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## **The Effects of Mixing Variables on Settling Rates and Particle Size Distribution of Dicalcium Phosphate Made by the Hydrolysis of Monocalcium Phosphate**

Marvin Noble Dokken  
*University of Tennessee - Knoxville*

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To the Graduate Council:

I am submitting herewith a thesis written by Marvin Noble Dokken entitled "The Effects of Mixing Variables on Settling Rates and Particle Size Distribution of Dicalcium Phosphate Made by the Hydrolysis of Monocalcium Phosphate." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

W. H. Baskervill, Major Professor

We have read this thesis and recommend its acceptance:

R. M. Boarts, Edgar D. Eaves

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

THE EFFECTS OF MIXING  
VARIABLES ON SETTLING RATES AND PARTICLE  
SIZE DISTRIBUTION OF DICALCIUM PHOSPHATE MADE  
BY THE HYDROLYSIS OF MONOCALCIUM PHOSPHATE

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A THESIS

Submitted to  
The Committee on Graduate Study  
of  
The University of Tennessee  
in  
Partial Fulfillment of the Requirements  
for the degree of  
Master of Science

---

by  
Marvin Noble Dokken

August 1942

July 31, 1942

To the Committee on Graduate Study:

I am submitting to you a thesis written by Marvin Noble Dokken, entitled "The Effects of Mixing Variables on Settling Rates and Particle Size Distribution of Dicalcium Phosphate Made by the Hydrolysis of Monocalcium Phosphate". I recommend that it be accepted for fifteen quarter hours credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

W.H. Baskerville  
Major Professor

We have read this thesis  
and recommend its acceptance:

Rm Boats

Edgar D. Caves

Accepted for the Committee

W.C. Smith  
Dean of the Graduate School

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THE EFFECTS OF MIXING VARIABLES ON SETTLING RATES  
AND PARTICLE SIZE DISTRIBUTION OF DICALCIUM  
PHOSPHATE MADE BY THE HYDROLYSIS OF  
MONOCALCIUM PHOSPHATE

SUMMARY

A process is under investigation for the manufacture of dicalcium phosphate by the hydrolysis of concentrated superphosphate containing recycled monocalcium phosphate. The hydrolysis also results in the formation of an aqueous solution of monocalcium phosphate and free phosphoric acid. The phases are separated, followed by washing and drying of the solid dicalcium phosphate. The wash water is used in the hydrolyzer. The solution is returned to the superphosphate production step, where phosphate rock and additional phosphoric acid are added, and where water is evaporated to form the solid superphosphate.

The solids can be separated from the solution by the use of either countercurrent thickeners or filters. In either case, increasing the size of the dicalcium phosphate particles would facilitate the separation. Pilot plant results have indicated that filtration rates vary widely under almost identical mixing conditions, presumably due to variations in particle size ranges. It was thought worthwhile, therefore, to study the effects of different mixing variables on the relative particle

sizes as indicated by the settling rates of the mixture.

Monocalcium phosphate and water were mixed in a small laboratory hydrolyzer under controlled conditions and the settling rates and compression points\* of the resultant slurries observed. Screen analysis of the settled slurries were made and the further size separations attempted with a hydraulic elutriator. Samples of the slurries were then examined under a microscope.

When the solid was added rapidly to water at 98° C. the settling rates decreased and the points of compression increased with an increase in mixing time beyond five minutes. When the solid was added slowly the settling rate increased with increasing time of addition, while the compression point was constant. Decreasing the ratio of water to monocalcium phosphate decreased the settling rates rapidly and increased the points of compression. For ratios of 0.65 and below, the slurries were in the compression stages as mixed. The settling rates were also decreased by increasing the  $P_2O_5$  and CaO contents of the original liquid, and by decreasing the particle size range of the monocalcium phosphate. Slurries made from fortified\*\* superphosphate settled more rapidly than did slurries made from

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\* The compression point is defined as the height of the slurry at the time the settling rate started to decrease rapidly divided by the original height of slurry.

\*\* Fortified superphosphate is defined as the superphosphate containing recycled monocalcium phosphate.

monocalcium phosphate.

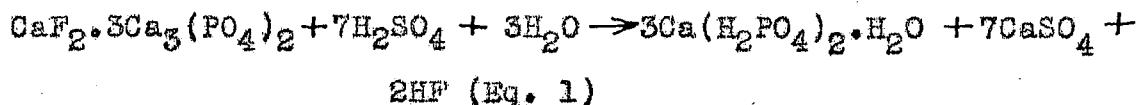
Induction periods observed in the settling-rate curves, the variations in the points of compression, the behavior of the solids in a hydraulic elutriator, and the microscopic examination indicated that the solids were present as extremely small particles of uniform size which combine to form flocs. The ultimate particle size was approximated to be 2.5 microns.

THE EFFECTS OF MIXING VARIABLES ON SETTLING RATES  
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PHOSPHATE MADE BY THE HYDROLYSIS OF  
MONOCALCIUM PHOSPHATE

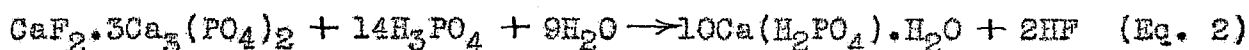
INTRODUCTION

Soil depletion is one of the major problems concerning farm economy which has received considerable attention in recent years. Crops gradually remove the elements of fertility from the soil, and erosion by wind or water removes the entire body of the soil. By using fertilizers and growing leguminous crops the fertility of the soil may be restored and erosion reduced to a large extent. Of the three essential elements for plant growth (nitrogen, phosphorus, and potassium), nitrogen may be restored by leguminous crops while phosphorus and potassium must be added artificially in the form of fertilizers. Phosphates have become the chief constituent of nearly all mixed fertilizers used today and for this reason any reduction in their cost of production, distribution, or application would be desirable.

At present, phosphatic fertilizers are usually produced by the reaction of phosphate rock with either sulphuric or phosphoric acid. Sulphuric acid and phosphate rock produce ordinary superphosphate. The principal reaction is as follows:



Phosphoric acid produces a more concentrated superphosphate, since both the rock and acid furnish  $\text{P}_2\text{O}_5^*$  to the product, which is called triple, or concentrated, superphosphate. The reaction may be represented by the following equation:



Both superphosphates contain water soluble monocalcium phosphate as the active fertilizing ingredient.

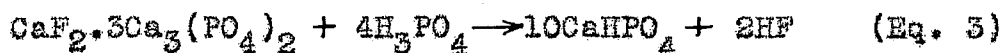
Another phosphatic material which may be used as fertilizer is dicalcium phosphate. Its  $\text{P}_2\text{O}_5$  content is slightly lower than that of triple superphosphate. Dicalcium phosphate is water insoluble but citrate soluble and therefore available to plants. It is known that readily soluble phosphates, as monocalcium phosphate, have a tendency to revert in the soil to less soluble phosphates<sup>12</sup>, thereby rendering utilization of the fertilizer by plants incomplete. Dicalcium phosphate does not revert to unavailable form as quickly as do superphosphates, and, being water insoluble, will not form high local concentrations which may injure the plants. Also, dicalcium phosphate being non-acidic and non-hygroscopic, has a decided advantage

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\* The quantity of phosphorous combined as compounds in a fertilizer is usually expressed as  $\text{P}_2\text{O}_5$ , the anhydride of phosphoric acid.

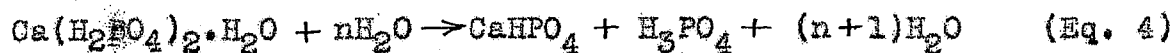
over superphosphates in that it will neither cake in the bags nor rot them. For these reasons dicalcium phosphate is more desirable as a fertilizer than are superphosphates.

For the reaction between phosphate rock and phosphoric acid, 1.4 moles of acid give one mole of  $P_2O_5$  in the product. A hypothetical reaction between phosphate rock and phosphoric acid to give dicalcium phosphate may be represented by the following equation:



This reaction would require 0.8 moles of phosphoric acid to give one mole of  $P_2O_5$  in the product, thus requiring only 57.2 per cent of the acid used in making triple superphosphate. Unfortunately, however, the direct reaction between theoretical amounts of phosphoric acid and phosphate rock as represented by equation 3 does not form dicalcium phosphate but rather a mixture of superphosphate and unreacted rock.

A possible method for the production of dicalcium phosphate is by the hydrolysis of monocalcium phosphate<sup>7</sup>. The reaction may be represented by the following equation:



By using a weight ratio of from one-half to two pounds of water per pound of monocalcium phosphate and mixing at 98° C. from 73 to 75 per cent conversion may be obtained<sup>6</sup>. The remaining monocalcium phosphate goes into solution.

A suggested cyclical process for utilization of the above reaction, the net result of which is the production of dicalcium phosphate by equation 3 is as follows<sup>7</sup>:

(1) A mixture of triple superphosphate and recycled monocalcium phosphate\* is treated countercurrently with hot water to form a solid containing a large amount of dicalcium phosphate and an aqueous  $\text{CaO-P}_2\text{O}_5$  solution.

(2) The solid and  $\text{CaO-P}_2\text{O}_5$  solution are separated, followed by washing and drying of the solid.

(3) The  $\text{CaO-P}_2\text{O}_5$  solution from step 2 is recycled and additional acid and rock are added to form the mixture of superphosphate and monocalcium phosphate used in step 1. Water is evaporated in this step so that the phosphoric acid will be of an optimum concentration for the superphosphate forming reaction. The wash water from step 2 is returned to the hydrolyzer.

The evaporation of the water could be accomplished in conjunction with the electric furnace production of phosphoric acid. This method of producing phosphoric acid involves burning phosphorous to give hot  $\text{P}_2\text{O}_5$  fumes and spraying water into them to hydrate the  $\text{P}_2\text{O}_5$  and to cool the gases. Instead of using water either the recycled solution or the mixture of recycled solution, fresh acid, and phosphate rock (in the form of a slurry) could be sprayed into the hot products of combustion. Thus, the heat of combustion of the phosphorus would be utilized to concentrate the by-product solution.

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\* Such a mixture will be referred to hereafter as fortified superphosphate.

Steps 1 and 2 had been investigated on both a laboratory and a pilot-plant scale and found to be workable<sup>7</sup>. They were carried out on the pilot-plant scale by mixing triple superphosphate and recycled wash water in a mixer-hydrolyzer at 98° C., filtering the slurry in a plate-and-frame filter press, and washing the solid (dicalcium phosphate) with fresh tap water. During operation it was noticed the filtering characteristics of the slurry varied considerably when different batches were mixed under as nearly the same conditions as possible. This variation was thought to be due to differences in the particle size of the dicalcium phosphate. Poor washing was obtained on the filter largely because of leakage.

It should be possible to increase the thoroughness of washing by using more than one filter in series, the cake being repulped between filters, and the filtrate from one filter being used as wash water for the next. The separation could also be affected by the use of countercurrent thickeners, with the underflow from the end thickener going to a filter. However, pilot-plant studies using thickeners showed their capacity was very limited because of the slow settling rates obtained.

Regardless of the method used to separate the solid and liquid phases it is desirable that they be separated as easily as possible. Since filtration and settling rates are dependent on the particle size, large particles would increase the rate in either case.



Attempts had been made to apply the inverted solubility curve of dicalcium phosphate to increase the crystal size by alternate heating and cooling<sup>7</sup>. It was thought that when a mixture of dicalcium phosphate and  $\text{CaO-P}_2\text{O}_5$  solution is cooled, the smallest dicalcium phosphate crystals present should go into solution; then when heating takes place, instead of more dicalcium seed crystals forming, the dicalcium phosphate should build up on the crystals already present. Microscopic examination showed no appreciable crystal growth by this method, probably because of the slow dissolution of dicalcium phosphate on cooling.

Because these pilot-plant studies had indicated larger particle sizes were desirable, and because variations in particle size had been obtained under almost identical mixing conditions, an investigation was undertaken to determine the effect of mixing variables on the particle size of dicalcium phosphate obtained. Since settling rates are dependent on particle size, settling-rate data were taken to use as the basis of comparison of particle size. Attempts were then made to use a short-column elutriator and a microscope for determining the ultimate particle size distribution.

## LITERATURE SURVEY

### Reaction Equilibria and Mechanism

Phase-equilibria data concerning the calcium phosphates in phosphoric acid solutions have been published<sup>6</sup> for a temperature range from 25 to 100° C., and in 2 to 98 per cent phosphoric acid solutions. The phase diagrams have been used to calculate the maximum conversion of monocalcium phosphate monohydrate into dicalcium phosphate, phosphoric acid, and water, on solution in different proportions of water at different temperatures. These calculated conversions are plotted in Fig. 1. It may be seen that the conversion increases with increasing temperatures, and at 100° C., varies from 73 to 78 per cent for weight ratios of monocalcium phosphate monohydrate to water of 0.35 to 3.8, with conversions falling off quite rapidly for ratios greater or less than these.

The suggested mechanism of the reaction to form dicalcium phosphate by the hydrolysis of monocalcium phosphate is as follows<sup>7,11</sup>;

(1) The monocalcium phosphate dissolves until the solution becomes supersaturated with respect to CaO.

(2) When the solution becomes supersaturated the CaO starts precipitating out as dicalcium phosphate while the monocalcium phosphate continues to dissolve. The conversion continues until equilibrium is reached.

The formation of dicalcium phosphate crystals may, therefore, be considered a process of crystallization. The following information concerning the theory of crystallization and effect

PER CENT CONVERSION

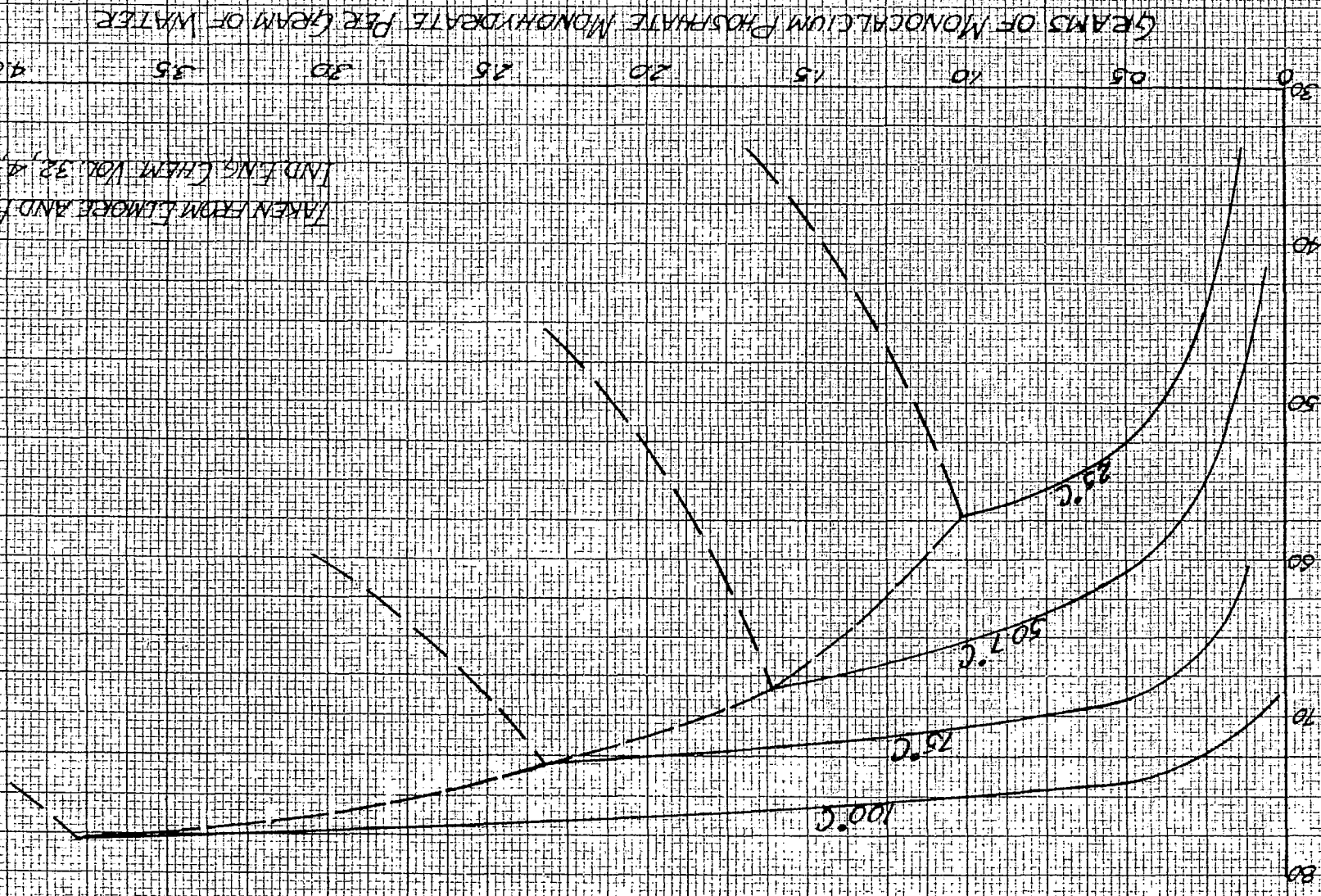


FIG. 1

PERCENTAGE CONVERSIONS OF MONOCALCIUM PHOSPHATE INTO DICALCIUM PHOSPHATE UNDER DIFFERENT CONDITIONS

M. N. S. 7/7/42

TAKEN FROM L. MORE AND F. A. R.  
IND. ENG. CHEM. VOL. 32, 4, (1940)

of particle size on settling rates was obtained from the literature.

### Crystallization

In any crystallization process the crystals must first form and then grow. The theory can be conveniently considered under three heads: (1) the formation of crystalline nuclei, (2) their resulting growth, and (3) the interrelation between formation and growth. If the laws and data for crystal formation and growth were complete, it should be possible to estimate in advance the size distribution of the product of a crystallization process. However, little quantitative information is available on crystal formation and growth so the following discussion is largely qualitative.

For crystal formation to take place a driving force in the form of a supersaturated solution must first be established. The degree of supersaturation required varies with the solute and impurities present. Solutions may be supersaturated under certain conditions to a considerable extent beyond the saturation point without the formation of any nuclei. The relationship between the concentration and the temperature at which crystals will spontaneously form from an unseeded solution takes the form of a so-called supersolubility curve, originally proposed by Miers<sup>9\*</sup>. These relationships are shown diagrammatically

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\*Perry, J. H., Chemical Engineers Handbook, 2nd edition, pg. 1767.

in Fig. 2. In the field between the normal and the supersolubility curve, equilibrium is considered to be metastable.

In order to form a nucleus several molecules in the solution must collide together in the configuration which is characteristic of the crystal of that substance. Until the supersaturation point is reached any small crystalline nuclei which are formed will immediately redissolve. However, the presence of dust particles, small solute crystals, mechanical shock, or in some cases crystals of other materials may lead to the formation of crystals that will continue to grow until normal equilibrium conditions are reached. When the supersaturation point is reached, crystal formation occurs spontaneously, giving a precipitate, and continues until the composition of the solution falls to the normal solubility curve. This type of crystal formation is said to take place from an unseeded solution. Crystal formation due to the presence of dust particles or crystals is said to take place from seeded solutions.

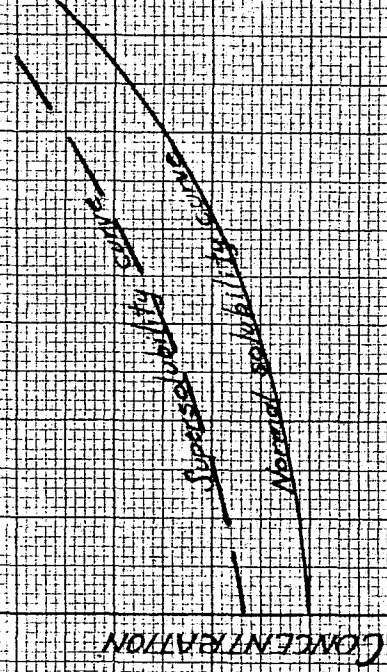
In addition to spontaneous nucleation new nuclei may originate in one or more of the following ways<sup>9\*</sup>:

1. By attrition of existing crystals. If crystals are agitated small fragments and corners may be broken off, becoming new nuclei.

2. Mechanical impact. If a supersaturated solution is vigorously stirred, the collision of crystals in the solution with each other or with the walls of the crystallizer may cause

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\*Ibid., p. 1770.



TEMPERATURE

FIG. 2

# DIAGRAMMATIC REPRESENTATION OF MIER'S THEORY

M.H.S. 7/7/42

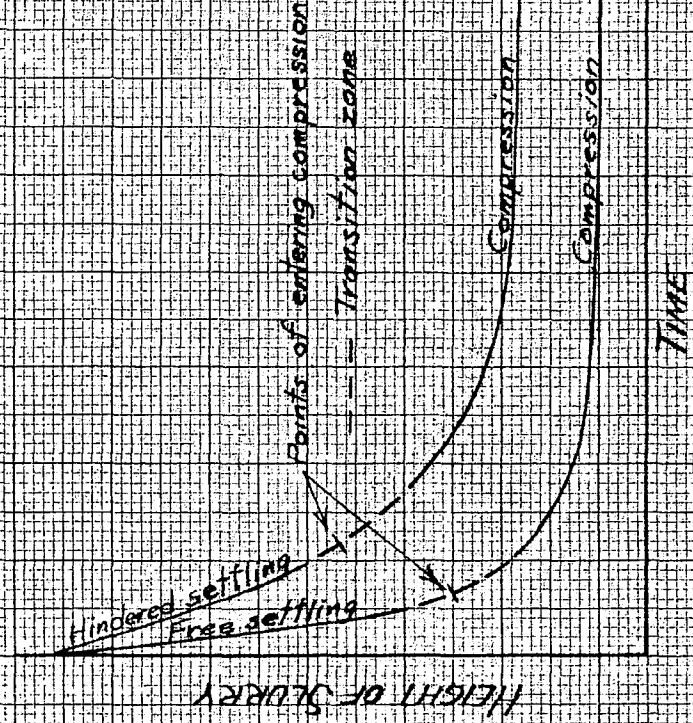


FIG. 3

# TYPICAL SETTLING CURVES OF SLURRIES

M.H.S. 7/7/42



formation of new nuclei.

3. New crystals may be formed due to the inoculating influence of the crystals already present. If a solution is supersaturated, small crystal fragments the size of spontaneous nuclei break off due to the tendency of disaggregation.

4. Local variations in conditions may cause nucleation in restricted zones. Examples would be the withdrawal of heat from the containing wall to increase supersaturation leading to lower temperatures near the wall, and evaporation leading to high concentration of solution at the surface.

Von Weiman<sup>3</sup> has shown that the size of crystals obtained by spontaneous crystallization from pure solutions is a function of the solubility, degree of saturation, and viscosity of the solution. The character and particle size of the crystals of precipitate are determined by the dispersion coefficient  $d$ , which is defined by the equation:

$$d = \frac{P}{S} u,$$

where,  $S$  = solubility of solute in mole/liter;  
 $P$  = moles of precipitate which must be removed from one liter of the supersaturated solution in order that its concentration may be reduced to the value of  $S$ ;  
 $u$  = viscosity of solution.

At low values of  $d$ , crystal formation is negligible, at medium values of  $d$  the crystals attain their maximum size, while high values of  $d$  give a large number of very small crystals.

In the case of an unseeded solution, it is possible in viscous solutions of relatively high molecular weight, to maintain a highly supersaturated solution indefinitely without the formation of nuclei. Solutions of moderate viscosities and low molecular weight are not capable of supporting supersaturation

of any great magnitude without nuclei formation. Spontaneous nucleation from unseeded solutions cannot be controlled and for this reason high supersaturations are avoided in industrial crystallizers.

The mechanism of crystal growth from solutions corresponds to crystal growth from a melt, except that the presence of a solvent introduces the concentration of the solution as a variable along with the temperature. The rate of crystal growth is controlled by the rate of diffusion of the reactants and products to and from the solid-liquid interface. This diffusional process is followed by a first-order interfacial reaction. The net rate of crystallization is dependent on both reactions and may be represented by the following equation<sup>9\*</sup>:

$$\frac{dW}{dt} = \frac{S(C-C_0)}{\frac{1}{K} - \frac{L}{k}}$$

where, W = weight;  
 t = time;  
 k = diffusion coefficient;  
 K = rate of reaction constant of the interfacial reaction;  
 S = surface area;  
 L = effective film thickness;  
 C = concentration of bulk of solution;  
 C<sub>0</sub> = concentration of a saturated solution.

In most cases it will be found that the diffusion rate is the controlling factor, since the rate of reaction taking place at the interface is usually very rapid in comparison with the diffusion rate. In the immediate vicinity of a growing crystal

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\*Ibid., p. 1773.



a zone of liquid no longer supersaturated is formed because of the removal of solute by the crystal. Further growth can occur only when the concentration of the solution in the immediate neighborhood of the growing crystal is increased by diffusion or convection. The growth of the crystal thus depends upon the rate of supply of dissolved material from the surrounding supersaturated solution.

The diffusional resistance is confined to a comparatively thin film surrounding the solid. Thus low viscosity and vigorous stirring attenuate the film, decrease the diffusional resistance, and increase the rate of crystal growth; while high viscosity and poor agitation decrease the diffusion rate.

For conditions of low supersaturation both crystal growth and formation are slow, but formation is relatively slower than growth, thus large crystals are obtained. For conditions of high supersaturation nuclei formation becomes faster relative to growth, thus small crystals are obtained. Agitation increases the nucleation rate more than growth rate which accounts for smaller crystals on stirring. Impurities in the solution may inhibit the formation of new nuclei and also affect crystal growth in that the impurities are absorbed on the crystal's surface thereby decreasing the growth rate.

#### Effect of Crystal Size on Settling Rates

In the separation of solids from liquids by settling,

the particle size is of great importance in that an increase in particle size will increase the settling rate considerably.

For a spherical body falling under viscous resistance in an infinitely large body of water, Stokes' Law for spherical particles applies, and is represented by the following equation<sup>1</sup>:

$$U = \frac{54.5D^2}{u} (p' - p),$$

where,  $U$  = velocity of fall, cm/sec;  
 $D$  = diameter of particle, cm;  
 $p'$  = density of solids, gms/cc;  
 $p$  = density of fluid, gms/cc;  
 $u$  = viscosity of fluid, poises.

In the case of non-spherical particles different values for the constant are used. Settling under the above conditions is called free settling. If, however, particles interfere with each other in settling, the process is called hindered settling and Stokes' Law no longer applies.

The settling of a fine suspension of solids in water or other fluids may be divided into three stages as follows<sup>2</sup>:

(1) the first part, or clarification zone, where the rate of settling is constant and the settling curve of height of slurry versus time is a straight line.

(2) the last part, or compression zone, where the slurry is approaching its ultimate level and the rate is getting slower and slower.

(3) the intermediate part, which is a transition zone between the first and last part.

During the initial period of constant rate settling, the particles settle more or less independently of each other. As settling continues the particles are loosely deposited on the bottom of the chamber, rest upon each other, and start to build a loose

layer of solid. When the layer reaches the top of the suspension the slurry is at the point of entering compression. Further settling is then effected by water passing through the interstices between the particles. Two types of settling curves, one obtained with hindered and one obtained with free settling, are shown in Fig. 5, page 14.

The difference between the rate of settling of an actual slurry and that of a lone spherical particle is due to the particles not being spherical and the large number of particles present in the fluid. Robinson<sup>10</sup> writes Stokes' Law in the following form for such case:

$$\frac{dH}{dt} = \frac{KD^2(P - P_s)}{u_s}$$

where,

H = height of suspension, cm;  
 t = time, sec;  
 D = average particle diameter, cm;  
 $P_s$  = density of suspension, gms/cc;  
 P = density of particles, gms/cc;  
 $u_s$  = viscosity of suspension, poises;  
 K = proportionality constant.

The reason given for writing the equation in this form is that the driving force which causes the settling is proportional, not to the difference between the specific gravity of the solid and the fluid, but to the difference between the specific gravity of the solid and the suspension surrounding the particle, and that the resistance to settling of the particle should be proportional to the viscosity of the suspension of the particles in the fluid surrounding the particle. Also, the settling coefficient should depend on the shape of the particles.

Many settling problems encountered in industry involve flocculated suspensions rather than individual particles. Flocculation is due to the force of attraction between particles causing two or more of them to aggregate into a floc. If the particles all bear a like charge, they repel each other and retain their individuality and are said to be dispersed. If the proper flocculating agent is added to the suspension so that the charge on each particle is neutralized the force of attraction exceeds that of repulsion, and the particles will aggregate into flocs. Large particles, although they still retain a charge are so heavy and their centers of attraction are so relatively far apart that they will not form flocs. The degree and type of flocculation produced influence the rate of settling and final height of slurry more than any other factor. The degree of flocculation depends on the following factors<sup>8</sup>:

- (1) the nature and preceding treatment of the slurry,
- (2) the character and concentration of the flocculating agent,
- (3) the concentration and temperature of the slurry,
- (4) the time elapsed after beginning of flocculation.

If a suspension of fine particles, in which the force of attraction exceeds that of repulsion, is allowed to stand undisturbed, flocculation proceeds. It is obvious that the flocs will settle faster than the individual particles, since

the rate of fall is proportional to the square of the radius. Thus, during the period when the flocs are beginning to form settling will be very slow. As flocculation continues the settling rate will increase until it reaches a more or less constant value. Flocs follow the same type of settling curves as individual particles but will not form as compact a mass on completion of settling.

In applying Stokes' or Robinson's formulas to flocs the variables cannot be determined directly so other methods have been developed for the prediction of settling rates. Egolf and McCabe<sup>5</sup> developed formulas for a suspension of flocculated particles of uniform size, in which, given the initial height, concentration, and viscosity of the medium one may predict the height of the suspension at any subsequent time. However, these equations are limited to the prediction of settling curves in which the concentration will not vary greatly from the concentration used in determining the factors given in the equations.

Work and Kohler<sup>13</sup> have presented general relations for the settling periods of suspensions over a wide range of concentrations and with different settling heights. By having data at one concentration for one initial height, settling rates can be predicted for any other initial height. Also, by having data for several concentrations settling rates may be predicted for any concentration provided the flocs are of uniform size.

## MATERIALS AND APPARATUS

Monocalcium Phosphate: The monocalcium phosphate used for the various studies was made by mixing theoretical amounts of hydrated lime and phosphoric acid in a rotary mixer. Two batches of 120 pounds each were made. Since some lime was carried off by steam during mixing, additional amounts were added until analysis of the product showed one mole of  $P_2O_5$  per mole of  $CaO$ .

The chemical and screen analyses of the two batches are given in Table I. Batch A was used for varying the mixing time, feeding time, and water to monocal\* ratio. Batch B was used for varying the concentration of the original solution and part of it was screened into various fractions for varying the particle size of the feed introduced.

Superphosphate: The superphosphate used was made by mixing theoretical amounts of recycled filtrate, phosphate rock and phosphoric acid. Chemical and screen analyses are given in Table I.

Hydrolyzer: The hydrolyzer was made of 4-inch brass tubing, 10 inches long, with a steam jacket of 5-inch steel pipe. The agitator consisted of a brass rod to which two brass paddles ( $1/8 \times 2 \times 9$  inches) were welded, and was ro-

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\*The word "monocal" will be used at times to denote monocalcium phosphate monohydrate.

TABLE I

CHEMICAL AND SCREEN ANALYSES OF MONOCALCIUM  
PHOSPHATE AND SUPERPHOSPHATE

## Chemical Analyses

	% Total CaO	% Total P <sub>2</sub> O <sub>5</sub>	% W.S. P <sub>2</sub> O <sub>5</sub>	% C.I. P <sub>2</sub> O <sub>5</sub>	% H <sub>2</sub> O
Monocalcium Phosphate					
Batch A	20.9	53.9			
Batch B	21.4	54.8	53.5	0.05	
Superphosphate	19.55	52.1	49.9	0.15	5.50

## Screen Analyses

	Wt. per cent retained on		
Screen Mesh	Monocalcium Phosphate		Superphosphate
	Batch A	Batch B	
60	0.0	0.0	0.0
100	21.8	28.4	55.6
150	19.3	21.0	10.0
200	24.1	23.5	14.1
-200	54.8	27.1	19.5

tated at 14 r.p.m. Temperature readings were taken with a thermometer placed at the exit end. Steam passing into the jacket was adjusted by a pressure-regulating valve in the steam line. The apparatus is shown pictorially in Fig. 4.

Settling-Rate Apparatus: One-liter graduated cylinders were used for taking settling-rate data. The volume equivalent to a height of one centimeter was 27.4 cubic centimeters. The cylinders were placed in a galvanized sheet metal container, 7 x 20 x 20 inches, heated by means of three 1000-watt heating coils. One of the heating coils was connected to a bimetallic Cenco-DeKhotinsky temperature regulator to hold the temperature constant. Clamps fitted with rubber stoppers were used to hold the cylinders in place and a small stirrer was used to agitate the water. The water level was held constant by adding a fine stream of clean water from a 55-gallon barrel and allowing any excess water to drain through an overflow pipe. Readings were taken by placing a mirror, mounted on wire, next to the cylinder at an angle of 45 degrees with the horizontal. The apparatus is shown pictorially in Fig. 5.

Screen Analysis Equipment: A Tyler Ro-Tap sieve shaker, adapted for wet screen analysis, was used for screen analysis of the slurries. Water from the city line was added through two spray nozzles screwed in the cover plate and removed through a  $\frac{1}{4}$ -inch brass tube soldered to the bottom pan. Tyler



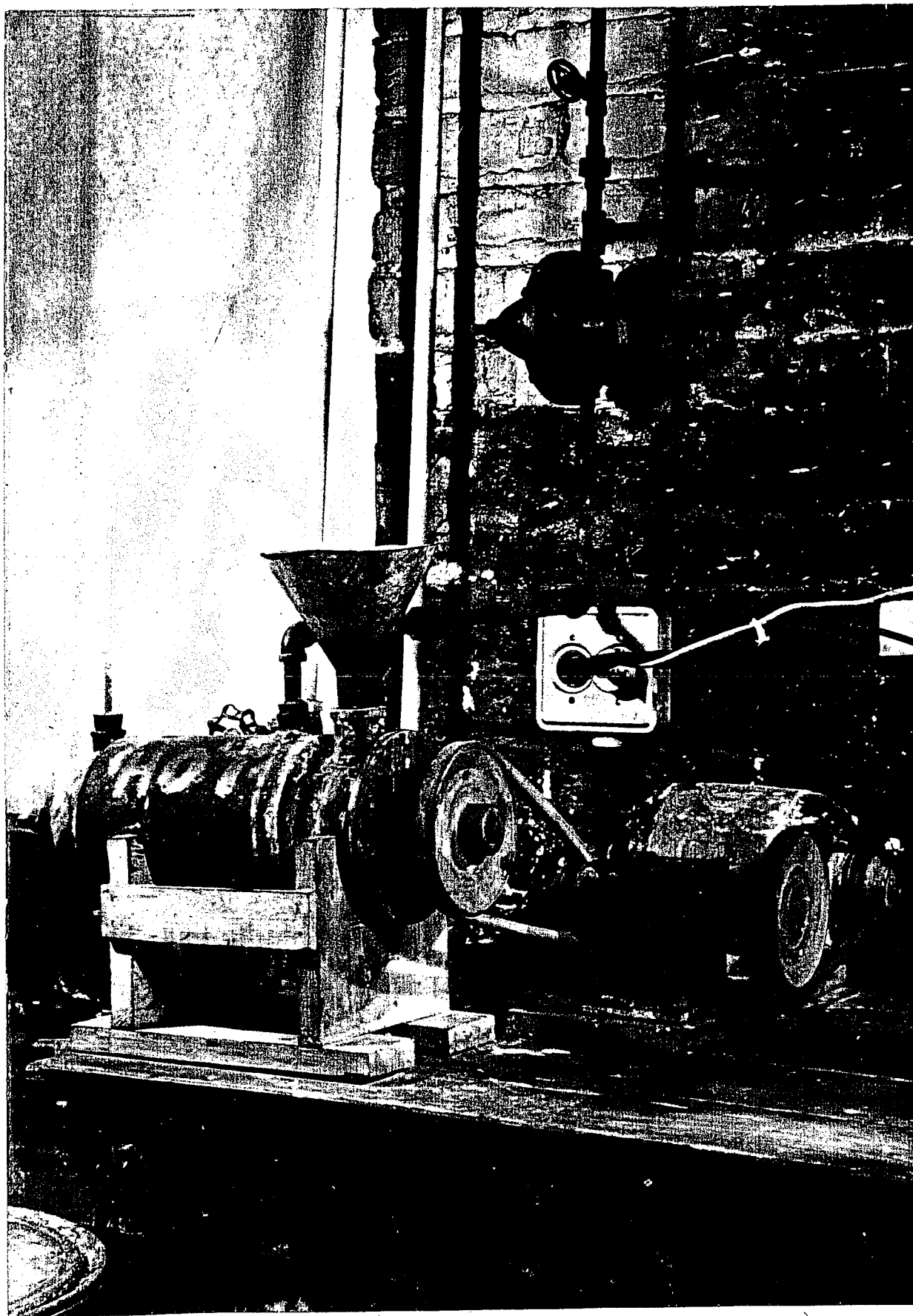


Fig. 4

Hydrolyzer

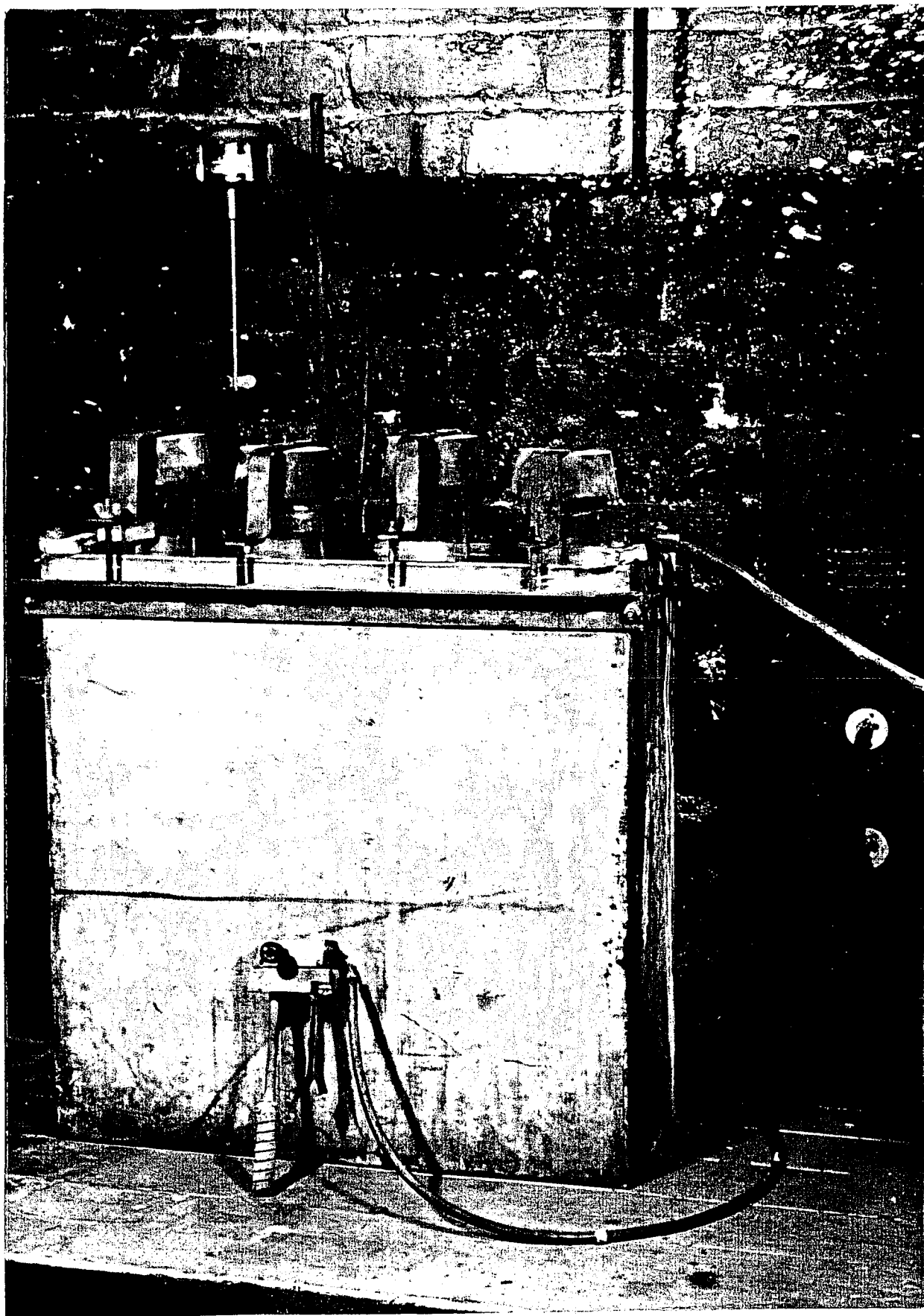


Fig.5

Settling-rate Apparatus

screens of the following sizes were used: 20, 35, 65, 100, 150, and 200 mesh.

Microscope: A Bausch and Lomb microscope with magnifying power of 537.5 diameters was used for microscopic examination of the particles obtained from the hydrolyzer. It was equipped with a filar micrometer for particle-size measurement.

Elutriator: Size separation of the -200 mesh particles from the hydrolyzer was carried out with a short-column, vertical, hydraulic elutriator<sup>4</sup>. The elutriation was performed in a Pyrex glass column, three inches high, and three and one-half inches inside diameter. The glass column was mounted in a brass holder, the bottom of which was in the shape of an inverted cone. A two-bladed, close-fitting stirrer, mounted on a hollow shaft, revolved inside the conical space. The top of the column was fitted with a trough to catch the water and particles which overflowed. At the upper end of the hollow shaft was mounted a dividing cone designed to give eight rates of water flow from the same source. Water from a constant-head cone was allowed to pass through a nozzle, strike the dividing cone, pass down through the hollow shaft and emerge at the bottom of the cone supporting the glass column. It then flowed upward through a celluloid straightening grid, into the glass column, and overflowed, carrying with it particles whose size was governed by the rate of water flow. The rate of water flow could be varied by catching different fractions

of the stream from the nozzle with the dividing cone, and also by changing the size of nozzle.

Viscosimeter: Viscosities of the solutions were determined with a Stormer viscosimeter, 1931 Model, Serial No. 1769. It was calibrated by determining the time required for the paddle to make 100 revolutions in aniline at different temperatures with the same weight as used in determining the time required to make 100 revolutions in the various solutions tested.

Pycnometer: Densities of the solutions were determined by using a 25 ml. pycnometer.

pH meter: A Beckman pH meter, Model M, Serial No. 4688, was used for obtaining pH readings of the various solutions.

## SETTLING-RATE STUDIES

### General Procedure

Runs were made using monocalcium phosphate for which the mixing time, feeding time, water to monocal ratio, size of feed, and concentration of  $P_2O_5$  and CaO in the original liquid were varied. Runs were also made using fortified superphosphate for which the mixing time was varied.

The desired amounts of liquid and solid were added to the hydrolyzer and mixed for the required time at a constant temperature of  $98^{\circ}$  C. The temperature was held constant during addition of the solid by allowing steam to by-pass the pressure regulator. Upon completion of mixing the entire mixture was drawn off in a liter cylinder, placed in the constant temperature settling-rate apparatus, and settling-rate data taken at  $98^{\circ}$  C. Samples of the supernatant liquid were taken upon completion of settling. A wet screen analysis of the slurry was then made with the Tyler Ro-Tap sieve shaker after washing the solid with 1000 ccs. of water by dilution and decantation at  $98^{\circ}$  C. to retard corrosion of the sieves. Runs were repeated until at least two of them gave practically identical settling-rate data.

### Definitions

Induction period: The initial period of slow settling during which the flocs are forming. The end of the induction period for each settling-rate curve is marked with

an arrow.

Point of compression: Height of slurry at the time the settling rate started to fall off rapidly divided by the original height of the slurry. Points on the settling-rate curves used for evaluating compression points are marked with arrows.

Apparent particle size: The size of settling particles as determined by substituting in the Stokes'-law equation. A sample of the method used for calculation is given in Appendix C. The values of  $u$  and  $p$  used for substitution in the equation were those determined for the supernatant liquid remaining on completion of settling, while the value of  $p'$  was taken from Perry's handbook<sup>9</sup> as that corresponding to pure dicalcium phosphate.  $U$  was taken as the settling velocity during the constant-rate period.

#### Effect of Varying Mixing Time

Object: The object of the first series of experiments was to compare the settling rates obtained when mixing mono-calcium phosphate and water for different periods of time.

Procedure: The mixing time was varied as follows: 2, 5, 10, 30, and 195 minutes. For all runs over two minutes the water was placed in the hydrolyzer, heated to 98° C., and the solid added as fast as possible. This required from 1 to 1½ minutes. The mixing time includes the time required for adding the solid with the exception of the two minute run, for

which the monocal was placed in the hydrolyzer and water at 98° C., added. For each run 750 grams of monocal and 750 grams of water were used.

Observations: When first starting the experimental runs considerable difficulty was encountered in obtaining reproducible results. This was found to be due to variations in the temperature during feeding. A variation of as little as 3 or 4 degrees affected the settling rates considerably. This was especially true if the temperature was allowed to go higher than 100° C., which resulted in a marked decrease in the rate. Allowing the temperature to fall below 96° C., appeared to increase the settling rate to a small extent. Runs were not made to determine specifically the effect of temperature on settling rates.

Results: Settling-rate curves plotted as height of slurry versus time for various mixing times are shown in Fig. 6. The settling rates during the more constant rate period, the average settling rates, the points of compression, and the apparent particle sizes are tabulated in Table II, page 46, (line numbers 1, 2, 3, 4, and 5). Negligible amounts of solid were retained on the sieves used in the wet screen analysis, (for sieve sizes, see Apparatus, page 27 ), so no attempt was made to dry and weigh the fractions. Separation of the -200 mesh slurry is described under Elutriator and Microscopic Studies.

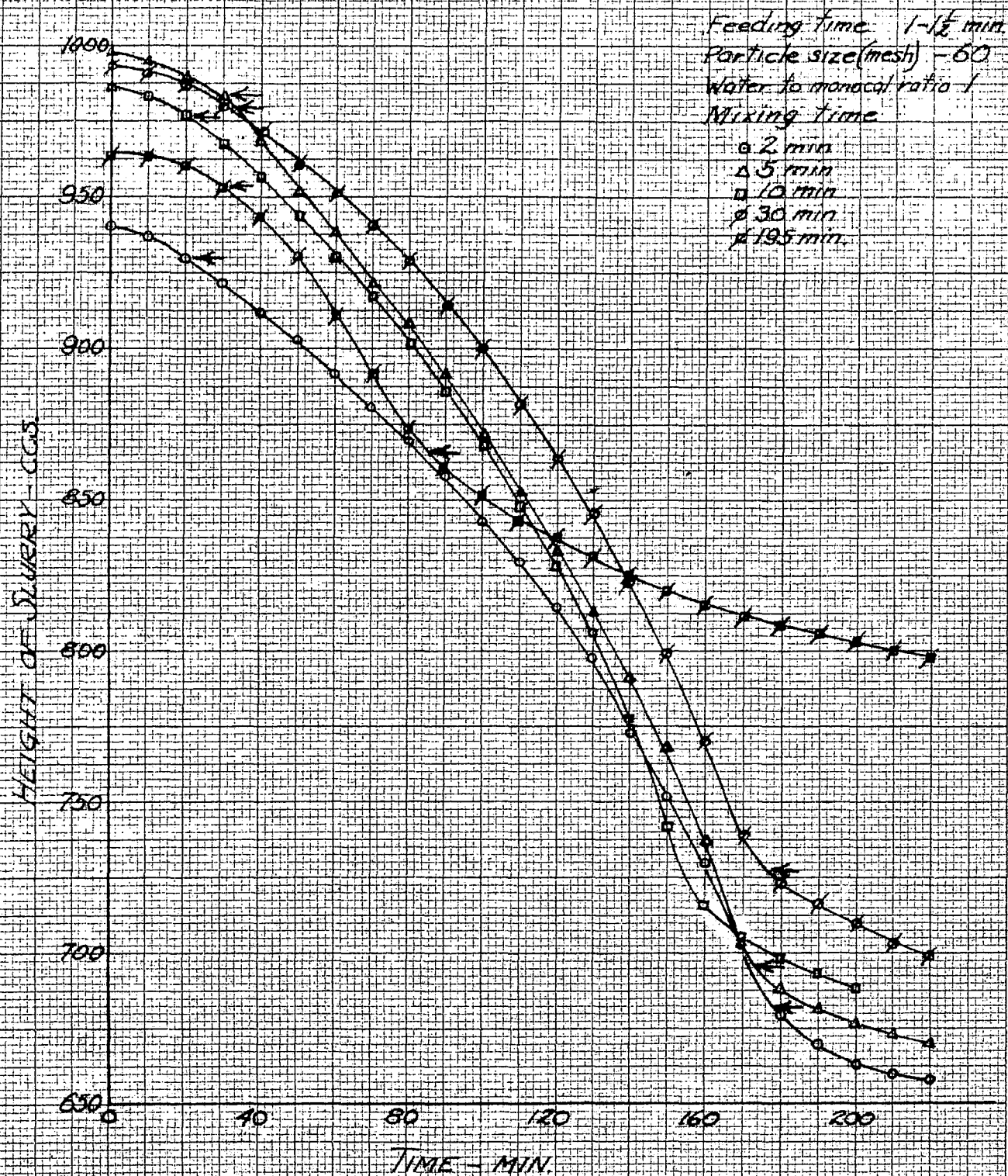


FIG. 6

SETTLING CURVES FOR VARIOUS MIXING TIMES WHEN  
 HYDROLYZING MONOCALCIUM PHOSPHATE



The settling-rate curves show that the material settled slowly at first and the settling rate gradually increased to a maximum value just before reaching the point of compression. Starting with the point representing the end of the induction period, until reaching the point of compression, settling velocities were determined. These velocities increased with a further increase in mixing time. Determinations of the average settling velocities, from the start of the settling until reaching the points of compression, show that the settling velocities decreased as the mixing time was increased beyond five minutes.

The apparent particle size was a maximum for a mixing time of ten minutes, decreasing with further increases in mixing time. The point of compression, was practically constant for all runs with mixing times of less than 30 minutes. However, for a mixing time of 195 minutes the point of compression was considerably higher, being 0.89 as compared to 0.70 for a five-minute mixing period.

#### Effect of Varying Feeding Time

Object: Because of the difficulty of obtaining reproducible results it was decided to add the monocal slowly with a vibratory feeder and mix for a period of 20 minutes. This method gave a more accurate control of temperature during feeding.

Procedure: The feeding time was varied as follows: 9, 30, and 87 minutes. The monocal was added to the hot water during the desired interval of time, mixed 20 minutes after completion of feeding, settling-rate data taken, and wet screen analyses made. For each run 750 grams of water and 750 grams of monocal were used.

Results: The settling-rate curves are plotted in Fig. 7, while settling velocities, compression points, and apparent particle sizes are tabulated in Table II (line numbers 6, 7 and 8). A feeding time variation of less than 30 minutes apparently had little effect since the 9 and 30 minute runs gave practically identical results. However, the curves showed an increase in the settling rate for a feeding time of 87 minutes. The point of compression was the same for all runs.

#### Effect of Varying Water to Monocal Ratio

Object: The amount of water used in the hydrolysis of monocalcium phosphate is an important factor since it must be evaporated from the final filtrate and also affects the degree of conversion. Therefore, runs were made to determine the effect of varying the water to monocal ratio on settling rates.

Procedure: The water to monocal ratio was varied as follows: 2, 1, 0.8, 0.65, and 0.5. For all runs with the exception of a ratio of two, 750 grams of monocal and the re-

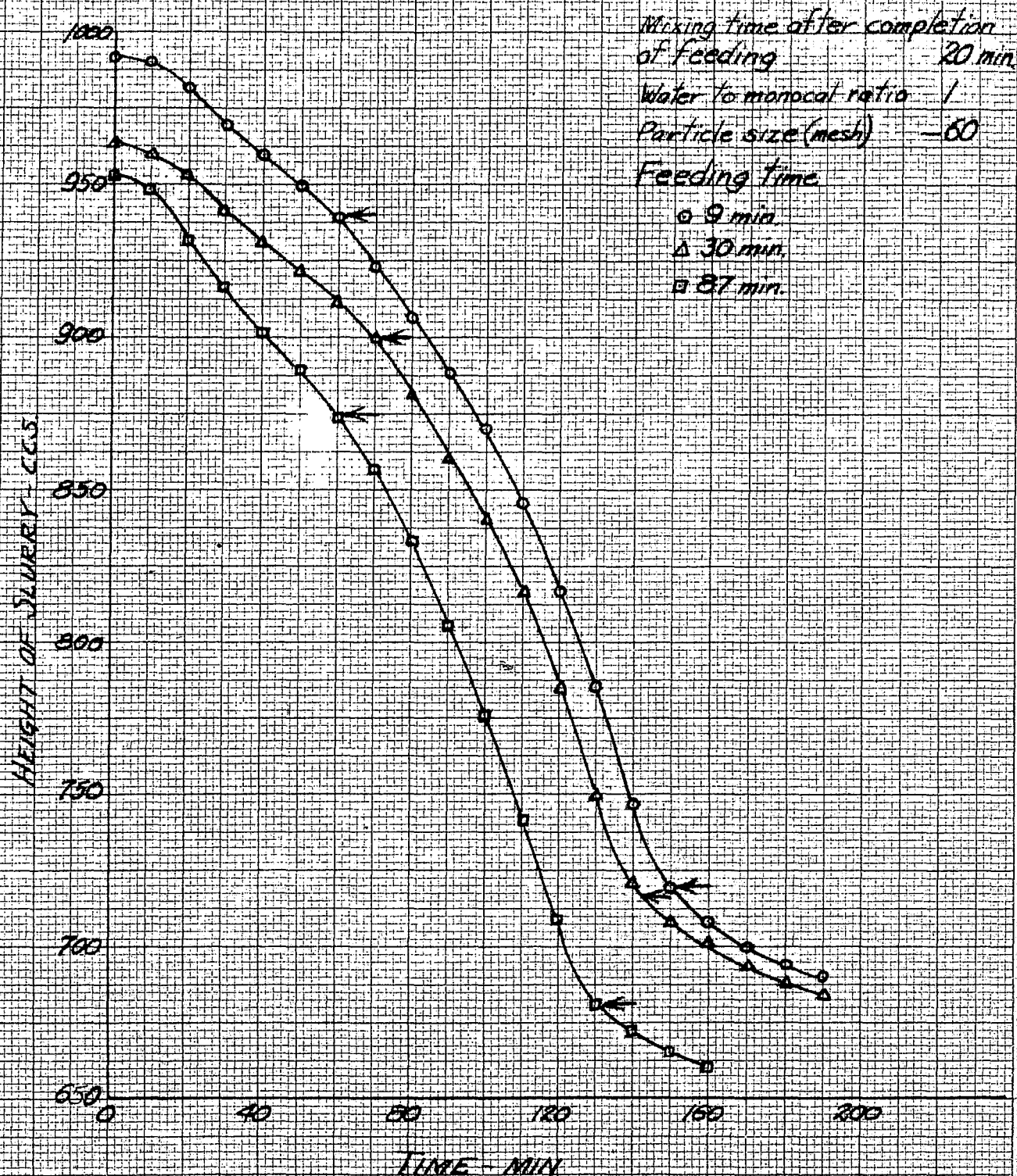


FIG 7  
 SETTLING CURVES FOR VARIOUS FEEDING TIMES WHEN  
 HYDROLYZING MONOCALCIUM PHOSPHATE

quired amount of water to give the desired ratio were used. For a ratio of two, 750 grams of water and 375 grams of monocal were used. The monocal was added over a period of ten minutes with a vibratory feeder and mixed ten minutes after addition was complete. Settling rates were then taken.

Results: The settling-rate curves for the first three ratios are plotted as height of slurry versus time in minutes in Fig. 8, while settling-rate results including the last two ratios are tabulated in Table II (line numbers 9, 10, 11, 12 and 13). As would be expected, settling rates decreased quite rapidly with a decrease in water to monocal ratio. Particularly noticeable was the longer induction period required as the ratio was decreased. For ratios of 0.65 and 0.5 the slurry settled at essentially constant rates of 0.06 and 0.0365 cm/hr., respectively, after passing the induction period. These settling rates may be considered analogous to those for higher ratios after entering the point of compression. Runs were attempted using a ratio of 0.4, but the slurry was so thick only part of it could be removed from the hydrolyzer so settling rates were not taken. It was intended to determine the ultimate height to which the slurry for a ratio of 0.65 would settle but after allowing it to settle for 225 hours it was necessary to use the equipment for other runs so the ultimate height was not found. However, judging by the rate of settling during the last 25 hours it was estimated the ultimate height would be 375 ccs.

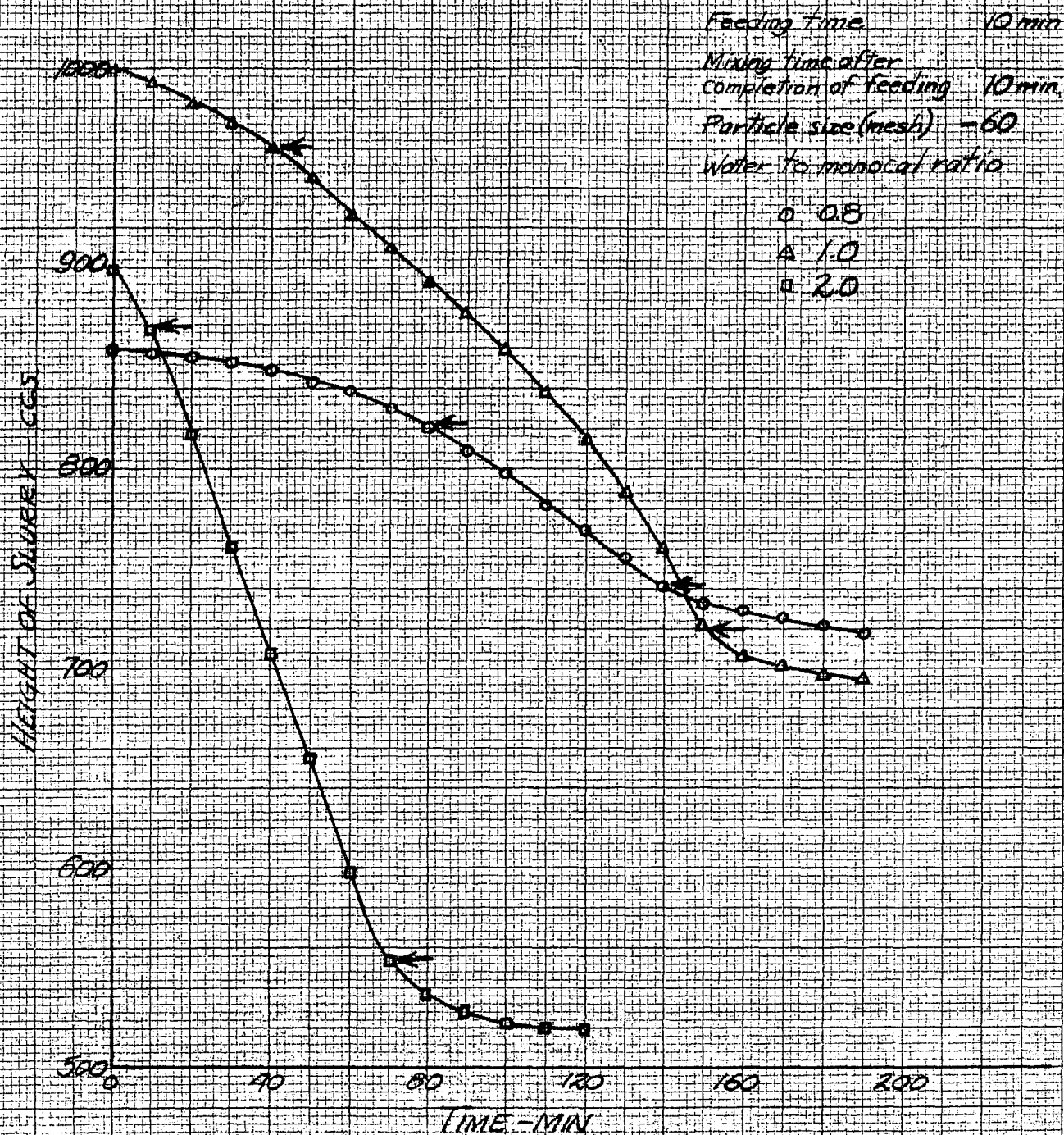


FIG 8

SETTLING CURVES FOR VARIOUS RATIOS WHEN  
 HYDROLYZING MONOCALCIUM PHOSPHATE

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The points of compression increased and the apparent particle sizes decreased with a decrease in water to monocal ratios from 2 to 0.8. For ratios of 0.65 and 0.5 there was no point of compression since the slurry was already in that stage.

#### Effect of Varying Particle Size of Feed

Object: In the pilot-plant operations for making dicalcium phosphate from monocalcium phosphate it was observed that the size of feed affected the particle size obtained. When using a feed size larger than 60 mesh a considerable number of large particles were formed which settled out immediately. When using feed smaller than 100 mesh these large particles were not obtained. Since variations in the particle size were apparently due to the size of feed particles introduced runs were made to determine their effect.

Procedure: The particle size of the feed was varied as follows: -200; -150, +200; -100, +150; -65, +100; and -35, +65 mesh. For each run 750 grams of monocal and 750 grams of water were used. The monocal was added as fast as possible (1-1½ minutes), mixed for ten minutes at 98° C., and settling rates taken.

Results: The settling-rate curves are plotted in Fig. 9, while settling velocities and points of compression are tabulated in Table II (line numbers 18, 19, 20, 21, and 22). The settling-rate curves show a decrease in the rate of settling



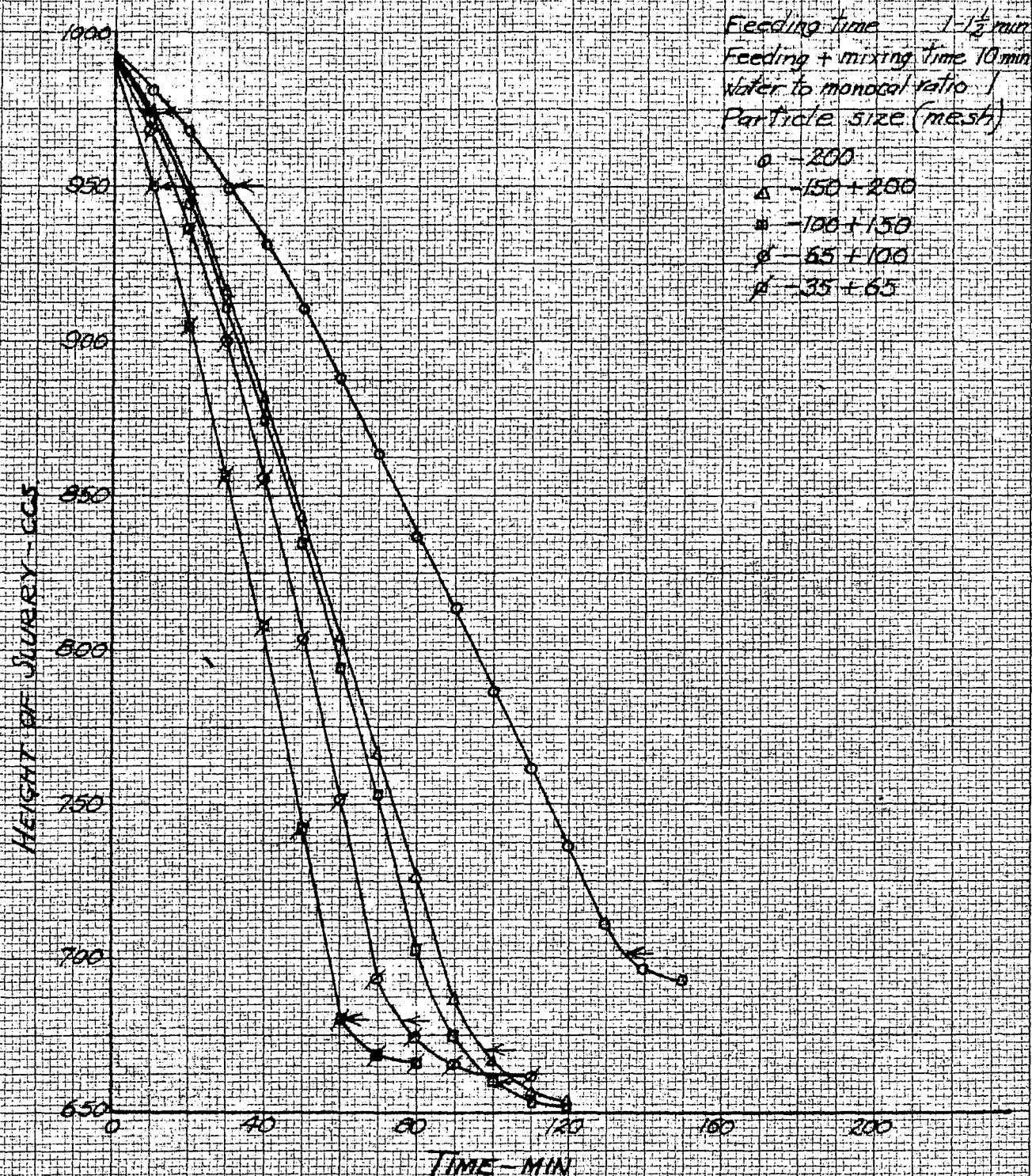


FIG 9

SETTLING CURVES FOR VARIOUS FEED SIZES WHEN  
 HYDROLYZING MONOCALCIUM PHOSPHATE

as the size of feed was decreased. The point of compression was essentially constant at 0.69 for all sizes with the exception of the -200 mesh settling-rate curve for which it was 0.71.

#### Effect of Varying Concentration of Original Solution

Object: In the proposed process for production of di-calcium phosphate from monocalcium phosphate the wash water from the filters is to be used to hydrolyze the monocal. This wash water will be a weak  $\text{CaO-P}_2\text{O}_5$  solution containing about one part of  $\text{CaO}$  to five of  $\text{P}_2\text{O}_5$ . It was thought that the concentration of this solution might affect the settling characteristics of the slurry obtained.

Procedure: Runs were made to determine the affect of the following percentage compositions on settling rates:  
 $\text{P}_2\text{O}_5 = 30, \text{CaO} = 6$ ;  $\text{P}_2\text{O}_5 = 20, \text{CaO} = 4$ ;  $\text{P}_2\text{O}_5 = 15, \text{CaO} = 3$ ;  
 $\text{P}_2\text{O}_5 = 10, \text{CaO} = 2$ . These solutions were made by mixing the desired amounts of phosphoric acid, lime and water. The amount of solution and monocal used for each run was calculated on the basis of the free water present to give a free water to monocal ratio of one.

The solution was placed in the hydrolyzer, heated to  $98^\circ \text{C.}$ , and the monocal added as fast as possible. Mixing was then continued for ten minutes at  $98^\circ \text{C.}$ , the slurry was removed, and settling-rate data taken.



Results: A plot of height of slurry versus time for the various concentrations is given in Fig. 10. Points of compression and settling velocities are tabulated in Table II (line numbers 14, 15, 16, and 17).

The curves in Fig. 10 show a marked decrease in settling rates as the concentration of the original solution is increased. The average rates varied from 4.70 cm./hr. for a concentration of 10 per cent  $P_2O_5$  and 2 per cent CaO to 0.365 cm./hr. for a concentration of 30 per cent  $P_2O_5$  and 6 per cent CaO. The points of compression were determined only for percentage compositions of  $P_2O_5 = 15$ , CaO = 3, and were 0.72 and 0.74 respectively. The slurries for other concentrations settled so slowly the point of compression was not found. Judging from the point of compression for concentrations of 0, 10, and 15 per cent  $P_2O_5$  the point of compression increases with an increase in concentration of the original liquid.

Feeding time 1-1/2 min  
 Mixing + feeding time 10 min  
 Particle size (mesh) -60  
 Concentrations

○ 10%  $F_2O_5$  2% CaO

△ 15%  $F_2O_5$  3% CaO

□ 20%  $F_2O_5$  4% CaO

◇ 30%  $F_2O_5$  6% CaO

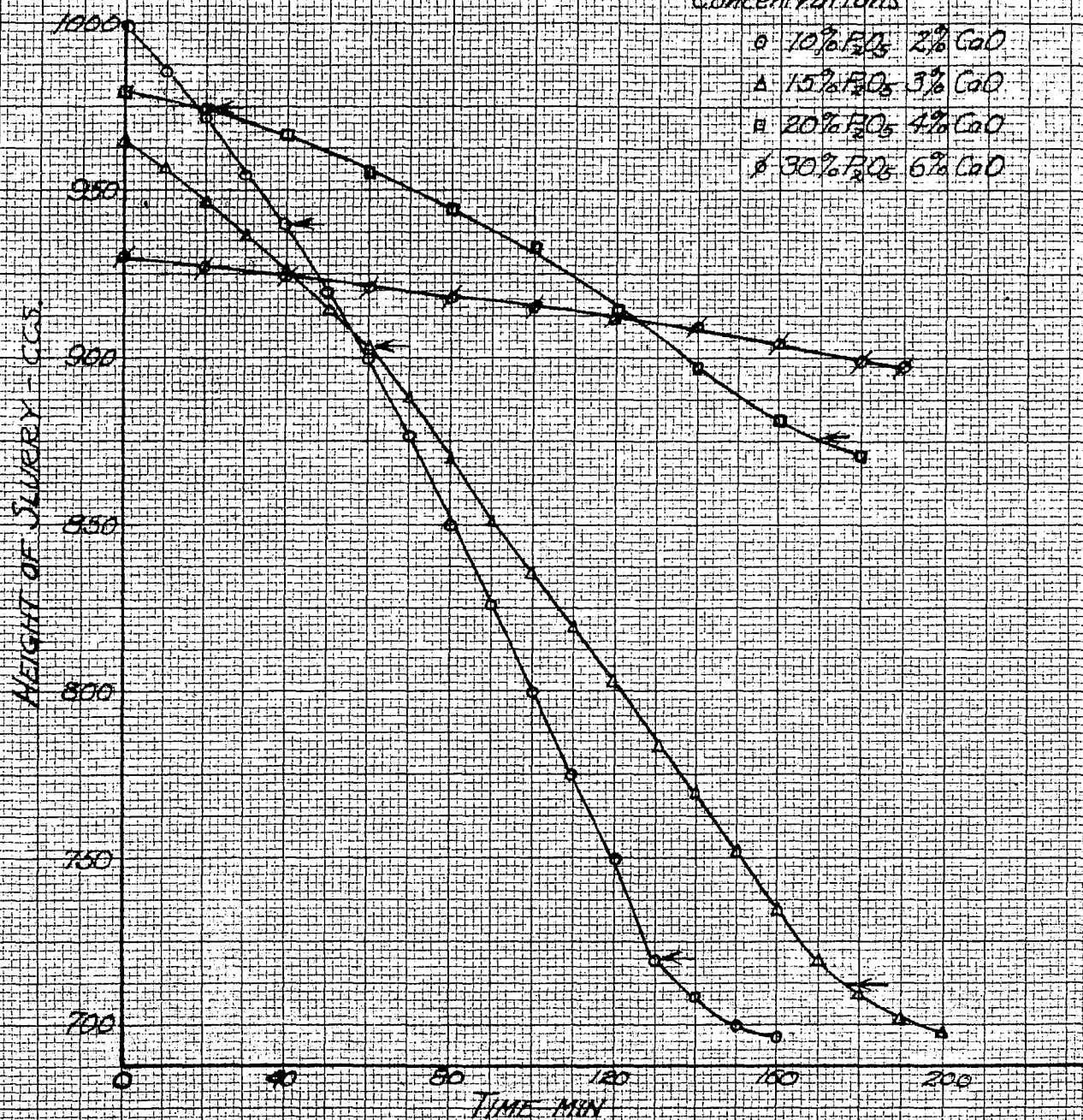


FIG 10  
 SETTLING CURVES FOR VARIOUS CONCENTRATIONS OF  
 ORIGINAL SOLUTION WHEN HYDROLYZING  
 MONOCALCIUM PHOSPHATE

### Effect of Varying Mixing Time Using Fortified Superphosphate

Object: Although triple superphosphate is essentially monocalcium phosphate there are some impurities present from the original rock<sup>7</sup>. These impurities are largely  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaCO}_3$ . The Fe, Al, and Ca impurities will be converted to phosphates during the hydrolysis reaction while the  $\text{SiO}_2$  will remain unchanged. Because of the impurities present and since the nature and preceding treatment of material are known to affect the degree of flocculation, different settling rates for dicalcium phosphate made from fortified superphosphate would be expected than for that made from practically pure monocalcium phosphate. Therefore, runs were made to determine the effect of varying mixing time when using fortified superphosphate.

Procedure: The mixing time was varied as follows: 5, 10, 30, and 195 minutes. The water was placed in the hydrolyzer, heated to  $98^\circ \text{C}$ ., and superphosphate added over a period of about one minute. Mixing was continued for the desired time. For each run 750 grams of water and 750 grams of superphosphate were used.

Results: A plot of height of slurry versus time is given in Fig. 11. Points of compression and settling velocities are tabulated in Table II (line numbers 23, 24, 25, and 26).

The settling rates and points of compression for the 10 and 30 minute runs were almost identical. For a mixing

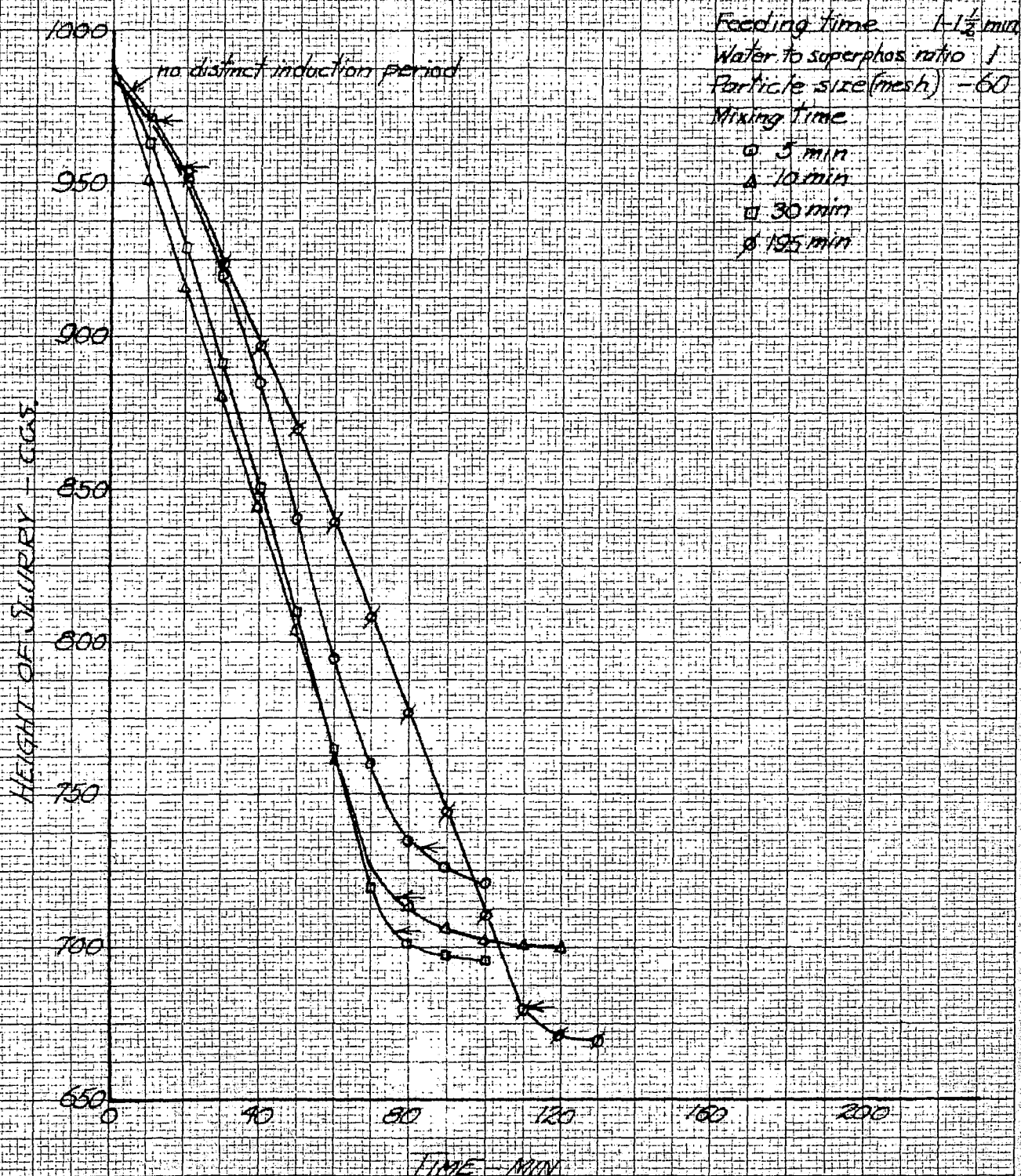


FIG 11

SETTLING CURVES FOR VARIOUS MIXING TIMES WHEN  
 HYDROLYZING FORTIFIED SUPERPHOSPHATE

time of 195 minutes the settling rate was less and the point of compression lower. For the five-minute mixing period consistent settling rates could not be obtained although mixing was carried out under as nearly identical conditions as possible. Since the viscosity, density, and pH of the liquid medium are known to affect the settling rates these values were determined for all the five minute runs. They were found to be the same for all cases within experimental error. The data tabulated and the curve of Fig. 11 for the five-minute mixing period represent an average of six runs.

# OF HYDROLYSIS

on ing	Settling Rate, <sup>c</sup> cm./hr.	Average <sup>d</sup> Settling Rate cm./hr.	Point of Compression ht./orig. ht.	Apparent Particle Diameter, (Mieron) (from Stokes' Law)
	3.40	3.16	0.72	—
	4.37	3.84	0.70	6.68
	4.15	3.67	0.72	7.53
	3.86	3.28	0.73	6.53
	3.44	2.55	0.89	6.10
	5.30	3.98	0.72	6.20
	5.40	3.80	0.74	—
	6.0	4.60	0.71	7.24
11.6	10.8	10.8	0.61	7.18
4.80	4.10	4.10	0.71	7.42
2.84	1.85	1.85	0.86	6.10
0.06	—	—	—	—
0.0365	—	—	—	—
5.30	4.70	4.70	0.72	—
3.58	3.20	3.20	0.74	—
1.46	—	—	—	—
0.365	—	—	—	—
11.5	11.2	11.2	0.69	—
9.4	9.0	9.0	0.69	—
7.8	7.4	7.4	0.68	—
7.7	7.3	7.3	0.68	—
5.4	4.9	4.9	0.71	—
7.6	6.6	6.6	0.74	—
8.3	8.2	8.2	0.72	—
8.3	8.2	8.2	0.71	—
6.8	6.1	6.1	0.69	—



SETTLING RATES OF PH

Line No. <sup>a</sup>	Solid Used	Mixing Conditions <sup>b</sup>		Weight Ratio H <sub>2</sub> O to Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	Particle Size Range of feed (Mesh)	Conc of H <sub>2</sub> L P <sub>2</sub> O <sub>5</sub> %
		Time of Addition Min.	Total Mixing Time Min.			
1	Monocal	0	2	1	-60	None
2	Batch A	1-1 $\frac{1}{2}$	5	1	-60	
3		1-1 $\frac{1}{2}$	10	1	-60	
4		1-1 $\frac{1}{2}$	30	1	-60	
5		1-1 $\frac{1}{2}$	195	1	-60	
6		9	29	1	-60	
7		30	50	1	-60	
8		87	107	1	-60	
9		10	20	2	-60	
10		10	20	1	-60	
11		10	20	0.8	-60	
12		10	20	0.65	-60	
13		10	20	0.5	-60	
14	Batch B	1-1 $\frac{1}{2}$	10	1	-60	10
15		1-1 $\frac{1}{2}$	10	1	-60	15
16		1-1 $\frac{1}{2}$	10	1	-60	20
17		1-1 $\frac{1}{2}$	10	1	-60	30
18		1-1 $\frac{1}{2}$	10	1	-35 + 65	None
19		1-1 $\frac{1}{2}$	10	1	-65 + 100	
20		1-1 $\frac{1}{2}$	10	1	-100 + 150	
21		1-1 $\frac{1}{2}$	10	1	-150 + 200	
22		1-1 $\frac{1}{2}$	10	1	-200	
23		1-1 $\frac{1}{2}$	5	1	-60	
24	Superphos	1-1 $\frac{1}{2}$	10	1	-60	
25		1-1 $\frac{1}{2}$	30	1	-60	
26		1-1 $\frac{1}{2}$	195	1	-60	

a One line may represent averages for several runs

b Includes time of addition

c Rate determined over interval from end of induction period to point of compression.

d Rate determined from start of settling until reaching point of compression

## ELUTRIATOR AND MICROSCOPIC STUDIES

### Introduction

Since practically all the slurry obtained from the various runs consisted of particles smaller than 200 mesh the use of screens would not give an accurate analysis of the particle size. It was thought that an accurate analysis could be obtained by using a hydraulic elutriator to separate the particles into definite size fractions and then measuring their sizes when placed under a microscope. This method was attempted but found to be rather unsatisfactory largely due to the very minute size of particles and to the failure to find a proper dispersion agent.

### Procedure

The particles which had passed through the -200 mesh sieve were stirred with a laboratory stirrer and during stirring a sample of approximately 50 grams (dry weight) was siphoned off. This slurry was placed in the elutriator and flow of water started. Attempts were made to find a dispersion agent so the overflow of water would carry individual particles rather than agglomerates, thereby effecting separation of the various particle sizes. Different concentrations of the following were tried: sodium silicate, calgon (sodium hexameta-phosphate), sodium hydroxide, and sodium oxalate. None of these showed dispersion to any extent and in some cases seemed



to favor agglomeration. Since an effective dispersion agent could not be found, elutriation was carried out without the use of a dispersion agent. The water velocity was started as slowly as could be obtained with the smallest nozzle. Samples of the overflow were taken at various times on a glass slide for observation under a microscope.

### Results

In operating the elutriator at a low water velocity the slurry would settle to about the middle of the glass column within five minutes, but after approximately ten hours operation particles would start coming over. This effect was observed for the solids obtained from experiments in which the mixing time, feeding time, and water to monocal ratio had been varied. Elutriation of the slurries from experiments with other mixing conditions were not attempted. In one case the elutriator was allowed to operate at the same low velocity for 50 hours. Essentially all the slurry was carried over during the period.

Examination of the particles under a microscope showed no appreciable difference in the individual particle size, but that they were present as agglomerates of various sizes. By use of a filar micrometer the individual particles were found to be approximately 2.5 microns in diameter.

## DISCUSSION

The type of settling rate curves obtained for the various runs correspond to those of flocculated particles as described in the literature survey. At the start of settling the particles were slowly forming aggregates, resulting in a slow rate of settling, and causing the induction period that was observed. As more and larger aggregates were formed the settling rate gradually increased to a constant value.

Since microscopic examination showed no appreciable difference in the particle size for runs in which the settling rates differed, the variations in settling rates must have been due to differences in the degree of flocculation. Small flocs would give a slower settling rate and higher compression point than large flocs because of the increased surface present for the adherence of liquid.

It may be seen that the settling rates decreased and points of compression increased for an increase in mixing time over five minutes when using monocalcium phosphate. This indicates that an increase in mixing time apparently tends to retard the formation of large flocs during settling or reduces the ultimate particle size. The results of the mixing time and feeding time studies show that the minimum overall time for feeding, mixing, and settling would be obtained by adding the feed as fast as possible and mixing only long enough for

equilibrium conditions to be obtained.

The increase in the settling rate, without any change in the point of compression, as the time required for adding the monocalcium phosphate was increased, indicates a possible increase in the ultimate particle size.

The results of the studies for variations in the water to monocal ratio show that the settling rates increased quite rapidly for an increase in the ratio. The small variation in apparent particle size for large variations in settling rates indicates the increase in settling rates for increased ratios is due to the decreased viscosity of the solution.

The results of the studies for variations in the concentration of  $P_2O_5$  and  $CaO$  in the original solution show that the settling rates increase for a decrease in the concentration of the original solution.

Since the solution used for hydrolysis would consist of wash water from the filter, an increase in the quantity of wash water would increase the settling rate because of both the higher water to monocal ratio and the lower concentration of  $P_2O_5$  and  $CaO$ . On the other hand, an increase in wash water rate would increase costs of concentrating the filtrate, which would likely be the governing factor.

Results of the runs for varying the particle size of feed show that a feed size at least large enough to be retained on a 35 mesh screen should be used to obtain good settling

rates. Too large a feed size would likely affect the degree of conversion for a given mixing time because the large particles would not have a chance to dissolve completely. It would probably be advisable to determine the conversion obtained for variations in the particle size of feed introduced.

In the mixing time studies using fortified superphosphate, a slower settling rate and lower compression point was obtained when mixing for 195 minutes than when mixing for 30 minutes. This result is not in accordance with the previous statement that smaller particle or floc sizes would result in slower settling rates and higher compression points. The lower compression point must have been due to some type of change in the relationship between individual particle size and floc size.

The composition of feed appeared to have an affect on the settling rate. On one occasion a run was made with monocalcium phosphate which had an excess of lime present. The resulting slurry reached the point of compression in ten minutes, representing a settling velocity of 48.3 cm./hr. This rate was 3.6 times that for the corresponding mixing conditions when monocal without an excess of lime was used. Further studies of this effect are recommended.

In the elutriator studies, separation of all the particles from the original sample with a single water velocity indicated that the flocs were made up of very small individual

particles. However, the water velocity for which all the particles were carried over was only the lowest obtainable with the nozzles used. It is probable that if a lower velocity could have been used some separation may have been obtained.

The slow settling rates obtained for the various mixing conditions indicate that a larger particle size of the dicalcium phosphate would be desirable. The settling rates also indicate that the use of countercurrent thickeners would not be feasible for washing the solids unless ratios of water to monocal of greater than unity could be used.

The apparent particle sizes as determined by Stokes'-law equation represent an approximation of the average size of flocs present during settling. The fact that the apparent particle sizes of the order of 6 or 7 microns were indicated, while the ultimate particle size was approximated to be 2.5 microns, is further evidence indicating the presence of flocs. An accurate determination of the apparent particle size could not be expected by use of this equation because of the loose structure of the flocs and the hindered settling which took place.

## CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were reached:

(1.) Variations in mixing time, feeding time, and water to monocalcium phosphate ratio had no effect on the ultimate particle size obtained as observed in a microscope. The ultimate particle size was approximated to be 2.5 microns.

(2.) Settling rates were affected by varying mixing conditions due to differences in the degree of flocculation. The following is an account of variations in settling rates and points of compression when using monocalcium phosphate:

(a.) When the solid was added rapidly to the hot liquid in the hydrolyzer, settling rates decreased and the points of compression increased with an increase in mixing time beyond five minutes.

(b.) When the solid was added slowly, the point of compression was constant for variations in feeding time. Settling rates for feeding times of 9 and 30 minutes were practically the same, but then increased with a further increase in feeding time to 37 minutes.

(c.) Settling rates decreased and points of compression increased with a decrease in the water to monocalcium phosphate ratio.

(d.) For feed sizes larger than 200 mesh, points of compression were constant, while the point of compression for a feed size smaller than 200 mesh was higher.

(e.) Settling rates decreased and points of compression increased with an increase in concentration of  $P_2O_5$  and  $CaO$  in the original solution.

(3.) When using fortified superphosphate the settling rates were practically constant for mixing times less than 30 minutes and decreased with an increase in mixing time beyond 30 minutes. Points of compression decreased with an increase in mixing time.

It is recommended that:

(1.) The effect of temperature during mixing on settling rates be determined.

(2.) Further settling-rate studies be made using fortified superphosphate.

(3.) Attempts be made to find a proper dispersion agent to disperse the dicalcium phosphate particles so an

accurate analysis of their size distribution can be made with the hydraulic elutriator.

(4.) Attempts be made to increase the particle size of dicalcium phosphate obtained to give faster settling rates and easier filtering properties. The particle size might possibly be increased by utilization of the inverted solubility curve, or by the use of a small excess of lime in the feed.

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## APPENDIXES

Appendix A-----Average Settling-rate  
Data Using Monocalcium  
Phosphate

Appendix B-----Average Settling-rate  
Data for Various Mix-  
ing Times when Using  
Superphosphate

Appendix C-----Sample Calculations of  
Apparent Particle Size

# PHOSPHATE

5	Water to monocal ratio			Size of feed (mesh)		Size of feed (mesh)		
	2.0	1.0	0.8	-200	-150,+200	-100,+150	-65,+100	
	2	3	6	3	2	2	2	4
900	1000	860	995	992	990	990	988	
870	993	858	983	975	973	970	950	
818	982	856	968	949	945	937	905	
760	973	854	950	917	912	900	857	
708	960	849	932	882	875	856	808	
656	945	843	911	843	835	804	742	
598	927	839	888	805	795	752	679	
554	910	831	864	767	754	694	669	
536	894	821	837	727	703	675	667	
529	878	809	814	687	675	666		
522	860	798	787	667	660	663		
521	839	783	762	657	653	662		
520	815	770	737	654	652			
	788	756	712					
	760	742	697					
	722	733	693					
	708	729						
	702	726						
	698	722						
	696	718						

AVERAGE SETTLING

(S)

Mixing conditions	Mixing time, min.					Feeding time, min.			Concen 10% P <sub>2</sub> O <sub>5</sub> 2% CaO
	2	5	10	30	195	9	30	87	
No. of runs used for averaging data	2	4	6	2	2	2	2	2	2
Time of settling, min.	←								
0	940	998	986	993	965	992	964	953	1000
10	937	995	983	991	961	990	960	948	985
20	930	990	977	987	958	982	953	932	972
30	922	983	968	980	953	970	942	917	955
40	912	968	957	971	944	960	932	902	940
50	903	952	944	961	931	950	922	890	920
60	892	938	930	951	911	939	912	874	900
70	881	922	918	941	892	923	900	857	877
80	870	908	902	929	873	907	882	833	850
90	858	892	887	914	862	888	861	806	826
100	843	872	868	900	852	869	840	776	800
110	830	853	848	882	843	846	817	742	775
120	815	833	828	864	838	817	785	709	750
130	798	813	807	846	832	785	750	681	725
140	773	792	777	823	825	747	722	673	710
150	752	768	742	799	820	720	708	666	700
160	730	737	715	770	816	708	702	661	697
170	700	701	705	738	812	700	694		
180	680	688	698	723	809	694	688		
190	670	682	693	717	806	690	684		
200	663	677	688	710	803				
210	660	673	683	703	800				
220	657	670		699	798				
230	653	667		695	796				
240									

\* Height of Slurry in Liter Cylinder

## APPENDIX B

AVERAGE SETTLING RATE DATA FOR VARIOUS  
MIXING TIMES USING SUPERPHOSPHATE

Mixing Time, Min.	5	10	30	195
No. of runs used to aver- age data	6	4	2	2
Time of settling, min.	Height of slurry*			
0	984	990	985	987
10	970	952	963	971
20	950	916	929	959
30	920	880	892	923
40	885	845	850	897
50	840	805	810	870
60	795	762	765	839
70	760	727	719	808
80	735	713	702	777
90	726	707	698	744
100	721	703	696	710
110		701		680
120		700		672
130				670

\*Height of slurry in liter cylinder for which 27.4 ccs. are equivalent to a height of one cm.

## APPENDIX C

SAMPLE CALCULATIONS OF APPARENT PARTICLE SIZE

Substitution in Stokes'-law equation for five-minute mixing time.

For Stokes'-law equation (see Page 18) :

$$U = \frac{54.5 D^2 (p' - p)}{u}$$

$$\text{Changing } U \text{ to cm./sec.} = \frac{4.37}{3600} = 0.001214$$

Substituting in equation

$$\frac{0.001214 = 54.5 D^2 (2.306 - 1.215)}{0.0219}$$

$$D^2 = 0.000000447$$

$$D = 0.000668 \text{ cm.} = 6.68 \text{ microns}$$