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EFFECT OF COAGULATION OF CLAY
ON FILTER CAKE RESISTANCE

by

Perialwar Regunathan

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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In Charge of Major Work

Head of Major Department

Dean of Graduate College

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LIST OF ABBREVIATIONS

Abbreviation	Meaning
conc.	concentration
expts.	experiments
F	dimensions of force
ft	feet
gal	gallons
g	grams
gpm	gallons per minute
gsfm	gallons per square feet per minute
in.	inches
L	dimension of length
ℓ	liters
lb	pounds
M	dimension of mass
mg	milligrams
mg/l	milligrams per liter
min	minutes
ml	milliliters
mv	millivolts
no.	number
ppm	parts per million parts by weight
sec	seconds
sq	square
T	dimension of time
vs.	versus
°C	degrees centigrade
°F	degrees Fahrenheit

INTRODUCTION

Surface waters often contain different types of impurities in suspension such as clay minerals, bacteria, algae and organic matter. When such waters are to be used for human consumption or industrial needs, it is necessary to remove these impurities to attain a degree of purity adequate for the intended usage. Common methods used for the removal of these solids are settling and filtration. There are two types of filtration: non-cake forming filtration and cake forming filtration. An example of the first type is rapid sand filtration. Slow sand filtration, precoat carbon filtration, and diatomite filtration belong to the second type.

Diatomite filtration consists of filtering water through a rigid, permeable septum over which a thin layer of porous, light material known as diatomite has been formed. Diatomite is composed of silicious remains of dead, decayed microscopic plants called diatoms. This diatomite is prepared by drying, grinding, and calcining the quarried diatomaceous earth. Several grades of diatomite of varying particle size and hydraulic characteristics are available.

The filtering cycle used in diatomite filtration is made up of three main parts: precoating, filtering, and backwashing. The precoating operation consists of placing a layer of clean diatomite on the septums. During the filtering operation small amounts of diatomite are added continuously to the raw water, and the suspended solids in the water are filtered together with this diatomite to form a porous, incompressible cake. The diatomite added during the filtration is known as body feed; the cake formed is known as the body feed layer, or filter cake. When a predetermined head loss across the filter is reached, the cake is removed from the septum and wasted. This operation is known as backwashing. The time of actual filtration between precoat and backwash is known as a filter run.

In diatomite filtration of municipal water supplies, the common practice is to filter the raw water without any pretreatment. Acceptable finished water quality can be obtained by selecting a suitable grade of diatomite and a body feed concentration. However, such practice can result in very short filter runs or very high diatomite usage depending upon the type and amount of colloids present in the raw water. This condition may be eliminated if the colloidal suspension is destabilized before filtration. Such pretreatment is used in rapid sand filtration plants; it consists of rapidly mixing a coagulant such as an aluminum or ferric salt with the raw water followed by slow mixing and allowing the agglomerated particles to settle out. This entire process of pretreatment is known to sanitary engineers as coagulation.

In treatment plants where coagulation is practiced, the optimum dose of coagulant is commonly determined by performing a jar test on the raw water. The apparatus used for this test consists of a six-place multiple stirrer and six jars. Equal amounts of raw water are poured in each jar, then different amounts of coagulant are added to each one. First the contents are rapidly mixed, then slowly mixed, and finally allowed to settle. Each step is done for an arbitrarily selected time. The lowest dose of coagulant causing a relatively high removal of colloids by settling is taken as the optimum dose.

A few water treatment plants have started using electrophoretic measurements as a means of determining the optimum coagulant dosage. In this procedure, the electrophoretic velocity of the colloids present in raw water is first measured. Then various amounts of a coagulant are added to different samples of the raw water and the change in velocity of the particles is observed. The electrostatic potential at the shear plane of the double layer, known as zeta potential, is calculated using this velocity and known expressions. The coagulant dose needed to reduce the potential to a preselected level is taken as the required alum dosage.

Besides these methods, colloid chemists have been using several different parameters to determine the coagulant dose required to destabilize a colloidal suspension. Examples of such parameters include refiltration time, scattering intensity, and subsidence rate. The refiltration time measurements consist of filtering a suspension through a filter paper and refiltering the filtrate through the cake formed during the first step. Time required to refilter a specific amount of filtrate is known as the refiltration time. If the first step of cake-forming filtration is timed for filtering a specific volume of suspension, it can be called filtration time.

PURPOSE AND SCOPE OF THIS RESEARCH

In rapid sand filtration plants, destabilization of the colloidal system found in surface waters has greatly aided in the removal of the colloids by settling and also has improved the filtrability of the settled water. However, improvements in filtrability by destabilization have not been widely employed in diatomite filtration plants. Use of coagulants such as aluminum or ferric salts may greatly reduce the probability of short filter runs or of increased body feed usage. A clay-aluminum sulphate system has been chosen to demonstrate the favorable effect of aluminum sulphate on cake-forming filtration. Aluminum sulphate is commonly referred to as alum by sanitary engineers.

Destabilization of colloids may occur through several mechanisms. La Mer (14) recently divided possible mechanisms into two categories: first, where the destabilization is achieved by reducing the repulsive potential of the colloids by the suppression of the electric double layer surrounding the colloids; second, where it is achieved by binding the particles together into three-dimensional networks by chemical bridges. The two categories have been named, respectively, coagulation and flocculation. This distinct division is evident in many cases. Action of indifferent electrolytes on lyophobic colloids can be termed as coagulation according to the above definition. Aggregation of electrically charged colloids by a similarly charged polyelectrolyte can be described as flocculation. The effect of polyvalent hydrolyzing metal salts such as aluminum salts on a colloidal suspension is, however, not completely clear. Again a clay-aluminum sulphate system has been chosen to study the various factors involved in the destabilization.

The specific objectives of this work are:

1. To demonstrate the effect of adding aluminum sulphate to a clay suspension on the hydraulic resistance of a diatomite filter cake. A pilot diatomite filter plant was used in this part of the study.

2. To study the relationship between these parameters of destabilization: refiltration time, electrophoretic mobility, jar test, and a seldom-used parameter known as filtration time.

3. To observe the effect of factors such as concentration of aluminum sulphate, clay concentration, pH, and mixing speed on the stability of a clay suspension using the above-mentioned parameters.

4. To gain further insight into the mechanism of destabilization caused by aluminum salts from the information gathered.

Results of this study indicate that the aggregation of clay particles can occur either by coagulation or flocculation or by both depending upon the clay concentration, alum concentration, and pH. Since the distinction cannot always be made, the term coagulation has been used for all cases where aggregation of particles was indicated by any of the parameters of destabilization.

LITERATURE REVIEW

Diatomite Filtration

U. S. Army Engineers developed a diatomite water filter unit for the use of field troops during World War II. After the war different types of the diatomite filters were applied to municipal use. Due to inadequate knowledge of this type of filtration, some of the early filters proved to be failures. However, as a result of research which has developed a theory of filtration, established design criteria and operational procedures, diatomite filters have now become more successful and acceptable.

Phillips (29) gathered together, analyzed, and summarized the results of all the important research which had been done on diatomite filtration of water up to 1957. His thesis stands as a concise report of the work done to that time. Since then, the bulk of the research on diatomite filtration has been carried out at Iowa State University.

A theory of diatomite filtration was presented as a result of this extensive research (2). An equation for head loss increase across a diatomite filter for constant rate filtration was developed based on Darcy's law.

$$H = K_3QW_1 + K_4C_DQ^2t \times 8.33 \times 10^{-6} \qquad (1)$$

where H = total head loss across the filter cake in feet of water

K_3, K_4 = constants for a given filter media including the coefficient of permeability of filter cake and the bulk density of material in the precoat layer and body feed layer respectively in $\frac{(\text{min})\ (\text{ft})^5}{(\text{lb}) \cdot (\text{gal})}$

Q = filtration rate in gsfm

W_1 = weight of precoat diatomite in $\frac{\text{lb}}{\text{ft}^2}$

C_D = concentration of body feed in ppm

t = time of filtration in min

Several studies were conducted to determine the effect of different types and amounts of solids in raw water on the permeability of diatomite filter cakes, as measured by the filter cake resistance, K_4. It was discovered in one study that the cake resistance values (K_4) obtained with raw water containing flocculent solids from trivalent iron salts and aluminum sulphate were approximately ten times as great as those obtained when the suspended solids were derived from bivalent iron salts (9). Microscopic examination of the solids revealed that the particle size of the floc from the trivalent iron was considerably larger than that from the bivalent salts. In another study the finer grades of diatomite gave higher K_4 values in the filtration of iron floc derived from ferrous sulphate than the coarser grades (8). However, the percent change in K_4 values for different grades of diatomite was not as great as the corresponding percent change in precoat resistance values (K_3).

Water containing different clay minerals, ball clay and Wyoming bentonite, was filtered through diatomite filters using two different grades of diatomites as well (31). Cake resistance values obtained with a Wyoming bentonite suspension were about ten times as great as those obtained with a ball clay suspension when the ratio of suspended solids concentration to body feed concentration was the same. Ball clay, which contains mostly kaolinite, was found to have a higher proportion of larger particles than Wyoming bentonite which contains mostly sodium montmorillonite. The swelling property of montmorillonite was suspected to have played an important role in increasing the filter cake resistance. All three studies emphasized the effect of the suspended solids characteristics on the permeability or diatomite filter cakes.

Dillingham et al. (7) have reported the development of a new equation for head loss increase across a diatomite filter during constant rate filtration. Most of the drawbacks of the previous equation were eliminated in the development of the new equation. During the theoretical development of the equation, the effect of factors such as initial dilution time, increasing area of cylindrical filter cakes during filtration and viscosity of water were considered and were included in the equation. The equation can be used with either English or metric units. The equation for cylindrical filter septum is shown below:

$$H = q\nu\xi \frac{w}{g} + \frac{R_s\sigma}{\phi} \ell n \left(1 + \frac{R_s\phi x}{R_o{}^2} \right) \qquad (2)$$

where:

$$\sigma = q^2 \nu \beta \frac{C_D}{g}$$

$$\phi = \frac{2q\gamma_w C_D (10)^{-6}}{\gamma_p}$$

$$x = t - \frac{(1 - e^{\delta t})}{\delta}$$

$$\delta = \frac{Q}{V_f}$$

$$R_o = R_s + L_p$$

$L_p = \dfrac{w}{\gamma_p}$

H = head loss across the cake in height of water column (L)

q = flow rate per unit septum area (LT^{-1})

ν = kinematic viscosity (L^2T^{-1})

ξ = filter aid resistance index (LF^{-1})

w = precoat weight per unit area (FL^{-2})

g = gravity constant (LT^{-2})

R_s = outer radius of septum (L)

β = filter cake resistance index (L^{-2})

C_D = body feed concentration, ppm by weight (dimensionless ratio)

γ_w = density of water (FL^{-3})

γ_p = density of precoat diatomite (FL^{-3})

t = time (T)

δ = dilution rate (T^{-1})

Q = flow rate (L^3T^{-1})

V_f = volume of filter housing (L^3)

$R_o = R_s + L_p$

L_p = thickness of precoat in the direction of flow (L)

Even though the equation is complicated, its use has been greatly simplified by the use of a computer program specifically written for computing β-indices from data collected during a filtration run.

Coagulation

Introduction

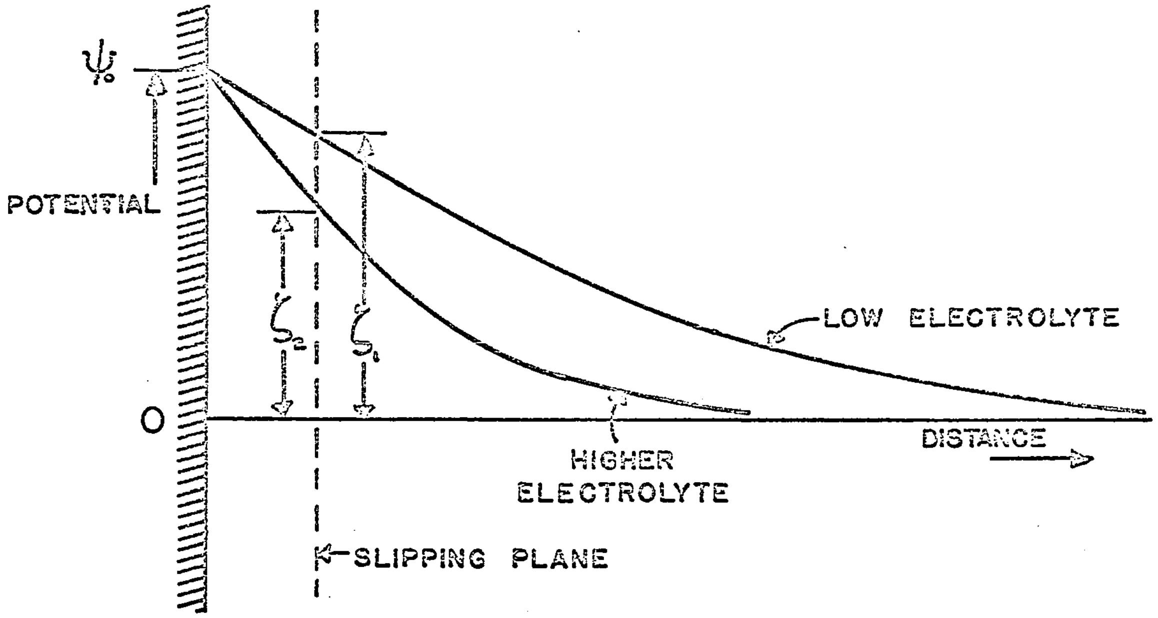
The stability of a lyophobic colloidal suspension can be attributed to the charge carried by the colloids, or more generally to the electrical double layer surrounding the particles. The clay colloids are known to be lyophobic colloids. This view of classical colloid chemistry that the high charge of colloids results in the stability of a suspension is still generally accepted (12). However, whether reduction of charge is essential to destabilization of a colloidal system is being questioned by recent researchers. The possibility of destabilization without charge reduction, such as by chemical bridging action between the colloids by long chain polymers is being discussed.

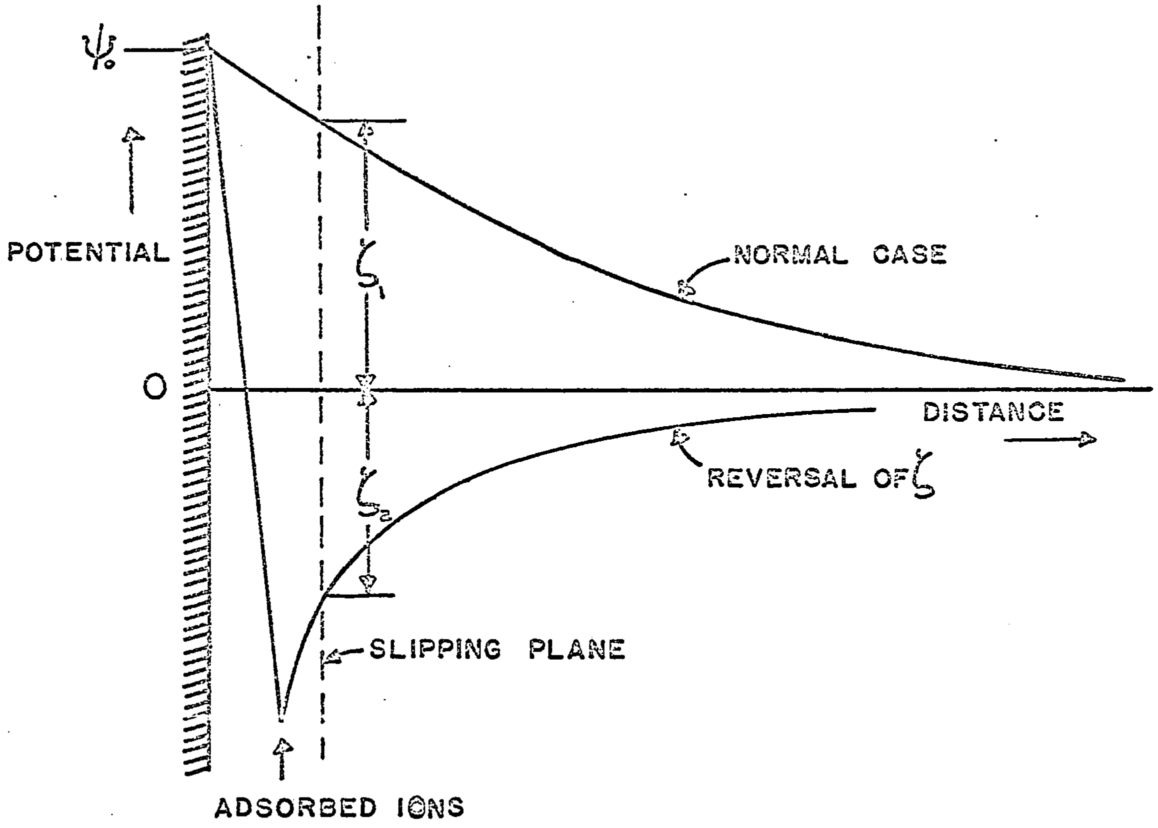
A number of workers have conducted research to shed light on the possible mechanisms of destabilization of a suspension. It is the purpose of this study to evaluate the coagulation of clay with aluminum sulphate. Therefore, a brief review of literature most pertinent to the destabilization mechanisms will be presented here.

Classical colloid chemistry has presented the effect of indifferent electrolytes on the electrical double layer surrounding the particle. The effect of indifferent electrolytes when added to a colloidal system is to reduce the thickness of the double layer; thus they change the zeta potential to a lower value even though the surface potential (Ψ_o) remains unchanged. This effect is shown in Figure 1. When the added electrolyte is made up of potential determining ions of the system (e.g., silver halide in a system of silver halide sol), the effect would be to change Ψ_o as

Figure 1. Distribution of potential in the double layer and the effect of an indifferent electrolyte (12)

Figure 2. Reversal of zeta potential by adsorption (12)


ψ_0
POTENTIAL
ζ_2
ζ_1
LOW ELECTROLYTE
O
HIGHER ELECTROLYTE
DISTANCE
SLIPPING PLANE


ψ_0
POTENTIAL
ζ_1
NORMAL CASE
O
DISTANCE
ζ_2
REVERSAL OF ζ
SLIPPING PLANE
ADSORBED IONS

well as to compress the double layer.

The reversal of charge by multivalent ions such as aluminum and thorium has been explained by a complicated variation of the potential in the double layer (Figure 2). This variation has been accepted as the effect of strong adsorbability of the ions or of the products of their hydrolysis. The adsorbed layer must possess a larger charge than is present on the wall for the zeta potential in the slipping plane to be reversed in charge.

Composition of the hydrolysis species of the coagulant

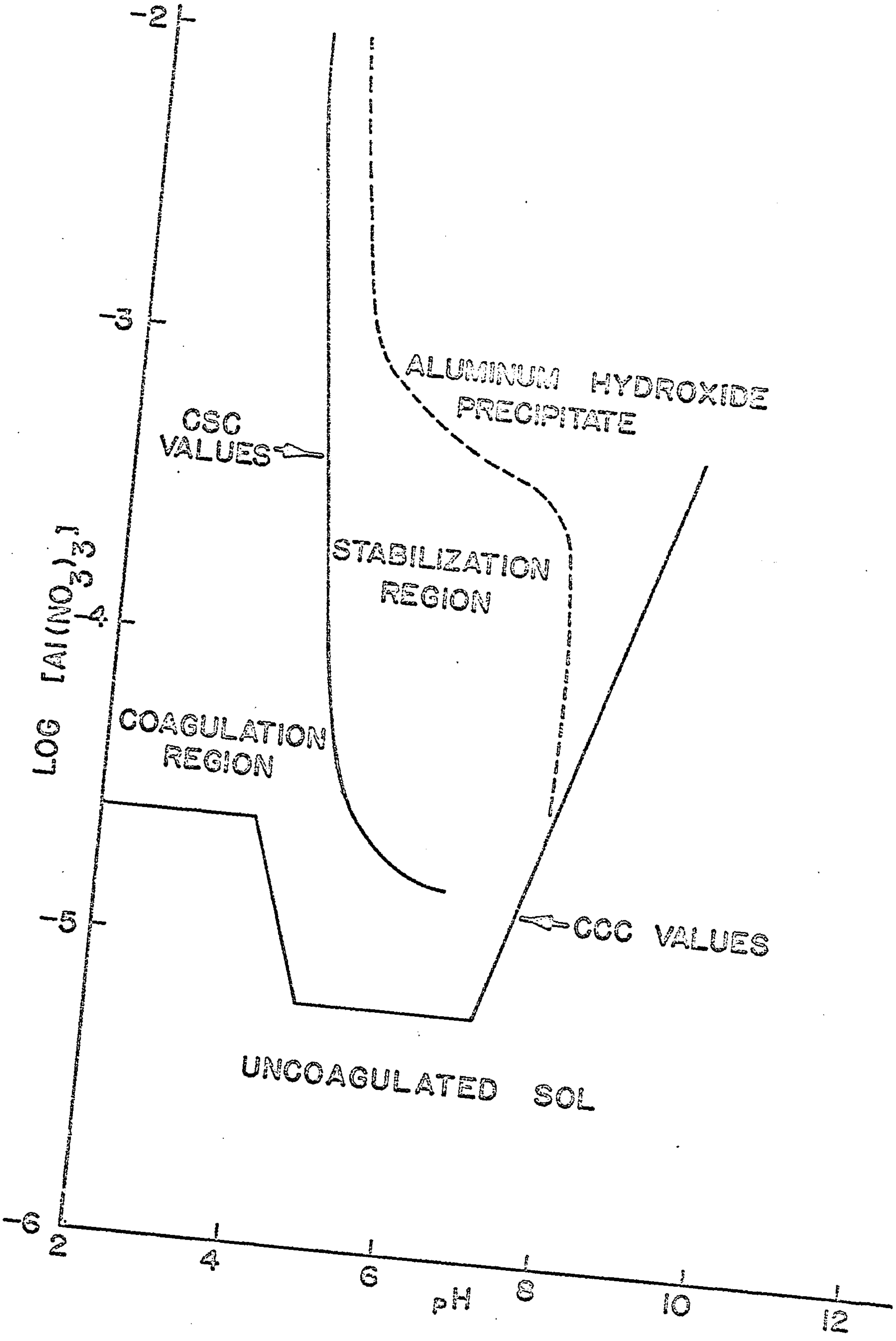
Matijevic and co-workers have conducted extensive studies on the coagulation of silver halide sols with metal ions such as aluminum (20, 22), thorium (18), zinc (19), and zirconium (21). These studies revealed that each of these ions was capable of coagulating and reversing the charge on the colloids, but only above a particular pH, characteristic of each metal ion. They concluded that the hydroxyl groups of the soluble species played an important role in the adsorption, and that the reversal of charge by a metal ion depended upon two parameters, metal ion concentration and the extent of its hydrolysis.

Aluminum nitrate was used to coagulate negatively charged silver halide sols for determining the charge and composition of hydrolyzed aluminum species present at different pH values (20, 22). Measurements of pH, scattered-light, and electrophoretic mobility were made for a series of systems containing a fixed amount of the sol and added acid or base but varying amounts of the coagulant. The lowest coagulant concentration which resulted in an increased amount of scattered light was termed as the critical coagulation concentration (CCC) at the corresponding pH value. Increased scattered light was used as an indication of aggregation. This procedure was repeated for several acid or base concentrations to obtain a relationship between pH and critical coagulation concentration.

The coagulant concentration above which the sol was observed to exhibit stability due to reversal of charge has been defined as the critical stabilization concentration (CSC). Such stabilization was indicated by a decrease in the amount of scattered light and reversed electrophoretic mobility values. By adopting a different procedure of keeping the coagulant concentration constant and systematically changing the amount of acid or base in any one series of tests, the relationship between pH and the critical stabilization concentration was determined. The entire aluminum nitrate-pH domain for silver iodide sol was established as the result of the study (19) (Figure 3). The dotted line shown in the figure represented the coagulant level at which precipitation was first observed. These levels were found by conducting the same tests but in the absence of the sol and observing the system for precipitation. Below the dotted line, all aluminum hydrolysis species were soluble.

The CCC values observed for pH values below 4.0 (Figure 3) were compared and found to agree with similar values obtained for different trivalent ions (22). Similarly, the CCC values observed for pH values between 5.0 and 7.0 were found to agree with the CCC values for tetravalent ions. As a result, it was concluded that the aluminum species present at pH levels below 4.0 was hydrated trivalent aluminum ion. Potentiometric titration tests conducted for aluminum salt solution with sodium hydroxide

Figure 3. Log $[A\ell(NO_3)_3]$ - - pH domain for a silver iodide sol (1 x 10^{-4}M) (20)


-2
-3
-4
-5
-6
LOG [Al(NO$_3$)$_3$]
2
4
6
8
10
12
pH
ALUMINUM HYDROXIDE PRECIPITATE
CSC VALUES
STABILIZATION REGION
COAGULATION REGION
CCC VALUES
UNCOAGULATED SOL

indicated the presence of a hydrolysis species with an Al to OH ratio of 1:2.5. From these it was concluded that $Al_8(OH)_{20}^{4+}$ would be the predominant species at pH levels between 5.0 and 7.0, since the tetravalent charge and the Al to OH ratio of 2.5 could be satisfied only by this particular species.

In an analysis of the chemistry of natural waters, Stumm (36) has discussed the nature and quantities of various hydrolysis products, as well as the solubility of aluminum hydroxide precipitate. At pH levels between 5.0 and 7.0, the concentration of all soluble species amounted to only 10^{-6} moles/liter. A comparison of this value with the values given by Matijevic (Figure 3) would reveal that the values presented by Matijevic were far greater. The solubility levels found by Packham (28) agreed reasonably well with the values presented by Stumm.

Alkalimetric titration experiments for aluminum perchlorate and ferric perchlorate solutions were performed by Stumm and Morgan (37). Their purpose was to study the net charge and the composition of the hydrolysis species of these metal ions. The results indicated that for a given metal ion concentration pH was the most important parameter in determining which hydrolysis species would be predominant, and thus in deciding the degree of coagulation to be expected. It was also asserted that when a metal salt was added in excess of its solubility, polynuclear hydrolysis products might occur as soluble kinetic intermediates in the transition to the precipitation of metal hydroxide.

Rapid mixing of alum with the colloids in water at speeds higher than the usual 100 rpm was found to be beneficial in the removal of turbidity by settling after mixing (32). Growth of insoluble hydroxides was observed to take place at a fast rate. If the hydrolysis product had to be adsorbed on the colloids before the coagulant was precipitated, it was argued that rapid mixing of the coagulant and colloids in the water would be essential for bringing the colloids and the soluble species nearer to each other within a short time.

When the present study was in progress, a report of work conducted with somewhat similar objectives was presented (27). An iron-silica system was used to study the effect of hydrolyzing polyvalent metal ions on the stability of lyophobic colloids. Measurements of adsorption, scattering intensity, and refiltration time were used as parameters to observe the extent of destabilization and restabilization of silica suspensions with different amounts of ferric perchlorate at various pH levels. The adsorption measurements were carried out only at low pH values by measuring the iron remaining in solution after adsorption on silica particles. The concentration of silica in suspension used in the study varied from 200 mg/l to 20,000 mg/l. Destabilization was found to occur at all pH levels regardless of the type of charge and nature of the hydrolysis products. At pH values above 3.0, a stoichiometric relationship was found to exist between the silica concentration and critical coagulation concentration values. Based on these results it was concluded that specific chemical forces must outweigh coulombic forces to result in specific adsorption of hydrolysis products on the interface of the colloids and eventually in aggregation. Restabilization of silica particles occurred only in the presence of greater than optimum coagulant amounts at pH values below 4.0. However, it was concluded that the restabilization phenomenon could not be evaluated at pH values above 4.0 because of the precipitation of insoluble hydroxides of iron.

Filtration as a parameter of destabilization

Filtering time had been used as a parameter by La Mer and co-workers (15, 16) to study the effect of various polyelectrolytes on the stability of highly concentrated phosphate slimes which consisted of fine colloidal particles from natural phosphate rocks. The filtering time was later replaced by refiltration time because, it was reported, the refiltration rate would fit the classical Kozeny-Carman equation for fixed-bed filtration (17). Since the thickness of filter cakes was found to be constant even with the addition of various polymer doses, they further simplified the equation to arrive at a relationship between the refiltration rate (Q) and the specific surface area (S) of slime particles. The relationship presented was $Q = K/S^2$ where K was a constant. Based upon a theory of adsorption of the polymers, considerations of floc geometry, and the simplified Kozeny-Carman equation, a quantitative theory was developed for filtration of suspensions treated with polymers (35). This theory predicted the variations of refiltration rate with different polymer concentrations. Thus, it was possible to calculate the optimum polymer concentration for destabilization of a suspension of known solids concentration. This development is discussed in more detail in a later chapter.

The mechanism of flocculation of slimes with polyelectrolytes proposed by La Mer consisted of a bridging mechanism. Some segments of the polyelectrolytes were visualized to be specifically adsorbed on the surface of the colloids. The segments that were not adsorbed hung out into the aqueous phase and were adsorbed on another colloid. A three-dimensional network of flocs consisting of polyelectrolyte molecules and colloids was eventually formed. This resulted in faster subsidence when settled, or a more porous cake when the suspension was filtered.

The bridging mechanism was later extended to the effect of aluminum perchlorate on silica suspensions (10). Aluminum perchlorate was used to destabilize the silica suspensions in the presence of various concentrations of a cationic polyelectrolyte. Since a small amount of the polyelectrolyte resulted in the same effect as that of a relatively larger amount of aluminum perchlorate, it was concluded that the mechanism of destabilization by aluminum salts may also be a bridging action. However, no other evidence was presented to support this conclusion about the mechanism.

It should be pointed out that all of La Mer's work was conducted at suspended solid concentrations higher than normally encountered in natural surface water supplies. The reported results show that the lowest concentration used was 400 mg/l, with concentrations as high as 250 g/l used in some studies.

Role of zeta potential or mobility in coagulation

Zeta potential measurements have been used either wholly or partly to control the coagulant doses in three water treatment plants where alum was used to coagulate turbid waters (25). Two plants have been successful in treating river waters with zeta potential as a parameter to determine optimum coagulant doses (32, 33). Sufficient alum was added to bring the zeta potential to a low negative value of about 5 mv, then a cationic polyelectrolyte to bring the value to zero or slightly positive value.

Activated silica was added to the water to produce tough floc. Adherence to this procedure has been reported to result in growth of large floc particles which have been removed easily by settling.

Electrophoretic mobility of colloids is the velocity of particles in an electric field, usually expressed in microns per second per volt per centimeter. Under known conditions of temperature, the zeta potential of the colloids can be calculated from the mobility value. Several researchers have attempted to correlate the zero mobility or zeta potential of colloids with optimum coagulant doses for turbidity removal. Black and associates (3, 4, 5, 30) used suspensions prepared with commercial clays and natural river sediments in their studies. The tests in their studies consisted of mixing different amounts of coagulant with a series of suspensions and conducting jar tests and mobility measurements on the coagulated but unsettled suspensions. Even though a correlation was found between low mobility levels and good coagulation conditions in some cases, good coagulation was often found to occur when the mobilities were highly positive or negative. They concluded that mobility alone cannot be used as a parameter for good coagulation.

In all their studies Black and co-workers made the mobility determinations several hours after the coagulant was mixed with the colloids. Kim, Ludwig, and Bishop (11) mixed aluminum sulphate solution with kaolinite suspensions and determined the mobility values at several time intervals. They found the mobility values changed after about an hour and stabilized at a constant value after about two hours. They attributed this phenomenon to the slow approach towards equilibrium of the CO_2 - HCO_3^- - $CO_3^=$ system. Packham (28) conducted studies similar to

Black's with natural clays but determined the mobilities soon after the mixing of coagulants. His results agreed in general with those of Black, differing only in some details. Matijevic (20), when investigating the coagulation of silver halide sol with aluminum nitrate, found charged sols on a few occasions, showing evidence for coagulation in scattering intensity measurements. He did not expect this and was not able to explain this phenomenon.

Effect of clay concentration on coagulation

The alum required to halve the turbidity (D_{50}) of a kaolinite suspension was used as a parameter to study the effect of clay concentration on coagulation (28). When 50 ppm kaolinite was used, the coagulant required showed an optimum pH value near 7.0. When the clay concentration was increased to 500 ppm, the required alum for halving turbidity below neutral pH was reduced to almost zero. Furthermore, at high pH values a lower alum concentration was required for 500 ppm of clay than for 50 ppm of clay. This phenomenon was attributed to the existance of larger interparticle distance at 50 ppm suspension.

Kim et al. (11) used kaolinite and bentonite in their study of the effect of clay concentration on coagulation. Using the parameter D_{50} they found the required alum dose increased with an increase in bentonite concentration but decreased with an increase in kaolinite concentration. This was attributed to the fact that bentonite is made up of small particles and has a larger number of particles per unit weight compared to kaolinite. The importance of interparticle distance would be predominant when the number of particles per unit volume was low as was the case with the kaolinite suspensions.

LABORATORY APPARATUS AND PROCEDURE

The work done to evaluate the coagulation of clay with alum in this study can be divided in two major parts: pilot plant studies and bench-scale studies. A pilot pressure diatomite filter was used in the pilot plant studies; a membrane filtration assembly, microelectrophoresis equipment and jar test apparatus were used in the bench-scale studies.

Pilot Plant Studies

Raw water

The turbid raw water used in all tests was prepared by continuously adding tap water and a clay slurry to a mix tank. The tank had a capacity of 50 gallons. The mixing was done by air-agitation. Tap water was added at a constant desired rate by using a float control valve.

The clay used in the entire study was Panther Creek bentonite[1], which contains mostly calcium montmorillonite. To prepare the clay slurry, the following procedure was adopted. About 180 g of the clay was mixed with approximately 45 gallons of distilled water in a 50 gallon tank by vigorous air-agitation for 36 hours. The mixing was then stopped; the larger particles of clay were allowed to settle for a period of 12 hours. Thirty gallons of supernatant clay suspension was then siphoned out and were used as the clay slurry for one filter run. The slurry used was also air-agitated during the filter run to keep the suspension in a uniform state. The slurry was fed at a constant desired rate. During the test three

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[1] Panther Creek Southern Bentonite, American Colloid Company, Merchandise Mart Plaza, Chicago 54, Illinois.

samples of the clay slurry were taken and used to determine the suspended solids concentration in the slurry. The clay concentration in the raw water was calculated from the pumping rate of clay slurry, the flow rate of tap water, and the concentration of the clay slurry. The clay concentration in the raw water varied from 11.0 mg/1 to 30.0 mg/1 during different pilot plant runs.

The university tap water is obtained from deep wells. This water has been treated for iron removal by aeration, sedimentation, and rapid sand filtration. A mineral analysis of the tap water conducted during the study is given below:

Total solids	528	mg/1
Alkalinity (as $CaCO_3$)	298	mg/1
Calcium	105	mg/1
Chloride	20.5	mg/1
Fluoride	0.5	mg/1
Iron	0.12	mg/1
Magnesium	36.4	mg/1
Manganese	0.05	mg/1
Nitrate	4.3	mg/1
Potassium	2.6	mg/1
Silica	26.0	mg/1
Sodium	18.0	mg/1
Sulphate	110.0	mg/1
Carbonate	none	

The temperature in the mix tank was controlled by a thermostat which actuated a relay and in turn a solenoid valve on the hot water feed line.

The mixing of hot and cold water took place before flowing through the flow rate regulator on the tank inlet line. The temperature of the water was maintained so that the filter effluent temperature would be at 68 ± 1.0° F.

Pilot filter plant

The construction and operation of the pilot plant used in this study was described in detail by Miley (24), LaFrenz (13) and Hawley (9). A few major changes were made in the pilot plant to facilitate coagulant addition and to simplify the operation of the plant. A brief description of the present pilot plant will be given here (Figures 4 and 5).

The raw water was prepared in the clay mix tank. It then flowed to either of the coagulation tanks where the alum could be added and mixed with the raw water. One of the tanks had a capacity of 22 gallons and was equipped with a rapid mixer. The speed of the mixer was 1780 rpm and the three-bladed paddle of the mixer had a diameter of 3.5 inches. The other coagulation tank, 36 in. diameter by 34 in. high, had a capacity which could be varied from about 32 to 152 gallons. A capacity of 38 gallons was used in this study. The mixing was done in this tank with a paddle having a diameter of 15 inches and rotating at 24 rpm. Fresh solutions of alum ($Al_2(SO_4)_3 \cdot 18H\ O$)[1] were prepared for every test in suitable concentrations and quantities. The solution was added to the raw water by means of a small positive displacement pump. The alum used was of analytical reagent grade and was used as received.

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[1] Aluminum sulphate (crystals) - - Analytical Reagent, Mallinckrodt Chemical Works, St. Louis, Missouri.

Figure 4. Schematic diagram of the pilot pressure diatomite filter plant

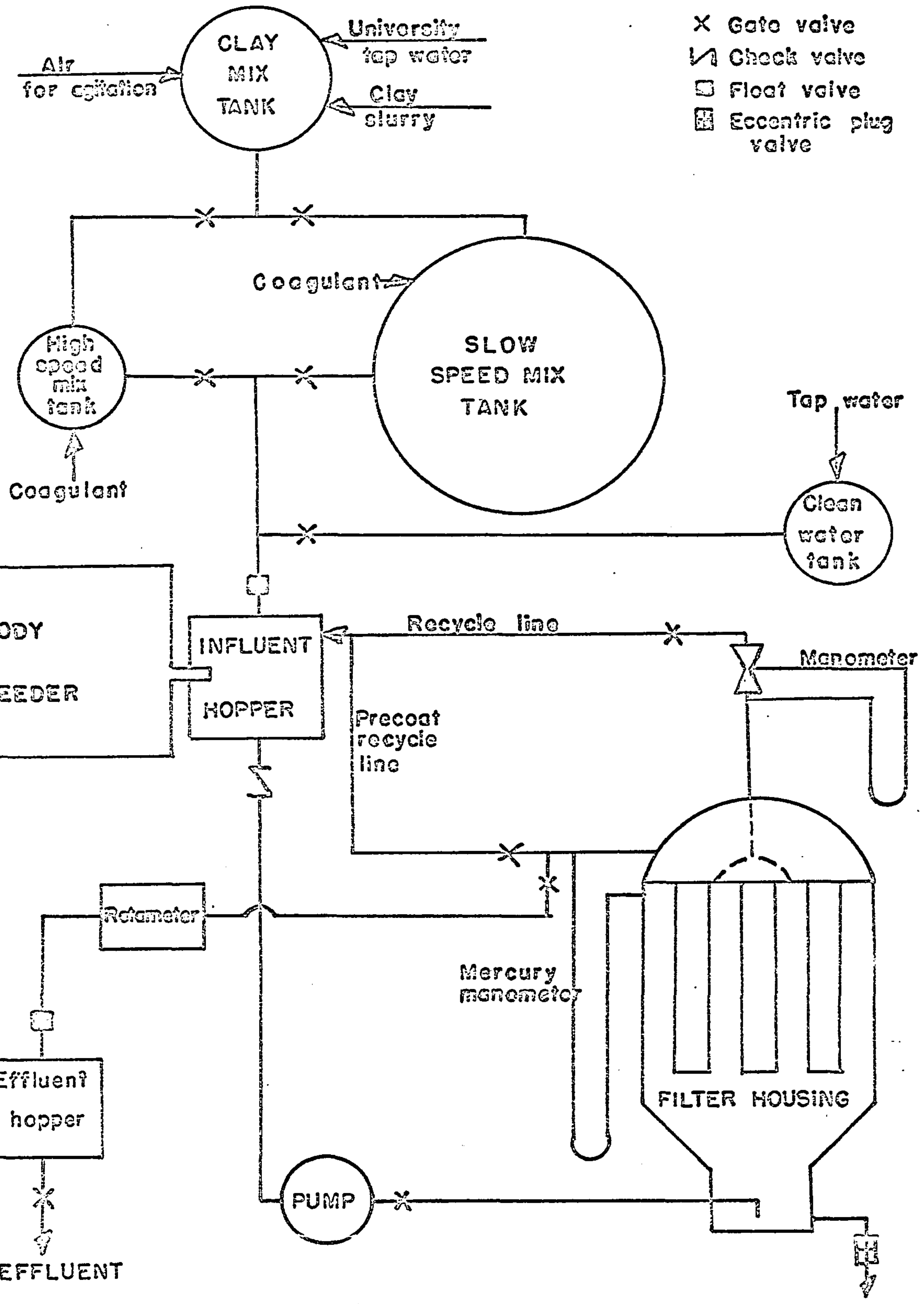
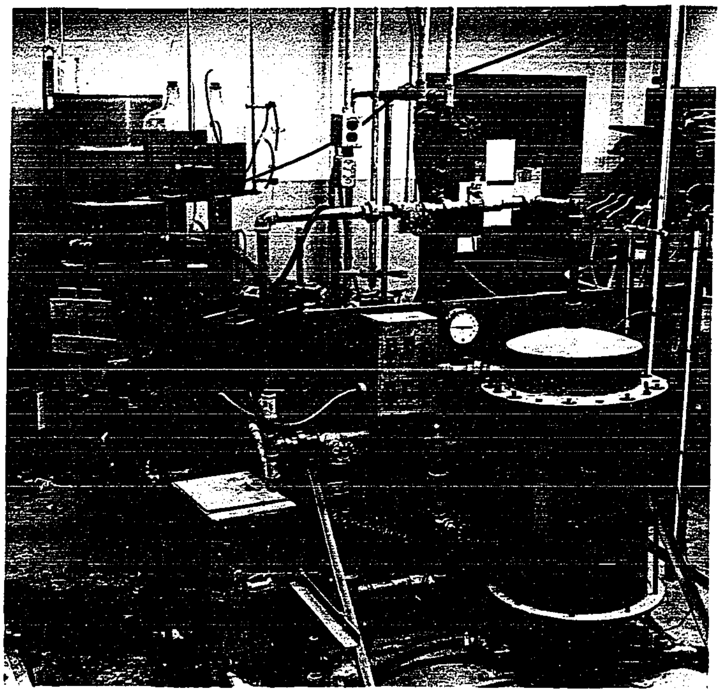
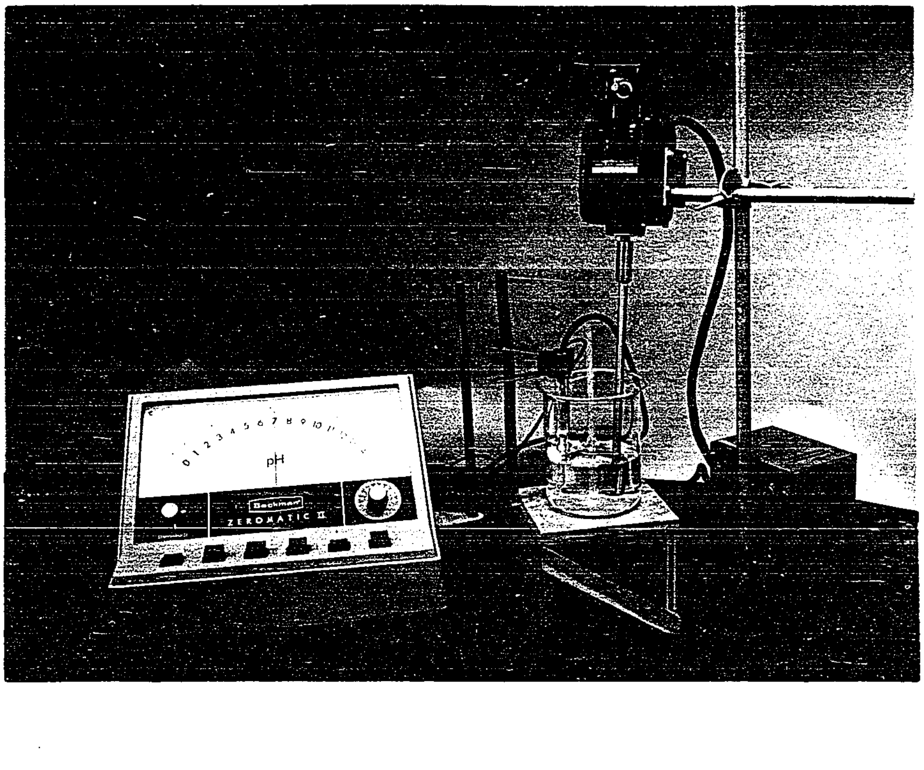

CLAY MIX TANK
University tap water
Air for agitation
Clay slurry
× Gate valve
Check valve
Float valve
Eccentric plug valve
Coagulant
High speed mix tank
SLOW SPEED MIX TANK
Coagulant
Tap water
Clean water tank
BODY FEEDER
INFLUENT HOPPER
Recycle line
Manometer
Precoat recycle line
Rotameter
Mercury manometer
FILTER HOUSING
Effluent hopper
PUMP
EFFLUENT

Figure 5. Photograph of the pilot pressure diatomite filter plant

Figure 6. Photograph of the mixing system used in the bench scale studies, and the pH meter




0 1 2 3 4 5 6 7 8 9 10 11
pH
Beckman
ZEROMATIC II

The water leaving either of the coagulation tanks entered a small hopper through a float valve. The body feed diatomite was added to the water flowing through the hopper. The water was pumped from the hopper through the filters, and thereafter through a flow meter and a flow regulator. The rate of flow through the filters was controlled at a constant rate by a float-type flow regulator and it was measured by the rotameter. The head loss across the filter cake was measured by a mercury manometer.

The body feeder used in this study was a dry, volumetric screw type feeder.[1] The feeder was fixed with a time clock which controlled it to run for a predetermined portion of each minute. The body feed rate could be varied from 35 to around 2000 mg/l at a flow rate of 1.0 gsfm. The body feed rate used in this study was generally below 65 mg/l.

The filter housing contained three filter septums and four dummy septums. The dummy septums were used to reduce the volume of filter housing and in turn the initial dilution time. The filter septums consisted of a sock, made from a synthetic fabric, stretched over a plastic frame. The septums were 3 1/2 inches in diameter and 14 inches in length, and provided a total filtering area of 3.24 sq ft.

Two recirculation lines were used in the pilot plant. One connected the effluent side of the filter housing to the hopper on the suction side of the pump. This was used during the precoating operation only. Another

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[1] BIF MODEL 25-01, BIF Industries, Division of New York Air Brake Company, Providence, Rhode Island.

recirculation line connected the inlet side of the housing to the same hopper on the suction side of the pump. This recirculation was used throughout the run so as to provide an upward velocity in the housing to facilitate even cake formation throughout the filtering area.

For the precoating operation and general washing of the filters, clean water was drawn from a tank having a capacity of 32 gallons. The university tap water was connected to this tank; the level in the tank was maintained by a float valve.

Metering equipment

To control the turbidity of the raw water and to measure the turbidity of the filter effluent continuously, two photoelectric turbidimeters[1] and an automatic recorder[2] were used throughout the study. The turbidimeters were known as low-range turbidimeters, and the output signals of the turbidimeters were continuously recorded on a multipoint recorder. Each turbidimeter was calibrated against the Jackson Candle Turbidimeter for the clay used in the study (1).

The turbidimeter is a 4-inch plastic tube, approximately 50 inches long. The water enters at the bottom and overflows at about one foot from the top. The photoelectric cells are mounted around the circumference at about mid depth of the tube. A light source and two lenses are fixed at the top, above the water surface. When the beam of light passes through the water, it is scattered by the particles in the water,

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[1] C. R. Low Range Turbidimeter, Hach Chemical Co., Ames, Iowa.

[2] Type 153 Universal Electronic Multipoint Recorder, Minneapolis-Honeywell Regulator Co., Philadelphia, Penn.

and this scattered light is picked up by the cells. This results in the production of a small potential which is measured by the recorder. The merits and details of the turbidimeter have been described elsewhere (6).

A multipoint, self-balancing potentiometer-recorder was used to record continuously the output of the photoelectric cells in the turbidimeters. The recorder has a full scale reading of 5 millivolts. Two variable resistors known as helipots are connected in parallel with the recorder and the turbidimeters. These sliding wire helipots have dials indicating the slide wire position. The dials can be set to get any desired scale reading in the recorder for a given output from the turbidimeter.

The Jackson Candle Turbidimeter is the standard instrument for measuring turbidity of suspensions (1). Any other instrument used should be calibrated against the Jackson turbidimeter using the solids to be subsequently measured. Accordingly, both the turbidimeters were calibrated for Panther Creek bentonite with several suspensions with different turbidity levels. A standard suspension with a turbidity higher than 25 units was prepared by mixing tap water with a known amount of concentrated clay slurry. Tap water was used in this calibration work since it would also be used in all pilot plant runs. The turbidity was measured with the Jackson Candle Turbidimeter. This suspension was then diluted with tap water in various proportions to obtain suspensions having desired turbidities. These suspensions were then circulated through the turbidimeters, and the readings in the recorder for a selected setting of the variable resistors were noted. A plot of turbidity versus the reading of the recorder was prepared and used during the subsequent experiments.

Operating procedure

The clay slurry pump was first started and the tap water valve was opened. The raw water prepared in the clay mix tank was allowed into either one of the coagulation tanks, so that raw water would be available when the filtering cycle had to be started. The precoating operation was started by pumping clean water into the filter housing system. Precoat diatomite was weighed and put into the hopper on the suction side of the pump. A precoat diatomite of 0.15 lb per sq ft of septum area was used in all the tests conducted in this study. The precoat slurry was recycled through the filter until a coat was formed on the septums and the water in the housing became clear.

The following procedure was adopted in starting the filtering operations: the filter effluent valve was first opened; the precoat recirculation valve was closed; filtration rate was set by adjusting the valve opening on the effluent side of the filter; the valve on the raw water line was opened and the valve on the clean water line was closed; the body feeder was started. The following data were noted periodically during a run:

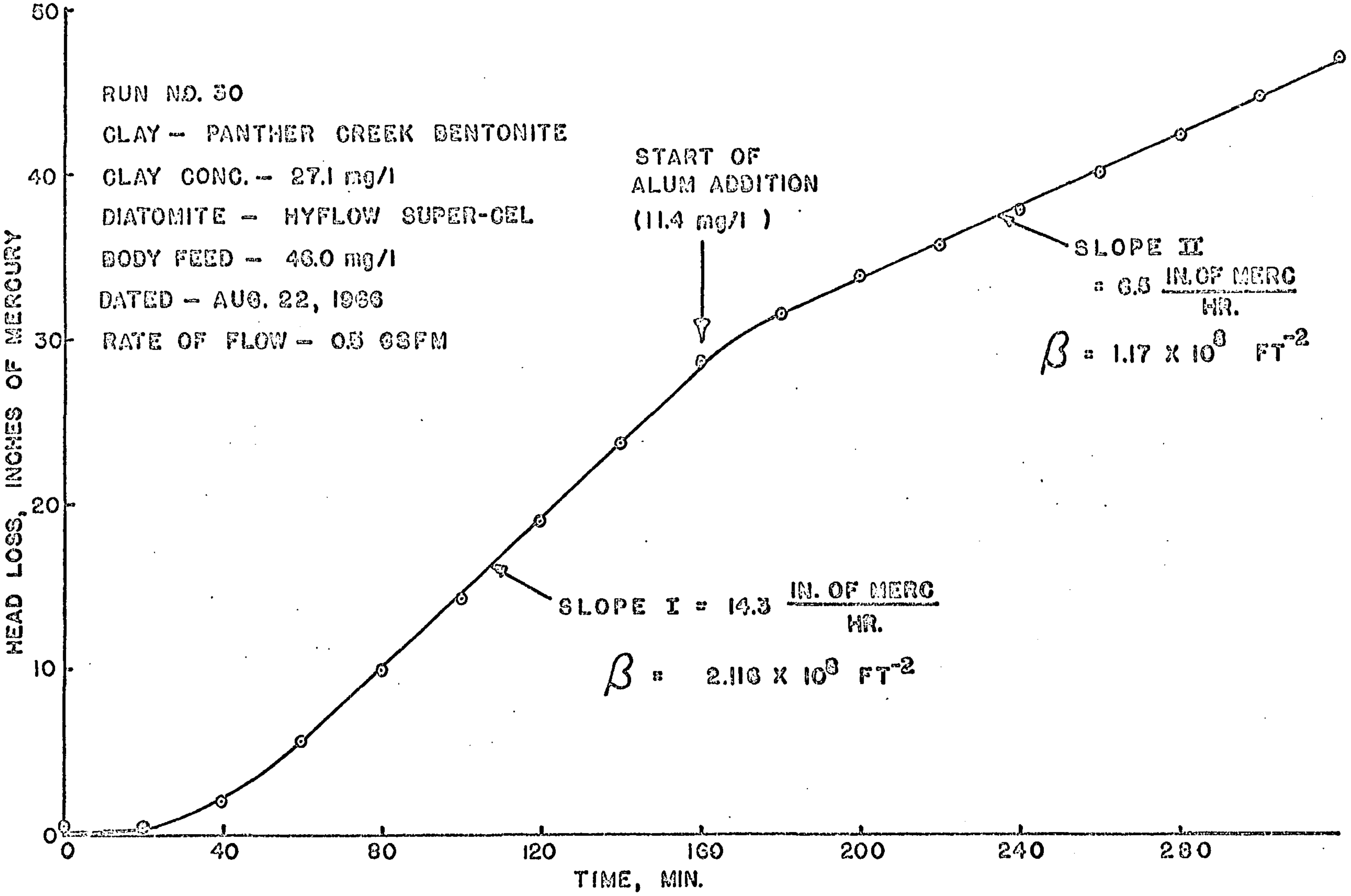
1. Clock time
2. Temperature of filter effluent
3. Clay slurry feed rate
4. Head loss in inches of mercury
5. Filtration rate of flow

The pH of the filter influent and effluent were noted during each run and it was noted to be relatively constant at 7.3 ± 0.3 during the study. A plot of head loss in inches of mercury versus the time of filtration in minutes was prepared while a run was in progress. When the linearity of the head loss curve was definitely established, alum solution feed to the raw water in the coagulation tank was started. This was normally at about two hours after the run was started. Observation of data listed above together with measurements of alum feed rate was continued until the head loss versus time relationship was again established in a linear form, but with a different slope. Data from a typical run are shown in Figure 7. The run was then terminated. The filter was backwashed by an air-gurgle type backwash. Before starting the next run, the whole system was cleaned twice by pumping the system full of clean tap water and draining it down.

The diatomite in the body feeder was changed after every run, so as to avoid any possible degradation of diatomite in the feeder. The body feed rate was measured by collecting and weighing two ten-minute samples, one before and another after the run.

The head loss-time data collected during each run were analyzed using a linear regression program and the Iowa State University digital computer. Two β-indices were determined, from the data collected before alum was fed to the raw water which would be the resistance of the filter cake formed without alum, a second from the rest of the data which would be the resistance of filter cake formed with the alum. The per cent change in the β index was calculated and taken as the effect of addition of that particular concentration of alum on filter cake resistance.

Figure 7. Typical head loss increase with time during a pilot filter run showing the effect of alum addition on the head loss increase


RUN NO. 30
CLAY – PANTHER CREEK BENTONITE
CLAY CONC. – 27.1 mg/l
DIATOMITE – HYFLOW SUPER-CEL
BODY FEED – 46.0 mg/l
DATED – AUG. 22, 1966
RATE OF FLOW – 0.5 GSFM
START OF ALUM ADDITION (11.4 mg/l)
SLOPE I = 14.3 IN. OF MERC / HR.
β = 2.116 X 10^8 FT^-2
SLOPE II = 6.5 IN. OF MERC / HR.
β = 1.17 X 10^8 FT^-2
HEAD LOSS, INCHES OF MERCURY
0
10
20
30
40
50
TIME, MIN.
0
40
80
120
160
200
240
280

Typical results are shown on Figure 7.

Bench Scale Studies

The bench scale work consisted of the evaluation of the coagulation of clay with alum using membrane filtration tests, electrophoretic measurements, and jar tests. Preparation of samples for filtration and electrophoretic measurements were carried out in exactly the same way; however, the preparation had to be somewhat altered for the jar tests because of the fact that larger quantities of suspension were required for one jar test. The procedure of preparing samples for filtration and electrophoretic work will be first presented here. Differences in procedure of sample preparation for jar tests will be discussed later.

Preparation of sample

A clay slurry was prepared for each series of tests in a manner similar to the pilot plant runs. However, the volume of slurry prepared was naturally much smaller. Twenty g of clay was mixed with 5 liters of distilled water for 12 hours by air-agitation. Then the mixing was stopped and settling of larger particles of clay was allowed to take place for 12 hours. Three liters of supernatant was siphoned out at the end of the settling period and was used for one series of filtration or electrophoretic tests.

Two liters of suspension with a desired clay concentration were prepared by mixing suitable amounts of clay slurry and distilled water. A one-to-seven mixture of tap water and distilled water was used instead of only distilled water to prepare the suspension in Series 14 and 15 of this study. The clay concentration of the suspension used in the bench scale studies varied from 26 mg/l to 208 mg/l. The prepared suspension was kept in a constant temperature bath at 30° C. (See Figure 10, p. 46.)

A 250 ml sample was drawn out of the prepared suspension and placed in a 600 ml beaker. The pH value of the sample was measured with the Beckman pH meter[1] and adjusted to a desired pH level. The pH adjustment was carried out by adding either HCl or NaOH of suitable normality. Solutions of acid and alkali of different strengths were prepared periodically and used as needed. Strengths of HCl solutions were 0.05 N and 1.0 N. Strengths of NaOH solutions were 0.05 N, 0.9 N, and 10.0 N. The pH meter itself was standardized every four hours using two different buffer solutions having a pH value reasonably close to the test pH level.

When the bench scale studies were about to be started it was noticed that the alum salt in the bottle had external moisture on the surface. For the first seven series of bench scale filtration tests, alum was dried in the oven before the alum solutions were prepared. However, it was realized that some of the molecular water in the structure of alum might have been driven out by this procedure. A sulfate analysis (1) of the oven-dried alum and desiccator-dried alum was made. The oven-dried alum was found to have lost some of the molecular water, whereas the desiccator-dried alum had not lost any water. So, the alum concentration recorded during the first seven series of filtration tests were

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[1] Beckman Zeromatic II pH Meter, Beckman Instruments, Inc., Fullerton, California.

accordingly corrected. One of the seven series of tests was repeated with desiccator-dried alum to see whether the correction was acceptable and it was found to be so. In all later filtration, electrophoresis, and jar tests the alum was left in the desiccator for one day before its use. Fresh stock solutions of suitable concentrations of alum were prepared and used every day.

The beaker containing the 250 ml sample was put under a rapid stirrer and required amount of alum solution was added while the suspension was mixed at a known speed (Figure 6). Distilled water was also added together with the alum solution, the total of these always being 10 ml. The clay concentration in the suspension after alum addition ranged from 25 mg/1 to 250 mg/1. If the pH of the suspension was altered by the addition of alum, it was brought back to the desired level by adding the required amount of NaOH solution having a suitable strength. After the pH adjustment, the mixing was continued at the same speed for 15 min. Then the sample was used for the filtration test or electrophoresis work. The rapid mixer used for this purpose was a laboratory mixer,[1] the speed of which could be varied from 0 - 5000 rpm by means of a motor controller. The speeds of mixing used in this study were 100, 1000, and 3000 rpm in different series. The paddle attached to the motor of the mixer had a shape similar to that of the paddle of the rapid mixer used in the pilot plant runs. The paddle had three blades horizontally fixed to the shaft. The diameter of revolution of the blades was 1 1/2 inches.

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[1] Electronically Controlled GT21 Laboratory Mixer, Gerald K. Heller Co., Las Vegas, Nevada.

Seven such samples could be taken out of the 2 liter suspension prepared. One out of every seven tests was made without any alum addition as a control test. In each series a total of 14 to 19 tests were conducted, and 4 or 5 of these tests were done to check the reproducibility of the readings observed. Thus 10 to 14 alum levels were tested in each series of tests. A plot of filtration time or refiltration time versus alum concentration was prepared. The lowest alum concentration producing the lowest time of filtration was termed the optimum alum level for that particular suspension.

Membrane filtration

The sample prepared in the above-described procedure was used either in filtration tests or electrophoresis tests. The filtration assembly used in this study is shown in Figure 8. The assembly consisted of a vacuum pump, a moisture trap flask, a mercury manometer and the membrane filter apparatus.[1] The vacuum pump was capable of producing a maximum suction pressure of 27 inches of mercury. The suction pressure was measured by the mercury manometer connected to the moisture trap flask. The suction pressure used in most of the filtration tests was 10 inches of mercury. Higher pressures were used in some of the initial filtration tests. Such deviations are noted in appropriate places. The membrane filter apparatus consisted of a top and a bottom portion of a filter holder held together by means of a clamp. The membrane filter was placed in between the top and bottom portions. Filter papers used were

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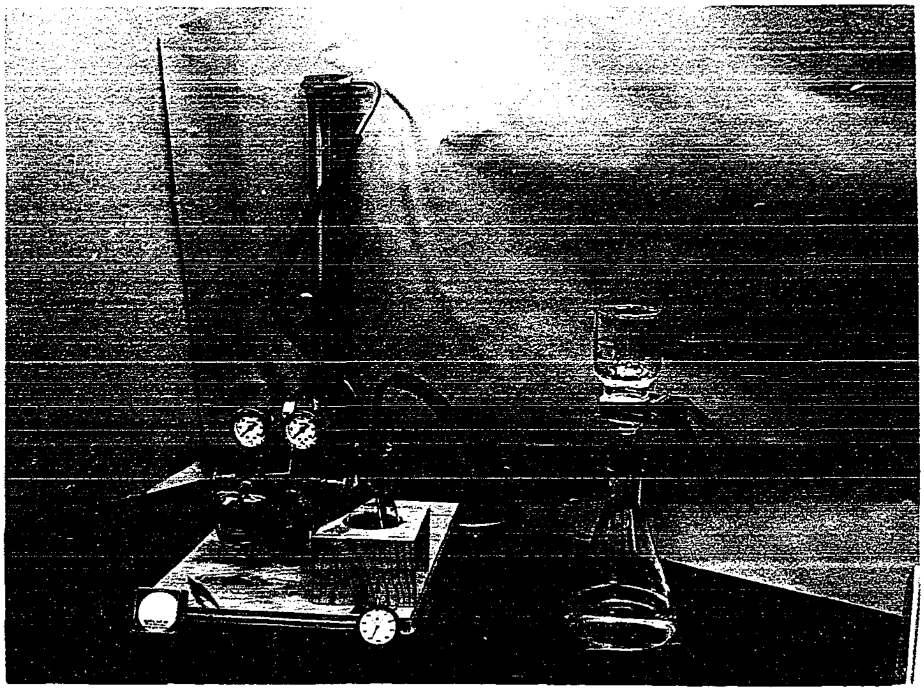
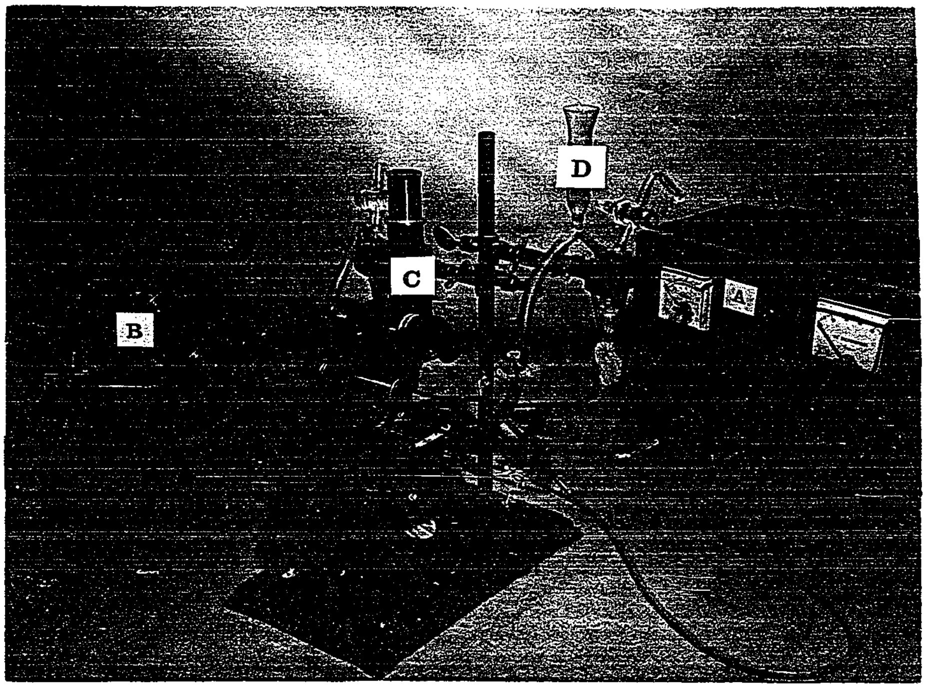
[1] Pyrex Filter Holder, Millipore Filter Corporation, Bedford, Mass.

Figure 8. Photograph of the membrane filtration assembly

Figure 9. Photograph of the components of the electrophoretic equipment

A - power supply
B - light source
C - microscope
D - pouring spout of the Brigg's cell assembly




D
C
B
A

of the grid type with a pore size 0.45 μ ± 0.02 μ and a diameter of 47 mm.[1] The entire filter apparatus was connected to a 1 liter suction flask where the filtrate was collected.

When the sample was being mixed, the filtration assembly was cleaned and connected together. One hundred or two hundred ml of the treated sample was poured into the top portion of the filter holder and the pump was started. A stop watch was also started at that time. The time taken to filter the sample through the membrane filter was noted as filtration time. Then 50 or 100 ml of the filtrate was slowly introduced back into the filter holder and the procedure was repeated. The time taken for this step of filtration was noted as refiltration time. Lower volumes were used for filtration and refiltration when the clay concentration of the suspension was higher than 50 mg/l, higher volumes for suspensions with lower clay concentrations.

When the filtrate was transferred back to the filter holder it was found to be necessary to exercise extreme care so as not to disturb the filter cake already formed during the first step. Whenever it was suspected that the cake had been disturbed, the refiltration time experiment was discarded for that test. The possibility of cake disturbance had not been reported by earlier investigators who used refiltration time as a parameter in ~~their~~ studies. This may have been due to the fact that much higher clay concentrations were used in their studies as compared to those used in the present study. Refiltration time experiments were discontinued

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[1] Type HA Filters, Millipore Filter Corporation, Bedford, Mass.

after 10 series of the filtration tests since both filtration and refiltration time indicated the same optimum coagulant dose. Thus in the last five series of filtration tests, only the filtration time of the suspensions was determined.

Microelectrophoresis

The apparatus used for making electrophoretic measurements consisted of a Brigg's cell and its components, a microscope, a light source, a power supply (Figure 9), and a conductivity bridge[1] and conductivity cell[2] (Figure 10).

A microscope with a 10 X ocular lens and a 10 X objective was used. An ocular micrometer was inserted in the eyepiece and calibrated to enable the timing of particles moving through a known distance. The Brigg's cell was mounted on the microscope platform with two clamps. A lamp focused to give rays of light perpendicular to the direction of viewing was placed at a distance from the microscope to shine directly at the Brigg's cell. The particles in the Brigg's cell scattered the light; these lighted specks of particles could be seen through the microscope and their movement be timed.

The width and depth of the Brigg's cell were found to be 2.13 cm and 0.1 cm respectively, thus having a cross-sectional area of 0.213 sq cm. The required movement of the fine adjustment in the microscope

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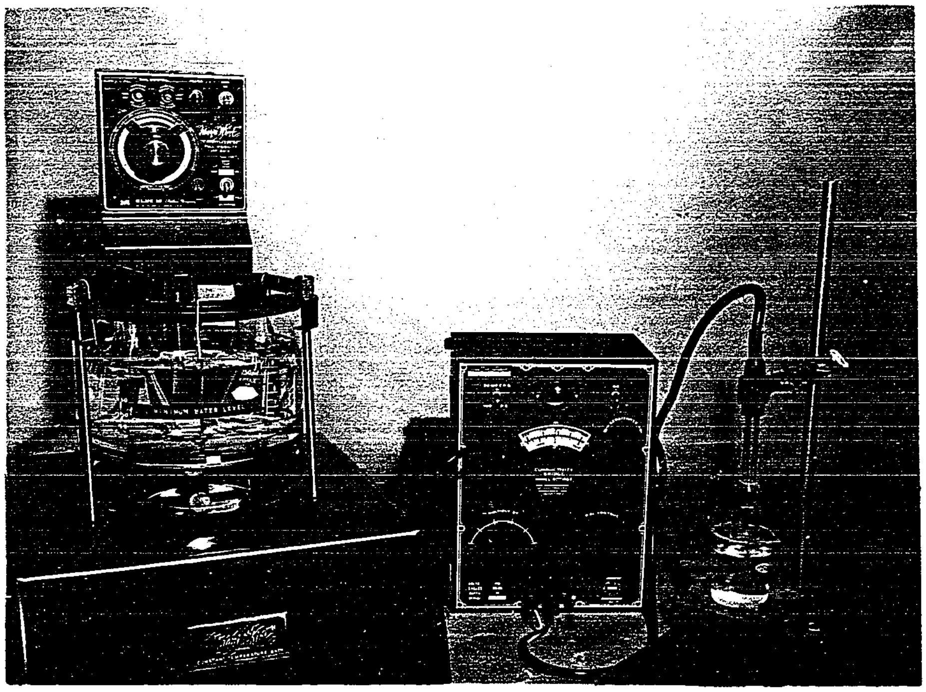
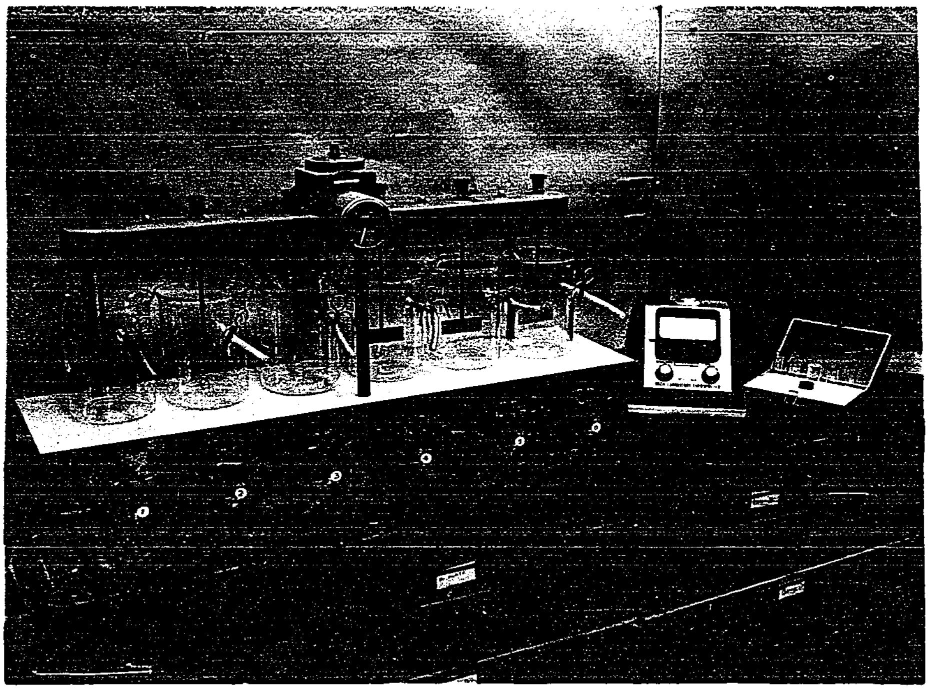
[1] Type RC-16B2 Conductivity Bridge, Industrial Instrument, Inc., 89 Commerce Road, Cedar Grove, N. J.

[2] Type A01 Glass Dip Cell, Industrial Instruments, Inc., 89 Commerce Road, Cedar Grove, N. J.

Figure 10. Photograph of the constant temperature bath, and the conductivity bridge and cell

Figure 11. Photograph of the jar testing apparatus and laboratory turbidimeter





for viewing the inner top and bottom of the cell when full of water was experimentally determined. Two stationary levels exist in an electrophoresis cell where the flow of liquid is zero, and the velocity of particles could be measured at these levels directly without interference from the flow of liquid. The movement required to reach the two stationary levels was calculated as 20 per cent of the total depth (30). This was found to be 150 micrometer divisions of the fine adjustment of the microscope from the bottom or top of the cell.

The Brigg's cell was connected with the two electrodes of the system with two pieces of surgical plastic hose. Sufficient mercury was added to each electrode vessel to cover completely the platinum wire of the electrodes. Mercuric nitrate solution (150 g/l) was then added to fill each electrode vessel to its constricted portion, then potassium nitrate solution (170 g/l) was added to fill each vessel. The electrode solutions were changed periodically as well as whenever a malfunction was suspected. The electrodes were connected to the power supply. A 400 volt D.C. power supply was constructed into a single unit by putting together various needed components. The direction of current could be reversed and the voltage output could be varied with adjustable knobs. The resistance of each suspension was measured with a conductivity bridge and a conductivity cell. The cell constant was found to be 0.1 cm^{-1} by using a standard reference solution of 0.1 N KCl at 25° C. (1)

Part of the sample after being mixed for 15 minutes was used for conductivity measurements. The temperature of the sample during this measurement was 25.0 ± 0.5° C. The rest of the sample was slowly transferred to the Brigg's cell assembly by pouring it into a spout in one end while a suction pressure was induced on the other end by means of an aspirator attachment. Then the valves were tightly closed and the microscope was focused at the bottom stationary layer. The power supply was switched on and the current was adjusted to a desired value. This desired value of current almost always resulted in a voltage output reading close to 400 volts. This level was not changed during the measurement. The direction of particle movement and current value in amperes were recorded. A stopwatch was used to time the particles traveling a given apparent distance on the ocular micrometer. This distance was normally chosen as 100 μ. When the particles moved very slowly and settled very fast, a distance of 20 μ was chosen. Normally, ten particles were timed in each direction, alternating the direction of movement after each observation by using the reversing switch. However, when the particles settled fast and it was difficult to find particles for timing, the number of observations had to be reduced to a value lower than ten. When the isoelectric point was occasionally reached, none of the particles moved noticeably and only a note of this fact was made. Readings at the upper stationary layer were occasionally taken to check the functioning of the apparatus. The temperature of suspension at the end of the test was measured by inserting a thermometer into the pouring spout of the cell assembly.

The temperatures measured at the beginning and at the end of the test were averaged. The times were then averaged and this value was used in calculating the electrophoretic mobility of the particles by using the following equation (30):

$$M = \frac{Ad}{tIR_s}$$

where M = electrophoretic mobility in $\frac{\mu \text{ cm}}{\text{volt sec}}$

A = area of cross section in sq cm

d = distance traveled in μ

t = time in seconds

I = current in amperes

R_s = specific resistance in ohm-cm.

The mobility values obtained by using the equation were corrected to 25° C assuming an inverse relation between viscosity and mobility.

Jar tests

The jar testing apparatus[1] used in this study consisted of a six-place multiple mixer and a base containing a light source to light the jars for visual observation of the contents (Figure 11). The mixer speed could be varied from 0 to 100 rpm. The paddles of the mixer were 3 inches in diameter. Two liter beakers were used as jars. A glass tube was attached to each jar so that the supernatant could be drawn out without disturbing the contents at the top or the bottom of the jars (Figure 11).

To prepare the clay slurry for the jar tests, a procedure similar to that for filtration tests was followed. Sixty g of clay was mixed with 15 liters of distilled water and 9 liters of supernatant was siphoned out after 12 hours of mixing and 12 hours of settling. This clay slurry was used with necessary dilution for four sets of jar tests. Each experimental series was made up of two sets of jar tests.

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[1] Multiple Laboratory Stirrer, Phipps and Bird, Inc., 303 South 6th Street, Richmond, Virginia.

In order to make one set of jar tests, at least 12 liters of suspension was needed. So, 13 to 16 liters of suspension with a desired clay concentration was prepared by mixing suitable amounts of clay slurry and distilled water, or a mixture of tap water and distilled water as the case may be, for the particular series. Two liters of suspension was placed in each jar and the pH value of the suspension was adjusted to a desired level by adding HCl or NaOH solution of required strength. After starting the rapid mixing at 100 rpm, different amounts of alum solutions were added to each jar and the pH values were adjusted back to the same value with NaOH solutions. Two pH meters operated by two persons were used for this purpose so as to complete it faster. This process normally took 3 to 5 minutes. After five minutes of rapid mixing at 100 rpm, the mixing speed was reduced to 35 rpm and this slow mixing was continued for 15 minutes. The mixing was then stopped and the particles were allowed to settle for 30 minutes. After this period the supernatant from each jar was drawn out and the turbidities were measured in a laboratory turbidimeter[1] (Figure 11). A plot of the turbidity remaining versus the alum concentration was prepared. The steep slope of the line was extended to zero turbidity level (e.g., Figure 18, p. 83), and the alum concentration at this point was taken as the optimum level for the particular suspension.

The turbidimeter used in this part of the study was a nephelometer using the principle that light passing through a suspension would be scattered by particulate matter. A light beam was sent upward through

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[1] Laboratory Turbidimeter-Model 1860, Hach Chemical Co., Ames, Iowa.

a tube containing the sample. The light which was reflected at 90° to the light beam was received by photocells which would send an electric current to be measured by the instrument. This turbidimeter was calibrated against the Jackson Candle Turbidimeter using Panther Creek bentonite as the suspended solids and distilled water as the dispersing medium. The instrument was found to be precise for measuring turbidities lower than 200 Jackson Turbidity units.

SUMMARY OF EXPERIMENTAL WORK

Pilot plant studies were first conducted for the purpose of demonstrating the effect of alum on filter cake resistance (β index). Eleven trial pilot filter runs (numbered 1 through 8, and 21 through 23) were made using two different clays and four different grades of diatomite in order to select a type of clay and a grade of diatomite which would be suitable for the purposes of this study. Results of these runs indicated the suitability of Panther Creek bentonite[1] as the suspended solid and Hyflo Super-Cel[2] as the grade of diatomite. The choice of clay was made on the basis of the ease with which it could be suspended and be free from complicating characteristics peculiar to it, such as the swelling of sodium montmorrillonite clays (31). Hyflo Super-Cel was selected as the grade of diatomite since it removed the clay particles completely and produced a reasonable head loss with sufficient body feed added to the raw water. The results of the trial runs are not reported since they are of no direct consequence to the purposes of the study.

Twenty-eight valid pilot filter runs were conducted. They are divided into two separate sets of runs, each differing from the other in level of clay concentration in raw water, level of body feed concentration, mixing speed, and rate of flow. The levels of factors that were held constant during each set of runs are shown in Table 1. The word "set" is used in connection with pilot plant studies to indicate a group

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[1] Panther Creek Southern Bentonite, American Colloid Co., Merchandise Mart Plaza, Chicago 54, Illinois.

[2] Filter aids, Johns-Mansville Corporation, New York, N. Y.

Table 1. Summary of constant factors in pilot filter runs

Set no.	Run no.	Speed of mixing	Average clay conc. mg/1	Average body feed conc. mg/1	Rate of flow gsfm
1	9 through 20	slow	12.0	38	1.0
2	24 through 40	rapid	26.0	50	0.5
-	41	rapid	17.1	25.4	1.0
-	42	slow	16.1	28.5	1.0

of filter runs. The word "series" is used in connection with bench scale studies (Table 3).

Slow mixing used in the first set of runs consisted of mixing raw water with the coagulant in the slow speed mix tank previously described. Rapid mixing was accomplished in the high speed mix tank previously described. An attempt was made to keep the clay concentration and the body feed concentration in the raw water at constant level during each set of filter runs. However, it was not always possible to arrive at a particular clay concentration or body feed concentration due to some of the inadequacies of the measurement procedure and the equipment used. Thus an average value of clay concentration and body feed concentration used in each set of filter runs are shown in Table 1. Clay concentration of the raw water and the body feed levels used in each run are shown in Table 3.

The bench scale studies were planned to evaluate the effect of several coagulation variables including speed of mixing, clay concentration, pH, and dissolved solids concentration in the water. These variables were studied using membrane filter tests, electrophoretic measurements and jar tests.

Fifteen series of bench scale studies were conducted. Table 2 summarizes the magnitude of the constant factors for each series of tests. Series 1 through 3 were conducted to study the effect of mixing speed; Series 2,4 through 8, and 12 to study the effect of clay concentration; Series 5,8 through 11, and 13 to study the effect of pH; while Series 14 and 15 were carried out to determine the differences between the effect of holding the pH constant and letting it vary during coagulation of water containing clay minerals and small amounts of dissolved solids.

Table 2. Summary of constant factors in bench scale tests

Series no.	Clay conc. (mg/l)	pH	Mixing for filtration and mobility expts. Speed (rpm)	Time (min)	Suspension volume filtered (ml)	Filtrate volume refiltered (ml)	Pressure difference inches of Hg, vacuum	Per cent tap water in suspension
1	25	7.0	100	15	200	100	10	0
2	25	7.0	1000	15	200	100	10	0
3	25	7.0	3000	15	200	100	10	0
4	50	7.0	1000	15	200	100	10	0
5	100	7.0	1000	15	100	50	10	0
6	150	7.0	1000	15	100	50	10	0
7	200	7.0	1000	15	100	50	10	0
8	100	3.5	1000	15	100	50	10	0
9	100	10.0	1000	15	100	50	10	0
10	100	4.1	1000	15	100	50	10	0
11	100	5.5	1000	15	100	--[a]	10	0
12	200	3.5	1000	15	100	--[a]	10	0
13	100	8.5	1000	15	100	--[a]	10	0
14	100	varying	1000	15	100	--[a]	10	12.5
15	100	7.3	1000	15	100	--[a]	10	12.5

[a] This test was not conducted in this series.

RESULTS AND INTERPRETATIONS

Pilot Plant Studies

Pilot filter runs

A summary of the pilot plant runs conducted during the period from April 2, 1966, to September 30, 1966, is reported in chronological order in Table 3. Numbers missing in the table are of the trial runs which are of no consequence to the results of this study. Table 3 presents clay concentration of the raw water, body feed concentration, alum concentration, starting time of alum feed, β-indices for cakes without and with alum, and per cent change in β-index resulting from alum addition. The clay concentration in the filter effluent is not shown in the table since, whether alum was added or not, the effluent turbidity was always lower than the university tap water turbidity. However, in a few filter runs, addition of alum was noted to result in a slight improvement in the quality of the effluent water as compared with the results without alum addition.

A plot of per cent change in the β-index versus alum concentration for runs 9 through 20 is shown in Figure 12. The clay concentration used in these runs averaged 12.0 mg/l. The slow speed mix tank was utilized for mixing the alum feed with the clay in raw water. Precipitation of aluminum hydroxide was noticed at alum concentration levels as low as 3.0 mg/l. The β-indices were noted to be increased for an alum addition greater than 3 mg/l (Figure 12). Since high-speed mixing had been found favorable for alum coagulation by previous researchers (32), the high-

Table 3. Summary of pilot filter runs

Run no.	Conc. of clay (mg/l)	Body feed conc. (mg/l)	Alum conc. (mg/l)	Starting time of alum feed (min)	β-index x 10^{-4} without alum (ft^{-2})	β-index x 10^{-4} with alum (ft^{-2})	Change in β-index (%)
9	14.3	36.0	1.0	150	5,186	5,419	+ 4.5
10	12.3	35.6	3.0	105	3,579	3,377	- 5.65
11	13.3	37.6	7.0	105	3,445	7,371	+114.0
12	11.5	41.0	4.0	150	3,006	6,651	+121.0
13	11.8	37.0	2.0	90	3,187	2,328	- 27.0
14	11.8	38.6	2.5	90	3,030	2,240	- 26.0
15	10.8	38.0	0.0		2,227	2,049	- 7.9
16	12.5	38.7	1.5	105	2,489	2,307	- 7.3
17	12.9	46.6	2.0	105	2,488	1,895	- 23.8
18	14.0	46.6	2.0	105	2,052	1,661	- 19.1
19	11.0	42.6	0.0		1,569	1,370	- 12.7
20	12.8	29.8	2.0	105	6,415	5,463	- 14.8
24	23.25	64.0	2.13	180	4,946	4,193	- 15.2
25	17.0	64.25	4.15	180	1,741	1,212	- 30.6

Table 3. (Continued)

Run no.	Conc. of clay (mg/1)	Body feed conc. (mg/1)	Alum conc. (mg/1)	Starting time of alum feed (min)	β-index x 10^{-4} without alum (ft^{-2})	β-index x 10^{-4} with alum (ft^{-2})	Change in β-index (%)
26[a]	26.1	0	4.15	67			
27[a]	26.1	0	0	67			
28	28.5	61.3	6.82	180	13,320	8,214	- 38.3
29[b]			11.4	180			
30	27.1	46.0	11.4	160	21,660	11,790	- 45.6
31	25.5	43.5	22.8	160	19,340	11,240	- 41.9
32	26.6	47.3	114.0	160	18,430	31,440	+ 70.6
33	26.2	49.2	6.73	140	24,140	13,060	- 45.9
34	30.2	50.0	6.48	120	37,520	29,360	- 18.6
35	27.8	48.8	0.0	140	20,660	28,260	+ 36.4
36	25.6	49.6	3.39	140	22,640	25,250	+ 11.5

---

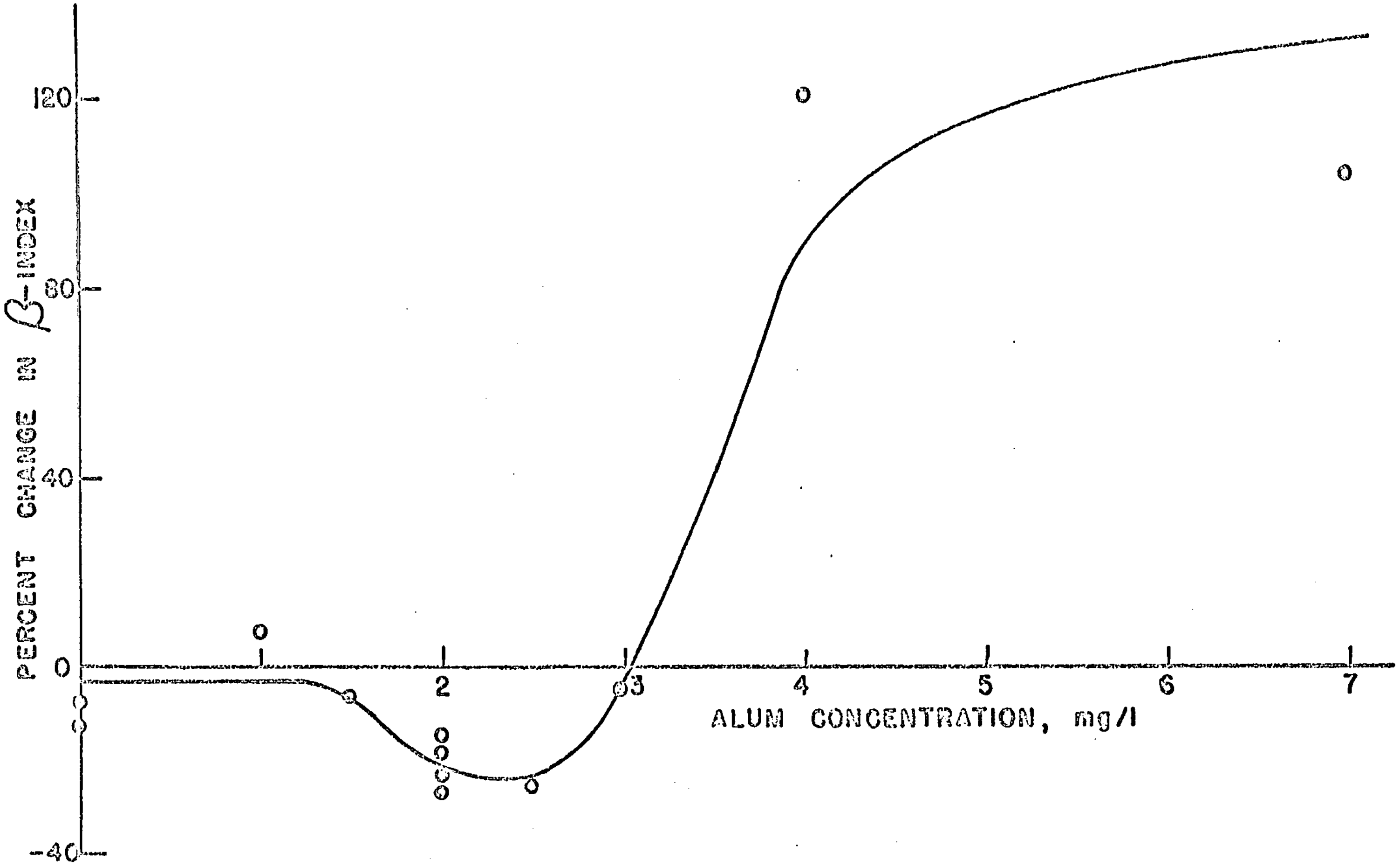
[a] Cracks developed in filter cakes.

[b] Discontinued due to mechanical failure.

Table 3. (Continued)

Run no.	Conc. of clay (mg/l)	Body feed conc. (mg/l)	Alum conc. (mg/l)	Starting time of alum feed (min)	β-index x 10^{-4} without alum (ft^{-2})	β-index x 10^{-4} with alum (ft^{-2})	Change in β-index (%)
37	24.0	52.8	16.3	160	13,420	7,963	- 40.7
38	24.9	54.4	45.0	160	12,840	17,960	+ 39.9
39	23.6	47.2	5.0	140	12,350	8,483	- 31.3
40	23.1	48.1	30.0	160	17,310	17,160	- 0.9
41	17.1	25.4	8.9	95	19,370	17,800	- 8.1
42	16.1	28.5	8.9	100	13,730	17,750	+ 29.7

Figure 12. Effect of alum concentration on diatomite filter cake resistance for filter runs in Set no. 1, Table 1


PERCENT CHANGE IN β-INDEX
120
80
40
0
-40
2
3
4
5
6
7
ALUM CONCENTRATION, mg/l

speed mixer was used in subsequent filter runs.

An inspection of Figure 12 would reveal that the largest decrease in the β-index of 27 per cent occurred when the alum concentration was 2.0 mg/l. At that alum concentration, the per cent decrease in β-index varied from 15 to 27 from run to run. Thus the effect of alum on filter cake resistance was neither convincing nor very significant considering a decrease of 8 and 13 per cent occurred at zero alum concentration. The reason for such a small effect may have been, besides the low mixing speed, the low clay concentrations used in runs 9 through 20. In the subsequent runs the clay concentration was increased to a higher value, about 25.0 mg/l. However, to accomplish this increase in clay concentration the rate of flow had to be reduced from 1.0 gsfm to 0.5 gsfm because of the fact that exceedingly large quantities of clay slurry would have had to be prepared to be able to maintain higher clay concentrations at higher flow rates.

The second set of filter runs, 24 through 40, are also summarized in Table 3. Different alum concentrations were used in the various filter runs of this set, from 0 to 114 mg/l. Clay concentration and body feed concentration were held relatively constant at 25.0 mg/l and 50 mg/l respectively. A plot of head loss in inches of mercury versus time was prepared during the run and the per cent change in the slope of the line and of the β-index as a result of the start of alum addition was determined. These per cent changes are plotted against the alum concentration used in each of the runs (Figures 13 and 14). In both Set no. 1 and Set no. 2, one or two filter runs were conducted without adding any alum during the entire run. The head loss-time curve was essentially linear in Set

Figure 13. Effect of alum concentration on the slope of the head loss-time relationship for filter runs in Set no. 2, Table 1

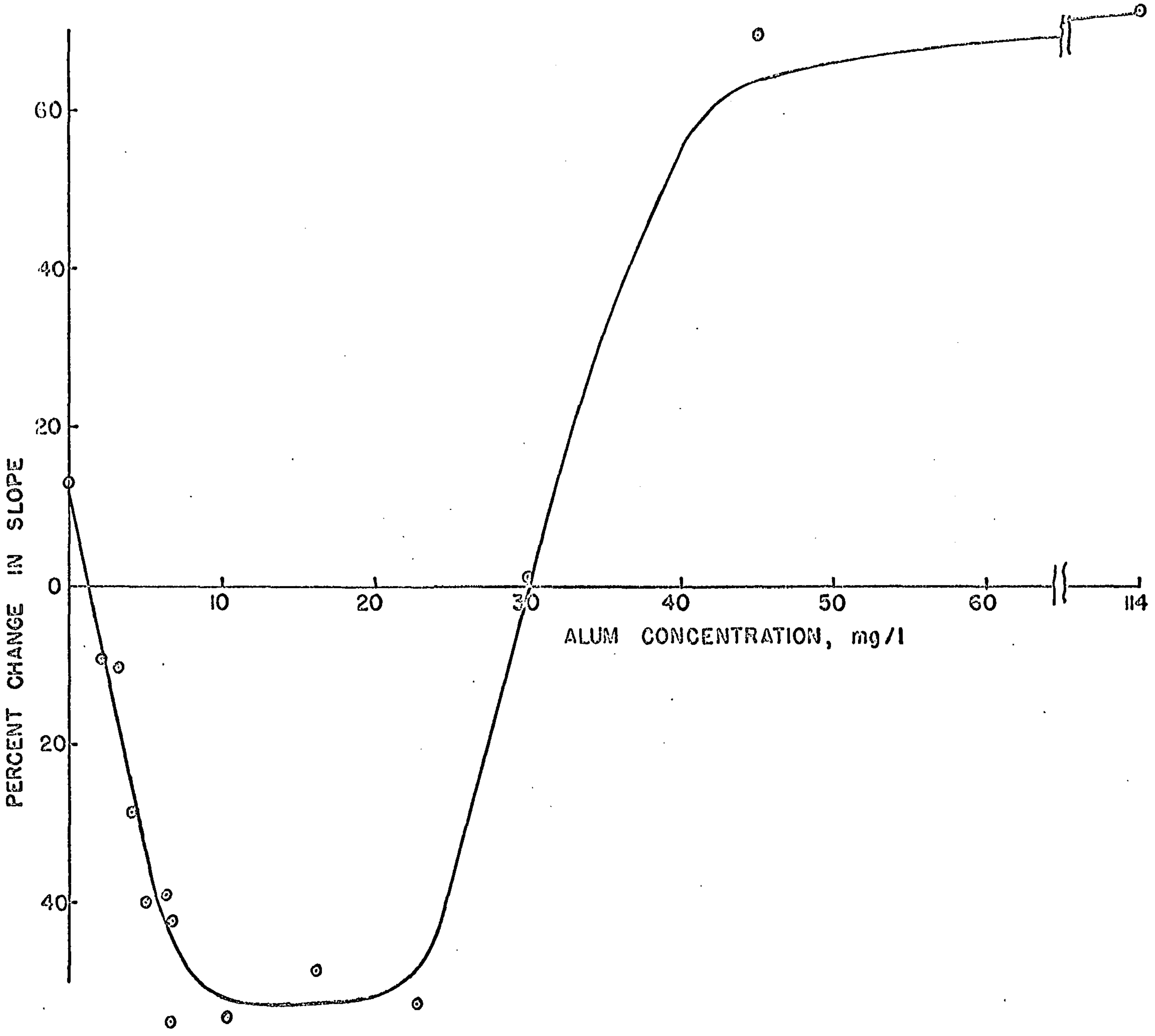
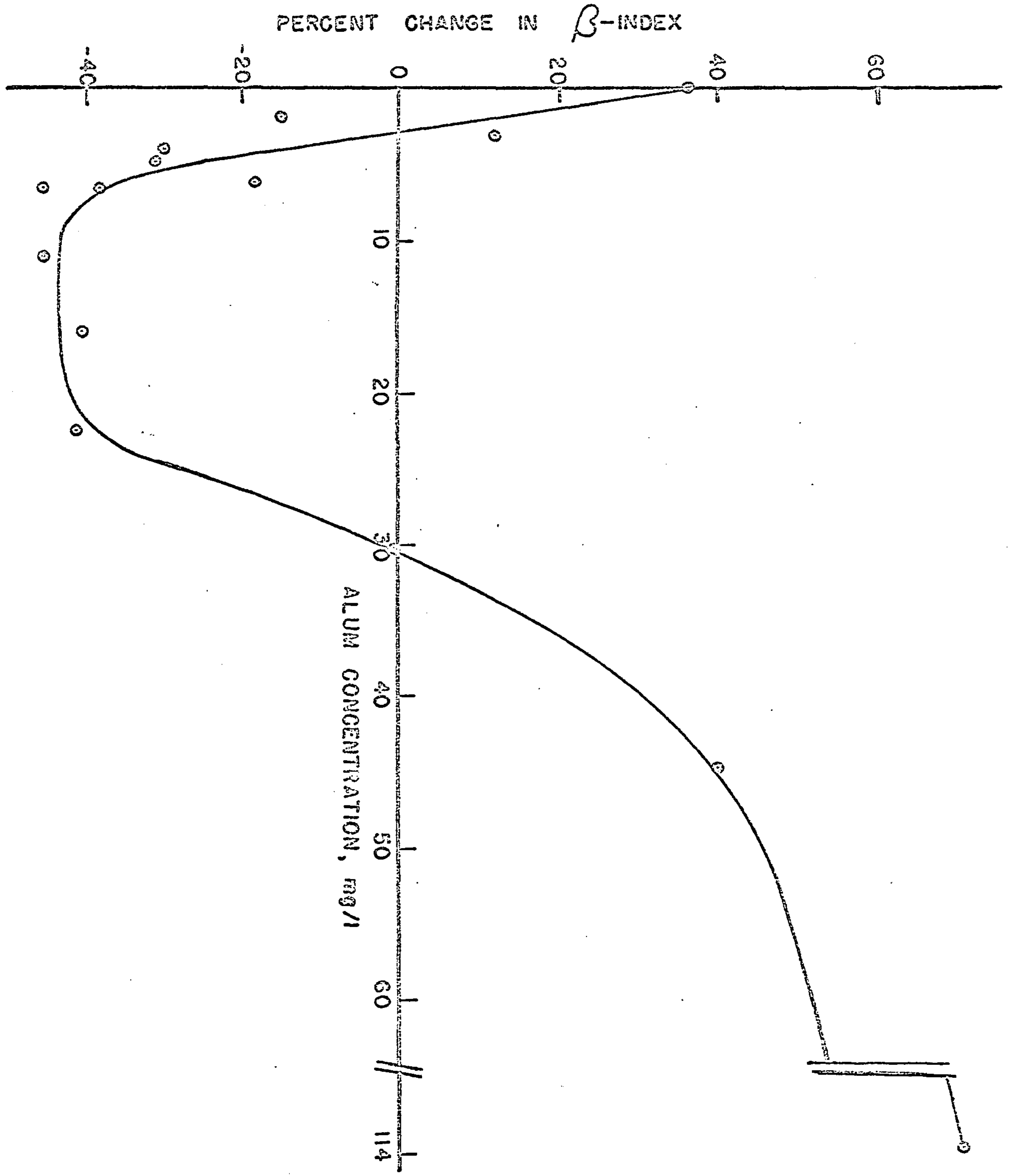

PERCENT CHANGE IN SLOPE
60
40
20
0
20
40
ALUM CONCENTRATION, mg/l
10
20
30
40
50
60
114

Figure 14. Effect of alum concentration on the diatomite filter cake resistance for filter runs of Set no. 2, Table 1


PERCENT CHANGE IN β-INDEX
-40
-20
0
20
40
60
10
20
30
40
50
60
114
ALUM CONCENTRATION, mg/l

no. 1, but showed a slight upward trend in Set no. 2. This was due to the low body feed levels which were used in the second set of runs. By dividing the run into two parts at an assumed time, the slopes and the β-indices of both parts of each run were calculated. The per cent changes in slope and β-index were noted as due to the addition of 0.0 mg/l of alum (Figures 12, 13, and 14).

Figures 13 and 14 differ significantly in actual values of per cent change. However, as expected, the trend of both the curves show a good similarity since the slope of the head loss line is actually a fairly reasonable indicator of the β-index.

Figure 14 shows that an addition of 10 mg/l of alum to the raw water results in a decrease in β-index of about 45 per cent. At alum concentrations lower than 10 mg/l, the change in filter cake resistance was lower than 45 per cent meaning that insufficient alum was present during these runs. The per cent reduction in the β-index shows a plateau at 45 per cent for alum concentrations between 10 mg/l and 23 mg/l. This leveling off may be attributed to the limitation of the accuracy of measuring instruments. The per cent change in the β-index steadily diminishes as the alum concentration is increased to greater levels than 23 mg/l, reaching the zero value at 30 mg/l and a high positive value of 72 per cent at 114.0 mg/l.

Runs 41 and 42 were conducted using clay and body feed concentrations, and rates of filtration closer to those used in the first set of filter runs (Table 1). The high-speed mix system was used in run 41 while the slow-speed system was used in run 42. Alum was fed at the same rate of 8.9 mg/l during both runs. As indicated in Table 3, the change in the β-index due to alum addition was -8 per cent in run 41 and was +29 per cent in run 42. This means that the high-speed mix system was better suited for the process of diatomite filtration after coagulation than the slow-speed mix system. However, it is not possible to compare the speeds of mixing and arrive at a required speed for effective reduction in cake resistance, since the speeds in these two systems were 24 rpm and 1780 rpm and the paddles differed from each other drastically. The speed of mixing was included as a factor to be investigated in the bench scale studies.

Concurrent bench scale observations

In order to find a method of predicting the optimum alum concentration as well as the general effect of alum on coagulation without conducting pilot filter runs, membrane filtration tests were conducted in conjunction with the pilot filter runs.

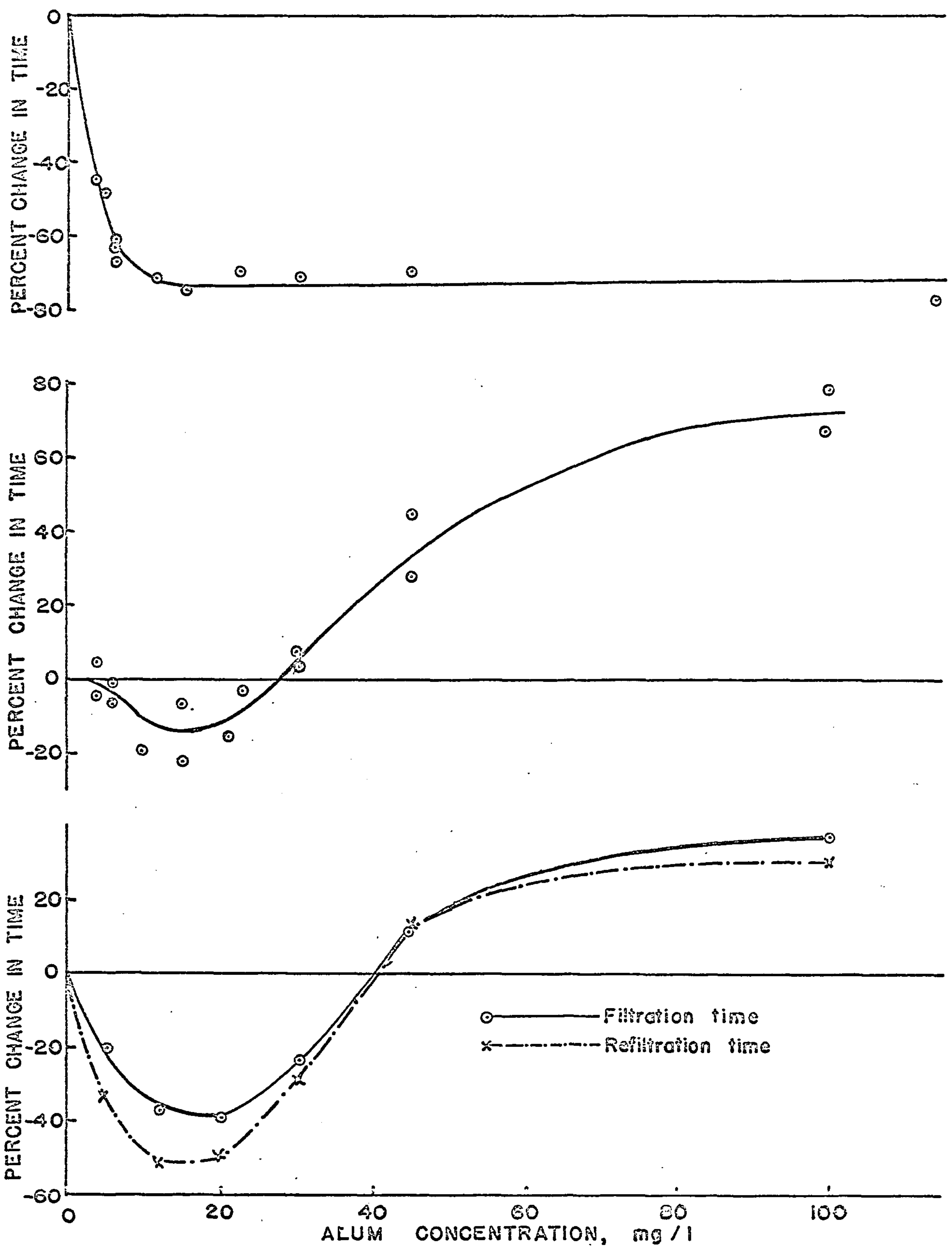
Two samples of water, one before and one after it entered the coagulation mix tank, were taken during each of the second set of pilot plant runs. Two fifty-ml samples were filtered through the membrane filters of pore size 0.45 μ at a pressure difference of 25.0 inches of mercury and the times of filtration were recorded. The sample taken before the water entered the mix tank contained no alum and the other sample contained the clay treated with the alum fed to the tank. The per cent changes in filtration time were calculated for each run and they were plotted against the alum concentration in raw water (Figure 15a). Figures 14 and 15a differ drastically at alum concentrations higher than 23 mg/1.

Figure 15. Results of bench scale filtration tests conducted concurrently with pilot filter runs of Set no. 2

a. Effect of alum concentration on filtration time of clay suspensions

b. Effect of alum concentration on filtration time for suspensions containing clay and diatomite

c. Effect of alum concentration on filtration time and refiltration time for suspensions mixed for longer time


PERCENT CHANGE IN TIME
0
-20
-40
-60
-80
PERCENT CHANGE IN TIME
80
60
40
20
0
-20
PERCENT CHANGE IN TIME
20
0
-20
-40
-60
Filtration time
Refiltration time
0
20
40
60
80
100
ALUM CONCENTRATION, mg / l

The reasons for this were investigated separately by conducting bench scale tests. Possible reasons included: the absence of diatomite body feed in filtration time tests, and the fact that samples were filtered without any slow mixing which the water would receive in the pilot plant during its detention in the filter housing and the piping.

In an attempt to evaluate which of the reasons was more important, filtration time tests were conducted in which the suspended solids sample after being treated with alum were mixed with fine diatomite particles. The diatomite was obtained by dispersing Hyflo Super-Cel, settling for two hours and decanting the diatomite in the supernatant. The samples were filtered through membrane filters. A pressure difference of 10 inches of mercury was used during these tests since in the presence of diatomite, higher pressure difference resulted in too small filtration times to be differentiated between each level of alum. The results of this series were plotted in the same way as before (Figure 15b). It can be seen that in the presence of diatomite, the filtration time shows a trend of decreasing and then increasing, although not comparable to the magnitude of the values shown in Figure 14.

Additional filtration time tests were conducted in which no diatomite was used but additional mixing time was provided. The suspended solids sample was mixed rapidly with alum for 10 minutes and slowly for another 10 minutes. These mixing times were selected because they were about equal to the detention time of the raw water in the coagulation tank and then in the filter housing. Samples treated with different alum doses were filtered and a plot similar to Figure 14 was prepared (Figure 15c). The refiltration time of the filtrate in each test was also measured and this was included in the plot. A comparison of Figures 14 and 15 is presented in the next section.

A jar test was conducted in conjunction with the second set of pilot plant runs and an alum concentration of 15 mg/l was found by visual observation of the floc formation to be the optimum concentration. This concentration lies in the middle of the optimum range of alum concentration found for filtration. However, the flocs formed with alum at and greater than the optimum level of 15 mg/l did not show very good settling characteristics, i.e., a significant amount of floc particles was seen in the supernatant after 30 minutes of settling. This may have been due to the fact that the clay concentration used was only 25 mg/l. This may not have resulted in an adequate density of floc.

A few electrophoretic measurements were made in conjunction with some of the second set of pilot filter runs on a trial basis to gain practice with the use of electrophoretic equipment. The data collected are not presented here. However, it should be mentioned that the particles were found to have the negative charge regardless of the amount of alum added up to 114.0 mg/l. Higher alum concentrations were not attempted in the pilot plant runs. This may mean that the increase in the β-index due to alum concentrations of 45 mg/l and 114 mg/l (Figure 14) was not due to restabilization induced by any charge reversal. It may have been only due to the precipitation of alum added in excess of the required amount. However, such conclusions cannot be verified as a result of this part of the study alone due to insufficient data.

Comparison of pilot filter runs and membrane filtration tests

The change in β-index with alum concentration observed in the pilot filter runs (Figure 14) does not correlate with the change in filtration times shown in Figures 15a and 15b. The trend of change in filtration time and refiltration time with alum concentration shown in Figure 15c coincides well with the trend noted in the pilot filter runs (Figure 14). The optimums indicated in Figures 14 and 15c are similar.

Thus the filtration time or refiltration time measurements can be used to predict the optimum alum concentrations required for a suspension to be filtered through the diatomite filters. The absence of diatomite in the membrane filtration tests does not interfere with the effect of coagulation of clay with alum on the filter cake resistance or the ability to predict the optimum alum dose by membrane filtration tests. The bench scale studies which follow were planned on the basis of this observation, i.e., without using any diatomite for the membrane filtration tests.

Bench Scale Studies

A summary of results obtained in the bench scale studies is presented in Table 4. The optimum alum concentration as predicted by different tests, and the electrophoretic mobility at these optimum alum concentrations for each series of tests are shown in the table. The series were numbered in the order in which they were conducted from November 14, 1966, to February 16, 1967. Due to physical limitations, the filtration tests, electrophoretic measurements, and jar tests were not carried out simultaneously, but in the order in which they are

Table 4. Summary of results of bench scale studies

Series no.	Clay conc. (mg/l)	pH	Mix speed (rpm)	Optimum alum conc. (mg/l)			Alum conc. for zero mobility (mg/l)	Mobility at optimum conc. $\frac{\mu \cdot cm}{volt \cdot sec}$	
				Filtration	Refiltration	Jar test		Filtration	Settling
1	25	7.0	100	16	16	10	--[a]	--[a]	--[a]
2	25	7.0	1000	13	13	--[a]	21	-1.5	-1.78
3	25	7.0	3000	13	13	--[a]	--[a]	--[a]	--[a]
4	50	7.0	1000	26	26	22	42	-1.35	-1.46
5	100	7.0	1000	52.5	52.5	30	--[b]	-1.30	-1.48
6	150	7.0	1000	78.5	78.5	30	--[b]	-0.94	-1.56
7	200	7.0	1000	105	105	32	--[b]	-1.0	-1.46
8	100	3.5	1000	8.0	8.0	8.0	80	-0.53	-0.53
9	100	10.0	1000	1095	1095	500	--[b]	-2.30	-2.53
10	100	4.1	1000	20.0	20.0	20.0	160	-0.27	-0.27
11	100	5.5	1000	40.0	--[a]	20.0	60	-0.45	-0.92
12	200	3.5	1000	16.0	--[a]	16.0	240	-0.64	-0.64
13	100	8.5	1000	100.0	--[a]	60.0	--[b]	-2.34	-2.44
14	100	varying	1000	60.0	--[a]	25.0	68	-0.26	-0.74
15	100	7.3	1000	60.0	--[a]	25.0	--[b]	-0.66	-0.815

[a] Corresponding test was not conducted.

[b] Zero mobility was never reached.

mentioned above.

Speed of mixing

The mixing speeds used during the first three series were 100, 1000 and 3000 rpm respectively. The mixing was done for a constant period of 15 minutes after adding the alum during each test. The suspension containing 25 mg/l of clay was prepared by mixing concentrated clay slurry and distilled water. This low clay concentration was selected to determine the effect of mixing since the interparticle distance would be larger. Thus, the mixing would be more beneficial in bringing the coagulant closer to the clay, and clay particles themselves closer to each other. The pH of the suspension was adjusted to a constant level of 7.0. The filtration times and refiltration times of the suspensions were measured for alum concentrations varying from 0 to 105 mg/l during each series.

The filtration and refiltration times for different alum levels of all three series are shown in Figures 16 and 17. The same optimum alum concentrations were indicated by both types of measurements. It can be seen from the figures that the optimum was 16 mg/l for 100 rpm and 13 mg/l for 1000 and 3000 rpm. Neither the filtration time curves nor the refiltration time curves show any drastic differences between the different speeds of mixing. The trend is, however, evident in that the optimum range of alum concentration somewhat widens out as the speed of mixing is increased. Visual observations of the alum-treated suspensions before filtration revealed that the floc produced at greater than optimum alum concentration was of a bigger size at lower speeds than at higher speeds. No visual difference was apparent in suspensions prepared at different

Figure 16. Effect of mixing speed and alum concentration on filtration time (Series no. 1, 2, and 3)

clay concentration = 25 mg/1
pH = 7.0

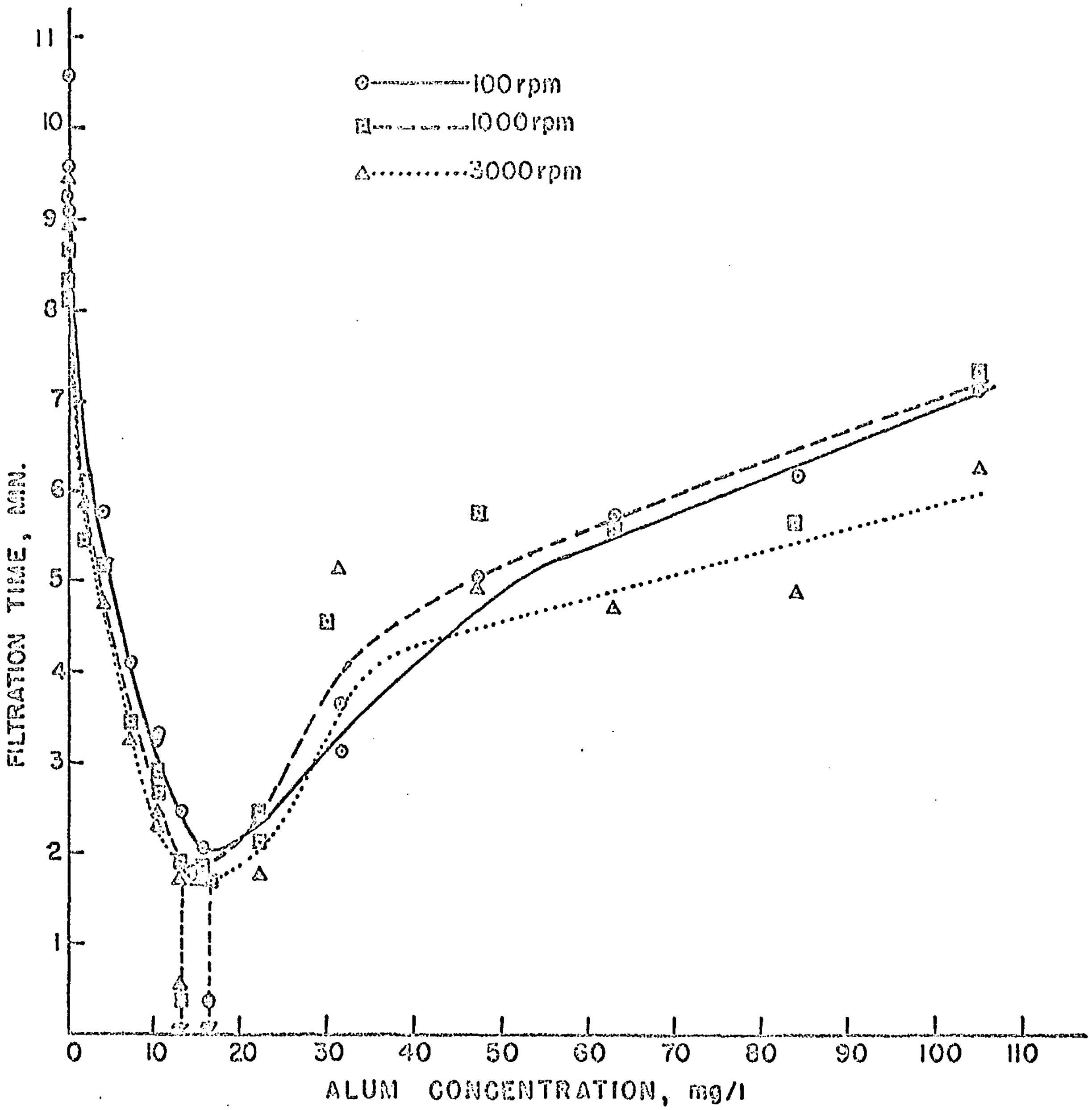
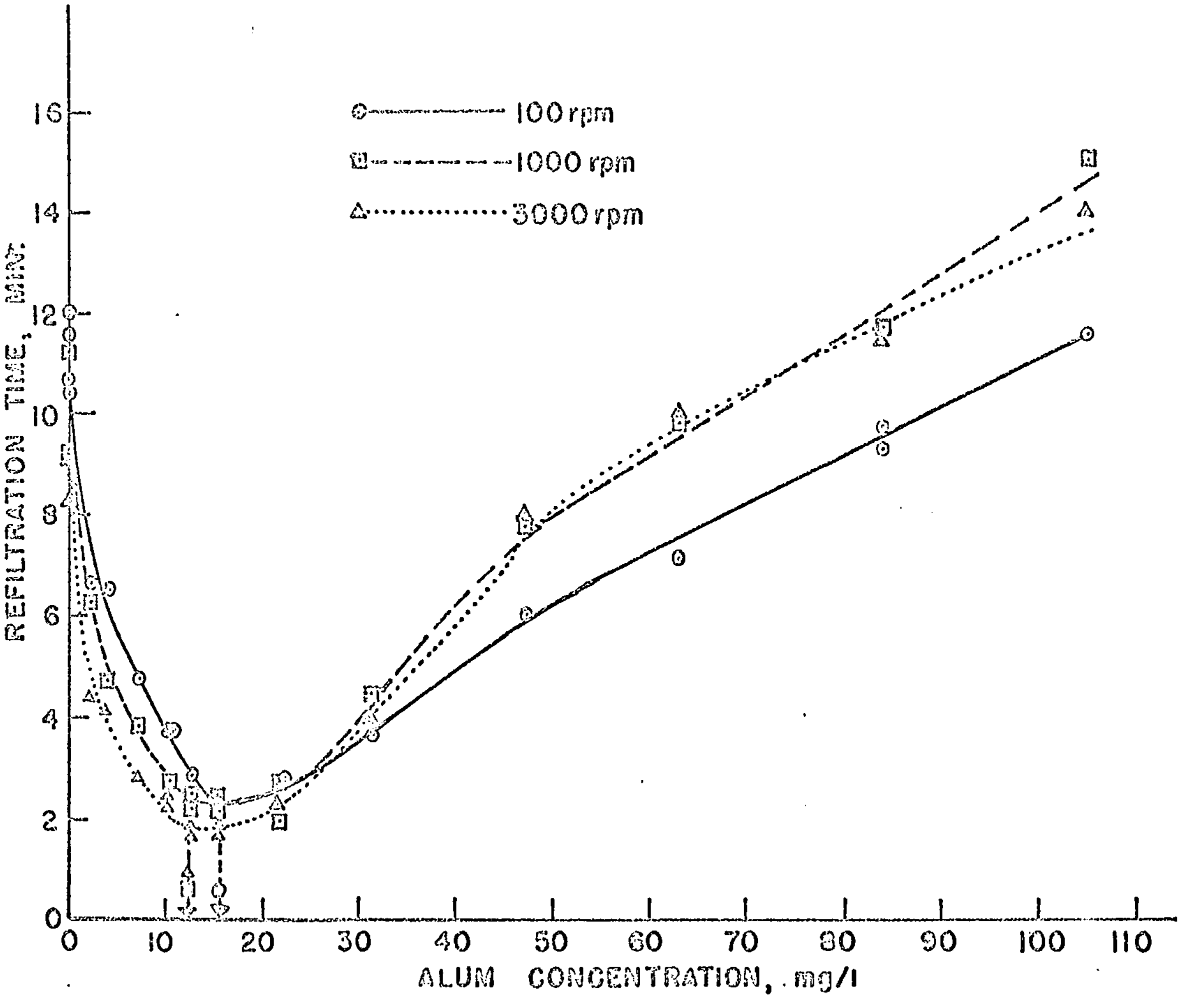

100 rpm
1000 rpm
3000 rpm
FILTRATION TIME, MIN.
11
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
110
ALUM CONCENTRATION, mg/l

Figure 17. Effect of mixing speed and alum concentration on refiltration time (Series no. 1, 2, and 3)

clay concentration = 25 mg/1
pH = 7.0


100 rpm
1000 rpm
3000 rpm
REFILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
0
10
20
30
40
50
60
70
80
90
100
110
ALUM CONCENTRATION, mg/l

speeds when the alum concentration was closer to or less than the optimum level.

It should not be concluded as a result of this study that the effect of high speeds of mixing in general is not very significant. The system used in this study might have been such that even a speed of 100 rpm was capable of getting the coagulant and clay particles close to each other. In an actual plant or in another system of mixing this may not be true. Since the optimum was shifted to a slightly lower value with a speed of mixing of 1000 rpm than with 100 rpm, all subsequent filtration tests were conducted using 1000 rpm.

The results shown in Figure 15a are somewhat different than those in Figure 16. These experiments differ in the type of mixing equipment used. The mixing in the pilot filter rapid mix tank appeared much more violent than in the bench scale mixing system. This may have been the cause of the observed differences.

Jar tests were conducted only at the maximum available speed of the apparatus, 100 rpm. All electrophoretic mobility experiments were conducted only with speed of mixing of 1000 rpm, since the filtration time data showed only small changes with speed of mixing. Therefore, it was expected that electrophoretic measurements would not reveal any significant differences at other mixing speeds.

Clay concentration

The concentration of clay in suspension used in Series 2 and 4 through 7 was 25, 50, 100, 150, and 200 mg/1 respectively. The pH was kept at a constant level of 7.0 in these five series. A speed of mixing of 1000 rpm for 15 minutes was used in the filtration and electrophoretic tests.

Plots have been prepared showing the variation of filtration time, refiltration time, electrophoretic mobility, and the turbidity remaining in the supernatant of the jar tests with alum concentration used in each series. Such plots for Series 2, 4, 5, 6, and 7 are shown in Figures 18 through 22, respectively. Filtration time and refiltration time show a recognizable minimum corresponding to an alum dose in all curves. This alum dose is termed as the optimum alum concentration for the process of filtration.

Turbidity remaining in the supernatant in jar tests is plotted against the alum concentration used in each jar. The turbidity curve shows a steep variation reaching a low value for a particular alum dose and then levels off for higher alum concentration. This steep part of the curve is extended to the zero turbidity value and the corresponding alum concentration is selected as the optimum level for settling.

The electrophoretic mobility at 25° C is also plotted against the alum concentration used in each series. The alum needed to reach zero mobility or, in other words, the isoelectric point is determined from the curve if it reaches that level. Also, the mobility values at optimum alum concentrations for filtration and settling can also be noted from the mobility curves.

These optimum alum doses and the corresponding mobility values are all shown in Table 4. From the values shown in the table, a stoichiometric relationship is evident between the optimum alum concentration for filtration and the clay concentration used in each series. However,

Figure 18. Effect of alum concentration on different parameters of coagulation (Series no. 2)

clay concentration = 25.0 mg/1
pH = 7.0

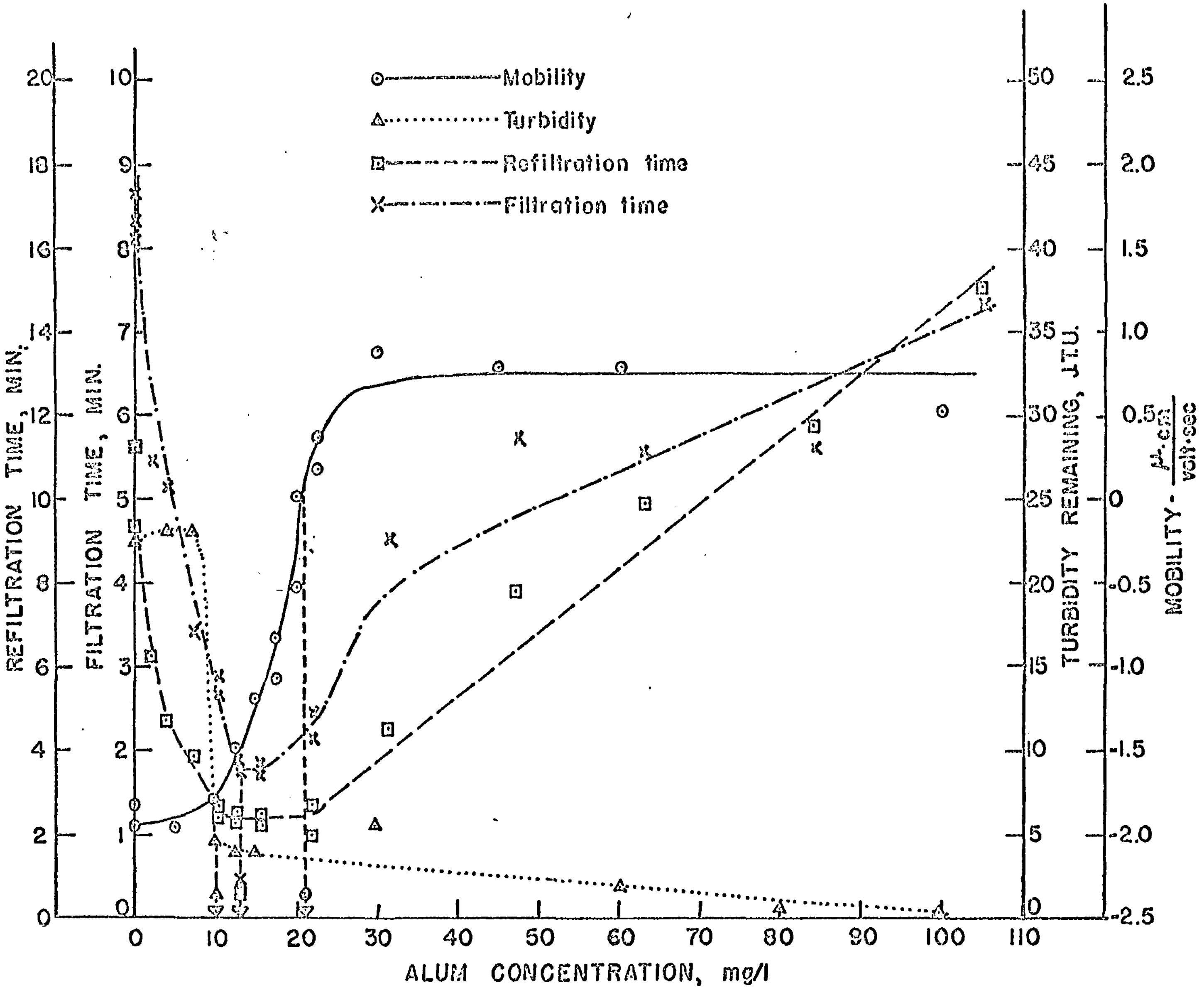

Mobility
Turbidify
Refiltration time
Filtration time
REFILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
20
FILTRATION TIME, MIN.
0
1
2
3
4
5
6
7
8
9
10
ALUM CONCENTRATION, mg/l
0
10
20
30
40
50
60
70
80
90
100
110
TURBIDITY REMAINING, J.T.U.
0
5
10
15
20
25
30
35
40
45
50
MOBILITY - μ·cm / volt·sec
-2.5
-2.0
-1.5
-1.0
-0.5
0
0.5
1.0
1.5
2.0
2.5

Figure 19. Effect of alum concentration on different parameters of coagulation (Series no. 4)

clay concentration = 50 mg/1
pH = 7.0

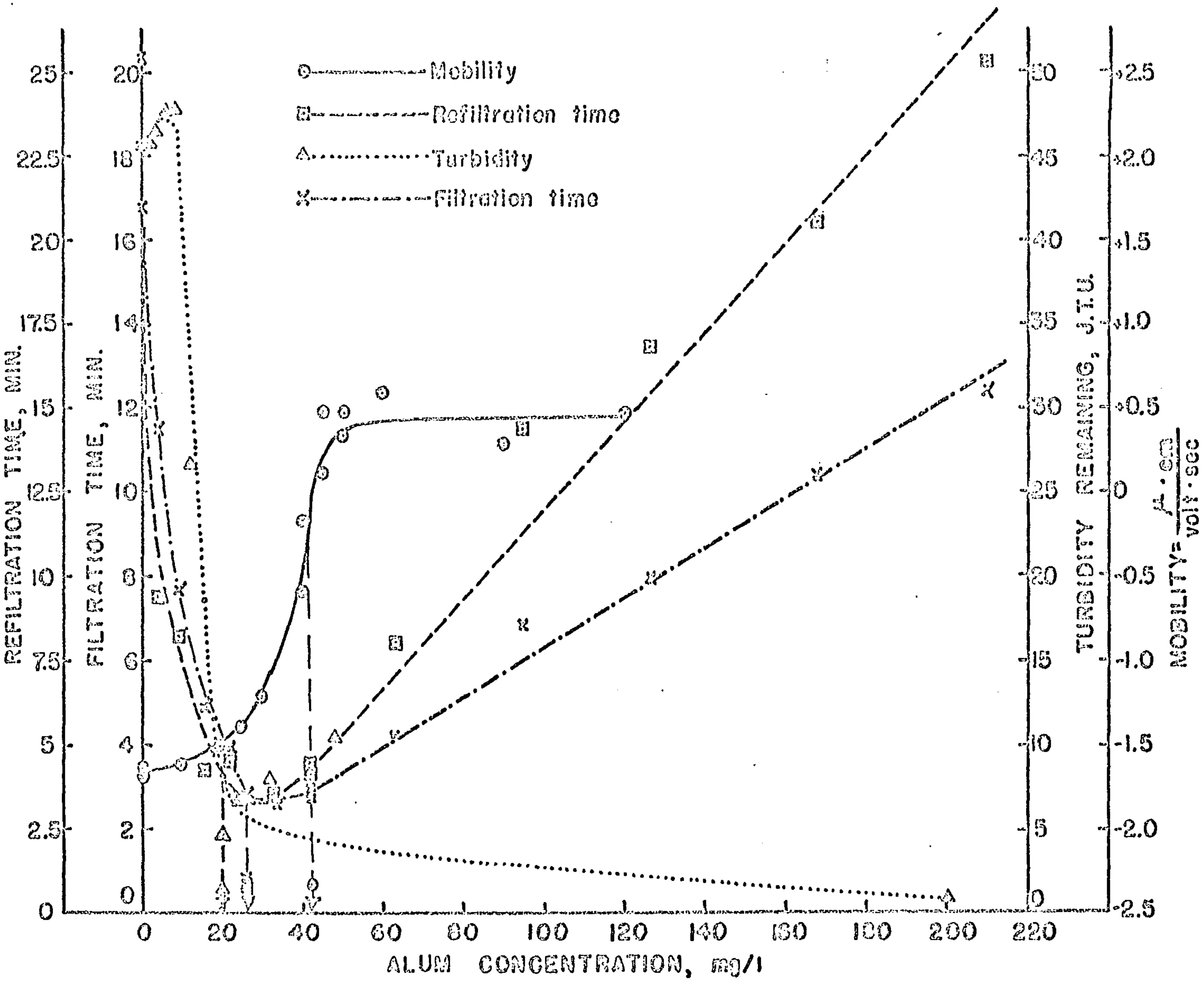

Mobility
Refiltration time
Turbidity
Filtration time
REFILTRATION TIME, MIN.
0
2.5
5
7.5
10
12.5
15
17.5
20
22.5
25
FILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
20
TURBIDITY REMAINING, J.T.U.
0
5
10
15
20
25
30
35
40
45
50
MOBILITY, $\frac{\mu \cdot cm}{volt \cdot sec}$
-2.5
-2.0
-1.5
-1.0
-0.5
0
+0.5
+1.0
+1.5
+2.0
+2.5
0
20
40
60
80
100
120
140
160
180
200
220
ALUM CONCENTRATION, mg/l

Figure 20. Effect of alum concentration on different parameters of coagulation (Series no. 5)

clay concentration = 100 mg/1
pH = 7.0

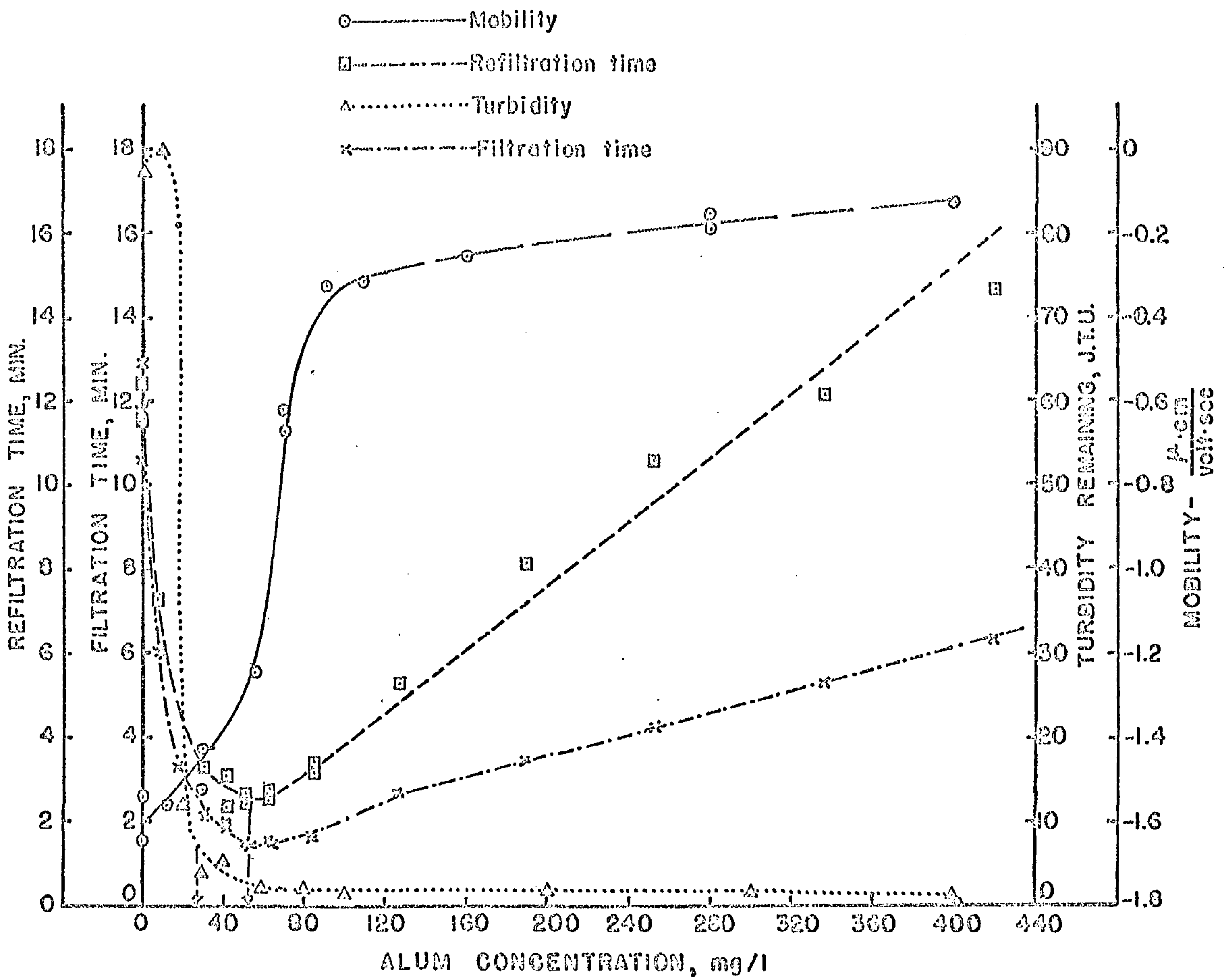

Mobility
Refiltration time
Turbidity
Filtration time
REFILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
FILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
TURBIDITY REMAINING, J.T.U.
0
10
20
30
40
50
60
70
80
90
MOBILITY- $\frac{\mu\cdot cm}{volt\cdot sec}$
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
0
40
80
120
160
200
240
280
320
360
400
440
ALUM CONCENTRATION, mg/l

Figure 21. Effect of alum concentration on different parameters of coagulation (Series no. 6)

clay concentration = 150 mg/1
pH = 7.0

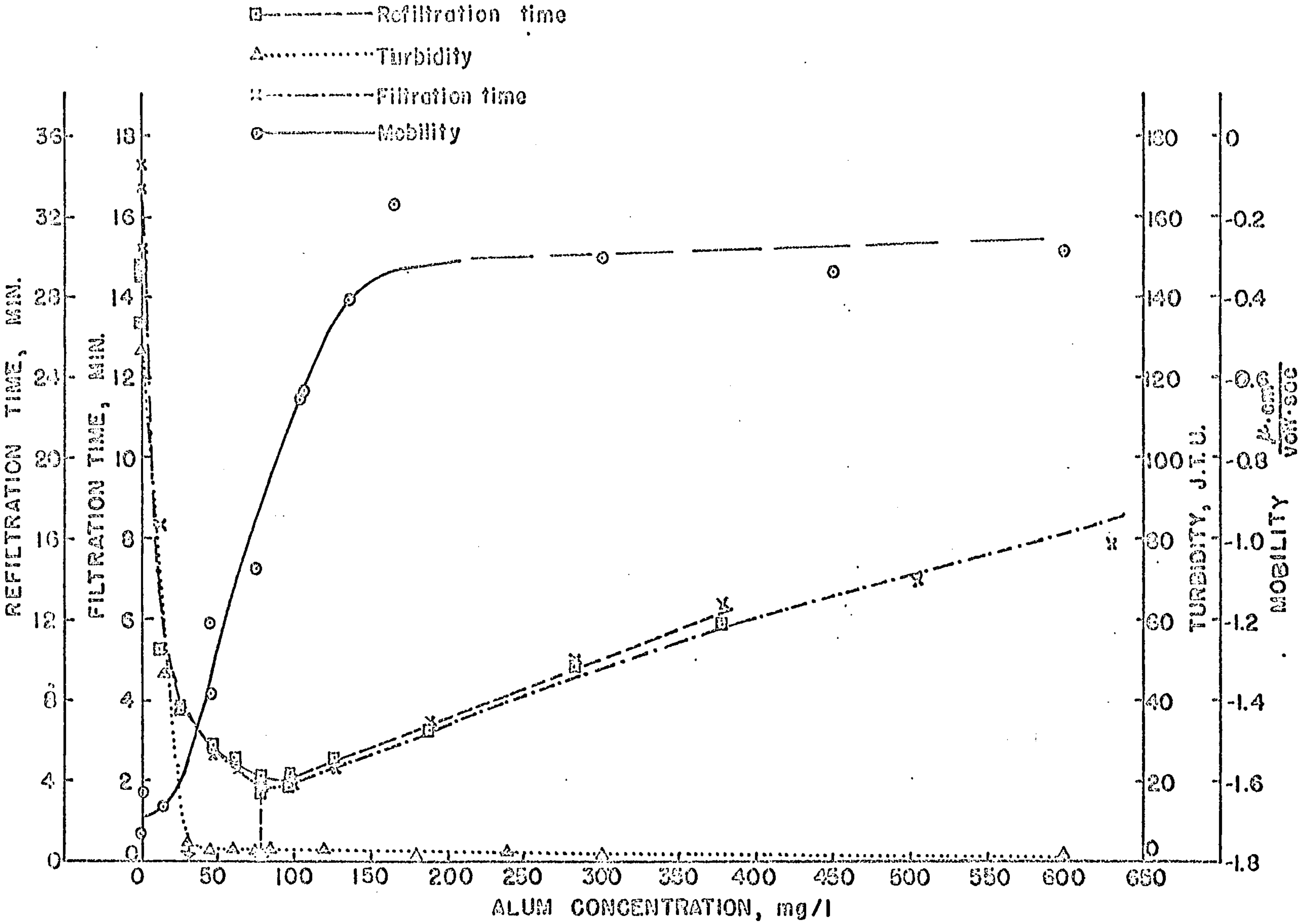
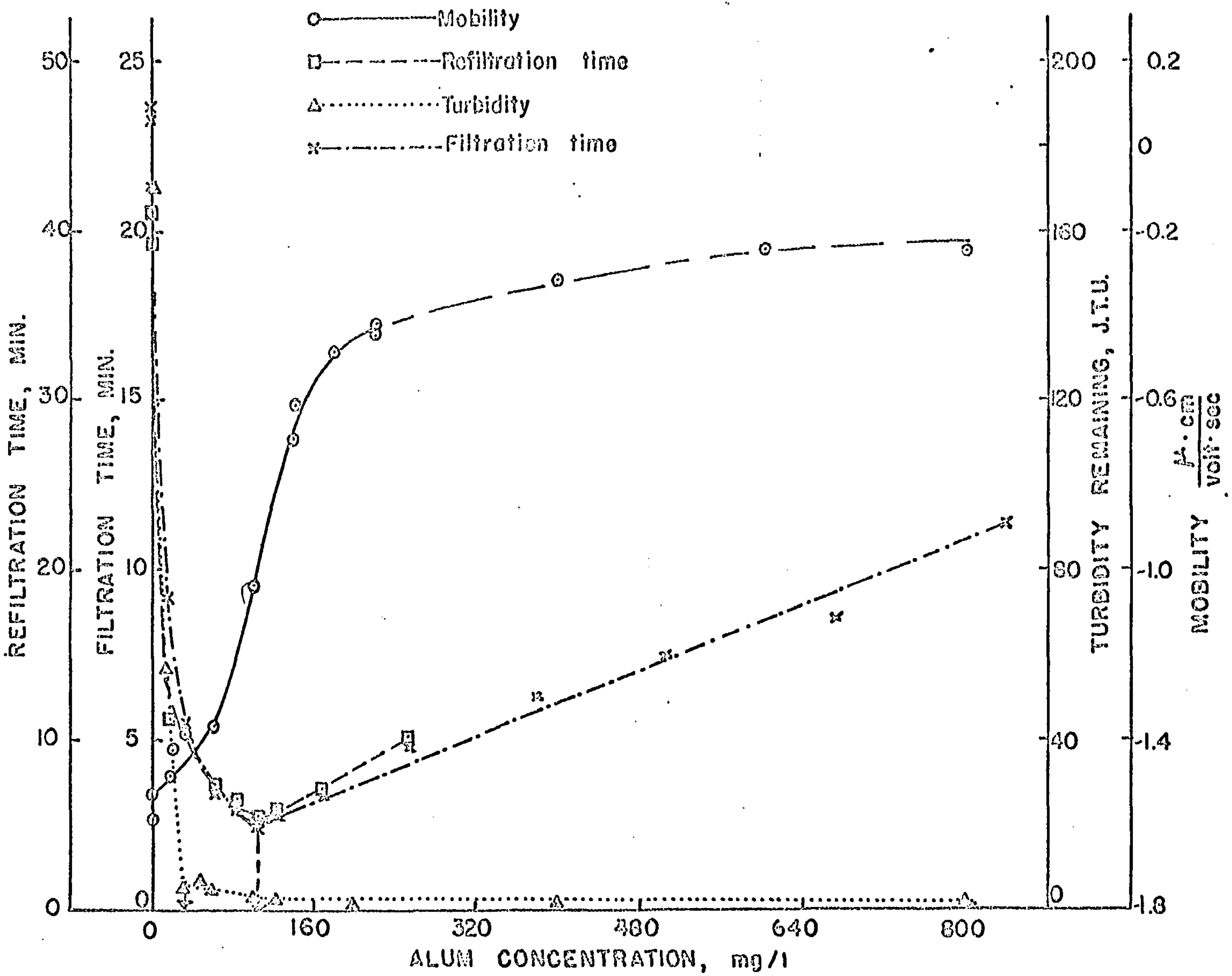

Refiltration time
Turbidity
Filtration time
Mobility
REFILTRATION TIME, MIN.
0
4
8
12
16
20
24
28
32
36
FILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
TURBIDITY, J.T.U.
0
20
40
60
80
100
120
140
160
180
MOBILITY $\frac{\mu \cdot cm}{volt \cdot sec}$
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
0
50
100
150
200
250
300
350
400
450
500
550
600
650
ALUM CONCENTRATION, mg/l

Figure 22. Effect of alum concentration on different parameters of coagulation (Series no. 7)

clay concentration = 200 mg/1
pH = 7.0


Mobility
Refiltration time
Turbidity
Filtration time
REFILTRATION TIME, MIN.
FILTRATION TIME, MIN.
TURBIDITY REMAINING, J.T.U.
MOBILITY $\frac{\mu \cdot cm}{volt \cdot sec}$
ALUM CONCENTRATION, mg/l
0
10
20
30
40
50
0
5
10
15
20
25
0
160
320
480
640
800
0
40
80
120
160
200
-1.8
-1.4
-1.0
-0.6
-0.2
0
0.2

no such relationship exists between the clay concentration and the optimum alum concentration for settling. This phenomenon will be discussed in detail in a later section of this chapter.

In Series 5, 6, and 7, when high alum concentrations, above 350 mg/l, were used, refiltration time measurements could not be conducted because the cake formed during the filtration step developed cracks when it was dewatered. This happened only at high alum concentrations where the cake was made up of excessive aluminum hydroxide precipitate. Such excessive precipitation also affected the mobility tests.

When high amounts of alum were added to clay suspensions of Series 5, 6, and 7, big floc particles were formed and these did not show any movement at all in the Brigg's cell when viewed through the microscope. Some floc were seen as big as 200 to 300 μ and they disappeared from focus because of settling. A few particles of smaller size were observed and timed, but these were by no means representative of average particles present in the water at these alum levels. Because of this, mobilities calculated for these tests are shown in dotted lines in Figures 20, 21, and 22. It can be noticed that the mobility curves in these figures did not reach or cross the isoelectric points, whereas in Figures 18 and 19, where clay concentrations were lower, the charge was reversed to the positive side. The significance of this will be interpreted in a later part of this chapter.

Series 8 and 12 were carried out with a constant pH of the suspension of 3.5. The clay concentration was 100 and 200 mg/l in Series 8 and 12 respectively. Mixing speed was 1000 rpm and mixing time was 15 minutes. The results of these two series are shown in Figures 23

Figure 23. Effect of alum concentration on different parameters of coagulation (Series no. 8)

clay concentration = 100 mg/1
pH = 3.5

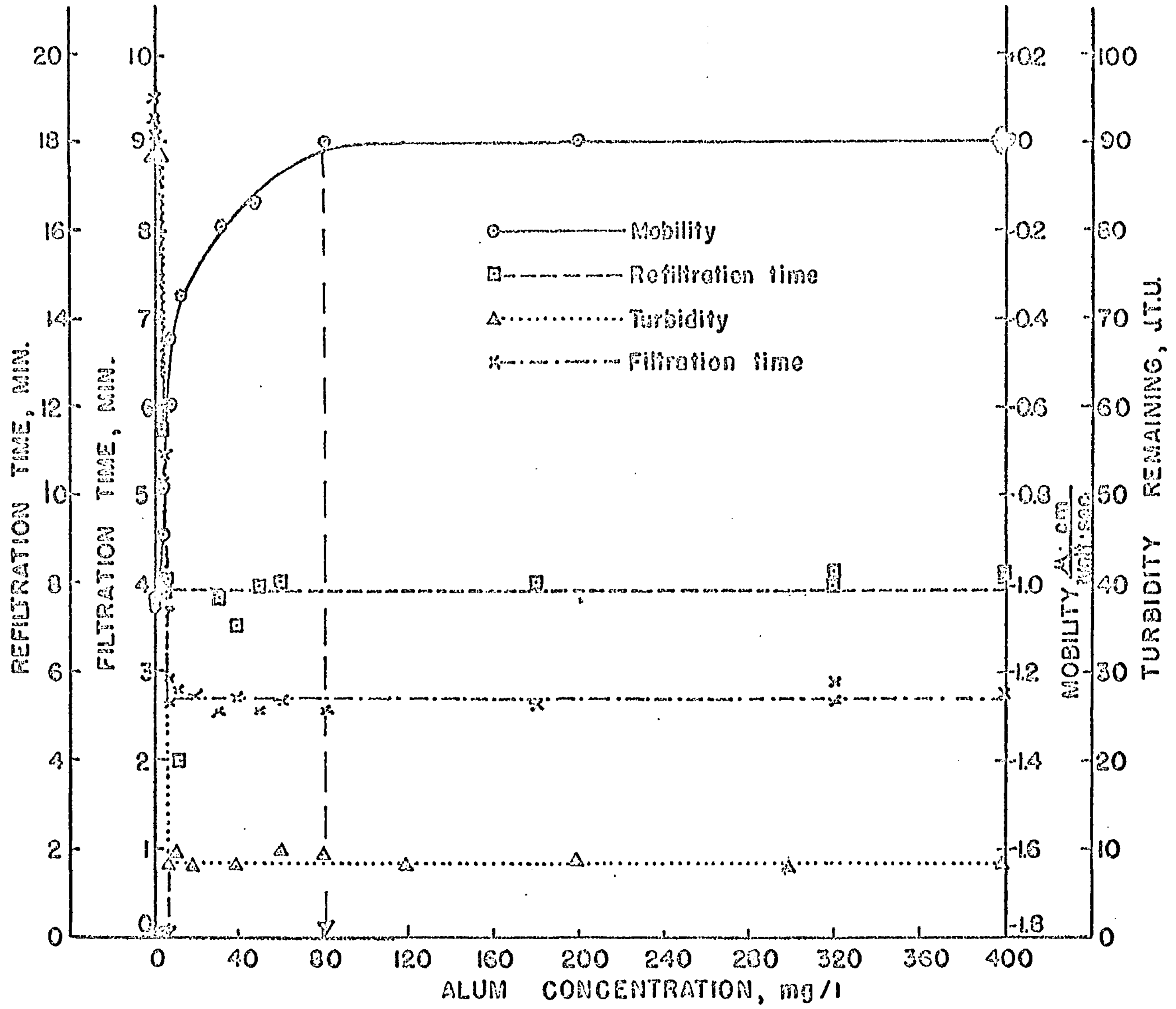
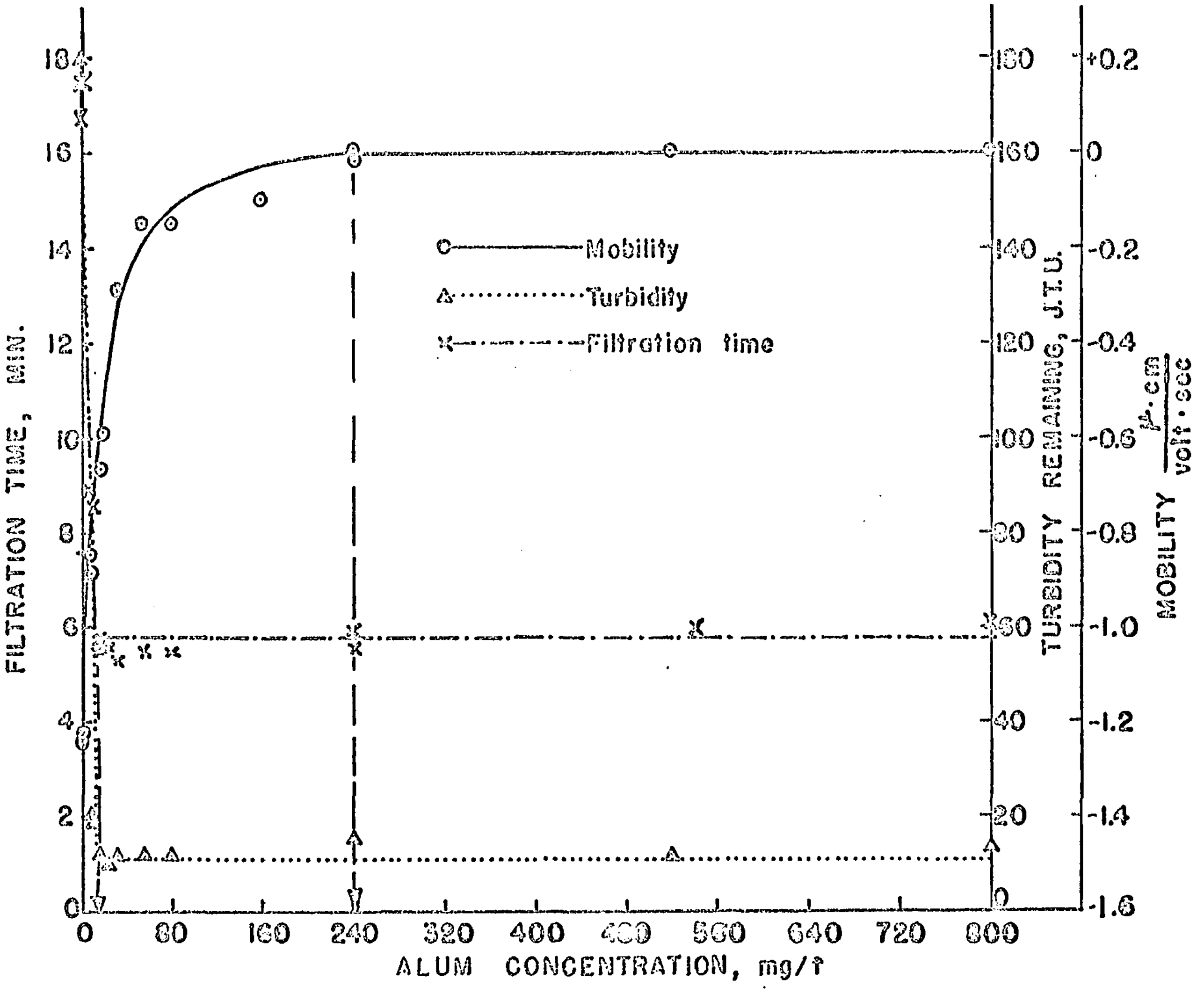

Mobility
Refiltration time
Turbidity
Filtration time
REFILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
20
FILTRATION TIME, MIN.
0
1
2
3
4
5
6
7
8
9
10
MOBILITY $\frac{\mu \cdot cm}{volt \cdot sec}$
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
TURBIDITY REMAINING, JTU
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400
ALUM CONCENTRATION, mg/l

Figure 24. Effect of alum concentration on different parameters of coagulation (Series no. 12)

clay concentration = 200 mg/1
pH = 3.5


Mobility
Turbidity
Filtration time
FILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
TURBIDITY REMAINING, J.T.U.
0
20
40
60
80
100
120
140
160
180
MOBILITY $\frac{\mu \cdot cm}{volt \cdot sec}$
-1.6
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0
+0.2
0
80
160
240
320
400
480
560
640
720
800
ALUM CONCENTRATION, mg/ℓ

and 24. These figures differ from the previous figures in that none of the curves show any type of minimum values. The filtration time, the refiltration time, and the turbidity remaining in the supernatant decrease rapidly with a small increase of alum concentration but stay at constant levels for higher alum doses. Optimums for filtration as well as for settling follow a stoichiometric relationship with the clay concentration as can be seen from the figures. Mobilities in both of the series reach the isoelectric point at higher alum concentrations than the corresponding optimum values for settling and filtration. However, the charge of the colloids is not reversed with higher alum concentrations in either series.

pH

The effect of pH on the coagulation of clay suspensions with alum was studied from the results of six series. The pH was kept at 3.5, 4.1, 5.5, 7.0, 8.5, and 10.0 in Series 8, 10, 11, 5, 13, and 9 respectively. The clay concentration of the suspension used in these tests was 100 mg/l. Mixing speed and time was kept at constant values of 1000 rpm and 15 minutes respectively.

The results of the filtration, mobility, and jar tests are shown in Figures 20, 23, and 25 through 28. Refiltration time measurements were discontinued after the tenth series for the following reasons. Both filtration time and refiltration time indicated exactly the same optimum dose for filtration (Table 4) and the trends of change in both the curves with alum concentration were very similar to each other in all ten series of tests. (Figures 16 through 23, 25 and 28)

Figure 25. Effect of alum concentration on different parameters of coagulation (Series no. 10)

clay concentration = 100 mg/1
pH = 4.1

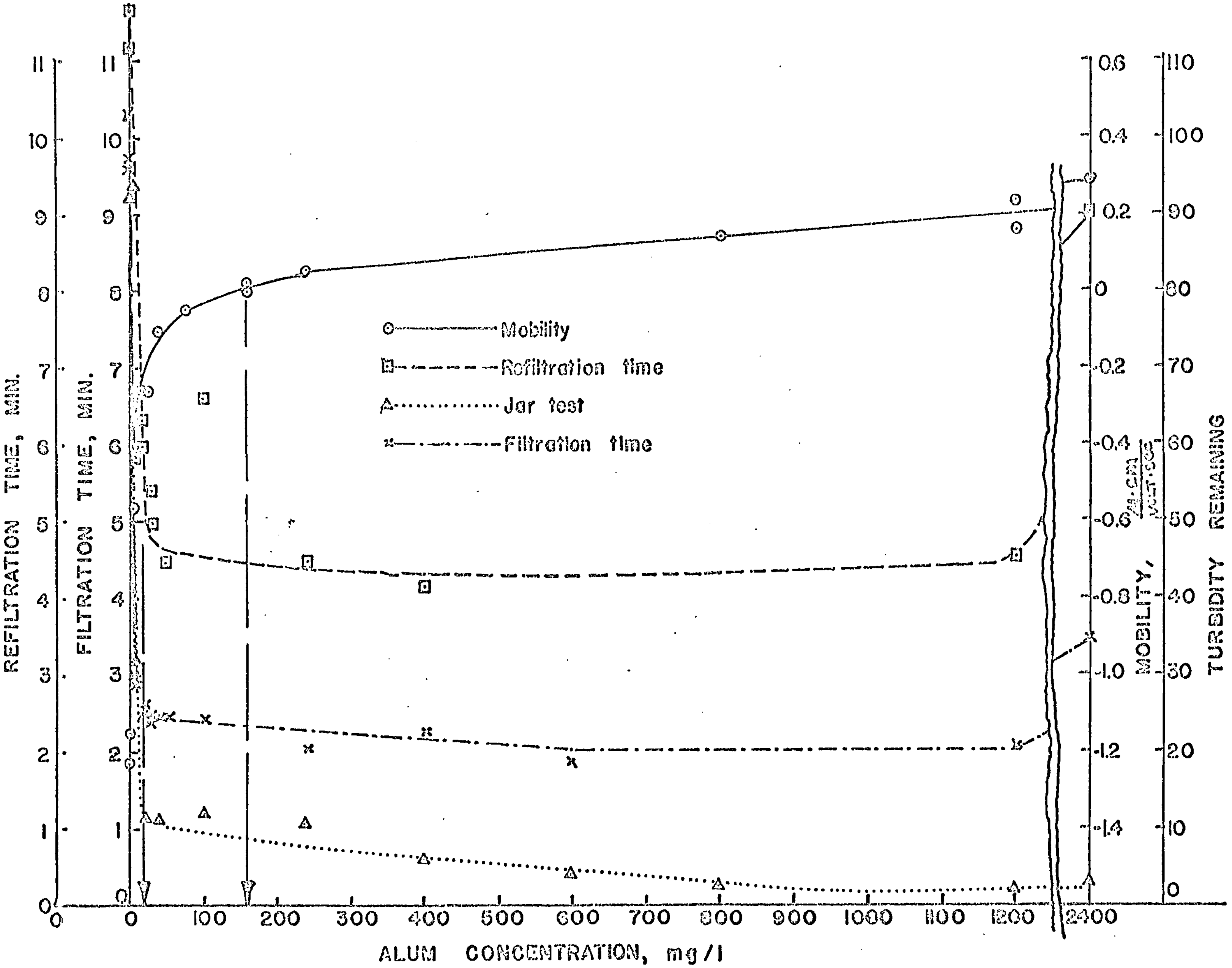

Mobility
Refiltration time
Jar test
Filtration time
REFILTRATION TIME, MIN.
FILTRATION TIME, MIN.
MOBILITY, μ·cm/volt·sec
TURBIDITY REMAINING
ALUM CONCENTRATION, mg/l
0 1 2 3 4 5 6 7 8 9 10 11
0.6 0.4 0.2 0 -0.2 -0.4 -0.6 -0.8 -1.0 -1.2 -1.4
0 10 20 30 40 50 60 70 80 90 100 110
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 2400

Figure 26. Effect of alum concentration on different parameters of coagulation (Series no. 11)

clay concentration = 100 mg/1
pH = 5.5

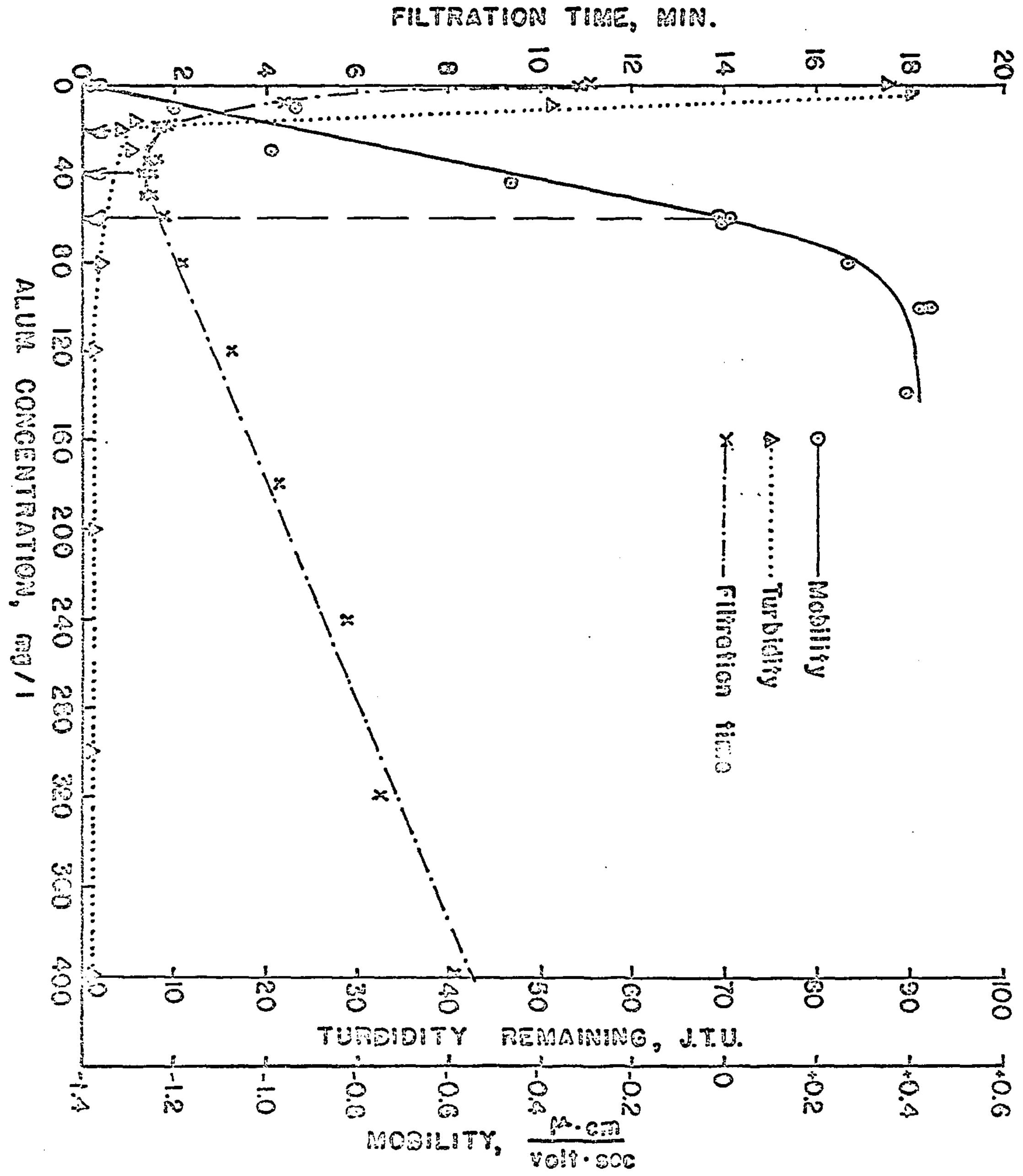

FILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
20
ALUM CONCENTRATION, mg/l
0
40
80
120
160
200
240
280
320
360
400
TURBIDITY REMAINING, J.T.U.
0
10
20
30
40
50
60
70
80
90
100
MOBILITY, μ·cm/volt·sec
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0
+0.2
+0.4
+0.6
Mobility
Turbidity
Filtration time

Figure 27. Effect of alum concentration on different parameters of coagulation (Series no. 13)

clay concentration = 100 mg/1
pH = 8.5

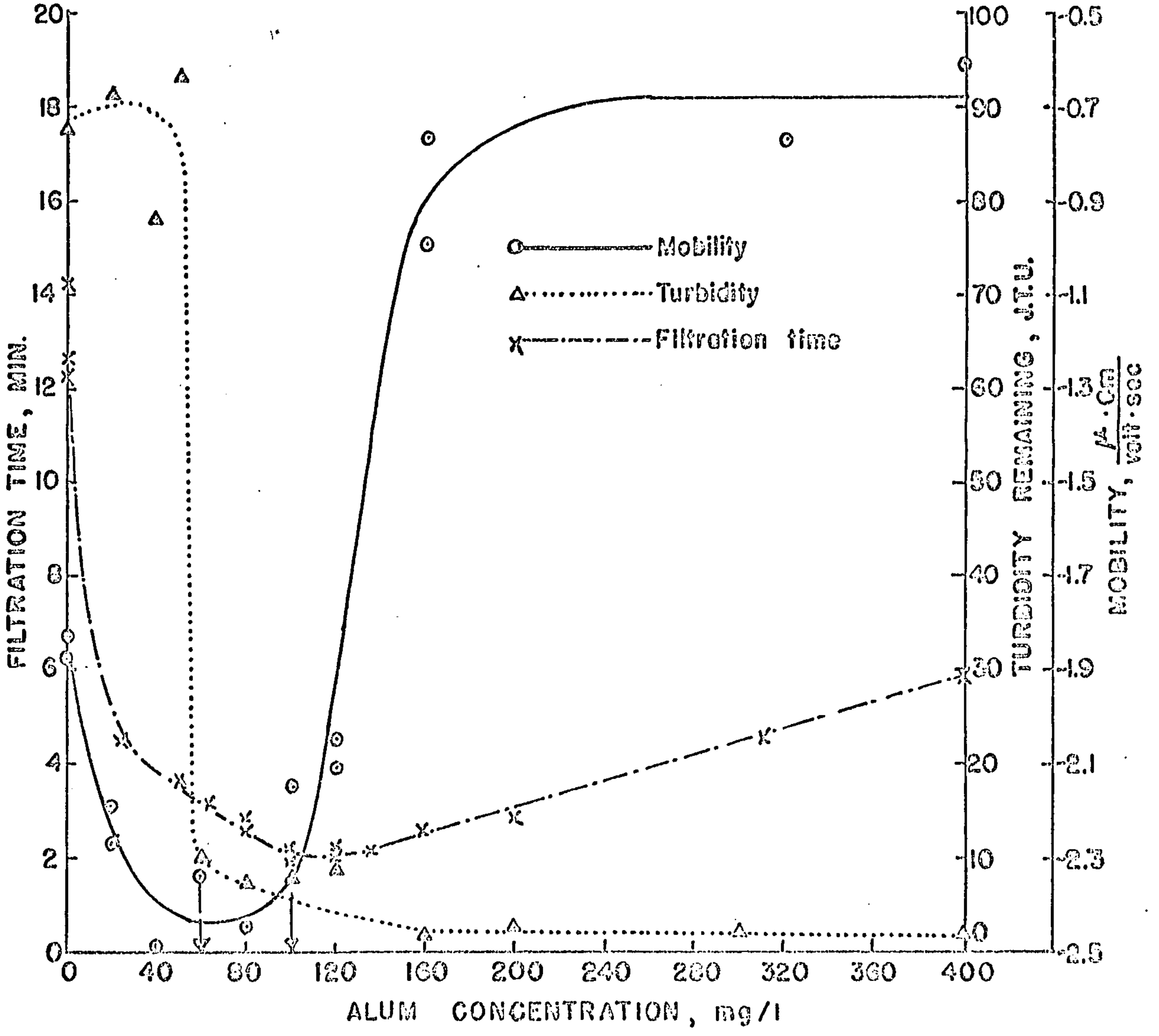
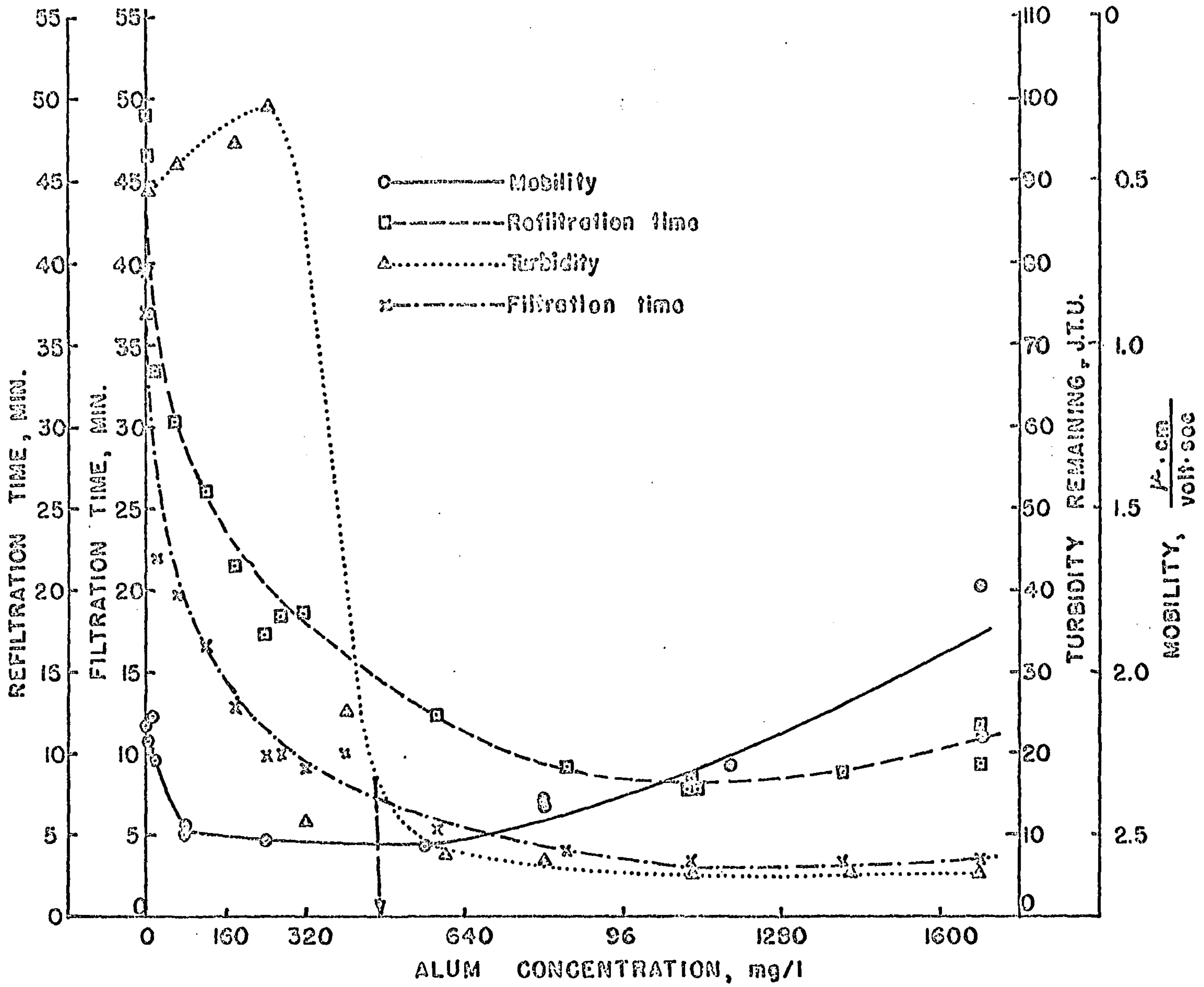

FILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
20
TURBIDITY REMAINING, J.T.U.
0
10
20
30
40
50
60
70
80
90
100
MOBILITY, $\frac{\mu \cdot cm}{volt \cdot sec}$
-2.5
-2.3
-2.1
-1.9
-1.7
-1.5
-1.3
-1.1
-0.9
-0.7
-0.5
ALUM CONCENTRATION, mg/l
0
40
80
120
160
200
240
280
320
360
400
Mobility
Turbidity
Filtration time

Figure 28. Effect of alum concentration on different parameters of coagulation (Series no. 9)

clay concentration = 100 mg/1
pH = 10.0


Mobility
Rofiltration time
Turbidity
Filtration time
REFILTRATION TIME, MIN.
FILTRATION TIME, MIN.
0
5
10
15
20
25
30
35
40
45
50
55
ALUM CONCENTRATION, mg/l
0
160
320
640
96
1280
1600
TURBIDITY REMAINING, J.T.U.
0
10
20
30
40
50
60
70
80
90
100
110
MOBILITY, μ·cm / volt·sec
0
0.5
1.0
1.5
2.0
2.5

Moreover, the filtration time test involved only one filtration step and there was no cake disturbance possibility to be concerned about, whereas the refiltration time test needed two steps of filtration, and thus, required twice the time. Furthermore, due to cake cracking or disturbance, the refiltration time frequently had to be discarded. Therefore, it was considered unnecessary to go through the troubles of refiltering, only to reach the same conclusion in the end.

Filtration time curves for pH 3.5 and 4.1 (Figures 23 and 25) show similarity in trend in that the curves of both these series dropped rapidly for small increases of alum concentration and then leveled off for higher alum doses. The jar tests follow exactly the same trend in both the series, giving the same optimums as the filtration time tests. The optimum value at pH 3.5 was only 8.0 mg/l of alum, where it was 20 mg/l for pH 4.1. The mobility curve for pH 3.5 reaches the isoelectric point when the alum dose is 80 mg/l and levels off there for higher alum doses. At a pH of 4.1, the charge is slowly reversed as the alum concentration is increased to be greater than 160 mg/l.

Series 5, 11, and 13, where pH levels used are 7.0, 5.5, and 8.5, can be grouped together because of the similarity of curves plotted with the results of these series (Figures 20, 26, and 27). All three filtration time curves exhibit minima, but at different alum concentrations for different pH values. The turbidity curves drop off sharply for small increases of alum concentrations and level off slowly for higher alum concentrations. Optimum values for filtration at pH values of 5.5, 7.0, and 8.5 are 40, 52.5, and 100 mg/l of alum respectively; for settling, corresponding values are 20, 30, and 60 mg/l respectively. The mobility of particles at pH 5.5 is reversed with alum doses higher than 60 mg/l. At pH 7.0, the trend of the mobility curve is similar to that of the curve at 5.5, but the charge itself is not reversed for higher alum concentrations. The mobility of particles at pH 8.5 is actually made more negative with the addition of small amounts of alum than with no alum addition. The mobility stays at this value up to an alum concentration of about 120 mg/l, then falls off to a lower negative value of 0.7 $\frac{\mu \cdot \text{cm}}{\text{volt} \cdot \text{sec}}$ and levels off at that value.

In Series 9 (pH = 10.0), very high alum concentrations had to be used (Figure 28) to go beyond the optimum level. The optimum for filtration as indicated by filtration time and refiltration time is 1095 mg/l and for settling by jar test is 500 mg/l. The mobility at pH 10.0 increased to a higher negative value with alum concentrations up to 1120 mg/l, but drops off to a lower negative value for 1680 mg/l of alum addition.

Thus, coagulation of clay suspensions can be seen to take place at all pH levels, even though required alum doses change when the pH is changed.

Dissolved solids in water

In all of the first thirteen series, clay suspensions were prepared by mixing suitable amounts of clay slurry and distilled water. The pH of the suspension was maintained at the desired level by adding either HCl or NaOH solutions of required strength. In Series 14 and 15, the clay suspension was prepared by mixing the clay slurry with a water containing tap water and distilled water in about a 1 to 7 ratio. The final content of tap water in the clay suspension was 12.5 per cent. Tap water used in all tests of both the series was drawn at one time and a mineral analysis was carried out. This mineral analysis is shown on page 24. Thus, the mineral concentrations in the clay suspension would be 1/8th of what is shown on that page. The pH of the clay suspension in tap water was 7.3 ± 0.05 units.

When alum was added in various concentrations to the clay suspension prepared in Series 14, the pH decreased but was not adjusted back to the same level. The pH values were measured and recorded. The first part of the filtration time showed a similarity to the curves obtained at neutral pH value for low alum concentrations (Figure 29). At alum concentrations higher than 120 mg/1, the pH dropped down below 4.75 and the filtration time curve leveled off at a constant value similar to the filtration time curves obtained at pH values of 4.1 and 3.5. The optimum for filtration occurs at an alum concentration of 60 mg/1 while the pH is 6.0. The optimum for settling is 25 mg/1. However, the turbidity curve increases to a hump at an alum concentration of 120 mg/1 and then levels off at a lower value. This deviation cannot be explained with the present data. This may have been due to the charge reversal of the colloids reaching a maximum positive value at about 120 mg/1. However, the charge reversal has not been noted to affect the settling process in the other series.

In Series 15, unlike Series 14, the pH was adjusted back to 7.3 with NaOH solution after the addition of alum. Series 15 (Figure 30) and Series 5 (Figure 20) can be compared since in both series conditions are quite similar, except that the pH maintained in Series 5 is 7.0 while in

Figure 29. Effect of alum concentration on pH and different parameters of coagulation (Series no. 14)

clay concentration = 100 mg/l
per cent tap water = 12.5

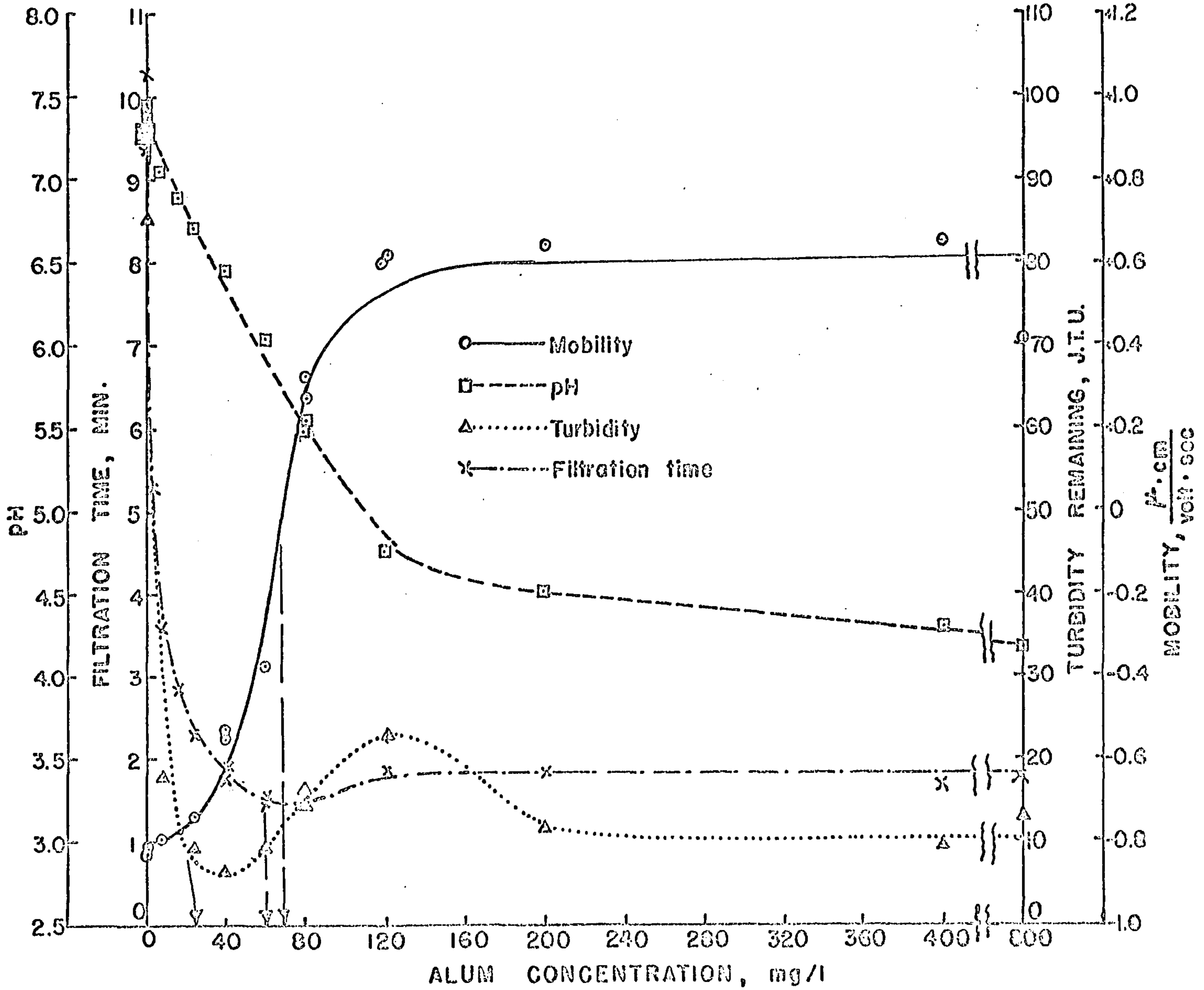
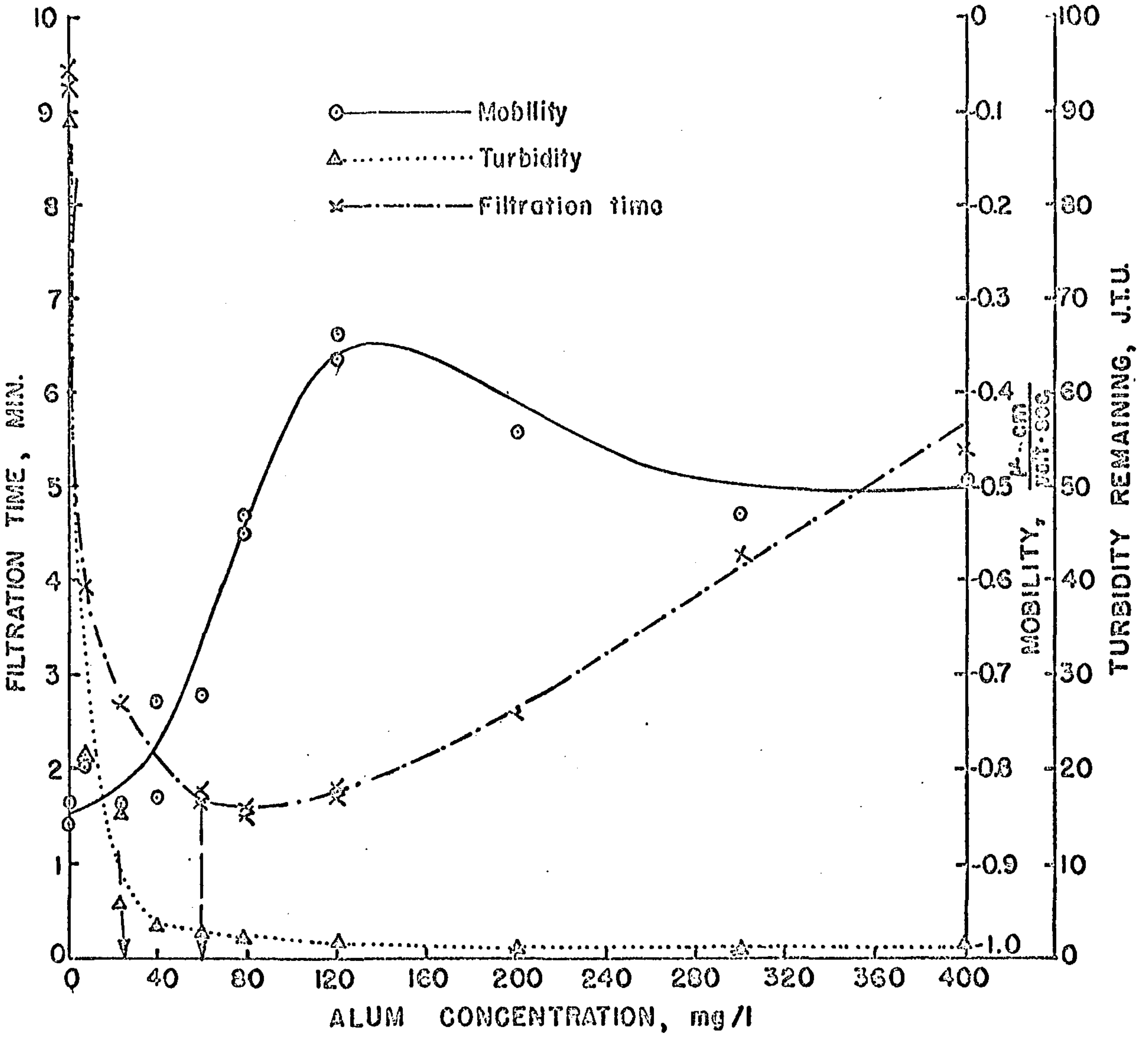

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
pH
11
10
9
8
7
6
5
4
3
2
1
0
FILTRATION TIME, MIN.
110
100
90
80
70
60
50
40
30
20
10
0
TURBIDITY REMAINING, J.T.U.
+1.2
+1.0
+0.8
+0.6
+0.4
+0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
MOBILITY, $\frac{\mu \cdot cm}{volt \cdot sec}$
Mobility
pH
Turbidity
Filtration time
0
40
80
120
160
200
240
280
320
360
400
600
ALUM CONCENTRATION, mg/l

Figure 30. Effect of alum concentration on different parameters of coagulation (Series no. 15)

clay concentration = 100 mg/1
pH = 7.3
per cent tap water = 12.5



Mobility
Turbidity
Filtration time
FILTRATION TIME, MIN.
0
1
2
3
4
5
6
7
8
9
10
ALUM CONCENTRATION, mg/l
0
40
80
120
160
200
240
280
320
360
400
MOBILITY, $\frac{\mu\text{-cm}}{\text{volt-sec}}$
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
TURBIDITY REMAINING, J.T.U.
0
10
20
30
40
50
60
70
80
90
100

Series 15 it is 7.3. Besides the pH, the only other difference is in the type of water used for dilution. Trends of curves obtained in both of these series are similar to each other. The optimum alum concentrations for filtration were 52.5 and 60.0 mg/l in Series 5 and 15 respectively; for settling they were 30.0 and 25.0 mg/l in the same order. The mobility curves remain negative for all alum concentrations in both series. However, the mobility value with no alum present was lower in Series 15 as compared to Series 5 because of the divalent cations present in the suspension prepared for Series 15.

As a result of this part of the study it can be concluded that the dissolved minerals in the water used in this part of the study do not significantly affect the process of coagulation. Also, addition of alkaline salts to keep the pH constant in a natural water may not be essential for the process of coagulation followed by settling or filtration.

Interpretations

Mechanism of coagulation

Coagulation of clay takes place at all pH levels and at all clay concentrations when sufficient alum is added to a clay suspension. Alum levels needed to effect coagulation have been found to depend upon clay concentration and the pH of the suspension. Filter cake resistance is greatly reduced by optimum coagulant dosage as measured by filtration time or refiltration time.

The destabilization of a clay suspension with alum can be visualized to be made up of two steps; one, the interaction of aluminum hydrolysis species and the clay colloids; and the second, the aggregation of clay colloids together to form larger particles. First the mechanism of interaction will be discussed and the discussion of mechanism of aggregation will follow.

The relationship between the optimum alum dose for filtration and clay concentration at pH 7.0 is shown in Figure 31 for the bench scale studies. In the range of clay concentration used in this study, 25 mg/l to 200 mg/l, the relationship is of a stoichiometric nature. The ratio of alum dose to clay concentration expressed in the same units is 0.525. This indicates that the forces involved may be of a chemical nature other than coloumbic.

To reach the isoelectric point for a suspension with a clay concentration of 25 mg/l it takes 21 mg/l of alum, whereas the alum required is 42 mg/l for 50 mg/l clay suspension (Figure 32). It is evident from Figure 32 that the isoelectric point was not observed with alum addition when the suspensions contained clay concentrations of 100 mg/l or higher. The significance of the dotted lines in this figure will be discussed later.

Changes in clay concentration should not greatly affect the potential distribution in the double layer of clay colloids if the same amount of indifferent electrolyte were present in the aqueous phase. If suppression of double layer by indifferent electrolyte were the mechanism involved in the observations made during this study, then all the curves shown for different clay concentration in Figure 32 should have coincided, i.e., resulted in one single curve. The fact that a reasonable stoichiometric displacement can be noticed among these curves (Figure 32)

Figure 31. Relationship between optimum alum concentration and clay concentration of the suspension at pH 7.0 (Series no. 2, 4, 5, 6 and 7)

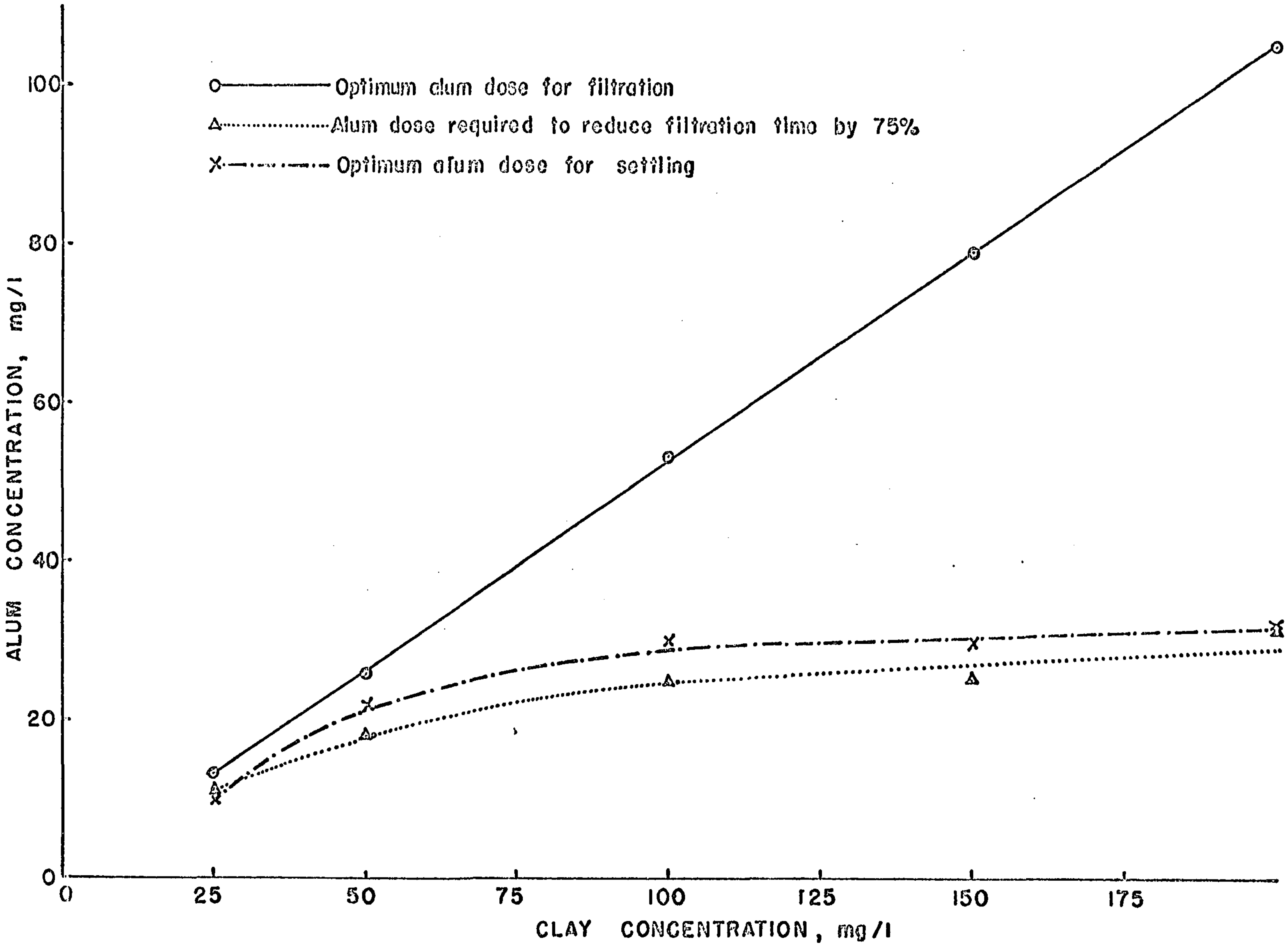
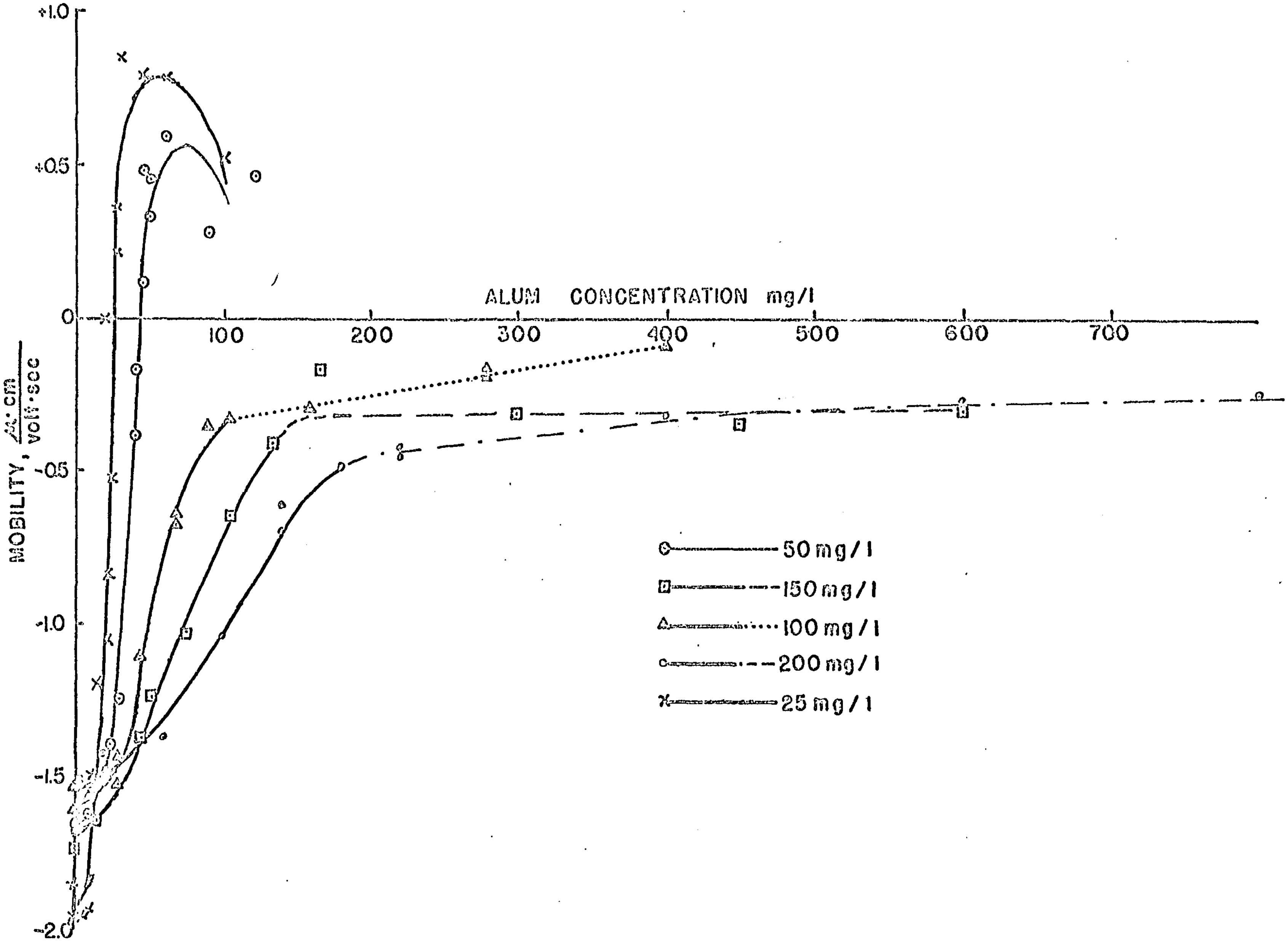

Optimum alum dose for filtration
Alum dose required to reduce filtration time by 75%
Optimum alum dose for settling
ALUM CONCENTRATION, mg/l
CLAY CONCENTRATION, mg/l
0
20
40
60
80
100
0
25
50
75
100
125
150
175

Figure 32. Effect of clay concentration and alum concentration on the mobility of particles at pH 7.0 (Series no. 2, 4, 5, 6 and 7)



+1.0
+0.5
0
-0.5
-1.0
-1.5
-2.0
MOBILITY, μ·cm / volt·sec
ALUM CONCENTRATION mg/l
100
200
300
400
500
600
700
50 mg/l
150 mg/l
100 mg/l
200 mg/l
25 mg/l

indicates that the mechanism of potential reduction of clay by alum is not suppression of the double layer. Thus the specific adsorption of the aluminum hydrolysis species present in the water at this pH due to chemical forces in the interface of the clay colloids seems to be a more acceptable explanation of the behavior.

The existence of a stoichiometric relationship between alum and clay has been checked at one other pH level. At pH 3.5, two series have been conducted with a clay concentration of 100 mg/l in one and 200 mg/l in the other (Series 8 and 12, Figures 23 and 24). The alum required for optimum filtration was 8.0 mg/l for 100 mg/l clay suspension and 16.0 mg/l alum for 200 mg/l clay. If the specific adsorption were the mechanism of coagulation, one would also expect a stoichiometric relation between clay concentration and the alum required to reach the isoelectric point. In both cases cited above, the isoelectric point was reached. However, 80 mg/l of alum was required to reach the isoelectric point in the case of the 100 mg/l clay suspensions, whereas the value was 240 mg/l for 200 mg/l of clay. The discrepancy from an exact stoichiometric relation may have been due to the very gradual approach of the mobility curve towards zero mobility (isoelectric point). Thus it is possible that a near-isoelectric point value may have been selected as the isoelectric point itself (Figures 23 and 24). The reason for the gradual approach towards the isoelectric point will be discussed in a later section.

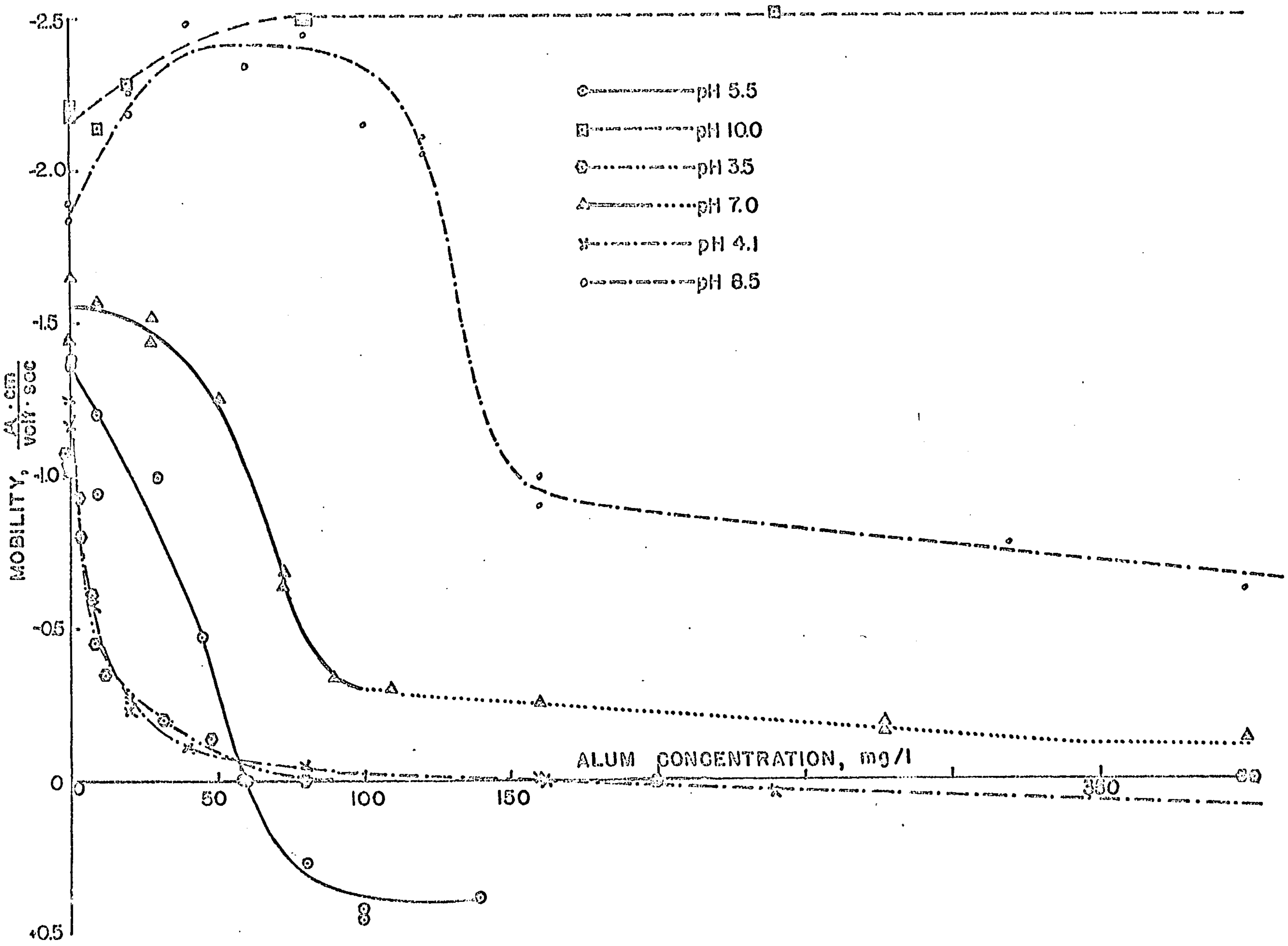
At pH 3.5 or lower, it has been well established that the aluminum ion is mostly in the form of hydrated trivalent ions, whereas the species present at pH levels between 5.0 and 7.0 has been concluded as $Al_8\ (OH)_{20}^{4+}$

by Matijevic (22). If suppression of double layer were the mechanism leading to coagulation, this would be best shown when the aluminum is present as the trivalent ion. The fact that the stoichiometric relationship held for the trivalent ion itself supports the adsorption mechanism even more strongly. Thus, there is no reason to believe that a stoichiometric relationship would not hold good at pH levels in between 3.5 and 7.0.

It is, however, possible to question whether a stoichiometric relationship would exist at pH levels higher than 7.0. The aluminum species present at these pH levels may exhibit a negative charge (36), which might affect the adsorptive process. However, the electrophoretic results obtained at pH 8.5 and 10.0 indicate the possibility of adsorption more strongly than the results obtained at other pH values. The negatively charged clay particles actually become more negative in the presence of alum at concentration levels up to 120 mg/l at pH 8.5 (Figure 33) and up to 1120 at pH 10.0 (Figure 28). This means that the chemical forces overcome the coloumbic repulsive forces to result in adsorption of the negatively charged aluminum species on the surface of the clay colloids resulting in a higher negative charge than in the presence of no alum. At alum concentrations of 160 mg/l at pH 8.5 and at 1680 mg/l at pH 10.0, the mobilities drop down to lower negative values than with zero alum. However, these alum concentrations were the lowest concentrations at which precipitation of visible floc was observed at their respective pH values. Thus, the mobility readings at higher alum concentrations represent not the charge characteristics of the clay colloids but the characteristics of solid aluminum hydroxide precipitate which also contains

Figure 33. Effect of pH and alum concentration on the mobility of particles (Series no. 5, 8, 9, 10, 11, and 13)

clay concentration = 100 mg/1


-2.5
-2.0
-1.5
-1.0
-0.5
0
+0.5
MOBILITY, $\frac{\mu \cdot cm}{volt \cdot sec}$
0
50
100
150
350
ALUM CONCENTRATION, mg/l
pH 5.5
pH 10.0
pH 3.5
pH 7.0
pH 4.1
pH 8.5

some clay particles. Thus a different surface charge might be expected.

The optimum alum dose for the process of filtration varies with pH. Such variation for a suspension having a clay concentration of 100 mg/l is shown in Figure 34. The required alum dose increases slowly from 8.0 mg/l to 100 mg/l as the pH is increased from 3.5 to 8.5. At pH 10.0, however, the alum required is comparatively very high, 1100 mg/l.

The mobility of the clay colloids and the filtration time for the clay suspension when no alum was added can be seen to vary with pH levels in Figure 35. The mobility curve approximates a linear relationship with pH. But, the filtration time varies with pH in a manner similar to the optimum alum dose, from 9.3 min at pH 3.5 to 13.0 min at pH 8.5 and to a high value of 38.3 min at pH 10.0. Refiltration time was also observed to vary in somewhat the same way. Not as many points were obtained for refiltration time, and also its variation with pH was erratic. It has been reported by other researchers (27) that refiltration time increased significantly with pH. However, no explanation was proposed.

First, it was suspected that the high value of filtration time at pH 10 observed in this study without alum might be due to the addition of sodium ions added as sodium hydroxide to maintain the pH at that level since some of the calcium montmorillonite might have been converted to sodium montmorillonite; and sodium montmorillonite yields higher resistance to filtration. However, a test conducted at pH 7.0 with an equivalent amount of sodium ions added as sodium chloride indicated no significant increase in the filtration time caused by the sodium ion concentration.

In view of this, there exist two other possible explanations.

Figure 34. Effect of pH on the optimum conditions of a suspension with a clay concentration of 100 mg/1 (from Series no. 5, 8, 9, 10, 11, and 13)

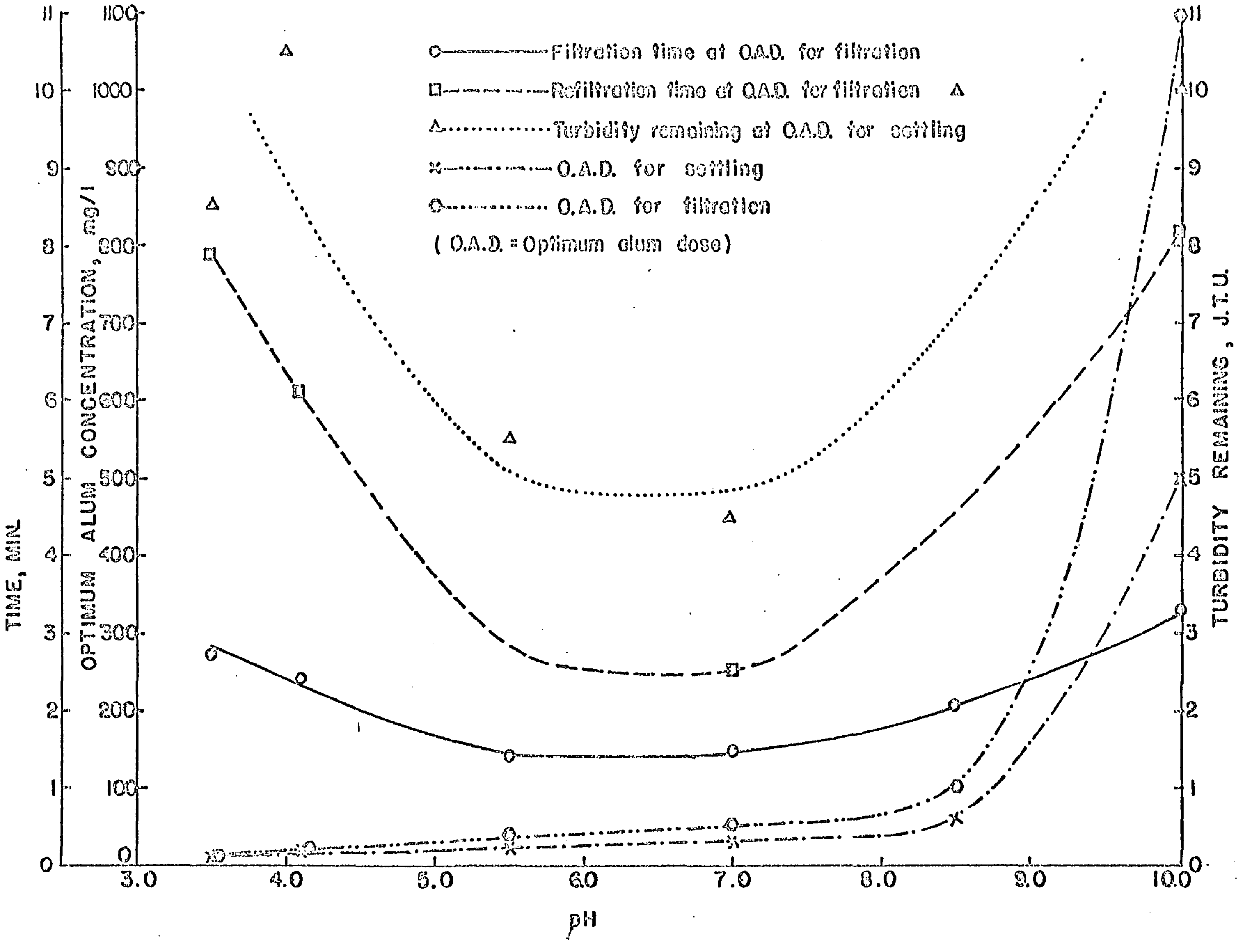
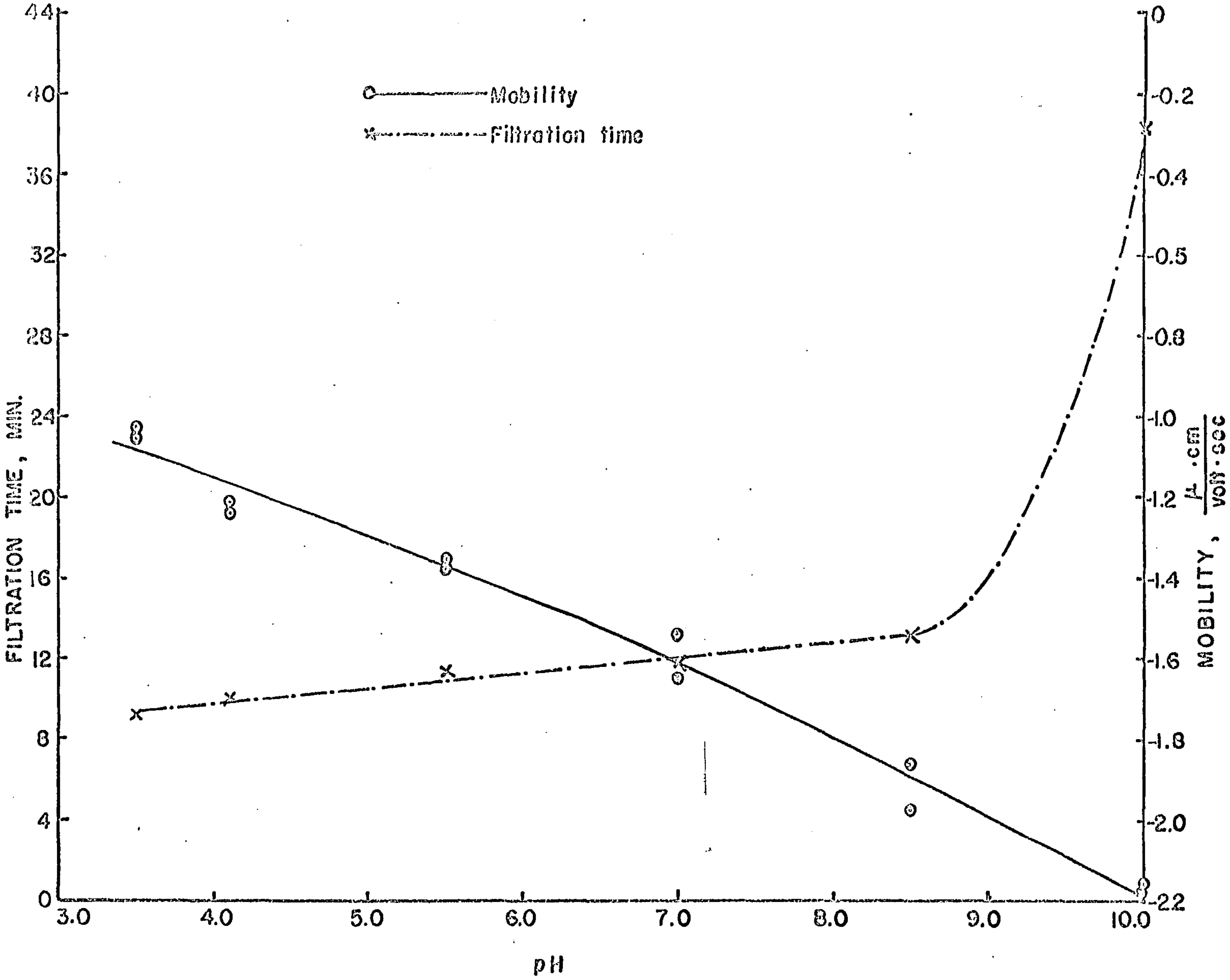

Filtration time at O.A.D. for filtration
Refiltration time at O.A.D. for filtration
Turbidity remaining at O.A.D. for settling
O.A.D. for settling
O.A.D. for filtration
(O.A.D. = Optimum alum dose)
TIME, MIN.
OPTIMUM ALUM CONCENTRATION, mg/l
TURBIDITY REMAINING, J.T.U.
pH
0
1
2
3
4
5
6
7
8
9
10
11
0
100
200
300
400
500
600
700
800
900
1000
1100
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0

Figure 35. Effect of pH on the mobility of clay particles and the filtration time of a suspension with a clay concentration of 100 mg/l and with no alum addition (from Series no. 5, 8, 9, 10, 11, and 13)


Mobility
Filtration time
FILTRATION TIME, MIN.
MOBILITY, $\frac{\mu \cdot cm}{volt \cdot sec}$
pH
0
4
8
12
16
20
24
28
32
36
40
44
0
-0.2
-0.4
-0.5
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0

One is based upon the mutual coagulation theory proposed by Olphen (26) for clay mineral suspension. Olphen has postulated that a dual double layer exists around the clay particles, one on the flat face of the clay minerals due to substitution of lower valent cations for higher valent cations in the lattice of the clay; and the other on the edge due to broken bonds and adsorption of potential determining ions. The charge on the edge can be positive in the acidic or near neutral pH range and negative in the alkaline pH levels even though the clays have a net negative charge on their surfaces. Due to this dual double layer it is possible for these particles to come near each other and form edge-to-face connections to grow to a bigger size when the charges on the face and edge are opposite to each other. Thus such self-aggregation is possible at acidic or near neutral pH values, but not likely in high alkaline pH values.

Another explanation for the observed variation of filtering time with pH and without alum can be based upon the variation of electrophoretic mobility itself with pH. The attractive forces between two colloids, such as Van der Waal's forces, are considered to be constant regardless of any variation in the characteristics of the bulk of the solution. Repulsive forces, however, are controlled by the contents of the dispersion phase. If the repulsive forces are greater than the attractive forces, the resultant force would pose a barrier of a certain magnitude over a certain distance opposing the aggregation of two particles, the magnitude and distance of the barrier being dependent upon the values of the attractive and repulsive forces. Particles containing enough kinetic energy would overcome this barrier to aggregate. As the barrier dimensions are increased as a result of an increase in the repulsive forces, the amount of self-aggregation would decrease. There may be a critical set of barrier dimensions which would prevent the self-aggregation almost altogether. This may be the reason for a high filtration time at pH 10.0, even though the mobility itself, which is an indication of repulsive forces, has not increased significantly for an increase in pH from 8.5 to 10.0.

It is not possible to distinguish which of the two explanations is responsible for the different degrees of self-aggregation occurring at various pH levels in Figure 35. Both of them probably have a significant effect on this phenomenon. The permeability of the cake formed by the removed solids would depend upon the size of the particles when other factors are held constant. When the size of the particles is decreased the surface area of the particles is increased for an equal weight of material. Thus the clay colloids present at pH 10.0, because of no or insignificant self-aggregation, would possess a larger surface area. Whichever may be the reason for the lack of self-aggregation at higher pH levels, the result would be an increased filtration time.

If adsorption of the aluminum hydrolysis product on the surface of the colloids is the prerequisite for destabilization, then the alum dose required for adequate adsorption would increase in proportion to the surface area of colloids. Since optimum alum dose for filtration (Figure 34) and filtration time of an uncoagulated suspension (Figure 35) vary similarly with the pH of the suspension, the optimum alum dose itself is directly dependent upon filtration time of the untreated suspension. The filtration time of the untreated suspension is directly dependent upon the specific surface area of the colloids. Therefore, the similarity of the figures indicates that the optimum alum dose depends upon the surface area posed by the clay colloids of the suspension and the specific adsorption theory is further supported.

Having established that the addition of alum to a clay suspension results in specific adsorption of the hydrolysis species on the clay colloids, the mechanism of aggregation of clay colloids after the adsorption will be discussed below.

The lowest filtration time or refiltration time obtainable for suspensions of the same clay concentration but at different pH levels are not one and the same. The variation of the optimum times are also shown in Figure 34. There seems to be an optimum range of pH during which the filtration time and refiltration time can be reduced to a lower value with alum than at other pH levels. This optimum pH range corresponds to 5.5 to 7.0. The existence of such a range can be explained by the predominance of different hydrolysis species at different pH levels and thus the possible differences in the mechanism of aggregation after the alum has been adsorbed on the surface of the colloids. It has already been discussed that the species predominant at low pH levels, about 4.0 or lower, would probably be the hydrated aluminum ion; at pH levels between 5.0 and 7.0 it would be $Al_8(OH)_{20}^{4+}$; and at alkaline pH levels, a negatively charged species such as $Al(OH)_4^-$ or $Al_2(OH)_8^{2-}$ probably exists (36). $Al_8(OH)_{20}^{4+}$ would be a higher positively charged and larger species than Al^{3+} or $Al(OH)_4^-$.

Because of these differences the mechanism of aggregation itself would probably be different. At lower pH values, the aggregation would have to be mostly by two clay particles coming nearer and being attached to each other due to the already reduced repulsive potentials because of specific adsorption of aluminum ions. There would not be any significant bridging action. At higher pH levels, the situation may be entirely different in that the aggregation may have to be due to the attraction of the aluminum species adsorbed on the clay and due to the bridging action of the coagulant species between two clay particles. At intermediate pH levels, both types of activity would necessarily have to be present. The bridging action would be more efficient due to the presence of larger species and the aggregation of clay particles by themselves would also occur since the adsorbed species would reduce the repulsive potential. Apparently the combination of both mechanisms results in a complete and efficient aggregation; this in turn results in a lower filtration and refiltration time at the intermediate pH levels as compared to lower or higher pH levels.

From the above discussion it is also evident that La Mer's definition of coagulation and flocculation (14) cannot be attributed to the mechanism of destabilization of the clay suspension with alum without accompanying qualifications. The mechanism of destabilization of clay suspensions with alum at higher pH levels may be similar to the definition proposed by La Mer for flocculation, i.e., bridging action. But, the mechanism at lower and neutral pH levels does not exactly fit into either one of the definitions proposed by La Mer for coagulation or flocculation. The potential reduction at the lower and neutral pH levels is accomplished not by suppression of double layer, but by specific adsorption. At near neutral pH levels, potential reduction by adsorption followed by aggregation of clay particles by attractive forces, as well as bridging action may take place. Thus it is not possible to categorize the mechanism of destabilization by alum according to the definitions proposed by La Mer (14).

Precipitation

Alum when added to a water precipitates out as aluminum hydroxide if the pH of the water after alum addition is near neutral. This has been found to be true by earlier researchers as well as treatment plant operators. This precipitate is normally expressed as a hydroxide, $Al(OH)_3$. However, this is only as a result of an elemental analysis. It can also be visualized as a hydrous aluminum oxide, $Al_2O_3 \cdot 3H_2O$. There has not been enough research work done to prove which of these two is correct. In this thesis, the precipitate would be referred to as aluminum hydroxide in all places, just to be consistent. The optimum pH for coagulation of waters has often been found to be also near neutral values. Because of this, precipitation has often been indicated as essential for the destabilization of a clay suspension. The coagulation observations at low and high pH levels in the present study, however, indicate that precipitation is not necessary, and also that it can adversely affect the process of filtration. This is discussed in detail below.

Figures 36 through 39 show the effect of alum concentration on the filtration and refiltration time of suspensions with different clay concentrations at pH 7.0. While the times shown by the curves are different for each clay concentration when the alum dose is below the optimum level,

Figure 36. Effect of alum concentration on filtration time of suspensions having different clay concentrations at pH 7.0 (Series no. 2 and 4)

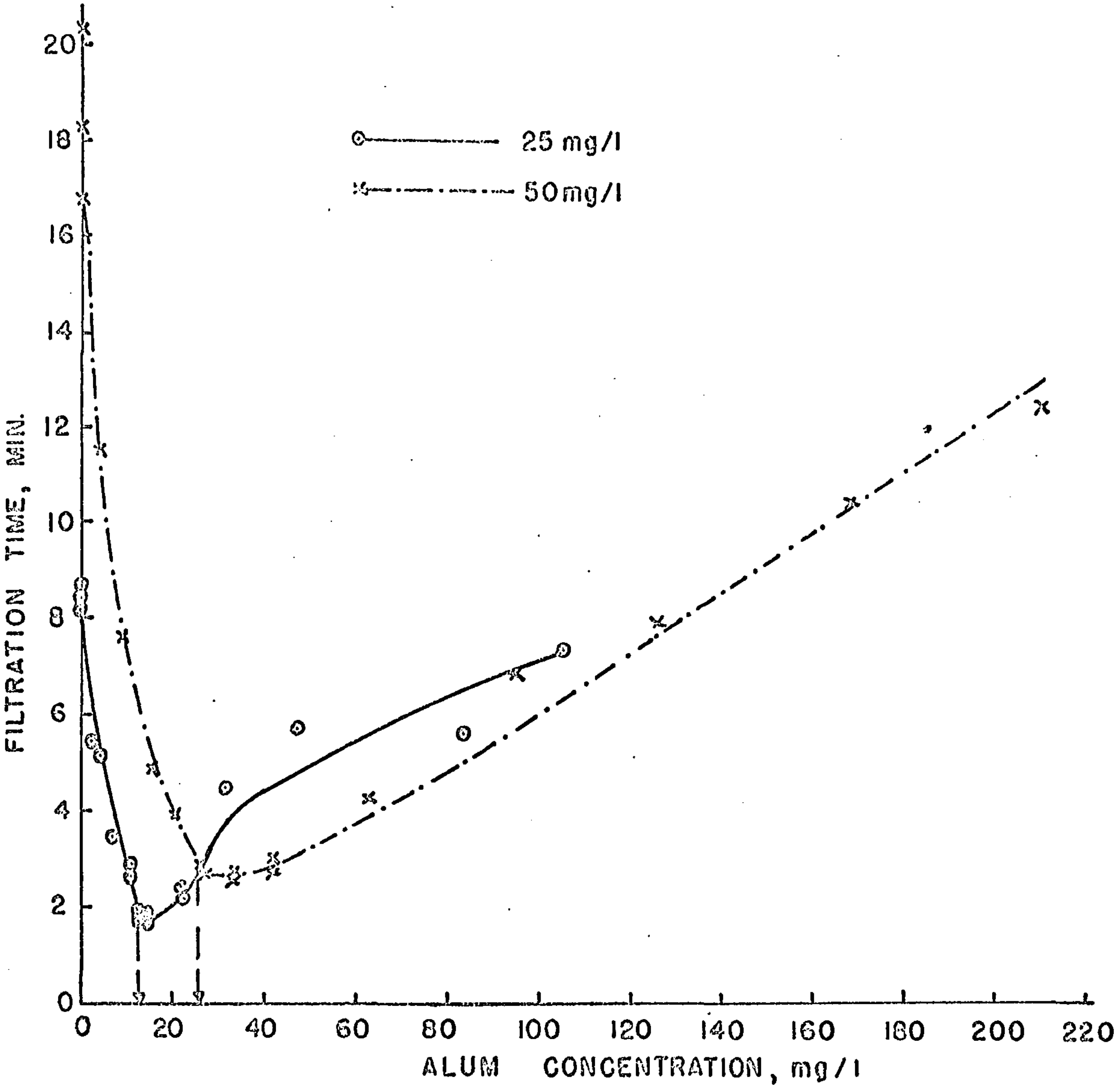

25 mg/l
50mg/l
FILTRATION TIME, MIN.
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160
180
200
220
ALUM CONCENTRATION, mg/l

Figure 37. Effect of alum concentration on the filtration time of suspensions having different clay concentrations at pH 7.0 (Series no. 5, 6, and 7)

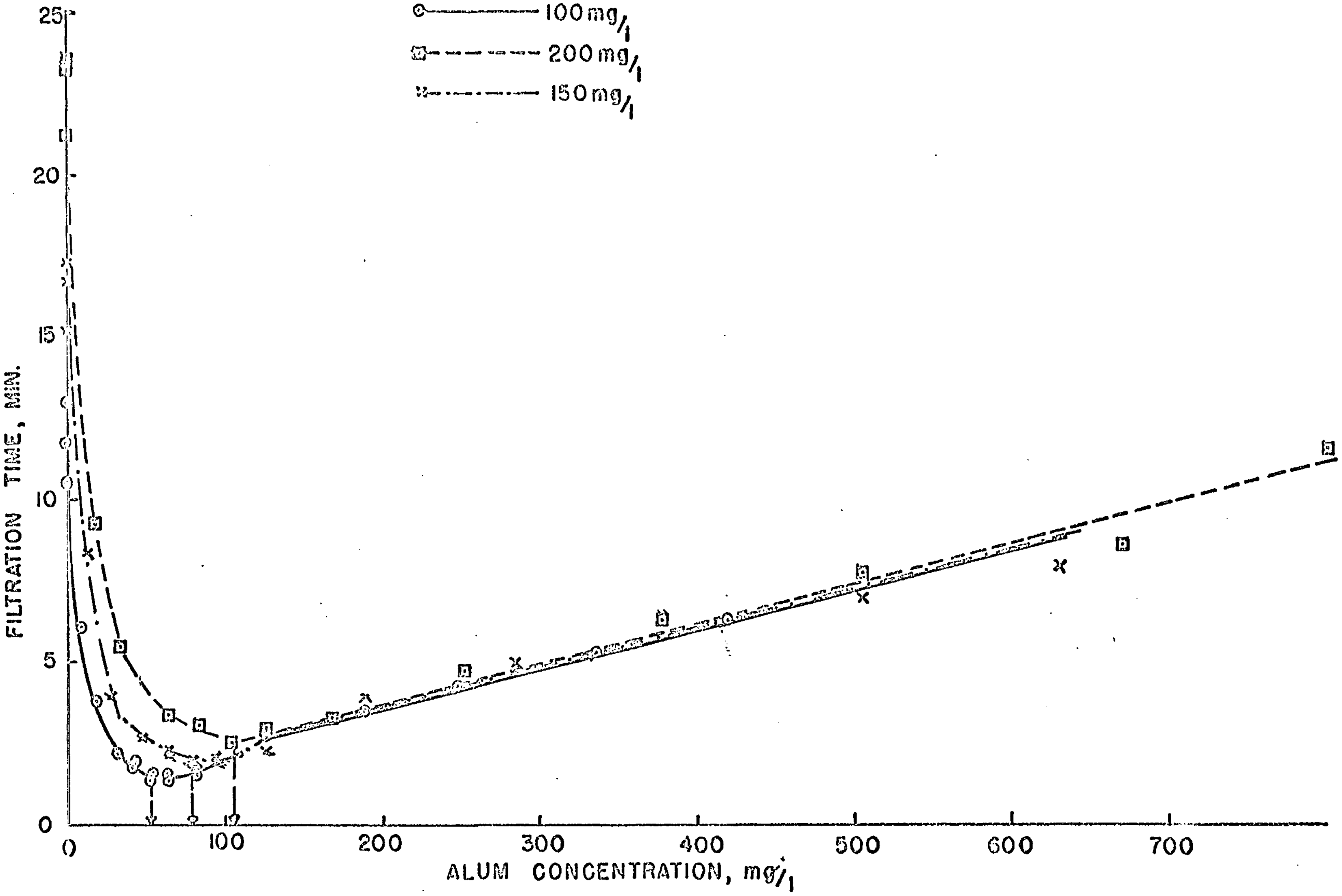

100 mg/l
200 mg/l
150 mg/l
FILTRATION TIME, MIN.
0
5
10
15
20
25
ALUM CONCENTRATION, mg/l
0
100
200
300
400
500
600
700

Figure 38. Effect of alum concentration on the refiltration time of suspensions having different clay concentrations at pH 7.0 (Series no. 2 and 4)

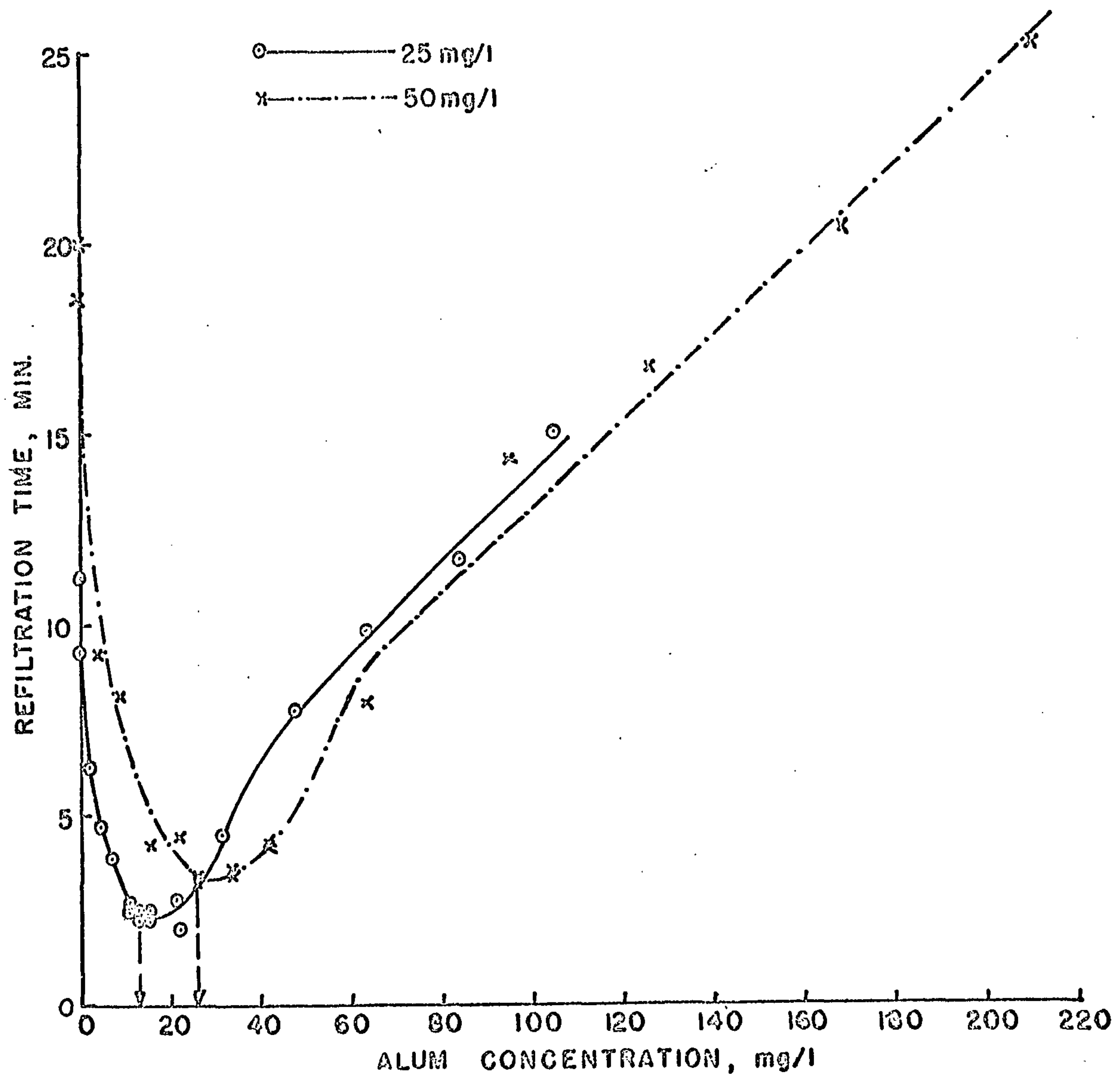
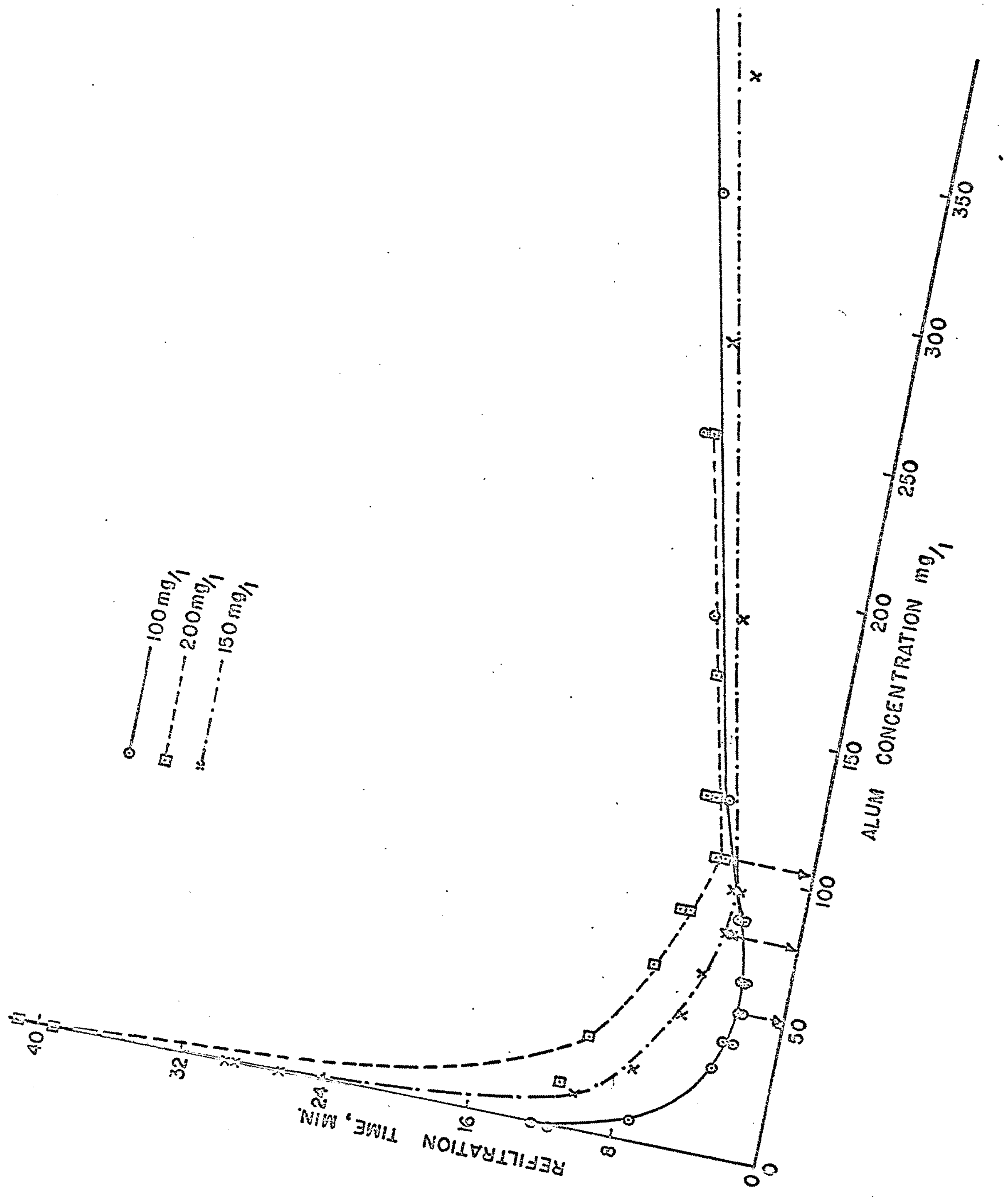

25 mg/l
50mg/l
REFILTRATION TIME, MIN.
0
5
10
15
20
25
0
20
40
60
80
100
120
140
160
180
200
220
ALUM CONCENTRATION, mg/l

Figure 39. Effect of alum concentration on the refiltration time of suspensions having different clay concentrations at pH 7.0 (Series no. 5, 6, and 7)

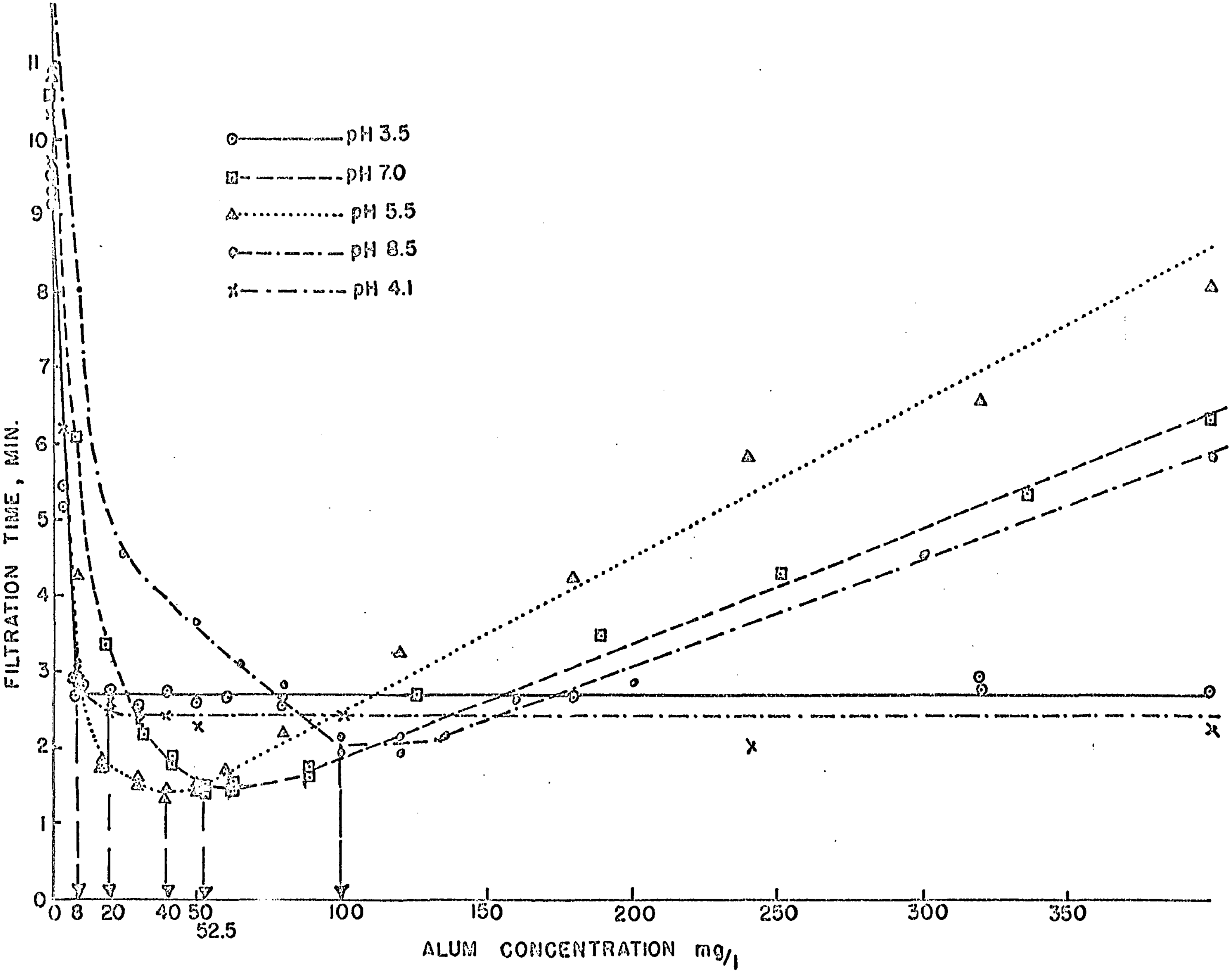

100 mg/l
200 mg/l
150 mg/l
REFILTRATION TIME, MIN.
0
8
16
24
32
40
ALUM CONCENTRATION mg/l
0
50
100
150
200
250
300
350

the curves tend to coincide with each other for alum concentrations above the optimum level. This means that if the alum concentration is above the optimum level, both the filtration time and refiltration time of the cakes formed depend only upon the alum concentration and not on the clay concentration. If the increases in time had been due to the restabilization of clay particles due to charge reversal, these increases should show the effect of clay concentration. Comparable jar tests show that the turbidity removal is not adversely affected by alum additions of such high levels, indicating that the destabilization of the suspension takes place at the high doses also (Figures 18 through 22). Since precipitation of floc can be visually observed at these high alum dosages, it can be concluded that the alum added in excess of the required amount precipitates out and affects the thickness and the porosity of the filter cakes.

Figure 40 summarizes the variation of filtration time with alum concentration at different pH levels. The filtration times at pH 10.0 are not included since they are beyond the range of this figure. Filtration time can be seen to increase for pH levels 5.5, 7.0, and 8.5 for alum concentrations higher than the optimum levels, while they stay at a constant level at pH values of 3.5 and 4.1. At pH 10.0 also they tend to increase when alum concentration is increased above the optimum.

Attempts were made to find out at what doses of alum, precipitation of aluminum hydroxide takes place. This was carried out by adding alum in increasing doses to distilled water containing no clay adjusted to constant pH, and by observing for precipitation with a light beam passed through the water. At pH levels 5.5 and 7.0, it proved to be impossible

Figure 40. Effect of pH and alum concentration on the filtration time of suspensions having a clay concentration of 100 mg/1 (Series no. 5, 8, 10, 11, and 13)



pH 3.5
pH 7.0
pH 5.5
pH 8.5
pH 4.1
FILTRATION TIME, MIN.
0
1
2
3
4
5
6
7
8
9
10
11
0
8
20
40
50
52.5
100
150
200
250
300
350
ALUM CONCENTRATION mg/l

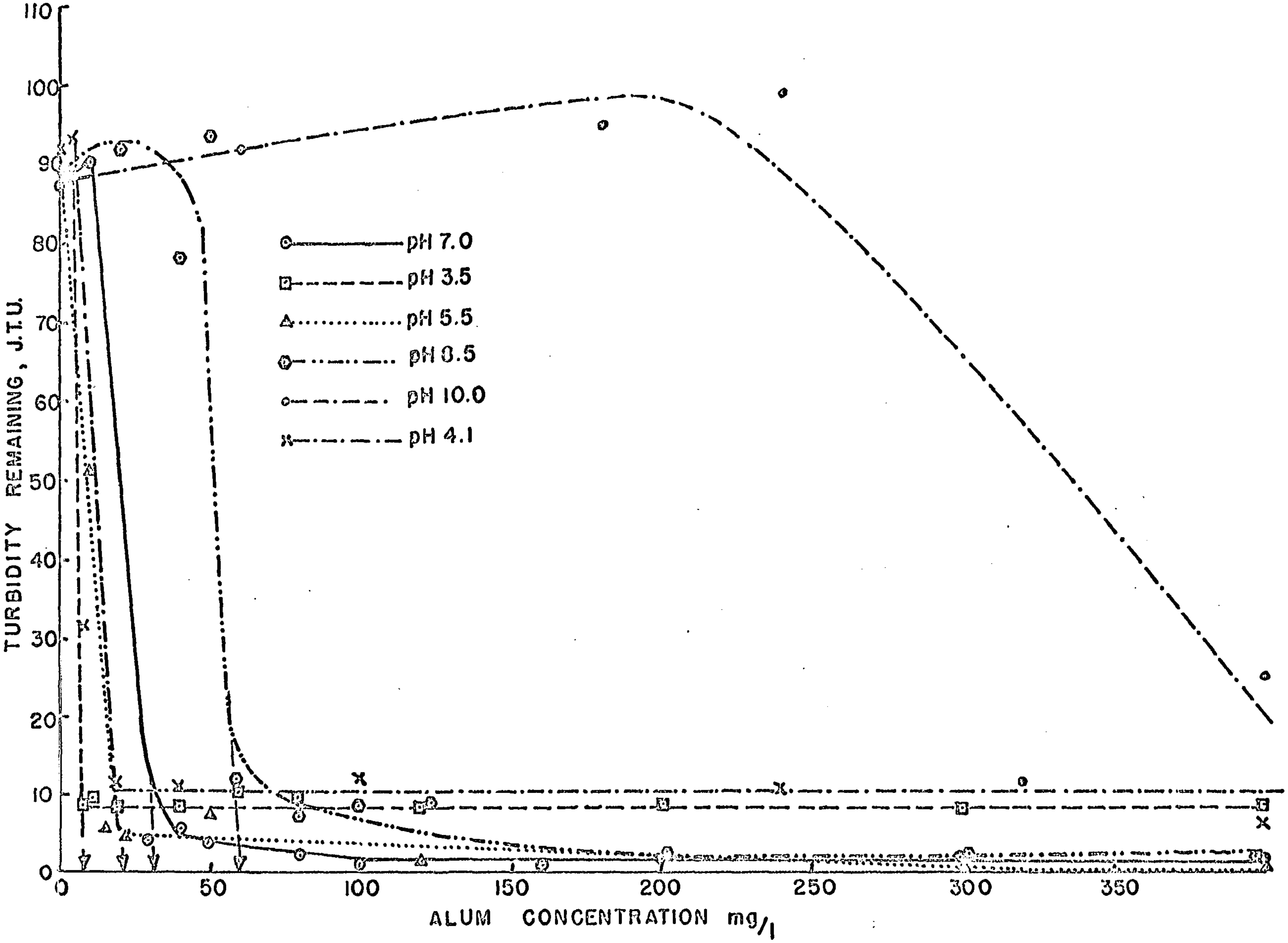
to distinguish the precise level of alum at which precipitation begins, since it seemed to start at very low doses, as low as 1.0 mg/l. Such low concentration for precipitation at these pH levels agree with the observations made by Packham (28) and the calculated values given by Stumm (36). When the pH was maintained at 4.1, concentrations of alum up to 1200 mg/l resulted in no precipitation; but when the concentration was doubled to 2400 mg/l, precipitation was clearly observed. The corresponding values at pH levels of 8.5 were 120 mg/l for no precipitation and 160 mg/l for precipitation; and at pH 10.0 they were 1420 mg/l and 1680 mg/l respectively. The precipitation levels coincide reasonably well with the values from the solubility diagram prepared by Stumm (36).

The filtration time curves at these different pH levels indicate that they either decrease or stay constant within the range where no precipitation occurs, but increase significantly for alum doses accompanied by precipitation (Figures 25, 27, and 28). But the jar tests again show no adverse effects on turbidity removals because of these high doses of alum (Figure 41). Precipitation of aluminum hydroxide, not restabilization of clay, can be concluded as being responsible for the observed increases in filtration time at high alum doses.

The above conclusion does not agree with the findings of Matijevic (20). The principal disagreement between the two studies lies in the disparity of levels of aluminum salt required for precipitation. While the precipitation levels observed in the present study agree well with the usual understanding of alum precipitation and the values shown by Packham (28) and Stumm (36), it was indicated by Matijevic (20) that much higher levels of aluminum salt were required to result in

Figure 41. Effect of pH and alum concentration on the turbidity of supernatant in jar tests (Series no. 5, 8, 9, 10, 11, and 13)

Initial clay concentration = 100 mg/1


TURBIDITY REMAINING, J.T.U.
0
10
20
30
40
50
60
70
80
90
100
110
ALUM CONCENTRATION mg/l
0
50
100
150
200
250
300
350
pH 7.0
pH 3.5
pH 5.5
pH 8.5
pH 10.0
pH 4.1

precipitation. The coagulant required for restabilization of sols obtained by Matijevic (Figure 3) were in the precipitation region indicated by the present study. Reasons for such disagreement cannot be readily explained.

At pH levels of 5.5 and 7.0, the optimum alum concentrations are in the region where precipitation was present. When alum is added to water, the soluble hydrolysis products would be expected to form first and these products would be progressing towards precipitation of insoluble hydroxide. If these kinetic intermediates can be brought to the surface of the colloids by rapid mixing, as it has been done in this study, adsorption of these on the clay colloids followed by aggregation of clay colloids can be effected. When alum concentrations higher than required for possible adsorption on the colloids are added to the suspensions, the excess alum would be expected to result in precipitation. This precipitation results in an increase of solid content of the water without aiding in aggregation and thus, increases the time required for filtration and refiltration.

Filtration time vs. refiltration time

The Kozeny-Carman equation for fixed bed filtration was used by Smellie and La Mer (35) to relate the characteristics of a suspension and the refiltration time through a cake formed with the contents of the suspension. The equation can be expressed as shown below:

$$q = \frac{\Delta P g_c \epsilon^3 A}{5L(1-\epsilon)^2 S^2 \mu} \tag{3}$$

where q = volume filtered, L^3T^{-1}

ΔP = pressure difference, FL^{-2}

g_c = Newton's law conversion factor, $LMF^{-1}T^{-2}$

ϵ = porosity factor

A = area, L^2

L = thickness, L

S = surface area per unit volume, L^{-1}

μ = viscosity of fluid, $ML^{-1}T^{-1}$

When filtering a known volume of water (V) through the bed, this can also be expressed as

$$\frac{V}{t} = \frac{\Delta P g_c \epsilon^3 A}{5L(1-\epsilon)^2 S^2 \mu} \qquad (4)$$

where t = refiltration time, T

Smellie and La Mer (35) assumed constant thickness and porosity of the cakes formed for suspensions having the same solids concentrations but different flocculant concentrations and arrived at a function from Equation 3, $q = \frac{K}{S^2}$ where K is a constant. This can also be expressed as

$$\frac{1}{t} = \frac{K^1}{S^2} \quad \text{or} \quad t = \frac{S^2}{K^1}$$

from Equation 4. Using this simplified relationship between refiltration rate and surface area and making several simplifying assumptions about the floc geometry, an equation relating the flocculant concentrations and the refiltration rates was derived.

$$\frac{P_o^{1/2}}{(q-q_o)^{1/8}} = A\,P_o + B \qquad (5)$$

where P_o = flocculant concentration, ppm

q = refiltration rate with the flocculant P_o

q_o = refiltration rate with no flocculant

A and B = constants containing the Langmuir adsorption constants and other constants characteristic of the suspension

A straight-line plot between $\frac{P_o^{1/2}}{(q-q_o)^{1/8}}$ and P_o was considered as a confirmation as to the accuracy of the theory developed for flocculation of slimes with polyelectrolytes. The slope and intercept of this line would respectively be A and B. This equation can be modified to express it in terms of refiltration times as

$$\frac{P_o^{1/2}}{(1/t - 1/t_o)^{1/8}} = A\,P_o + B \tag{6}$$

where t and t_o are the refiltration times needed to refilter a constant volume of filtrate resulting from filtering a suspension treated with a flocculant or coagulant concentration of P_o and of untreated suspension respectively.

Filtration time (i.e., time of cake formation) can be expressed in the following form (23) neglecting the effect of the filter paper.

$$t_f = \frac{\mu}{g_c(\Delta P)}\left[\frac{c\,\alpha}{2}\left(\frac{V}{A}\right)^2\right] \tag{7}$$

where t_f = filtration time, T

c = concentration of solids, ML^{-3}

α = average specific cake resistance, LM^{-1}

The specific cake resistance through a unit thickness of filter cake, α_L is equal to (23):

$$\alpha_L = \frac{kS^2(1-\epsilon)}{\epsilon^3 \rho_p} \tag{8}$$

where ρ_p = density of the particles, ML^{-3}

k = constant

The average specific cake resistance, α, can be approximated to be equal to the average values of the factors in the right hand side of Equation 8. So, inserting the expression for α into Equation 7, the following equation is obtained

$$t_f = \frac{\mu kcV^2(1-\epsilon)}{2g_c(\Delta P)A^2\epsilon^3\rho_p} S^2 \tag{9}$$

Under constant conditions, similar to those assumed by Smellie and La Mer, a simplified equation of $t_f = K''S^2$ can also be derived for filtration time from Equation 9. The assumptions made above in arriving at this equation are neither correct nor acceptable. They are presented only to show that filtration time and refiltration time can be expected to give the same results of optimum coagulant concentrations.

As mentioned earlier, Smellie and La Mer prepared plots of $\frac{P_o^{1/2}}{(q-q_o)^{1/8}}$ versus P_o and obtained straight line relationship for the data collected for phosphate slimes treated with polyelectrolytes. This was taken as indication of proof that the assumptions made in developing the bridging theory were correct.

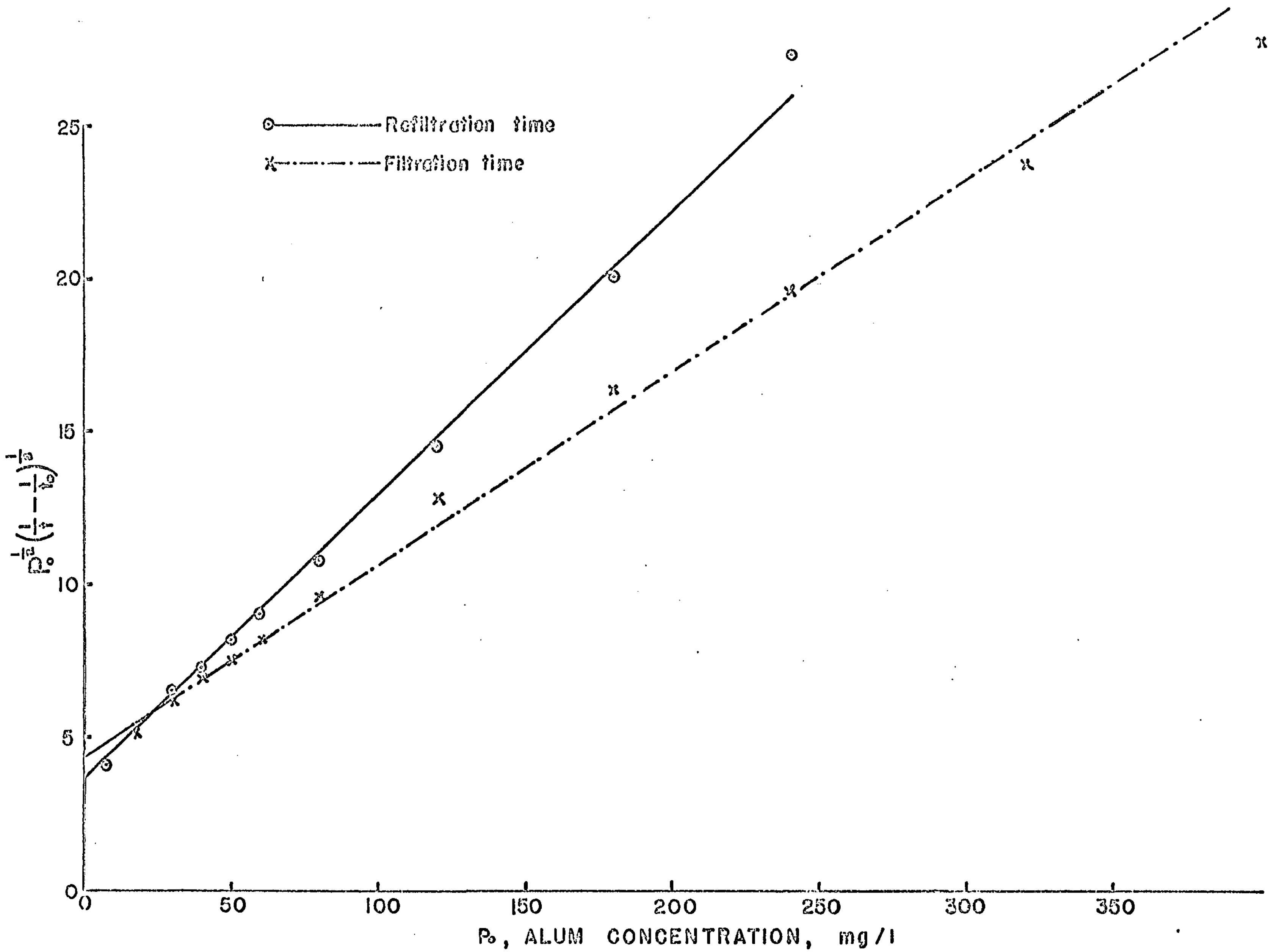
The filtration and refiltration data collected during the present study were used to prepare plots of $\frac{P_o^{1/2}}{(1/t - 1/t_o)^{1/8}}$ versus P_o, where the times were either filtration time or refiltration time. Fairly good straight line relationships were obtained for both types of filtration for the series of tests conducted at and near neutral pH levels, but curvi-linear plots resulted for the tests at lower and higher pH levels. Examples of straight line plots and curvi-linear plots are shown in Figures 42 and 43 respectively.

Smellie and La Mer assumed constant porosity and thickness of the cakes formed in a series of tests regardless of polyelectrolyte concentrations used in each test. The thickness of cakes formed during the tests performed at or near neutral pH levels in the present study were visually observed to increase with alum concentration because of precipitation of excess alum. This observation invalidates the assumptions made by Smellie and La Mer. So, it was actually amusing to note that straight relationships were obtained only in those series where the cake thickness was observed to increase. This indirectly means that the test itself is an insensitive one for deviations from the assumptions.

Furthermore, from the example figures (Figures 42 and 43) it can be noticed that the relationships have a tendency to reach the origin, i.e., the (0,0) point, whether a straight line or a curvi-linear relationship was obtained. This was found to be true in all the figures. The reason for this may be found in Equation 6. When P_o is equal to zero, the intercept, B, also has to be zero according to the equation. Thus, the line should pass through the origin. However, the value of B cannot be equal to zero according to the theoretical development (35). This may have resulted due to some inaccuracies in the assumptions made during the development of the bridging theory.

Figure 42. Relationship between alum concentration, P_o and $\frac{P_o^{1/2}}{(1/t - 1/t_o)^{1/8}}$ (see Equation 6)

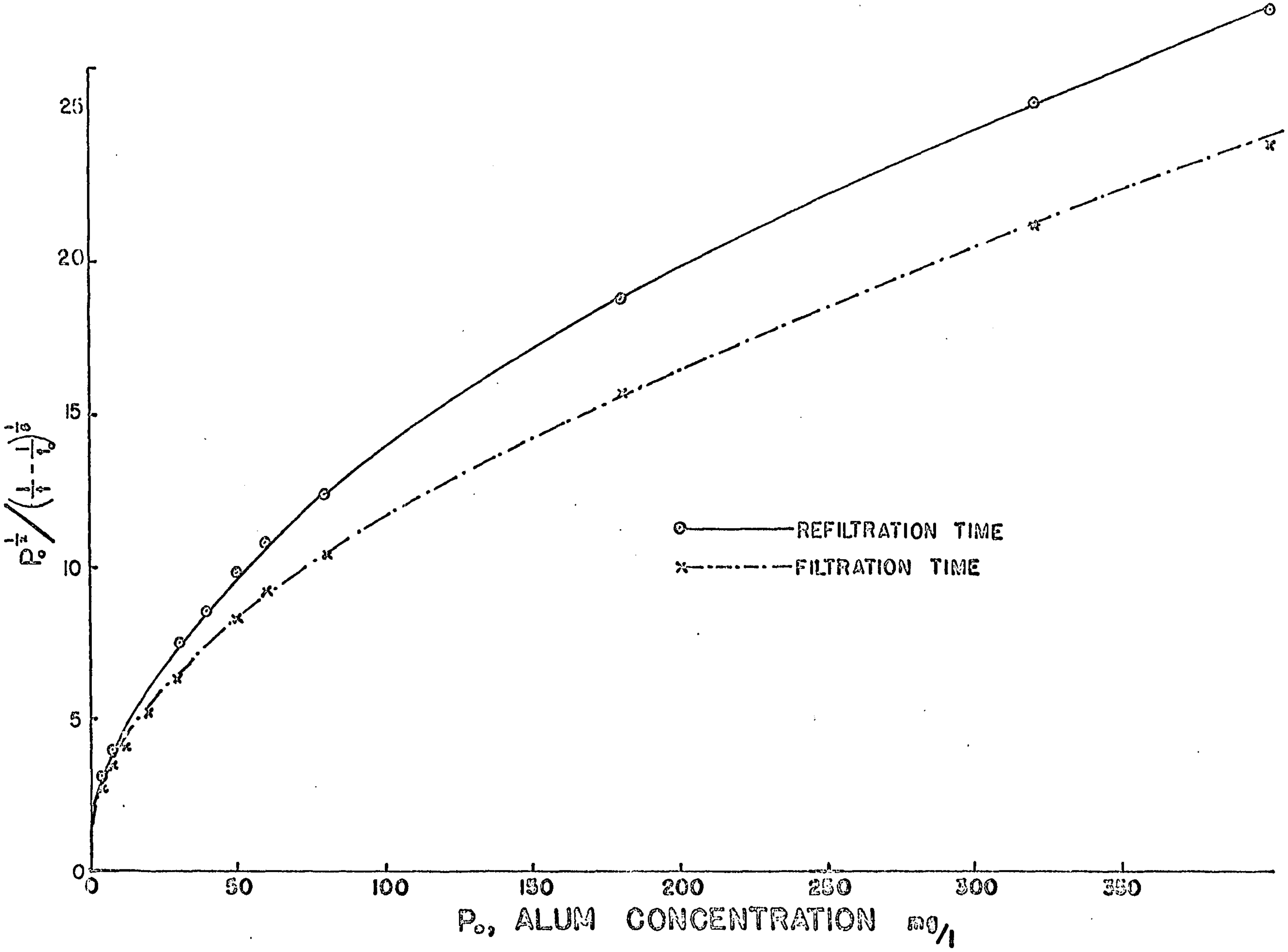
Series no. = 5
clay concentration = 100 mg/1
pH = 7.0



Refiltration time
Filtration time
$\Omega_0^{\frac{1}{a}}\left(\frac{1}{t}-\frac{1}{t_0}\right)^{\frac{1}{a}}$
0
5
10
15
20
25
0
50
100
150
200
250
300
350
P_0, ALUM CONCENTRATION, mg/l

Figure 43. Relationship between alum concentration, P_o and $\dfrac{P_o^{1/2}}{(1/t - 1/t_o)^{1/8}}$ (see Equation 6)

Series no. = 8
clay concentration = 100 mg/l
pH = 3.5


$P_o^{\frac{1}{n}} / \left(\frac{1}{t} - \frac{1}{t_o}\right)^{\frac{1}{\beta}}$
0
5
10
15
20
25
0
50
100
150
200
250
300
350
P_o, ALUM CONCENTRATION mg/l
REFILTRATION TIME
FILTRATION TIME

The discussion above leads to two conclusions; both filtration time and refiltration time are comparable parameters and, La Mer's flocculation theory of the bridging mechanism does not hold true for the mechanism of destabilization of clay suspensions with alum. While it is true that both filtration time and refiltration time tests are equally acceptable parameters, it should be pointed out that filtration time test was found to be a simpler, faster and less technique-dependent as compared to the refiltration time test.

Mobility as a parameter of coagulation

The mobility values indicated that only in seven out of thirteen series, the isoelectric point was reached; and the charge of the colloids was reversed to a positive value in only five of these. The neutralization of charge was observed in the pH range of 3.5 to 7.0 and the charge reversal was noted in the pH range of 4.1 to 7.0. Matijevic (20), on the basis of extensive studies, concluded that the hydroxyl groups of the coagulating species were essential for adequate adsorption for the charge reversal phenomenon to occur. The $Al_8(OH)_{20}^{4+}$ species suggested by Matijevic in the pH range of 4.0 to 7.0 would fit the requirement of the hydroxyl ion in its structure. At pH levels lower than 4.0, the charge would be neutralized by the trivalent ionic species but not be reversed due to the lack of hydroxyl groups in the species. The fact the charge reversal was not observed at these pH levels suggests that multilayer adsorption might be essential for charge reversal, and that the hydroxyl groups are essential to multilayer adsorption. The hypothesis cannot be definitely proved by the experimental data, however. At pH levels higher than 7.0, the hydrolysis species $Al(OH)_4^-$ proposed by Stumm (36) would meet the requirement of hydroxyl groups in its structure but would not reduce the charge of the colloids when adsorbed because of its negative charge.

At pH 7.0, the charge of the particles was reversed when alum concentrations higher than the optimum were used, and when the clay concentration was equal to or lower than 50 mg/l (Figure 32). However, at higher clay concentrations, a similar expected charge neutralization or reversal could not be accurately observed because the floc grew to such a large size that settling of the large floc in the Brigg's cell prevented accurate mobility observations. The observed floc in these cases was believed to be aluminum hydroxide precipitate containing some clay particles. A few smaller flocs did not settle down and they were timed. Since they were by no means representative of all the particles present, these results are shown as dotted lines in the respective figures (Figures 20, 21, 22, and 32).

The lowest amount of alum required to reach the isoelectric point in different series of tests are compared with the respective optimum alum doses for filtration and settling in Table 4. The amount required to reach the isoelectric point was always found to be higher than the optimum values. However, it should be noted that the alum doses required to reach the isoelectric point are in the broad optimum range of alum concentration observed during filtration and the settling tests. This means that adhering to the usage of the isoelectric point as the indicator of coagulation would result in wastage of alum; but the process would work efficiently as far as the reduction of cake resistance or turbidity are concerned.

However, the isoelectric point was not reached in six series of tests. Adopting the isoelectric point as a coagulation parameter would not work under the conditions maintained in these series. The condition common to these series is that the pH is either equal to or greater than 7.0. Thus, when dealing with highly alkaline waters, the use of the isoelectric point as an indicator would definitely be meaningless.

Another factor which has been reported in Table 4 is the mobility value at an alum dose equivalent to the optimum levels for filtration and settling. There is absolutely no direct correlation between the mobility values and the optimum alum doses. The only common factor in these mobility values is that they are all negative; but they vary from -0.27 to -2.53 $\frac{\mu \cdot \text{cm}}{\text{volt} \cdot \text{sec}}$. This points out that use of a constant zeta potential or mobility as an indicator of coagulation is not desirable. Thus, it may be concluded that even though the electrophoretic measurements may serve as an important tool in understanding the process of coagulation, it cannot be indiscriminately used as a parameter of coagulation.

Jar tests vs. filtration tests

The difference in the effect of aluminum hydroxide precipitation on jar tests and filtration studies has been discussed in an earlier section of this chapter. One other difference noted in the results of these different tests is in the optimum alum levels observed for settling and filtration. The optimum level required for settling is always less than the corresponding optimum level for filtration (see Table 4 and Figures 31 and 34).

When an arbitrary time for settling is chosen for the jar tests, it follows that a particular extent of aggregation, so as to reach a certain size which will settle within that time, is also chosen. If this extent of aggregation results in essentially complete turbidity removal in the allotted time, the jar test loses its sensitivity to detect higher degrees of aggregation for higher alum doses. Alum doses higher than the optimum dose for settling do not result in any further significant reduction in turbidity, even though faster and better aggregation might take place. These progressive increases in size of particles are sensed by the filtration tests however, since there is no fixed level of filtering time attempted in the tests. The alum level required for reducing the filtering time by 75 per cent of its no-alum-value (i.e., a fixed degree of aggregation) at pH 7.0 for different clay concentrations is shown in Figure 31. It can be seen that this curve and the curve of the optimum level for settling coincide quite reasonably.

These two curves, for optimum settling and for 75 per cent reduction in filtration time, differ more and more from the optimum level curve for filtration as the clay concentration is increased (Figure 31). This phenomenon can be explained by the importance of interparticle distance. As the clay concentration is increased, one would expect the interparticle distance to decrease proportionately and the probability of collision of any two particles to increase significantly. More and more collisions would be expected to result in a greater particle aggregation even though the same ratio of alum to clay concentration is present. Thus, a particular extent of aggregation would take place at a lower ratio of alum concentration to clay concentration if the clay concentration were increased. On the other hand, the optimum alum dose for filtration does not measure a fixed degree of aggregation. Rather, it measures the greatest observable degree of aggregation and is dependent upon the complete adsorption of the aluminum species.

A recent paper (34) concludes that coagulant doses for filtration optimums are lower than the optimums for settling alone. However, the procedure followed in that study compared the process of settling with the combination of settling followed by filtration. Thus it is not possible to directly compare the results of that study with the present study, where the settling process has been compared against the filtration process alone.

SUMMARY AND CONCLUSIONS

Surface waters have been traditionally treated by coagulation followed by settling and rapid sand filtration for the removal of suspended matter from the water. In municipal diatomite filtration plants, however, the process used for the removal of particulate matter has been one of cake forming filtration, commonly without any pretreatment. Because of this, coagulation studies conducted by sanitary engineers have been directed towards the effect of coagulant doses on the process of settling; the effect of coagulation on filtration, or a combination of settling and filtration has not been adequately studied.

The commonly used test for evaluating coagulant dosage has been the jar test which is essentially a measurement of the effectiveness of settling resulting from various coagulant doses in a predetermined schedule of mixing and settling. While this test can be successfully applied to the operation of a treatment plant in the hands of a good operator, its application as a research tool has not been significant since it does not adequately show the progressive effect of increasing coagulant dose near the optimum dose. Refiltration experiments have been successfully applied to study the effect of polyelectrolytes on coagulation of phosphate slimes (17). The use of electrophoretic mobility as an indicator of coagulation has also been reported recently (33).

A clay-alum system has been chosen to study the different parameters of coagulation with a hydrolyzing salt, and also to investigate the mechanisms involved in the process of coagulation itself. The type of clay used was Panther Creek bentonite, which contains mostly calcium montmorillonite.

If filtration can be used as a parameter of coagulation of a suspension, it indirectly points out the feasibility of a process where coagulation can be followed by a cake-forming type of filtration, namely diatomite filtration. Diatomite filtration is quite versatile in the sense that most types of particulate matter can be removed with proper selection of diatomite grade and body feed levels. However, when certain clay minerals were removed by diatomite filtration, rapid head loss increases and short filter runs have been noted, even with high body feed levels. Thus the control of characteristics of suspended matter in water by coagulation could result in longer filter runs or lower body feed levels. The clay-alum system has also been chosen here to demonstrate the feasibility of the process of coagulation followed by diatomite filtration.

The specific objectives of this study have been:

1. To demonstrate the effect of adding aluminum sulphate to a clay suspension, prepared with university tap water, upon the resistance of a diatomite filter cake containing the coagulated or uncoagulated clay.

2. To study the relationship between the following parameters of coagulation: refiltration time, electrophoretic mobility, jar test, and a seldom-used parameter known as filtration time.

3. To observe the effect of factors such as concentration of aluminum sulphate, clay concentration, pH, and mixing speed on the coagulation of a clay suspension using the above-mentioned parameters.

4. To gain further insight into the mechanism of coagulation caused

by aluminum salts by compiling and drawing conclusions from the information gathered.

A pilot pressure diatomite filter plant was used to carry out the first of the objectives listed above. Two sets of filter runs were conducted during this part of the study. The factors that were different from one set to another included clay concentration, body feed concentration, filtration rate, and speed of mixing of alum with the raw water. Alum dose levels were varied from filter run to filter run, within a set, to study the effect of alum concentration on the filter cake resistance. The β-index, which is a measure of specific cake resistance, was computed for each filter run and the per cent change in the β-index was calculated due to each alum concentration.

In order to accomplish the rest of the objectives, bench scale studies were made using a membrane filtration assembly, electrophoretic equipment, and a jar testing apparatus to measure the effect of coagulation of clay with alum. The observed measurements included filtration time, refiltration time, electrophoretic mobility, and the turbidity of the supernatant in jar tests. Fifteen series of tests were carried out, each being done to test the effect of one or more factors that might be important in coagulation. Factors tested included mixing speed, clay concentration, pH, and the dissolved mineral concentration in the water.

The following conclusions have been reached as a result of this study:

1. The resistance of a diatomite filter cake containing Panther Creek bentonite can be changed significantly by the coagulation of the clay with aluminum sulphate. The magnitude and the direction of change

depend upon the clay concentration, alum concentration, body feed concentration, and the speed of mixing the alum with the raw water.

2. There is an optimum alum concentration which can be used to obtain the greatest reduction in the filter cake resistance. With the addition of an optimum amount of alum to water, either longer filter runs or lower body feed levels can be achieved.

3. The hydrolysis species of aluminum ions are adsorbed on the surface of the clay particles, regardless of the type and magnitude of charge exhibited by the species and the clay particles. The change of repulsive potential does not take place due to the suppression of the electrical double layer surrounding the particle alone; rather it is mainly due to the specific adsorption of the aluminum species on the surface of the colloids.

4. Aggregation of clay particles takes place as a result of the adsorption of the aluminum species. The level of alum required for maximum aggregation is dependent upon many factors such as pH, the type and charge of aluminum species, and the clay concentration.

5. At low pH levels (3.0 to 4.0) the adsorption of the coagulating species reduces the repulsive potential of the particles and the clay particles aggregate together as a result of natural attractive forces.

6. At high pH levels (above 7.0) the negative charge of the colloids is not reduced by the adsorption of the negatively charged aluminum species. However, aggregation is observed. In this case, aggregation may take place due to the adsorption of an aluminum hydrolysis species molecule on the surface of more than one clay particle, or due to the interaction of a molecule of species adsorbed on one particle with

another molecule adsorbed on a second particle. This interpretation is similar to the bridging model developed by Smellie and La Mer (35).

7. At intermediate pH levels (5.0 to 7.0) both the mechanisms may be expected to take place, since the adsorption of a large polyvalent hydrolysis species reduces the repulsive potential. Such a combination of both mechanisms seems to result in the most effective coagulation.

8. The filtration time and refiltration time tests are equally valuable parameters for predicting the progress of coagulation and the optimum coagulant level. The filtration time experiments are relatively simple and fast. The refiltration time tests are highly technique-dependent because of the possibility of cake disturbance when the filtrate is poured back over the filter cake. They consume more time compared to filtration time tests.

9. The restabilization of a clay colloidal suspension with high doses of alum is not observed in the results of this work. However, precipitation of aluminum hydroxide in excess of the amount of alum required for adsorption results in increases of filtration time and refiltration time. The precipitation of excess alum does not affect the process of settling adversely.

10. The use of mobility or zeta potential as an indicator of the optimum alum dose may not be possible if the pH of the water is higher than neutral, since the isoelectric point is not reached at these pH levels. At lower pH values, the use of the isoelectric point as an indicator may result in wastage of alum. No correlation between optimum alum doses and mobility values has been observed in this study.

11. The jar tests do not indicate the progressive effect of increasing alum doses on coagulation as well as the filtration or refiltration time tests.

12. The mutual coagulation of clay colloids and the interparticle distance are two factors which play a major part in the degree of coagulation obtained with a certain dose of alum. These would be most evident when less than optimum alum doses are added. These factors affect the required alum dose significantly.

RECOMMENDATIONS

The following recommendations are made as a result of this investigation:

1. Pilot scale studies should be conducted using natural waters containing clay minerals, algae, and color in suspension and a coagulant, such as alum, in order to further establish the practicability of the use of alum for reducing cake resistance.

2. Similar bench scale studies and pilot scale studies should be conducted in the laboratory using different types of suspended solids, such as sodium montmorillonite and kaolinite.

3. Attempts should be made to construct or secure equipment capable of feeding body feed at different rates with more accuracy; similarly, the development of devices to feed suspended solids slurry at the desired levels with ease should be attempted.

4. The feasibility of using commercially available multiple filtration devices in a manner similar to the jar testing apparatus, for conducting bench scale coagulation studies should be considered.

5. The effect of mixing speed and time on the coagulation of a suspension should be studied utilizing a variable speed mixer in pilot plant studies.

6. The use of a microscope with accessories to screen the image in microelectrophoretic measurements should be investigated to avoid enormous eyestrain to the operator and possible errors in the readings due to this.

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