide, CaO -----	0.07
Magnesium Oxide, MgO -----	0.20
Potassium Oxide, K ₂ O -----	0.35
Ignition Loss -----	14.00

United Clay Mines Corp., Trenton, N. J.

Transformer Oil. Wemco C, 22,000 volts dielectric strength. Distributed by Westinghouse Electric Supply Co., Roanoke, Va. Used as an insulating and cooling medium in transducer housing of G. E. ultrasonic generator.

Varnish. Clear, "Lin-X" variety. Manufactured by Sherwin-Williams Co., Cleveland, Ohio; distributed by Brown Stores Co., Inc., Blacksburg, Va. Used as primary coat in painting of panel board.

Water. Tap, analysis in Table V. Obtained from college water supply, Blacksburg, Va. Used as suspension medium for ball-clay hydrosols employed in experimental tests.

TABLE V

Analysis of College Water Supply, Blacksburg, Virginia

Qualitative Analysis	Quantitative Analysis ppm
pH - 7.4	-
Methyl orange alkalinity -----	200
HCO ₃ -----	244
Cl (halide) -----	1.45
Nitrates and nitrites -----	None
Free CO ₂ -----	28.2
Total dissolved solids -----	240.0
Volatile matter -----	84.0
Mineral residue -----	156.0
Dissolved silica as SiO ₂ -----	2.4
Iron and aluminum oxides -----	3.0
Calcium -----	45.19
SO ₄ ion -----	7.08
Magnesium -----	24.42
Soap hardness -----	204.0
Calculated hardness -----	223.0

Department of Chemistry, Virginia Polytechnic Institute,
Blacksburg, Va. Sept. 27, 1939.

Apparatus

The apparatus used in this investigation is considered under the following eleven subheadings:

- (1) ultrasonic generator; (2) transducer housing;
- (3) panel board; (4) suspension preparation equipment;
- (5) oil cooling unit; (6) coagulating tube;
- (7) crystal probe assembly; (8) equipment for continuous comparison mechanical coagulation tests;
- (9) equipment for batch comparison mechanical coagulation tests; (10) equipment for measurement of settling rates; and (11) auxiliary equipment.

Ultrasonic Generator. An ultrasonic generator is an instrument which converts high frequency electrical power into high frequency mechanical vibrations. This is accomplished with a power oscillator which drives a quartz crystal at its resonant frequency. The ultrasonic generator used in this investigation, catalogue No 8665966 G3, was manufactured by the General Electric Company, Schenectady, New York, and was consigned to the Virginia Polytechnic Institute, for experimental research, through the General Electric Supply Corporation, Roanoke, Virginia. The generator consisted of one unit; a cabinet housing the power amplifier upon which was

directly mounted the oil-filled, quartz crystal, transducer. Sets of plug-in coils, matched to these respective crystals were also supplied. Instructions designated as GEI-29578-B accompanied the generator. The front view of the generator is shown in Figure 12, and the rear in Figure 13. A sectional view of the test cavity and transducer housing supplied with the generator is shown in Figure 14.

Transducer Housing. Since it was desired to use the ultrasonic generator for periods of over an hour at a time, it was considered advisable to cool the transformer oil in the transducer housing by means of continuous flow through a cooling unit. This cooling was necessitated by the heat developed in the transformer oil due to the vibration of the crystal and conversion of sound waves into heat by attenuation. The transducer housing supplied with the generator was not designed to permit this continuous flow of transformer oil, so a housing was designed and constructed out of polystyrene plastic to accomplish this advantage. A drawing of the constructed housing is shown in Figure 15 and a photograph of it in Figure 16. All parts of the transducer assembly supplied with the generator, except



FIGURE 12. FRONT VIEW OF GENERAL ELECTRIC
ULTRASONIC GENERATOR WITH CONTINUOUS-
FLOW TRANSDUCER HOUSING IN POSITION.

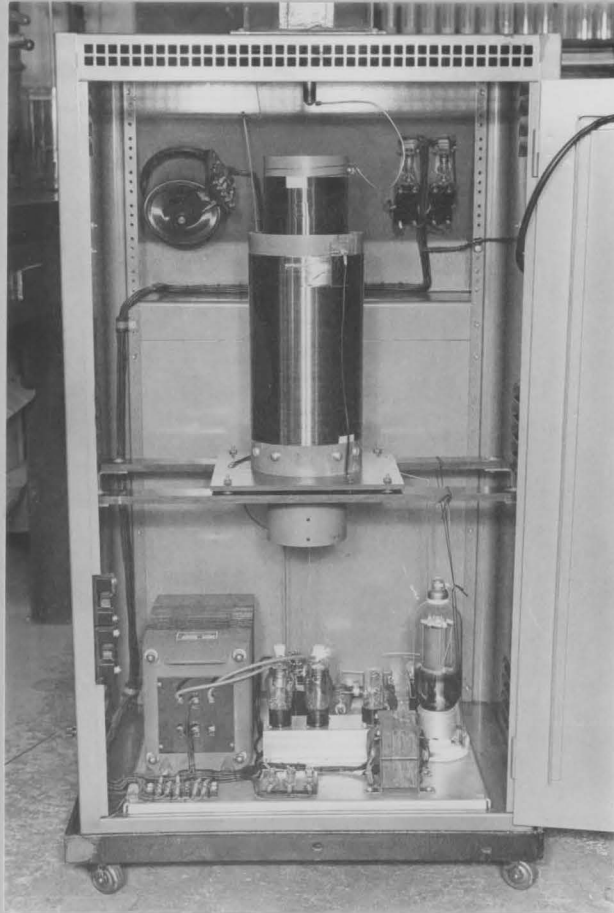
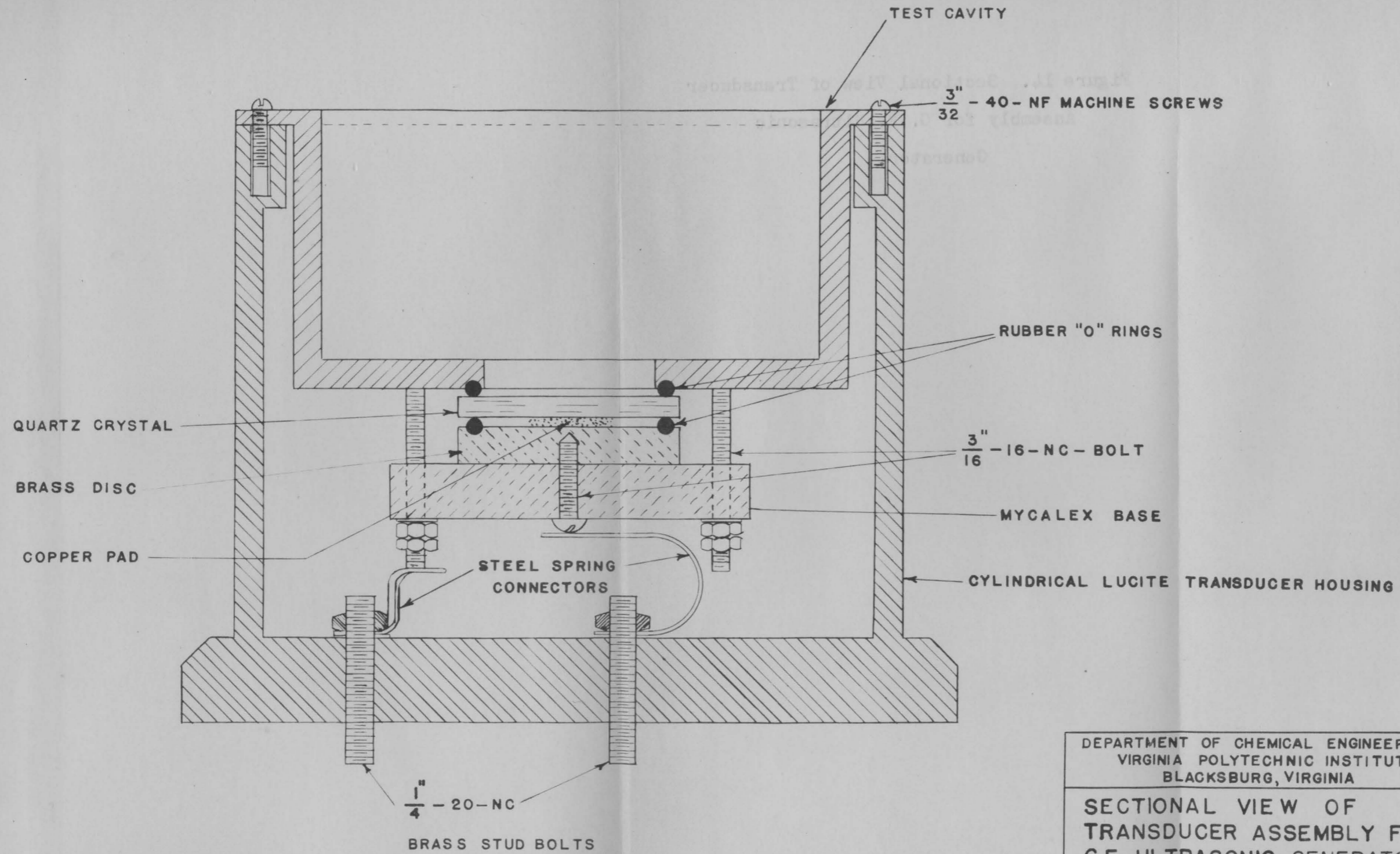


FIGURE 13. REAR VIEW OF GENERAL ELECTRIC
ULTRASONIC GENERATOR SHOWING INSIDE
OF CABINET.



DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA		
SECTIONAL VIEW OF TRANSDUCER ASSEMBLY FOR G.E. ULTRASONIC GENERATOR		
SCALE: FULL	DATE	CASE NO 51
DRAWN BY: CWE	10-3-51	FILE 539
CHECKED BY: <i>RJ</i>	4-29-52	FIGURE 14
APPROVED BY: <i>RJ</i>	7-29-52	SHEET NO

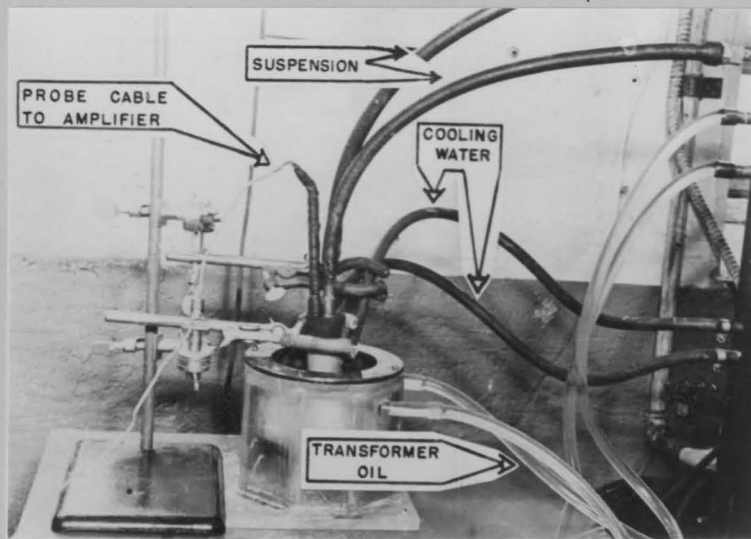


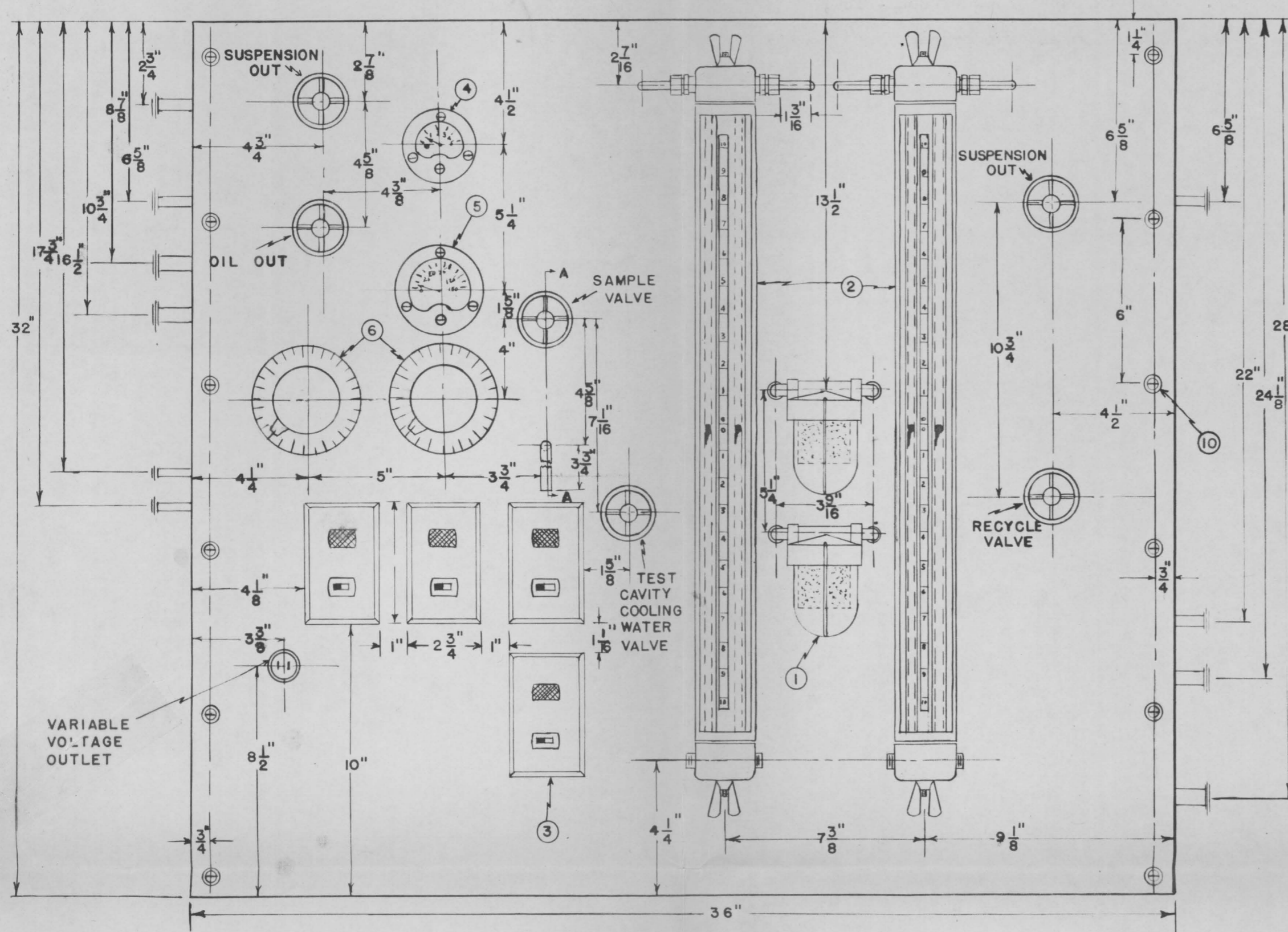
FIGURE 16. CONTINUOUS-FLOW TRANSDUCER HOUSING WITH COAGULATING TUBE IN POSITION.

the cylindrical housing, were used in connection with the constructed housing.

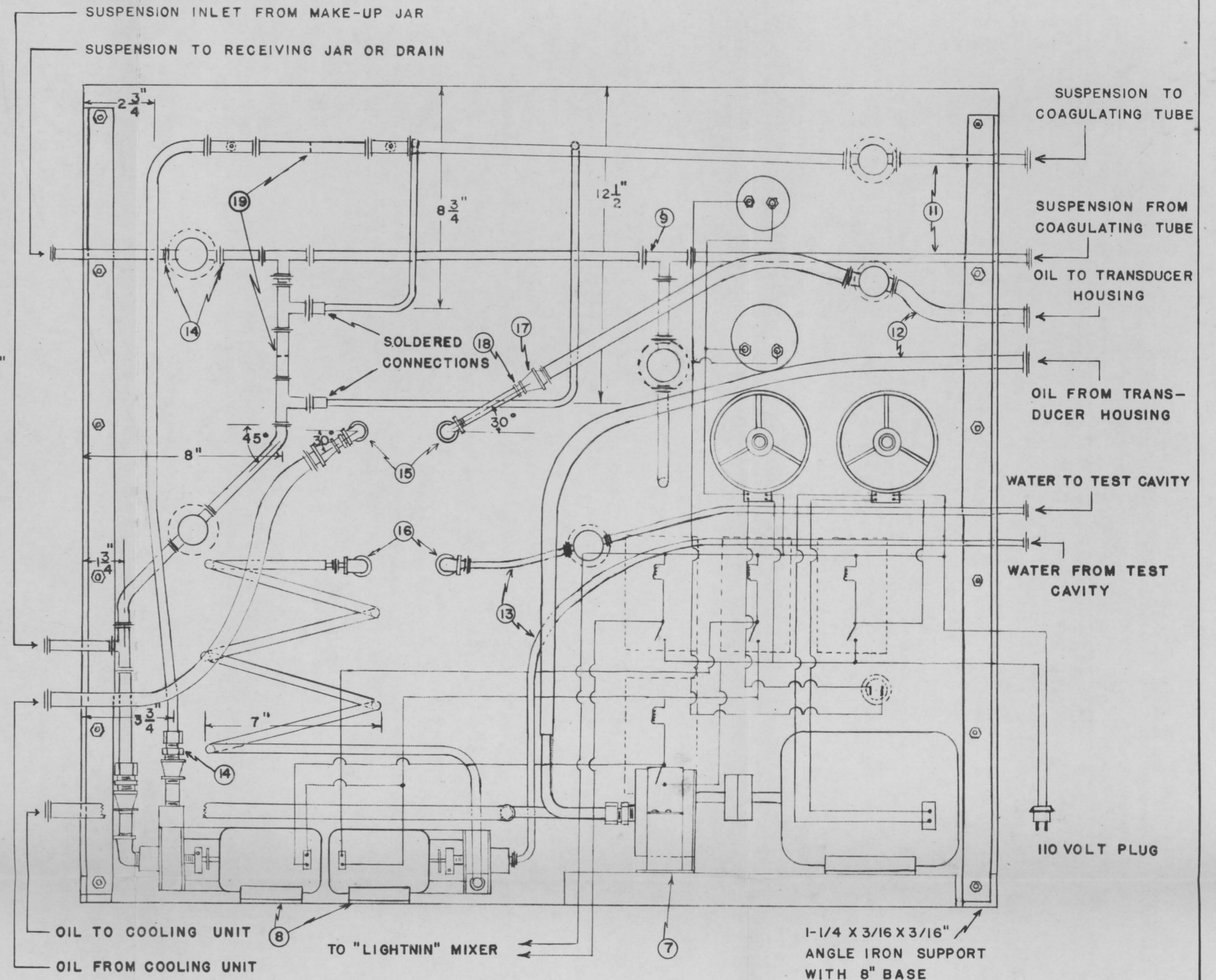
Panel Board. The panel board system used in this investigation comprised the major portion of apparatus for measurement, regulation, and distribution of the ball-clay suspension, transformer oil, and cooling water. Figure 17 is a detailed drawing of the front and rear of the panel board system. Figure 18 is a photograph of the front view of the panel board. Illustrated in Figure 19 is a diagrammatic flow diagram for suspension, transformer oil and cooling water. Figure 20 is an elevation view of the entire experimental equipment. A list of the fittings used on the panel board is given in Table VI. Described below are the various pieces of apparatus which comprised the panel board system.

Ammeter. Radio frequency, type NT-33, 25 cycles to 20 megacycles. Manufactured by Westinghouse Electric Corp., Newark, N. J. Used to measure current to Waring blender.

Angle Iron. Mild steel, 1-1/4 x 1-1/4 x 3/16-inch; two 38-inch lengths required. Obtained from Noland Co., Roanoke, Va. Used to support panel board.



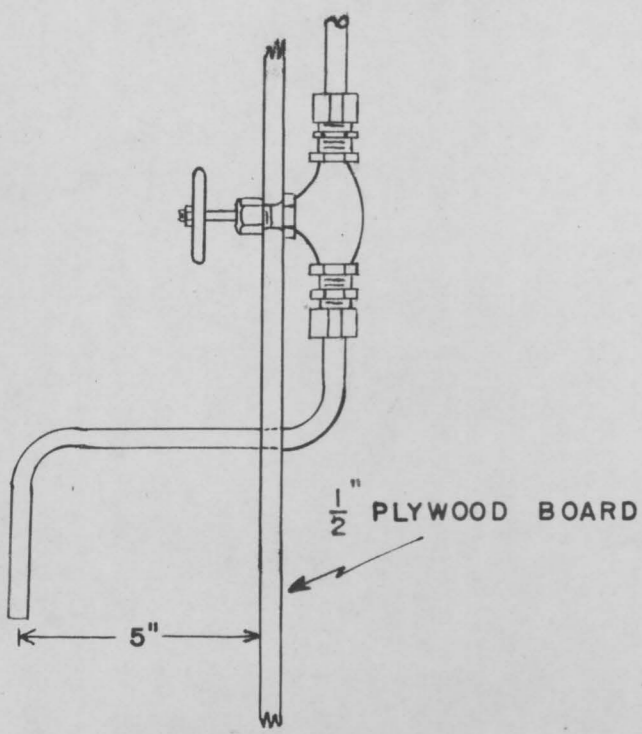
FRONT ELEVATION



REAR ELEVATION

LEGEND:

- | | |
|------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| ① CARTER CERAMIC FILTER | ⑪ 3/8" O.D. X 1/4" I.D. COPPER TUBING |
| ② 20" MERIAM MERCURY MANOMETER | ⑫ 1/2" O.D. X 3/8" I.D. COPPER TUBING |
| ③ PILOT LIGHT SWITCH | ⑬ 1/4" O.D. X 1/8" I.D. COPPER TUBING |
| ④ AMMETER, 0-5 AMPS A.C. | ⑭ BRASS COMPRESSION ADAPTER |
| ⑤ VOLTMETER, 0-150 VOLTS A.C. | ⑮ 1/8"-90° BLACK IRON ELL |
| ⑥ AUTO-TRANSFORMER, 0-130 V., 5 AMPS | ⑯ 1/8"-90° GALVANIZED STEEL ELL |
| ⑦ GEAR PUMP WITH 1/8 HP MOTOR | ⑰ 1/4" X 3/8" BLACK IRON REDUCER |
| ⑧ FISHER MIDGET CIRCULATING PUMP | ⑱ 1/8" X 1/4" BLACK IRON BUSHING |
| ⑨ BRASS COMPRESSION TEE | ⑲ ORIFICE, CONSISTING OF FOUR PUNCHED INDENTATIONS INTO TUBING AROUND COMMON CIRCUMFERENCE |
| ⑩ 1-1/2" X 32 OVAL HEAD MACHINE SCREW, FINISHING WASHER, AND NUT | |



SECTION A-A

DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA		
PANEL LAYOUT FOR CONTINUOUS-FLOW, ULTRASONIC COAGULATION SYSTEM		
SCALE: 3"=1'-0"	DATE: 9-12-51	CASE NO 51
DRAWN BY: C.W.E.	CHECKED BY: [Signature]	FILE 539
APPROVED BY: [Signature]	DATE: 4-27-52	FIGURE 17
		SHEET NO

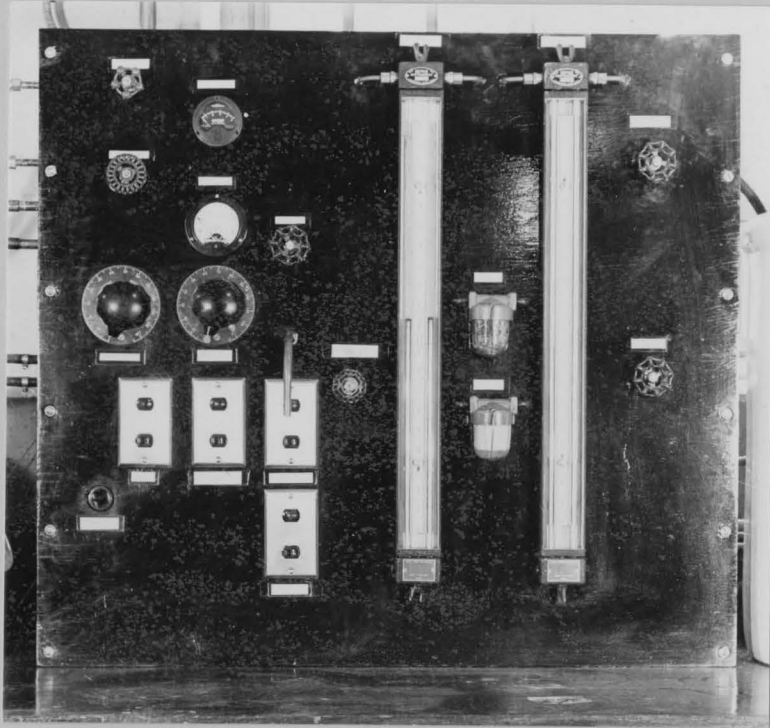
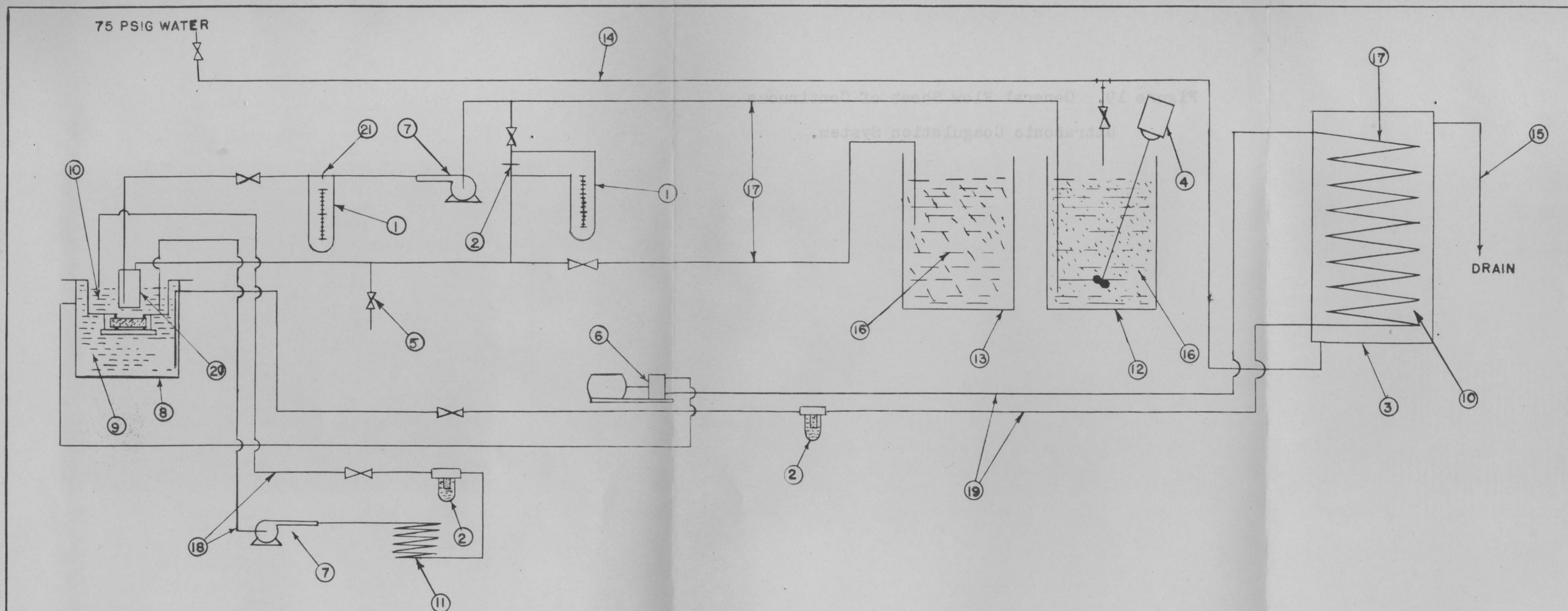


FIGURE 18. FRONT VIEW OF PANEL BOARD.



LEGEND:

- | | | |
|---------------------------------|--------------------------------------|---------------------------------------|
| ① 20" MERIAM MERCURY MANOMETER | ⑧ TRANS DUCER HOUSING | ⑮ 1" BLACK IRON PIPE |
| ② CERAMIC FILTER | ⑨ TRANSFORMER OIL | ⑯ 3/8" AD. X 1/4" I.D. COPPER TUBING |
| ③ COOLING UNIT | ⑩ WATER | ⑰ 1/4" O.D. X 1/8" I.D. COPPER TUBING |
| ④ LIGHTNIN MIXER MODEL CV2 | ⑪ AIR COOLING COIL - ⑰ | ⑱ 1/2" O.D. X 3/8" I.D. COPPER TUBING |
| ⑤ SAMPLE VALVE | ⑫ 15 GALLON SUSPENSION MAKE-UP JAR | ⑳ COAGULATING TUBE |
| ⑥ GEAR PUMP WITH 1/8 H.P. MOTOR | ⑬ 20 GALLON SUSPENSION RECEIVING JAR | ㉑ ORIFICE |
| ⑦ CENTRIFUGAL PUMP | ⑭ 1/2" GALVANIZED PIPE | |

DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG VIRGINIA		
GENERAL FLOW SHEET OF CONTINUOUS ULTRASONIC COAGULATION SYSTEM		
SCALE: NONE	DATE	CASE NO 51
DRAWN BY: C.W.E.	9-11-51	FILE 539
CHECKED BY: <i>D.T.</i>	4-29-52	FIGURE 19
APPROVED BY: <i>A.J.</i>	4-29-52	SHEET NO



FIGURE 20. VIEW OF EXPERIMENTAL EQUIPMENT ARRANGEMENT.

TABLE VI

Fittings Used in Panel Board System

Amount	Name	Description	Supplier
2	Reducer	1/2 x 1/4-inch black iron	Noland Co., Roanoke, Va.
2	Bushing	1/4 x 1/8-inch galvanized steel	Noland Co., Roanoke, Va.
3	Nipple	1/8-inch by 3-inch, black iron	Noland Co., Roanoke, Va.
2	90° ell	1/8-inch, black iron	Noland Co., Roanoke, Va.
2	Street ell	1/8-inch, black iron	Noland Co., Roanoke, Va.
1	Close nipple	1/8-inch, black iron	Noland Co., Roanoke, Va.
2	Nipple	1/8-inch by 2-inch, black iron	Noland Co., Roanoke, Va.
2	90° ell	1/8-inch, galvanized steel	Noland Co., Roanoke, Va.
2	Nipple	1/4-inch by 2-inch, galvanized steel	Noland Co., Roanoke, Va.
2	Reducer	3/8-inch x 1/4-inch, galvanized steel	Noland Co., Roanoke, Va.
1	Street ell	1/4-inch, galvanized steel	Noland Co., Roanoke, Va.
10	Adapter	1/4-inch, brass compression	W. B. Clements Co., Roanoke, Va.
14	Adapter	3/8-inch, brass compression	W. B. Clements Co., Roanoke, Va.
6	Adapter	1/2-inch, brass compression	W. B. Clements Co., Roanoke, Va.
7	Tee	3/8-inch, brass compression	W. B. Clements Co., Roanoke, Va.
1	Valve	3/8-inch, needle	Noland Co., Roanoke, Va.
2	Valve	1/2-inch, globe	Noland Co., Roanoke, Va.
3	Valve	3/8-inch, globe	Noland Co., Roanoke, Va.
1	Valve,	1/4-inch, gate	Noland Co., Roanoke, Va.

Auto-Transformers. 0-135 volts, 5 amperes; two required. Manufactured by Superior Electric Co., Bristol, Conn.; distributed by Fisher Scientific Co., Silver Spring, Md. Used to control speeds of Waring blender and transformer oil gear pump motors.

Copper Tubing. 1/4-inch O. D. by 1/8-inch I. D., annealed; 7-1/2 feet required. Manufactured by Revere Copper and Brass Co., Inc., New York, N. Y.; distributed by W. B. Clements Co., Roanoke, Va. Used in construction of cooling water lines for transducer cavity.

Copper Tubing. 3/8-inch O. D. by 1/4-inch I. D., annealed; 18 feet required. Manufactured by Revere Copper and Brass Co., Inc., New York, N. Y.; distributed by W. B. Clements Co., Roanoke, Va. Used in construction of suspension flow lines.

Copper Tubing. 1/2-inch O. D. by 3/8-inch I. D., annealed; 14 feet required. Manufactured by Revere Copper and Brass Co., Inc., New York, N. Y.; distributed to W. B. Clements Co., Roanoke, Va. Used in construction of transformer oil lines to cooling unit.

Filters. Ceramic, 1/8-inch fittings, catalogue No F760s; two required. Manufactured by Carter Carburetor Corp., St. Louis, Mo. Used to filter transformer oil and cooling water while flowing.

Machine Screws. Oval head, No 10-32 x 1-1/2-inch, with hex-nuts and finishing washers; twelve required. Obtained from Lucas Motor Co., Blacksburg, Va. Used to fasten panel board to supporting angle irons.

Manometers. Double head, U-type, cleanout, 20-inch range; two required. Obtained from Meriam Instrument Co., Cleveland, Ohio. Used to measure pressure drop across flow rate and recycle orifices.

Plug. Male, standard light fixture. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used in connection with variable voltage outlet for Waring blender.

Plywood. 32 x 36 x 1/2-inch. Obtained from New River Lumber Co., Blacksburg, Va. Used as panel board.

Pump. Gear, with 1/8-horsepower motor, assembled on angle iron base in one unit. Obtained from the Department of Electrical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used to pump transformer oil to and from cooling unit.

Pumps. Circulating, monel metal, model B, catalogue No 13-874-93; two required. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for pumping suspension and cooling water.

Socket. Standard light fixture, 115 volts, 15 amperes. Obtained from Blacksburg Hardware Co., Inc., Blacksburg, Va. Used for variable voltage outlet for Waring blender.

Switches. Tumbler, catalogue No GT-1391; plate, wall, two opening, P and S Chrome-X, catalogue No GT-1791-B; pilot light and bracket, catalogue No GT-1377; four each required. Obtained from General Electric Supply Corp., Roanoke, Va. Used on motors in experimental equipment.

Voltmeter. AC, 0-150 volts, model 332-JP.

Manufactured by Triplet Electric Instrument Co., Bluffton, Ohio. Used to measure voltage to Waring blender.

Wire. No 14, enameled copper. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used for wiring of switches to motors and power supply.

Suspension Preparation Equipment. The equipment required for the preparation of a four per cent by weight ball-clay hydrosol consisted essentially of a 15 gallon stoneware jar equipped with a "Lightnin" mixer, overhead water outlet, and a stick graduated for 96 pounds of water, clamped to the jar. A 50-mesh screen was used to remove + 50 mesh particles, by dry sieving, from the ball-clay before initial dispersion. A Waring blender, equipped with a "Micro" head, was used to disperse the clay while in continuous flow, after it had been initially dispersed with the "Lightnin" mixer. A 325-mesh screen was used to remove + 325 mesh particles, by wet sieving, from the suspension while in continuous flow through the blender. Figure 21 is a plan view of the suspension make-up jar and accessories. Figure 22 is

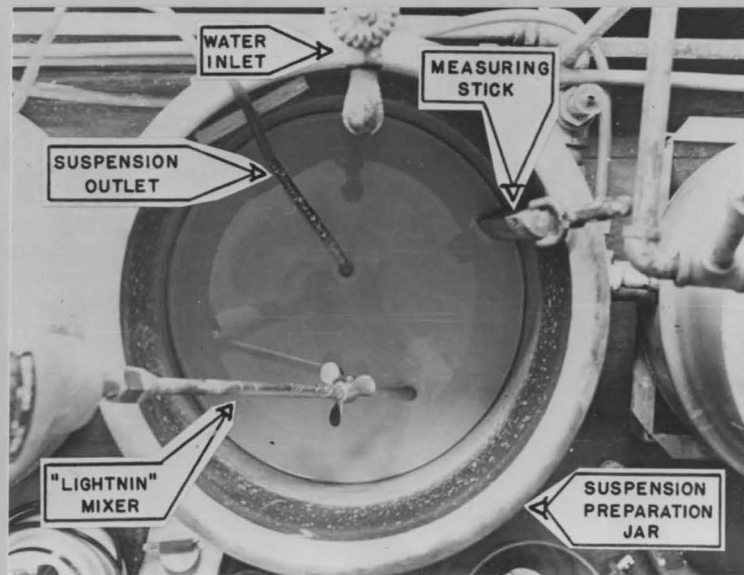
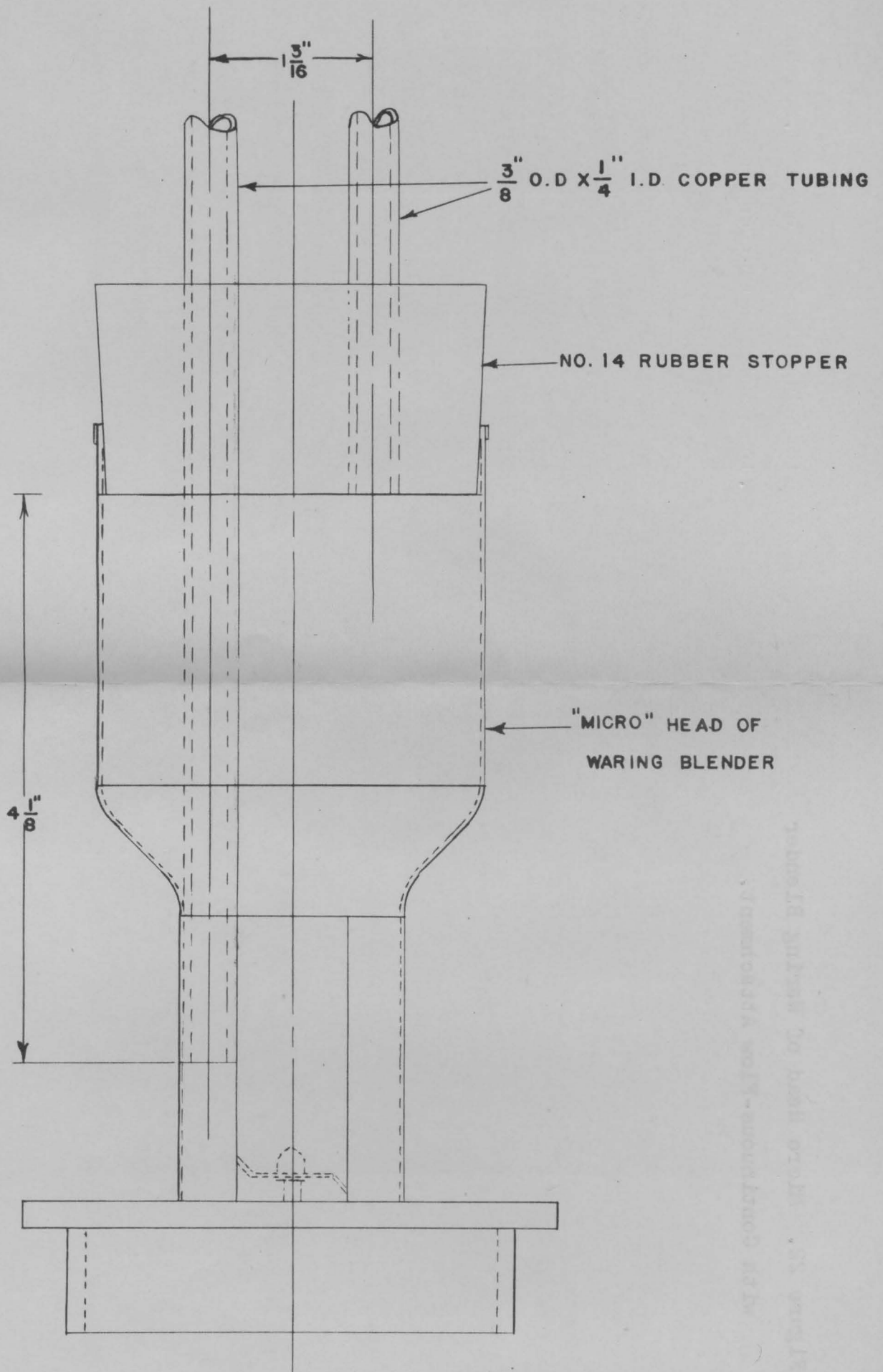


FIGURE 21. PLAN VIEW OF SUSPENSION MAKE-UP JAR.



DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA		
MICRO HEAD OF WARING BLENDER WITH CONTINUOUS-FLOW ATTACHMENT		
SCALE: FULL	DATE	CASE NO 51
DRAWN BY: CWE	10-4-51	FILE 539
CHECKED BY: DJ	4-29-52	FIGURE 22
APPROVED BY: DJ	4-29-52	SHEET NO

a drawing of the adaption of the "Micro" head of the Waring blender for continuous flow. Described below is the apparatus comprising the suspension preparation equipment.

Clamps. Brass, extension, wide range V-jar, catalogue No 18-702; two required. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to hold graduating stick and 325 mesh screen to suspension make-up jar.

Gyratory Riddle. Combs type, equipped with 1/6-horsepower, 110-volt, single-phase motor, 860 rpm, model 5KH65ABO4, type KH. Manufactured by Great Western Manufacturing Co., Leavenworth, Kansas. Used for screening of ball-clay.

Mixer. "Lightnin", with built in 1/8 horsepower, single-phase motor, serial No 500993Z, model No CV2. Manufactured by Mixing Equipment Co., Inc., Rochester, N. Y. Used to disperse ball-clay in water.

Rubber Tubing. Gum rubber, 5/8-inch O. D. by 5/16-inch I. D.; three feet required. Obtained from the Department of Chemistry, Virginia

Polytechnic Institute, Blacksburg, Va. Used for transporting ball-clay suspension from panel board lines to "Micro" head of Waring blender.

Scale. 115 pound capacity, model 31-0851-FB, serial No 1788. Manufactured by Toledo Scale Co., Toledo, Ohio. Used for weighing of ball-clay for suspension preparation.

Sieve. Tyler standard, 50 mesh. Manufactured by W. S. Tyler Co., Cleveland, Ohio. Used to remove +50 mesh particles from ball-clay by dry sieving.

Sieve. Tyler standard, 325 mesh. Manufactured by W. S. Tyler Co., Cleveland, Ohio. Used to remove +325 mesh particles from ball-clay by wet sieving.

Stick. Pine, 20 inches long, graduated for 96 pounds of water and clamped to suspension make-up jar. Obtained from New River Lumber Co., Blacksburg, Va. Used for graduation of suspension make-up jar.

Stoneware Jar. 15 gallon capacity. Obtained from Blacksburg Hardware Co., Inc., Blacksburg, Va. Used to contain ball-clay suspension during preparation and use.

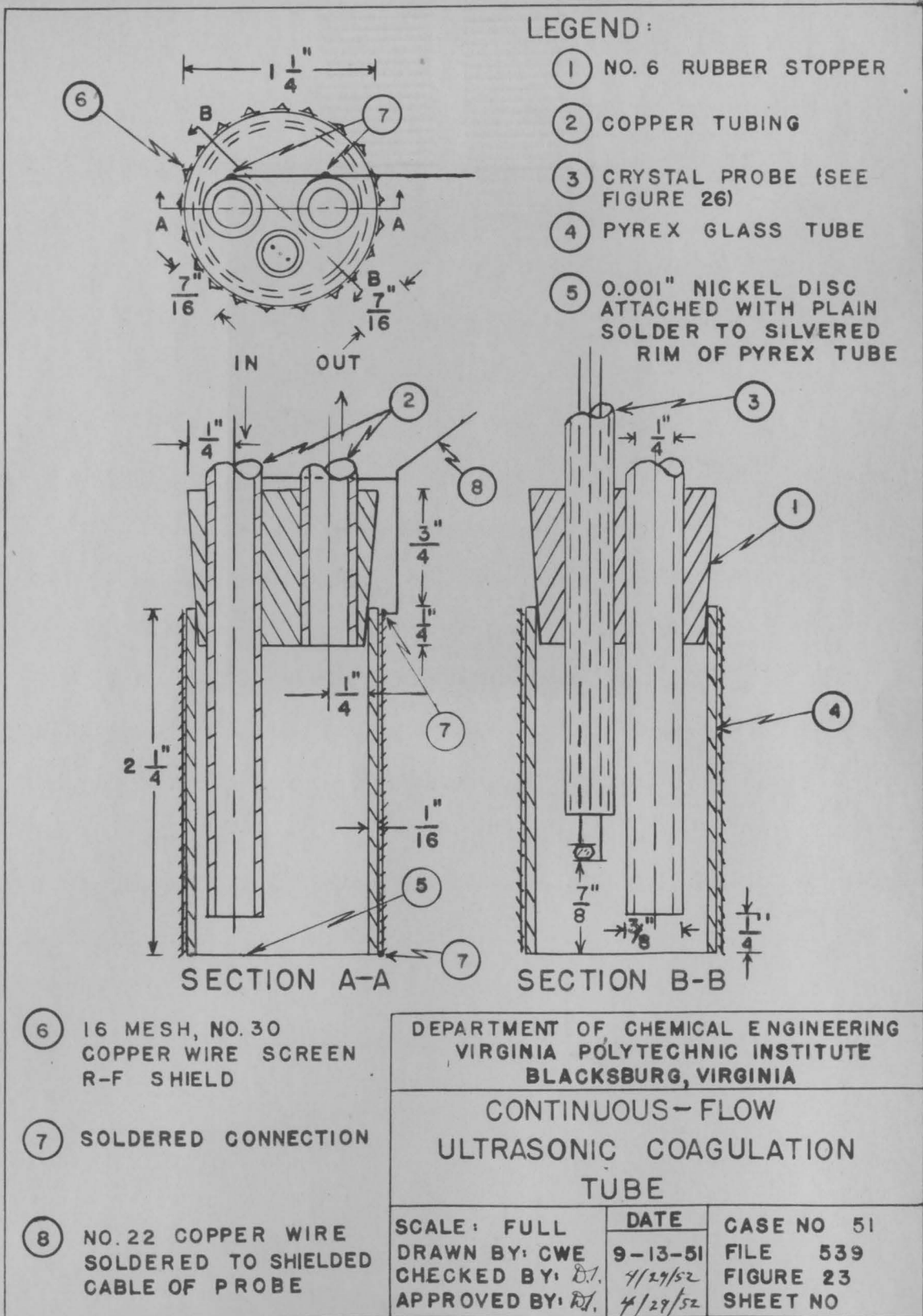
Stopper. Rubber, No 14. Obtained from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Va. Used in connection with continuous-flow attachment for "Micro" head of Waring blender.

Waring Blender. 115 volts, 60 cycle, 3 amperes, catalogue No 700, with "Micro" head. Obtained from Waring Products Corp., New York, N. Y. Used to disperse ball-clay in water and for continuous comparison mechanical coagulation tests.

Oil Cooling Unit. The transformer oil cooling unit consisted of a 15 gallon steel drum containing a coil of 40 feet of 3/8-inch O. D. by 1/4-inch I. D. copper tubing. Tap water entered the unit at the bottom and drained off the top. The transformer oil was circulated through the copper coil, entering at the top and leaving at the bottom. Thermometer wells were present in the inlet and outlet lines of both the oil and water. The cooling unit was constructed in the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va.

Coagulating Tube. A descriptive drawing of the coagulating tube designed and constructed for this

investigation is shown in Figure 23. Figure 24 shows the tube, containing a four per cent by weight ball-clay hydrosol, being insonated at 300 kilocycles. Figure 25 shows the insert for the top of the coagulating tube. Figure 16, page 107, is a view of the coagulating tube in position for experimental tests. The only special technique used in the construction of this tube was the bonding of a 0.001-inch nickel disc bottom to the pyrex coagulating tube. This was accomplished by first applying chloroplatinic acid to a ground rim of the tube and then reducing this acid to metallic platinum in a blast burner flame. By keeping the rim of the tube at red heat for about two minutes after the metallic platinum had formed, it was possible to fuse this platinum into the glass. A 0.001-inch nickel disc was cut to the same outside diameter as the pyrex tube and tinned with solder around the circumference, approximately 1/8-inch from the periphery. Liquid "Tri-Flux" was applied to the platinized glass rim and tinned nickel surfaces and the nickel disc was placed in position on the tube with the tinned and platinized surfaces touching. Application of heat from a soldering iron, applied around the rim of the



LEGEND:

- ① NO. 6 RUBBER STOPPER
- ② COPPER TUBING
- ③ CRYSTAL PROBE (SEE FIGURE 26)
- ④ PYREX GLASS TUBE
- ⑤ 0.001" NICKEL DISC ATTACHED WITH PLAIN SOLDER TO SILVERED RIM OF PYREX TUBE

- ⑥ 16 MESH, NO. 30 COPPER WIRE SCREEN R-F SHIELD
- ⑦ SOLDERED CONNECTION
- ⑧ NO. 22 COPPER WIRE SOLDERED TO SHIELDED CABLE OF PROBE

DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA		
CONTINUOUS-FLOW ULTRASONIC COAGULATION TUBE		
SCALE: FULL	DATE	CASE NO 51
DRAWN BY: CWE	9-13-51	FILE 539
CHECKED BY: <i>D.J.</i>	7/29/52	FIGURE 23
APPROVED BY: <i>D.J.</i>	4/29/52	SHEET NO

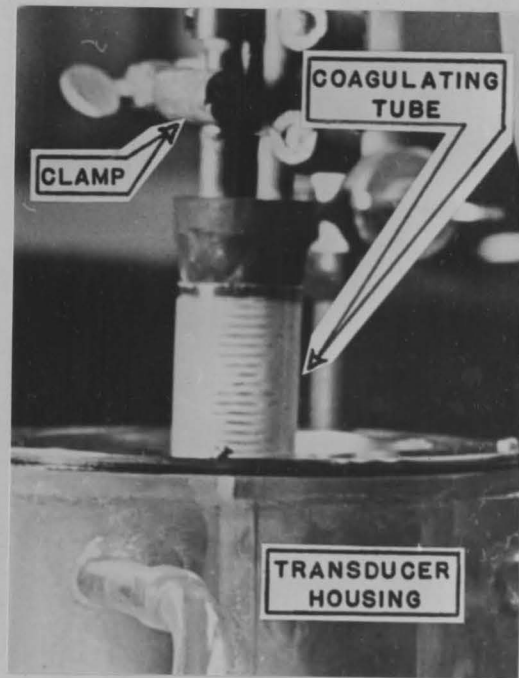


FIGURE 24. COAGULATING CHAMBER CONTAINING
FOUR PER CENT BY WEIGHT TENNESSEE NO 9
BALL-CLAY HYDROSOL BEING INSONATED
AT 300 KILOCYCLES.

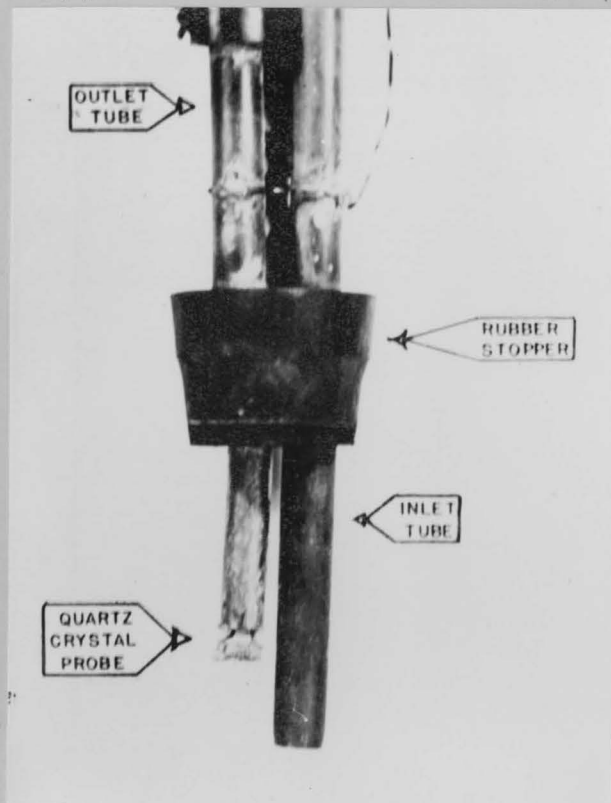


FIGURE 25. INSERT FOR TOP OF COAGULATING CHAMBER.

nickel disc, caused fusion and bonding of the solder to the platinized glass.

Crystal Probe Assembly. A descriptive drawing of the crystal probe used in this investigation is shown in Figure 26. The quartz crystal employed was obtained from a hill outside of Blacksburg, Virginia. Photographs of the top and bottom faces of this crystal are shown in Figures 27 and 28, respectively. A circuit diagram with a list of parts for the amplifier used in connection with the quartz crystal probe is shown in Figure 29. Figure 30 is a photograph of the amplifier and voltmeter used to increase and measure the output of the probe crystal.

Equipment for Batch Ultrasonic Coagulation Tests.

The chamber used for the batch insonation of a ball-clay hydrosol consisted of a 0.001-inch nickel bottom, pyrex glass tube. This tube was 12 inches high with an outside diameter of 1-1/4 inches and a wall thickness of 1/16-inch.

Equipment for Continuous Mechanical Coagulation Tests. The equipment for the continuous mechanical coagulation tests consisted of a Waring blender equipped with a "Micro" head and continuous flow

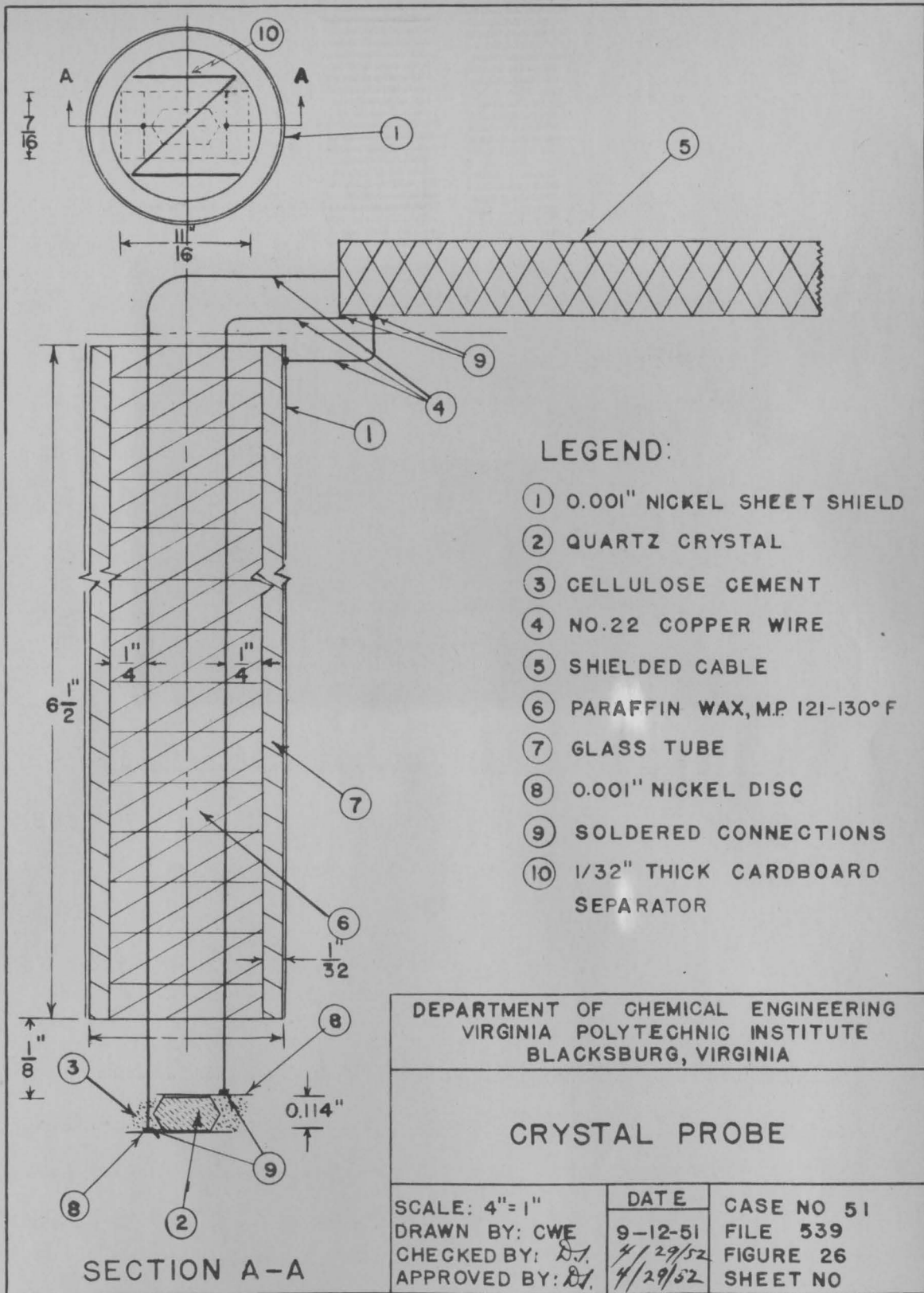
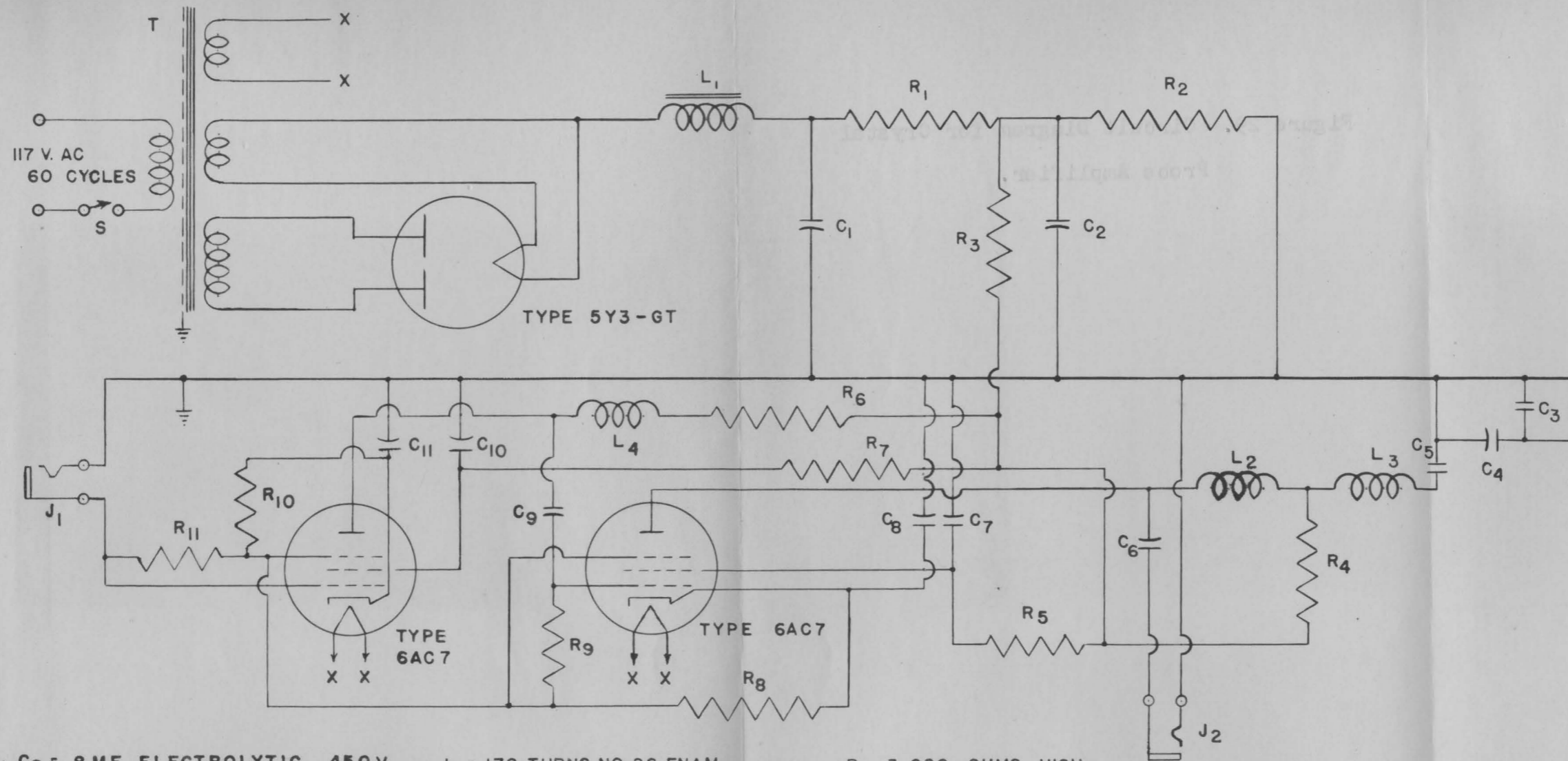




FIGURE 27. TOP FACE OF QUARTZ PROBE CRYSTAL.



FIGURE 28. BOTTOM FACE OF QUARTZ PROBE CRYSTAL.



$C_1, C_2 = 8 \text{ MF, ELECTROLYTIC, 450 V.}$
 $C_3 = 20 \text{ MF, ELECTROLYTIC, 350 V.}$
 $C_4, C_5 = 0.5 \text{ MF, PAPER, 400 V.}$
 $C_6 = 0.1 \text{ MF, MICA, 400 V.}$
 $C_7 = 0.5 \text{ MF, PAPER, 400 V.}$
 $C_8 = 20 \text{ MF, ELECTROLYTIC, 200 V.}$
 $C_9 = 0.1 \text{ MF, PAPER, 600 V.}$
 $C_{10} = 0.1 \text{ MF, MICA, 400 V.}$
 $C_{11} = 0.5 \text{ MF, PAPER, 400 V.}$
 $J_1 = \text{JACK FOR CRYSTAL PROBE}$
 $J_2 = \text{JACK FOR VOLTMETER}$
 $L_1 = \text{FILTER CHOKE, 1 HENRY}$

$L_2 = 178 \text{ TURNS NO. 26 ENAM.}$
 CLOSE WOUND ON 1/2" SLUG
 TUNED FORM
 $L_3 = 118 \text{ TURNS NO. 26 ENAM.}$
 CLOSE WOUND ON 1/2" SLUG
 TUNED FORM
 $L_4 = 56 \text{ TURNS NO. 26 ENAM.}$
 CLOSE WOUND ON 1/2" SLUG
 TUNED FORM
 $R_1 = 450 \text{ OHMS, 100 WATTS}$
 $R_2 = 30,000 \text{ OHMS, HIGH-}$
 WATTAGE

$R_3 = 3,000 \text{ OHMS, HIGH-}$
 WATTAGE
 $R_4 = 5,600 \text{ OHMS, 1 WATT}$
 $R_5 = 22,000 \text{ OHMS, 1 WATT}$
 $R_6 = 1,800 \text{ OHMS, 1 WATT}$
 $R_7 = 56,000 \text{ OHMS, 1 WATT}$
 $R_8 = 78 \text{ OHMS, 1 WATT}$
 $R_9 = 270,000 \text{ OHMS, 1 WATT}$
 $R_{10} = 220 \text{ OHMS, 1 WATT}$
 $R_{11} = 1 \text{ MEGOHM, 0.5 WATT}$
 $S = \text{SWITCH, DOUBLE-POLE,}$
 DOUBLE-THROW
 $T = \text{POWER TRANSFORMER,}$
 375-0-375 VOLTS, RMS, 150 MA.

DEPARTMENT OF CHEMICAL ENGINEERING
 VIRGINIA POLYTECHNIC INSTITUTE
 BLACKSBURG, VIRGINIA

CIRCUIT DIAGRAM FOR
 CRYSTAL PROBE AMPLIFIER

SCALE: NONE	DATE	CASE NO 51
DRAWN BY: CWE	9-12-51	FILE 539
CHECKED BY: <i>[Signature]</i>	4-29-52	FIGURE 29
APPROVED BY: <i>[Signature]</i>	4-29-52	SHEET NO

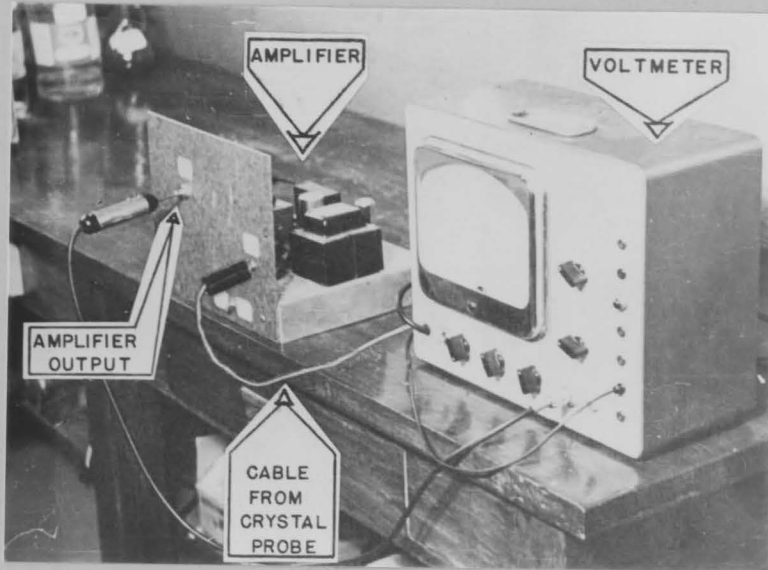


FIGURE 30. AMPLIFIER AND VOLTMETER ASSEMBLY FOR PROBE VOLTAGE MEASUREMENTS.

adaptation as illustrated in Figure 22, page 119.

The blender motor was connected to a variable voltage outlet so that the motor speed could be varied. Figure 31 shows the blender in position for experimental control tests.

Equipment for Batch Mechanical Coagulation Tests.

The equipment used for the batch mechanical coagulation tests consisted of a variable speed stirrer motor, obtained from Fisher Scientific Co., Silver Spring, Maryland, clamped to a tripod base, 24-inch ring stand. Inserted in the stirrer motor was a 16-inch long impeller with four blades at an angle of 10 degrees and covering a circle of diameter two and one-half inches. A nine and one-quarter inch high by six and one-quarter inch diameter glass jar, graduated to 15 centimeters in height, was used to contain the suspension undergoing testing. The 16-inch impeller, used for mechanical agitation, was centered in the glass jar, three inches from the bottom. Figure 32 shows the equipment arrangement for the batch control tests.

Equipment for Measurement of Settling Rates. For the measurement of settling rates of the test samples, 24 low form, 100 milliliter Nessler tubes, obtained

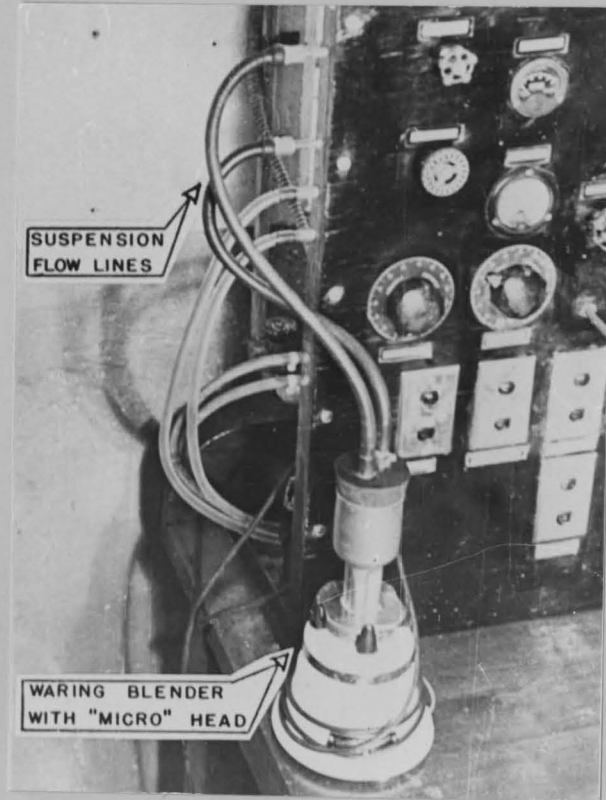


FIGURE 31. EQUIPMENT ARRANGEMENT FOR
CONTINUOUS MECHANICAL COAGULATION
TESTS.

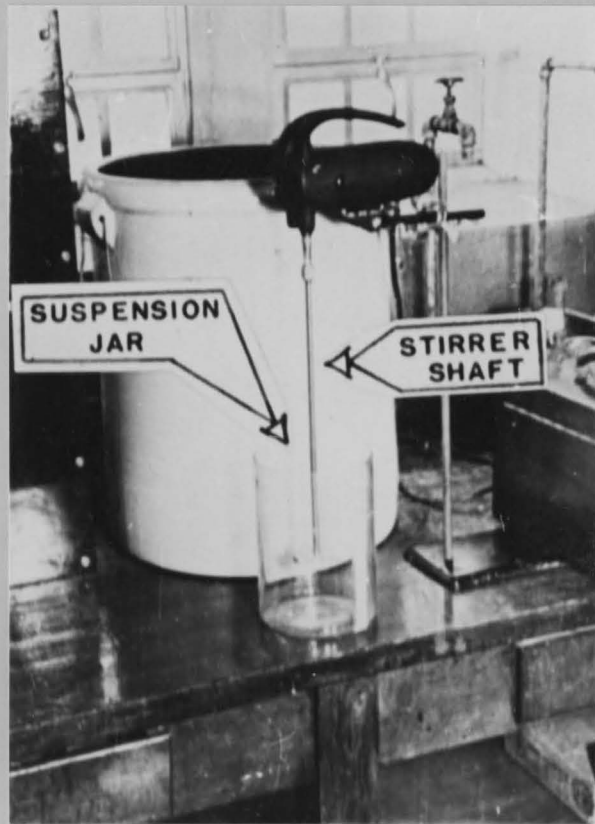


FIGURE 32. EQUIPMENT ARRANGEMENT FOR BATCH MECHANICAL COAGULATION TESTS.

from Fisher Scientific Co., Silver Spring, Maryland, were used. These tubes were graduated at five centimeter intervals and up to fifteen centimeters in height by heating and fusing marks made with ceramic marking ink into the glass. The tubes were placed in a low form Nessler tube rack for settling tests. A millimeter scale was used to measure the height of the settling suspension samples between the five centimeter graduations. Figure 33 shows the Nessler tubes containing some settling suspension samples.

Auxiliary Equipment. Equipment not previously discussed and that of an auxiliary nature, is described below:

Cable. Shielded, No 26 axial wire. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used as a lead from quartz crystal probe to amplification unit.

Clamp Holders. Universal, castaloy, catalogue No 18-822; three required. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to hold extension clamps to ring stand.

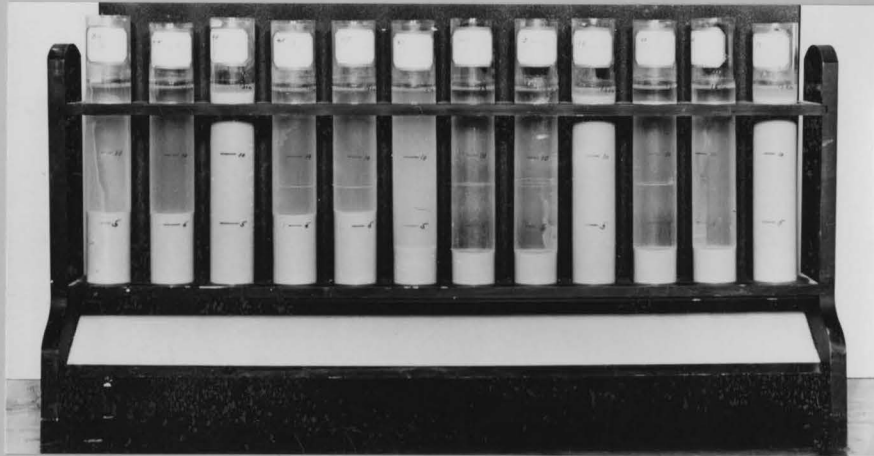


FIGURE 33. GRADUATED NESSLER TUBES CONTAINING TEST SAMPLES UNDERGOING SETTLING.

Clamps. Brass, 1/2, 5/8, and 3/4-inch sizes, tubing clamps. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used to connect rubber and tygon tubing to copper tubing lines.

Clamps. Brass, extension, wide range V-jar, catalogue No 18-702, three required. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to hold coagulating tube and water cooling lines in transducer cavity.

Extension Cord. 10 amperes - 250 volts, 15 amperes - 125 volts, 31/32-inch diameter female plug. Obtained from the Department of Electrical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used to connect General Electric ultrasonic generator to power supply.

pH Meter. Coleman, glass electrode, model No 3D, instrument No 2331. Manufactured by Coleman Electric Co., Inc., Maywood, Ill. Used for pH measurements of clay samples.

Ring Stand. Rectangular, cast iron base, six by nine inches, with copper plated steel rod, 24 inches long. Obtained from Fisher Scientific

Co., Silver Spring, Md. Used to support clamps for coagulating tube and cooling water lines.

Rubber Tubing. Gum rubber, 5/8-inch O. D. by 5/16-inch I. D. Obtained from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Va. Used for transporting clay suspension from panel board lines to coagulating tube and "Micro" head of Waring blender.

Signal Generator. 9.5 kilocycle to 30 megacycle range, type 605-B, serial No 1454. Manufactured by General Radio Co., Cambridge, Mass.; obtained from the Department of Electrical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used as source of radio-frequency energy for calibration of quartz crystal probe amplifier.

Stoneware Jar. 20-gallon capacity. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used to receive ball-clay suspension after flow through testing apparatus.

Thermometers. Glass, mercury indicating fluid, 32 - 212 °F range with 2 degree subdivisions; two required. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for measurements of suspension and room temperatures.

Thermometers. Weston, 30 - 150 °F range with 2 degree subdivisions; four required. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for measurement of oil and water temperature in and out of cooling unit.

Timer. Electric, 115 volts, 5 watts, 60 cycle, readings in minutes and hundredths of a minute. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure the settling time of test samples.

Tygon Tubing. 1/2-inch O. D. by 3/8-inch I. D.; six feet required. Obtained from Julius Blum and Co., Inc., New York, N. Y. Used to connect oil lines on panel board to transducer housing for continuous transformer oil flow.

Voltmeter. Hickok, vacuum tube, model 209A, serial No 6-13232. Manufactured by Hickok Electric Instrument Co., Cleveland, Ohio; obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Va. Used to measure amplified voltage from crystal probe.

Voltmeter. Weston, vacuum tube, type 1800-A,
instrument serial No 799, meter model No 861.
Instrument manufactured by General Radio Co.,
Cambridge, Mass.; meter manufactured by Weston
Electric Instrument Corp., Newark, N. J.; obtained
from the Department of Electrical Engineering,
Virginia Polytechnic Institute, Blacksburg, Va.
Used to calibrate crystal probe amplifier.

Method of Procedure

The method of procedure by which the experimental phase of this investigation was pursued is considered under the headings of literature review, records and reports, design and construction, exploratory investigations, and plan of evaluation.

Literature Review. A review of the literature was made on published information pertinent to this investigation. The procedure consisted of preparing a separate card for each abstract that was considered appropriate. Main attention was focused on articles dealing with coagulation, ultrasonics, and clay hydrosols. Photographic copies were made on 35 millimeter film of articles of considerable interest, particularly when a large number of charts or figures were contained in the article. Also, Ozalid copies were made from carbon copies of translated German articles on acoustic coagulation which were available on the Virginia Polytechnic Institute campus. Furthermore, a list of domestic and foreign patents on ultrasonic processes for the period 1929 to 1950 were obtained from the United States Patent Office in Washington, D. C.

Records and Reports. All original data and notes for this investigation were kept in bound notebooks with consecutively numbered pages. Separate sheets of drawings and data tables were attached to the notebook pages by means of drafting tape. Weekly reports were submitted to Dr. Dudley Thompson containing the progress of the investigation. Furthermore, quarterly progress reports were prepared for submission to the General Electric Company.

Design and Construction. Consideration of the facilities necessary for the evaluation of a continuous-flow, ultrasonic coagulation unit, was prerequisite to a design drawing and construction of the equipment. Those facilities decided upon were: (1) equipment for preparing a ball-clay suspension; (2) a panel board on which valves, tubing, switches, and meters could be mounted; (3) a pumping system to keep the ball-clay suspension in continuous flow; (4) a coagulating tube, placed in the ultrasonic field of the generator, through which the suspension could flow continuously; (5) a crystal probe for measurement of relative pressure amplitudes of the ultrasonic waves in the coagulating tube; (6) a system for obtaining samples of the suspension

while in continuous flow; (7) two separate cooling systems: one for the transformer oil in the transducer housing of the ultrasonic generator and the other for the water in the test cavity of the transducer housing; (8) a system for subjecting a ball-clay suspension, in continuous flow, to mechanical agitation for comparison coagulation tests; (9) a system for batch mechanical agitation of a ball-clay suspension for comparison coagulation tests; and (10) a system for batch ultrasonic treatment of a ball-clay suspension for comparison coagulation tests.

Suspension Preparation Equipment. Since the suspension undergoing testing would be in continuous flow, it was necessary to prepare a large enough amount to last for at least one series of tests, with an additional amount available as a safety factor. Accordingly, it was decided to prepare 100 pounds of the suspension at a time, so a 15 gallon stoneware jar was considered adequate. A valve was installed above the jar, on an extension from the water line, in order to enable ready availability of the aqueous suspension medium. A 1/8-horsepower "Lightnin" mixer, style

131941, was attached to the jar, and operated at a speed of 900 revolutions per minute in order to keep the suspension well dispersed during the period of testing, as well as to initially disperse the ball-clay in the water. Figure 21, page 118, is a plan view of the suspension make-up jar.

In order to insure complete dispersion of the mixture of ball-clay and water, it was passed continuously through the "Micro" head of a Waring blender, operating on 120 volts and at a speed of 17,550 revolutions per minute, for a period of 30 minutes, using a 5.2 pound per minute flow rate for a four per cent by weight ball-clay hydrosol. This continuous dispersion was in addition to 15 minutes of initial dispersion with the "Lightnin" mixer, the first six minutes of which comprised the time of addition of the ball-clay to the water. Figure 22, page 119, is a drawing of the "Micro" head of the Waring blender with continuous-flow attachment.

A 325-mesh screen was placed under the discharge of the ball-clay from the Waring blender

before it was returned to the make-up jar. This screen was used to remove sand and undispersed ball-clay particles over 325 mesh so as to obtain a more uniform suspension which would be known to be under 325 mesh or 38 microns.

Panel Board. A panel board was used to support the majority of apparatus required for control, measurement, and regulation of the flow of ball-clay hydrosol, transformer oil, and transducer cavity cooling water. A one-half-inch thick plywood board, having the dimensions of 36 by 32 inches, was considered adequate. It was mounted on a nine-foot long by 29-inch wide by 33-inch high table by means of two 1-1/4 x 3/16 x 3/16-inch angle irons and 12 machine bolts. Figure 17, page 109, is a detailed drawing of the front and rear of the panel board system. On the panel board were attached valves for: (1) regulation of suspension flow; (2) regulation of suspension recycle; (3) taking of samples of suspension while in continuous flow; (4) regulation of flow of cooling water for transducer cavity; and (5) regulation of transformer oil flow for transducer housing. Two Meriam

manometers were mounted on the panel board for measurement of pressure drop across orifices in the suspension flow and recycle lines. Four switches were also mounted, and used for:

- (1) oil pump motor;
- (2) suspension pump motor;
- (3) cooling water pump motor; and
- (4) suspension make-up stirrer motor.

Two auto-transformers were mounted to regulate the voltage and consequently the speed of the oil pump and Waring blender motors. Copper tubing was mounted behind the panel board to contain the flowing suspension, transformer oil, and cooling water while travelling through the panel board regulating network.

Suspension Flow System. The system necessary to keep the suspension of ball-clay and water in continuous flow, as well as recycle it, consisted essentially of a Fisher centrifugal circulating pump, drawing the suspension from the make-up jar, pumping it through the panel board regulating and distributing network and through the testing apparatus, and discharging it into a 20-gallon stoneware jar. The flow rate orifice was calibrated at 67 and 81 °F in order to determine the effect of

temperature, if any, on the calibration values. However, no detectable change in calibration values was observed for the two temperatures used which represented the approximate limits of the experimental temperatures encountered.

Coagulating Tube. In subjecting a ball-clay hydrosol in continuous flow to an ultrasonic field, it was desired to have a special container, the bottom of which would permit maximum transmission of the ultrasonic waves from the transducer cavity to the ball-clay hydrosol flowing through this container. In a previous investigation, Thompson⁽¹⁴⁷⁾ has shown that a 0.001-inch nickel sheet gave the best transmission in comparison with a number of other materials such as copper, aluminum, and glass. Accordingly, a 0.001-inch nickel disc was bonded to one end of a 2-1/4-inch high by 1-1/4-inch outside diameter, 1-1/8-inch inside diameter pyrex glass tube. Figure 23, page 124, is a drawing of the coagulating tube. The diameter of this tube was limited by the opening of 1-1/2-inches in the transducer cavity through which ultrasonic energy was transmitted from the quartz transducing

crystal. A tube 2-1/4 inches in height of which the top 1/4-inch was occupied by a stopper containing inlet and outlet lines and crystal probe, was used. Such a tube was used in order to limit the attenuation of the ultrasonic energy through the ball-clay hydrosol to approximately one order of magnitude in order that the results could be related to a limited range of intensity of insonation. The significance of this consideration may be illustrated by Equation 11, page 72:

$$I_x = I_0 e^{-2\alpha x}$$

Using this equation and an attenuation coefficient, α , of 0.26 cm⁻¹, obtained from Figure 6b, page 74, for a four per cent by weight or 1.58 per cent by volume kaolin hydrosol, it can be calculated that for a two-inch suspension height the intensity of ultrasonic waves travelling through this distance is decreased by a factor of 1/14; whereas for a one-foot height of suspension, the intensity is decreased by a factor of approximately 10⁻⁷.

Crystal Probe. There was no assurance that the power delivered from the power tube of the ultrasonic generator, of which the plate current meter reading was an indication, was the same as that delivered to the faces of the transducing crystal nor that this is converted without loss to ultrasonic energy. Further losses may occur as the ultrasonic energy is transmitted from the crystal to the bottom of the container housing the sample to be treated, as well as when it is transmitted through the bottom of the container. Therefore, the actual ultrasonic energy entering the sample under test is not necessarily directly related to the power indicated by the panel meter. Consequently, a more direct and accurate method of measurement was sought. A number of quartz crystals were obtained from the hills around Blacksburg, Virginia, and the smallest and most perfect one selected to be used in a probe that would pick up the ultrasonic vibrations acting on the hydrosol in the coagulating chamber and transform them into electrical impulses which could be amplified and measured. The quartz crystal was

sealed between two, 0.001-inch thick nickel discs by means of cellulose cement. Leads were soldered to the nickel discs and led through a shielded cable to an amplification unit. The probe was inserted in the coagulation chamber and held stationary by a rubber stopper at the top of the chamber such that an X-cut axis of the crystal was parallel to the direction of propagation of the ultrasonic waves. Figure 26, page 128, is a drawing of the quartz crystal probe.

Procurement of Samples for Settling Tests.

Since the ball-clay hydrosol undergoing testing was in continuous flow, it was necessary to have a sample valve and copper tubing line extending from the return line of the coagulating chamber. The sample line was at such a height that a rack of low form Nessler tubes, used to contain the settling samples of the treated hydrosol, could be placed underneath and samples obtained by turning the sample valve and allowing the hydrosol to flow into the Nessler tubes. The sample valve is shown in detail in Figure 17, page 109.

Measurement of Settling Rates. In the determination of the height of a settling sample, low form Nessler tubes were used which were graduated to a height of 15 centimeters at one centimeter intervals. The procedure was to first graduate a plastic tube with an external diameter a fraction of an inch less than the internal diameter of the Nessler tubes. The graduations were made at five centimeter intervals, starting at the extreme bottom of the plastic tube. This tube was then placed in the Nessler tube to be graduated and the assembly placed in a wooden cradle. A T-square was guided by this cradle normal to the tube assembly so that graduation marks could be drawn on the Nessler tube using the graduated plastic tube as an indicator. The graduations were made by means of a drafting pen and ceramic marking ink at five centimeter intervals and up to fifteen centimeters in height from the inside bottom of the Nessler tube. The ceramic marking ink was permanently fused into the glass tube by heating to red heat and holding it at that for approximately one minute. For the actual measurement of the settling suspension

height, a centimeter scale, graduated in tenths of a centimeter, was used, with the graduations on the Nessler tube serving as a guide. Figure 33, page 137, shows the graduated Nessler tubes containing settling ball-clay samples.

Transformer Oil Cooling System. For the purpose of dissipating the heat developed in the transformer oil of the transducer housing due to the vibration of the quartz transducing crystal and conversion of sound waves into heat by attenuation, it was necessary to circulate the oil through a cooling unit. The transducer housing supplied with the generator was not designed to permit this continuous flow of transformer oil, so a housing was designed and constructed out of polystyrene plastic to accomplish this advantage. Figure 16, page 106, is a drawing of the continuous-flow housing. The oil was drawn from this housing by means of a gear pump, sent to a water cooling unit, through a ceramic filter, and returned to the transducer housing. A transformer oil flow rate of 4.85 pounds per minute was used through the experimental tests. A potential of 50 volts applied to the gear pump motor by means

of an auto-transformer gave the pump sufficient speed to obtain the 4.85 pound per minute flow rate of transformer oil. The water flow rate through the cooling unit was 20.3 pounds per minute. Operating the ultrasonic generator at 500 kilocycles and 100 milliamperes plate current, equilibrium temperatures of the transformer oil in and out of the transducer housing were 70 and 75 °F, respectively, with water temperatures in and out of the cooling unit of 60 and 64 °F, respectively. Since the tap water temperature throughout the experimental tests varied between 66 and 68 °F and since the maximum intensity of insonation used did not appreciably exceed that corresponding to 100 milliamperes plate current at 500 kilocycles, the cooling system used was considered adequate to protect the quartz transducing crystal from overheating in that the temperature was not allowed to rise continuously but rather kept within a range of approximately 70 to 75 °F.

Test Cavity Water Cooling System. During the operation of the ultrasonic generator, at 500 kilocycles and 100 milliamperes plate current for example, it was observed that the water in the test

cavity of the transducer housing rose approximately 4 °F per minute. Therefore, it was necessary to circulate the water through a cooling coil in order to keep the temperature under control so as to protect the quartz transducing crystal. This circulation was done at a rate of 3.25 pounds per minute through an air cooling coil, consisting of eight feet of 3/8-inch outside diameter, 1/4-inch inside diameter copper tubing, by means of a Fisher centrifugal circulating pump, Model B. The test cavity water cooling system is shown in Figure 17, page 109. Using this system it was observed that a maximum equilibrium temperature of approximately 90 °F could be maintained in the transducer cavity with the ultrasonic generator operating at maximum output.

Continuous Mechanical Agitation System. For the purpose of comparison coagulation tests, one of the systems chosen was the treatment of a ball-clay hydrosol, in continuous flow, with mechanical agitation supplied by a Waring blender equipped with a "Micro" head containing a continuous flow attachment as shown in Figure 22, page 110, and having an operational blade speed up to 17,500 revolutions

per minute. This type of treatment was chosen for comparison coagulation tests as it was the most nearly comparable to continuous ultrasonic treatment which is essentially a particular type of mechanical agitation.

Batch Mechanical Agitation System. Another type of comparison coagulation tests was made on a batch scale employing relatively mild agitation at stirrer speeds between 14 and 120 revolutions per minute. In this type of treatment, a ball-clay hydrosol was contained in a nine and one-quarter inch high by six and one-quarter inch inside diameter glass jar at a height of 15 centimeters. Suspensions were stirred for periods of 5 to 60 minutes and the subsequent settling rates measured. Figure 32, page 135, shows the equipment arrangement for batch mechanical agitation.

Batch Ultrasonic System. The same type of nickel bottom treatment chamber was used as in the continuous-flow tests (Figure 23, page 124), except that the chamber was approximately one foot in height in order to permit a suspension height of

15 centimeters so that the settling of the suspension could be on the same basis as for the continuous ultrasonic tests.

Exploratory Investigations. Because of practical limitations on the comprehensiveness of this investigation, it was necessary to obtain information which would be helpful in fixing certain variables as well as supplying information to direct the choice of experimental tests to be made. Exploratory investigations were conducted on the following: (1) type of hydrosol to be used; (2) electron microscopic observations of ball-clay particles; (3) suspension flow rate; and (4) crystal probe calibration.

Type of Hydrosol to be Used. In the choice of a hydrosol for experimental tests, the following criteria were set up: (1) dispersed phase of single definite composition; (2) settling rate between one and five centimeters per hour; and (3) hydrophobic suspension. It was desired to use a single substance of definite composition as the dispersed phase in order that the experimental results may be taken as representative of materials of comparable particle size and density. A

settling rate of between one and five centimeters per hour was desired so as to allow for a relatively significant increase in settling rate without consuming an impractical amount of time for measurements. A hydrophobic suspension was desired so as to have particles of fairly definite size and shape. In hydrophilic suspensions such as bentonite and gelatin, the size and shape of the particles is difficult to determine due to their tendency to form gel-like structures resulting in very little optical heterogeneity. Tests were conducted on settling rate of kaolin, ball-clay, and bentonite hydrosols. The settling rate of the ball-clay hydrosol was within the desired range of one to five centimeters per hour. A ball-clay hydrosol also satisfied the other criteria advanced. More specific tests were conducted varying the concentration of ball-clay in an aqueous suspension medium. Four to seven and one-half per cent by weight ball-clay hydrosols fell within the desired limits of one to five centimeters per hour settling rate. It was decided to use a four per cent by weight ball-clay hydrosol for the experimental tests.

since this concentration gave the longest period of constant hindered settling.

Electron Microscopic Observation of Ball-Clay Particles. In the course of this investigation it was desired to determine the size and shape of ball-clay particles, the essential composition of which was the crystalline mineral kaolinite. Since it was observed that the range of particle size was below the limit of resolution of the optical microscope, an electron microscope was used with subsequent enlargement of the photographs obtained therewith. Suspensions were prepared using a concentration of approximately 0.001 gram ball-clay per millimeter of water. The ball-clay was thoroughly dispersed by means of an ultrasonic field at 300 kilocycles and 100 milliamperes plate current for a period of approximately one minute using a 0.001-inch thick nickel bottom container. Electron photomicrographs were made which showed the appearance of hexagonal kaolinite particles. Two limitations are apparent in the above required procedure of electron microscopic observation. One is the extreme dilution of the sample which was

necessary due to the low penetrability of an electron beam. It would be practically impossible to obtain any contrast with a suspension concentration above about 0.01 gram per millimeter. The other limitation was the necessary dryness of the sample due to the vacuum required for an electron beam. Therefore, the photomicrograph is not necessarily representative of the condition of the ball-clay in aqueous suspension concentration of four per cent by weight.

Suspension Flow Rate. A series of tests were made at 5, 4, 3, 2, 1, and 1/2 pounds per minute flow rate of a four per cent by weight ball-clay hydrosol and established that no difference in settling rate was caused by the different flow rates alone.

Crystal Probe Calibration. Since the amplified output of the quartz crystal probe involved a function introduced by the amplifier, it was necessary to calibrate the amplifier so that the actual output of the probe crystal could be determined. This calibration was accomplished by feeding a given voltage to the amplifier at 300, 500,

750, and 1000 kilocycles by means of a General Radio signal generator, type 605-B, and measuring the amplified output by means of a Weston, vacuum tube, voltmeter, type 1800-A. Also, the relation between amplified probe voltage and ultrasonic generator plate current was determined with the probe in position for experimental tests. Furthermore, if it is assumed that the voltage given off by the crystal is proportional to the pressure amplitude of the ultrasonic waves, then by squaring this voltage, values of relative intensity can be obtained since the relative intensity is proportional to the square of the pressure amplitude at a given frequency⁽¹⁶⁴⁾.

Plan of Evaluation. In the continuous ultrasonic treatment of a four per cent by weight ball-clay hydrosol, the variables of frequency, intensity of insonation, flow rate, and recycle rate were investigated to determine their effect on coagulation and settling rate. Continuous and batch mechanical agitation comparison coagulation tests were also made along with batch ultrasonic comparison coagulation tests. Furthermore, control and reproducibility tests were conducted.

Figure 34 shows the standard form used in recording the experimental data. Described in the following paragraphs is the plan of evaluation of the experimental variables investigated.

Effect of Frequency. Since four quartz crystals with resonant frequencies of 300, 500, 750, and 1000 kilocycles were supplied with the General Electric ultrasonic generator, it was decided to use all of them in the continuous ultrasonic tests. In order to evaluate the effect of frequency on coagulation, the constant hindered settling rate, obtained from a plot of level of sedimentation versus time, was plotted against frequency, holding the flow rate and intensity of insonation constant. Since it would be impractical to represent each combination of intensity of insonation and flow rate, selected data were plotted which were considered to be representative of the effect of frequency.

Effect of Intensity of Insonation. In the experimental tests conducted, the intensity of insonation, of which the amplified and actual probe output voltages were an indication at a

given frequency, was varied holding the frequency and flow rate constant. Specifically, the amplified probe voltages as shown in Table IX, page 180, were used, which necessarily corresponded to the other calibration values shown in the table. These amplified probe voltages were read directly during the experimental tests and controlled by the plate current rheostat on the ultrasonic generator. In an analysis of the effect of intensity of insonation on coagulation, selected plots were made of constant hindered settling rate versus plate current, amplified probe voltage, and actual probe voltage at constant flow rate and frequency.

Effect of Flow Rate. Six flow rates of 5, 4, 3, 2, 1, and 1/2 pounds per minute of a four per cent by weight ball-clay hydrosol were used at different frequencies and intensities of insonation. Selected data were plotted as constant hindered settling rate versus flow rate at constant frequency and intensity of insonation.

Effect of Recycle Rate. Recycle rates of one and two pounds per minute of a four per cent by weight ball-clay hydrosol were used for the

continuous ultrasonic tests at a flow rate of four pounds per minute and an amplified probe voltage of 1.5 volts at the four different frequencies used. Selected data were plotted as constant hindered settling rate versus recycle rate.

Continuous Mechanical Agitation Coagulation Tests. For the continuous mechanical agitation coagulation tests, a four per cent by weight ball-clay hydrosol was used at flow rates of 5, 4, 3, 2, 1, and 1/2 pounds per minute and stirrer speeds ranging from 2,860 to 17,550 revolutions per minute. Selected data were plotted in the form of settling rate curves and compared with the continuous ultrasonic tests.

Batch Mechanical Agitation Coagulation Tests. The series of batch mechanical agitation coagulation tests comprised the treatment of a four per cent by weight ball-clay hydrosol on a batch scale at stirrer speeds of 14.5 to 120 revolutions per minute and agitation times of 5 to 60 minutes.

Selected data were plotted in the form of settling rate curves and compared with the continuous ultrasonic tests.

Batch Ultrasonic Coagulation Tests. A series of tests were made on a batch ultrasonic scale at 300 kilocycles with an amplified probe voltage of 5.40 volts and with times of insonation of one and two minutes. The data were compared with the continuous ultrasonic tests.

Data and Results

The data and results of this investigation, an evaluation of a continuous-flow, ultrasonic coagulation unit employing a ball-clay hydrosol, were divided into two main divisions: (1) exploratory calibrations and investigations and (2) experimental data and results.

Exploratory Calibrations and Investigations.

Values for the calibration of the flow rate orifice at 67 °F are given in table VII and the plotted calibration chart in Figure 35. Values for the calibration of the recycle rate orifice at 67 °F are given in Table VIII and the plotted calibration chart in Figure 36. Settling

TABLE VII

Calibration Values for Flow Rate Orifice

Pressure Drop Across Orifice, in. Hg	Flow Rate, ^a lb/min
12.90	5.42
10.70	4.77
8.80	4.40
7.00	3.99
6.30	3.60
4.65	3.25
3.60	2.78
2.00	2.06
1.00	1.47
0.30	0.78

^a Of four per cent by weight ball-clay hydrosol at 67 °F.

PRESSURE DROP ACROSS ORIFICE, INCHES OF MERCURY

14
12
10
8
6
4
2
0

0 1 2 3 4 5 6

SUSPENSION FLOW RATE, POUNDS PER MINUTE

SUSPENSION: 4 POUNDS
TENNESSEE NO. 9
BALL-CLAY IN 96
POUNDS WATER.
TEMPERATURE: 67 °F

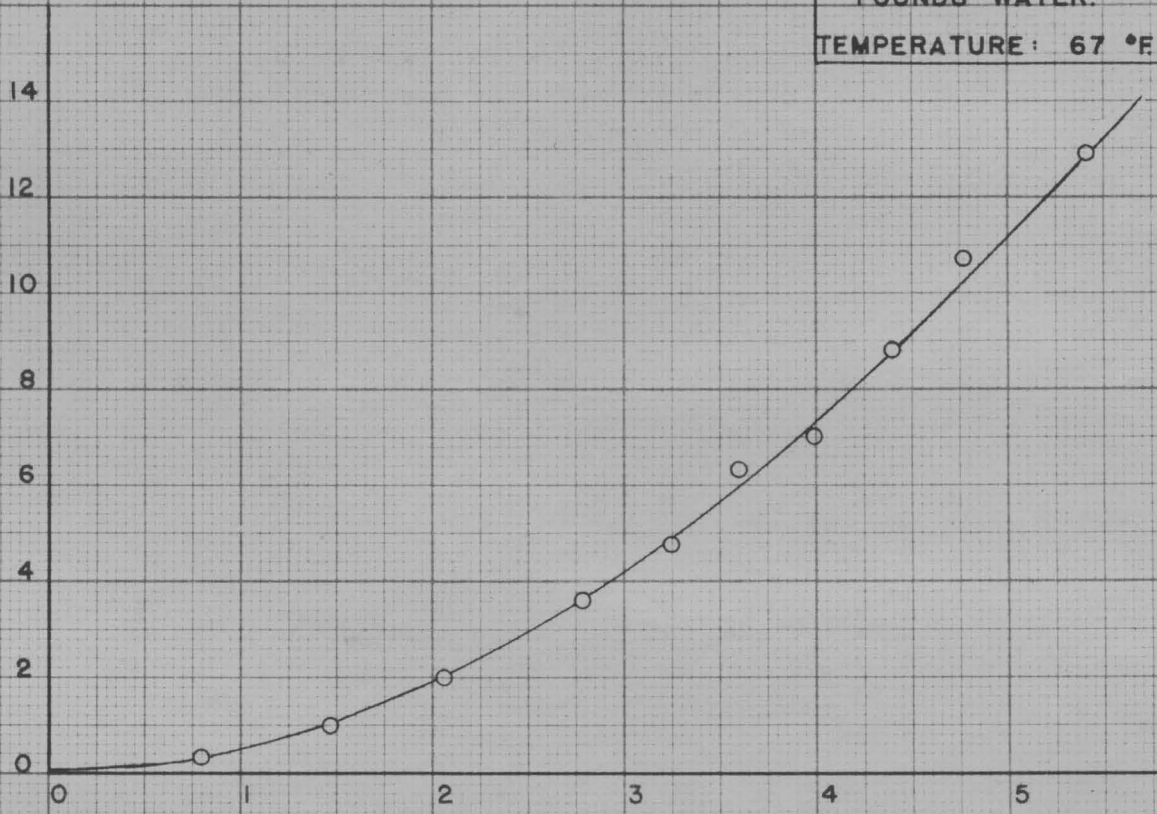


FIGURE 35. CALIBRATION OF ORIFICE FOR RATE OF FLOW.

TABLE VIII

Calibration Values for Recycle Orifice

Pressure Drop Across Orifice, in. Hg	Recycle Rate, ^a lb/min
8.00	2.98
7.00	2.71
6.00	2.54
5.00	2.28
4.00	2.03
3.00	1.83
2.00	1.65
1.00	1.18
0.40	0.70

^a Of four per cent by weight ball-clay hydrosol at 67 °F.

SUSPENSION: 4 POUNDS
TENNESSEE NO. 9
BALL-CLAY IN 96
POUNDS WATER.
TEMPERATURE: 67 °F

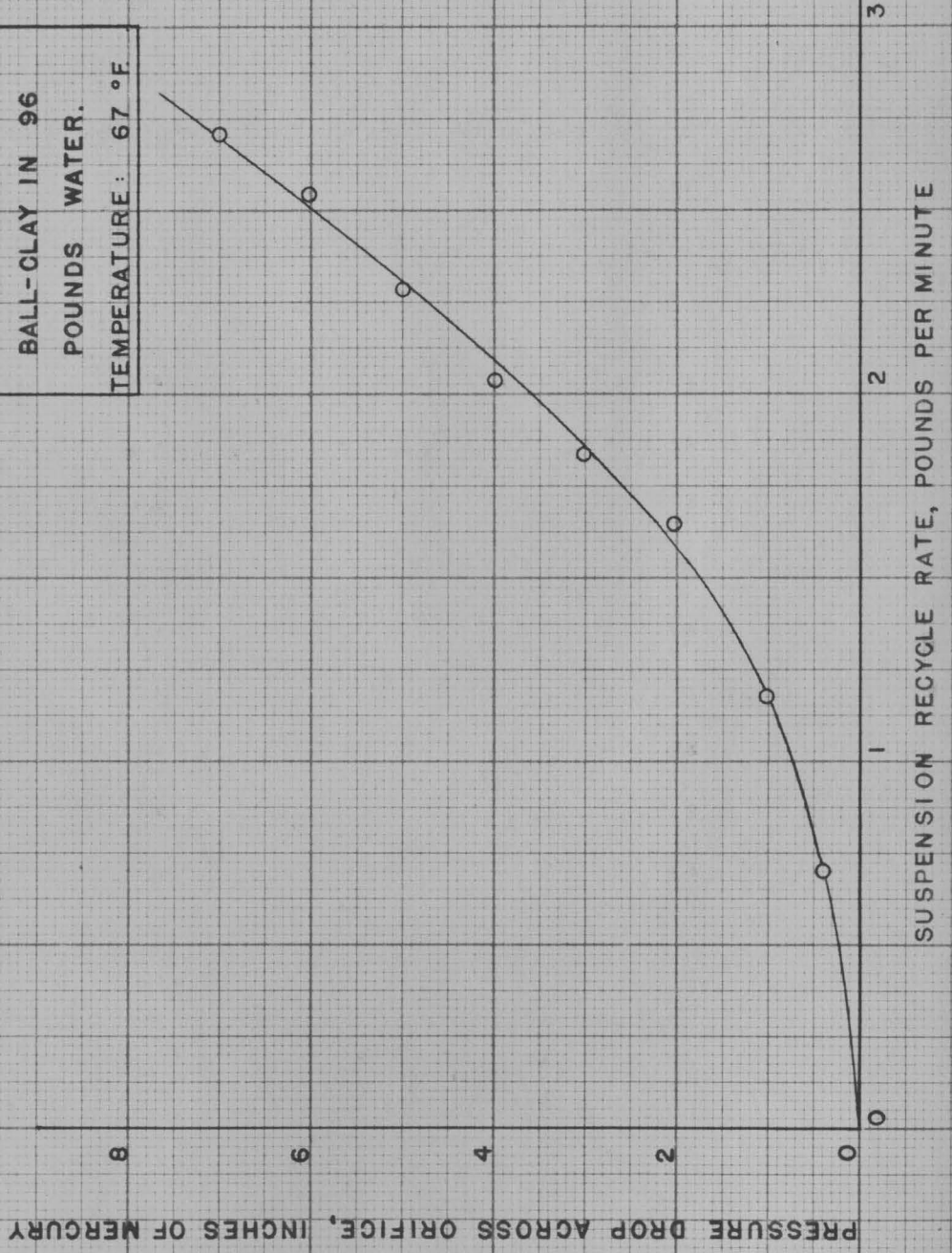


FIGURE 36. CALIBRATION OF ORIFICE FOR RATE OF RECYCLE.

rate curves for exploratory tests conducted on kaolin, ball-clay, and bentonite hydrosols are given in Figure 37. In Figure 38 are settling rate curves for ball-clay hydrosols at different concentrations. Figure 39 is an electron photomicrograph of Tennessee No 9 ball-clay particles. Calibration curves for the crystal probe amplifier at 300, 500, 750, and 1000 kilocycles are shown in Figures 40 to 43, respectively. The relationship between amplified probe voltage and General Electric ultrasonic generator plate current is shown in Figure 44 for 300, 500, 750, and 1000 kilocycles. Table IX contains calibration values for the quartz crystal probe.

Experimental Data and Results. The experimental data and results of this investigation were divided into nine sections: (1) 300-kilocycle continuous ultrasonic coagulation tests; (2) 500-kilocycle continuous ultrasonic coagulation tests; (3) 750-kilocycle continuous ultrasonic coagulation tests; (4) 1000-kilocycle continuous ultrasonic coagulation tests; (5) continuous mechanical coagulation tests; (6) batch mechanical coagulation tests; (7) 300-kilocycle batch ultrasonic

○- KINGSLEY KAOLIN HYDROSOL, PH: 7.51
X- TENNESSEE NO.9 BALL-CLAY HYDROSOL, PH: 7.82
Δ- BENTONITE HYDROSOL, PH: 9.20
CONCENTRATION: 5 GRAMS CLAY PER 100 GRAMS TAP WATER
DISPERSION: WARING BLENDER "MICRO" HEAD, 17,550 RPM,
ONE-HALF MINUTE.
TEMPERATURE: 72 °F.

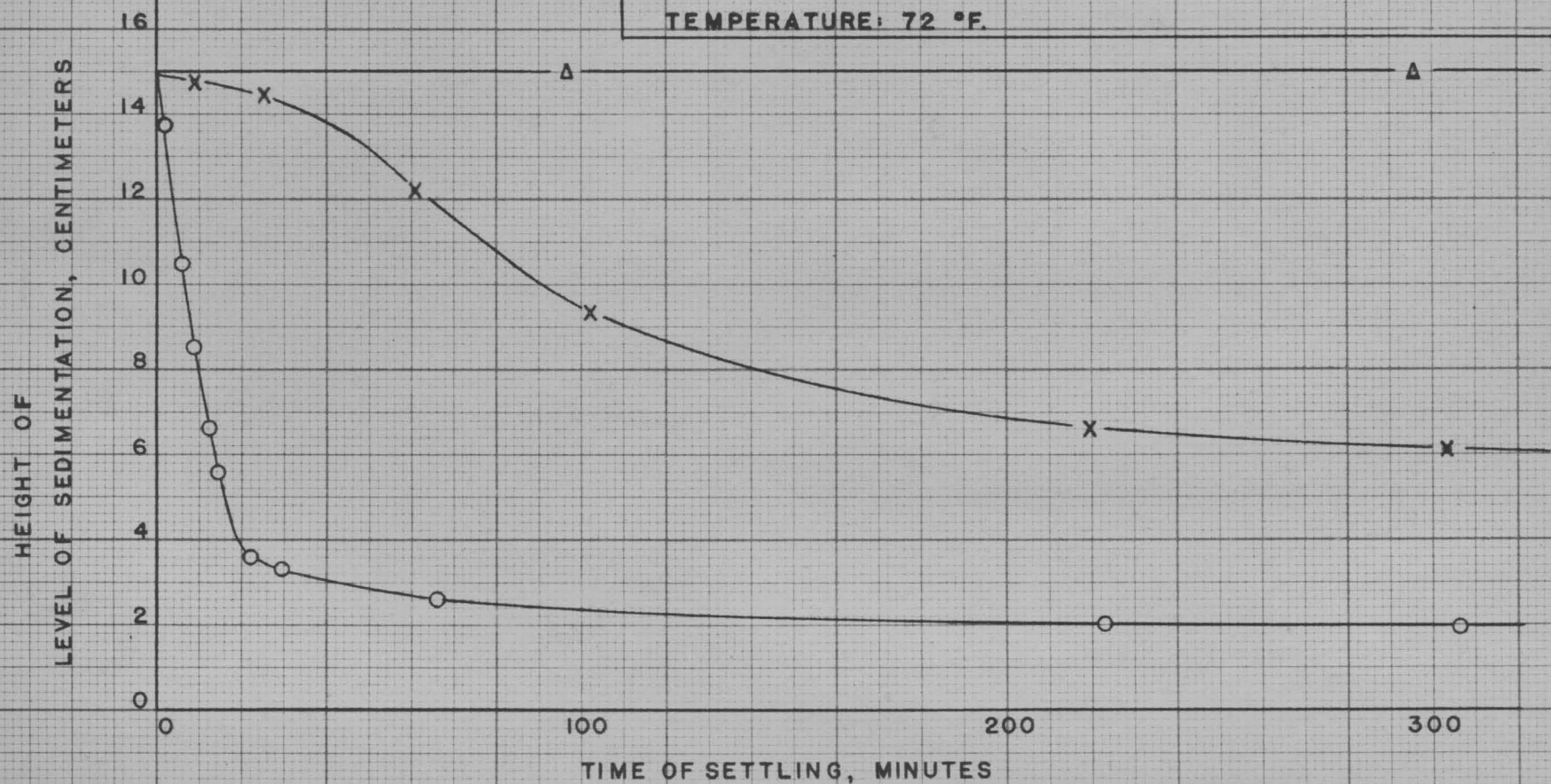
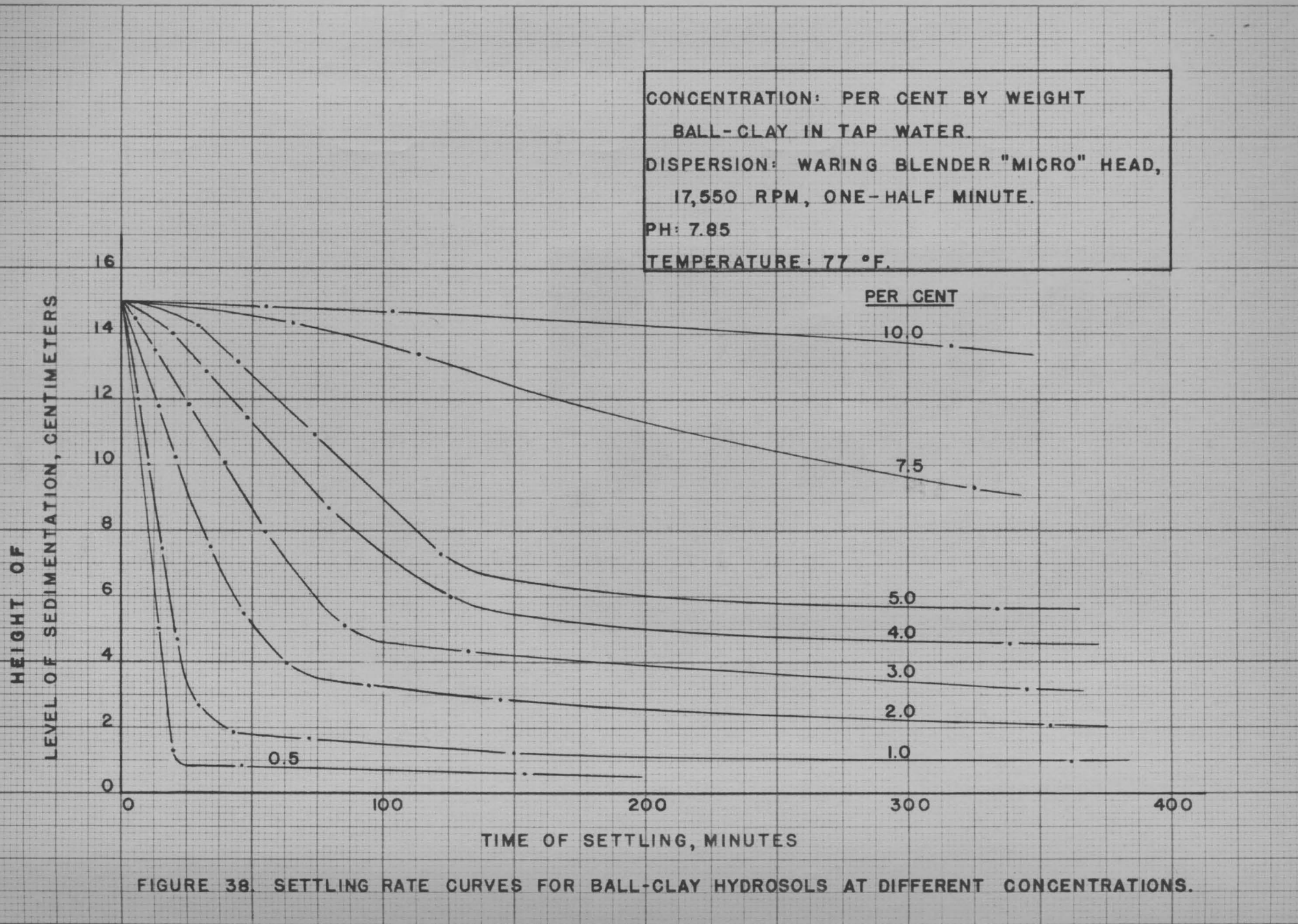


FIGURE 37. SETTLING RATE CURVES FOR KAOLIN, BALL-CLAY, AND BENTONITE HYDROSOLS.



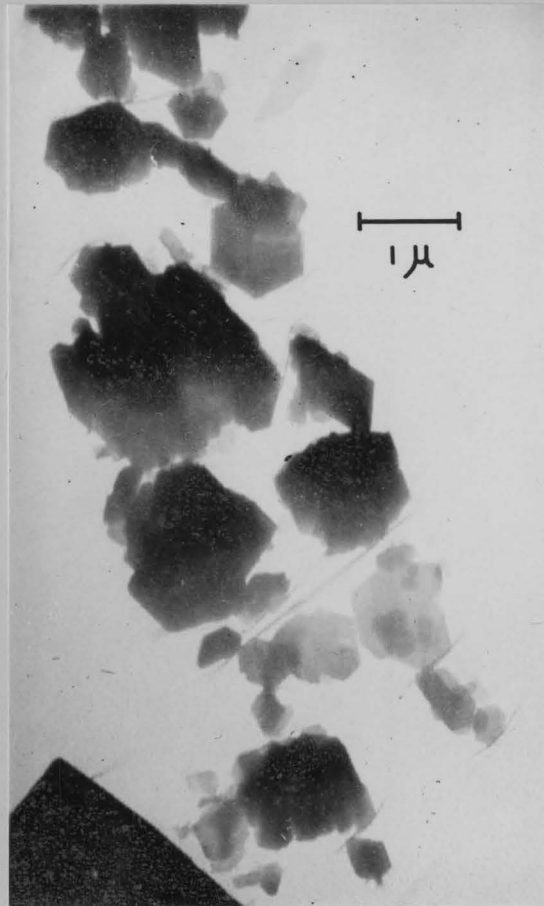


FIGURE 39. ELECTRON PHOTOMICROGRAPH OF TENNESSEE NO 9 BALL-CLAY PARTICLES.

EUGENE DIETZGEN CO.
MADE IN U. S. A.

NO. 340 120 DIETZGEN GRAPH PAPER
20 X 20 PER INCH

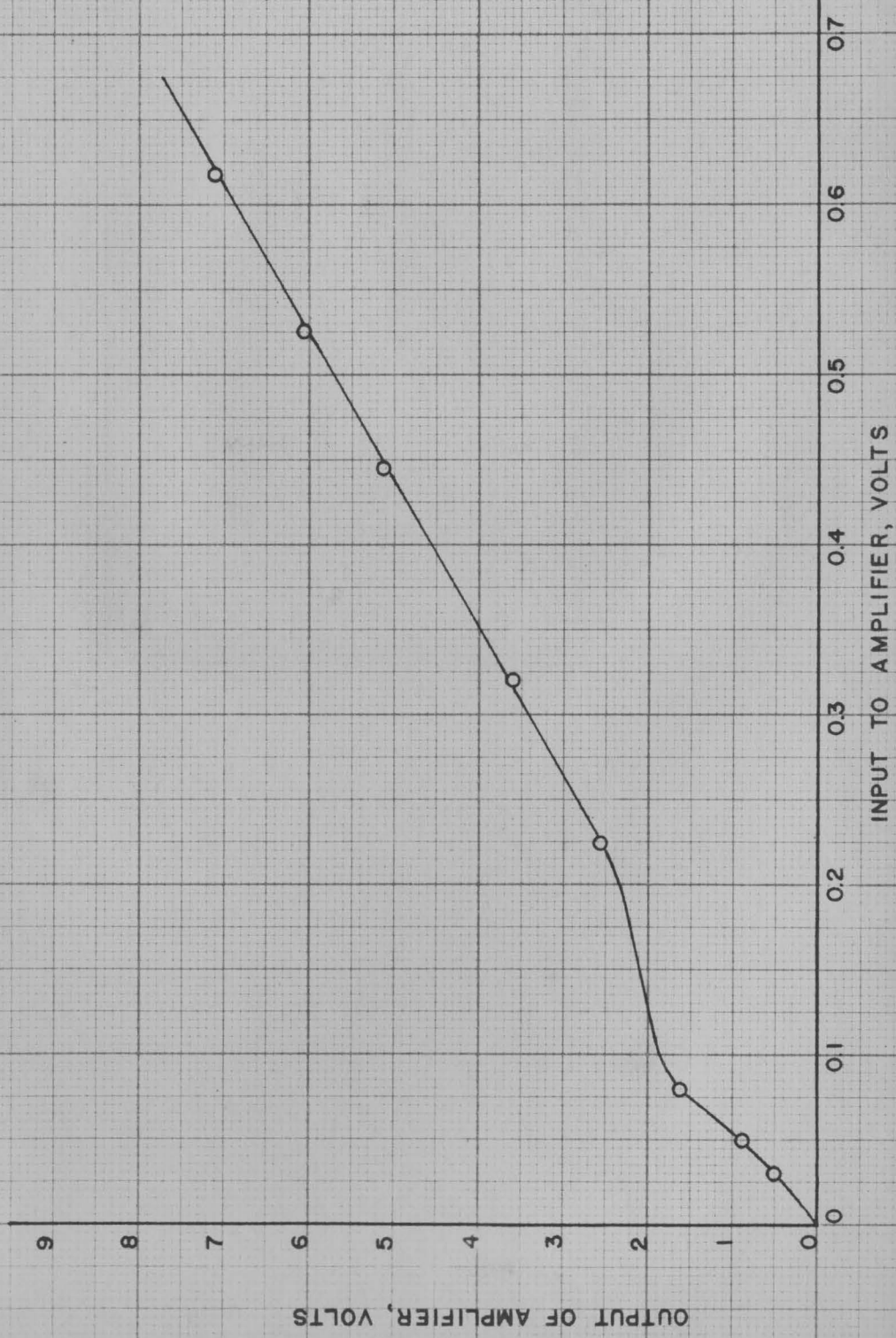


FIGURE 40. CALIBRATION CURVE FOR CRYSTAL PROBE AMPLIFIER AT 300 KC.

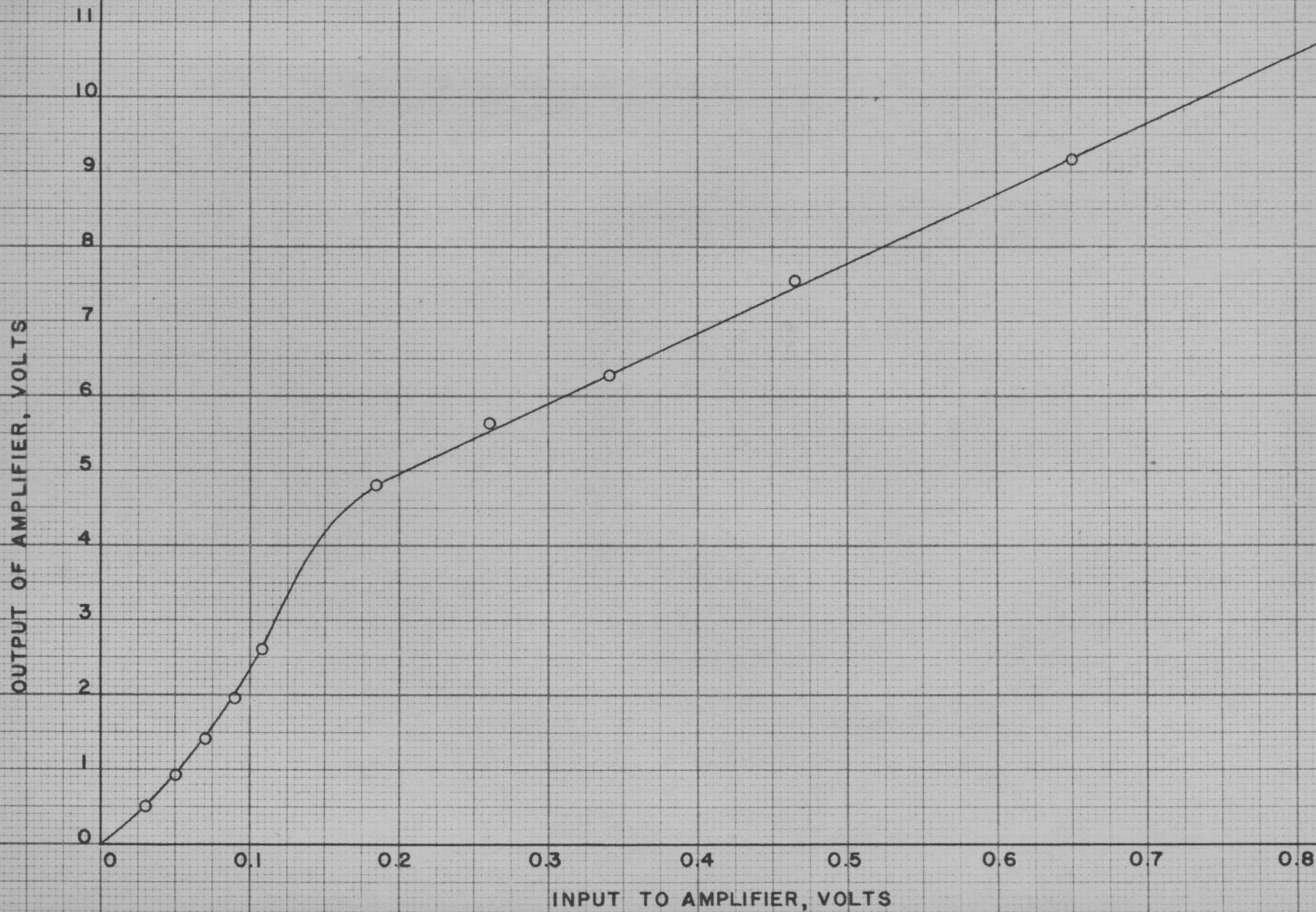


FIGURE 41. CALIBRATION CURVE FOR CRYSTAL PROBE AMPLIFIER AT 500 KC.

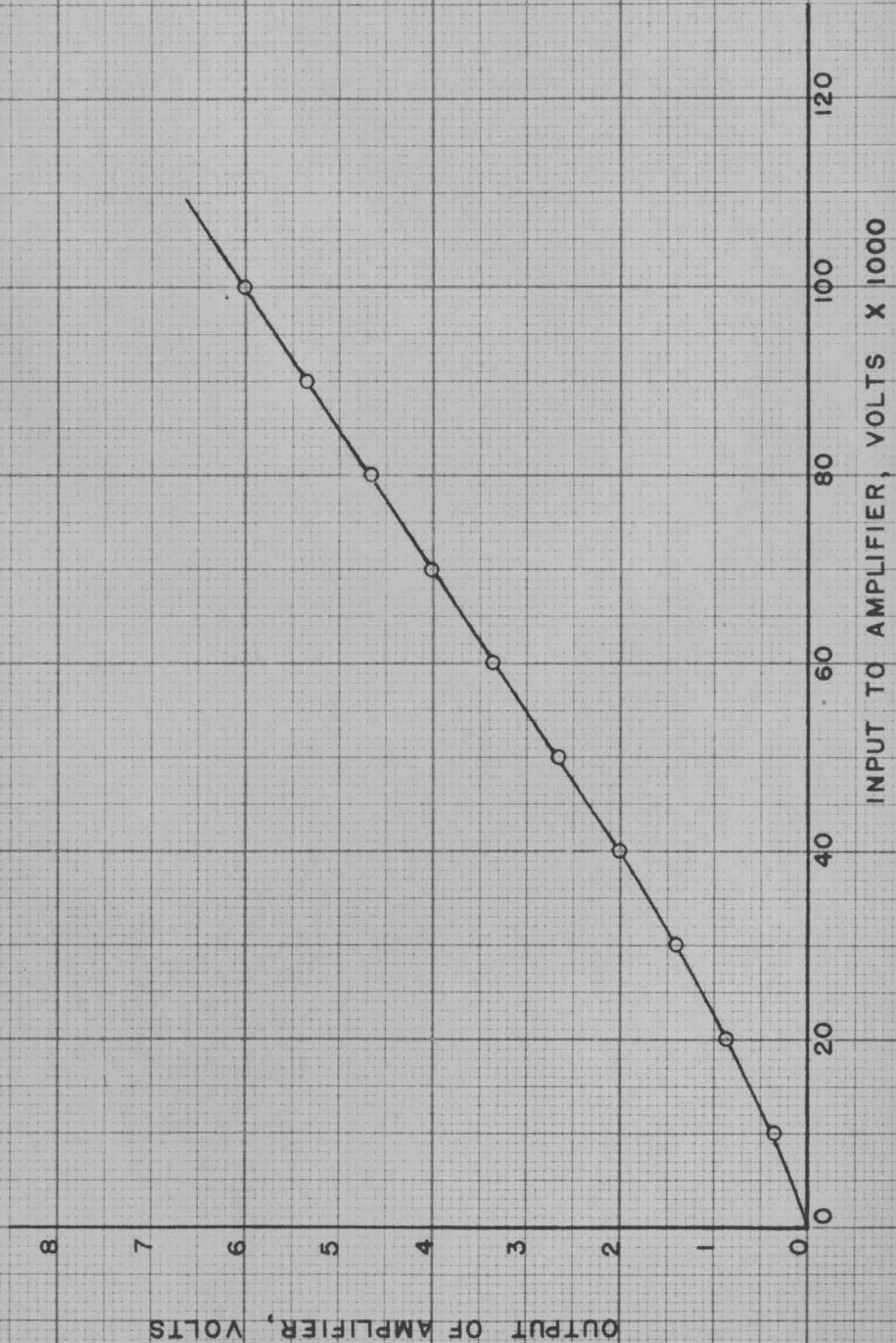


FIGURE 42. CALIBRATION CURVE FOR CRYSTAL PROBE AMPLIFIER AT 750 KC.

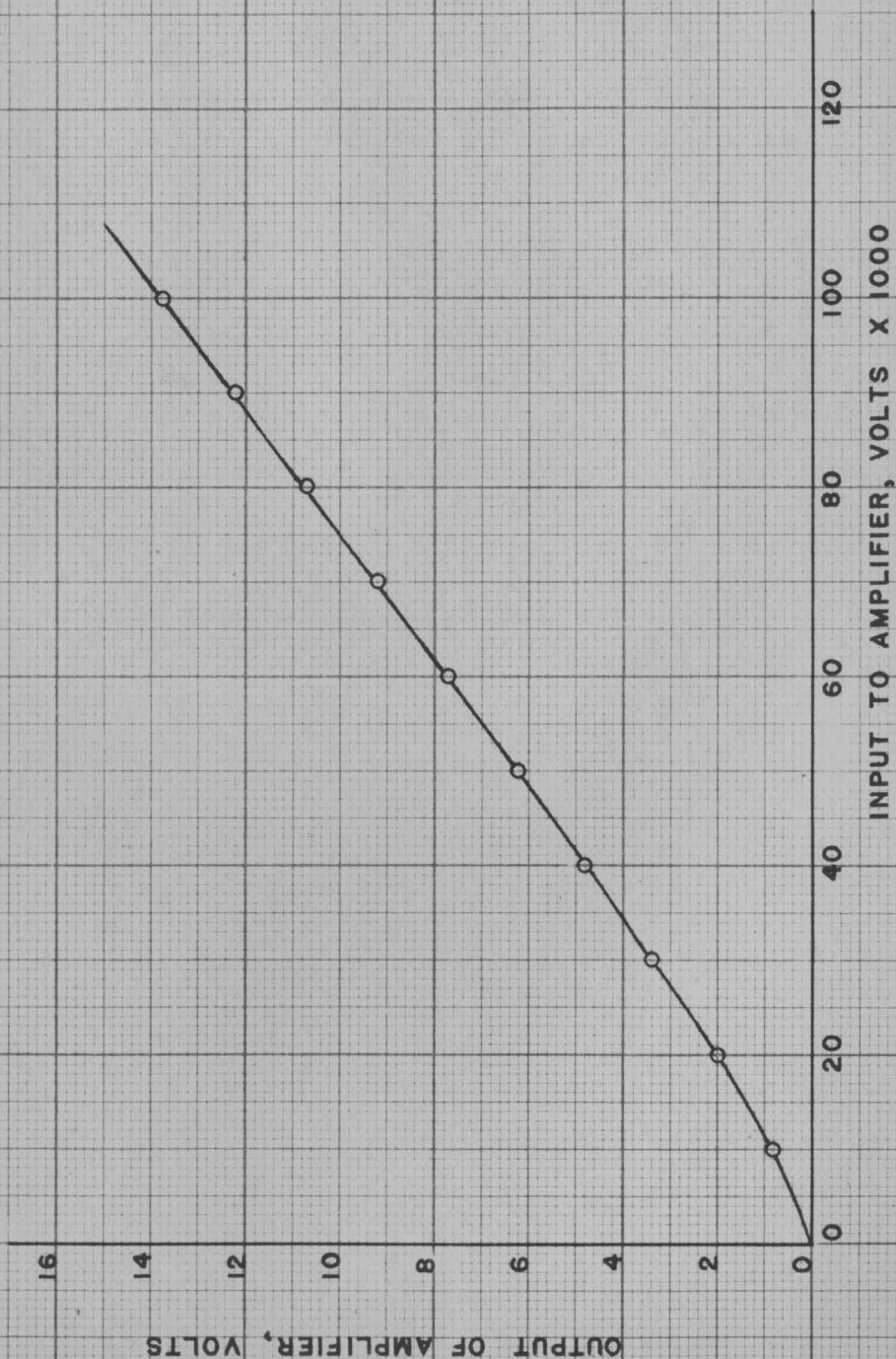


FIGURE 43. CALIBRATION CURVE FOR CRYSTAL PROBE AMPLIFIER AT 1000 KC.

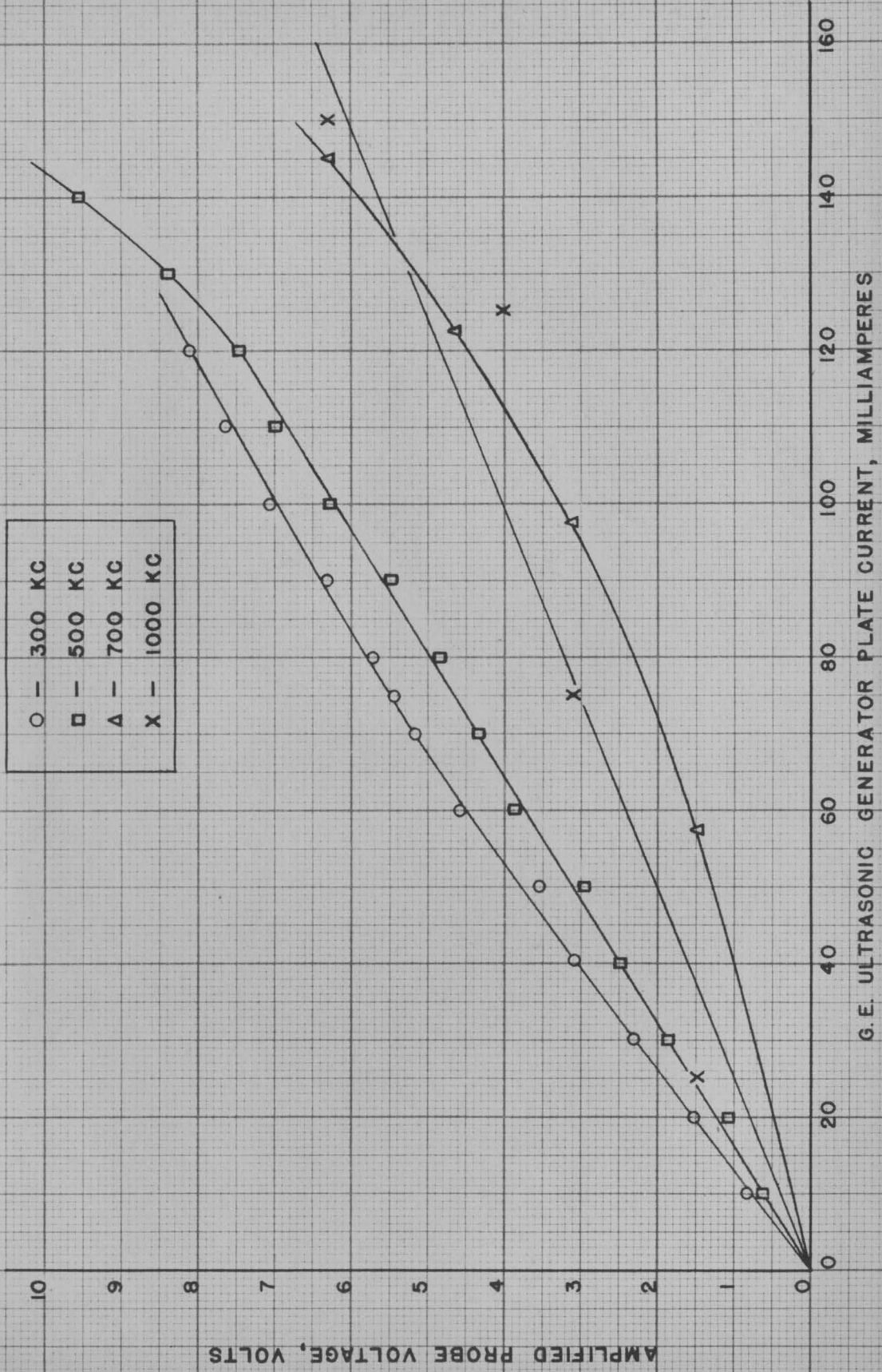


FIGURE 44. RELATIONSHIP BETWEEN AMPLIFIED PROBE VOLTAGE AND G.E. ULTRASONIC GENERATOR PLATE CURRENT.

TABLE IX

Quartz Crystal Probe Calibration Values

Frequency, kc	Plate Current, ma	Amplified Probe Output, volts	Actual Probe Output, millivolts
300	10.0	0.85	48.0
	20.0	1.50	76.0
	30.0	2.30	175.0
	40.5	3.10	272.5
	60.2	4.65	407.5
	70.0	5.20	450.0
	80.0	5.72	500.0
	90.0	6.30	547.5
	110.0	7.65	665.0
	120.0	8.08	700.0
	130.0	8.45	735.0
500	140.0	8.75	760.0
	160.0	9.45	820.0
	25.0	1.50	74.0
	50.0	3.10	122.5
	75.0	4.65	177.5
750	100.0	6.30	340.0
	150.0	9.45	682.5
	57.5	1.50	32.0
	97.5	3.10	56.4
1000	122.5	4.65	80.0
	145.0	6.30	105.0
	25.0	1.50	16.5
	75.0	3.10	28.5
	125.0	4.65	39.0
	150.0	6.30	50.3

coagulation tests; (8) reproducibility tests; and (9) control tests. The data are presented graphically as settling rate curves plotted from the initial observations.

300-Kilocycle Continuous Ultrasonic Coagulation Tests. The experimental information for the 300-kilocycle continuous ultrasonic coagulation tests is shown in Table X along with data taken from the settling rate curves. Figure 45 is representative of the range of settling characteristics obtained with different flow rates for constant intensities of insonation. Figure 46 is representative of the range of settling characteristics obtained with different intensities for insonation for constant flow rates. Both figures indicate an increase in constant hindered settling rate for the test samples over the control. In Figure 47 is shown the settling characteristics obtained with one and two pound per minute recycle rates at a four pound per minute flow rate and constant intensity of insonation. The settling rate curves indicate that recycling hinders the constant hindered settling rate relative to the nonrecycled test.

TABLE X

Data on Continuous Ultrasonic Coagulation of a Ball-Clay Hydrosol at 300 kc, Tests Nos 1-35

Test No	Flow Rate, ^a lb/min	Recycle Rate, ^c lb/min	Plate Current, ^b ma	Amplified ^c Probe Voltage, volts	Initial pH ^d	Final pH ^e	Point I ^f Height, cm	Point I ^f Time, min	Point II ^g Height, cm	Point II ^g Time, min	Point III ^h Height, cm	Point III ^h Time, min	Constant Hindered Settling Rate, cm/hr
1	5	0	20.0	1.50	7.95	8.12	14.0	25.0	9.5	75.0	7.5	97.5	5.50
2	4	0	20.0	1.50	7.95	8.06	14.0	25.3	-	-	7.3	101.0	5.46
3	3	0	20.0	1.50	7.95	8.05	13.1	39.0	9.5	77.5	7.8	96.5	5.62
4	2	0	20.0	1.50	7.95	8.03	13.5	33.0	9.8	75.0	7.7	96.5	5.30
5	1/2	0	20.0	1.50	7.95	8.08	13.3	42.0	-	-	7.5	101.0	6.02
6	5	0	40.5	3.10	7.95	8.09	13.7	27.9	-	-	7.6	94.0	5.55
7	4	0	40.5	3.10	7.95	8.06	14.0	26.0	-	-	7.0	102.0	5.33
8	3	0	40.5	3.10	7.95	8.09	13.5	31.0	9.1	79.0	7.4	97.0	5.52
9	2	0	40.5	3.10	7.95	8.15	13.7	29.0	9.6	95.0	7.5	95.0	5.26
10	1/2	0	40.5	3.10	7.95	8.14	13.5	40.0	-	-	8.2	90.0	6.44
11	5	0	60.2	4.65	7.95	8.10	14.2	25.0	9.8	73.5	7.1	100.0	5.52
12	4	0	60.2	4.65	7.95	8.09	12.9	42.0	8.9	84.0	7.3	98.0	5.79
13	3	0	60.2	4.65	7.95	8.10	13.4	32.0	9.0	80.0	7.5	96.0	5.48
14	2	0	60.2	4.65	7.95	8.11	13.2	40.0	-	-	6.9	107.0	5.79
15	1/2	0	60.2	4.65	7.95	8.15	13.5	38.0	-	-	7.7	94.0	6.15
16	5	0	90.0	6.30	7.95	8.15	13.9	27.0	-	-	6.8	102.0	5.76
17	4	0	90.0	6.30	7.95	8.11	12.8	42.0	8.5	82.5	6.8	99.0	6.02
18	3	0	90.0	6.30	7.95	8.02	14.2	25.0	-	-	7.6	97.0	5.44
19	2	0	90.0	6.30	7.95	8.09	14.0	28.0	10.1	69.0	7.5	92.0	6.50
20	1/2	0	90.0	6.30	7.95	8.11	14.0	33.0	9.9	74.5	8.1	90.0	5.99
21	1	0	10.0	0.85	7.75	7.94	13.6	38.0	-	-	7.3	117.0	4.90
22	1	0	20.0	1.50	7.75	7.89	13.7	36.0	9.5	88.0	7.2	115.0	4.88
23	1	0	30.0	2.30	7.75	7.79	14.0	38.0	10.0	88.0	7.8	112.0	4.84
24	1	0	40.5	3.10	7.75	7.79	14.1	30.0	9.3	89.0	7.3	109.0	4.92
25	1	0	60.0	4.63	7.75	7.83	13.9	37.0	-	-	7.5	107.5	5.48
26	1	0	70.0	5.20	7.75	7.81	14.0	37.0	-	-	7.5	111.0	5.46
27	1	0	80.0	5.72	7.75	7.86	14.0	34.0	-	-	7.5	105.0	5.58
28	1	0	90.0	6.30	7.75	7.86	14.3	32.0	-	-	7.3	115.0	5.00
29	1	0	110.0	7.65	7.75	7.86	14.0	28.0	-	-	7.5	99.0	5.52
30	1	0	120.0	8.08	7.75	7.89	13.9	34.0	-	-	7.7	105.0	5.24
31	1	0	130.0	8.45	7.75	7.93	13.5	34.0	-	-	7.6	94.0	5.62
32	1	0	140.0	8.75	7.75	8.05	14.4	26.0	-	-	7.8	97.0	5.57
33	1	0	160.0	9.45	7.75	8.06	14.6	30.0	-	-	7.5	110.0	5.37
34	4	2	20.0	1.50	7.95	8.08	14.0	27.0	10.6	68.0	7.7	99.0	5.37
35	4	1	20.0	1.50	7.95	8.07	14.0	35.0	10.5	81.0	8.1	109.0	4.55

Temperatures: Suspension make-up, 67 °F; room, 81-83 °F range over approximately 5 hours.

^a Of four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.

^b Of General Electric Ultrasonic Generator, catalogue No 8665966 G3.

^c From voltmeter connected to quartz crystal probe amplifier.

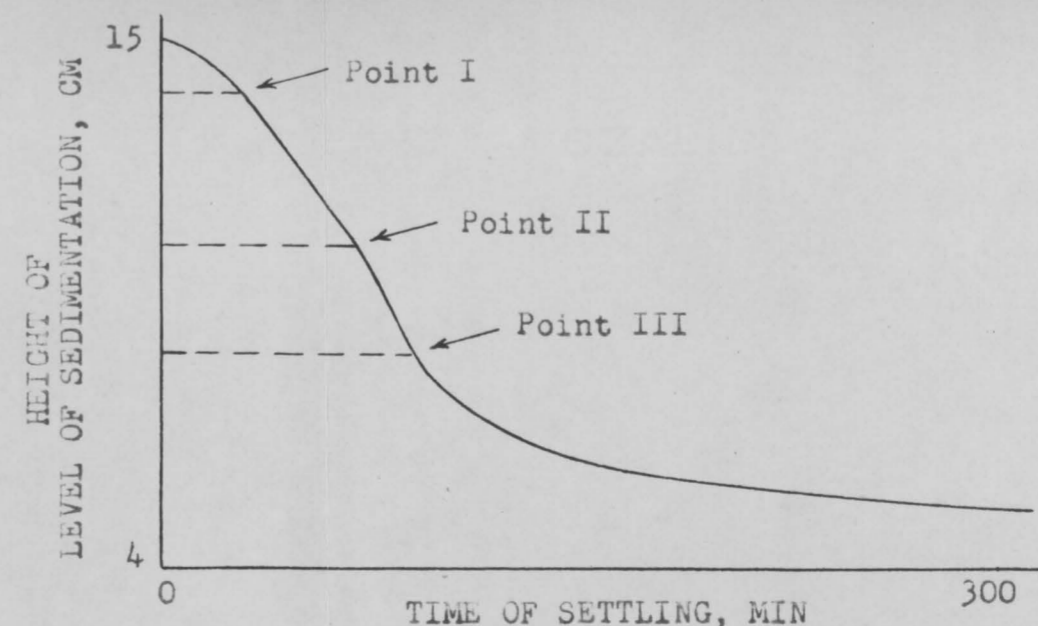
^d Suspension make-up.

^e Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.

^f Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time after insonation.

^g End of constant hindered settling period and beginning of increased rate settling period.

^h End of increased rate settling period and beginning of compaction settling period.



GENERALIZED SETTLING RATE CURVE

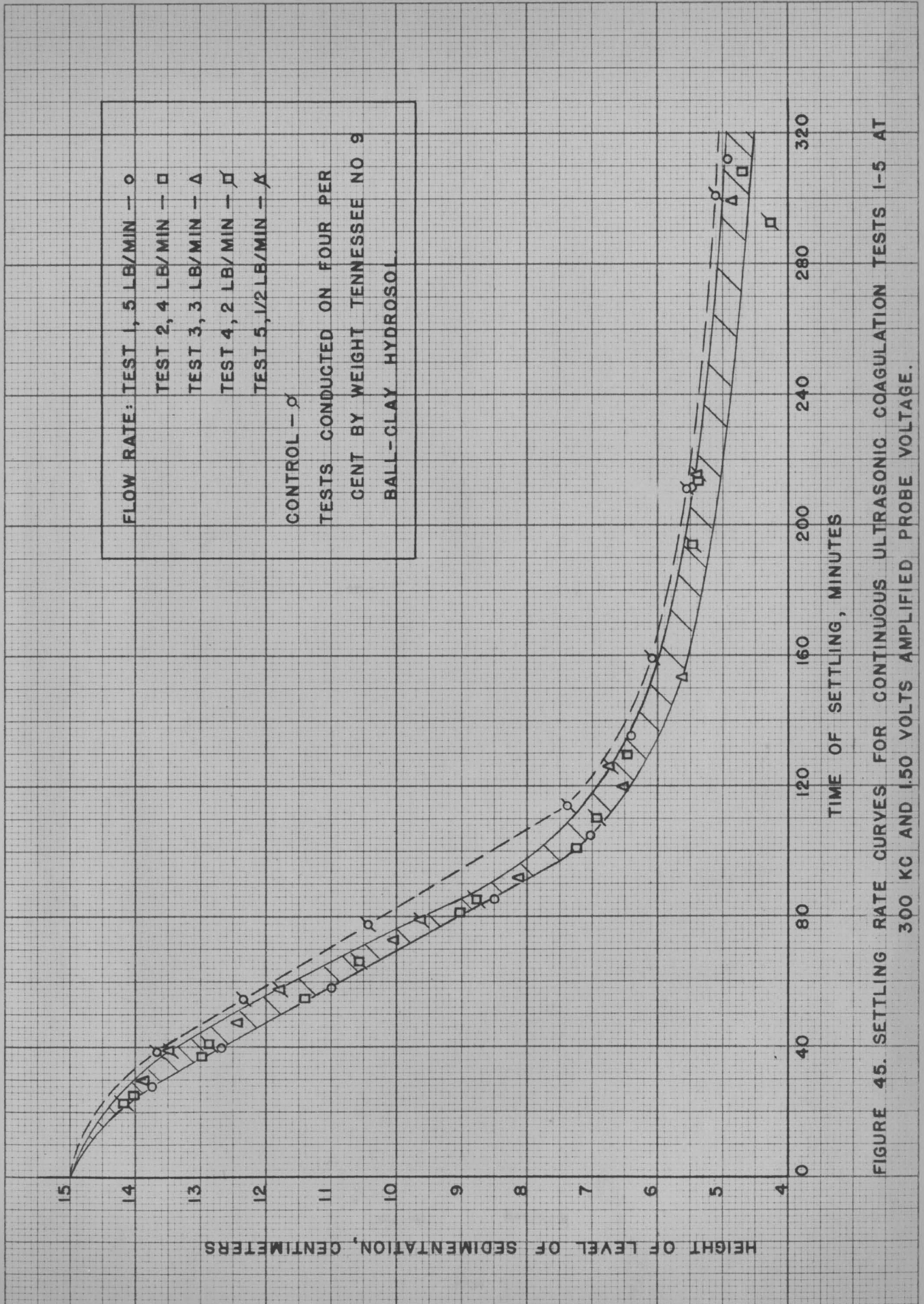


FIGURE 45. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 1-5 AT 300 KC AND 150 VOLTS AMPLIFIED PROBE VOLTAGE.

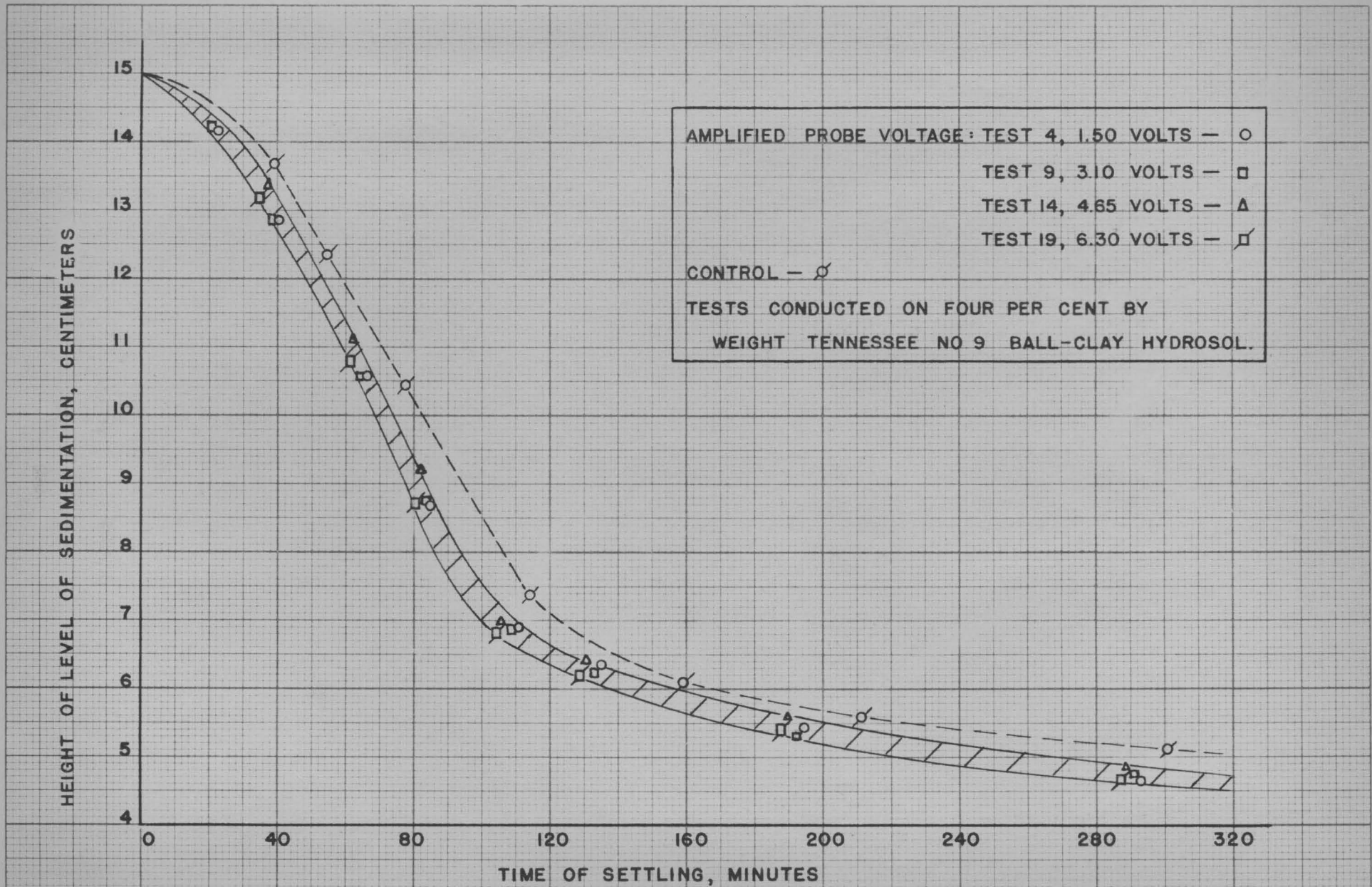


FIGURE 46. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 4, 9, 14, AND 19 AT 300 KC AND 2 POUNDS PER MINUTE FLOW RATE.

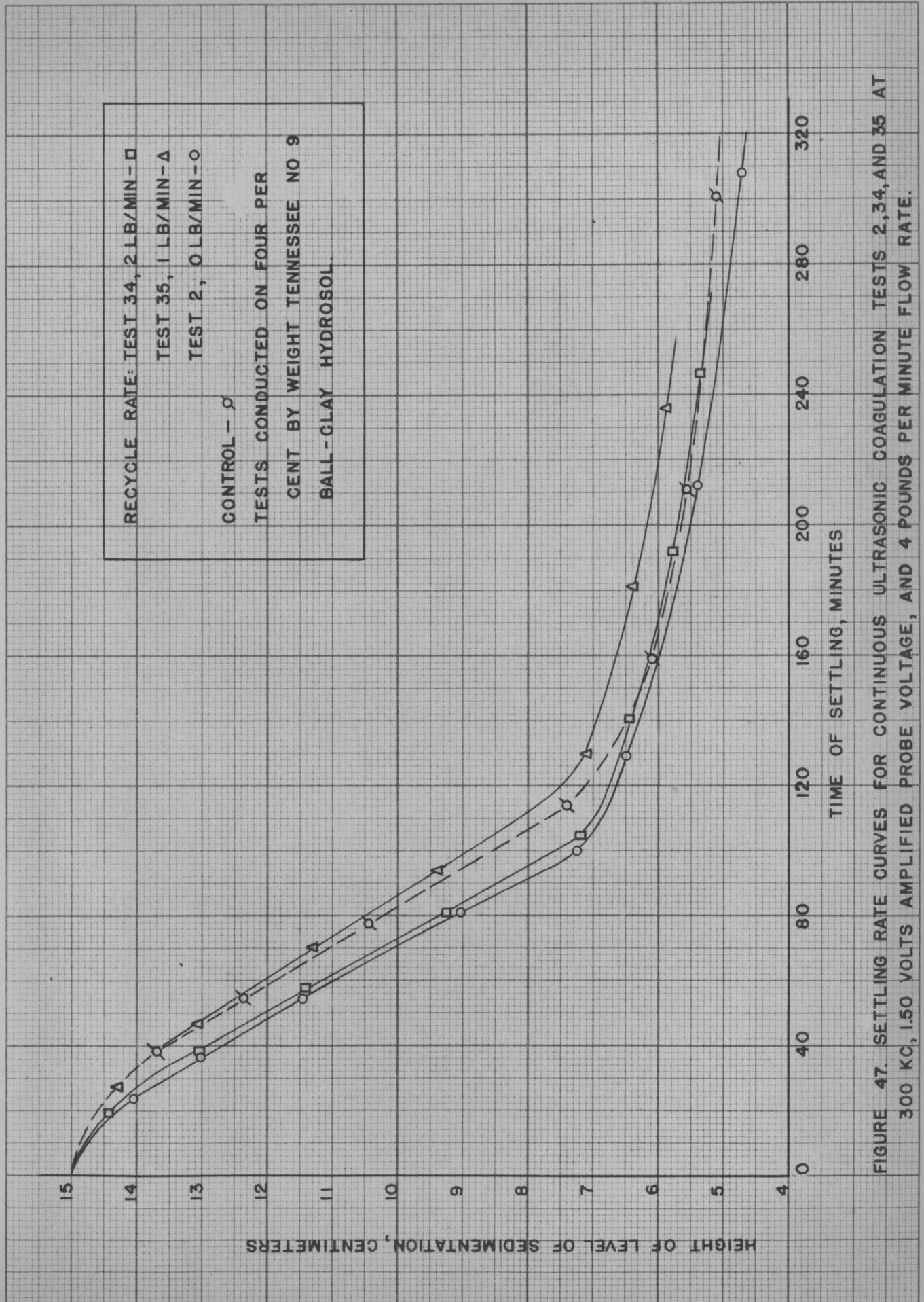


FIGURE 47. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 2, 3, 4, AND 35 AT 300 KC, 1.50 VOLTS AMPLIFIED PROBE VOLTAGE, AND 4 POUNDS PER MINUTE FLOW RATE.

500-Kilocycle Continuous Ultrasonic Coagulation

Tests. The experimental information for the 500-kilocycle continuous ultrasonic coagulation tests is shown in Table XI along with data taken from the settling rate curves. Figure 48 is representative of the range of settling characteristics obtained with different flow rates for constant intensities of insonation. Figure 49 is representative of the range of settling characteristics obtained with different intensities of insonation for constant flow rates. Both figures show a slight increase in constant hindered settling rate for the test samples over the control. The one and two pound per minute recycle rate tests at a four pound per minute flow rate and constant intensity of insonation had practically the same settling characteristics as the nonrecycled test at the same flow rate and intensity of insonation; however, the constant hindered settling rate was less for the recycled tests.

TABLE XI

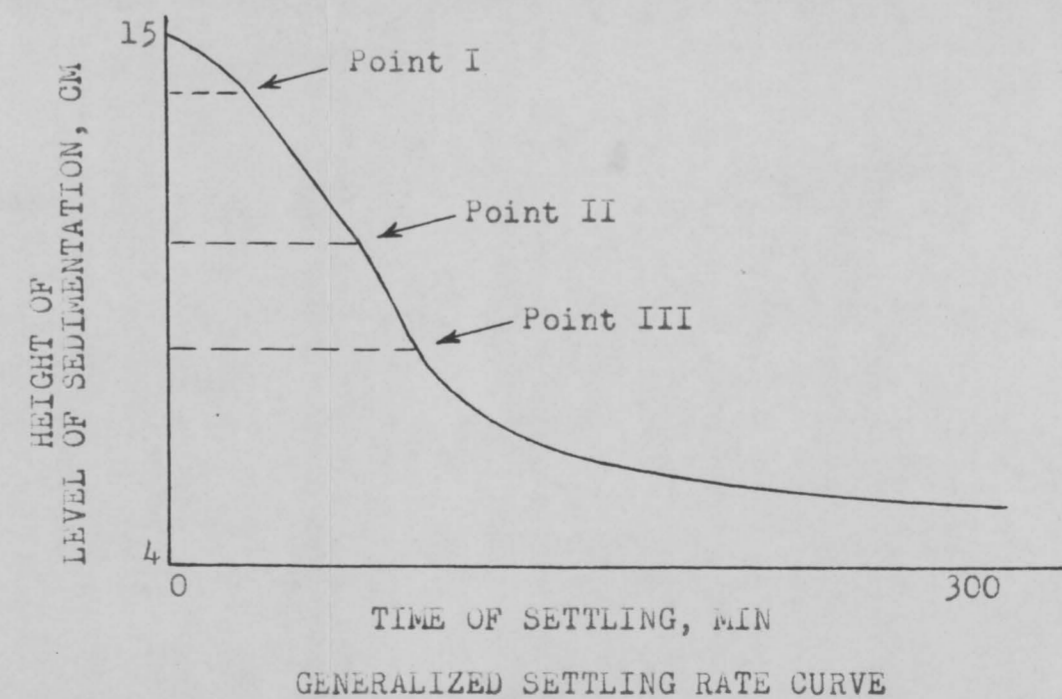
Data on Continuous Ultrasonic Coagulation of a Ball-Clay Hydrosol at 500 kc, Tests Nos 36-67

Test No	Flow Rate, ^a lb/min	Recycle Rate, ^a lb/min	Plate Current, ^b ma	Amplified ^c Probe Voltage, volts	Initial pH ^d	Final pH ^e	Point I ^f Height, cm	Point I ^f Time, min	Point II ^g Height, cm	Point II ^g Time, min	Point III ^h Height, cm	Point III ^h Time, min	Constant Hindered Settling Rate, cm/hr
36	5	0	25.0	1.50	7.65	7.71	14.2	25.0	9.8	88.0	7.2	124.0	4.16
37	4	0	25.0	1.50	7.65	7.75	13.2	40.0	-	-	7.5	120.0	4.32
38	3	0	25.0	1.50	7.65	7.80	13.8	36.0	-	-	6.8	137.0	4.14
39	2	0	25.0	1.50	7.65	7.78	13.5	37.0	-	-	8.7	104.0	4.35
40	1	0	25.0	1.50	7.65	7.82	13.6	38.0	-	-	6.8	131.0	4.43
41	1/2	0	25.0	1.50	7.65	7.90	13.6	40.0	9.2	98.0	7.1	122.0	4.55
42	5	0	50.0	3.10	7.30	7.41	13.0	31.0	-	-	6.8	101.0	5.35
43	4	0	50.0	3.10	7.30	7.40	13.5	27.0	-	-	6.8	106.0	5.12
44	3	0	50.0	3.10	7.30	7.43	13.8	26.0	-	-	7.1	106.0	5.01
45	2	0	50.0	3.10	7.30	7.40	13.8	32.0	-	-	7.0	107.0	5.42
46	1	0	50.0	3.10	7.30	7.41	14.7	21.0	-	-	10.8	59.0	4.80
47	1/2	0	50.0	3.10	7.30	7.35	14.3	27.0	9.4	80.0	7.1	99.0	5.60
48	5	0	75.0	4.65	7.65	7.75	13.3	36.0	-	-	7.8	112.0	4.30
49	4	0	75.0	4.65	7.65	7.69	13.7	37.0	-	-	6.9	136.0	4.18
50	3	0	75.0	4.65	7.65	7.79	14.0	31.0	10.1	88.0	8.0	116.0	4.16
51	2	0	75.0	4.65	7.65	7.81	13.6	34.0	-	-	7.8	113.0	4.38
52	1	0	75.0	4.65	7.65	7.83	13.3	46.0	-	-	7.1	124.0	4.90
53	1/2	0	75.0	4.65	7.65	7.91	13.8	40.0	-	-	8.0	107.0	5.24
54	5	0	100.0	6.30	7.30	7.40	14.3	18.0	9.5	73.0	7.0	98.0	5.30
55	4	0	100.0	6.30	7.30	7.39	13.7	25.0	-	-	7.0	98.0	5.30
56	3	0	100.0	6.30	7.30	7.35	14.1	17.5	10.1	64.0	8.5	78.0	5.24
57	2	0	100.0	6.30	7.30	7.40	13.9	34.0	-	-	8.1	82.0	7.59
58	1	0	100.0	6.30	7.30	7.39	14.3	18.0	-	-	7.9	77.0	6.65
59	1/2	0	100.0	6.30	7.30	7.41	13.4	38.0	-	-	8.5	77.0	7.99
60	5	0	150.0	9.45	7.30	7.40	14.0	21.0	9.5	73.0	6.7	103.0	5.20
61	4	0	150.0	9.45	7.30	7.42	13.8	24.0	-	-	8.0	91.0	5.26
62	3	0	150.0	9.45	7.30	7.39	12.3	53.0	-	-	5.7	140.0	4.55
63	2	0	150.0	9.45	7.30	7.40	14.6	13.0	-	-	7.1	105.0	4.96
64	1	0	150.0	9.45	7.30	7.42	14.7	15.0	10.0	66.0	8.0	85.0	5.70
65	1/2	0	150.0	9.45	7.30	7.41	14.1	23.0	-	-	8.0	79.0	6.56
66	4	2	25.0	1.50	7.65	7.91	14.0	27.0	10.3	81.0	8.3	108.0	4.18
67	4	1	25.0	1.50	7.65	7.86	13.8	33.0	10.0	88.0	8.3	111.0	4.21

Temperatures: Suspension make-up:
Tests Nos 36-41 inc., 48-53 inc., and 66-67 inc., 68 °F.
All other tests at 500 kc, 67 °F.

Room:
Tests Nos 36-41 inc., 48-53 inc., and 66-67 inc., 82-85 °F range
over approximately 5 hours.
All other tests at 500 kc, 78-79 °F range over approximately 5 hours.

- a Of four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.
- b Of General Electric Ultrasonic Generator, catalogue No 8665966 G3.
- c From voltmeter connected to quartz crystal probe amplifier.
- d Suspension make-up.
- e Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.
- f Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time after insonation.
- g End of constant hindered settling period and beginning of increased rate settling period.
- h End of increased rate settling period and beginning of compaction settling period.



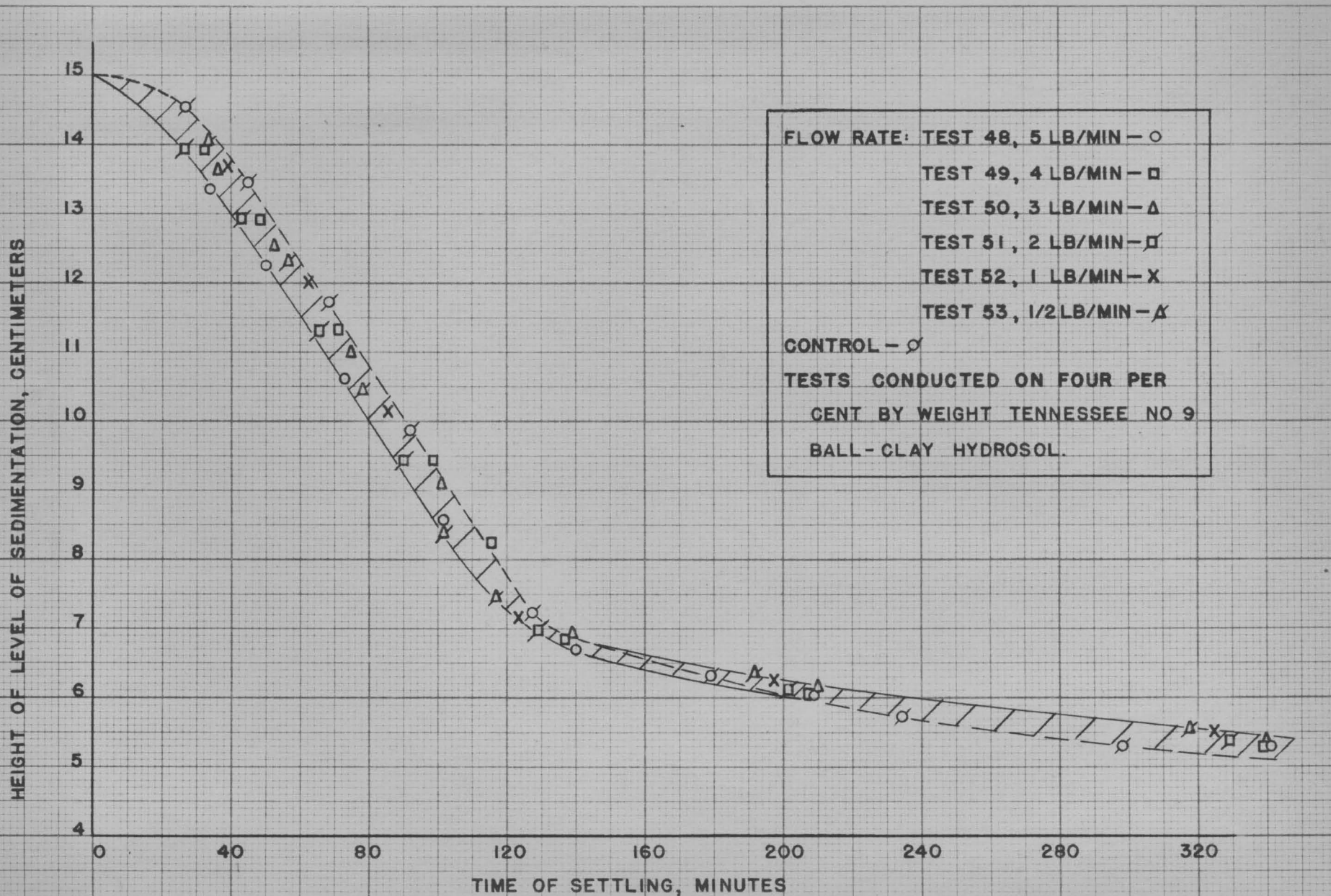


FIGURE 48. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 48-53 AT 500 KC AND 4.65 VOLTS AMPLIFIED PROBE VOLTAGE.

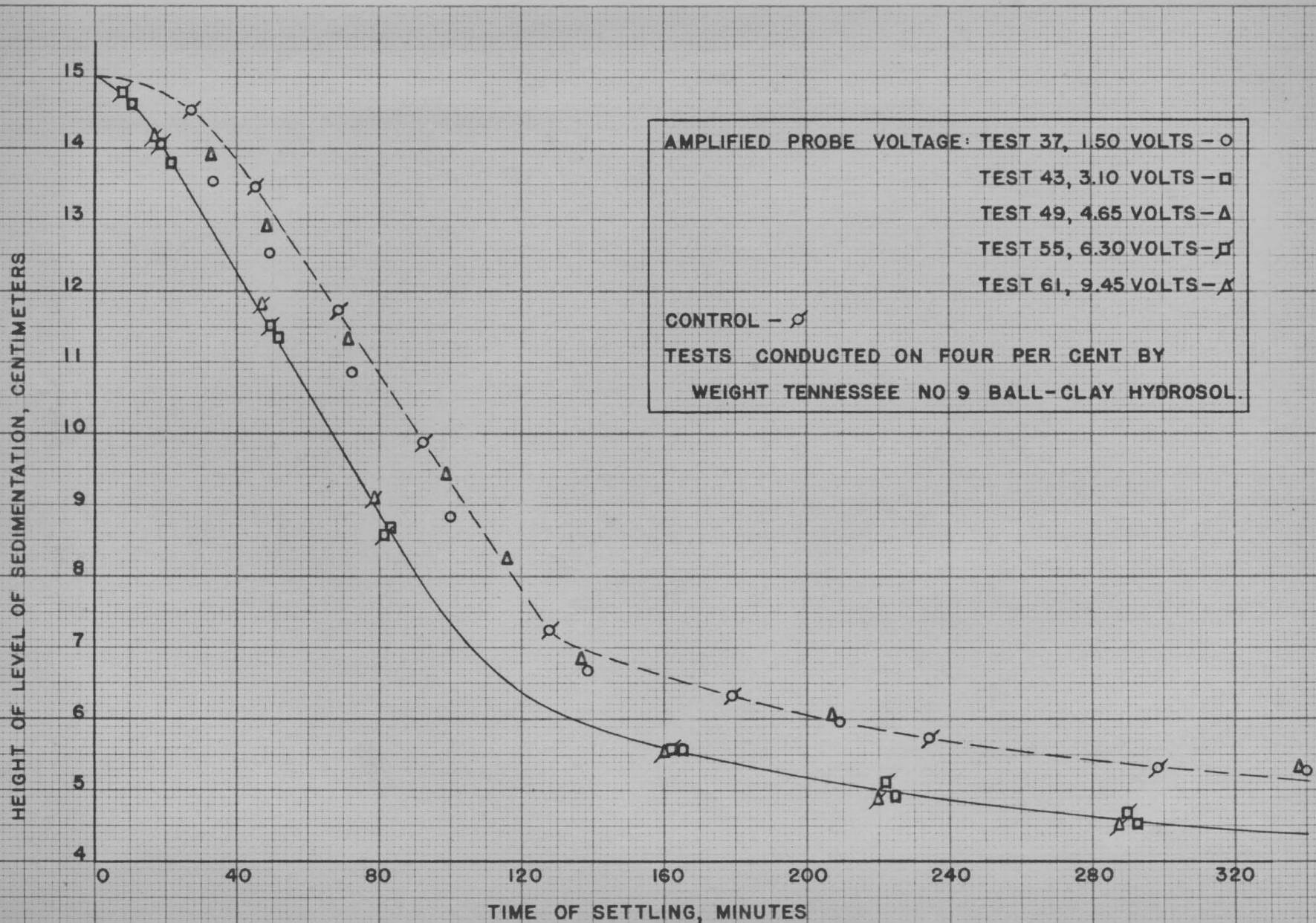


FIGURE 49. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 37, 43, 49, 55, AND 61 AT 500 KG AND 4 POUNDS PER MINUTE FLOW RATE.

750-Kilocycle Continuous Ultrasonic Coagulation

Tests. The experimental information for the 750-kilocycle continuous ultrasonic coagulation tests is shown in Table XII along with data taken from the settling rate curves. Figure 50 is representative of the range of settling characteristics obtained with different flow rates for constant intensities of insonation. Figure 51 is representative of the range of settling characteristics obtained with different intensities of insonation for constant flow rates. Both figures show a marked increase in constant hindered settling rate for the test samples over the control. In Figure 52 is shown the settling characteristics obtained with one and two pound per minute recycle rates at a four pound per minute flow rate and constant intensity of insonation. The settling rate curves indicate that recycling hinders the constant hindered settling rate relative to the nonrecycled test.

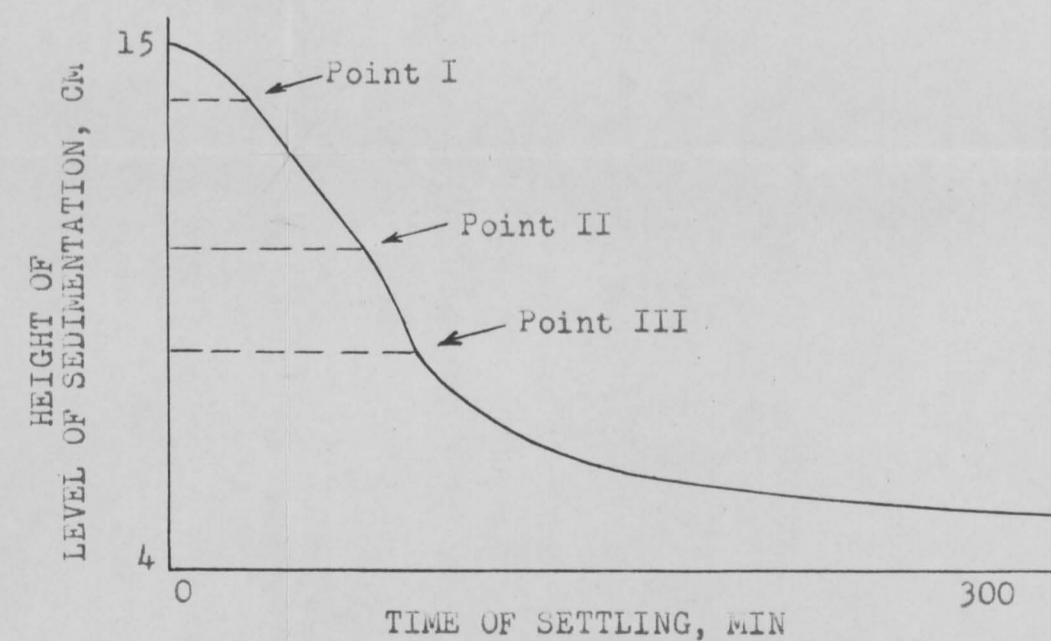
TABLE XII

Data on Continuous Ultrasonic Coagulation of a Ball-Clay Hydrosol at 750 kc, Tests Nos 68-93

Test No	Flow Rate, ^a	Recycle Rate, ^a	Plate Current, ^b	Amplified ^c	Initial pH ^d	Final pH ^e	Point I ^f	Point II ^g	Point III ^h	Constant Hindered Settling Rate,			
	lb/min	lb/min	ma	Probe Voltage, volts			Height, cm	Time, min	Height, cm		Time, min	Height, cm	Time, min
68	5	0	57.5	1.50	7.95	8.10	13.2	32.0	9.0	74.0	7.3	90.0	6.02
69	4	0	57.5	1.50	7.95	8.05	13.9	26.0	10.2	66.0	7.1	97.0	5.58
70	3	0	57.5	1.50	7.95	8.01	13.3	32.0	-	-	7.2	93.5	5.87
71	2	0	57.5	1.50	7.95	8.06	12.6	29.0	9.5	65.0	7.6	79.5	5.70
72	1	0	57.5	1.50	7.95	8.21	13.7	32.0	-	-	7.8	91.0	5.99
73	1/2	0	57.5	1.50	7.95	8.11	14.0	28.0	9.1	75.0	8.0	85.0	6.27
74	5	0	97.5	3.10	7.95	8.01	13.9	30.0	10.0	72.0	7.9	91.0	5.79
75	4	0	97.5	3.10	7.95	8.02	14.1	20.0	10.3	63.0	7.5	90.0	5.33
76	3	0	97.5	3.10	7.95	8.05	13.1	29.0	-	-	7.9	79.0	7.58
77	2	0	97.5	3.10	7.95	8.01	13.9	25.0	9.5	70.0	7.7	84.0	5.92
78	1	0	97.5	3.10	7.95	8.20	13.2	25.0	-	-	6.9	98.0	5.14
79	1/2	0	97.5	3.10	7.95	8.22	13.0	28.0	-	-	7.9	84.0	6.62
80	5	0	122.5	4.65	7.95	8.11	13.0	36.0	-	-	7.3	96.0	5.72
81	4	0	122.5	4.65	7.95	8.15	13.8	25.0	-	-	6.8	100.0	5.62
82	3	0	122.5	4.65	7.95	8.09	13.8	26.0	9.1	78.0	7.5	93.0	5.48
83	2	0	122.5	4.65	7.95	8.05	13.9	28.0	10.1	69.0	8.3	85.0	5.65
84	1	0	122.5	4.65	7.95	8.20	14.0	32.0	9.7	78.5	7.9	96.0	5.65
85	1/2	0	122.5	4.65	7.95	8.21	13.6	32.0	-	-	8.7	76.0	6.62
86	5	0	145.0	6.30	7.95	8.12	14.2	26.0	10.4	67.5	7.4	96.0	5.50
87	4	0	145.0	6.30	7.95	8.20	13.5	34.5	9.0	82.5	7.6	96.0	5.57
88	3	0	145.0	6.30	7.95	8.10	13.7	32.5	9.7	77.0	8.1	92.5	5.44
89	2	0	145.0	6.30	7.95	8.20	14.2	22.0	10.0	68.0	8.3	85.0	5.46
90	1	0	145.0	6.30	7.95	8.19	13.7	30.5	9.8	73.0	7.7	92.0	5.50
91	1/2	0	145.0	6.30	7.95	8.19	13.5	34.0	-	-	7.8	97.5	5.42
92	4	2	57.5	1.50	7.95	8.20	14.7	13.0	10.5	70.0	7.6	96.0	4.49
93	4	1	57.5	1.50	7.95	8.16	13.8	30.0	11.1	67.0	8.6	99.0	4.45

Temperatures: Suspension make-up, 66 °F; room, 80-82 °F range over approximately 5 hours.

- ^a Of four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.
- ^b Of General Electric Ultrasonic Generator, catalogue No 8665966 G3.
- ^c From voltmeter connected to quartz crystal probe amplifier.
- ^d Suspension make-up.
- ^e Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.
- ^f Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time after insonation.
- ^g End of constant hindered settling period and beginning of increased rate settling period.
- ^h End of increased rate settling period and beginning of compaction settling period.



GENERALIZED SETTLING RATE CURVE

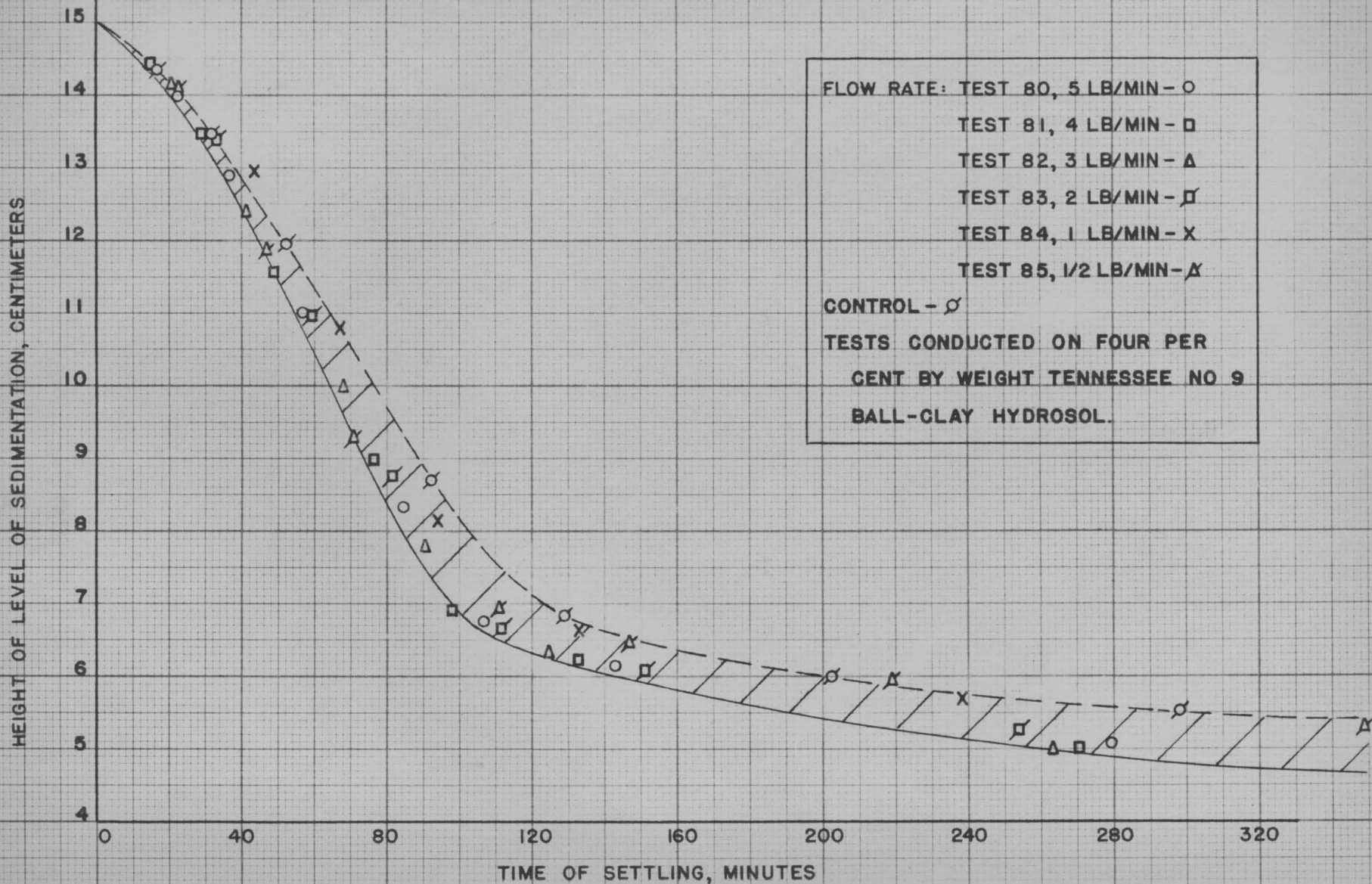


FIGURE 50. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 80-85 AT 750 KC AND 4.65 VOLTS AMPLIFIED PROBE VOLTAGE.

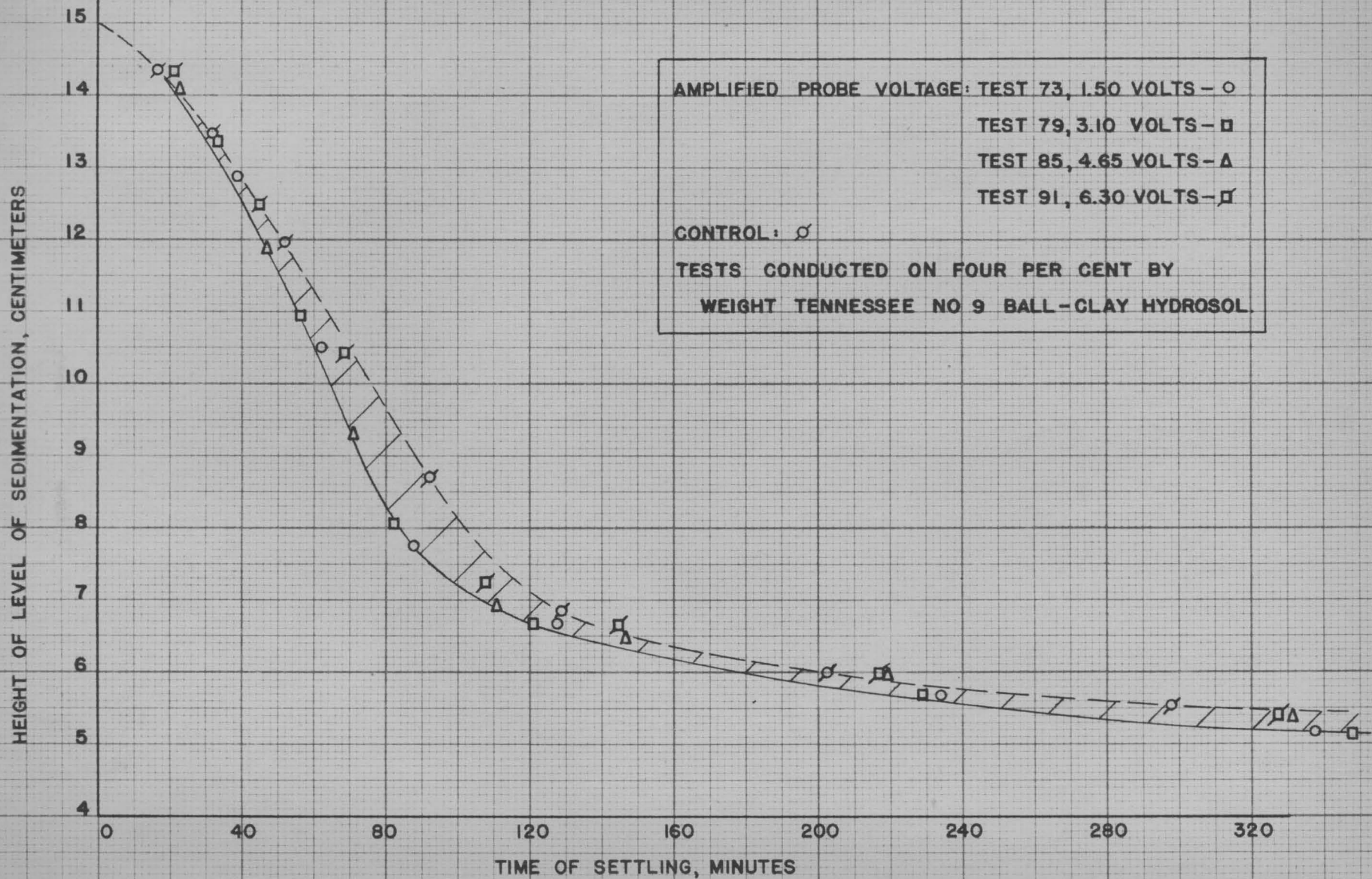


FIGURE 51. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 73,79,85 AND 91 AT 750 KC AND 1/2 POUND PER MINUTE FLOW RATE.

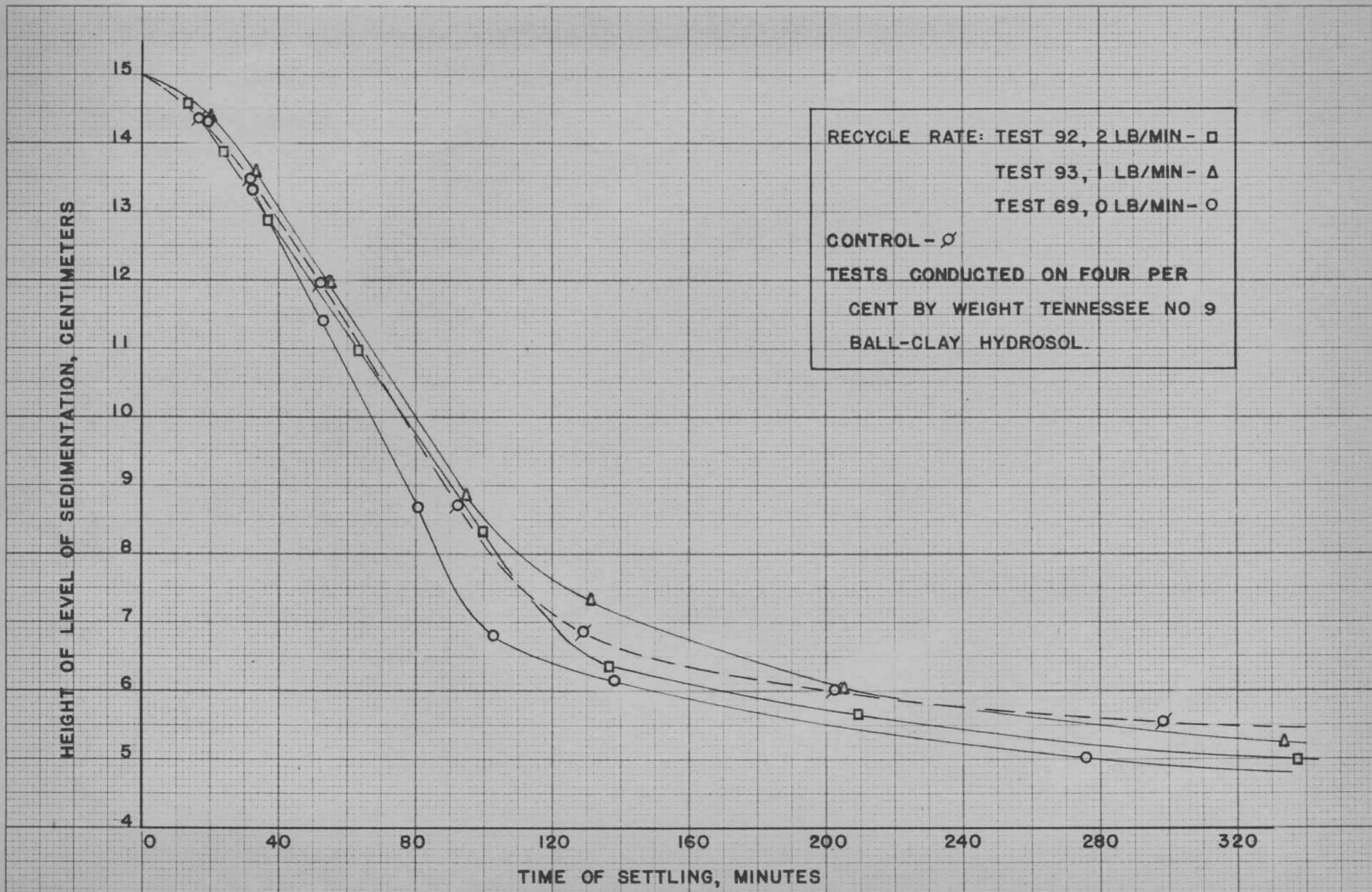


FIGURE 52. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 69, 92, AND 93 AT 750 KC, 1.50 VOLTS AMPLIFIED PROBE VOLTAGE, AND 4 POUNDS PER MINUTE FLOW RATE.

1000-Kilocycle Continuous Ultrasonic Coagulation

Tests. The experimental information for the 1000-kilocycle continuous ultrasonic coagulation tests is shown in Table XIII along with data taken from the settling rate curves. Figure 53 is representative of the range of settling characteristics obtained with different flow rates for constant intensities of insonation. Figure 54 is representative of the range of settling characteristics obtained with different intensities of insonation for constant flow rates. Very little increase in constant hindered settling rate is shown in the figures for the test samples over the control. The one and two pound per minute recycle rate tests at a four pound per minute flow rate and constant intensity of insonation had practically the same settling characteristics as the nonrecycled test at the same flow rate and intensity of insonation; however, the constant hindered settling rate was less for the recycled tests.

TABLE XIII

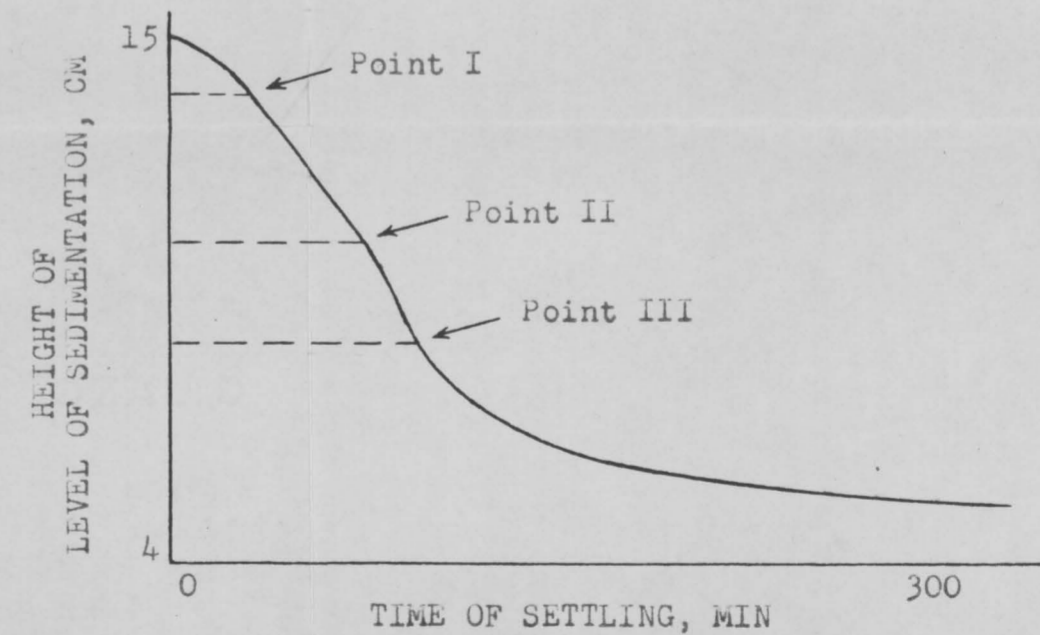
Data on Continuous Ultrasonic Coagulation of a Ball-Clay Hydrosol at 1000 kc, Tests Nos 94-119

Test No	Flow Rate, ^a lb/min	Recycle Rate, ^a lb/min	Plate Current, ^b ma	Amplified ^c Probe Voltage, volts	Initial pH ^d	Final pH ^e	Point I ^f Height, cm	Point I ^f Time, min	Point II ^g Height, cm	Point II ^g Time, min	Point III ^h Height, cm	Point III ^h Time, min	Constant Hindered Settling Rate, cm/hr
94	5	0	25.0	1.50	7.85	7.80	14.0	22.0	10.7	65.0	8.0	94.0	4.66
95	4	0	25.0	1.50	7.85	7.90	13.3	31.0	-	-	7.0	103.0	5.08
96	3	0	25.0	1.50	7.85	7.80	14.3	22.5	9.4	84.0	7.5	103.0	4.80
97	2	0	25.0	1.50	7.85	7.87	14.1	22.0	-	-	8.7	89.0	4.84
98	1	0	25.0	1.50	7.85	7.85	13.9	30.0	-	-	7.3	109.5	5.00
99	1/2	0	25.0	1.50	7.85	7.81	14.4	25.5	9.2	90.0	7.8	106.0	4.88
100	5	0	75.0	3.10	7.85	7.90	14.0	22.0	10.5	66.5	7.4	99.5	4.66
101	4	0	75.0	3.10	7.85	7.80	13.5	27.5	-	-	7.5	99.0	5.04
102	3	0	75.0	3.20	7.85	7.84	13.7	25.5	-	-	7.6	94.0	5.26
103	2	0	75.0	3.20	7.85	7.71	14.1	23.5	9.8	79.0	7.5	104.5	4.62
104	1	0	75.0	3.30	7.85	7.89	14.0	34.5	9.0	95.5	7.6	109.0	4.98
105	1/2	0	75.0	3.00	7.85	7.80	13.5	40.0	-	-	8.3	104.0	4.86
106	5	0	125.0	4.65	7.85	7.85	14.2	23.0	10.6	68.0	7.4	99.0	4.80
107	4	0	125.0	4.65	7.85	7.92	13.5	29.5	-	-	7.5	95.0	4.96
108	3	0	125.0	4.65	7.85	7.88	14.4	16.5	9.3	82.0	7.7	96.0	5.71
109	2	0	125.0	4.65	7.85	7.90	14.1	23.5	9.5	81.0	7.5	102.0	4.80
110	1	0	125.0	4.65	7.85	7.80	-	-	-	-	8.0	110.0	-
111	1/2	0	125.0	4.60	7.85	7.91	14.1	29.0	-	-	8.3	104.0	4.80
112	5	0	150.0	6.30	7.85	7.76	14.6	10.0	10.6	64.0	7.4	99.5	4.49
113	4	0	150.0	6.30	7.85	7.69	13.5	29.5	-	-	7.7	94.0	5.20
114	3	0	150.0	6.20	7.85	7.69	14.6	18.0	9.0	85.5	7.4	103.5	4.88
115	2	0	150.0	6.20	7.85	7.89	14.1	24.5	9.8	79.0	7.5	105.0	4.86
116	1	0	150.0	6.25	7.85	7.70	14.0	28.0	9.4	86.0	7.7	100.0	4.79
117	1/2	0	150.0	6.30	7.85	7.84	13.7	29.5	10.0	73.5	7.8	96.0	5.08
118	4	2	25.0	1.50	7.85	7.96	13.2	32.5	-	-	6.9	112.0	4.73
119	4	1	25.0	1.50	7.85	7.94	12.7	40.0	-	-	7.0	113.0	4.73

Temperatures: Suspension make-up:
 Tests Nos 118-119 inc., 68 °F.
 All other tests at 1000 kc, 65 °F.

Room:
 Tests Nos 118-119 inc., 82-86 °F range
 over approximately 5 hours.
 All other tests at 1000 kc, 79-81 °F range
 over approximately 5 hours.

- ^a Of four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.
- ^b Of General Electric Ultrasonic Generator, catalogue No 8665966 G3.
- ^c From voltmeter connected to quartz crystal probe amplifier.
- ^d Suspension make-up.
- ^e Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.
- ^f Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time after insonation.
- ^g End of constant hindered settling period and beginning of increased rate settling period.
- ^h End of increased rate settling period and beginning of compaction settling period.



GENERALIZED SETTLING RATE CURVE

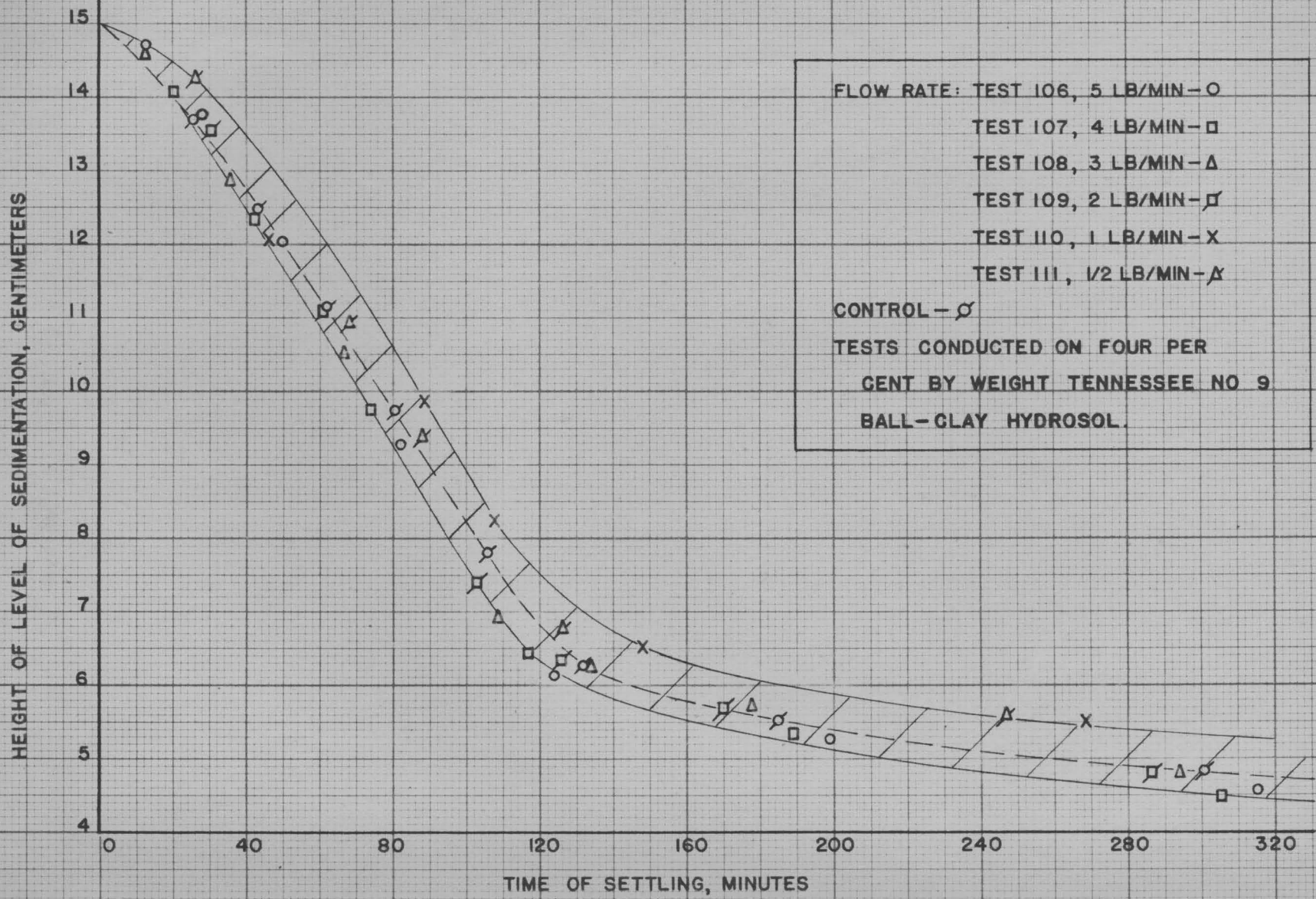


FIGURE 53. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 106-III AT 1000 KG AND 4.65 VOLTS AMPLIFIED PROBE VOLTAGE.

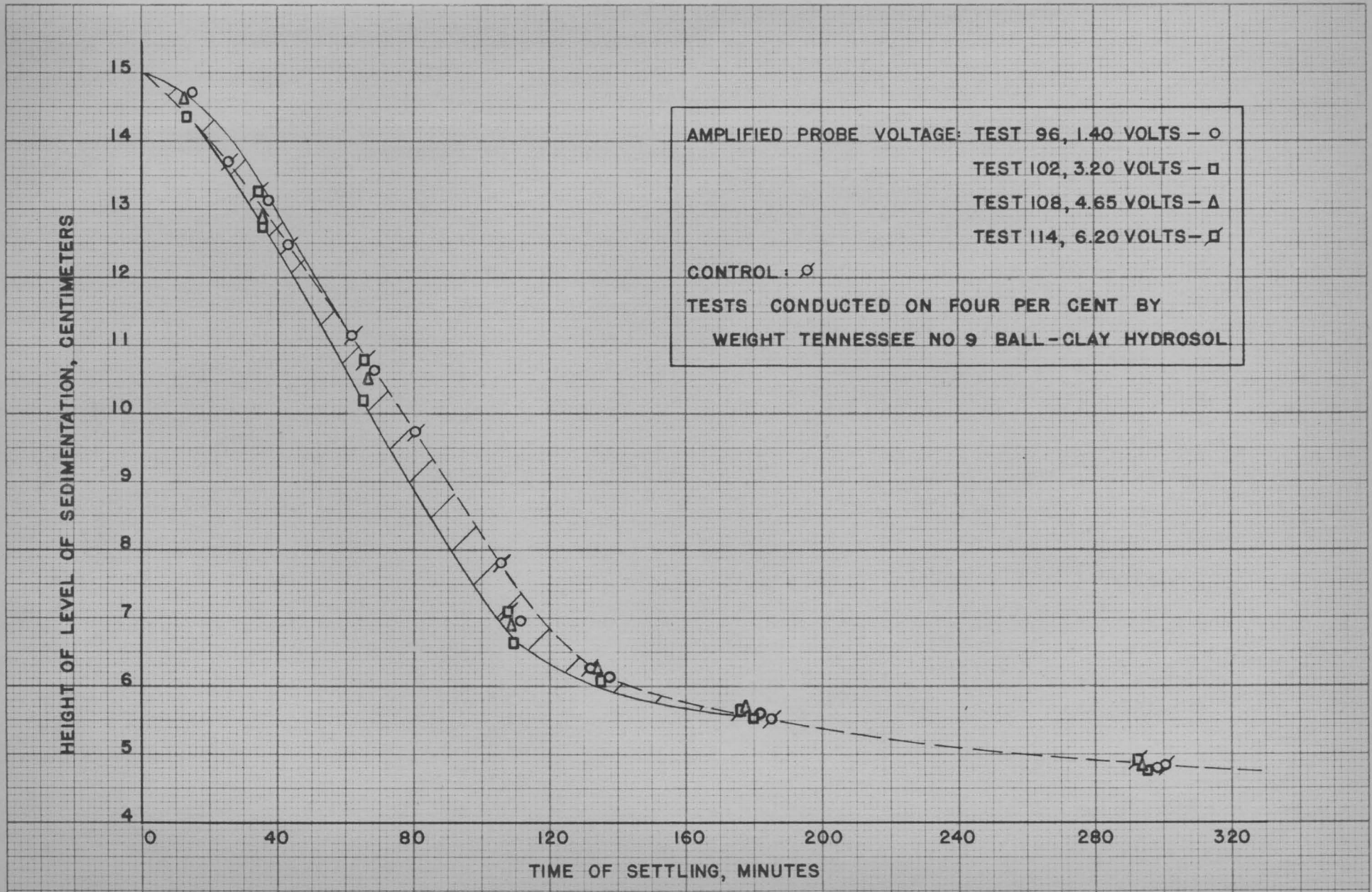


FIGURE 54. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC COAGULATION TESTS 96, 102, 108, AND 114 AT 1000 KC AND 3 POUNDS PER MINUTE FLOW RATE.

Continuous Mechanical Coagulation Tests. The experimental information for the continuous mechanical coagulation tests is shown in Table XIV along with data taken from the settling rate curves. Figure 55 is representative of the range of settling characteristics obtained with different flow rates for the 2,860 and 11,110 revolution per minute stirrer speed tests. Figure 56 is representative of the range of settling characteristics obtained with different flow rates for the 14,820 and 17,550 revolution per minute stirrer speed tests. Figures 57 and 58 show the extremes, at the five and the one-half pound per minute flow rates, respectively, of the settling characteristics obtained with different intensities of insonation. In general, increasing stirrer speed and/or decreasing flow rate tended to decrease the constant hindered settling rate. The one and two pound per minute recycle rate tests at a four pound per minute flow rate and stirrer speeds of 2,850 and 14,820 revolutions per minute were not conclusive; however, the constant hindered settling rate was less for the recycled tests than for the non-recycled tests.

TABLE XIV

Data on Continuous Mechanical Coagulation of a Ball-Clay Hydrosol, Tests Nos 120-147

Test No	Flow Rate, ^a lb/min	Recycle Rate, ^a lb/min	Applied Voltage, ^b volts	Speed, ^c rpm	Initial pH ^d	Final pH ^e	Point I ^f Height, cm	Time II ^g Time, min	Height, cm	Time III ^h Time, min	Height, cm	Time, min	Constant Hindered Settling Rate, cm/min
120	5	0	30	2,860	7.80	8.00	14.1	20.0	9.1	80.0	6.9	104.0	5.14
121	4	0	30	2,860	7.80	8.05	14.2	16.5	9.2	76.0	6.9	100.5	5.08
122	3	0	30	2,860	7.80	7.95	14.2	24.0	-	-	7.0	105.0	5.30
123	2	0	30	2,860	7.80	7.97	14.2	26.5	9.9	78.5	7.6	105.0	5.00
124	1	0	30	2,860	7.80	8.01	14.0	32.0	9.0	96.5	7.4	114.0	4.66
125	1/2	0	30	2,860	7.80	7.99	14.0	31.5	9.0	93.0	7.2	114.5	4.86
126	5	0	60	11,110	7.80	8.10	14.0	20.0	-	-	7.0	100.0	5.35
127	4	0	60	11,110	7.80	8.10	13.9	25.5	-	-	7.1	102.0	5.33
128	3	0	60	11,110	7.80	8.02	13.2	41.0	9.1	85.0	7.5	101.5	5.00
129	2	0	60	11,110	7.80	8.01	13.6	38.0	-	-	7.6	109.5	5.00
130	1	0	60	11,110	7.80	7.97	13.7	30.5	9.4	82.0	7.4	102.0	5.08
131	1/2	0	60	11,110	7.80	8.02	13.8	29.5	-	-	8.5	91.0	5.16
132	5	0	90	14,820	7.80	7.99	14.1	24.0	9.7	76.0	7.5	99.0	5.10
133	4	0	90	14,820	7.80	8.05	14.2	29.0	-	-	7.8	105.5	5.04
134	3	0	90	14,820	7.80	8.02	14.0	32.0	-	-	7.5	109.0	5.08
135	2	0	90	14,820	7.80	8.09	14.0	25.0	-	-	7.4	102.0	4.94
136	1	0	90	14,820	7.80	8.02	14.2	32.0	-	-	7.4	112.0	4.96
137	1/2	0	90	14,820	7.80	8.00	13.9	32.5	-	-	7.7	105.5	5.16
138	5	0	120	17,550	7.80	8.05	13.8	26.5	-	-	7.5	102.0	5.08
139	4	0	120	17,550	7.80	8.02	13.9	25.5	-	-	7.4	101.5	5.16
140	3	0	120	17,550	7.80	8.03	13.9	35.5	9.8	85.5	7.0	117.0	4.90
141	2	0	120	17,550	7.80	8.05	14.0	26.5	10.0	76.0	7.3	104.0	4.90
142	1	0	120	17,550	7.80	8.04	13.7	38.5	10.0	84.5	7.4	113.0	4.84
143	1/2	0	120	17,550	7.80	8.10	13.3	49.5	-	-	7.7	118.5	4.94
144	4	2	30	2,860	7.80	8.10	13.5	29.5	8.6	93.0	7.4	107.5	4.68
145	4	1	30	2,860	7.80	8.12	13.7	28.5	-	-	7.0	115.0	4.64
146	4	2	90	14,820	7.80	8.01	14.1	22.0	10.3	70.5	7.2	106.5	4.92
147	4	1	90	14,820	7.80	8.02	14.1	23.5	10.6	68.5	7.0	110.0	4.96

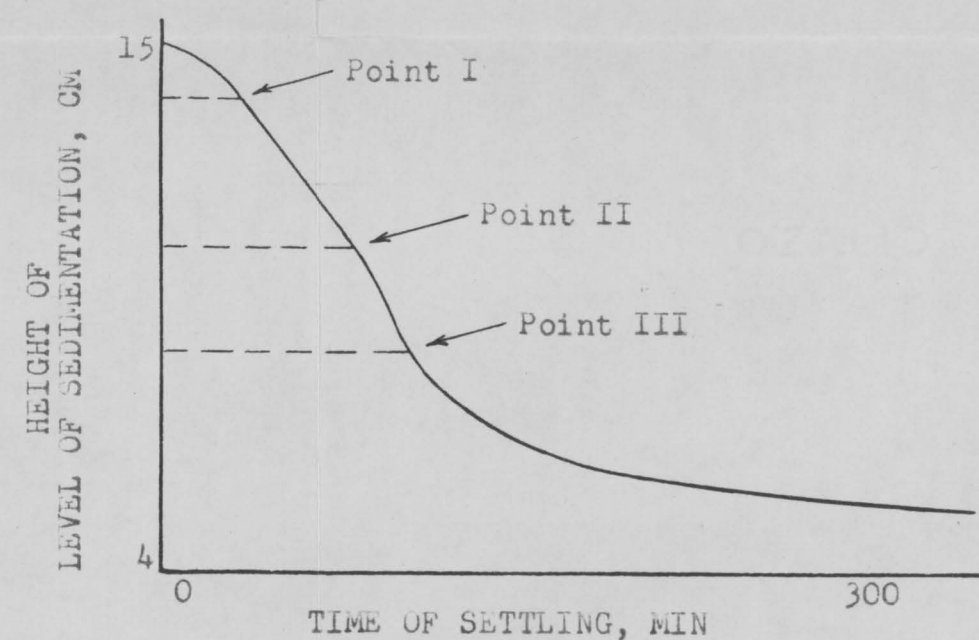
Temperatures: Suspension make-up, 66 °F.

Room:

Tests Nos 144-147 inc., 82-86 °F range
over approximately 5 hours.

All other continuous mechanical tests, 82-83 °F range
over approximately 5 hours.

- a Of four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.
- b To Waring blender motor.
- c Of blades in "micro" head of Waring blender.
- d Suspension make-up.
- e Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.
- f Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time after insonation.
- g End of constant hindered settling period and beginning of increased rate settling period.
- h End of increased rate settling period and beginning of compaction settling period.



GENERALIZED SETTLING RATE CURVE

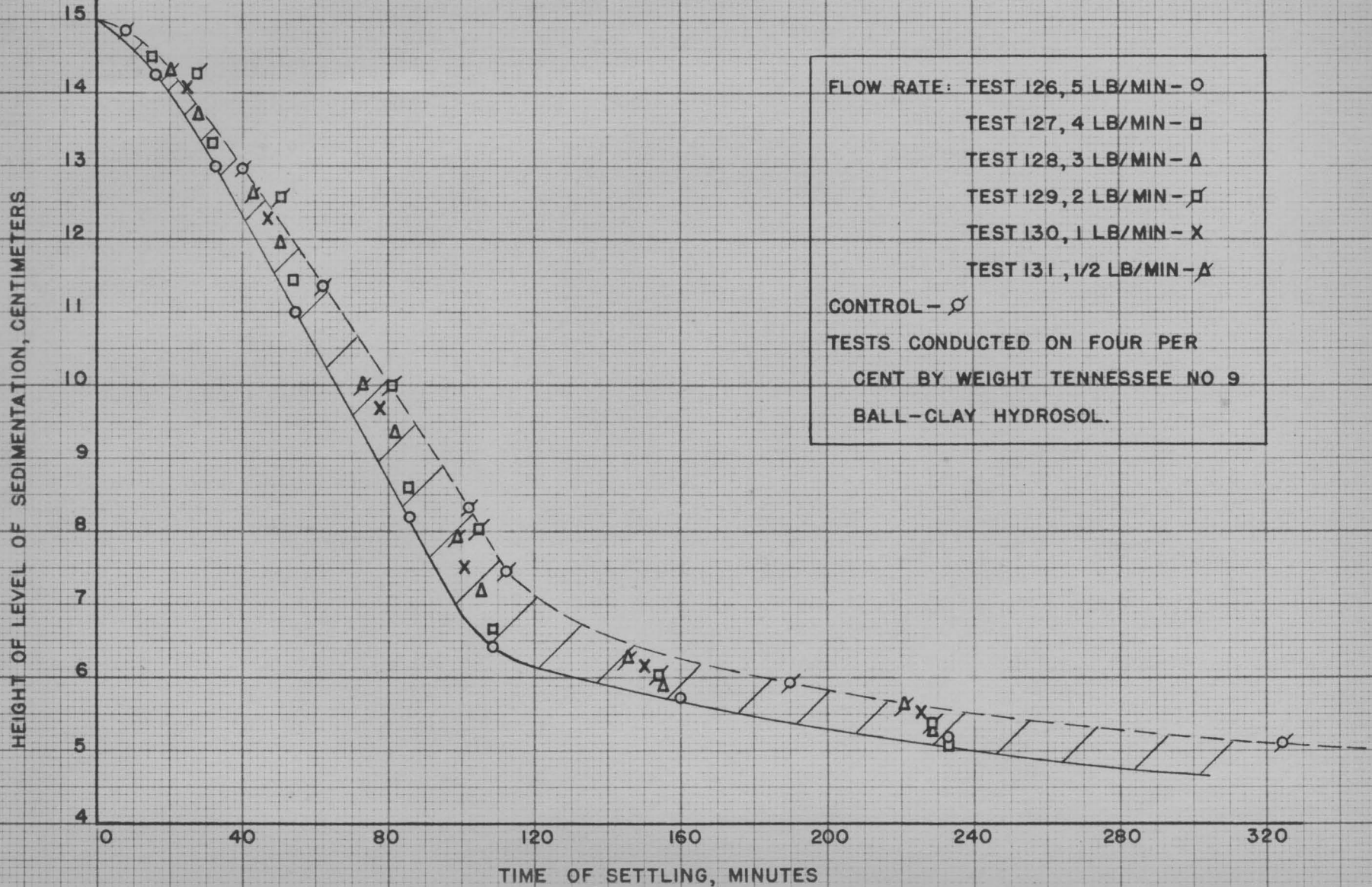


FIGURE 55. SETTLING RATE CURVES FOR CONTINUOUS MECHANICAL COAGULATION TESTS 126-131 AT 11,110 RPM STIRRER SPEED.

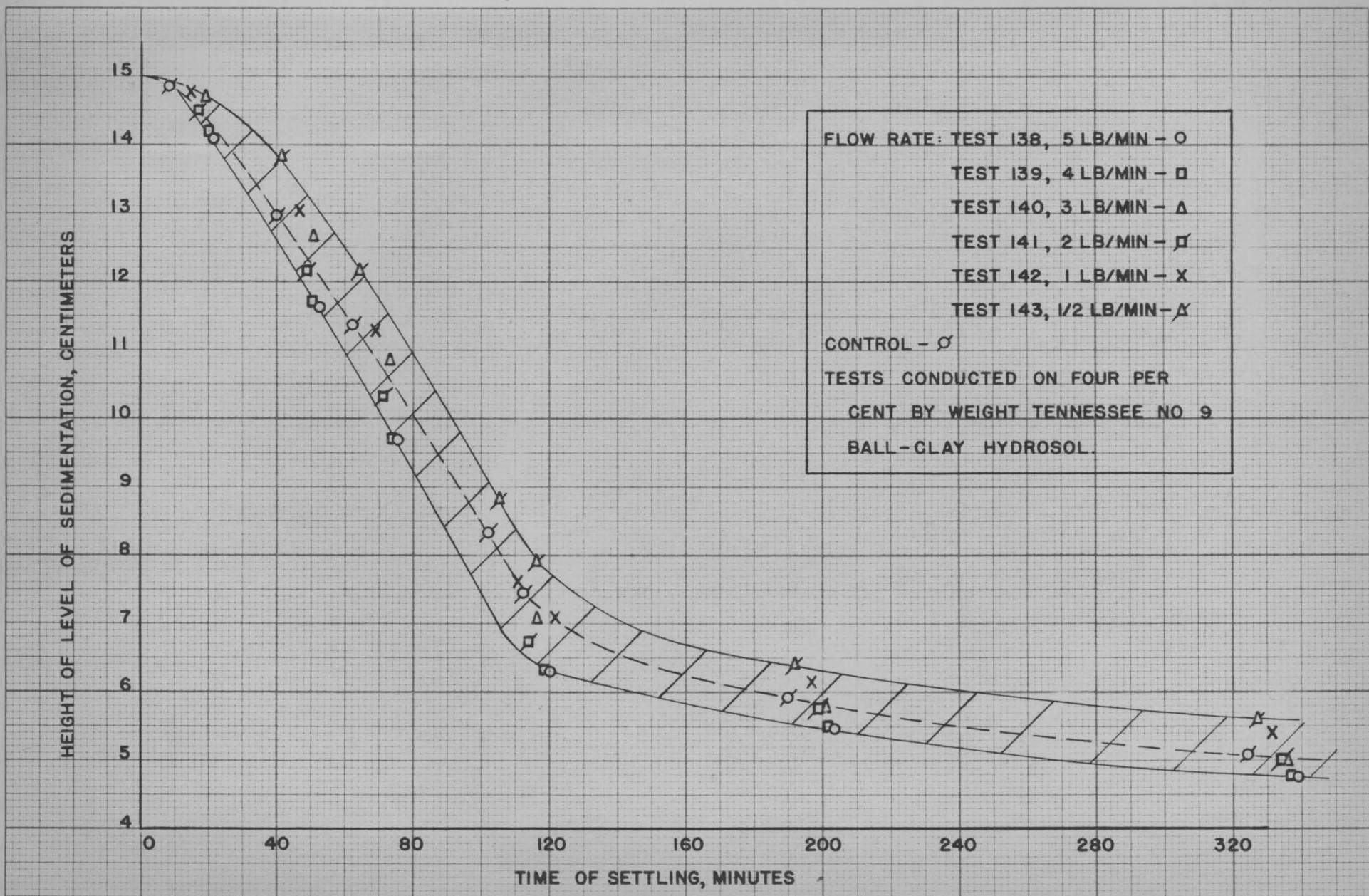


FIGURE 56. SETTLING RATE CURVES FOR CONTINUOUS MECHANICAL COAGULATION TESTS 138-143 AT 17,550 RPM STIRRER SPEED.

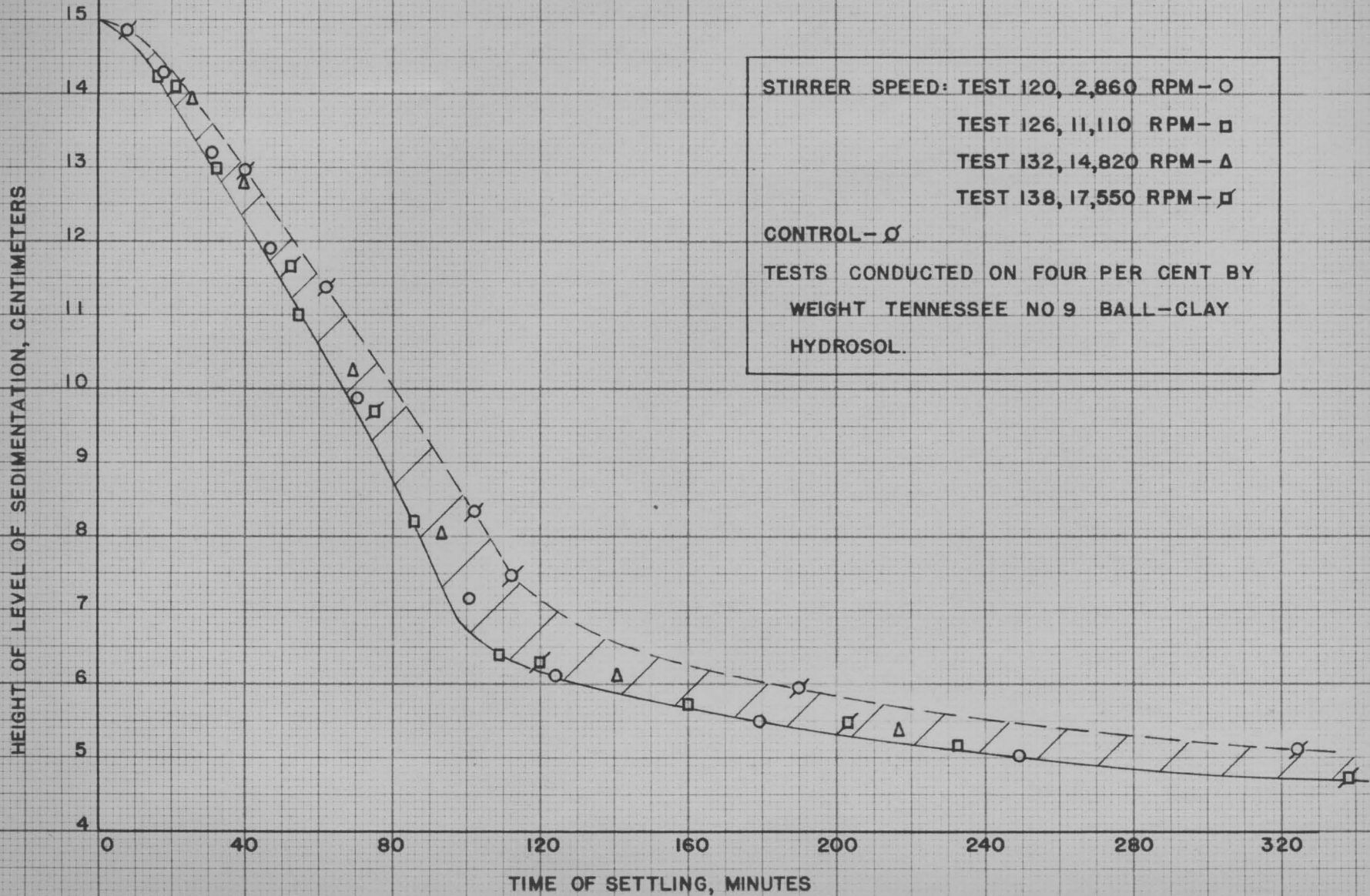


FIGURE 57. SETTLING RATE CURVES FOR CONTINUOUS MECHANICAL COAGULATION TESTS 120, 126, 132, AND 138 AT 5 POUNDS PER MINUTE FLOW RATE.

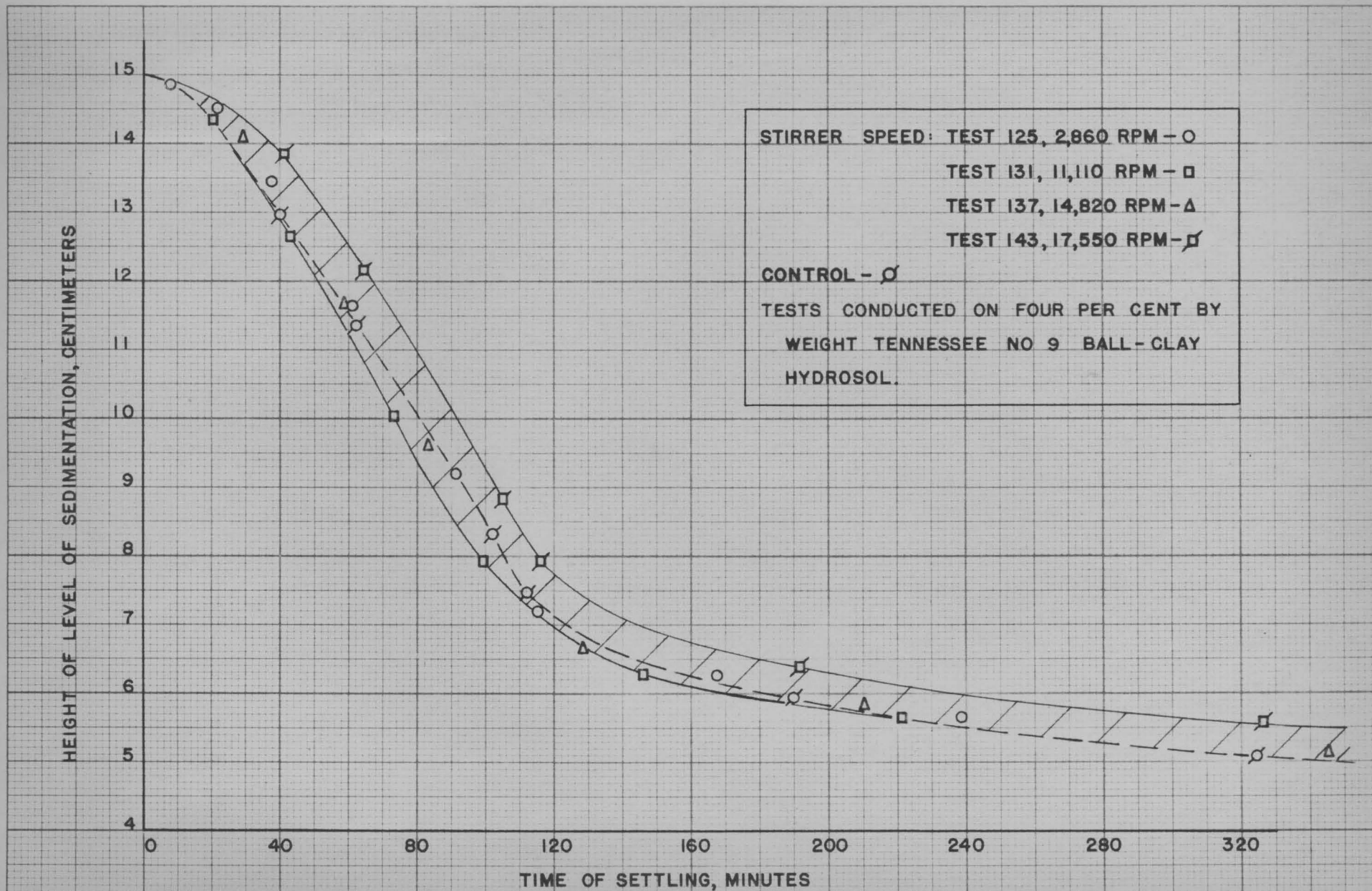


FIGURE 58. SETTLING RATE CURVES FOR CONTINUOUS MECHANICAL COAGULATION TESTS 125, 131, 137 AND 143 AT 1/2 POUND PER MINUTE FLOW RATE.

Batch Mechanical Coagulation Tests. The experimental information for the batch mechanical coagulation tests is shown in Table XV along with data taken from the settling rate curves. Figure 59 shows the settling rate curves obtained for different agitation times at 29 revolutions per minute stirrer speed. The settling rate curves as well as the constant hindered settling rate values indicate that this method of treatment hinders rather than increases coagulation. Since no single control test was made for the batch mechanical coagulation tests, the continuous mechanical coagulation control test was used as its pH corresponded more closely to the pH of the batch mechanical coagulation tests than the other control tests.

300-Kilocycle Batch Ultrasonic Coagulation Tests. The experimental information for the 300-kilocycle batch ultrasonic coagulation tests is shown in Table XVI along with information taken from settling rate curves. The 300-kilocycle batch ultrasonic coagulation tests in themselves were not conclusive; however, a considerably higher constant hindered settling rate was obtained by batch ultrasonic treatment than by continuous ultrasonic treatment.

TABLE XV

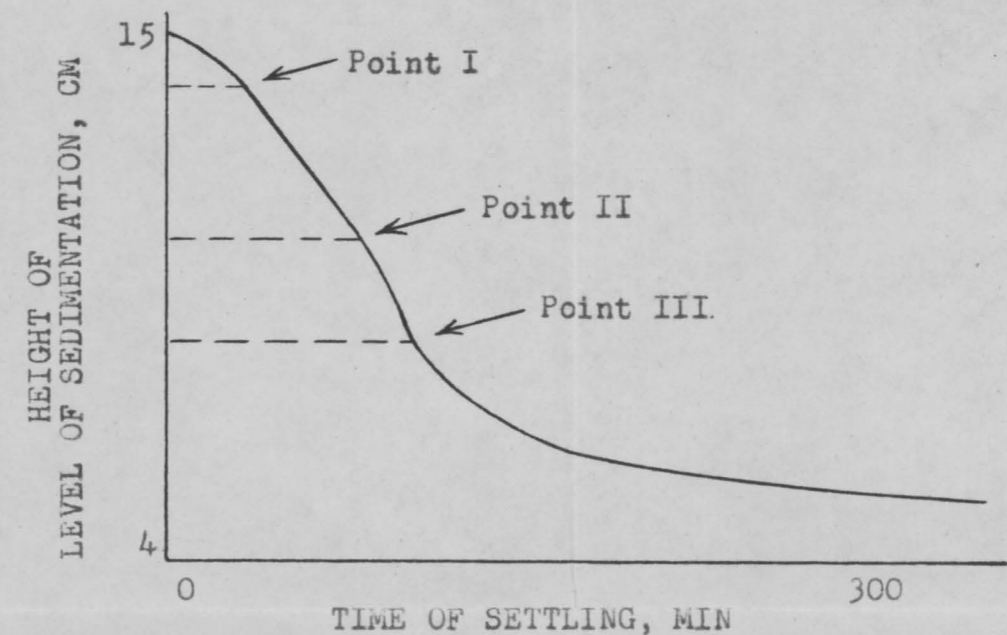
Data on Batch Mechanical Coagulation of a Ball-Clay Hydrosol, Tests Nos 148-156

Test No	Stirrer Speed, ^a rpm	Agitation Time, min	Initial pH ^b	Final pH ^c	Point I ^d Height, cm	Point I ^d Time, min	Point II ^e Height, cm	Point II ^e Time, min	Point III ^f Height, cm	Point III ^f Time, min	Constant Hindered Settling Rate, cm/hr
148	29.0	5.0	7.90	8.10	13.3	36.0	10.6	82.0	8.1	118.0	3.54
149	29.0	10.0	7.85	7.96	13.4	28.0	-	-	9.0	83.0	4.80
150	29.0	30.0	7.70	7.80	13.4	64.0	-	-	8.5	196.0	2.21
151	29.0	60.0	7.80	7.98	13.5	60.0	-	-	7.5	177.0	3.33
152	60.0	5.0	7.70	7.85	13.7	25.0	9.2	84.0	8.0	97.0	4.69
153	60.0	10.0	7.86	8.00	13.3	44.0	-	-	8.3	130.0	3.51
154	60.0	30.0	7.86	8.02	13.1	65.0	-	-	8.5	138.5	3.77
155	120.0	5.0	7.85	7.98	14.0	44.0	10.6	136.0	8.2	196.0	2.24
156	14.5	60.0	7.85	8.03	12.5	81.0	9.8	152.0	8.7	180.0	2.29

Temperatures: Suspension make-up:
 Test No 155, 66 °F.
 Tests Nos 150, 151, 152, 154, and 156, 67 °F.
 Tests Nos 149 and 153, 68 °F.
 Test No 148, 69 °F.

Room:
 Test No 148, 82-83 °F.
 Test Nos 149 and 151, 82-86 °F.
 Test No 150, 81 °F.
 Tests Nos 152 and 153, 82-85 °F.
 Test No 154, 80-82 °F.
 Tests Nos 155 and 156, 82-84 °F.
 Range over approximately 5 hours.

- a Fisher "Jumbo" stirrer impeller centered in coagulating jar three inches from bottom; jar containing four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.
- b Suspension make-up.
- c Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.
- d Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time at beginning of agitation.
- e End of constant hindered settling period and beginning of increased rate settling period.
- f End of increased rate settling period and beginning of compaction settling period.



GENERALIZED SETTLING RATE CURVE

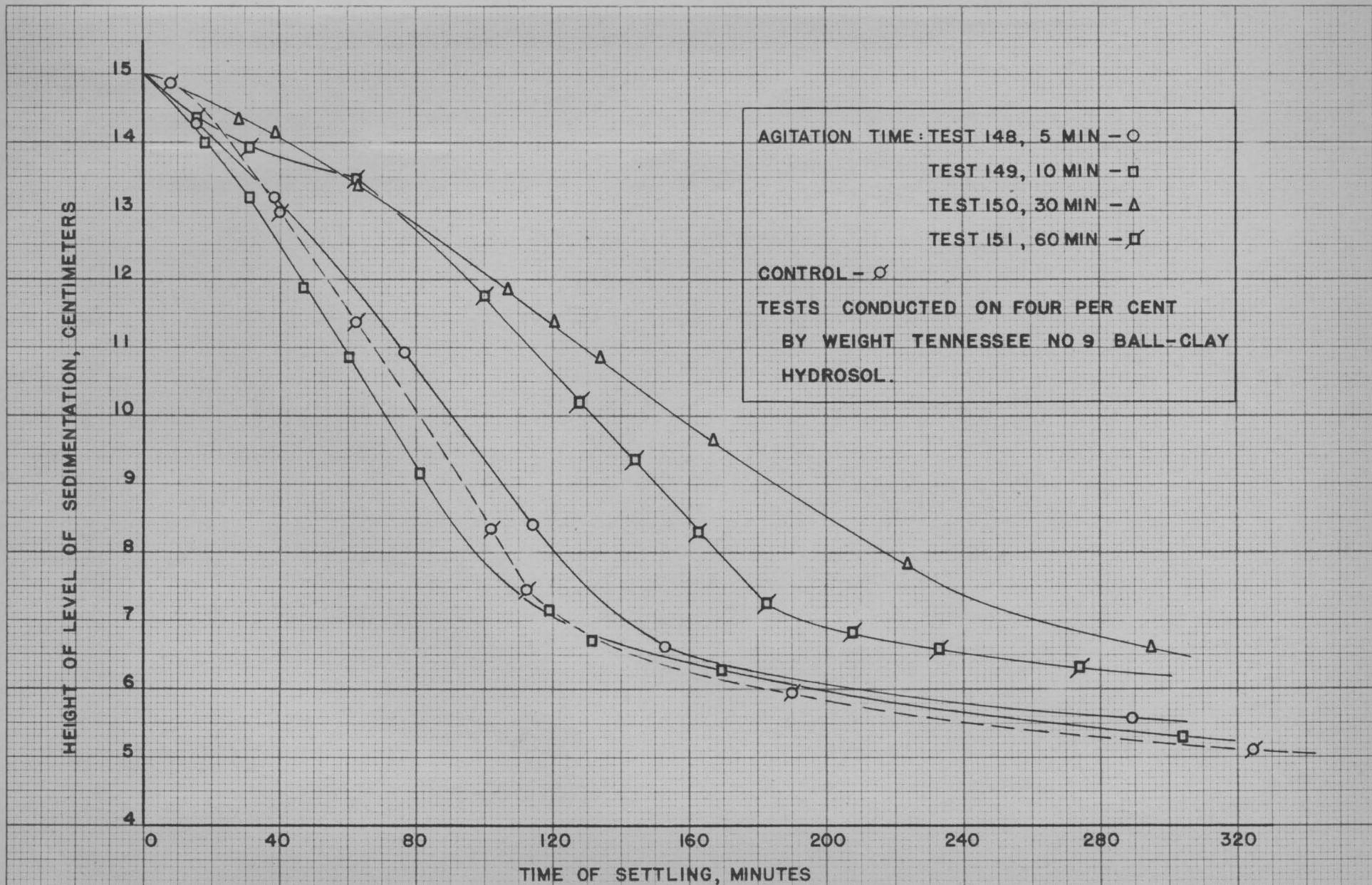


FIGURE 59. SETTLING RATE CURVES FOR BATCH MECHANICAL COAGULATION TESTS 148-151 AT 29 RPM STIRRER SPEED.

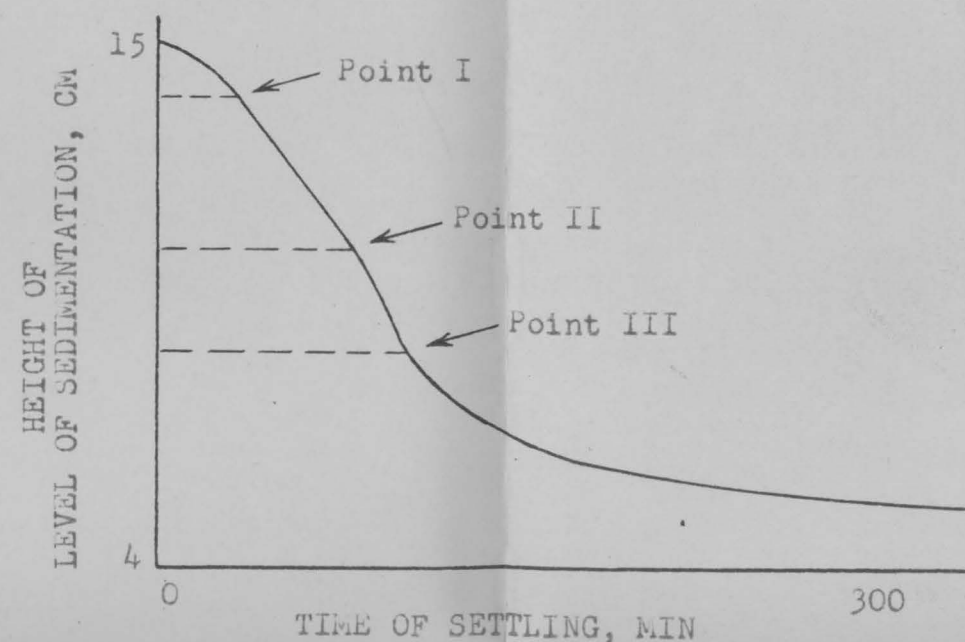
TABLE XVI

Data on Batch Ultrasonic Coagulation of a Ball-Clay Hydrosol at 300 kc, Tests Nos 157-160

Test No	Time of Insonation, min ^a	Plate Current, ma ^b	Probe Voltage, volts ^c	Initial pH ^d	Final pH ^e	Point I ^f Height, cm	Point I ^f Time, min	Point II ^g Height, cm	Point II ^g Time, min	Point III ^h Height, cm	Point III ^h Time, min	Constant Hindered Settling Rate, cm/hr
157	1	75.0	5.40	7.85	7.92	13.1	28.5	-	-	8.5	67.0	7.07
158	1	75.0	5.40	7.85	7.93	13.8	24.0	-	-	7.5	78.0	7.04
159	2	75.0	5.40	7.85	7.91	13.5	28.0	-	-	7.9	73.0	7.43
160	2	75.0	5.40	7.85	7.95	14.2	39.0	-	-	8.0	77.0	9.82

Temperatures: Suspension make-up, 66 °F; room, 81-83 °F range over approximately 5 hours.

- ^a Of four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water, insonated in a 33 mm O. D. by 29 mm I. D., 0.001-inch nickel bottom pyrex glass tube at a height of 15 cm.
- ^b Of General Electric Ultrasonic Generator, catalogue No 8665966 G3.
- ^c From voltmeter connected to quartz crystal probe amplifier.
- ^d Suspension make-up.
- ^e Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.
- ^f Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time after insonation.
- ^g End of constant hindered settling period and beginning of increased rate settling period.
- ^h End of increased rate settling period and beginning of compaction settling period.



GENERALIZED SETTLING RATE CURVE

Comments: Tests Nos 157 and 159 allowed to settle in nickel bottom tubes. Tests Nos 158 and 160 transferred to Nessler tubes for settling.

Reproducibility Tests. The experimental information for the reproducibility tests made at 300 kilocycles is shown in Table XVII along with data taken from the settling rate curves. Figure 60 is representative of the comparison obtained between the reproducibility tests and the experimental tests.

Control Tests. The experimental information for the control tests is shown in Table XVIII along with data taken from the settling rate curves. The settling rate curves themselves have already been presented in connection with the settling rate curves for the corresponding series of tests.

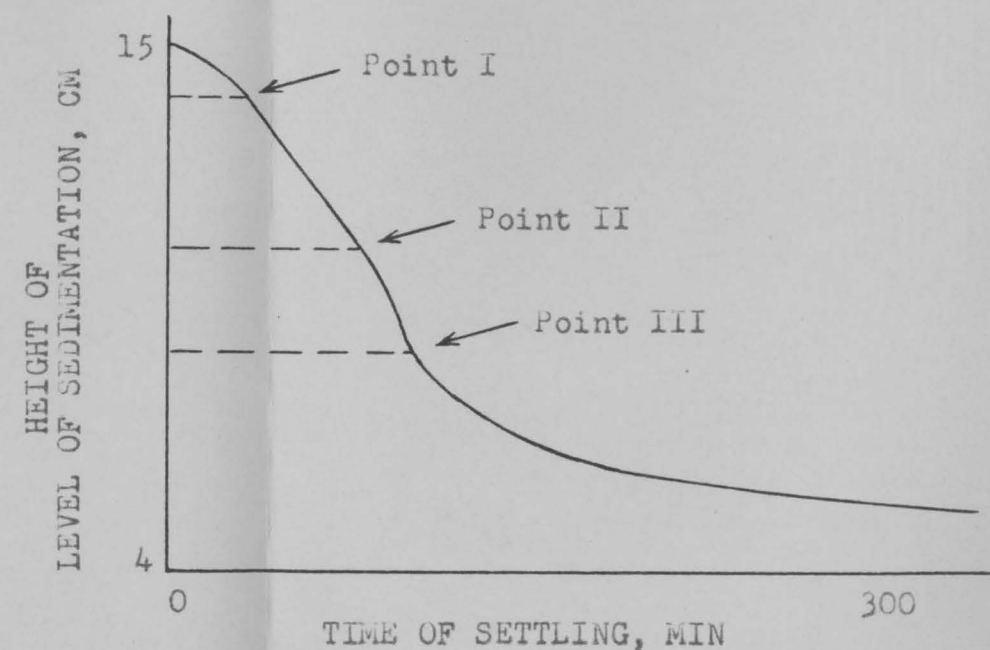
TABLE XVII

Data on Continuous Ultrasonic Coagulation Reproducibility at 300 kc, Tests Nos 161-163

Test No ^a	Flow Rate, ^b lb/min	Recycle Rate, ^b lb/min	Plate Current, ^c ma	Amplified ^d Probe Voltage, volts	Initial pH ^e	Final pH ^f	Point I ^g Height, cm	Point I ^g Time, min	Point II ^h Height, cm	Point II ^h Time, min	Point III ⁱ Height, cm	Point III ⁱ Time, min	Constant Hindered Settling Rate, cm/hr
161	5	0	20.0	1.50	7.92	8.06	14.2	22.0	-	-	7.6	96.0	5.44
162	3	0	20.0	1.50	7.92	8.10	14.4	24.0	10.3	72.0	7.7	97.0	5.21
163	2	0	40.5	3.10	7.92	8.06	14.1	24.5	9.5	77.5	7.6	97.5	5.26

Temperatures: Suspension make-up, 68 °F; room, 80-83 °F range over approximately 5 hours.

- a Reproducibility corresponding to Tests Nos 1, 3, and 9, respectively.
- b Of four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.
- c Of General Electric Ultrasonic Generator, catalogue No 8665966 G3
- d From voltmeter connected to quartz crystal probe amplifier.
- e Suspension make-up.
- f Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.
- g Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time after insonation.
- h End of constant hindered settling period and beginning of increased rate settling period.
- i End of increased rate settling period and beginning of compaction settling period.



GENERALIZED SETTLING RATE CURVE

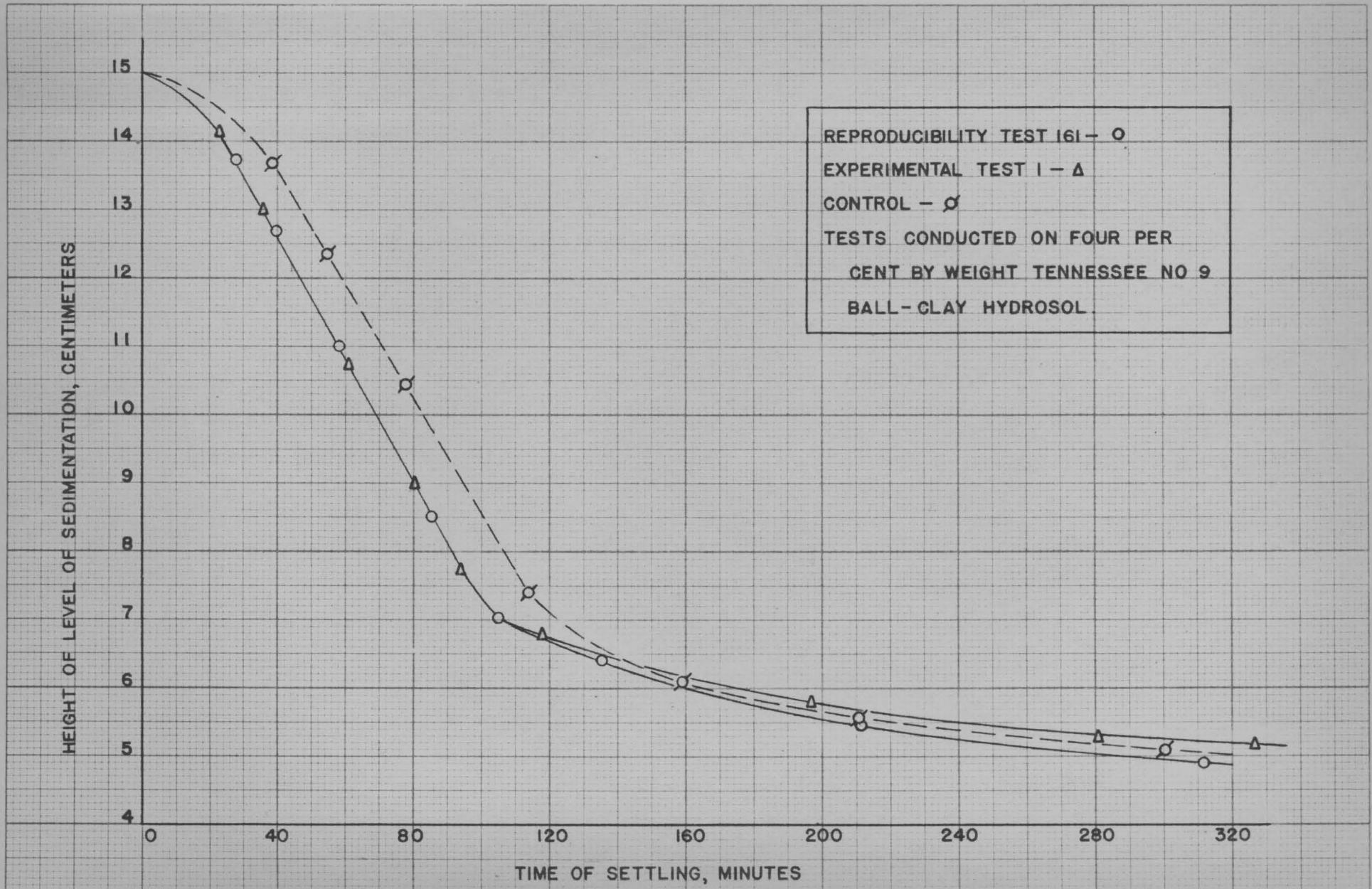


FIGURE 60. SETTLING RATE CURVES FOR CONTINUOUS ULTRASONIC REPRODUCIBILITY TEST 161 AND EXPERIMENTAL TEST I AT 300 KG, 1.50 VOLTS AMPLIFIED PROBE VOLTAGE, AND 5 POUNDS PER MINUTE FLOW RATE.

TABLE XVIII

Data on Control Settling of a Ball-Clay Hydrosol, Tests Nos 164-168

Test No	Type ^a	Initial pH ^b	Final pH ^c	Suspension Make-Up Temperature, °F	Room ^d Temperature, °F	Point I ^e Height, cm	Point I ^e Time, min	Point II ^f Height, cm	Point II ^f Time, min	Point III ^g Height, cm	Point III ^g Time, min	Constant Hindered Settling Rate, cm/hr
164	300 kc	7.75	7.65	67	81-83	13.8	37.0	-	-	7.0	119.0	5.00
165	500 kc	7.65	7.73	68	82-85	14.1	36.0	11.2	76.0	8.0	115.0	4.40
166	750 kc	7.95	8.05	66	80-82	13.7	30.0	-	-	7.6	105.0	4.71
167	1000 kc	7.85	7.88	65	82-86	14.0	22.0	10.0	91.0	7.3	112.0	4.88
168	Continuous Mechanical	7.80	8.10	66	82-83	14.0	26.5	9.5	87.0	7.2	116.0	4.57

^a Refers to series of tests being made when control was taken, using four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.

^b Suspension make-up.

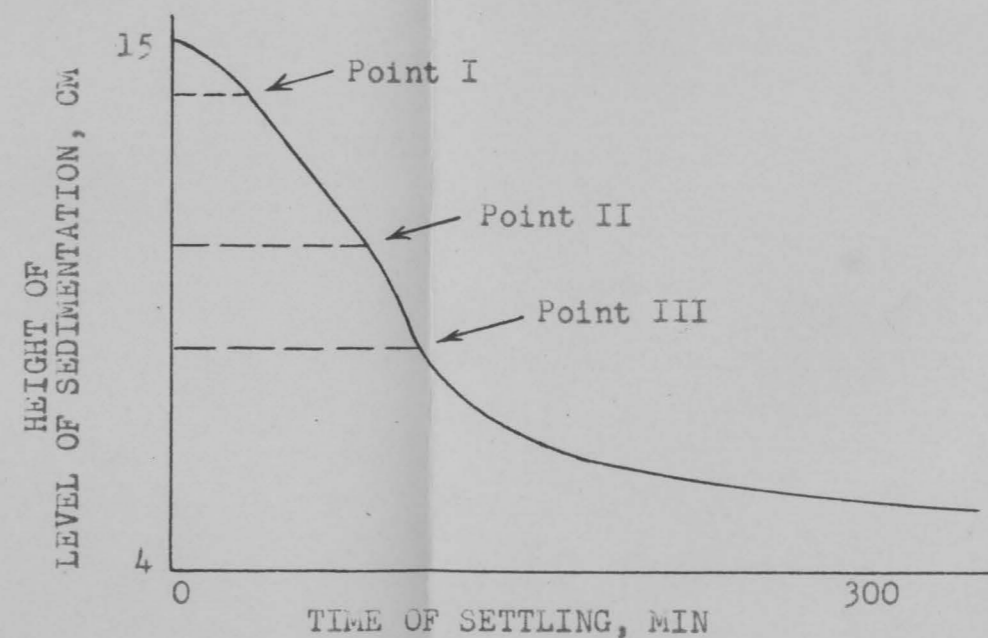
^c Of supernatant liquid after level of sedimentation had dropped approximately 10 cm.

^d Range over approximately 5 hours.

^e Beginning of constant hindered settling period of ball-clay hydrosol; settling starting from 15 cm in height and zero time.

^f End of constant hindered settling period and beginning of increased rate settling period.

^g End of increased rate settling period and beginning of compaction settling period.



GENERALIZED SETTLING RATE CURVE

Sample Calculations

In this section are presented samples of calculations used in the determination as well as interpretation of results.

Calculation of Time of Contact from Flow Rate. For the continuous ultrasonic tests the volume of the coagulation used was 29 milliliters. Assuming ball-clay to have a specific gravity the same as kaolinite, which is 2.59⁽⁸⁶⁾, and using the density of water at an average experimental temperature of 66.5 °F, which is 62.3 pounds per cubic foot⁽²⁾, the time of contact for a four per cent by weight ball-clay hydrosol at any flow rate may be calculated as follows:

$$T_c = (m)(V_c)(D_h)/u \quad (12)$$

where:

T_c = time of contact, sec

V_c = volume of coagulation chamber, cu ft
= (29 ml)/(28,317 ml/cu ft), cu ft
= 0.001025 cu ft

D_h = density of ball-clay hydrosol, lb/cu ft

u = flow rate, lb/min

m = 60 sec/min

The density of the ball-clay hydrosol may be calculated as follows:

$$D_h = 100 / (V_w + V_{b-c}) \quad (13)$$

where:

$$\begin{aligned} V_w &= \text{volume of 96 lb water at } 66.5 \text{ }^\circ\text{F, cu ft} \\ &= (96 \text{ lb}) / (62.3 \text{ lb/cu ft}) = 1.54 \text{ cu ft} \end{aligned}$$

$$\begin{aligned} V_{b-c} &= \text{volume of 4 lb ball-clay, cu ft} \\ &= (4 \text{ lb}) / (2.59)(62.4 \text{ lb/cu ft}), \text{ cu ft} \\ &= 0.0248 \text{ cu ft} \end{aligned}$$

$$D_h = 100 / (1.54 + 0.02) = 64.1 \text{ lb/cu ft}$$

Therefore:

$$T_c = (60)(0.001025)(64.1)/u = 3.93/u \text{ sec}$$

For the continuous mechanical tests, the volume, V_c , of the coagulation chamber used was 311.5 milliliters or 0.011 cubic foot. The time of contact at any flow rate may be calculated from Equation 12 as follows:

$$T_c = (m)(V_c)(D_h)/u$$

$$T_c = (60)(0.011)(64.1)/u = 42.2/u \text{ sec}$$

Relative Intensity of Insonation. The data taken in the laboratory in regards to relative intensity of insonation was the amplified output of a quartz crystal probe. Since there was a possibility that an additional function would be introduced between the actual output and amplified output of the crystal probe, the amplifier was calibrated by means of a signal generator and vacuum tube voltmeter. From a knowledge of the actual output of the quartz crystal, the relative intensity of insonation at a given frequency could be represented, assuming that the actual output of the probe crystal was directly proportional to the pressure amplitude of the ultrasonic waves acting on the crystal. The following equation⁽⁸⁾:

$$J = P^2/2\rho v \quad (14)$$

where:

J = sound intensity, ergs/sq cm-sec

P = pressure amplitude, dynes/sq cm

ρ = density of medium of transmission,
gm/cu cm

v = velocity of sound in medium of
transmission, cm/sec

shows that with density and velocity constant, the intensity is directly proportional to the square of the

pressure amplitude at a given frequency. Consequently, the relative intensity of insonation at a given frequency may be represented as follows:

$$J' \propto (P')^2 \quad (15)$$

where:

J' = relative intensity of insonation

P' = actual probe output, millivolts

Values of actual probe outputs were obtained from the amplifier calibration curves, Figures 40 to 43 included, pages 175 to 178 included.

Calculation of Constant Hindered Settling Rate. The settling rate curves plotted from experimental data contained a straight line portion representing a constant hindered settling rate, abbreviated C.H.S.R. The following equation relates the constant hindered settling rate to the slope of the straight line:

$$\text{C.H.S.R.} = (m)(R)(-\tan \theta) \quad (16)$$

where:

C.H.S.R. = constant hindered settling rate, cm/hr

R = ratio of units of abscissa and ordinate on settling rate curves, cm/min

= 0.05 cm/min

θ = slope of straight line representing C.H.S.R., degrees

m = 60 sec/min

Therefore:

$$\text{C.H.S.R.} = 30(-\tan \theta)$$

Values of C.H.S.R. are given for each test in Tables X to XVIII included, pages 182 to 212 included.

Average Particle Size of Ball-Clay in Suspension.

If a particle of definite shape is considered, starting from rest and settling in a stagnant fluid, the particle will accelerate under the influence of gravity. As it accelerates, the fluid offers a greater and greater frictional resistance. A time will be reached when the resisting force is exactly equal to the force of gravity, the acceleration will become zero, and the particle will

settle at a definite constant velocity. The equation for this constant velocity, known as Stokes' law, is as follows:

$$V_m = (\rho_s - \rho_l)gD^2/18\mu \quad (17)$$

where:

V_m = terminal constant velocity, cm/sec

ρ_s = density of particle, gm/cu cm

ρ_l = density of fluid, gm/cu cm

g = gravitational acceleration, cm/sec²

D = diameter of particle, cm

μ = viscosity of fluid, gm/cm-sec

Stokes' law, however, assumes that the following four conditions exist:

1. Spherical particles
2. No influence exerted between particles or between particles and liquid
3. Monodisperse particles
4. Particles within 3 to 100 micron range.

The four per cent by weight ball-clay hydrosol used in this investigation did not conform to the above four conditions. Figure 38, page 173, shows that as the concentration of the ball-clay hydrosol increased from

one to four per cent by weight, the settling rate decreased, indicating interaction between the particles and a consequent hindered settling. Furthermore, the particles were not spherical nor monodisperse.

According to Brown⁽²⁶⁾, when many particles are present there is a mutual interference in the motion of the particles, and the velocity of motion or rate of settling is considerably less than that computed by the equations derived on the assumption of free motion of the solid particles. The particle is actually settling through a slurry or suspension of particles in a fluid rather than through the simple fluid itself. Therefore, the bulk density of the slurry, calculated by dividing the mass of the fluid and suspended matter by the volume occupied by the slurry, should be used instead of the density of the clear liquid. Likewise, the bulk viscosity of the slurry should be used instead of the viscosity of the clear liquid. With the above mentioned substitutions, Equation 17 becomes:

$$V_h = (\rho_s - \rho_b)gD^2/18\mu_b \quad (18)$$

where:

- V_h = constant hindered settling rate, cm/sec
- ρ_b = bulk density of suspension, gm/cu cm
- μ_b = bulk viscosity of suspension, gm/cm-sec

Since the suspension used did not contain spherical particles, an additional factor must be introduced to account for their shape. This factor is known as the sphericity⁽²⁵⁾ and the shape of the particle may be defined in terms of it. The following equation⁽²⁵⁾ shows the significance of this factor:

$$D_s = D_{avg} / \psi^n \quad (19)$$

where:

D_s = diameter of sphere having same volume as particle, cm

D_{avg} = average screen size of particles, cm

ψ = ratio of surface area of sphere having same volume as particle to surface area of particle

n = ratio of specific surfaces

The value " D_s " should be used for "D" in Equation 18 when nonspherical particles are involved.

In the case of suspensions encountered in this investigation, it was desired to find the average particle size of the ball-clay preparatory to additional calculations concerning the settling particles. It should be realized, however, that since the test samples varied in settling rate, the average particle size

also varied from one test to another. Therefore, it was desired to calculate the average particle size for a number of test samples which represented the range of settling rates encountered.

A sample calculation for Test 4 (Table X, page 182) is presented herewith. The constant hindered settling rate was 5.3 centimeters per hour or 0.00147 centimeters per second. The bulk density of the hydrosol as calculated from Equation 13 was 64.1 pounds per cubic foot or 1.053 grams per cubic centimeter. The density of the ball-clay particles was 2.59 grams per cubic centimeter. The bulk viscosity was 1.2 centipoises⁽³⁷⁾ or 0.012 grams per centimeter-second. By rearranging Equation 18, the calculation for "D_s" is as follows:

$$\begin{aligned} D_s &= \sqrt{(18)(V_h)(\mu_b)/(\rho_s - \rho_b)g} \\ &= \sqrt{(18)(0.00147)(0.012)/(2.59 - 1.05)(980)} \\ &= 4.59 \times 10^{-4} \text{ cm} \end{aligned}$$

It was known from the electron micrograph of Figure 38, page 174, that the ball-clay particles were hexagonal and disc-shaped, but it was difficult to determine the thickness of these discs. An assumption of a thickness to diameter ratio of one to eight was

used in the literature⁽⁹⁶⁾ and was considered satisfactory for these calculations. Consequently, a value for " D_s/D_{avg} " of 0.575 was obtained from Brown⁽²⁵⁾ by extrapolation. Therefore, the average diameter of the ball-clay particles may be calculated as follows:

$$\begin{aligned} D_{avg} &= D_s/0.575 \\ &= (4.59 \times 10^{-4})/0.575, \text{ cm} \\ &= 7.99 \times 10^{-4} \text{ cm or } 7.99 \text{ microns} \end{aligned}$$

Theoretical Minimum Height of Settled Hydrosol. The theoretical minimum height of a four per cent by weight ball-clay hydrosol, based on the volume occupied by the ball-clay particles alone, may be calculated from the following equation:

$$H_{tm} = (C_v)(H_t) \quad (20)$$

where:

H_{tm} = theoretical minimum height of settled hydrosol particles, cm

C_v = volume concentration of hydrosol, gm ball-clay/gm water

H_t = total original height of hydrosol, cm

= 15 cm

The volume concentration of the ball-clay hydrosol may be calculated as follows:

$$C_v = V_{b-c} / (V_{b-c} + V_w) \quad (21)$$

where:

$$C_v = \text{volume concentration of hydrosol,} \\ \text{gm ball-clay/gm water}$$

$$V_{b-c} = \text{volume of 4 lb ball-clay, cu ft} \\ = 0.0248 \text{ cu ft}$$

$$V_w = \text{volume of 96 lb water at } 66.5 \text{ }^\circ\text{F, cu ft} \\ = 1.54 \text{ cu ft}$$

$$C_v = 0.0248 / (0.0248 + 1.54), \text{ gm ball-clay/gm} \\ \text{water} \\ = 0.0158 \text{ gm ball-clay/gm water}$$

Consequently:

$$H_{tm} = (0.0158)(15), \text{ cm} \\ = 0.237 \text{ cm}$$

Practical Minimum Height of Settled Hydrosol. The practical minimum height of the settled ball-clay hydrosol was based on tetrahedral packing of the ball-clay particles at the end of the compaction settling period. Using the average particle diameter of 7.99 microns from

Test 4, it was first desired to find the average volume of a hexagonal, disc-shaped, particle; the solution of which is as follows:

$$V = \pi r^2 T \quad (22)$$

where:

V = average volume of particle, cu cm

r = particle radius, cm

$$= 4.0 \times 10^{-4} \text{ cm}$$

T = average particle thickness, cm

$$= (7.99 \times 10^{-4})/8, \text{ cm}$$

$$= 9.99 \times 10^{-5} \text{ cm}$$

Therefore:

$$V = (\pi)(4.0 \times 10^{-4})(9.99 \times 10^{-5}), \text{ cu cm}$$

$$= 5.03 \times 10^{-11} \text{ cu cm}$$

From a knowledge of the average cross sectional area of the inside of the Nessler tubes, which was 6.56 square centimeters, and the height of 15 centimeters to which the tubes were initially filled with hydrosol, the average hydrosol volume of the Nessler tubes was found to be 98.4 cubic centimeters. Consequently, the total volume of ball-clay particles in a single test sample was found to be 1.55 cubic centimeters

by multiplication of the average volume of the Nessler tubes by the volume concentration calculated from Equation 21. Therefore, the number of particles present in 98.4 cubic centimeters may be calculated as follows:

$$N_t = V_t/V \quad (23)$$

where:

$$N_t = \text{total number of particles in} \\ 98.4 \text{ cu cm of hydrosol}$$

$$V_t = \text{total volume of particles, cu cm} \\ = 1.55 \text{ cu cm}$$

$$V = \text{average volume of one particle,} \\ \text{cu cm} \\ = 5.03 \times 10^{-11} \text{ cu cm}$$

$$N_t = 1.55 / (5.03 \times 10^{-11}) \\ = 3.087 \times 10^{10}$$

On the basis of tetrahedral packing of the ball-clay particles at the end of the compaction settling period, the following equation⁽⁹⁶⁾ results:

$$N = 1/0.71(D_{avg})^3 \quad (24)$$

where:

$$N = \text{number of particles per cu cm} \\ = 1/(0.71)(7.99 \times 10^{-4}) \\ = 2.76 \times 10^9$$

From the foregoing information the practical minimum height may be calculated as follows:

$$H_{pm} = N_t / (N)(A_i) \quad (25)$$

where:

H_{pm} = practical minimum height of settled ball-clay hydrosol based on tetrahedral packing, cm

A_i = inside cross sectional area of Nessler tube, sq cm
= 6.56 sq cm

$$H_{pm} = (3.087 \times 10^{10}) / (2.76 \times 10^9)(6.56),$$

cm

$$= 1.71 \text{ cm}$$

Thickness of Double Layer Surrounding Ball-Clay Particles. It was considered that at the beginning of compaction settling, the double layers surrounding the ball-clay particles were in contact and uniform distribution in the form of tetrahedral packing was present. As compaction settling progressed, the double layers, which are composed of water and ions attached to the particles, are squeezed out due to the particles coming closer and closer together as they settle under the influence of gravity. For Test 4, the height at which

compaction settling began was 7.7 centimeters. By multiplying this height by the cross sectional area of the Nessler tubes (6.56 square centimeters), a volume of 50.5 cubic centimeters was obtained which represented the volume occupied by the ball-clay particles at the beginning of compaction settling. Therefore, since 3.087×10^{10} particles were present in 50.5 cubic centimeters, it can be calculated that 6.12×10^8 particles were present per cubic centimeter. Equation 24 can be revised and the average particle diameter, including the double layer, may be calculated as follows:

$$D'_{avg} = \sqrt[3]{1/(0.71 N)}$$

where:

$$\begin{aligned} D'_{avg} &= \text{average diameter of particles} \\ &\quad \text{including double layer, cm} \\ &= \sqrt[3]{1/(0.71)(6.12 \times 10^8)}, \text{ cm} \\ &= 13.2 \times 10^{-4} \text{ cm or } 13.2 \text{ microns} \end{aligned}$$

Since the average particle diameter without the double layer was 7.99 microns, the thickness of the double layer was found to be 2.6 microns.

Center-to-Center and Edge-to-Edge Distance of Ball-Clay Particles at Beginning of Increased Rate Period.

Using the data for Test 4, the height of the settled ball-clay particles at the beginning of the increased rate

settling period was 9.8 centimeters. By multiplying this height by the average cross sectional area of the Nessler tubes (6.56 square centimeters), a value of 64.3 cubic centimeters was obtained which represented the volume occupied by the ball-clay particles at the beginning of increased rate settling. Therefore, since 3.087×10^{10} particles were present in 64.3 cubic centimeters, it can be calculated that 4.8×10^8 particles were present per cubic centimeter. Equation 24 can be revised to find the average center-to-center distance of the particles assuming uniform distribution:

$$D_{c-c} = \sqrt[3]{1/(0.71 N)}$$

where:

$$\begin{aligned} D_{c-c} &= \text{average center-to-center distance} \\ &\quad \text{of ball-clay particles at} \\ &\quad \text{beginning of increased rate} \\ &\quad \text{settling, cm} \\ &= \sqrt[3]{1/(0.71)(4.8 \times 10^8)} \\ &= 14.32 \times 10^{-4} \text{ cm or } 14.32 \text{ microns} \end{aligned}$$

The edge-to-edge distance may be calculated by subtraction of the average diameter of the ball-clay particles, including the double layer, from the center-

to-center distance. This results in an average edge-to-edge distance of the ball-clay particles at the beginning of the increased rate settling period of 1.12 microns.

IV. DISCUSSION

An analysis and discussion of the results obtained are included in this section of the thesis together with recommendations for future work and a summary of the limitations imposed on the investigation.

Discussion of Results

On a batch scale, as much as 500 per cent increase in hindered settling rate⁽¹⁵⁵⁾ of an aqueous suspension has been reported for periods of insonation of approximately ten minutes. In this investigation it was desired to ascertain the effect of ultrasonic coagulation on a basis of continuous flow of the suspension through the sound field and concurrently to reduce the time of insonation.

It is pointed out that the pH of the test samples of ball-clay was approximately 7.8 ± 0.2 in contrast with an isoelectric point for the clay suspension of approximately 3.5. Since the coagulation of the clay at its isoelectric point was so rapid that measurements could not be made with desired accuracy, although other properties of the suspension were desirable, a pH of approximately 7.8 was employed. A desired initial

settling rate of between one and five centimeters per hour could thus be obtained.

Data obtained in this investigation indicated that the application of ultrasonic energy to a continuously flowing ball-clay hydrosol is practicable and facilitates coagulation with a subsequent increase in settling rate being realized. Under optimum experimental conditions a maximum increase in hindered settling rate of 81.8 per cent over the control was obtained. An increase in hindered settling rate was found with increasing time of insonation within the 0.786- to 7.86-second insonation range. Comparison of continuous and batch insonation indicated that periods of treatment greater than 7.86 seconds would continue to increase the settling rate. In fact, increases in hindered settling rate up to 101.4 per cent were obtained on a batch basis with two minute insonation. A careful analysis of the data leads to the conclusion that the optimum conditions of time, frequency, and intensity of insonation have not been achieved.

Presented in the following paragraphs is a discussion of the variables investigated and the settling phenomena evident, followed by a discussion of the results obtained.

Variables. The experimental variables that were involved in the different series of coagulation tests are as follows:

Continuous Ultrasonic Coagulation

Time of Insonation
Intensity of Insonation
Frequency of Insonation
pH
Temperature

Batch Ultrasonic Coagulation

Time of Insonation
Intensity of Insonation
Frequency of Insonation
Treatment after Insonation
pH
Temperature

Continuous Mechanical Coagulation

Time of Agitation
Intensity of Agitation
pH
Temperature

Batch Mechanical Coagulation

Time of Agitation

Intensity of Agitation

pH

Temperature

Those experimental variables meriting special consideration are: (1) time of insonation and time of agitation; (2) intensity of insonation; (3) pH; and (4) temperature.

Time of Insonation and Time of Agitation. The time of insonation and time of agitation for the continuous ultrasonic and continuous mechanical tests, respectively, were determined from the flow rate of the ball-clay hydrosol under treatment. Table XIX shows the flow rates and corresponding times of contact for the continuous ultrasonic and continuous mechanical tests. The time of contact, or treatment, for the continuous ultrasonic tests ranges from 0.786 to 7.86 seconds in comparison with one and two minutes for the batch ultrasonic tests, 8.44 to 84.4 seconds for the continuous mechanical tests, and 5 to 60 minutes for the batch

TABLE XIX

Tabulations of Flow Rates and Corresponding Times of Contact
for Continuous Ultrasonic and Continuous Mechanical
Coagulation Tests

<u>Ultrasonic^a</u>			<u>Mechanical^b</u>		
Flow Rate, lb/min	Time of Contact, sec min		Flow Rate, lb/min	Time of Contact, sec min	
5	0.786	0.0131	5	8.44	0.141
4	0.983	0.0164	4	10.55	0.176
3	1.310	0.0220	3	14.07	0.234
2	1.970	0.0328	2	21.10	0.352
1	3.930	0.0655	1	42.20	0.704
$\frac{1}{2}$	7.860	0.1310	$\frac{1}{2}$	84.40	1.410

^a Volume of coagulation chamber was 29 ml

^b Volume of coagulation chamber was 311.5 ml

mechanical tests. These differences in time of treatment are important in comparing the different methods of coagulation employed.

Intensity of Insonation. Four ways were considered whereby an estimate of the relative intensity of insonation at a given frequency could be obtained. These were (1) plate current from ultrasonic generator; (2) amplified voltage output of quartz probe; (3) actual voltage output of quartz probe; and (4) calculated relative intensity. The plate current readings gave only an inaccurate indication of the amount of energy being delivered by the quartz transducing crystal of the ultrasonic generator. The amplified probe voltage readings indicated the quantity of energy acting on the ball-clay hydrosol, but contained an extraneous function contributed by the amplifier. The actual probe output voltage excluded any amplification factor. The calculated relative intensity was based on the direct proportionality of the square of the actual probe voltage at a given frequency to the intensity of insonation.

In consideration of relative intensity at a given frequency, the following conditions were assumed: (1) the probe crystal was essentially acted upon by the pressure amplitude over the distance of one node, and (2) the relative intensity at a given frequency was directly proportional to the square of the actual output voltage of the quartz probe crystal. The following facts tend to substantiate the foregoing conditions and the validity of calculations of relative intensity:

(1) fairly smooth curves were obtained, Figure 44, page 179, from a plot of amplified probe voltage versus plate current; (2) the amplifier calibration curves in Figures 40 to 43, pages 175 to 178, were essentially straight line functions; (3) the output voltage of a piezoelectric crystal is directly proportional to the pressure amplitude of the ultrasonic waves acting upon it⁽¹⁶⁶⁾; and (4) relative ultrasonic intensity at a given frequency is directly proportional to the square of the pressure amplitude of the ultrasonic waves⁽⁸⁾. Since only proportionalities could

be advanced relating relative intensity to probe voltage measurements, the calculation of relative intensities was not accomplished. Values of actual probe output voltage (directly proportional to pressure amplitude at a given frequency) were used in correlations incorporating intensity of insonation.

pH. The initial pH of the ball-clay hydrosol was 7.8 ± 0.2 and the final pH of the test samples was 7.9 ± 0.3 . It was doubtful if such small changes in pH would have any predominate effect on the settling characteristics of the ball-clay hydrosol. An attempt was made to correlate pH with constant hindered settling rate for the continuous ultrasonic coagulation tests, however, no relationship was found to exist. It was considered that the small change in pH encountered was not a major factor.

Temperature. The temperatures involved in the experimental tests ranged from a suspension make-up temperature of approximately 67°F to a final temperature of approximately 83°F , resulting in a 16°F differential. The suspension make-up temperature did not vary more than 4°F and the room

temperature 7 °F for the different series of tests. The effect of temperature on coagulation and settling rate in this investigation was not known, but according to Lewis, Squires, and Broughton⁽⁸⁸⁾, the general influence of temperature on coagulation is small in comparison with other more important influences, since the kinetic energy of the system, which would affect the probability of collision, increases very little with a rise in temperature.

Interpretation of Settling Characteristics. All of the settling rate curves conformed to a general form which is shown in Figure 61. Three distinct transition points were evident. Point I represents the beginning of constant hindered settling period. Point II represents the end of a constant hindered settling period and the beginning of an increased rate settling period. Point III represents the end of an increased rate settling period and the beginning of a compaction settling period. A series of calculations were made to determine the significance of the shape of the settling rate curves. Table XX is a tabulation of these calculations. The following is an explanation of the significance of

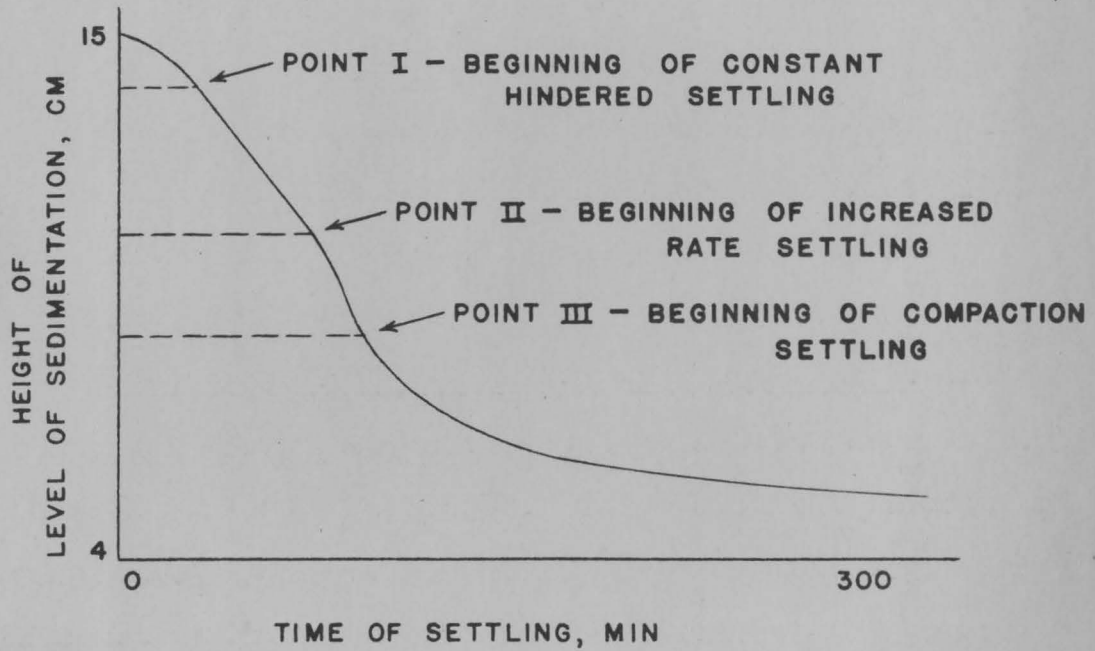


FIGURE 6I. GENERALIZED SETTLING RATE CURVE SHOWING DIFFERENT PHASES OF SETTLING.

TABLE XX

Tabulation of Calculations Interpreting the Settling of Ball-Clay Hydrosols

Test No	Constant Hindered ^a Settling Rate, cm/hr	Average Particle Size, microns	Practical ^b Minimum Height, cm	Height at Beginning of Compaction Settling, cm	Thickness of ^c Diffuse Double Layer, microns	Beginning of Increased Rate Period		
						Height, cm	Center to Center Distance, microns	Edge to Edge ^d Distance, microns
36	4.16	7.07	1.71	7.2	2.18	9.8	12.66	1.23
112	4.49	7.36	1.71	7.4	2.32	10.6	13.52	1.52
167	4.88	7.68	1.71	7.3	2.40	10.0	13.84	1.36
130	5.08	7.83	1.71	7.4	2.49	9.4	13.85	1.04
4	5.30	7.99	1.71	7.7	2.60	9.8	14.32	1.12
71	5.70	8.28	1.71	7.6	2.67	9.5	14.68	1.04
19	6.50	8.84	1.71	7.5	2.83	10.1	16.00	1.50

^a Of four per cent by weight Tennessee No 9 ball-clay in Blacksburg, Va. tap water.

^b Calculated final height of particles at end of compaction settling period.

^c Difference between average center-to-center distance of particles at beginning of compaction settling and average particle diameter calculated from constant hindered settling rate.

^d Difference between average center-to-center distance of particles at beginning of increased rate settling and average particle diameter including double layer.

these calculations and their relation to the shape of the settling rate curves.

Average Particle Size. The average particle size of the ball-clay was calculated using a modified Stokes' law employing bulk viscosity and bulk density of the hydrosol. A tabulation of the average particle size for a number of constant hindered settling rate values is shown in Table XX. Figure 62 is a plot of constant hindered settling rate versus average particle size. Actually, the constant hindered settling rate is directly proportional to the square of the particle size, but for the range of particle sizes encountered, the relationship is practically linear. Consequently, the average particle size would bear approximately the same relationship as the constant hindered settling rate with a variable with which the latter is correlated.

Practical Minimum Height of Settled Hydrosol. By practical minimum height is meant the height of the settled particles at the end of the compaction settling period. Such a height was not reached experimentally, but it was desired to calculate

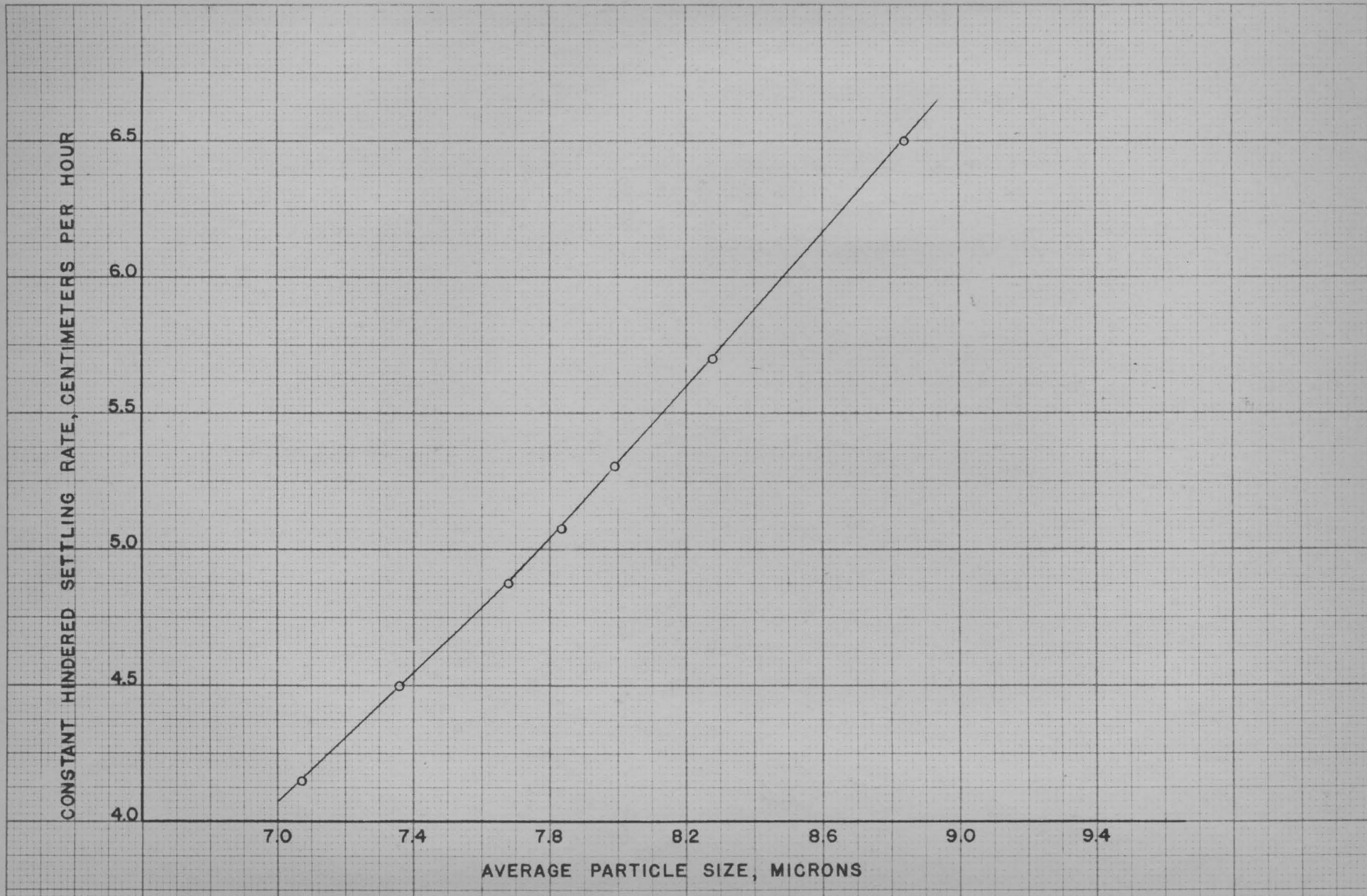


FIGURE 62. RELATION BETWEEN CONSTANT HINDERED SETTLING RATE AND AVERAGE PARTICLE SIZE OF BALL-CLAY PARTICLES IN FOUR PER CENT BY WEIGHT TENNESSEE NO 9 BALL-CLAY HYDROSOL.

it in order to obtain an idea of what portion of the settling comprised a compaction settling period. It is believed that at the beginning of compaction settling the double layers, comprised of water and ions attached to the particles, come into contact. As settling progresses with a marked decrease in rate, water is eliminated from the double layers as the particle-to-particle distance decreases. The calculated height of 1.71 centimeters represents the limit to which the suspension could settle, starting from a height of 15 centimeters. The practical minimum height was constant for the particle size range of 7.07 to 8.84 microns as this range was not large enough to make any appreciable differences in the calculations.

Thickness of Diffuse Double Layer. From a knowledge of the size of the ball-clay particles and the height at which compaction settling began, it was possible to calculate the thickness of the diffuse double layers surrounding the particles based on the assumption that the double layers are touching at the beginning of compaction

settling. A tabulation of those double layer thicknesses calculated for a range of particle sizes is shown in Table XX. Figure 63 shows that the thickness of the double layers is directly proportional to the average particle size.

Increased Rate Settling Period. After the settling rate curves had been plotted, an increased rate settling period was evident at the end of the constant hindered settling period. This increased rate settling period was not evident in all of the settling rate curves, but it unmistakably existed for about fifty per cent of the curves; not being peculiar to any particular series of tests. The reason that this increased rate was not evident in all of the settling tests is attributed to the fact that insufficient data were taken. From a knowledge of the height at which the increased rate settling period began, it was possible to calculate the average center-to-center and edge-to-edge distance, including the double layer, of the ball-clay particles at this point. Table XX contains a tabulation of these calculations. The range

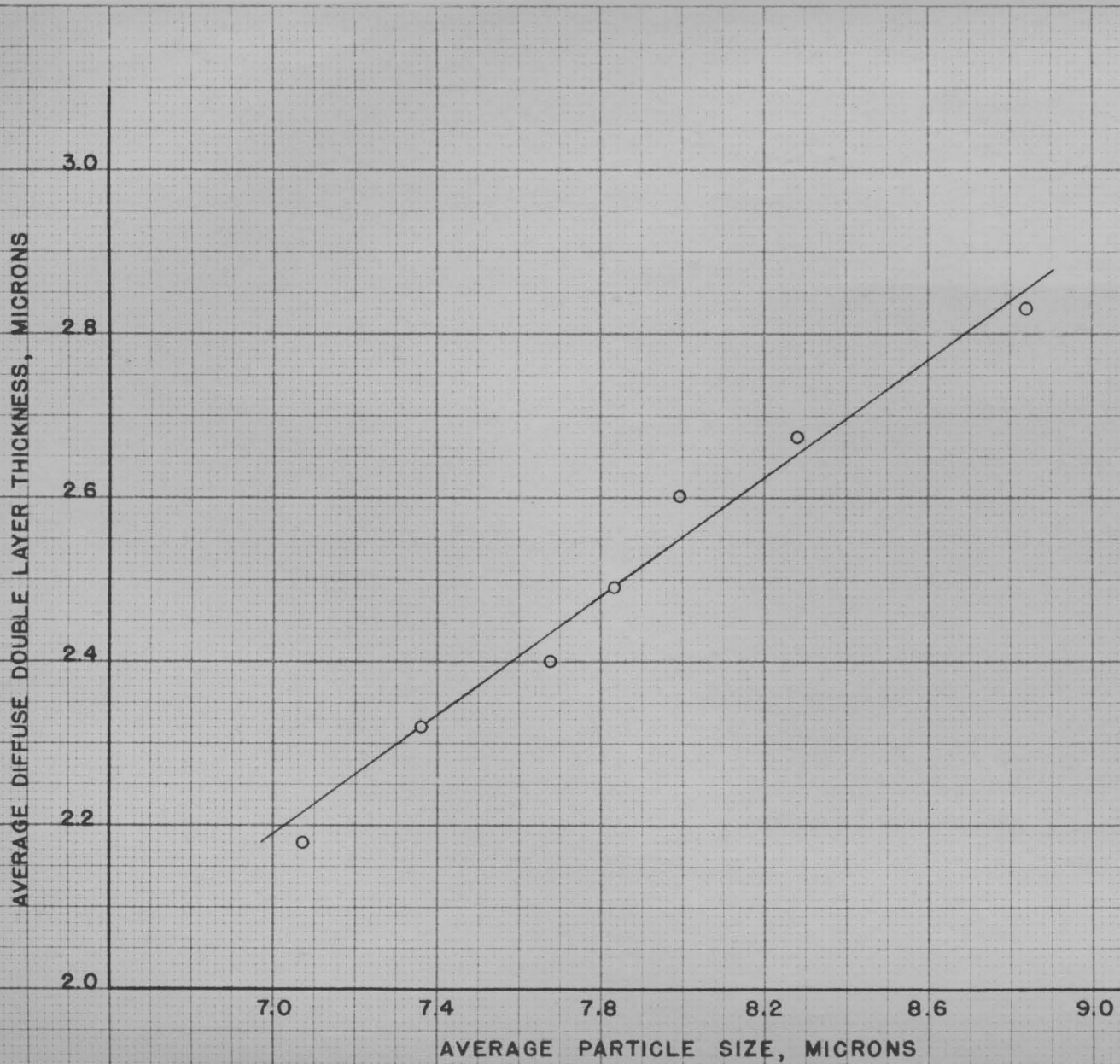


FIGURE 63. RELATION BETWEEN AVERAGE DIFFUSE DOUBLE LAYER THICKNESS AND AVERAGE PARTICLE SIZE OF BALL-CLAY PARTICLES IN FOUR PER CENT BY WEIGHT TENNESSEE NO 9 BALL-CLAY HYDROSOL.

of average edge-to-edge distances of the ball-clay particles for seven tests was compared with a chart representing potential energies of repulsion and attraction between suspended particles. This chart was calculated by Freundlich and Rubin and is shown in Figure 64. It was found that the range of edge-to-edge distances apart, calculated from the experimental (1.23 to 1.50 microns) data, corresponded to those values on this chart at which existed a maximum of attractive forces between the particles. This would explain the increase in settling rate. As the particles settle from an initial height of 15 centimeters, through a constant rate period, a concentration is reached where the secondary and gravitational forces of attraction between particles predominate over the electrostatic forces of repulsion between them, and the particles are brought together thereby increasing their size and settling rate. This phenomenon continues to exist until the beginning of the compaction settling period.

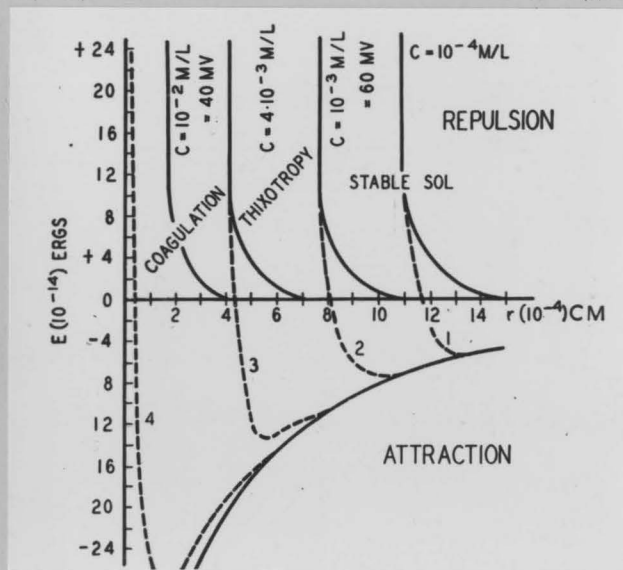


FIGURE 64. POTENTIAL ENERGIES OF ATTRACTION AND REPULSION IN COLLOIDAL SYSTEMS.

HAUSER, E. A.: "COLLOID PHENOMENA," P. 218. MC GRAW-HILL BOOK CO., INC., NEW YORK, N. Y., 1939. 1 ED.

Effect of Time of Insonation on Constant Hindered Settling Rate for Continuous Ultrasonic Coagulation Tests. Inasmuch as the major portion of settling of the ball-clay test samples occurred during the constant hindered settling period, it was considered that this period was the most valid in the evaluation of the coagulation tests. In Figure 65 are shown plots of constant hindered settling rate versus flow rate for each of the four frequencies used. Each curve is essentially representative of the function obtained for the frequency for which it was plotted. Figure 66 is a plot of constant hindered settling rate versus flow rate for the 500-kilocycle tests with intensity of insonation, in terms of amplified probe voltage, as a parameter. The highest individual increases in constant hindered settling rate were obtained at 500 kilocycles at the longer times of insonation (lower flow rates) and higher intensities of insonation as shown in Figure 66. The maximum increase of 81.8 per cent was obtained at 500 kilocycles with a 7.86-second time of insonation (1/2-pound per minute flow rate) and 6.30-volt amplified probe voltage intensity level. In both Figures 65 and

CONSTANT HINDERED SETTLING RATE, CENTIMETERS PER HOUR

8.0
7.0
6.0
5.0
4.0
3.0

FREQUENCY:

- - 300 KC
- - 500 KC
- △ - 750 KC
- ◻ - 1000 KC

AVERAGE CONTROL: ----

TESTS CONDUCTED ON FOUR PER
CENT BY WEIGHT TENNESSEE NO 9
BALL-CLAY HYDROSOL

0 1 2 3 4 5
FLOW RATE, POUNDS PER MINUTE

FIGURE 65. EFFECT OF FLOW RATE ON CONSTANT HINDERED SETTLING RATE FOR CONTINUOUS
ULTRASONIC COAGULATION TESTS AT 4.65 VOLTS AMPLIFIED PROBE VOLTAGE.

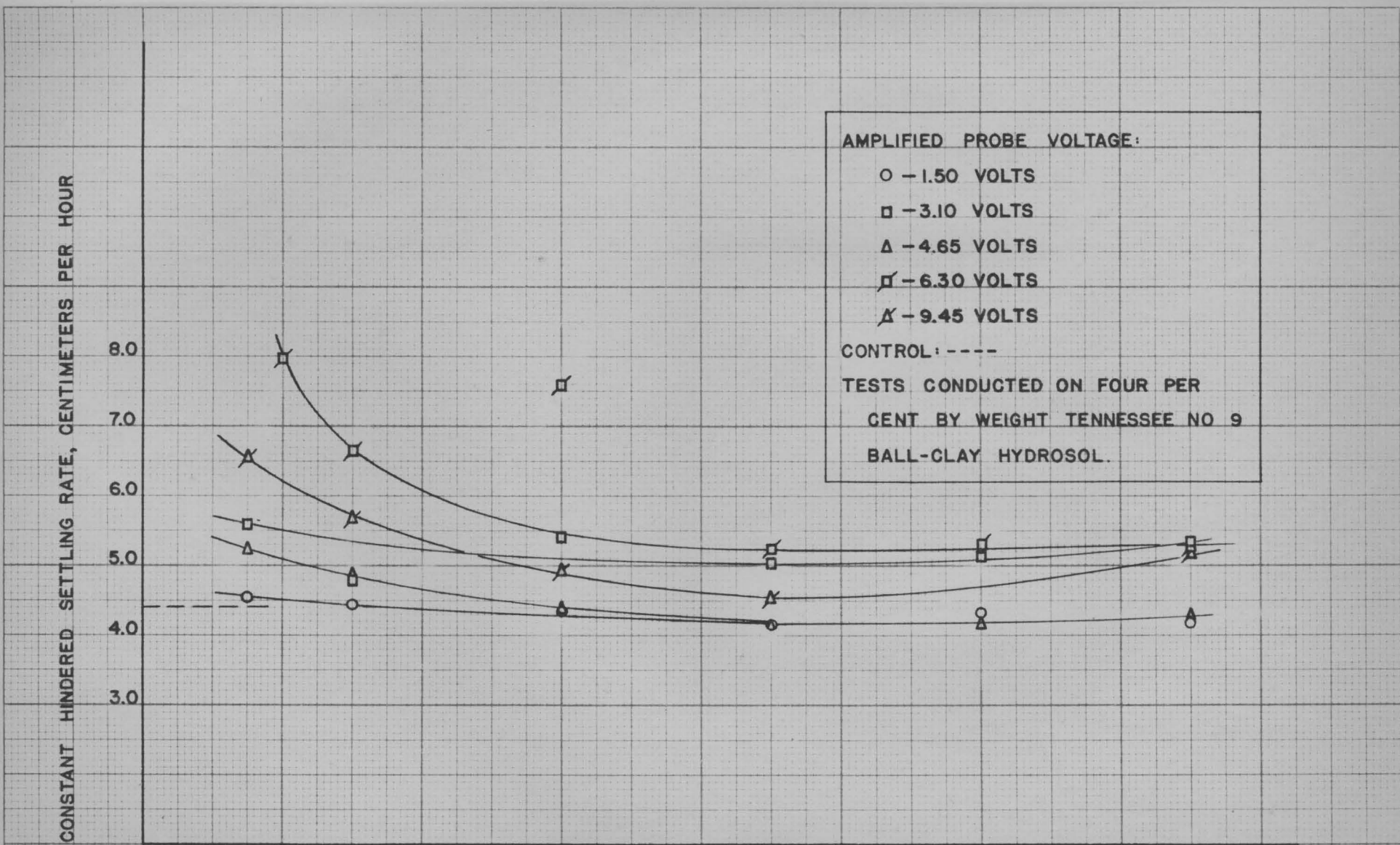
CONSTANT HINDERED SETTLING RATE, CENTIMETERS PER HOUR

AMPLIFIED PROBE VOLTAGE:
○ - 1.50 VOLTS
□ - 3.10 VOLTS
△ - 4.65 VOLTS
◻ - 6.30 VOLTS
⋈ - 9.45 VOLTS
CONTROL: ----
TESTS CONDUCTED ON FOUR PER
CENT BY WEIGHT TENNESSEE NO 9
BALL-CLAY HYDROSOL.

-250-

0 1 2 3 4 5
FLOW RATE, POUNDS PER MINUTE

FIGURE 66. EFFECT OF FLOW RATE ON CONSTANT HINDERED SETTLING RATE FOR CONTINUOUS ULTRASONIC COAGULATION TESTS AT 500 KC.



66 there was an increase in constant hindered settling rate towards the one-half-pound per minute flow rate or 7.86-second time of insonation. Consequently, times of insonation above the maximum of 7.86 seconds used for the continuous ultrasonic coagulation tests in this investigation are indicated. This is substantiated by Thompson⁽¹⁵⁵⁾ whereby he obtained increases in hindered settling rate up to 500 per cent in the batch insonation of a phosphate tailing suspension for periods of ten minutes.

In Figure 67 is shown the effect of recycle rate on constant hindered settling rate for the continuous ultrasonic coagulation tests. It can be seen from the curves in Figure 67 that recycling of the ball-clay hydrosol decreased the constant hindered settling rate in comparison with nonrecycling. A minimum value of constant hindered settling rate was reached at the one-pound per minute recycle rate and an increase over this minimum was observed for the two-pound per minute recycle rate, although the constant hindered settling rates obtained by recycling were all below those for the nonrecycled tests. From the foregoing it appears

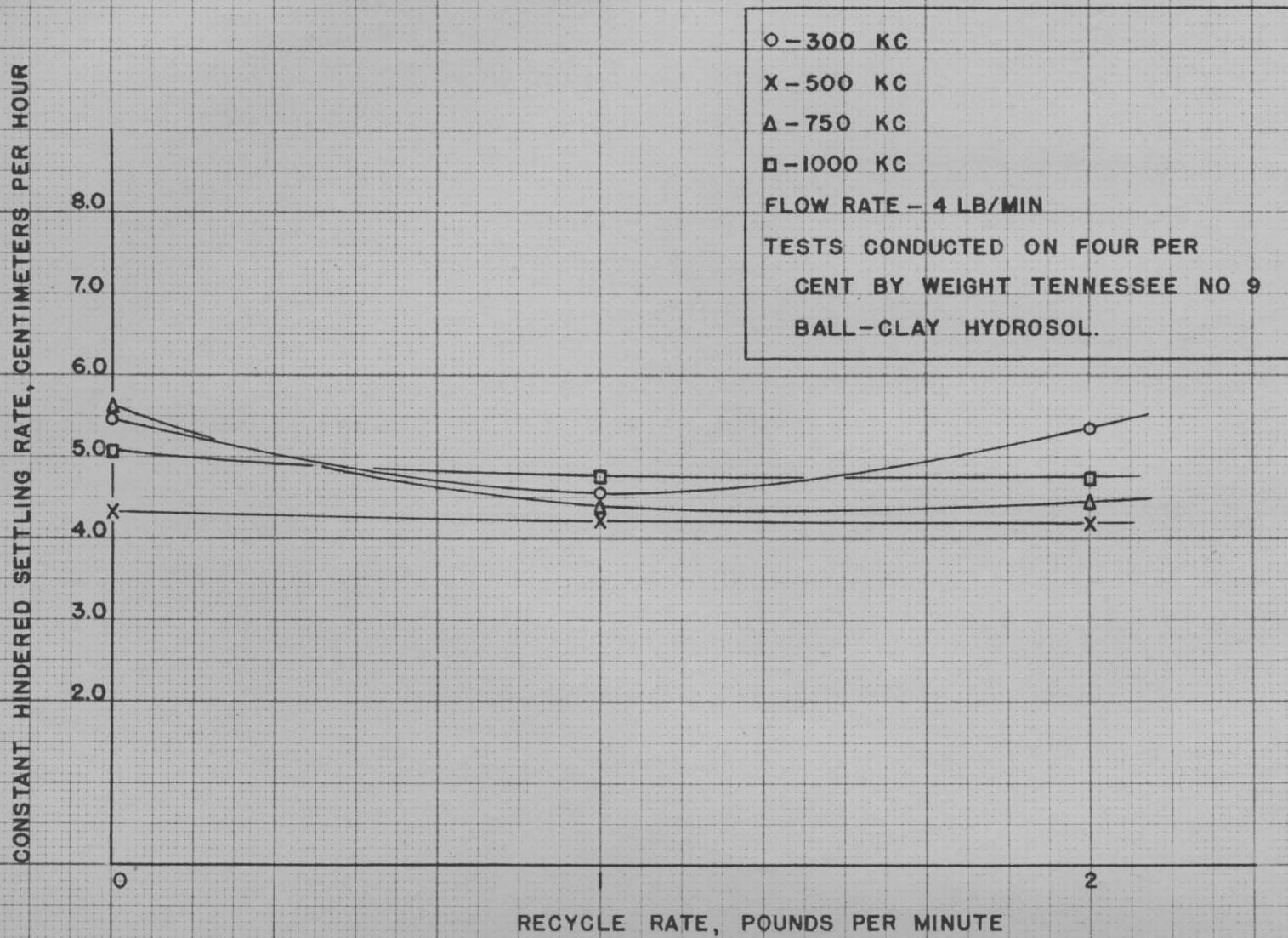


FIGURE 67. EFFECT OF RECYCLE RATE ON CONSTANT HINDERED SETTLING RATE FOR CONTINUOUS ULTRASONIC COAGULATION TESTS.

probable that larger recycling over the two-pound per minute rate used would result in constant hindered settling rates higher than those for the nonrecycled tests.

Effect of Intensity of Insonation on Constant Hindered Settling Rate for Continuous Ultrasonic Coagulation Tests. In Figure 68 is shown the effect of intensity of insonation, in terms of actual probe voltage, on constant hindered settling rate for the continuous ultrasonic coagulation tests at 300 kilocycles. Essentially the same relationship was obtained by using ultrasonic generator plate current and amplified probe voltage as the independent variable because both were essentially directly proportional to the actual probe voltage at a given frequency. Following are correlations of intensity of insonation and constant hindered settling rate at the different frequencies employed.

300-Kilocycle Tests. For the 300-kilocycle tests in Figure 68, it can be seen that for flow rates of 5, 4, 2, and 1 pound per minute there was an increase in constant hindered settling rate with intensity of insonation and for flow

CONSTANT HINDERED SETTLING RATE, CENTIMETERS PER HOUR

FLOW RATE:

○ - 5 LB/MIN

□ - 4 LB/MIN

△ - 3 LB/MIN

◻ - 2 LB/MIN

X - 1 LB/MIN

△ - 1/2 LB/MIN

CONTROL: ----

TESTS CONDUCTED ON FOUR PER CENT BY WEIGHT TENNESSEE NO 9 BALL-CLAY HYDROSOL.

8.0
7.0
6.0
5.0
4.0
3.0

0 200 400 600

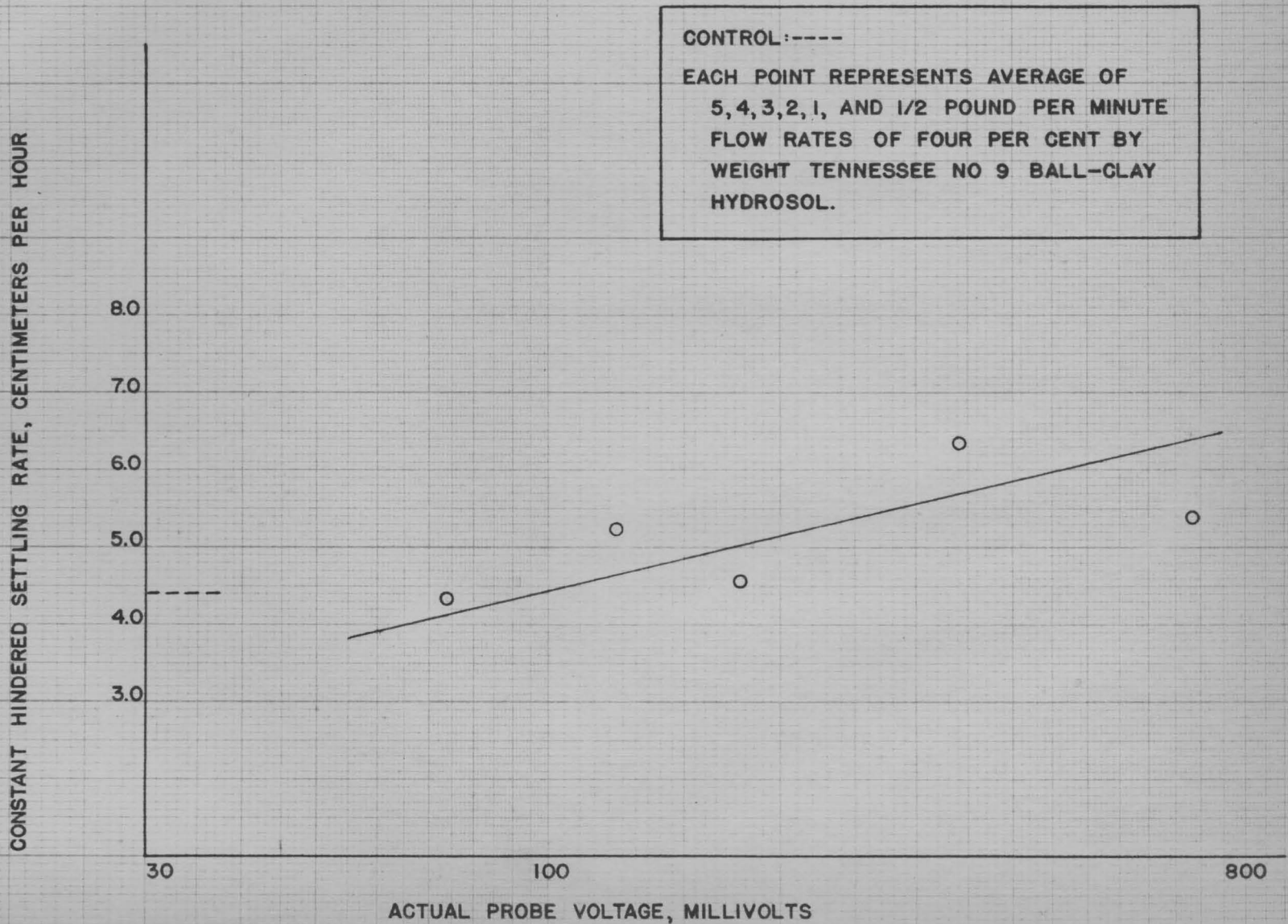
ACTUAL PROBE VOLTAGE, MILLIVOLTS

FIGURE 68. EFFECT OF INTENSITY OF INSONATION, IN TERMS OF ACTUAL PROBE VOLTAGE, ON CONSTANT HINDERED SETTLING RATE FOR CONTINUOUS ULTRASONIC COAGULATION TESTS AT 300 KC.

rates of 3 and 1/2 pound per minute there was a decrease. The general interpretation is that there was an over-all tendency for an increase in constant hindered settling rate with intensity of insonation.

500-Kilocycle Tests. Since the 500-kilocycle correlations were considerably scattered, an average of constant hindered settling rates for all flow rates at a particular intensity of insonation was made and plotted against the intensity of insonation. Figure 69 shows the effect of intensity of insonation, in terms of actual probe voltage, on constant hindered settling rate for the 500-kilocycle continuous ultrasonic coagulation tests. The curve in Figure 69 shows an increase in constant hindered settling rate with an increase in intensity of insonation.

750-Kilocycle Tests. In Figure 70 is shown the effect of intensity of insonation, in terms of actual probe voltage on constant hindered settling rate for the 750-kilocycle continuous ultrasonic coagulation tests. The correlation



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FIGURE 69. EFFECT OF INTENSITY OF INSONATION, IN TERMS OF ACTUAL PROBE VOLTAGE, ON CONSTANT HINDERED SETTLING RATE FOR CONTINUOUS ULTRASONIC COAGULATION TESTS AT 500 KC.

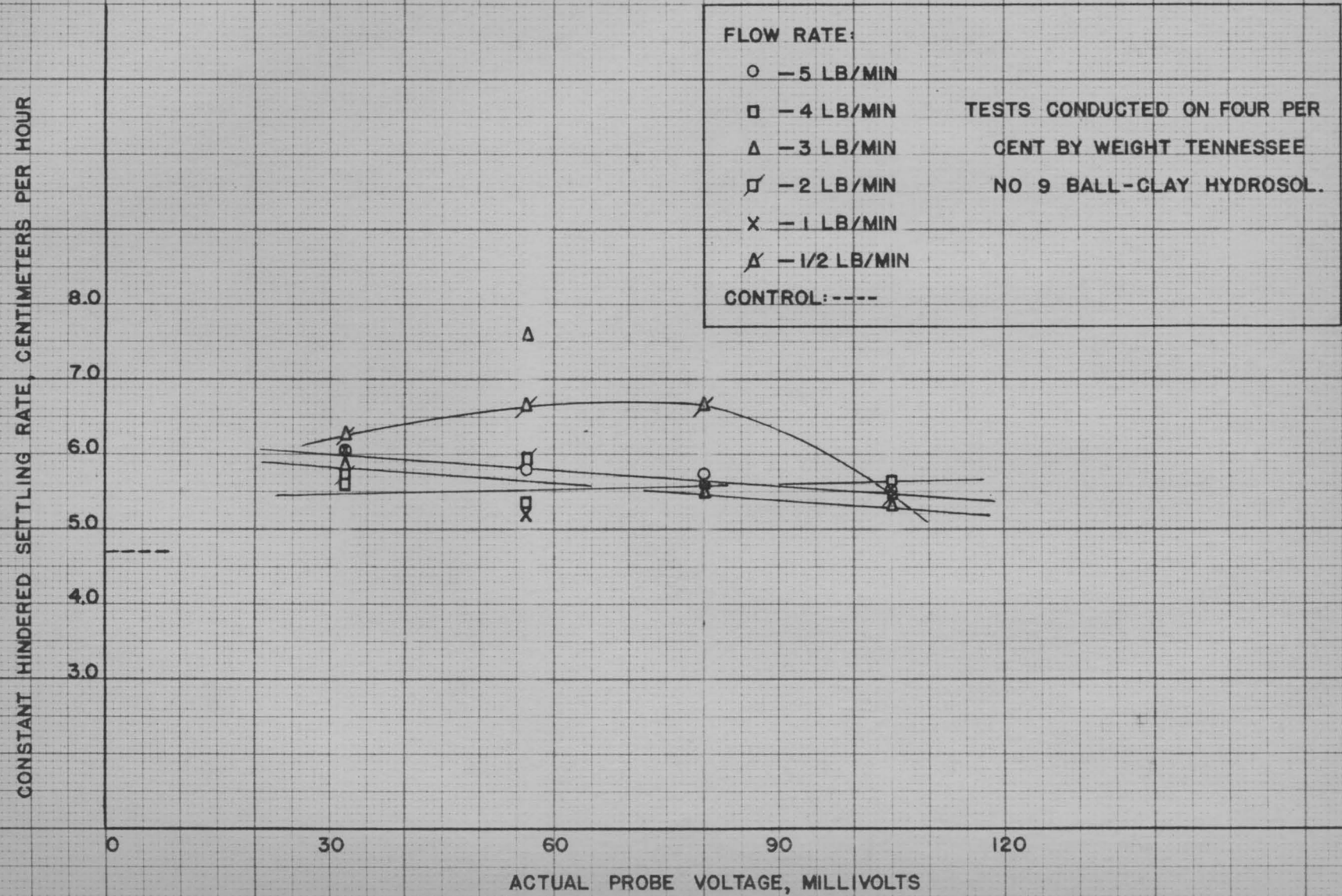


FIGURE 70. EFFECT OF INTENSITY OF INSONATION, IN TERMS OF ACTUAL PROBE VOLTAGE, ON CONSTANT HINDERED SETTLING RATE FOR CONTINUOUS ULTRASONIC COAGULATION TESTS AT 750 KC.

indicates a decrease in constant hindered settling rate with increasing intensity of insonation.

1000-Kilocycle Tests. For the 1000-kilocycle tests there was also a decrease in constant hindered settling rate with increasing intensity of insonation, however, the decrease was not as pronounced as in the 750-kilocycle tests.

Significance of Correlations. There was an increase in constant hindered settling rate with intensity of insonation at 300 and 500 kilocycles and a decrease at 750 and 1000 kilocycles. Consequently, since the actual sound intensity is proportional to the product of both the square of the pressure amplitude and the square of the frequency, in contrast to the relative intensity at a given frequency which is proportional only to the square of the pressure amplitude, it appears that the actual intensity is a significant factor.

Effect of Frequency of Insonation on Constant

Hindered Settling Rate for Continuous Ultrasonic

Coagulation Tests. Figure 71 shows the effect of frequency of insonation on the increase (over the control) in constant hindered settling rate for the continuous

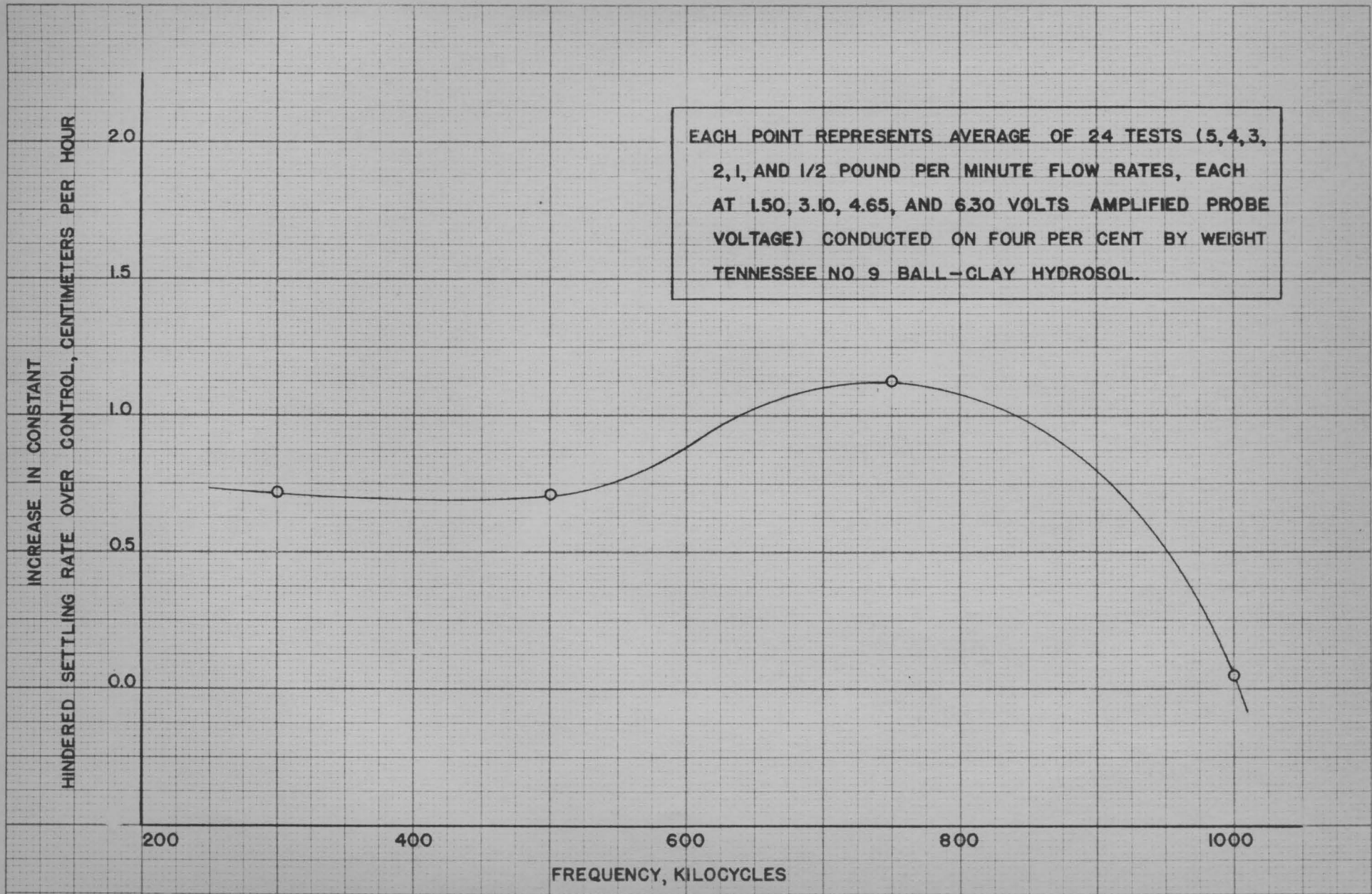


FIGURE 71. EFFECT OF FREQUENCY ON INCREASE IN CONSTANT HINDERED SETTLING RATE OVER CONTROL FOR CONTINUOUS ULTRASONIC COAGULATION TESTS.

ultrasonic coagulation tests. Each point represents an average of 24 continuous-flow tests at the particular frequency plotted. Figure 71 shows that for an average of all similar tests a maximum increase in constant hindered settling rate occurred at 750 kilocycles. For every particle size range there is a favorable frequency or range of frequencies in which the vibration amplitude of the suspended particles is variable, resulting in collision and orthokinetic coagulation⁽²²⁾. From experimental evidence, the 750-kilocycle frequency falls in this category.

Batch Ultrasonic Coagulation Tests. By 300-kilocycle batch insonation of a ball-clay hydrosol for periods of one and two minutes, an average increase (over the control) in constant hindered settling rate of 60.7 per cent was obtained. For the continuous ultrasonic coagulation tests, in which periods of insonation of 0.786 to 7.86 seconds were used, an average increase (over the control) in constant hindered settling rate of 11 per cent was obtained at 300 kilocycles. The batch ultrasonic tests indicate that periods of insonation above the maximum of 7.86 seconds used for the continuous ultrasonic tests would give a more appreciable

increase in constant hindered settling rate than was obtained for the latter. Furthermore, periods of insonation above the two minutes used in the batch ultrasonic tests appear profitable. This finding is consistent with the reported results of Thompson⁽¹⁵⁵⁾ who has shown that increases in hindered settling rate up to 500 per cent could be obtained by batch insonation of a phosphate tailing suspension for periods of ten minutes.

Continuous Mechanical Coagulation Tests. The continuous mechanical coagulation tests employed in this investigation showed only an increase of 2 to 17 per cent in hindered settling which was not believed to be significant. Increasing stirrer speed and/or increasing time of agitation tended to decrease the constant hindered settling rate. Recycling of the ball-clay hydrosol had no apparent advantage.

Batch Mechanical Coagulation Tests. A series of tests were made on a batch scale applying a stirrer speed of 14.5 to 120 revolutions per minute to a four per cent by weight ball-clay hydrosol. The stirring had the effect of decreasing the constant hindered settling rate, indicating the inefficiency of this

method of treatment. Figure 72 shows the effect of the product of stirrer speed and time of agitation on constant hindered settling rate for the batch mechanical tests. The constant hindered settling rate was found to reach a minimum at a product of approximately 900. A fairly definite relationship was obtained between the constant hindered settling rate and the product of stirrer speed and time of agitation. This would indicate that the product was more significant than either the stirrer speed or time of agitation, which by themselves, did not bear any definite relationship with the constant hindered settling rate.

Reproducibility Tests. It was desired to determine to what extent the continuous ultrasonic tests could be reproduced. A series of repeat tests were made at 300 kilocycles with the experimental conditions as close as possible to the original tests. By comparing the results of the reproducibility tests in Table XVII, page 210, with the results of the original tests in Table X, page 182, it can be seen that they compare quite closely. Figure 60, page 211, is a graphical representation of this comparison.

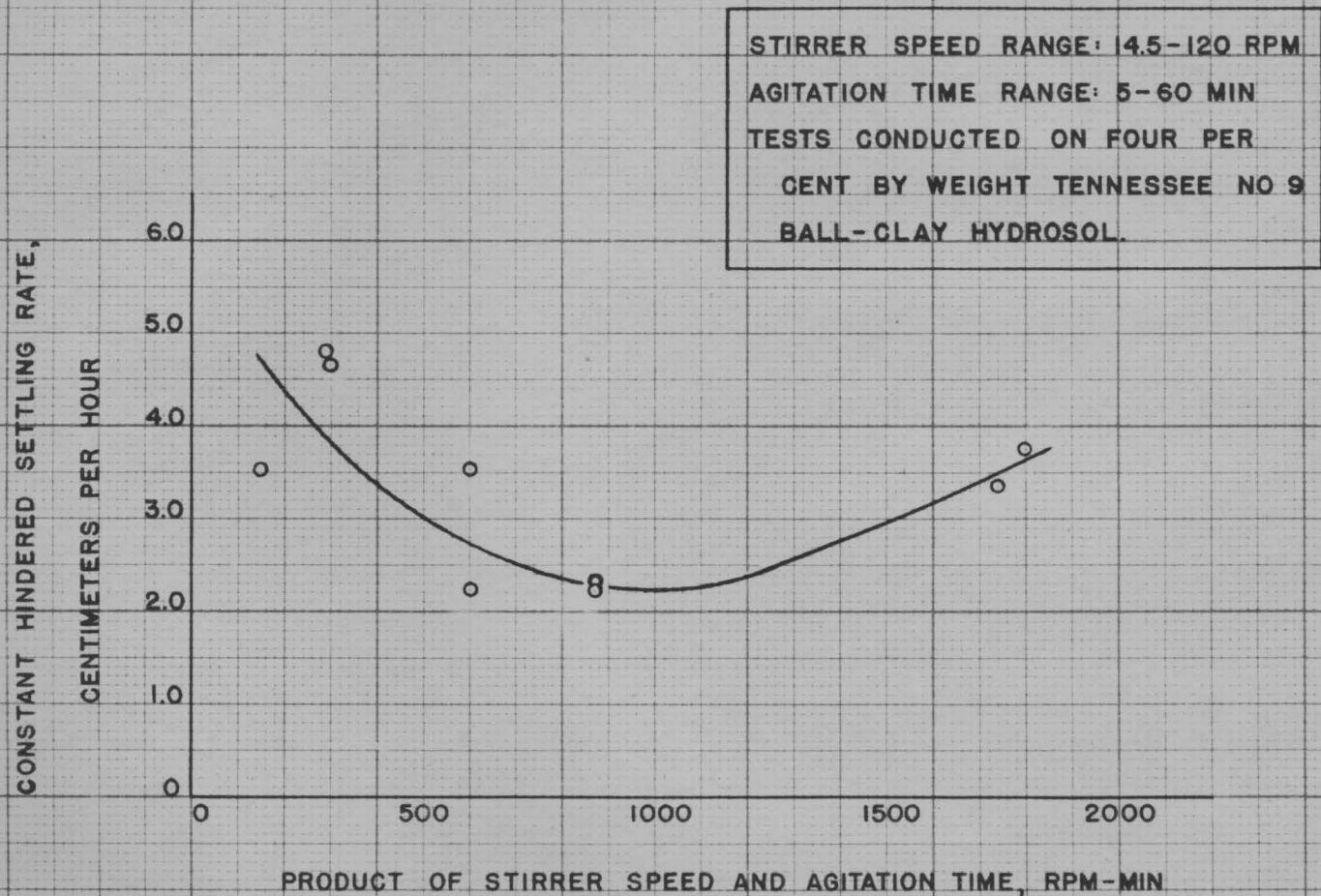


FIGURE 72. EFFECT OF PRODUCT OF STIRRER SPEED AND AGITATION TIME ON CONSTANT HINDERED SETTLING RATE FOR BATCH MECHANICAL COAGULATION TESTS.

Comparison of Different Methods of Coagulation.

The methods of coagulation employed involved only mechanical energy. The essential phenomenon that was imposed on the ball-clay particles was an increase in collision. In this respect insonation appeared to have an advantage over mechanical agitation as was indicated by the increases in settling rate. A probable reason for the advantage of insonation over mechanical agitation is that in the former case a phenomenon of microagitation is exhibited. This microagitation has the effect of causing particles of different sizes to vibrate at different displacement amplitudes resulting in orthokinetic coagulation; a particular frequency being favorable for each particle size range⁽²²⁾. In the mechanical agitation method of treatment there was no positive action in causing particles to collide; only a gross stirring caused by rotating blades.

Influence of Suspension Environment on Coagulation.

Kruyt⁽⁸⁵⁾ has recognized two factors controlling the coagulation of colloidal particles: (1) probability of collision and (2) probability of adhesion. Collision may be accentuated by insonation superimposed on the Brownian movement. Adhesion depends upon the

existence of a predominance of attractive forces between the particles⁽⁸⁵⁾. The major forces which are present between colloidal particles are: (1) gravitational forces of attraction; (2) surface or secondary forces which result in attraction; and (3) a like electric charge on the particles which results in a repulsive force. The smaller the electric charge or zeta potential of the particles, the greater will be their adherence. In this investigation the ball-clay hydrosol pH was approximately 7.8 in contrast to the isoelectric pH of approximately 3.5 at which the zeta potential is practically zero. Nevertheless, coagulation was exhibited by insonation indicating adherence of the particles after the collisions caused by micro-agitation and orthokinetic forces. The average size of the ball-clay particles in suspension was approximately seven microns, being outside of the colloidal range (1 to 500 millimicrons) in which electrostatic forces of repulsion predominate over secondary and gravitational forces of attraction, thereby preventing adhesion. Since the ball-clay particles were outside the colloidal range, it appears probable, that with respect to adhesion, the electrostatic forces of

repulsion assumed a minor role in contrast with secondary and gravitational forces of attraction.

The theory at present accepted⁽⁷⁶⁾ is that by insonation of charged colloidal particles surrounded by an electric double layer, the particles acquire a velocity with respect to the suspension medium and the double layer loses its spherical symmetry resulting in a dipole. These dipoles are all lying in the same direction, that is, the direction in which the sound is being propagated. The dipole forces between two particles which follow each other in the same line are attractive, those between particles that are lying side by side are repulsive. The former will occur more frequently than the latter, and the result will be a higher coagulation rate.

Evaluation of Continuous-Flow Insonation. Four considerations are of particular importance in an evaluation of continuous-flow insonation: (1) there was an increase in constant hindered settling rate with increasing time of insonation within the 0.786- to 7.86-second insonation range; (2) at 500 kilocycles with a 7.86-second insonation and 6.30-volt amplified probe voltage intensity level, a maximum increase in constant hindered settling rate of 81.8 per cent over

the control was obtained which most nearly approximated the maximum increase of 101.4 per cent obtained on a batch scale with a two minute insonation; (3) the most consistent increases (over the control) in constant hindered settling rate were obtained at 750 kilocycles resulting in a range of 9.4 to 61.0 per cent increase with an average of 23.5 per cent increase; and (4) insonation was shown to be more advantageous to coagulation than mechanical agitation.

The foregoing results indicate, on the basis of the ball-clay hydrosol used for experimental tests, that the application of ultrasonic energy to a continuously flowing ball-clay hydrosol is practicable and facilitates coagulation with a subsequent increase in settling rate being realized. Times of insonation on a continuous-flow basis above the 7.86 seconds used in this investigation are indicated. Certain conditions of time, intensity, and frequency of insonation gave a maximum increase in settling rate. The 750-kilocycle frequency appeared to be the most favorable based on the consistent increases in settling rate obtained. A careful analysis of the data leads to the conclusion

that the optimum conditions of time, intensity, and frequency of insonation have not been achieved.

Barium Titanate Transducer. Comparison of continuous insonation with batch insonation indicated that the time of contact was the most important factor. It is believed that times of contact above 7.86 seconds for the continuous ultrasonic treatment would result in a greater coagulation effect than was obtained. In order to have longer times of contact as well as a practical mass velocity of the suspension through the treatment chamber, either larger scale equipment or a change in design is necessary. In this connection, a recent development in the field of piezoelectric crystals is worthy of investigation. It has been shown that a crystal of piezoelectric barium titanate can be molded into any desired shape⁽⁷⁸⁾. A tabular crystal of this type could be used with advantages of both a higher mass velocity and a larger time of contact than was obtainable in this investigation. The barium titanate crystal could be coupled directly to its load and insonation would be perpendicular to the direction of flow.

Recommendations

An evaluation of ultrasonic coagulation on a continuous-flow basis employing a ball-clay hydrosol for experimental tests raised a number of questions to which no answer was provided, thereby indicating possibilities for future investigations. Specific recommendations for future investigations are presented.

Time of Insonation. It is recommended that a four per cent by weight ball-clay hydrosol be insonated on a continuous-flow basis for periods of 10 seconds to 10 minutes. The results of this investigation indicated that times of insonation on a continuous-flow basis above 7.86 seconds would produce a greater coagulation effect than was obtained. Previous investigators have obtained favorable results on a batch scale with 10-minute periods of insonation.

Transducer. It is recommended that the phenomenon of ultrasonic coagulation be further investigated using a cylindrical barium titanate transducing element. Since the design of a reaction chamber employing this element has a wide variety of possibilities, the time of insonation could be controlled by the length of the

element as well as by the directions and rates of flow. The barium titanate element could be coupled directly to its load and insonation would be perpendicular to direction of flow.

Measurement of Ultrasonic Intensity. It is recommended that the determination of ultrasonic intensity for each frequency be made with a probe incorporating a separately calibrated barium titanate crystal. The probe would give an accurate and direct indication of absolute pressure amplitude enabling the calculation of absolute ultrasonic intensities.

Data. It is recommended that settling rate data be taken at ten minute intervals, up to, and for about thirty minutes after, the beginning of the compaction settling period. Such a procedure would give an accurate determination of the transition points encountered in the settling of a ball-clay hydrosol.

Temperature. It is recommended that the effect of temperature on the settling characteristics of a four per cent by weight ball-clay hydrosol be investigated for the range of 60 to 90 °F. Such a determination would indicate the relative importance of

temperature variations which would normally be encountered, on coagulation and settling rate.

Limitations

In this investigation there were many limitations that may be noted in connection with the experimental work. The most important ones are recorded in the following paragraphs.

Coagulation Chamber. The coagulation chamber employed for continuous-flow insonation was limited to two inches in height because of the attenuation of ultrasonic energy in a four per cent by weight ball-clay hydrosol. This limitation prevented times of insonation greater than about eight seconds under the operating conditions that were established.

Measurement of Pressure Amplitude. The accuracy obtainable in the measurement of pressure amplitude with the improvised natural quartz crystal probe was limited with respect to: (1) frequency response, (2) wave length response, and (3) imperfections in shape and composition of crystal.

Frequency. Only frequencies of 300, 500, 750, and 1000 kilocycles were investigated for continuous-flow insonation. These frequencies corresponded to the crystals supplied with the General Electric ultrasonic generator.

Suspension. A single hydrosol consisting of four per cent by weight Tennessee No 9 ball-clay in tap water was used in this investigation. Practical considerations in the analysis of the variables of time, intensity, and frequency of insonation necessitated limiting the investigation to a single hydrosol.

Measurement of Settling Rate. Two inherent errors were involved in the measurement of settling rate: refraction and parallax. Refraction resulted from the thickness of the glass between graduations on the outside of the settling tubes and the inside level of sedimentation. Parallax errors resulted from the position of the observer in reading the values for the height of the level of sedimentation. Different positions would result in slightly different values for a given height. It is believed, however, that these errors were on the order of one millimeter.

V. CONCLUSIONS

Ultrasonic coagulation of a four per cent by weight Tennessee No 9 ball-clay hydrosol, particle size range two-tenths to eight microns, at a pH of 7.8 \pm 0.2 employing a General Electric ultrasonic generator, catalogue No 8665966 G3, led to the following conclusions:

A. For continuous insonation:

1. At 300 kilocycles, an intensity of insonation of 20.0 milliamperes plate current, and increasing time of insonation within the range 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.30 to 6.02 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 5.00 centimeters per hour.

2. At 300 kilocycles, an intensity of insonation of 40.5 milliamperes plate current, and increasing time of insonation within the range 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.26 to 6.44 centimeters per hour, whereas the uninsonated control

exhibited a constant hindered settling rate of 5.00 centimeters per hour.

3. At 300 kilocycles, an intensity of insonation of 60.2 milliamperes plate current, and increasing time of insonation within the range 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.48 to 6.15 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 5.00 centimeters per hour.

4. At 300 kilocycles, an intensity of insonation of 90.0 milliamperes plate current, and increasing time of insonation within the range 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.44 to 6.50 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 5.00 centimeters per hour.

5. At 500 kilocycles, an intensity of insonation of 25.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 4.14 to 4.55

centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.40 centimeters per hour.

6. At 500 kilocycles, an intensity of insonation of 50.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 4.80 to 5.60 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.40 centimeters per hour.

7. At 500 kilocycles, an intensity of insonation of 75.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 4.16 to 5.24 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.40 centimeters per hour.

8. At 500 kilocycles, an intensity of insonation of 100.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling

rates were obtained ranging from 5.24 to 7.99 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.40 centimeters per hour.

9. At 500 kilocycles, an intensity of insonation of 150.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 4.55 to 6.56 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.40 centimeters per hour.

10. At 750 kilocycles, an intensity of insonation of 57.5 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.58 to 6.27 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.71 centimeters per hour.

11. At 750 kilocycles, an intensity of insonation of 97.5 milliamperes plate current, and increasing time of insonation within the range of

0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.33 to 6.62 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.71 centimeters per hour.

12. At 750 kilocycles, an intensity of insonation of 122.5 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.48 to 6.62 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.71 centimeters per hour.

13. At 750 kilocycles, an intensity of insonation of 145.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.57 to 5.42 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.71 centimeters per hour.

14. At 1000 kilocycles, an intensity of insonation of 25.0 milliamperes plate current, and

increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.08 to 4.88 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.88 centimeters per hour.

15. At 1000 kilocycles, an intensity of insonation of 75.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 5.04 to 4.86 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.88 centimeters per hour.

16. At 1000 kilocycles, an intensity of insonation of 125.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 4.96 to 4.80 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.88 centimeters per hour.

17. At 1000 kilocycles, an intensity of insonation of 150.0 milliamperes plate current, and increasing time of insonation within the range of 0.786 to 7.86 seconds, constant hindered settling rates were obtained ranging from 4.88 to 4.86 centimeters per hour, whereas the uninsonated control exhibited a constant hindered settling rate of 4.88 centimeters per hour.

18. Based on the individual controls, average increases in constant hindered settling rate for the 300, 500, 750, and 1000 kilocycle tests were 11, 17, 23.5, and 1 per cent, respectively.

B. For batch insonation:

1. At 300 kilocycles, an intensity of insonation of 75 milliamperes plate current, and a time of insonation of one minute, a constant hindered settling rate of 7.07 centimeters per hour was obtained, whereas the uninsonated control exhibited a constant hindered settling rate of 4.87 centimeters per hour.

2. At 300 kilocycles, an intensity of insonation of 75 milliamperes plate current, and a time of insonation of two minutes, a constant hindered settling rate of 9.82 centimeters per hour was obtained, whereas the uninsonated control exhibited a constant hindered settling rate of 4.87 centimeters per hour.

C. For continuous mechanical agitation employing a Waring blender with "Micro" head:

1. At a stirrer speed of 2,860 revolutions per minute and increasing time of agitation within the range of 8.44 to 84.4 seconds, constant hindered settling rates were obtained ranging from 5.14 to 4.66 centimeters per hour, whereas the untreated control exhibited a constant hindered settling rate of 4.57 centimeters per hour.

2. At a stirrer speed of 11,110 revolutions per minute and increasing time of agitation within the range 8.44 to 84.4 seconds, constant hindered settling rates were obtained ranging from 5.35 to 5.08 centimeters per hour, whereas the

untreated control exhibited a constant hindered settling rate of 4.57 centimeters per hour.

3. At a stirrer speed of 14,820 revolutions per minute and increasing time of agitation within the range 8.44 to 84.4 seconds, constant hindered settling rates were obtained ranging from 5.08 to 4.96 centimeters per hour, whereas the untreated control exhibited a constant hindered settling rate of 4.57 centimeters per hour.

4. At a stirrer speed of 17,550 revolutions per minute and increasing time of agitation within the range 8.44 to 84.4 seconds, constant hindered settling rates were obtained ranging from 5.08 to 4.90 centimeters per hour, whereas the untreated control exhibited a constant hindered settling rate of 4.57 centimeters per hour.

D. For batch mechanical agitation employing a nine and one-quarter inch high by six and one-quarter inch diameter glass jar containing hydrosol undergoing stirring by means of an impeller with four blades at an angle of 10 degrees and covering a circle of diameter two and one-half inches:

1. At a stirrer speed of 14.5 revolutions per minute and a time of agitation of 60 minutes, a constant hindered settling rate of 2.29 centimeters per hour was obtained, whereas the untreated control exhibited a constant hindered settling rate of 4.71 centimeters per hour.

2. At a stirrer speed of 29 revolutions per minute and increasing time of agitation within the range 5 to 60 minutes, constant hindered settling rates were obtained ranging from 4.80 to 2.21 centimeters per hour, whereas the untreated control exhibited a constant hindered settling rate of 4.71 centimeters per hour.

3. At a stirrer speed of 60 revolutions per minute and increasing time of agitation within the range 5 to 30 minutes, constant hindered settling rates were obtained ranging from 4.69 to 3.51 centimeters per hour, whereas the untreated control exhibited a constant hindered settling rate of 4.71 centimeters per hour.

4. At a stirrer speed of 120 revolutions per minute and a time of agitation of 5 minutes, a constant hindered settling rate of 2.24

centimeters per hour was obtained, whereas the untreated control exhibited a constant hindered settling rate of 4.71 centimeters per hour.

E. Comparison of the constant hindered settling rates obtained by insonation and mechanical agitation indicated increases, based on the individual controls, of up to 81.8 per cent for continuous insonation, 101.4 per cent for batch insonation, 17 per cent for continuous mechanical agitation, and 2 per cent for batch mechanical agitation.

VI. SUMMARY

A summary of the investigation, an evaluation of continuous ultrasonic coagulation employing a ball-clay hydrosol, is given in the following paragraphs:

Purpose of Investigation. On a batch scale, as much as 500 per cent increase in hindered settling rate of an aqueous suspension has been reported for periods of insonation of approximately ten minutes. In this investigation it was desired to ascertain the effect of ultrasonic coagulation on a basis of continuous flow of the suspension through the sound field and concurrently to reduce the time of insonation. It was the purpose of this investigation to design, construct, and evaluate a continuous-flow, ultrasonic coagulation unit, employing a ball-clay hydrosol for experimental tests.

Plan of Experimentation. The plan of experimentation consisted of subjecting a continuously flowing four per cent by weight ball-clay hydrosol to an ultrasonic field and observing the effects on settling rate produced subsequent to insonation. Variables of time, intensity, and frequency of insonation were investigated on a continuous-flow basis. Batch ultrasonic and continuous and batch

mechanical agitation tests were conducted for comparison of settling rates with the continuous ultrasonic tests.

Results and Conclusions. Data obtained in this investigation indicated that the application of ultrasonic energy to a continuously flowing ball-clay hydrosol facilitates coagulation with a subsequent increase in settling rate being realized. Under optimum experimental conditions a maximum increase in hindered settling rate of 81.8 per cent over the control was obtained. The consistently highest increases in hindered settling rate were obtained at 750 kilocycles resulting in a range of 9.4 to 61 per cent increase with an average of 23.5 per cent increase. An increase in hindered settling rate was found with increasing time of insonation within the 0.786- to 7.86-second insonation range. Comparison of continuous and batch insonation indicated that periods of treatment greater than 7.86 seconds would continue to increase the settling rate. In fact, increases in hindered settling rate up to 101.4 per cent were obtained on a batch scale with two minute insonation. Furthermore, the microagitation and orthokinetic effects produced by insonation were shown to be more advantageous to coagulation and settling rate than

the gross stirring produced by mechanical agitation.

A careful analysis of the data suggests that the optimum conditions of time, intensity, and frequency of insonation have not been achieved.

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