EFFECT OF POLYELECTROLYTES ON

COLOR AND TURBIDITY REMOVAL

By

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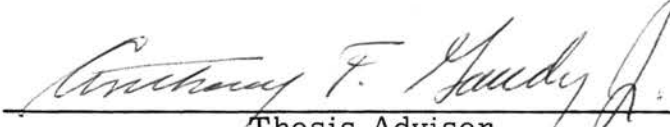Bachelor of Science

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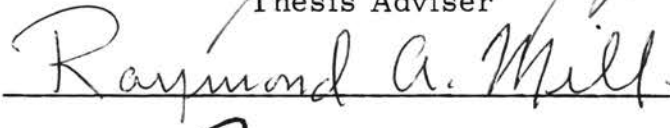for the degree of
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ACKNOWLEDGMENT

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CHAPTER I

INTRODUCTION

One of the essential processes of the majority of water treatment plants involves the addition of a chemical coagulant which causes aggregation of some fine particles and adsorption of others to produce a larger particle called a "floc". The settling rate of this floc is dependent on many factors, but principally on its size and density. Considerable research over the past years has been directed toward achieving more rapid flocculation. A major contribution to this effort was the discovery that activated silica induces the formation of large, dense, and tough floc. There had been no serious competitor to activated silica for water clarification until the recent introduction of natural and synthetic materials called "polyelectrolytes". It was soon apparent that these materials were effective coagulant aids, which produce a large and rapidly settling floc when used with standard chemical coagulants.

Production of both natural (starch) and synthetic (polycationic and polyanionic) polyelectrolytes for use in water treatment has been developed by several large chemical companies in the past 10 years.

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Literature Review

Colloidal Solutions

There are several natural and artificial processes which give rise to a stable dispersion of one substance in another. Such dispersions are made up of a "disperse phase" or a "discontinuous phase" consisting of minute particles in the size range of 1 to 100 millimicron, and a "continuous phase" or "dispersion medium" in which the particles are uniformly spread out. Such systems have well marked physico-chemical properties and are termed "Colloids Systems" (1). Colloidal dispersions of solids in liquids are often referred to as "sols" or "suspensoids".

The colloidal matter may be broadly classified into two main types, that giving rise to "turbidity" and that giving rise to "color". The substances which give rise to turbidity are mainly composed of mineral clay. The turbidity includes both coarse and truly colloidal matter. Coarse turbidity is not as much a problem as colloidal turbidity because, on allowing the suspension to stand quiescently, most of it settles out. Color in water is composed of some metallic hydroxides and organic compounds. Color particles also fall within the colloidal range.

Color and turbidity can be removed from water effectively under suitable conditions. In the case of many sols, when an electrolyte is added in small concentrations, the stability is disturbed,

and aggregation and precipitation of the suspended colloidal particles occur, the process being known as "Coagulation".

Basic Mechanisms of Coagulation Including Instability and Stability Factors.

The two most important instability factors are Brownian movement and Van der Waals forces of attraction. Brownian movement is the movement imparted to the suspended sol particles because of their impact with rapidly moving molecules of the medium. It is, therefore, essentially a thermal effect that tends to drive particles closer to each other and even causes them to penetrate the force fields surrounding each particle. Although the nature of the Van der Waals forces is not well understood, they may be described as molecular cohesive forces that increase in intensity as the particles approach each other.

The most important stabilizing factors are hydration and the zeta potential. Hydration is the result of a characteristic possessed by some particles of attracting relatively large numbers of solvent molecules to their surface. This prevents contact between the particles by "sandwich action". Zeta potential refers to the surface charge of colloidal particles which causes the particles to migrate in an electrical field to the pole of opposite charge. Zeta potential may be the result of selective adsorption of ions from the solution or of residual valence forces, or both (2) (3).

Theoretically, as long as the zeta potential is great enough to

produce repulsive forces in excess of the Van der Waals forces, the particles cannot coalesce (4).

Electrophoretic studies (4) (5) (6) have shown that rapid coagulation of a colloid sol usually take place shortly before the zeta potential has been completely neutralized for the coagulation of either organic color or turbidity. It has also been found that when turbidity is present as clay, the metallic ions in the diffuse double layer surrounding a clay particle constitute an ion-exchange system and an equilibrium exists between them and other ions in solution (3).

Flocculation

As defined by Herbert E. Hudson, Jr. (7), flocculation is part of coagulation and includes: (1) addition of coagulating or flocculating materials; (2) their dispersion throughout the fluid; (3) agitation to bring the colloidal turbidity particles in contact with the coagulating agents and with each other; (4) agitation to unite the individual particles into more or less tightly bound agglomerates or flocs of suitable size and density. The last two agitation phases are termed flocculation.

The probability of collision and adhesion between colloidal particles, governing the size and density of agglomerates or floc, is determined by agitation or energy input (8).

It is generally held that upon the addition of certain chemicals to water, an insoluble, gelatinous flocculent precipitate will be formed increasing the probability of particle adhesion. These chemicals,

reagents, or flocculants act in water by entrapment of the agglomerated particles through one or a combination of three possible mechanisms (9).

1. The first class of flocculants, called "electrolytes", reduce the magnitude of the zeta potential so that the Van der Waals forces allow cohesion of colloidal particles (1). This neutralization of the zeta potential makes the particles able to approach each other and facilitates further entrapment by one of the two other flocculating agencies given below.

2. The second class of flocculants, called coagulants, form in water, an insoluble, gelatinous, and voluminous hydroxide precipitate, which in its formation and descent through the water adsorbs and entrains suspended and colloidal matter, hastens its sedimentation, and removes particles more completely than by plain sedimentation (10). In other words, the coagulant destabilizes the colloidal turbidity and color and agglomerates the fine particles; the flocs grow to a large size and settle quickly. However, the floc is formed only at a definite pH range (11) (1).

3. The third class of flocculants are called "polyelectrolytes". They consists of either natural or synthetic long chain, high molecular weight organic polymers that have many active sites along the length of the polymer chain.

Three general classes of polyelectrolytes can be obtained, depending on the sign of the electrical charges: (1) anionic (2) cationic

(3) nonionic. The basic polyacrylamide structure (11) (13) is given below:

$$- CH - CH_2 - CH - CH_2 - CH - CH_2 -$$
$$\quad | \qquad\qquad | \qquad\qquad | $$
$$\quad CO \qquad\quad CO \qquad\quad CO \qquad\qquad polyacrylamide$$
$$\quad | \qquad\qquad | \qquad\qquad | $$
$$\quad NH_2 \qquad\quad NH_2 \qquad\quad NH_2$$
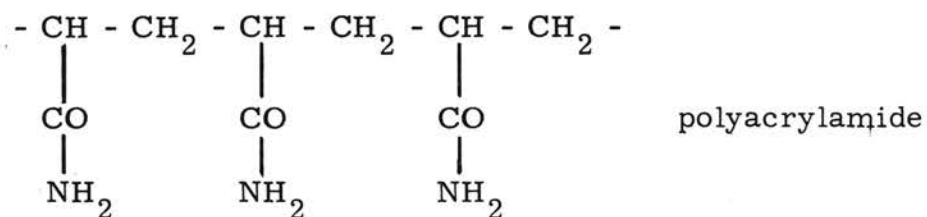
Upon acidification with acrylic acid the anionic polyelectrolyte is formed:

$$- CH - CH_2 - CH - CH_2 - CH -$$
$$\quad | \qquad\qquad | \qquad\qquad | $$
$$\quad CO \qquad\quad CO \qquad\quad CO \qquad\qquad substituted\ anionic\ chain$$
$$\quad | \qquad\qquad | \qquad\qquad | $$
$$\quad NH_2 \qquad\quad NH_2 \qquad\quad O\ -$$
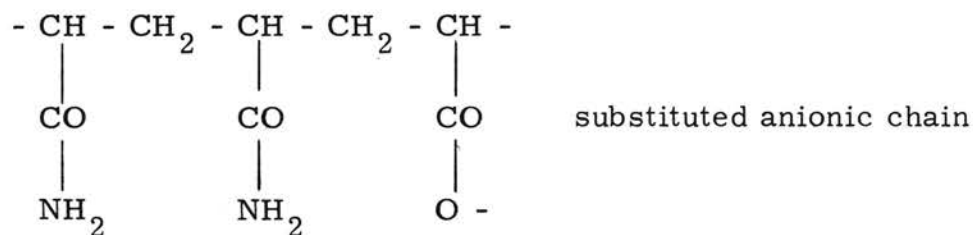
Upon addition of quaternary amine the cationic polyelectrolyte is formed:

$$- CH - CH_2 - CH - CH_2 - CH - CH_2 -$$
$$\quad | \qquad\qquad | \qquad\qquad | $$
$$\quad CO \qquad\quad CH_2 \qquad\quad CO \qquad\qquad substituted\ cationic\ chain$$
$$\quad | \qquad\qquad | \qquad\qquad | $$
$$\quad NH_2 \qquad R - N - R' \qquad NH_2$$
$$\qquad\qquad\qquad | $$
$$\qquad\qquad\qquad R''$$
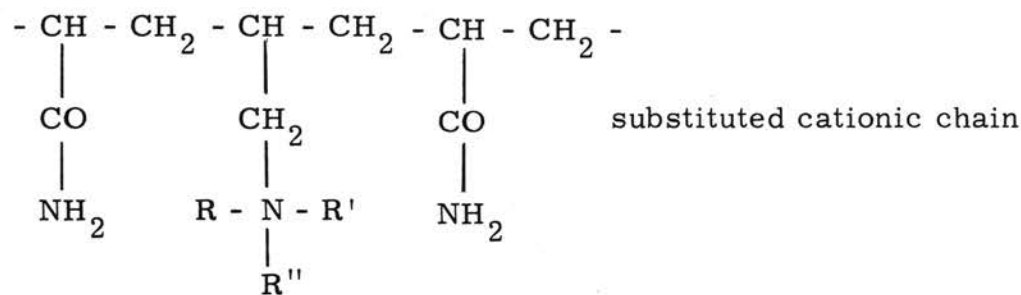
Depending upon the nature of the polymer and the particulate matter to be flocculated, polymers adsorbed on mineral surfaces may be held by at least three distinct types of bonding: (1) Hydrogen Bonding, (2) Electrostatic Site-Bonding, (3) Double-Layer Interaction (5) (12). When two or more solid particles are attached to different active sites along the polymer chain then the polymer is said to form

a bridge between the particles. When a single particle is bonded to an active site on each of several polymer molecules the polymers are said to form a bridge between themselves (14).

Effect of the Three Basic Types of Polyelectrolyte on Turbidity.

Cohen, Rouke and Woodward (13) have investigated the utility of some anionic, cationic, and nonionic polyelectrolytes in coagulation of surface waters and of laboratory-prepared turbid water. The salient facts emerging from this study are as follows:

Anionic

1. "Anionic is not a coagulant, but a true coagulant aid, which required the concomitant use of a metal coagulant."

2. "The benefit which can be ascribed to the use of anionic is a greatly increased size of floc, which produces an increased rate of settling."

3. "It has not been shown in the laboratory tests that either the coagulant dose or the flocculation time can be substantially reduced without some sacrifice of final water quality."

4. "For some waters the effective range of concentration of anionic is limited. Doses exceeding this concentration produce a dispersion rather than a coagulation."

5. "The activity of anionic appears to be independent of physical and chemical water characteristics, such as pH, alkalinity, hardness,

and turbidity; the only requisite is that a floc be produced by a metal coagulant."

Cationic

"The difference in charge, cationic as opposed to anionic, endows cationic with certain behavior of which anionic is incapable."

1. "In addition to its activity as a coagulant aid, cationic can perform as a true coagulant when the suspended particles are negatively charged."

2. "Because of this positive charge, suitable negative ions in solution can be effectively precipitated or complexed."

3. "The ability to coagulate living organisms, such as certain algae, provides cationic with an advantage lacking in anionic."

4. "Cationic is inactive in demineralized or slightly mineralized water."

Nonionic

"The naturally derived polyelectrolyte, nonionic has been shown to be considerably less effective or versatile as a coagulant aid than either anionic or cationic."

Coagulant Aids for Potable Water Treatment.

In 1957, the U.S. Public Health Service, in response to requests from health and water works officials and others having responsibility in the field of water supply, established the Technical

Advisory Committee on Coagulant Aids for Water.

On the basis of information submitted by the manufacturers, the Technical Advisory Committee on Coagulant Aids for Water Treatment has concluded that the following products may be used in water treatment without adverse physiological effects on those using the water, when used in the concentration recommended by the manufacturer, and provided the products continue to meet the quality specifications furnished the Committee.

The Committee emphasized that its findings bear only on health aspects of the use of these products and do not constitute endorsement or indicate effectiveness in proposed use. Products reviewed by the Committee and found to conform to Committee requirements are given in Table I.

Guide for Selection of Flocculant Aid.

On the basis of information obtained from the producers and purveyors, and some data (9) found in the literature, Table II has been prepared to facilitate the selection of reagents most likely to be effective for water of known characteristics. It is emphasized that actual selection of any flocculant aid should not be made without laboratory tests for the particular waters in question.

Columns 1 through 3 give manufacturer, trade name of the polyelectrolyte and its chemical composition.

Columns 4 and 5 give the ionic character of each flocculant

TABLE I

COAGULANT AIDS APPROVED BY USPHS
FOR POTABLE WATER TREATMENT

Manufacturer	Product	Max. Concentration Recommended by Manufacturer	
American Cyanamid Co.	Magnifloc - 990	1	mg/l
Allyn Chemical Co.	Claron	1.5	mg/l
	Claron - 207	2	mg/l
Betz Laboratories Inc.	Poly-Floc 4D	25	mg/l
The Burtonite Co.	Burtonite - 78	5	mg/l
Dow Chemical Co.	Purifloc N17	1	mg/l
Dearborn Chemical Co.	Aquafloc - 422	1	mg/l
Drew Chemical Corp.	Alchem Coagu-Aid 252	5	mg/l
	Alchem Coagu-Aid 262	5	mg/l
Electric Chemical Co.	Ecco Suspension Catalyzer - 146	3.5	mg/l
Hagan Chemicals and Controls Inc.	Hagan Coagulant Aids		
	2	1	mg/l
	7	0.75	mg/l
	11	4	mg/l
	18	15	mg/l
	801	6	mg/l
	952	8	mg/l
Hercules Powder Co.	Carboxymethylcellulose	1	mg/l
Illinois Water Treatment Co.	Illco IFA 313	10	mg/l
Ionac Chemical Co.	Wisprofloc - 20	5	mg/l
	Wisprofloc - 75	5	mg/l
Kelco Company	Kelgin W	2	mg/l
	Kelcosol	2	mg/l
Key Chemicals Inc.	Key - Floc - W	25	mg/l
Metalene Chemicals Co.	Metalene Coagulant P - 6	5	mg/l
National Starch & Chemical Corp.	Floc Aid 1038	5	mg/l
	Floc Aid 1063	5	mg/l
North American Mogul Products Co.	Mogul CO - 980	2	mg/l
	Mogul CO - 982	1.5	mg/l
	Mogul CO - 983	1	mg/l
Nalco Chemical Co.	Nalcolyte - 110	5	mg/l
O'Brien Industries Inc.	O'B - Floc	10	mg/l
Stein, Hall & Co., Inc.	Jaguar	0.5	mg/l

and the mechanism of flocculation accompanying it.

After finding the proper dosage, the cost can be calculated from columns 6 and 11.

Column 7 gives the range of pH effectiveness most likely to be effective for each flocculant.

From the information in column 8, solutions of the selected flocculants can be prepared using a standard mixing procedure. The standard mixing procedure adopted in the present research can be described as a slow sifting of the chemicals into the vortex created by a rotating stirring mechanism. Slow mixing is continued until all solids have been dissolved or dispersed; this may take up to one hour.

Multipoint addition or stage feeding as given in column 9 has been found to be a major factor in decreasing the amount of chemical required for a given application. It has been recommended that these coagulant aids be added after flash mixing of the primary coagulant chemical; at this time pinpoint floc is just beginning to form (13).

The amount of flocculant to be used in a test is given in column 10. In some cases, the use of too much polyelectrolyte interferes with coagulation. Optimum results are in most cases obtained with small additions (13).

The last column 12 contains additional information pertinent to stock solution stability.

TABLE II

A GUIDE FOR SELECTION OF COAGULANT AIDS

Manufacturer	Flocculant	Composition	Ionic Character	Mechanism	Form	Range of pH Effectiveness	Strength of Solution	Method of Addition	Commercial Dosage	Price per Pound	Additional Information
Dow Chemical Co.	Purifloc N 17	Synthetic high molecular weight polymers of polyacrylamide	Nonionic	Bridging	White granule solid 35 lb/cu. ft.	All pH's	Less than 1% dilute to 0.05% or less	Stage Feeding	0.002 to 1 mg/l	$1.40 in 50 lb. bag	Stock stable for a period of 1 year if properly stored. Stock solution 1% stable for 2 months.
Nalco Chemical Co.	Nalcolyte 110	High molecular weight polymer	Nonionic	Bridging	White coarse powder 9 lb/cu. ft.	Over 5	Up to 15% dilute to 1% prior to introducing	Single point addition	0.5 to 5 mg/l	$0.42 in 25 lb. bag	Prevent microbiological growth by adding calcium or sodium hypochloride. Stock solution is stable for 24 hours.
American Cyanamid Co.	Magnifloc 990	Synthetic high-molecular weight polymers of polyacrylamide	Nonionic	Bridging	White fine powder 30 lb/cu. ft.	All pH's	Not over 0.5% dilute to 0.01% or less prior feeding	Stage feeding	0.1 to 0.5 mg/l	$1.55 in 100 lb drum or 50 lb bag	Addition after the rapid mixing at maximum concentration of 1 mg/l
Ionac Chemicals and Control Inc.	Wisprofloc 20	Complex organic polymeric compound of selected and treated amorphous starch	Nonionic	Bridging	Free flowing white powder 20 lb/cu. ft.	3 - 12	0.5 to 2%	Stage feeding	0.5 to 5 mg/l	$0.30 to $0.47 in 50 lb. bag	Addition after the rapid mixing. Indefinitely stable in dry form. Stock solution is stable for 24 hours.
The North American Mogul Products Co.	Mogul Claracel CO-980	Activated bio-colloid described as aluminate-carbohydrate coordination complexe	Cationic	Coagulation bridging	Dark brown liquid 74 lb/cu. ft.	5.0 to 10.5	Any concentration	Distribution to several points	0.5 to 5 mg/l	$0.26 in 525 lb. drum	Addition where pinpoint floc is just starting to form. Stock is stable for a period of a year
The North American Mogul Products Co.	Mogul Claracel CO-982	Activated bio-colloid described as aluminate-carbohydrate coordination complexe	Cationic	Coagulation bridging	Light cream colored liquid 90 lb/cu. ft.	4.0 to 8.0 >9.5 (lime softening without Mg removal	Any concentration	Distribution to several points	0.5 to 5 mg/l	$0.26 in 625 lb. drum	Addition where pinpoint floc is just starting to form. Stock is stable for a period of a year.
The North American Mogul Products Co.	Mogul Claracel CO-983	Synthetic organic polymers of the poly-amide types	Nonionic	Bridging	Colorless liquid 63 lb/cu. ft.	2 to 12	1 to 5%	Distribution to several points	0.5 to 5 ppm	$0.40 in 450 lb. drum	Addition where pinpoint floc is just starting to form. Stock is stable for a period of a year.
Hagan Chemicals and Controls Inc.	Hagan 2	Polyelectrolyte	Nonionic	Bridging electrolytic	Free flowing amber granular solid 32 lb/cu. ft.	All pH ranges generally most effective 5.5 to 9.0	0.5%	Stage feeding	0.06 to 0.5 mg/l	$1.25 in 30 lb. drum	Addition after the primary coagulants. Stock solution is stable for 3 months
Hagan Chemicals and Controls, Inc.	Hagan 18	Polyelectrolyte and specially processed bentonite	Nonionic	Bridging electrolytic	Light tan free flowing granular solid 65 lb/cu. ft.	All pH ranges generally most effective 5.5 to 9.5	3%	Stage feeding	3 to 15 mg/l	$0.09 in 100 lb. bag	With and after the primary coagulants should be investigated. Stock solution is stable for 3 months.

TABLE II (cont.)

A GUIDE FOR SELECTION OF COAGULANT AIDS

Manu-facturer	Flocculant	Composition	Ionic Character	Mecha-nism	Form	Range of pH Effec-tiveness	Strength of Solution	Method of Addition	Commer-cial Dosage	Price per Pound	Additional Information
Hagan Chemicals and Controls Inc.	Hagan 952	Polyelectrolyte	Anionic	Bridging electroly-tic	Viscous light amber liquid 65 lb/cu. ft.	All pH ranges generally most ef-fective 5. 5 to 9. 5	Any con-centration	Multiple points of addition	0. 25 to 8 mg/l	$0. 17 in 480 lb. drum	Addition after the pri-mary coagulants. Stock solution stable for 24 hours.
Illinois Water Treatment Co.	IFA-313	Gel	Nonionic	Bridging	Viscous yel-lowish liquid	All pH's	1. 25%	Single point of addition	1 to 10 pounds per ton of pre-cipitated solids	$0. 20 in 450 lb. drum	Addition after the floc has formed
Methalene Chemical Co.	Metha-lene Co-agulant P-6	Aluminum trihydrate combined with acti-vated organic ma-terial	Cationic	Coagula-tion bridging	Viscous white liquid with caustic odor 90 lb/cu. ft.	6. 5 to 10. 5	Any concentra-tion	Single point of addition	3. 0 to 5. 0 mg/l	$0. 13 in 55 gal. drum	Stock solution is stable for 6 months. Add regular coagulants prior coagulant aid
The Burtonite Co.	Burtonite 78	Purified endersperm of such leguminous seed as guar	Nonionic	Bridging	Creamed free-flowing pow-dered solid 4. 25 lb/cu. ft.	All ranges	0. 25% to 0. 5%	Stage feeding	2 to 5 mg/l	$0. 35 in 100 lb. bag	Stock solution is stable for 24 hours. Used in combination with regu-lar coagulants
National Hercules Powder Starch & Chemical Co.	Hercules CMC	Purified sodium car-boxymethylcellulose	Anionic	Bridging electro-lytic	White powder	4. 0 to 7. 5	0. 2%	Stage feeding	0. 25 to 1 mg/l	$0. 57	Used in combination with regular coagulants
	Floc Aid 1063	Modified cationic starch derivative	Cationic	Coagu-lation bridging	White flasky solid	3 to 11	0. 5 or less	Stage feeding	1 to 5 mg/l	$0. 35 in 50 lb. bag	Stock solution is stable for a period of a year.
Betz Laboratories Inc.	Poly-Floc 4D	Synthetic high mo-lecular weight of acrylamide	Nonionic	Bridging	Straw colored viscous liquid 65 lb. ft.	All pH's	15% or less	Either single point of addition or stage feeding	5 to 25 mg/l	$0. 18 in 50 gal. drum	Addition of some clays aid the performance
Kelco Company	Kelgin W	Natural high polymer or treated sodium alginate	Anionic	Coagula-tion Bridging	Ivory colored granular pow-der 50 lb/cu. ft.	5 to 10	0. 5% to 1% stock dilute to 0. 05% or less	Stage feeding	0. 05 to 0. 30 mg/l	$1. 00 to $1. 50 in 100 lb.	Used in combination with regulat coagulants.
Kelco Company	Kelcosol	Natural high polymer of treated sodium	Anionic	Coagula-tion bridging	Cream colored fibrous powder 50 lb/cu. ft.	5 to 10	0. 5% to 1% stock dilute to 0. 05% or less	Stage feeding	0. 05 to 0. 30 mg/l	$1. 00 to $1. 50 in 50 lb.	Used in combination with regular coagulants

TABLE II (cont.)

A GUIDE FOR SELECTION OF COAGULANT AIDS

Manu-facturer	Flocculant	Composition	Ionic Character	Mecha-nism	Form	Range of pH Effec-tiveness	Strength of Solution	Method of Addition	Commer-cial Dosage	Price per Pound	Additional Information
Stein, Hall and Co. Inc.	Jaguar	Guar gum (nonionic straight chain galactomannans)	Nonionic	Bridging electroly-tic	- - -	0.5 to 11.0	0.25% to 0.50% stock dilute to 0.01% to 0.10%	Stage feeding	0.01 to 0.5 mg/l	$0.34 to $0.70	Properties such as rate of hydration, dispersi-bility, mesh, size, etc. can be varied to meet requirements for a spe-cific application.
O'Brien Industries Inc.	O'B Floc	Starch derivative	Nonionic	Bridging	White flasky powder	All pH's	2% or less	Stage feeding	0.5 to 2 mg/l	$0.40 in 50 lb. bag	Addition after the rapid mixing.

Purpose and Scope of the Present Investigation

The purpose and scope of this particular study were: (1) to compare the effectiveness of selected commercial polyelectrolytes on the removal of colloidal particles which cause color (organic colloidal particles) and turbidity (clay colloidal particles) in water; (2) to determine the effect of polyelectrolytes in conjunction with alum as the primary coagulant; (3) to determine the value of polyelectrolytes in reducing primary coagulant dose.

CHAPTER II

MATERIALS AND METHODS

Removal of Color

General

Color due to organic matter is a fairly common constituent of
many natural waters. The materials causing color in water are not
known to be injurious to health, but color is reduced for aesthetic
reasons. The 1946 USPHS Drinking Water Standards (15) recommend,
for public water supplies, a maximum color concentration of 20 units
on the platinum-cobalt scale. Most municipalities, however, endeavor
to maintain lower concentrations, 10 units or even less.

Apparatus Employed

1. Multiple stirrer

The apparatus used for mixing and flocculating the samples was
the multiple stirrer*. It consists of six glass stirrers with a paddle
at the stirring ends. Each stirrer extends into a glass jar containing
the sample to be agitated. The stirrers can be lifted through a certain

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*Standard Phipps and Bird Jar Test Apparatus; a product of
Phipps and Bird.

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distance so that the jars can be removed and replaced without undue disturbance. The stirrers are connected to a prime-mover consisting of a variable-speed motor and can be made to rotate from 0 to 120 rpm. The sample containers used in the present study were 600 ml capacity pyrex glass jars.

2. Spectrophotometer

A spectrophotometer* was used to measure the color. This optical instrument consists of two major components: a spectrometer and a photometer. A spectrometer is usually called a monochromator and the color of the monochromatic light it produces is expressed in terms of wavelengths (λ). The photometer measures the intensity of the monochromatic beam produced by the associated monochromator. In the present study distilled water was used as a reference. The cuvette size was 19 x 105 mm.

The instrument was read on the % transmittance scale and the values obtained were converted to optical density by means of a conversion chart which had been previously prepared.

The instrument was calibrated to measure in terms of platinum-cobalt color standards. Platinum-cobalt color standards of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 100 units were prepared according to the procedure given in Standard Methods for the Examination of Water and Waste Water (17). The optical density corresponding to

———————
*Coleman Model 6D Junior Spectrophotometer; a product of the Coleman Instruments Inc.

each color standard was then measured and a calibration curve was thus obtained.

The accuracy of the instrument was found to be ± 1 unit on the % transmittance scale corresponding to ± 4 standard color units. All optical density readings were made at a wavelength of 400 mμ since this was found to be the wavelength of maximum absorption for the synthetic colloidal color solution (tea) employed (see page 20).

3. pH Meter

A line operated pH meter* was used and temperature corrections were made manually with the Temperature Adjustment Control. The meter was standardized daily using standard buffer solution (pH - 6.86).

Materials

Stillwater tap water was used for preparing test solutions; it had the average physical and chemical characteristics given in Table III.

The colloidal organic matter dispersed in water to obtain the desired colored waters was Cains orange pekoe tea as commercially sold.

The alum** employed for running the tests was $Al_2(SO_4)_3 \cdot 18H_2O$

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*Beckman Zeromatic pH Meter; a product of Beckman Instruments Inc.

**Aluminum Sulfate $Al_2(SO_4)_3 \cdot 18H_2O$; a product of Allied Chemical Co.

TABLE III

PHYSICAL AND CHEMICAL CHARACTERISTICS
OF STILLWATER TAP WATER

Hardness (as $CaCO_3$ ppm)	185
Alkalinity (as $CaCO_3$ ppm)	153
Turbidity units	6.3
pH	8.05

as obtained commercially. The alum was obtained from Stillwater Water Treatment Plant.

Samples of polyelectrolytes in concentrated form were obtained from the manufacturers. The designation and identification of the 10 polyelectrolytes selected for study are given in Table IV.

Preparation of Solutions

1. Colored Water

A standard colored solution was obtained by brewing one pound of tea in 20 liters of tap water for a period of 24 hours. To insure a solution free from impurities due to tea leaves and free from particles above the colloidal range, the solution was filtered through Whatman filter paper, no. 41. The color of the water obtained was approximately 10,000 standard units. The pH of this stock solution was taken daily and showed a constant value of 4.7 $\pm$ 0.5 for a period of 6 days. At the end of this period of 6 days, a microbial growth could be observed and the pH was 5.1. This stock solution was thrown away and an identical one was prepared. This second solution remained stable throughout the experimental period.

To obtain a color in the final test water equal to the average color value of most natural waters of 100 color units (16) it was necessary to dilute the prepared stock colored water. The stock solution was diluted with tap water having the physical and chemical characteristics given in Table III. The 100 unit color solution obtained from mixing stock tea solution and tap water had a pH value of 7.6 $\pm$ 0.5.

TABLE IV

IDENTIFICATION OF THE TEN COAGULANT AIDS STUDIED

Designation of Coagulant Aid	Trade Name	Manufacturer
Nonionic A	Wisprofloc - 20	Ionac Chemical & Controls Inc.
Nonionic B	Hagan - 2	Hagan Chemical & Controls Inc.
Nonionic C	Magnifloc - 990	American Cyanamid Co.
Nonionic D	Nalcolyte - 110	Nalco-Chemical Co.
Nonionic E	Purifloc N17	Dow Chemical Co.
Anionic F	Kelcosol	Kelco Company
Anionic G	Hagan - 952	Hagan Chemical & Controls Inc.
Anionic H	CMC 7H	Hercules Powder Co.
Cationic I	Floc Aid - 1063	National Starch & Chemical Co.
Cationic J	Mogul CO - 982	The North American Mogul Products Co.

The pH was checked twice daily.

2. <u>Alum</u> <u>solution</u>

Ten grams of commercial alum $Al_2(SO_4)_3 \cdot 18H_2O$ were dis-
solved in 2000 ml of distilled water. Therefore one ml of the solution
contained 5 mg alum.

3. <u>Coagulant</u> <u>Aid</u> <u>Solution</u>

Coagulant aid solutions were prepared according to the speci-
fications given by the manufacturers (see Table II column 8). Stock
solutions were prepared daily.

Experimental Procedure

For all flocculation studies a standard jar test stirring appara-
tus which accomodates six jars was used and the test procedure was
standardized to permit comparisons between individual coagulation
runs. A typical test was performed in the following manner: 500 ml
portions of well mixed test solution were put in 600 ml beakers and
placed on the apparatus and stirring was begun. Measured amounts
of alum and the polyelectrolyte under study were pipetted from the
prepared stock solutions. This procedure provided a means of adding
the dosing chemicals quickly while the stirrer was operating.

The stirrer was run at 100 rpm for 2 min. after addition of
coagulating chemicals; then the speed was reduced to 15 rpm for 15
min. The apparatus was then turned off, the paddles removed from
the beakers and the contents were allowed to settle for 30 min. From

the beginning of slow stirring, rapidity of floc formation and the increase in floc were noted. At the end of this period of slow stirring, floc size was observed and rated as given below:

    a) small
    b) fair
    c) good
    d) very good
    e) excellent.

At intervals of 5, 10, and 30 min. of the settling period, settling characteristics of the flocs were observed. At the end of the settling period the degree of clarification was determined by withdrawing samples one inch below the surface of the water from each of the six beakers and measuring the amount of color in each sample spectro-photometrically.

All tests were run at a temperature of 22.5 °C ±1.5.

Removal of Turbidity

General

Turbidity is a fairly common constituent of many natural waters and is found normally as a clay. The 1946 USPHS Drinking Water Standards (15) recommend, for public water supplies, a maximum turbidity concentration of 10 units on the silica scale.

Apparatus Employed

1. Multiple Stirrer

The apparatus used for mixing and flocculating the samples was the same as described under materials and methods for removal of color (see page 16).

2. Hellige Turbidimeter

The Hellige turbidimeter* was used throughout the study to measure turbidity. This optical instrument operates on the principle of equalizing the intensities of direct and scattered light. This is obtained by controlling a knob which moves over a circular scale and changes a slit opening admitting light. The scale reading is correlated with turbidity values using standard colloidal solutions, and standard charts are prepared and supplied by the manufacturer. The charts can be used for finding turbidity values of samples in silica units expressed in parts per million (ppm).

A viewing tube of 20 mm depth was used for all the experiments. The accuracy of the instrument was observed to be ± 2.5 units on the silica scale.

3. pH Meter

The pH meter used for the study on color removal and described on page 18 also served for the present investigation on removal of turbidity.

4. Water Demineralizer

A mixed bed, cartridge type water demineralizer** was used

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*The Hellige Turbidimeter; a product of Hellige Inc.

**Bantam Demineralizer Model BD-1; a product of Barnstead Still and Sterilizer Co.

in the preparation of synthetic waters of known turbidity.

Materials

In order to obviate the need to consider effects of changes in the quality of the raw water and to provide a more precise basis for comparison it was decided to use demineralized water for making the turbid suspensions. Distilled water was passed through a demineralizer. This water, essentially free of extraneous ions, was used for preparing the stock turbidity solutions. The pH value of the demineralized water was 5.3 ± 0.5.

The colloidal material dispersed in water to obtain turbid solutions was pure kaolin clay*. Microscopic determination of particle size distribution is shown in Fig. 1. It is seen that 85% of the particles were smaller than 1μ and 50 per cent were smaller than 0.6μ. Two thirds of the particles fall in the range of 0.43μ to 1μ.

The chemicals (alum and polyelectrolytes) used for the present study were the same as those used for removal of color and are described on pages 18 and 22.

Preparation of Solutions

1. Turbid water

Colloidal kaolin clay powder was suspended in demineralized

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*Kaolin NF Colloidal; a product of Chemical Products Inc.
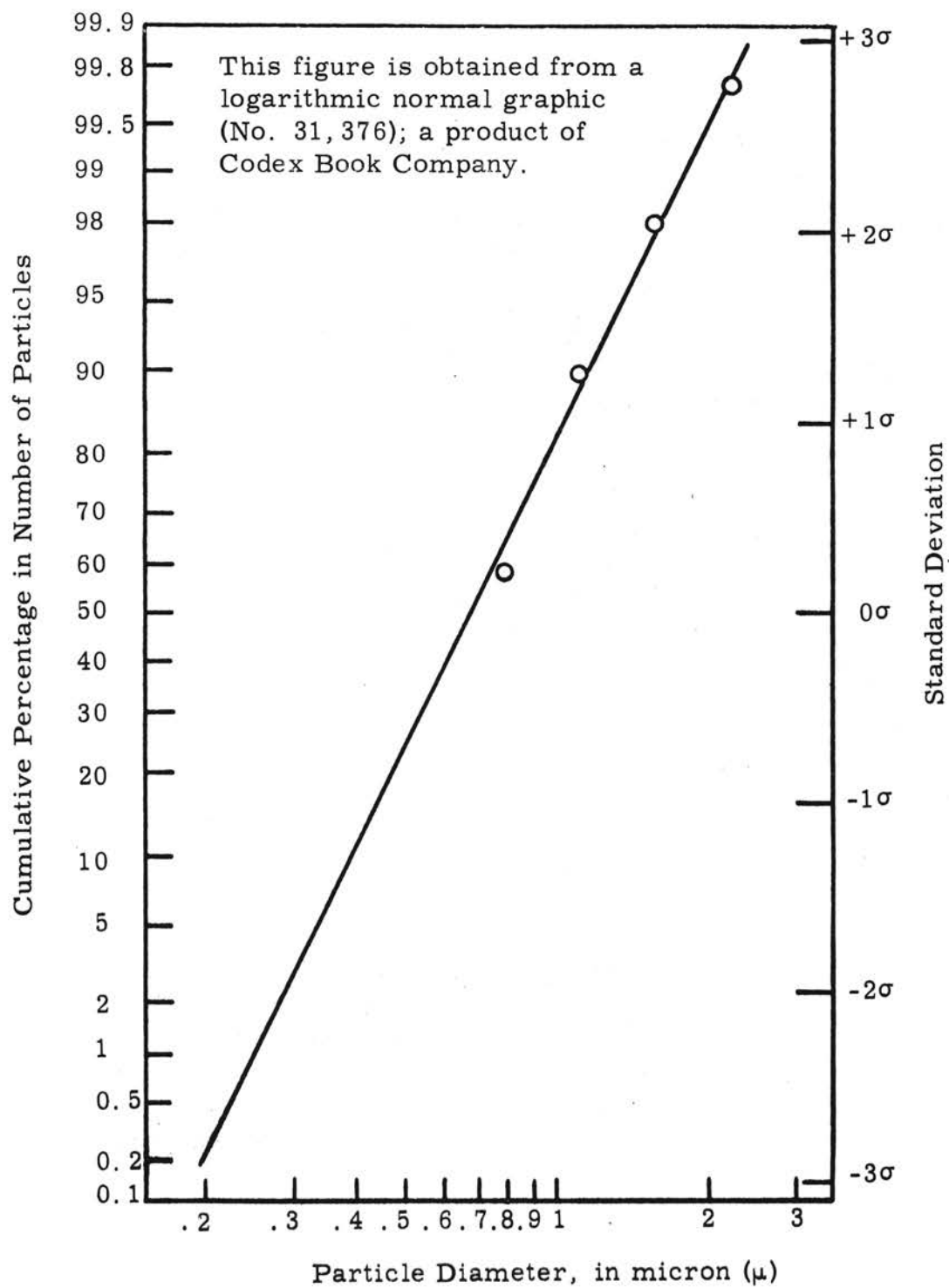
Fig. 1 – Particles Size Distribution.

water, and allowed to stand for 48 hours. The supernatant was siphoned and filtered through glass wool. The filtrate comprised the stock turbidity suspension. The pH of the stock suspension remained at 6.3 ± 0.5.

All the experiments on removal of turbidity were conducted by diluting the stock turbidity with demineralized water to yield 100 silica units of turbidity. The pH of this suspension was 5.8 ± 0.5.

2. Alum solution

The stock solution of alum prepared for removal of color was also used for the experiments on removal of turbidity.

3. Polyelectrolyte solution

As noted previously, solutions of polyelectrolytes were prepared according to the recommendations of the manufacturers and are given in Table II column 8.

Experimental Procedure

Such experimental conditions as rate and time of mixing and stirring, time of settling, etc., were maintained constant for all the tests. The standard procedure adopted was the same as that used for the studies on removal of color (see page 22).

The degree of turbidity removal was determined by withdrawing samples one inch below the surface of the water from each of the six beakers used in each experiment and the amount of turbidity remaining in each sample was measured with the turbidimeter. For

all experiments the temperature of the flocculating suspension was maintained at 24° C ±2.

CHAPTER III

RESULTS

Removal of Color

Flocculation with alum

Prior to evaluation of the effect of the polyelectrolytes it was
necessary as a basis of comparison to determine the optimum dosage
of aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ when used alone. Figure 2
shows the results of jar tests on colored water using alum up to a
dosage of 230 mg/ℓ. The curve shows the residual color as well as the
color removed. Although the floc was classified as "small", color
removal of 90% was obtained at alum dosages of 150 mg/ℓ and above.
The floc appeared during slow stirring and reached its "small" size
at the end of the flocculation period. Most of the floc particles re-
mained in suspension during the 30 minute settling period. In this
study, the first appearance of floc was at a dosage of 30 mg/ℓ of alum.

Flocculation with Alum and Polyelectrolytes

The effects of various concentrations of each polyelectrolyte
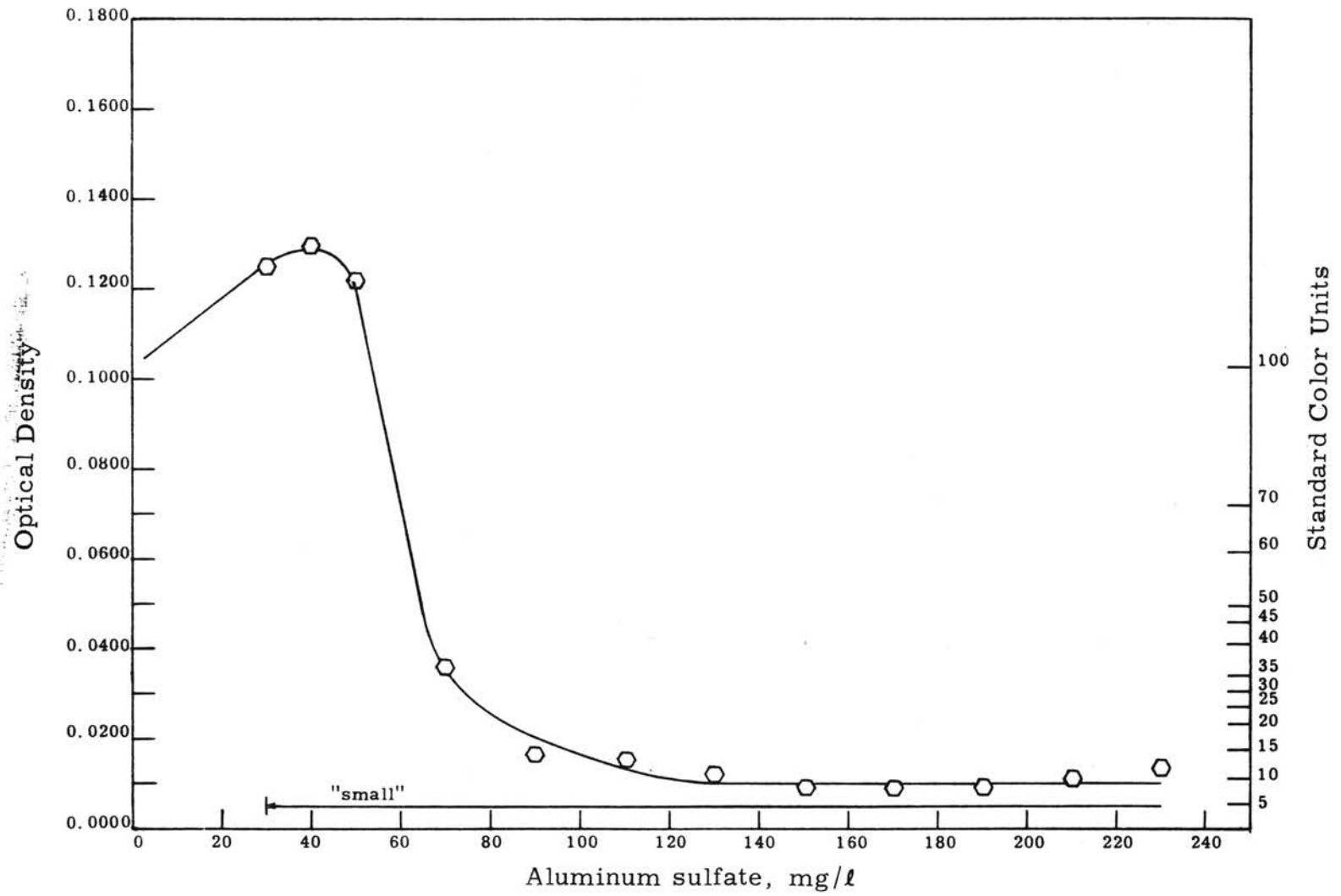on color removal in conjunction with specific dosages of alum are

Fig. 2 — Effect of aluminum sulfate on color removal.

shown in Figures 3 through 12. For comparison purposes the dosage curve for alum alone (Figure 2) is also plotted on each figure. Experiments to determine the effect of the coagulant aid alone were also run. These results are not plotted but are noted on each figure. The quality of the floc is also noted.

The selection for a proper range of dosages of polyelectrolytes was first made according to the specifications given by the manufacturers (Table II). In most cases, the range of dosages was found not to be adequate for the water used in this study, and random tests were run to determine the lowest possible dose.

In Figures 3 through 12, the dotted curve is an attempt to represent the removal of color for a practical or recommended dosage of polyelectrolyte to be used in conjunction with alum. This curve was drawn from consideration of the effects of maximum and minimum dosages of polyelectrolyte and is not necessarily confined within the zone bounded by maximum and minimum curves because at times, an increase in polyelectrolyte dosage resulted in an inhibition of flocculation. In cases where an increase in polyelectrolyte dosage had a negligible effect, only dotted curve is plotted. Thus, the dotted curve represents the minimum polyelectrolyte dosage recommended by the author for the most effective results.

Nonionic A

Coagulant aid A was tested in dosages of 0.6 to 5.0 mg/ℓ (Figure 3). Without addition of alum, the coagulant aid did not cause

formation of floc or color removal. The 0.6 mg/ℓ dose hindered floc

formation up to 40 mg/ℓ of alum. With dosages of 40 to 50 mg/ℓ of

alum, the 0.6 mg/ℓ dose of coagulant aid reduced the color only to a

small extent and did not improve the size of the floc. At the 30 mg/ℓ

dose of alum, 0.6, 1.2, 2.0 mg/ℓ of coagulant aid did not start floc

formation or improve removal of color. In general, at low dosages

(30 to 50 mg/ℓ) of alum and dosages of 3.0 to 5.0 mg/ℓ of nonionic A,

the floc was improved and rated from "very good" to "excellent" and

the color was considerably reduced. At alum dosages over 60 mg/ℓ,

the coagulant aid at any of the tested dosages gave an "excellent" floc

and color removed was approximately the same. The floc formation

was rapid and the floc became bulky. The floc, rated as "excellent",

settled instantly. It is also interesting to note that at dosages from

75 mg/ℓ of alum and above, the color removed by alum alone was

slightly greater than that found in conjunction with the coagulant aid

even though the coagulant aid increased the size of the floc particles.

Nonionic B

Coagulant aid B was tested at dosages of 0.05 to 0.50 mg/ℓ

(Figure 4). Without addition of alum, the coagulant aid did not cause

formation of floc or color removal. The coagulant aid hindered floc

formation from 30 to 40 mg/ℓ of alum. The 0.05 mg/ℓ dose of co-

agulant aid in conjunction with alum did not aid the coagulation or floc

formation. It is interesting to note that removal of color at the dosage

of 0.05 mg/ℓ of coagulant aid was less than for alum alone. Between
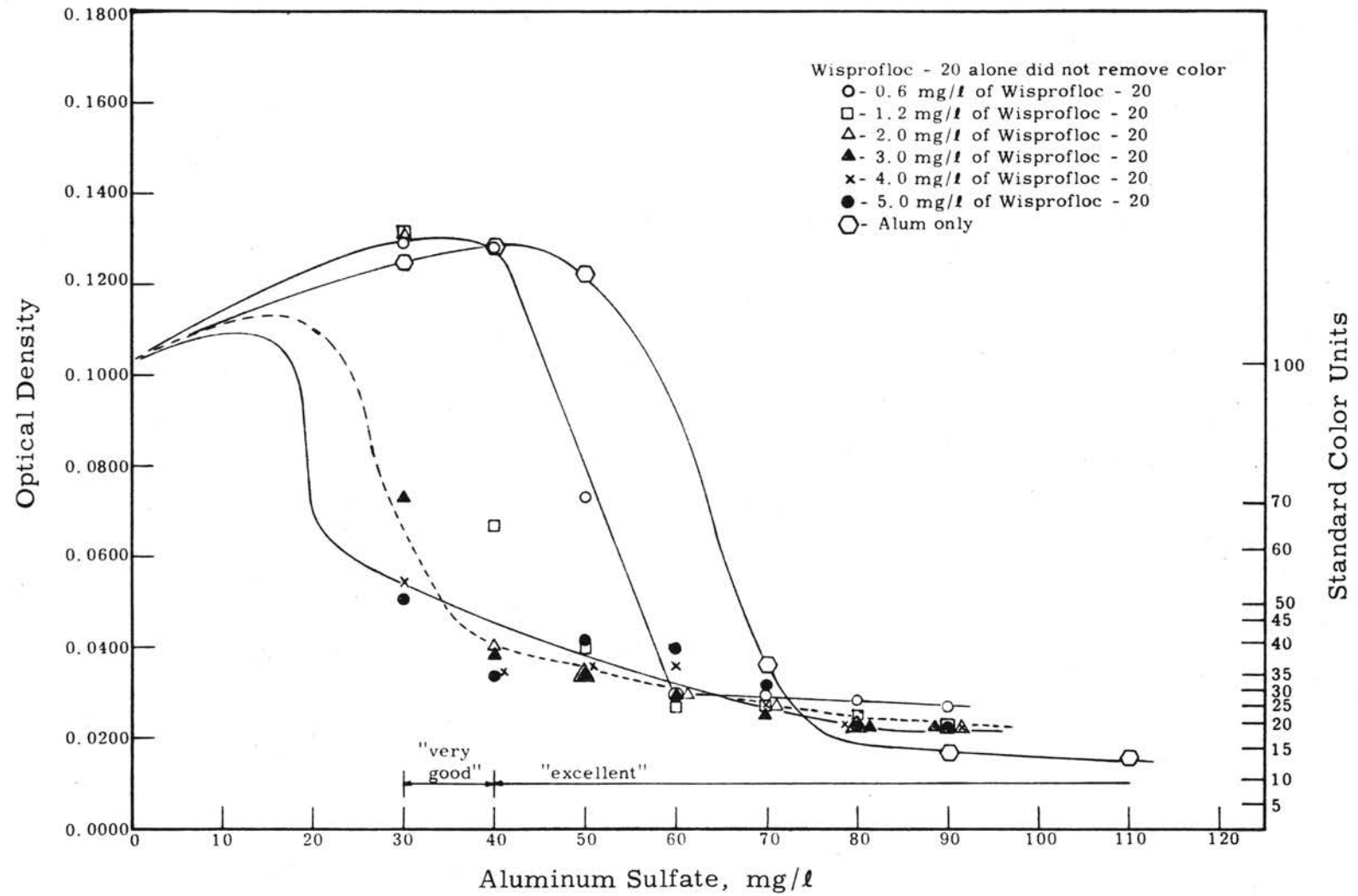
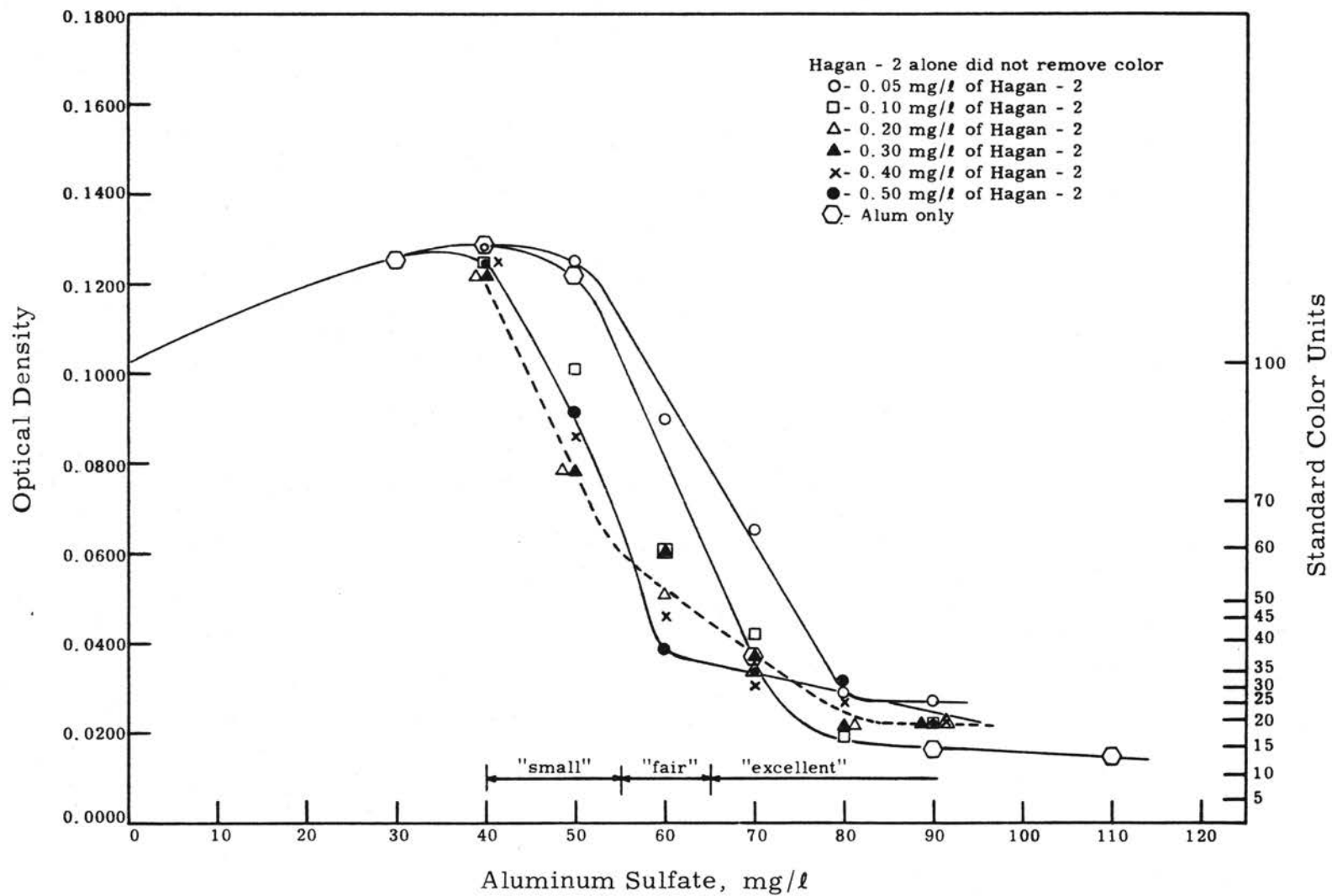Fig. 3 — Effect of polyelectrolyte "A" on color removal and alum flocculation.

Fig. 4 – Effect of polyelectrolyte "B" on color removal and alum flocculation.

dosages of 0.10 to 0.50 mg/ℓ of coagulant aid and 40 to 60 mg/ℓ of alum, only slight improvement in the size of the floc and removal of color was obtained. In general, at alum doses above 70 mg/ℓ the coagulant aid gave a floc of an "excellent" size at any concentration. However, color removal by coagulant aid and alum is less than with alum alone above 70 mg/ℓ. The floc, rated "excellent", settled within 10 minutes.

Nonionic C

Coagulant aid C was tested in dosages of 0.1 to 0.6 mg/ℓ (Figure 5). Without addition of alum the coagulant aid did not cause formation of floc or color removal. Dosages of 0.1 to 0.3 mg/ℓ of coagulant aid in conjunction with alum at 40 mg/ℓ did not show floc formation or removal of color. The 0.1 mg/ℓ dose of coagulant aid hindered floc formation at dosages from 30 to 50 mg/ℓ of alum. Above 50 mg/ℓ of alum, this 0.1 mg/ℓ dose of coagulant aid improved the formation of floc but removal of color was essentially the same as with alum alone. Between doses of 40 and 60 mg/ℓ of alum, an increase in dosages of coagulant aid improved floc formation and color removal. Dosages of 0.3 to 0.6 mg/ℓ of coagulant aid in conjunction with alum removed much more color than alum alone and increased the size of the floc in the range of 40 to 60 mg/ℓ of alum dosage. At higher doses of alum, (60 mg/ℓ and above), color removal due to addition of coagulant aid was comparable to alum alone but the size of the floc was greatly improved. In this range of dosage, the floc was
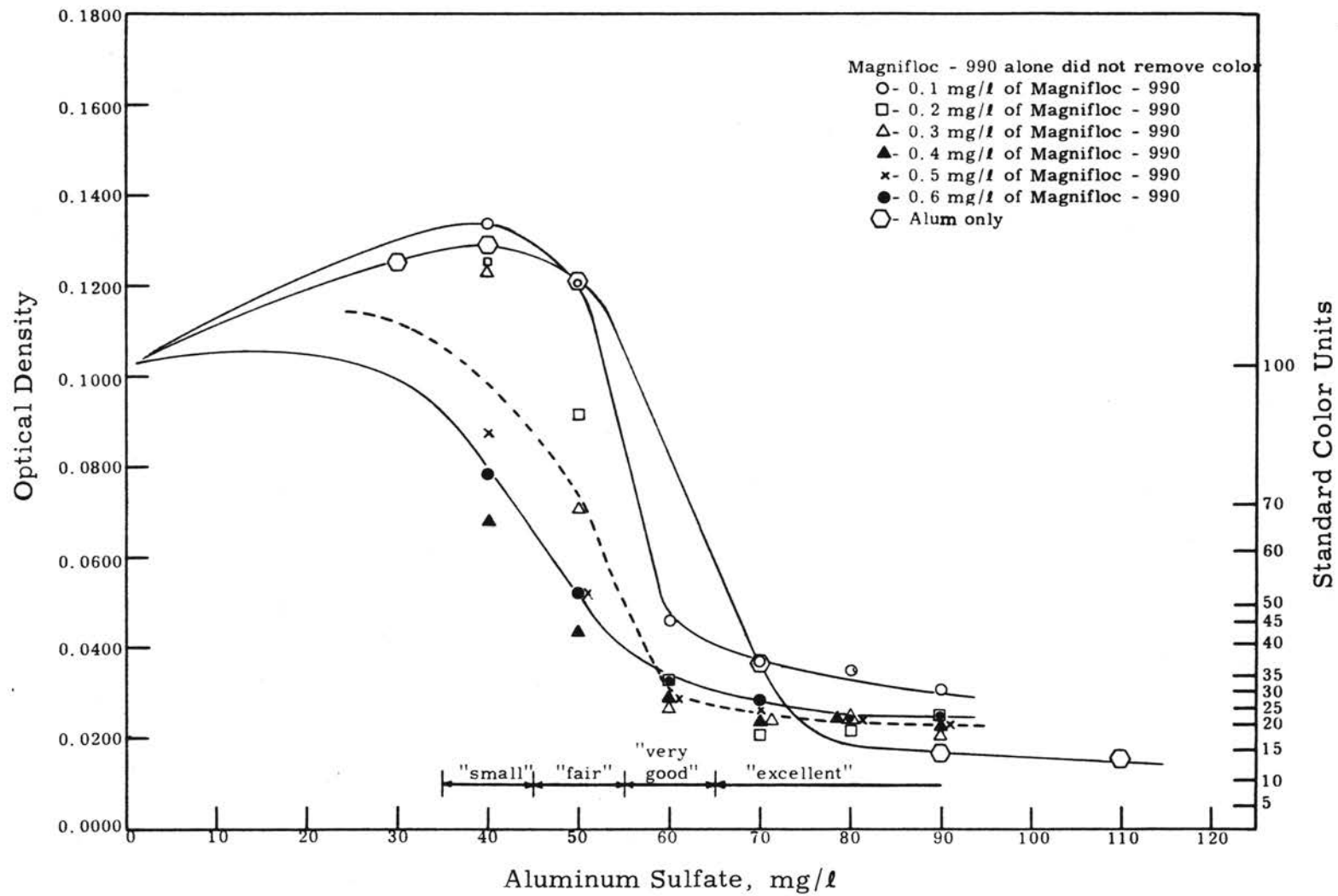
Fig. 5 – Effect of polyelectrolyte "C" on color removal and alum flocculation.

rated as "excellent" and settled within 10 minutes.

Nonionic D

Coagulant aid D was tested in dosages of 0. 2 to 2. 6 mg/ℓ (Figure 6). Without addition of alum, the coagulant aid did not cause formation of floc or removal of color. The 0. 2 mg/ℓ dose of coagulant aid hindered formation of floc at alum doses from 30 to 50 mg/ℓ. Above 50 mg/ℓ of alum, this 0. 2 mg/ℓ dose of coagulant aid did not aid appreciably the formation of floc and removal of color was essentially the same as with alum alone. In general, increasing dosages of coagulant aid improved formation and size of floc and removal of color. Dosages of 0. 5 to 2. 6 mg/ℓ of coagulant aid yielded a significant improvement in the size of the floc. Dosages of 30 to 60 mg/ℓ of alum in conjunction with coagulant aid removed the color much more efficiently than alum alone. Above an alum dosage of 70 mg/ℓ, this coagulant aid improved the size of the floc but the color removed was the same as alum alone. The floc was rated as "excellent" and settled within 15 minutes.

Nonionic E

Coagulant aid E was tested in dosages of 0. 2 to 1. 2 mg/ℓ (Figure 7). Without addition of alum, the coagulant aid did not cause formation of floc or removal of color. Addition of coagulant aid hindered formation of floc at dosages of alum from 30 through 40 mg/ℓ. It is interesting to note that in general, the increase from 0. 2 to 0. 6 mg/ℓ of coagulant aid improved removal of color but an increase from 0. 6
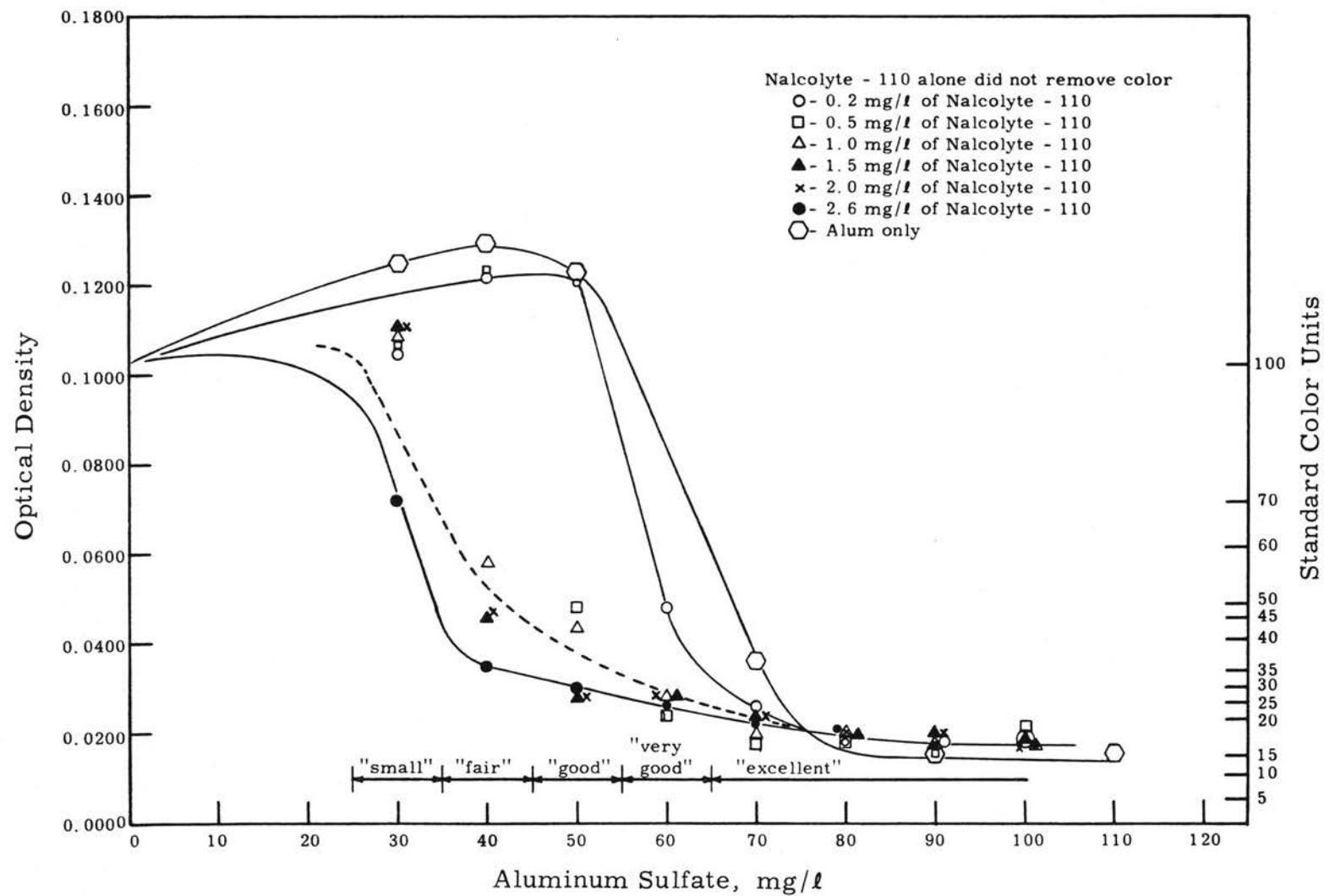
Fig. 6 — Effect of polyelectrolyte "D" on color removal and alum flocculation.

to 1.2 mg/ℓ of coagulant aid removed less color. The floc was rapidly formed and was large and bulky. The floc had a tendency to rise rather than settle. The floc particles were very large and it seemed that the floc formation occurred too fast for the alum to entrap the color colloids. Up to a dosage of 70 mg/ℓ of alum, this coagulant aid improved the floc to an "excellent" size but did not aid appreciably in removing color. Above 70 mg/ℓ of alum the coagulant aid formed a very large but light floc and removed less color than alum alone.

Anionic F

Coagulant aid F was tested in dosages of 0.6 to 5.0 mg/ℓ (Figure 8). Without addition of alum, the coagulant aid did not cause formation of floc or removal of color. Dosages of 0.6 to 5.0 mg/ℓ of coagulant aid yielded a major improvement in the size of the floc. Dosages of 40 to 70 mg/ℓ of alum in conjunction with the coagulant aid removed the color much better than alum alone. However it should be noted that at any concentration of alum, an increase in dosage of coagulant aid did not yield a notable increase in the size of the floc or removal of color. Above 70 mg/ℓ of alum, this coagulant aid, while improving the size of the floc did not aid in removing color; the color removed was slightly less than with alum alone. The floc was of large size and did not break up upon agitation. Settling of these floc particles occurred instantly.

Anionic G

Coagulant aid G was tested in dosages of 4.0 to 9.0 mg/ℓ
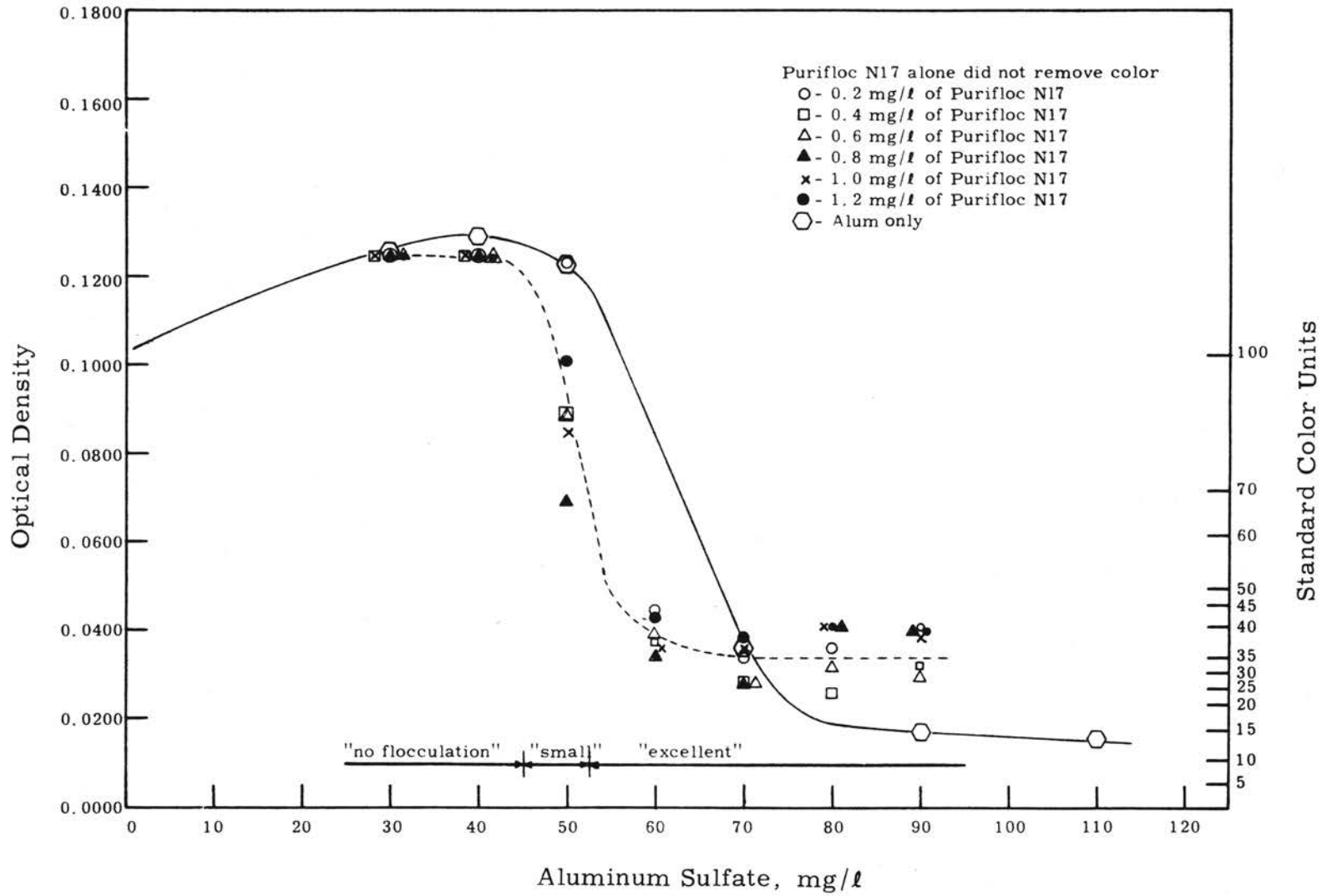
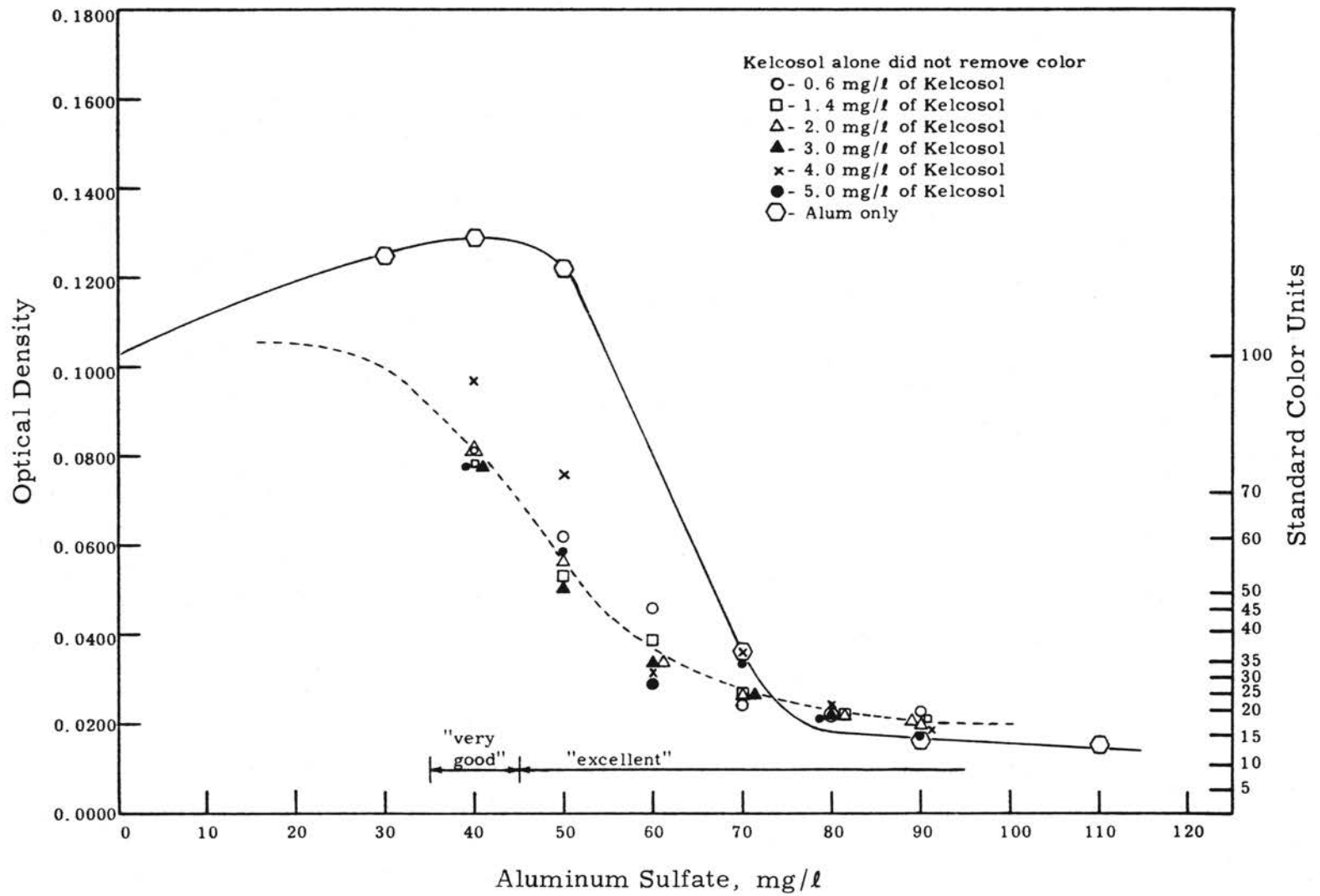Fig. 7 — Effect of polyelectrolyte "E" on color removal and alum flocculation.

Fig. 8 – Effect of polyelectrolyte "F" on color removal and alum flocculation.

(Figure 9). Without addition of alum, the coagulant aid did not cause formation of floc or removal of color. The reduction in color and improvement in size of the floc increased with increasing concentrations of the coagulant aid in the range of alum dosages from 40 to 60 mg/ℓ. Above 60 mg/ℓ of alum, any concentration of coagulant aid yielded improvement in the size of the floc, but color was removed slightly less than with alum alone. The floc was built up slowly during the period of flocculation or slow stirring. The floc was rated as "very good" and settled within 30 minutes.

Anionic H

Coagulant aid H was tested in dosages of 0.20 to 1.30 mg/ℓ (Figure 10). Without addition of alum, the coagulant aid did not cause formation of floc or removal of color. Coagulant aid hindered formation of floc at alum dosages from 30 through 40 mg/ℓ. Dosages of 0.20 to 1.30 mg/ℓ of coagulant aid in conjunction with dosages of alum in the range of 40 to 60 mg/ℓ improved appreciably the size of the floc and the removal of color. Above 70 mg/ℓ of alum the coagulant aid yielded an improvement in floc size but gave less color reduction than alum alone. At concentrations of alum above 70 mg/ℓ, the coagulant aid appeared to inhibit the action of alum. In general, at any concentration the same color removal pattern was found, except for the 0.20 mg/ℓ dose where the color reduction was slightly less than for other dosages. The largest color reduction was found to be 75% and this occurred when using the coagulant aid with alum dosages of 80 mg/ℓ
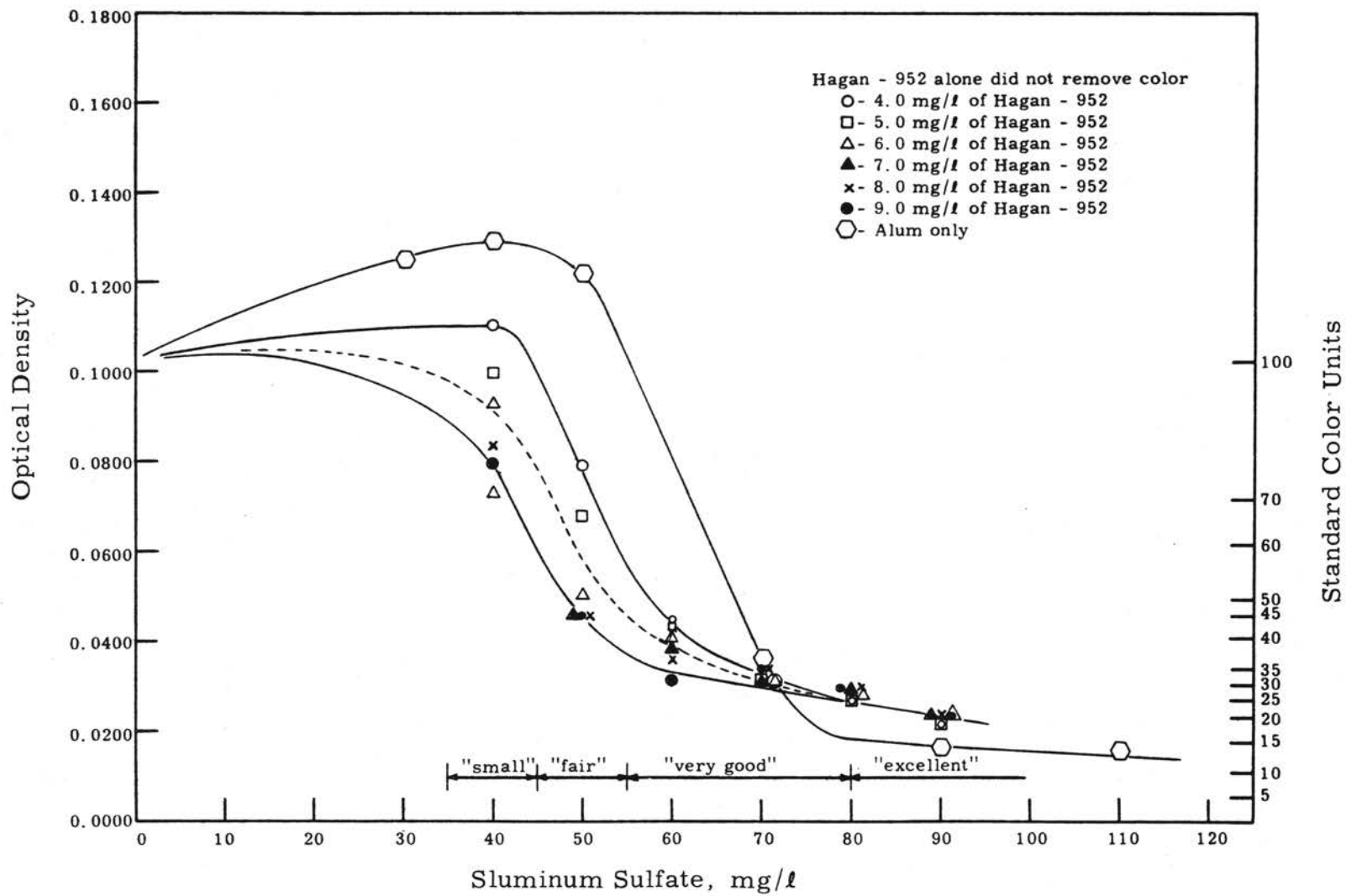
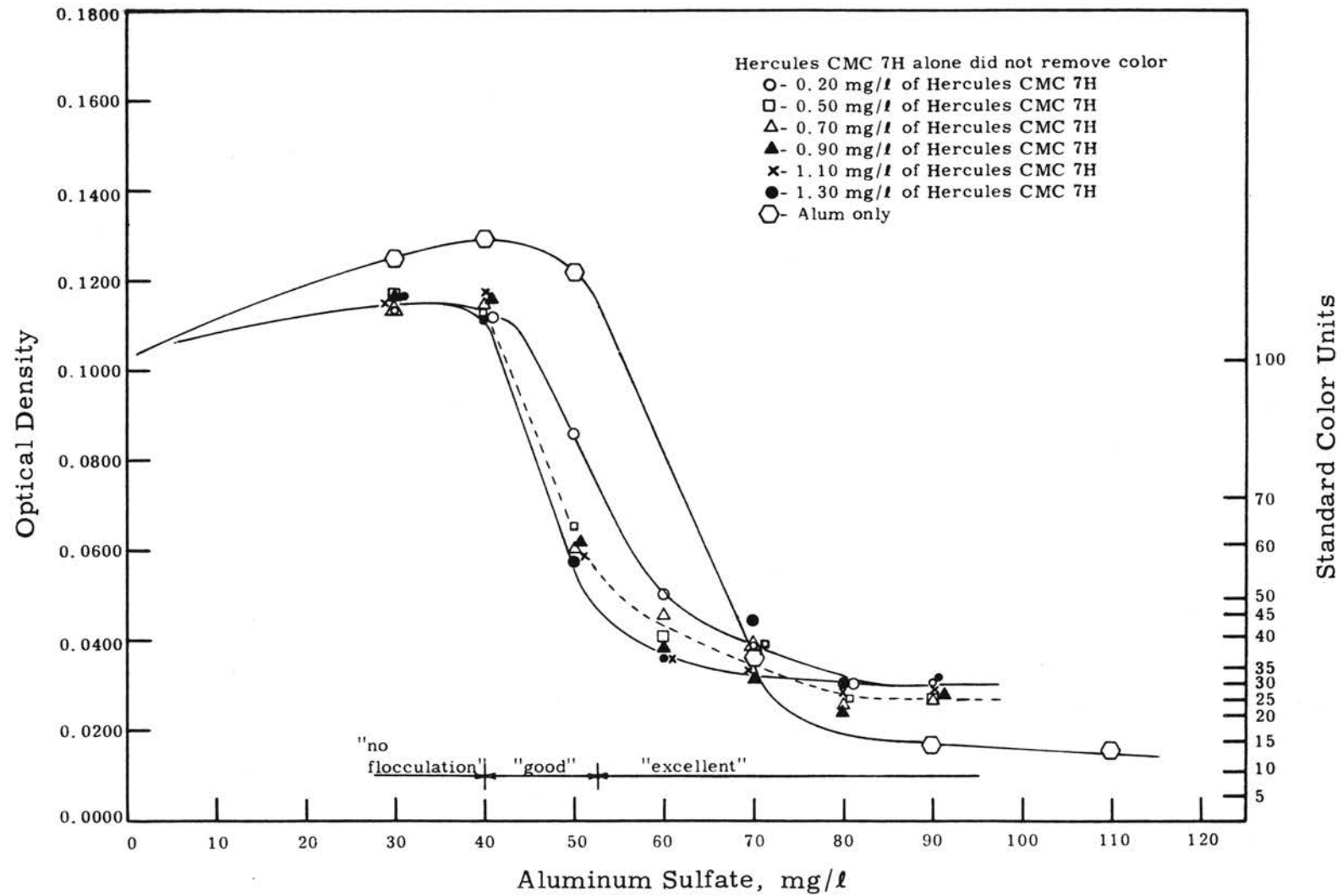Fig. 9 — Effect of polyelectrolyte "G" on color removal and alum flocculation.

43

Fig. 10 — Effect of polyelectrolyte "H" on color removal and alum flocculation.

and above. The floc was of "excellent" quality and settled in 10 minutes.

Cationic I

Coagulant aid I was tested in dosages of 5.0 to 50.0 mg/ℓ (Figure 11). Without addition of alum, the coagulant aid did not cause formation of floc or removal of color. Reduction of color in the lower range of alum dosage was evident. Most of the color was reduced between dosages of 30 to 40 mg/ℓ of alum. Dosages of coagulant aid of 5, 10, and 20 mg/ℓ with 30 mg/ℓ of alum did not reduce the color but at 40 mg/ℓ of alum any dosages of coagulant aid yielded appreciable color reduction. The maximum color reduction by alum in conjunction with coagulant aid was 85%. In these systems, there was an abundance of large floc which settled completely within 10 minutes.

Cationic J

Coagulant aid J was tested in dosages of 2.0 to 12.0 mg/ℓ (Figure 12). Without addition of alum, the coagulant aid did not cause formation of floc or removal of color. Dosages from 40 to 60 mg/ℓ of alum in conjunction with coagulant aid yielded a significant color reduction at all concentrations of the coagulant aid above 2.0 mg/ℓ. However even this lower dosage of coagulant aid was more effective than alum alone in the 40 to 60 mg/ℓ alum dose range. Also, at 40 mg/ℓ of alum an increase in concentration of coagulant aid resulted in a reduction of color. Above 70 mg/ℓ of alum, the coagulant aid appeared to inhibit the action of alum; the color reduction was less than
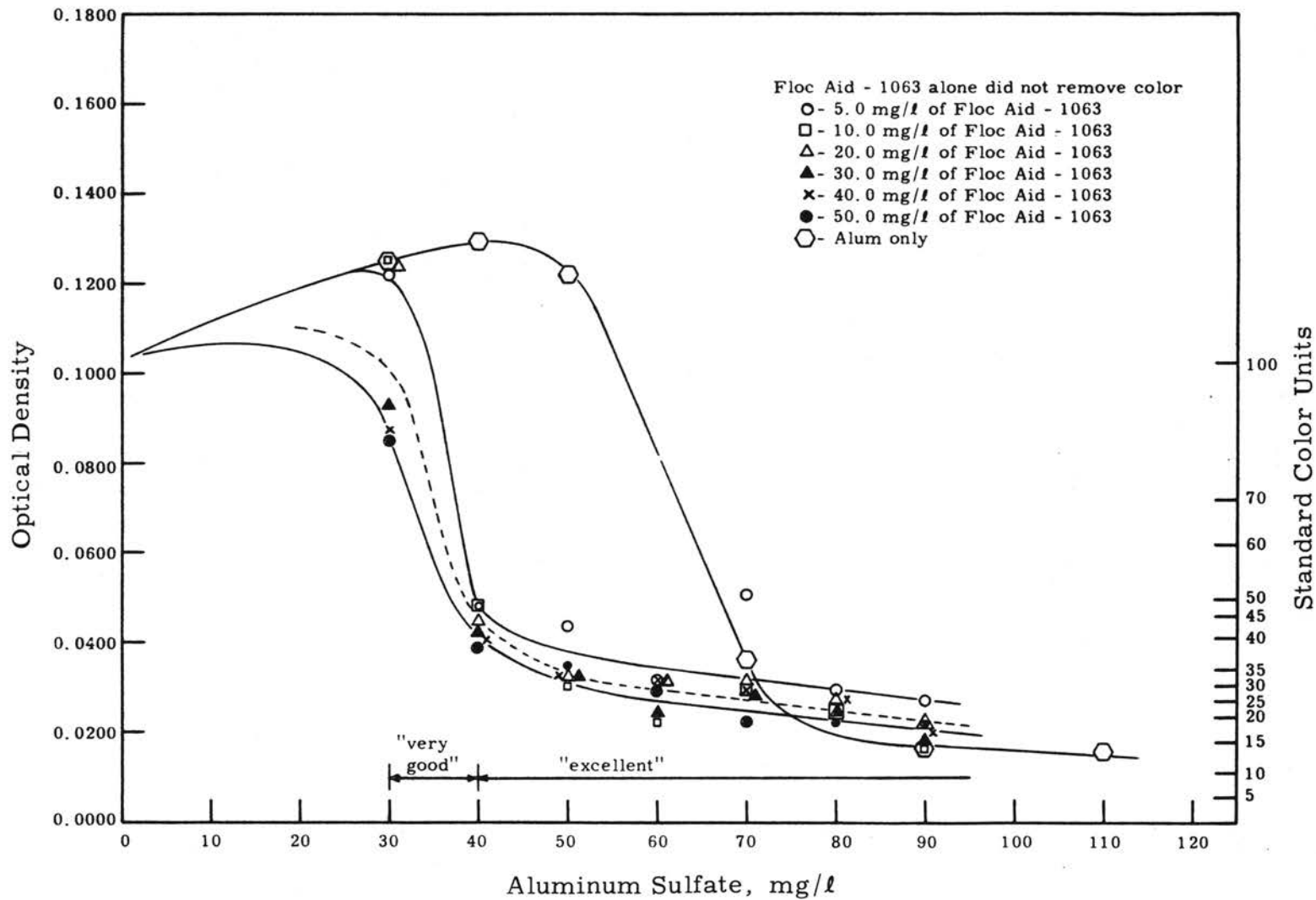
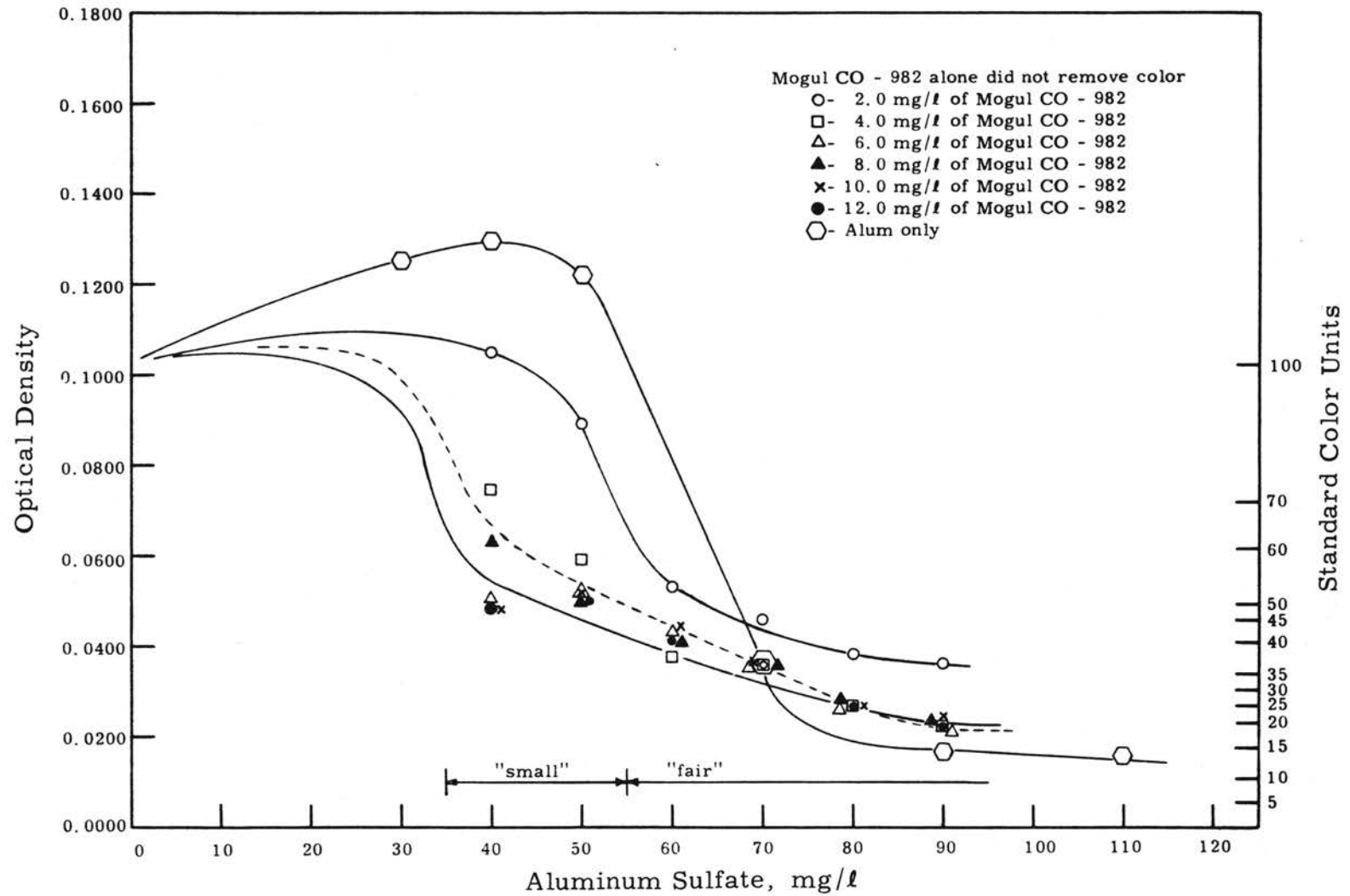Fig. 11 — Effect of polyelectrolyte "I" on color removal and alum flocculation.

Fig. 12 — Effect of polyelectrolyte "J" on color removal and alum flocculation.

for alum alone. The floc at any concentration of coagulant aid was not greatly increased in size and after the 30 minute settling period some floc appeared in suspension. The maximum color reduction obtained using the coagulant aid in conjunction with alum was 83%

Removal of Turbidity

Flocculation with Alum

Optimum dosage of aluminum sulfate $Al_2(SO_4)_3 18H_2O$ was determined as a basis of comparison for turbidity removal. Figure 13 shows the results of jar tests on turbid water using alum up to a dosage of 220 mg/ℓ. The curve shows the residual turbidity as well as the turbidity removed. Although the floc was rated as "small", turbidity removal was 83% at a dosage of 220 mg/ℓ of alum. The floc appeared during slow stirring and reached its final "small" size at the end of the flocculation period. The floc remained in suspension during the entire 30 minute settling period. In this study, the first appearance of floc was observed at 20 mg/ℓ of alum.

Flocculation with Alum and Polyelectrolytes

The effects of various concentrations of each polyelectrolyte selected for removal of turbidity in conjunction with specific dosages of alum are shown in Figures 14 through 23. For the purpose of comparison, the dosage curve for alum alone (Figure 13) is also
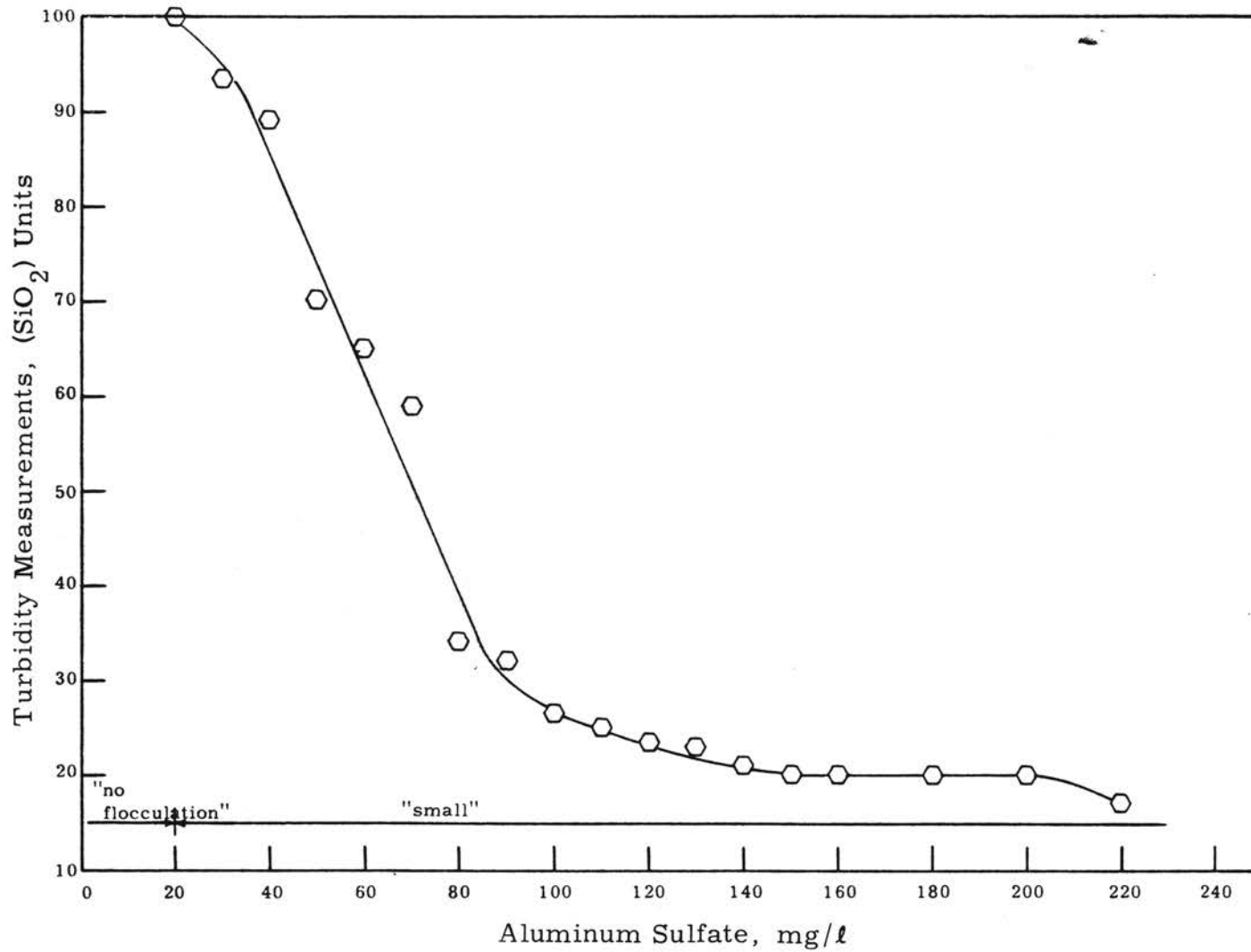
Fig. 13 — Effect of Aluminum sulfate on turbidity removal.

plotted on each figure. Experiments to determine the effect of the coagulant aid alone were also run. These results are plotted if removal of turbidity was obtained or simply noted if no reduction was shown. The quality of the floc is also noted.

The selection for a proper range of dosages of polyelectrolytes was first made according to the specifications given by the manufacturers (Table II). In most cases, the range of dosages was found not to be adequate for the water used in this study, and random tests were run to determine the lowest possible dose.

In Figures 14 through 23, the dotted curve is an attempt to represent the removal of turbidity for a practical or recommended dosage of polyelectrolyte to be used in conjunction with alum. This curve was drawn from consideration of the effects of maximum and minimum dosages of polyelectrolyte and is not necessarily confined within the zone bounded by maximum and minimum curves because at times, an increase in polyelectrolyte dosage resulted in an inhibition of flocculation. In cases where an increase in polyelectrolyte dosage had a negligible effect, only dotted curve is plotted. Thus, the dotted curve represents the minimum polyelectrolyte dosage recommended by the author for the most effective results.

Nonionic A

Coagulant aid A was tested in dosages of 0.6 to 5.0 mg/ℓ (Figure 14). Without addition of alum, the coagulant aid did not cause formation of floc or turbidity removal. First appearance of floc, in

the presence of coagulant aid, appeared at a dosage of 10 mg/ℓ of alum. The coagulant aid in dosages of 10 to 40 mg/ℓ of alum did not significantly aid the coagulation but helped in removing more turbidity than alum alone. Above 40 mg/ℓ of alum, the coagulant aid helped coagulation by providing a large and well-formed floc; the floc settled within 10 minutes. From dosages of 40 to 80 mg/ℓ of alum, the coagulant aid helped in removal of turbidity but, from 80 mg/ℓ of alum and above, the coagulant aid removed less turbidity than alum alone. At the higher alum dosages, only the size of the floc was improved. In this experiment, the maximum turbidity removed by alum and coagulant aid was 74%. At any alum concentration, increase in dosage of coagulant aid did not yield a notable increase in the size of the floc or removal of turbidity. Floc was built up slowly during the entire 15 minute flocculation period.

Nonionic B

Coagulant aid B was tested in dosages of 0.2 to 2.0 mg/ℓ (Figure 15). Without addition of alum, the coagulant aid did not cause formation of floc or removal of turbidity. Dosages of 20 to 80 mg/ℓ of alum in conjunction with the coagulant aid did not aid floc formation but aided considerably the removal of turbidity. The floc was rated only as "fair" and "good" and remained in suspension after the 30 minutes allowed for settling. Above 80 mg/ℓ of alum, the coagulant aid removed slightly less turbidity than alum alone. At any alum concentration increase in dosages of coagulant aid did not yield a notable improvement in the size of the floc or removal of turbidity. At alum
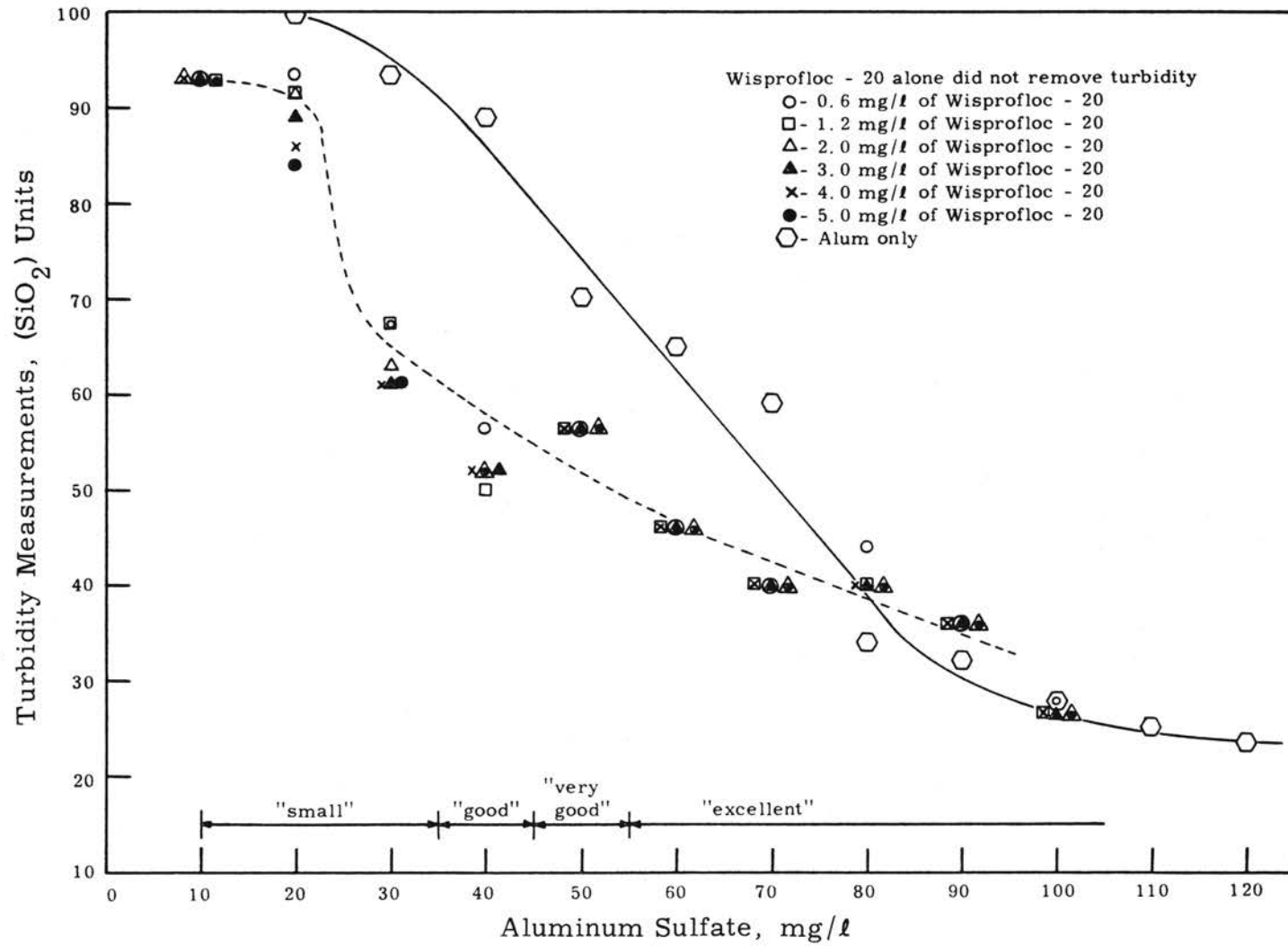
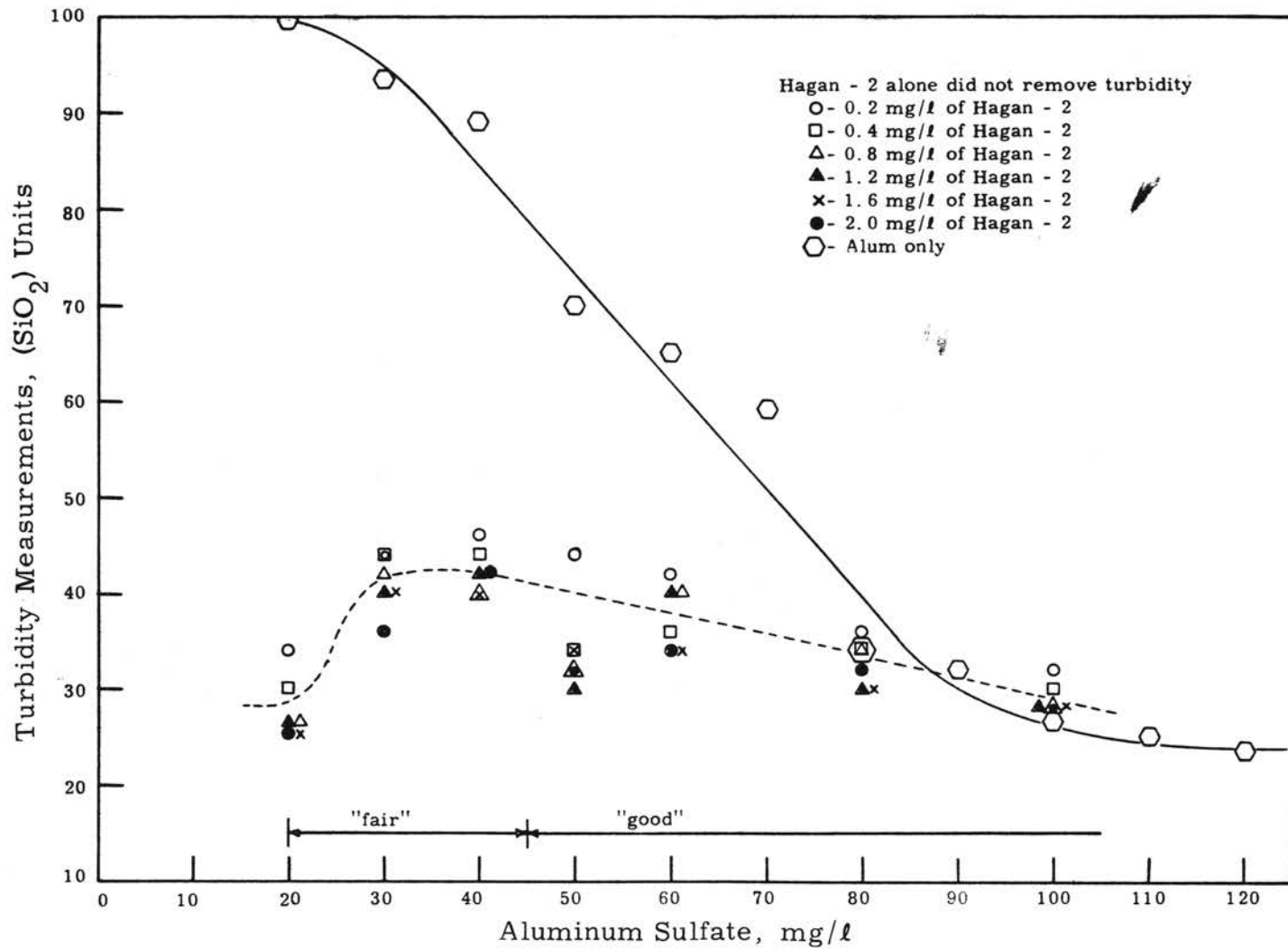Fig. 14 — Effect of polyelectrolyte "A" on turbidity removal and alum flocculation.

Fig. 15 — Effect of polyelectrolyte "B" on turbidity removal and alum flocculation.

dosages of 20 to 80 mg/ℓ, the addition of coagulant aid greatly improved removal of turbidity compared to that obtained by alum alone. Maximum turbidity removed by the coagulant aid in conjunction with alum was 72%. Floc built up slowly during the period of flocculation.

Nonionic C

Coagulant aid C was tested in dosages of 0.1 to 0.6 mg/ℓ (Figure 16). Without addition of alum, the coagulant aid did not cause formation of floc or removal of turbidity. Coagulant aid with alum dosages from 20 to 60 mg/ℓ improved the turbidity removal and floc formation. From alum dosages of 80 mg/ℓ and above, the coagulant aid inhibited the action of the primary coagulant and less turbidity was removed than by the alum alone. At any concentration of coagulant aid tested, the "small" floc particles formed during slow stirring were eventually agglomerated into one very large floc particle. This large floc particle reached its maximum size during the first minute of flocculation. During slow stirring in the flocculation period this single floc particle did not move in the suspension but trembled slowly at the bottom of the jar. In general, an increase in coagulant aid decreased the amount of turbidity removed. In these experiments, the maximum turbidity removed by the coagulant aid in conjunction with alum was about 64% and is much less than the turbidity removal obtained by alum alone.

Nonionic D

Coagulant aid D was tested in dosages of 0.3 to 2.5 mg/ℓ (Figure 17). Without addition of alum, the coagulant aid did not cause
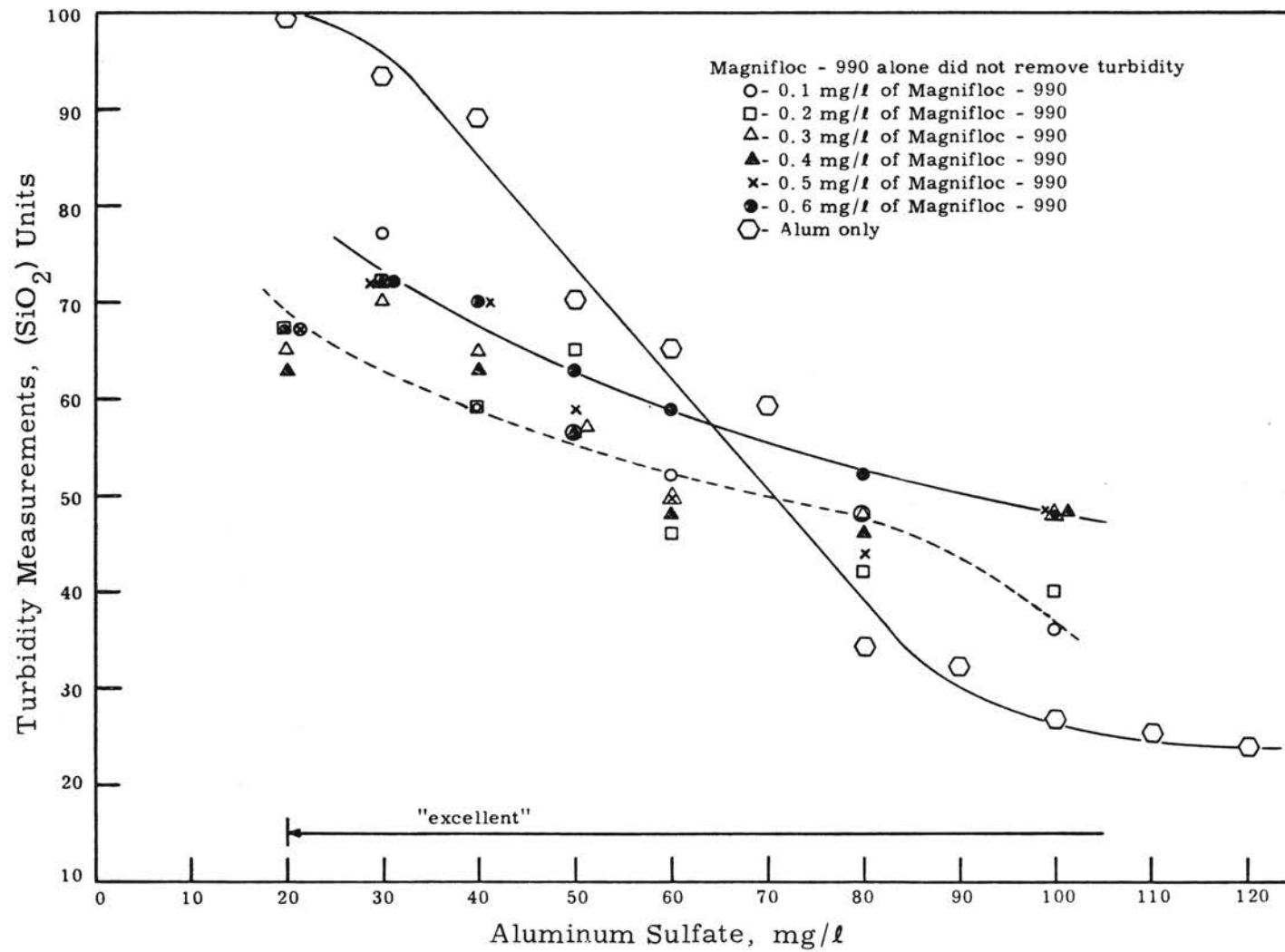
Fig. 16 — Effect of polyelectrolyte "C" on turbidity removal and alum flocculation.

formation of floc or removal of turbidity. Dosages of 20 to 80 mg/ℓ of alum with the coagulant aid did not aid appreciably the formation of floc and helped only slightly in removing turbidity. From dosages of 80 mg/ℓ of alum and above, the coagulant aid improved the floc only to a size rated as "good" and the turbidity removed was the same as for alum alone. The floc particles built up slowly during the period of flocculation. Floc particles were abundant and dense and settled within the 30 minutes allowed for settling. The maximum turbidity removed by alum and coagulant aid was 77%; this value was obtained with the lowest dose (0.3 mg/ℓ) of coagulant aid. At any alum concentration, an increase of coagulant aid dosage reduced the removal of turbidity.

Nonionic E

Coagulant aid E was tested in dosages of 0.2 to 1.2 mg/ℓ (Figure 18). Without addition of alum, the coagulant aid did not cause formation of floc or removal of turbidity. The dose of alum needed to start flocculation was reduced with addition of coagulant aid. The individual floc particles agglomerated during the slow stirring period into a very large single floc particle which laid at the bottom of the jar. This single particle of floc formed and settled within the first 5 minutes of the slow stirring period. In the presence of coagulant aid, turbidity removal was very good at low dosages (5 to 60 mg/ℓ) of alum compared to result obtained for alum alone. The maximum turbidity removal obtained in these experiments was 74% with the lowest
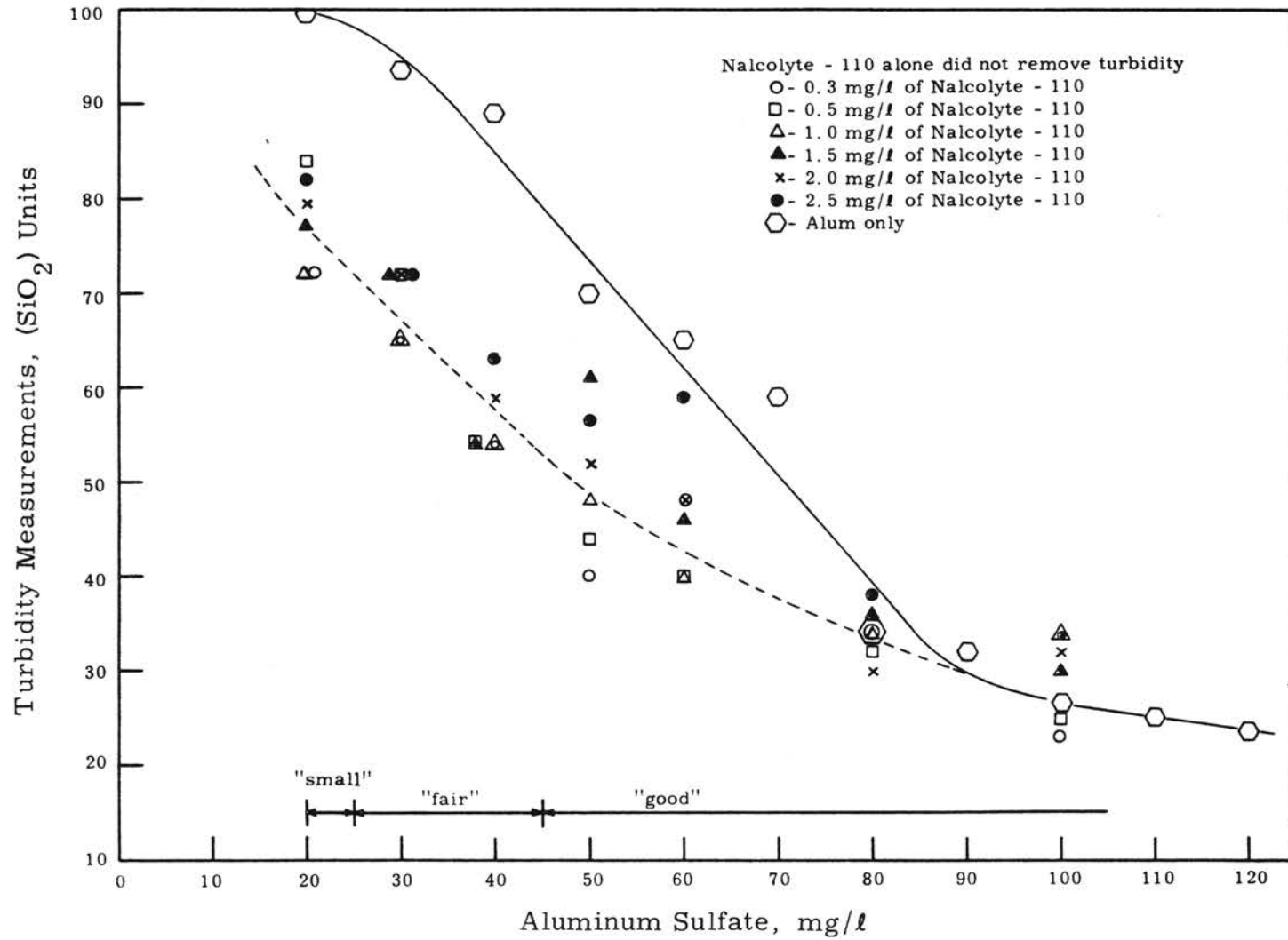
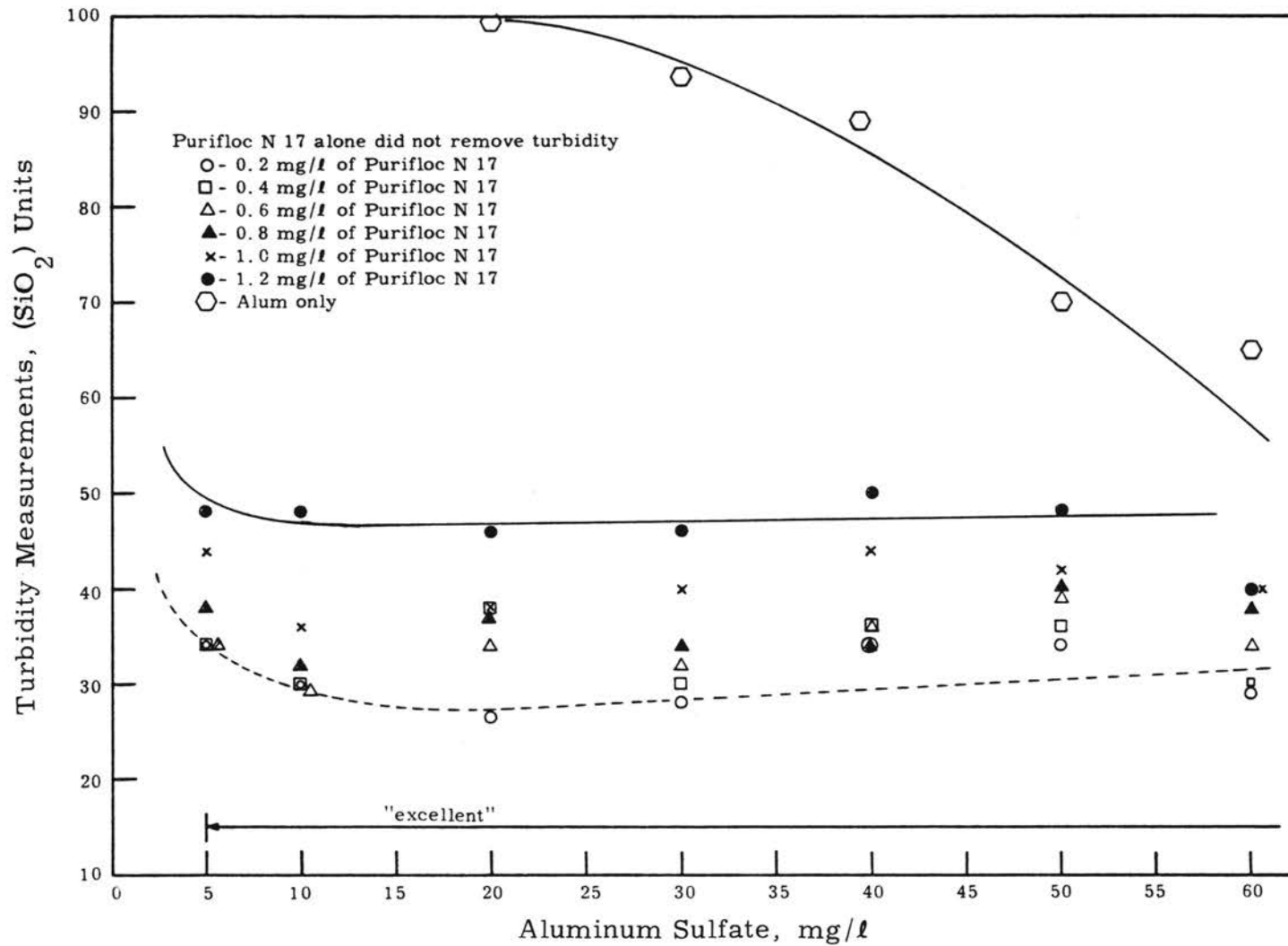Fig. 17 — Effect of polyelectrolyte "D" on turbidity removal and alum flocculation.

Fig. 18 — Effect of polyelectrolyte "E" on turbidity removal and alum flocculation.

coagulant aid dose 0.3 mg/ℓ. However, an increase in coagulant aid dosage inhibited the action of alum such that final turbidity was higher for the high dosages than at the low dosage.

Anionic F

Coagulant F was tested in dosages of 0.2 to 1.2 mg/ℓ (Figure 19). Without addition of alum, the coagulant aid did not cause formation of floc or removal of turbidity. The dose of alum needed to start flocculation was reduced with addition of coagulant aid. Large well-formed floc was obtained almost instantly after addition of the coagulant aid. The floc particles were not bulky; they were well defined and settled immediately after the stirrers were removed from the beakers. Turbidity was reduced by 85% at an alum dosage of 5 mg/ℓ and 0.2 mg/ℓ of coagulant aid; it is seen that turbidity removal was far better than by alum alone. At a dosage of 2 mg/ℓ of alum, there was a greater reduction in turbidity at the two lowest dosages (0.2 and 0.4 mg/ℓ) of coagulant aid than there was at the higher dosages. At higher dosages of alum, any dosages of coagulant aid removed the same amount of turbidity.

Anionic G

Coagulant aid G was tested in dosages of 2.0 to 12.0 mg/ℓ (Figure 20). Without addition of alum, the coagulant aid did not cause formation of floc or removal of turbidity. With addition of coagulant aid, pinpoint floc formation did not appear until an alum dosage of 40 mg/ℓ. Any dosage of coagulant aid in conjunction with alum gave very fine and
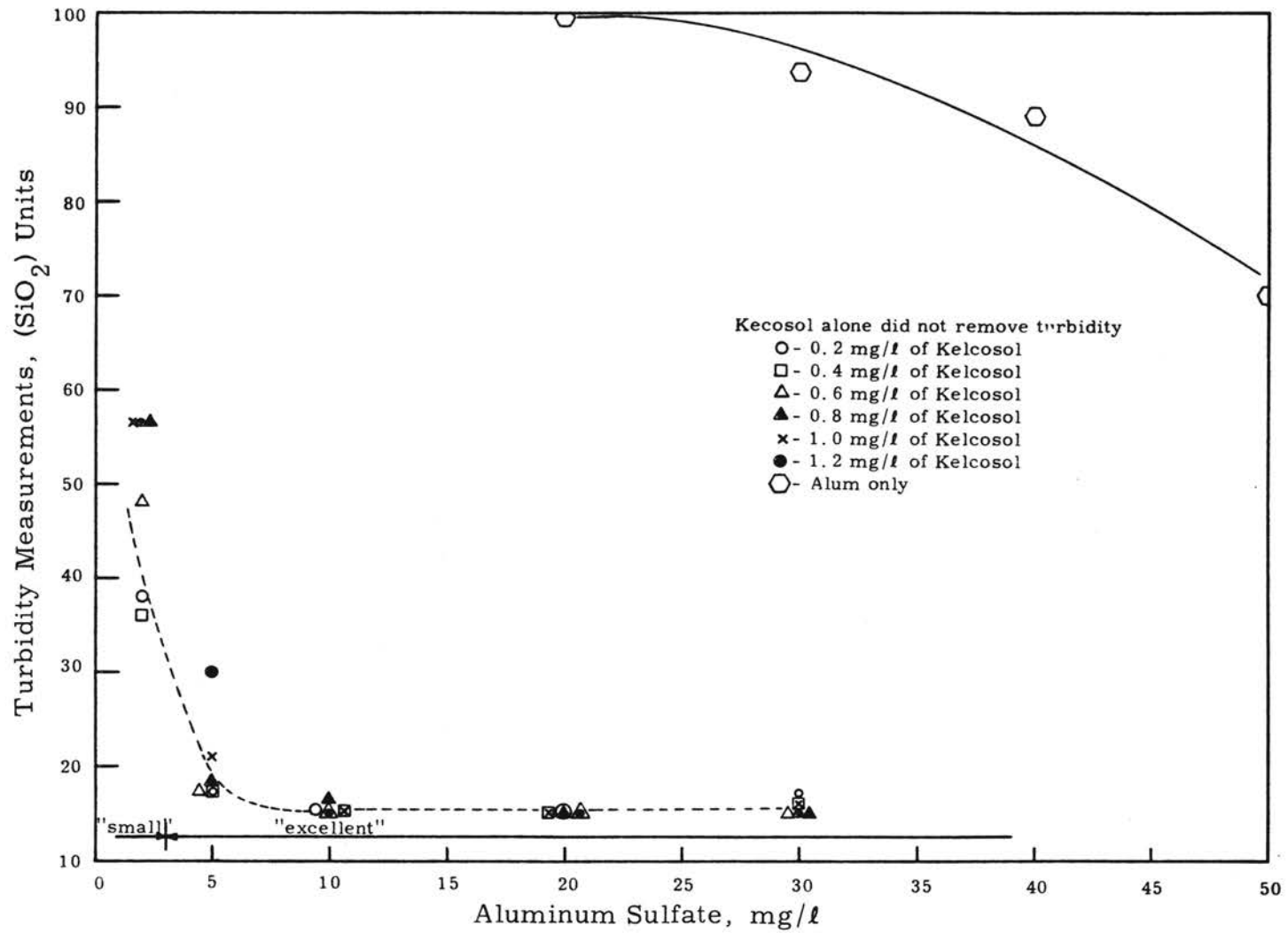
Fig. 19 — Effect of polyelectrolyte "F" on turbidity removal and alum flocculation.

poorly formed floc particles. After 30 minutes, most of the floc particles remained in suspension. The floc built up slowly during all the period of flocculation. This coagulant aid did not help to remove turbidity and the values obtained were the same as for alum alone. At a dose of 10 mg/ℓ of coagulant aid the action of alum was inhibited and the turbidity removed was very much less than for alum alone.

Anionic H

Coagulant aid H was tested in dosages of 0.2 to 1.30 mg/ℓ (Figure 21). Without addition of alum, the coagulant aid did not cause formation of floc or removal of turbidity. With addition of coagulant aid, only 2 mg/ℓ of alum were needed to start formation of floc and reduction of alum dosages appeared to be feasible with addition of a small dose of coagulant aid. The size of the floc could be classified only as "good" but it was dense and well formed. These floc particles were abundant and settled within 30 minutes. Floc particles appeared during slow stirring and built up slowly during the period of flocculation. At dosages of 2 and 5 mg/ℓ of alum, an increase in concentration of the coagulant aid yielded decreasing amounts of turbidity removal. From an alum dosage of 10 mg/ℓ and above, any concentration of coagulant aid reduced turbidity to the same value. In general, the coagulant aid in conjunction with alum did not improve the size of the floc but reduced the turbidity very much. At an alum dosage of 30 mg/ℓ, the coagulant aid reduced turbidity by 84%
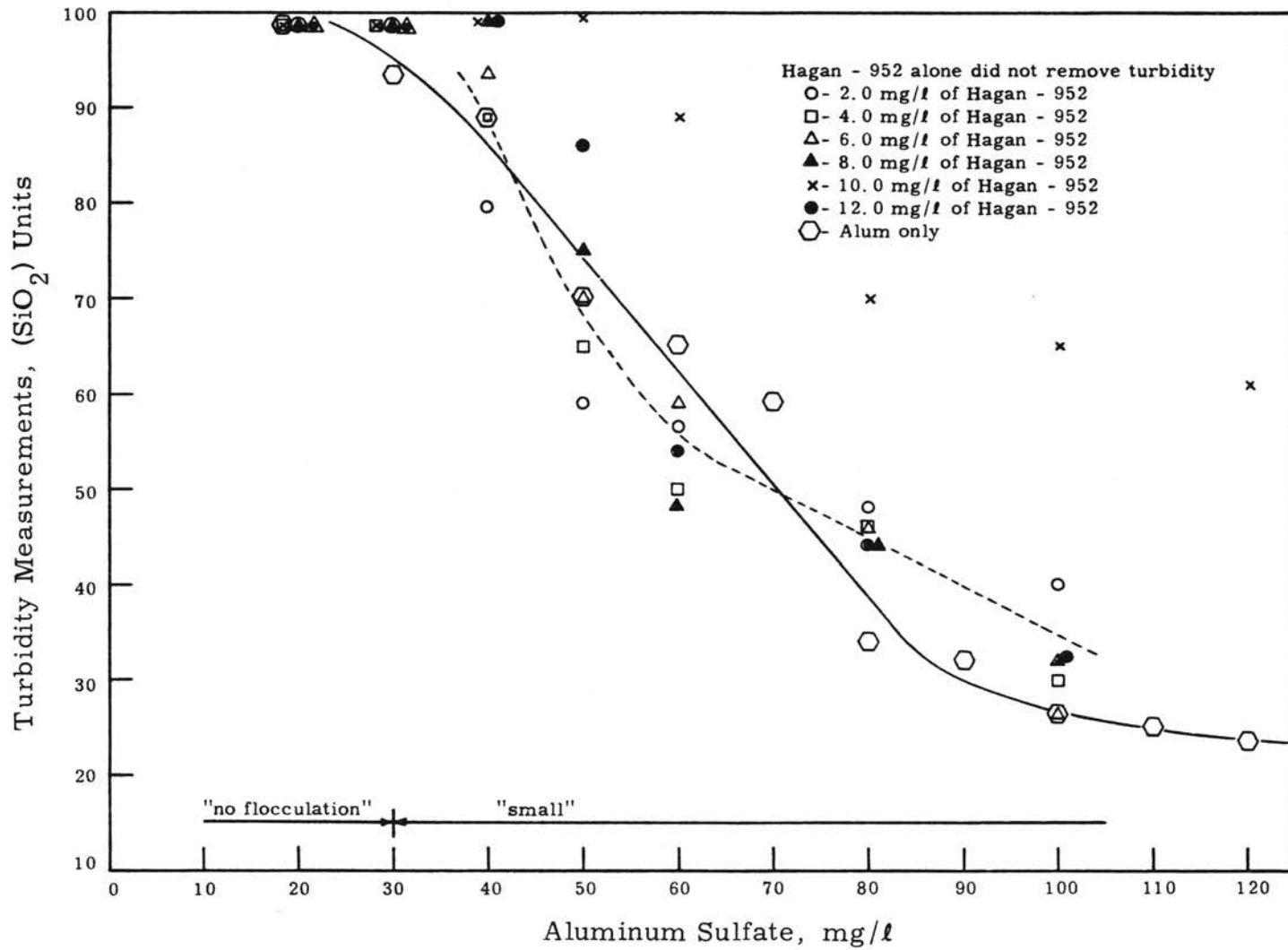
Fig. 20 — Effect of polyelectrolyte "G" on turbidity removal and alum flocculation.
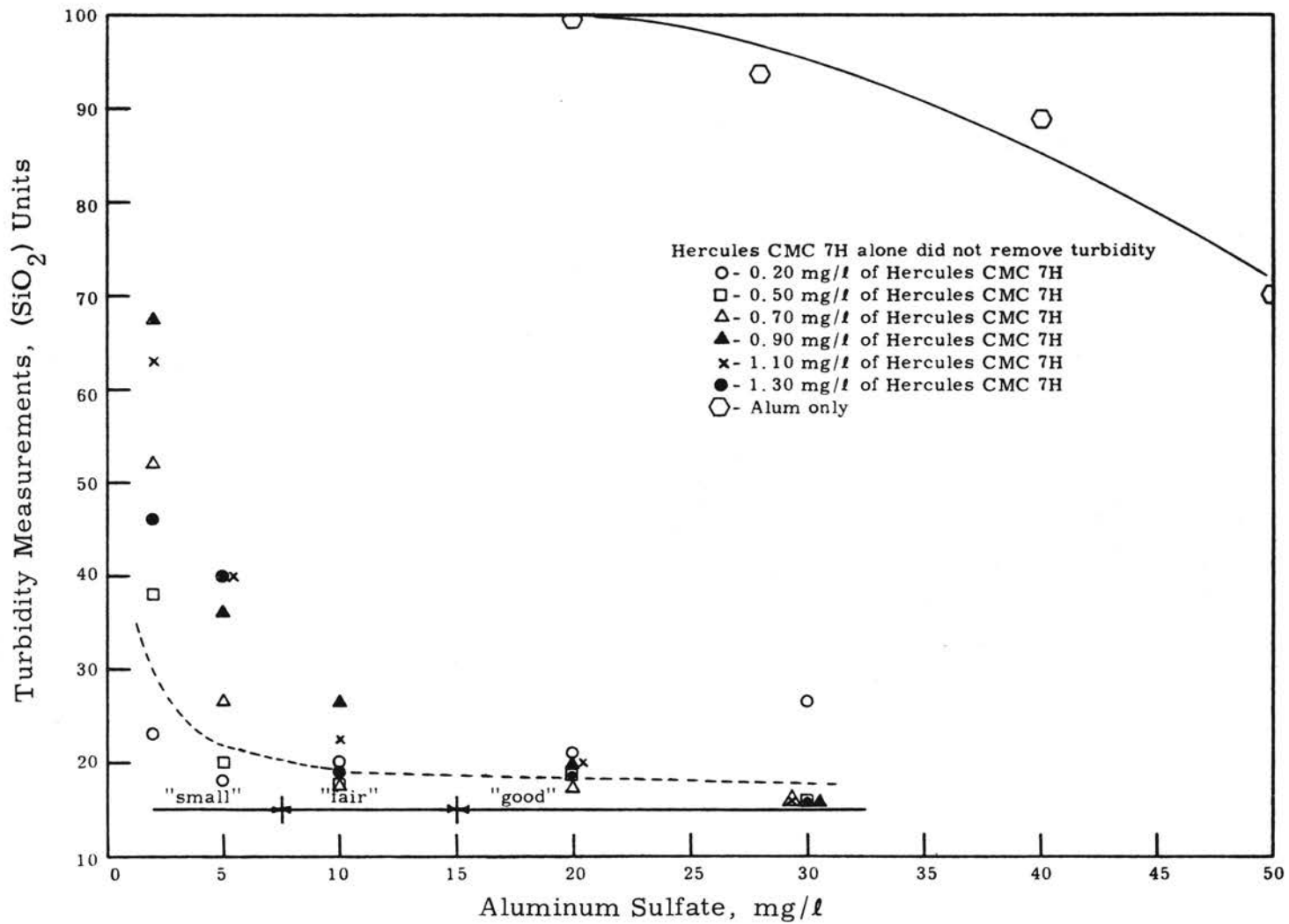
Fig. 21 — Effect of polyelectrolyte "H" on turbidity removal and alum flocculation.

Cationic I

Coagulant aid I was tested in dosages of 4.0 to 24.0 mg/ℓ (Figure 22). Without addition of alum, the coagulant aid showed a floc formation passing from "excellent" to "small" with dosages of 4 to 48 mg/ℓ. The maximum turbidity removal was found to occur at a relatively low dosage (8 mg/ℓ) of coagulant aid. The floc which produced maximum turbidity removal was very large and its final size was reached in the first 5 minutes of slow stirring. Increasing dosages of the coagulant aid also increased the time of formation of floc. Above 36 mg/ℓ of coagulant aid, the particles remained "small". The floc which was rated as "excellent", settled instantly whereas the "small" floc remained in suspension. The 8 mg/ℓ dose of coagulant aid yielded 83% removal of turbidity.

The coagulant aid in conjunction with alum also yielded a very large floc but less reduction of turbidity was obtained. The formation of floc was rapid but turbidity removal was less than with alum alone. Increasing coagulant aid dosages when used in conjunction with alum yielded decreasing amounts of turbidity removal. In conjunction with coagulant aid, more benefit was obtained at dosages of 20 to 60 mg/ℓ of alum than at dosages of 60 to 90 mg/ℓ. This cationic polyelectrolyte can be used as a true coagulant and is more effective alone than when used in conjunction with alum.

Cationic J

Coagulant aid J was tested in dosages of 2.0 to 20.0 mg/ℓ
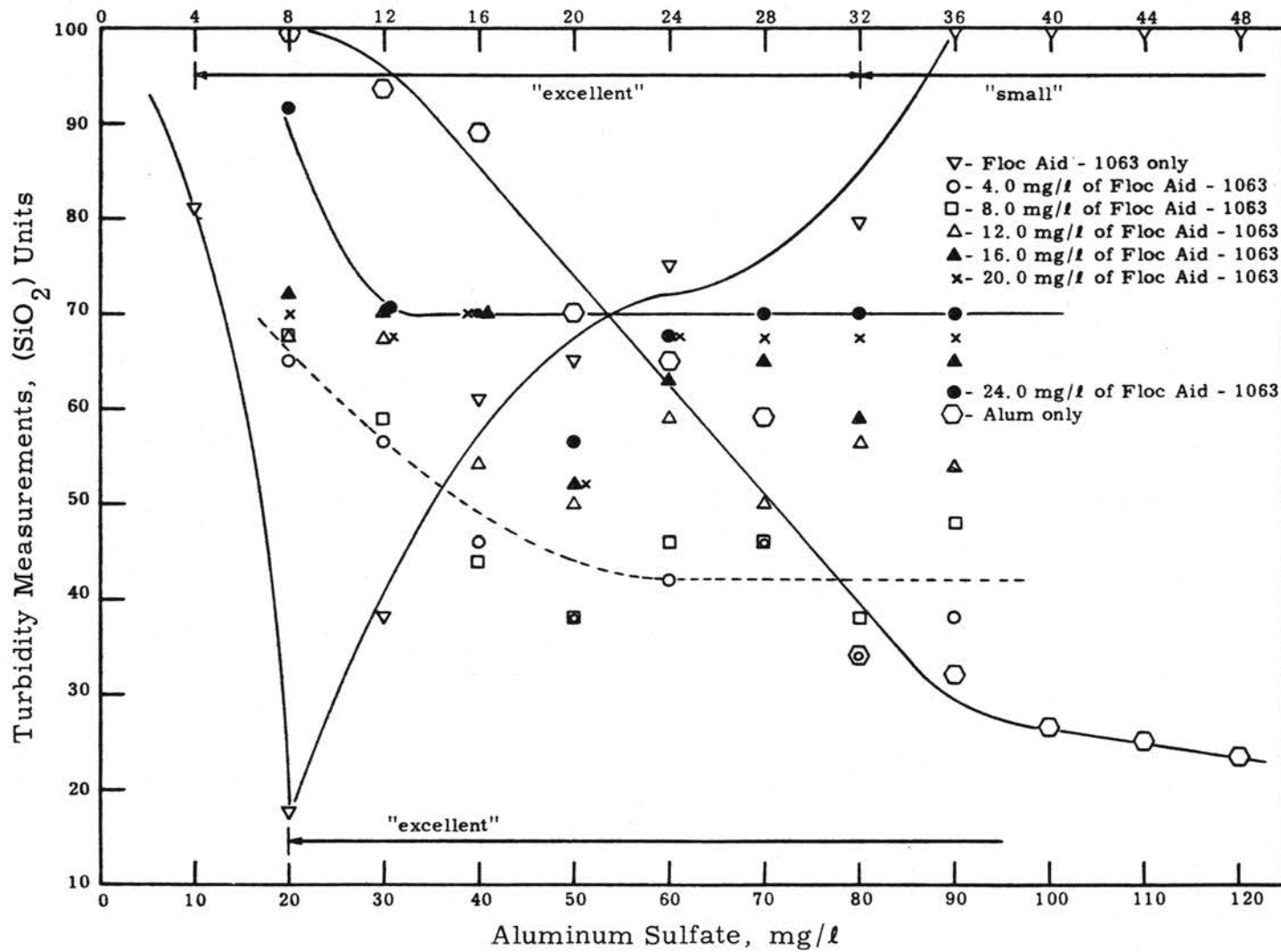
Fig. 22 — Effect of polyelectrolyte "I" on turbidity removal and alum flocculation.

(Figure 23). Without addition of alum, the coagulant aid did not cause formation of floc or removal of turbidity. The coagulant aid appeared to inhibit the action of alum by retarding pinpoint floc formation. In general, the coagulant aid inhibited the action of alum and removal of turbidity was much less than with alum alone. Increase in coagulant aid dosage also reduced the amount of turbidity removed. The size of the floc particles were not improved by addition of coagulant aid and remained "small", similar to the floc of alum. The floc was totally in suspension after the 30 minutes allowed for settling. In general, cationic J in conjunction with alum yielded less reduction of turbidity than alum alone, increased the time required to form floc and did not increase its size.
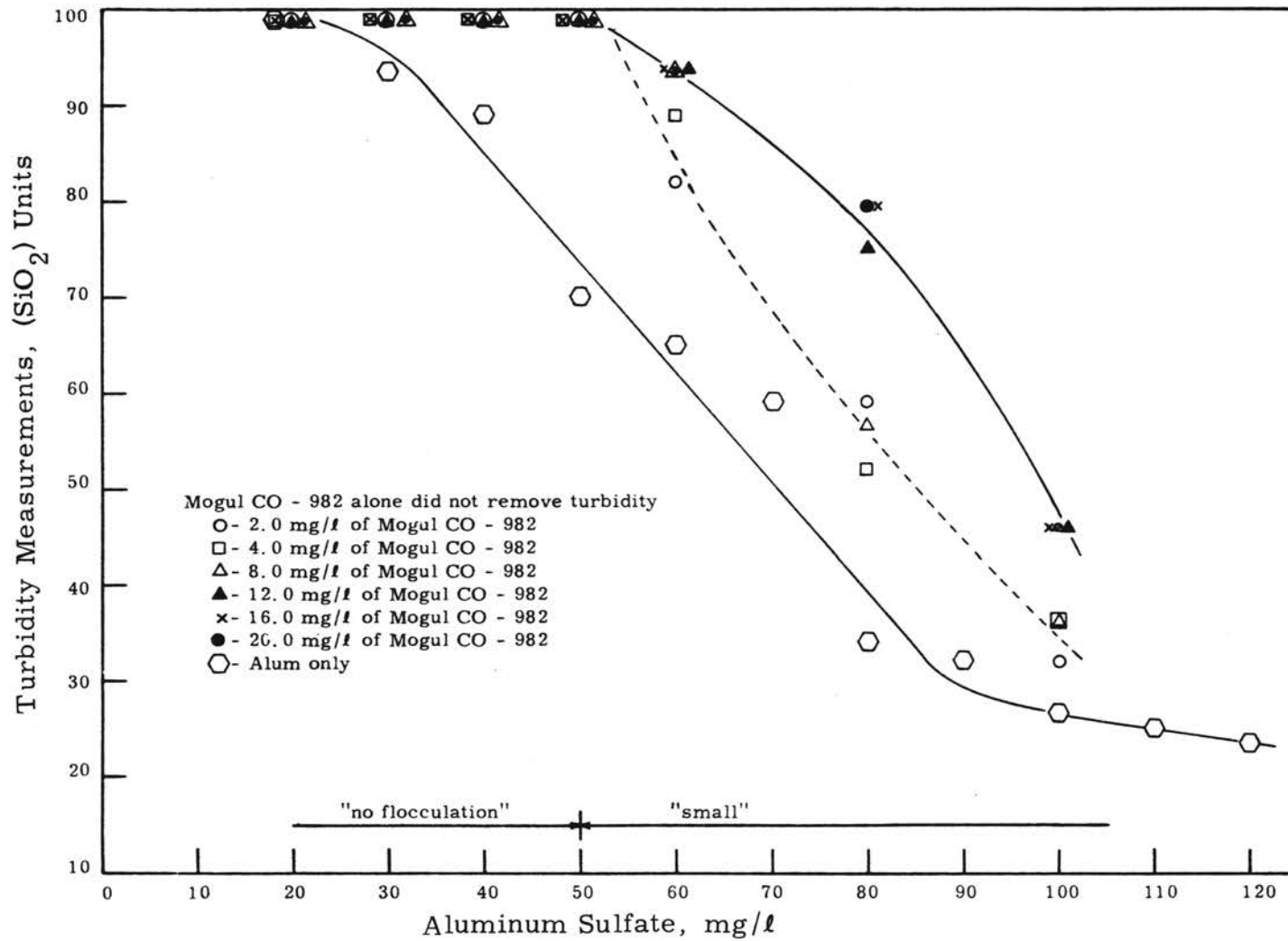
Fig. 23 — Effect of polyelectrolyte "J" on turbidity removal and alum flocculation.

CHAPTER IV

DISCUSSION

Removal of Color

In all experiments, the nonionic, anionic, or cationic polyelectrolytes when used alone, did not cause formation of floc nor removal of color. Optimum removal of color by alum alone was 91% and this value was higher than any found when alum was used in conjunction with polyelectrolytes. However, the floc obtained with alum alone was "small" and remained in suspension even after the 30 minutes allowed for settling.

The nonionic and anionic polyelectrolytes when used in conjunction with alum reacted differently in forming floc: For nonionic A and anionic F the floc particles were immense, heavy and settled instantly; nonionic E floc particles were very large but light and they sometimes floated to the surface instead of settling; nonionic B, C, D, and anionic H gave an "excellent" size of floc which settled within 10 minutes; anionic G formed an "excellent" but light floc which required 30 minutes to settle. Rapidity of floc formation is dependent to some extent on the size of the particles formed: Very large floc particles like those formed with nonionics A, E, and anionic F, were made

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instantaneously after addition of the reagents; flocs from nonionics
B, C, and anionic H reached their final size within 5 minutes; nonionic
D and anionic G floc particles built up slowly during the 15 minutes
allowed for flocculation.

Below 70 mg/ℓ of alum, the floc particles of nonionic A and
anionic F were very large and removal of color was also very much
improved. However, the large floc particle formed by nonionic E pro-
duced negligible color removal. Rated as "small" to "very good", the
floc particles of nonionics B, C, and anionic H improved, appreciably,
the removal of color. For nonionic D and anionic G the floc particle
built up slowly, but nonionic D was found to be more efficient in re-
moving color than anionic G.

At 70 mg/ℓ of alum or above, all nonionic and anionic polyelec-
trolytes formed floc particles of "excellent" size which increased the
rate of settling, but the final clarity of the water was poorer than that
obtained for alum alone.

Nonionics B, E, and anionic H inhibited the primary coagulant
(alum) in that they increased the alum dose required for marginal
flocculation to 40 mg/ℓ. In general, inhibition by nonionic and anionic
polyelectrolytes was observed at 70 mg/ℓ of alum and above, where
removal of color was less than that for alum alone.

Of the two cationics tested, cationic I formed an immense floc
which settled instantaneously; whereas cationic J did not improve the
size of the floc and these floc particles remained in suspension.

Formation of the floc with cationic I was instantaneous whereas with cationic J the floc built up slowly throughout the flocculation period. Color removal by cationic I was also much better than with cationic J. The final clarity of water obtained from these two cationics was comparable with that obtained with nonionics and anionics and therefore was less than that for alum alone.

In general, between alum dosages of 30 to 70 mg/ℓ, increase in size of floc and removal of color resulted from increased dosages of nonionic, anionic, or cationic polyelectrolytes. This increase in benefits was greater for some and less for others, but in general any of these three types of polyelectrolytes, yielded some benefit in either color removal or floc formation. Above 70 mg/ℓ of alum, for nonionic, anionic, and cationic polyelectrolytes, removal of color was less than that for alum alone.

It would have been desirable if color could have been removed to the practical value of 10 units (in this study 90% removal). Although this value of 90% removal of color was not obtained, the size of the floc particles was improved when polyelectrolytes were used in conjunction with alum.

These experiments, using polyelectrolytes with alum, exposed two major points of interest: First, more color was removed at alum concentrations between 30 to 60 mg/ℓ with polyelectrolytes than when alum was used alone; second, floc particles in this same range of alum dosage were also increased in size and settled faster.

In the low range of alum dosage with addition of polyelectrolytes, it was noted that color removal was from 40% to 60% better than with the same dosage of alum alone. If one assumes that the per cent color removed is independent of the initial color concentration, it is conceivable that the desired 90% color removal could be obtained if multistage treatments were practiced. In any case, the addition of polyelectrolytes was beneficial in that a better floc was produced. Furthermore, if per cent color removal is truly independent of initial color concentration, it can be calculated that a savings in alum would be obtained despite the use of a multistage operation.

The present study on removal of color involved the simultaneous addition of the polyelectrolyte and alum. However, Black (18) in his study has shown that the order and rate of addition of the primary coagulant and polyelectrolytes are important factors in the removal of color. He explains the fact that alum requires time to initiate coagulation and gather the colloidal particles of color. Since in the present experiments the polyelectrolytes alone did not remove color, it is felt that their function is to act as gatherers of larger particles and that the addition of polyelectrolytes should be made one minute or more after flash mixing of alum. However it would appear that greater agitation than is provided in the usual flocculation period should be employed (so long as it is gentle and does not tear the floc) in order to bring the polyelectrolyte and the tiny floc formed by alum into contact. Such a mode of operation should provide for better removal of

color and reduce the number of multistages required.

From the result of the present study, nonionic, anionic, and cationic polyelectrolytes appear to have a limited range of dosage for maximum benefit to floc formation and color removal. In general, most of the color removal occurred between the alum dosage at which pinpoint floc was formed and an alum dosage 20 mg/ℓ above this point. At the alum dosage where formation of floc began, an increase in concentration of polyelectrolyte resulted in a greater reduction of color, but as the alum concentration was increased, an increase in polyelectrolyte dosage did not increase color removal. In general, color removal and formation of floc were closely related and maximum benefit from addition of the chemicals is obtained in a limited range.

Removal of Turbidity

Of the nonionic, anionic, and cationic polyelectrolytes tested, only cationic I caused formation of floc and removal of turbidity when used without alum.

Optimum removal of turbidity obtained by alum alone was 83% and this value is less than the 10 units (90% in the present study) recommended for public supplies. The flocs obtained with alum alone were "small" and most of them remained in suspension. Only anionic F and H polyelectrolytes acting in conjunction with alum were found to increase (only slightly) the removal of turbidity while the rest did not. Thus, the permissible maximum value of 10 silica units of turbidity in

the clarified water was not obtained in any of the experiments run.

Each of the various polyelectrolytes tested in conjunction with alum formed floc particles of different sizes. Nonionics C, E, and anionic F formed immense floc particles which settled instantly. Non-ionic A gave "excellent" floc particles which settled within 10 minutes. Anionic H formed relatively "small" but heavy flocs which also settled within 10 minutes. Nonionic D also produced a small but relatively heavy floc which settled within 30 minutes. Nonionic B, anionic G, and cationic J did not improve, appreciably, the size of the floc and the floc particles which were formed remained in suspension.

Rapidity of floc formation was dependent to some extent on the size of the particles formed. Very large floc particles like those caused by nonionic C and anionic F were formed instantly but the large particles by nonionic E were slowly formed. Anionic H formed a relatively good floc particle in the first 5 minutes of flocculation, whereas the flocs formed by nonionics A, B, D, anionic G, and cationic J built up during the entire period allowed for flocculation.

The large floc formed with nonionic C did not appreciably remove the turbidity. However, the large floc produced by nonionic E and anionic F removed practically all of the turbidity at alum dosages from 0 to 10 mg/ℓ. A probable reason for this difference in removal may be that completeness of flocculation had not been achieved due to lack of foundation material on which the remaining colloids must adhere. This lack of foundation floc could in turn be attributed to the

rapidity of settling of the floc which was formed. Therefore, the advantage of adding polyelectrolyte which may be gained by a reduction in flocculation time was offset by the poorer clarity obtained in the supernatant. In addition to these three polyelectrolytes, anionic H and nonionic D also produced a relatively settleable floc which removed turbidity. However, anionic H removed nearly all turbidity which it was capable of removing in the range of 0 to 10 mg/ℓ of alum whereas nonionic D was found to be less effective in this range. The floc particles formed by the following four polyelectrolytes remained in suspension but removal of turbidity was effected to different degrees: Nonionic A did not appreciably remove turbidity whereas nonionic B was most effective in alum concentrations of 0 to 20 mg/ℓ; on the other hand, anionic G and cationic J inhibited floc formation and turbidity removal was much less than for alum alone. The use of cationic I alone caused an instantaneous production of very large floc particles which yielded a turbidity removal of 83%. This amount of turbidity removal was produced by a dosage of 8 mg/ℓ which was found to be optimum because further increases in dosage inhibited coagulation i.e. showed less removal of turbidity. These floc particles settled instantly.

When used in conjunction with alum, cationic I also formed very large flocs which settled instantly. The formation of flocs was very fast but removal of turbidity was much less than that observed for cationic I alone. It would therefore seem that cationic I could be used better solely as a true coagulant rather than as an aid to coagulants.

In general, addition of nonionic, anionic, or cationic polyelectrolytes reduced the usual dose of alum required to start the formation of floc except for anionic G and cationic J which increased the alum dosage.

It is interesting to note that an increase, beyond the optimum dosages, of nonionic, anionic, or cationic polyelectrolytes, always inhibited coagulation in varying degrees; a greater inhibition was observed at lower concentrations of alum.

In their study, Mueller and Burbank (19) found that nonionic polyelectrolytes were the most effective from the standpoint of settling rate and turbidity removal. However, Cohen (13) reported that the nonionics were less effective as coagulant aids than anionic or cationic polyelectrolytes. The present study indicates that there is not much difference between nonionic and anionic polyelectrolytes. It was also found that all polyelectrolytes are not equally effective in removing the turbidity of a specific water. Cohen (13) tested various waters and concluded that effectiveness of all polyelectrolytes are different with different waters. From the foregoing discussion it can be stated that each water must be examined individually in order to determine the most effective polyelectrolyte as well as its optimum dosage.

In the present study, none of the polyelectrolytes yielded 90% removal of turbidity when used in conjunction with alum and floc was improved by only seven of the ten tested, i.e. nonionics A, C, D, E, anionics F, G, and cationic I.

The prediction made for removal of color, i.e. that even with

multistage operation a savings in alum could be effected by addition of polyelectrolytes, can also be applied to removal of turbidity since both color and turbidity are colloidal in nature. Four of the polyelectrolytes tested showed that a considerable savings in alum dosage is possible. Anionics F and H removed 83% of the turbidity at an alum dosage of only 5 mg/ℓ and nonionics B and E removed 75% of the turbidity at an alum dosage of 20 mg/ℓ.

Comparison of color and turbidity removal

In general, nonionic and anionic polyelectrolytes when used in conjunction with alum were equally effective in removal of color and in removal of turbidity. However, the floc particles obtained in the color studies were tougher and more discrete than those obtained in the turbidity experiments. In the discussion which follows, the color or turbidity removal for a particular polyelectrolyte is reported relative to the control i.e. removal of color or turbidity by alum alone.

Nonionic A gave, in both cases, a large floc which settled fast but color was removed to a greater extent than turbidity.

Nonionic B, in the case of color removal, gave a floc which settled within 10 minutes whereas in the case of turbidity removal, the floc remained in suspension. However, both turbidity and color removal were improved. In the case of turbidity removal, a savings in alum dosage is feasible.

Nonionic C, in both cases, gave an "excellent" size of floc which

settled rapidly but color was removed much more than turbidity.

Nonionic D, gave a color floc which settled within 10 minutes whereas the turbidity floc settled within 30 minutes. Color was reduced much more than turbidity.

Nonionic E, in both cases, formed immense floc particles. Turbidity was removed very much at lower dosages of alum whereas color removal was not improved at all. In the case of turbidity removal a saving in alum is feasible.

Anionic F, in both cases, produced a very large floc which settled instantly. Turbidity and color was reduced very much in both cases. In the case of turbidity, a savings in alum seems feasible.

Anionic G, in the case of color removal, produced a floc which barely settled within 30 minutes. However, in the case of turbidity removal, the floc remained in suspension. Anionic G improved color removal but did not improve turbidity removal.

Anionic H, in the case of turbidity removal, produced a relatively "small" but heavy floc whereas in the case of color removal it produced an "excellent" floc. However, both flocs settled within 10 minutes. In both cases color and turbidity removal was improved. A saving in alum dosage is feasible in the case of turbidity removal.

Cationic I, in the case of turbidity removal, was very effective when used alone. Used with alum the effectiveness was greatly reduced. Whether used with or without alum, it produced an "excellent" size of floc which settled instantly. In the case of color, when used

alone, cationic I did not cause formation of floc or removal of color. Used in conjunction with alum it produced an "excellent" floc which settled within 10 minutes. The color was also greatly reduced.

Cationic J, in the case of color, produced a "small" floc which remained in suspension. In the case of turbidity, the flocs were also "small" and remained in suspension. Color removal was improved but for turbidity removal, an apparent inhibition of the chemicals occurred and reduction of turbidity was less than that for alum alone.

In summary, reduction of 90% color or turbidity seemed possible on the assumption that multistage operation could be used. In general, a savings in alum would be obtained in spite of the use of multistage operation. In any event, the tests run on turbidity showed that four of the polyelectrolytes (nonionics B, E, and anionics F, H) effected extreme reduction in alum dosage.

CHAPTER V

SUMMARY AND CONCLUSIONS

Removal of Color

The data presented clearly demonstrate that polyelectrolytes are effective coagulant aids and the following conclusion may be drawn:

1. The experiments show that nonionic, anionic, and cationic polyelectrolytes are not coagulants but are true coagulant aids which require the use of a primary coagulant.

2. The polyelectrolytes when used in conjunction with alum react differently on floc formation. Four of them gave immense floc particles; four others produced large and well formed flocs; one produced large but light flocs; and one produced small flocs.

3. Some of the polyelectrolytes tested were more effective than others in reducing color below that of the control curve.

4. At certain dosages, the polyelectrolytes give a better rate of floc settling but a poorer final clarity of water than obtained with alum alone.

5. A few of the polyelectrolytes prevented or inhibited floc formation in that they caused the pinpoint floc to appear at a higher dosage of alum.

6. In general, the polyelectrolytes increased the rate of settling to value greater than that obtained with alum alone.

7. With most of the polyelectrolytes, the floc formation was instantaneous or built up within the first 5 minutes of flocculation. Thus, flocculation time could be reduced by use of these polyelectrolytes.

8. Although the addition of polyelectrolytes effected some reduction in alum dosage, this reduction was not appreciable, under the experimental condition herein employed if a final color concentration of 10 units is used as a basis of comparison.

9. Each polyelectrolyte has a limited range of dosage for maximum benefit of floc formation or removal of color.

10. At low concentrations of alum, an increase in polyelectrolyte dosage led to greater or lesser increase in floc formation and color removal, in accordance with the polyelectrolyte used. However, as alum concentration was increased, little or no benefit or even inhibition of coagulation was noted.

11. In general, nonionic, anionic, and cationic type polyelectrolytes, in conjunction with alum, have all been shown to be effective in improving floc formation, settling rate, and color removal.

Removal of turbidity

1. Nonionic and anionic polyelectrolytes are not true coagulants but are coagulant aids which need a metal coagulant (e.g. alum) to initiate coagulation.

2. One cationic polyelectrolyte served as a primary coagulant as well as a coagulant aid.

3. Four distinctly different types of floc were found to result from the addition of the various polyelectrolytes with the metal coagulant alum. These were:

(a) Huge, bulky flocs that settle instantaneously

(b) Large, well-formed flocs that settle rapidly

(c) Small but dense flocs that also settle at a relatively rapid rate

(d) Small, poorly formed flocs that settle slowly or remain in suspension.

4. Flocs of settleable size normally formed within the first 5 minutes of flocculation. Therefore the rapidity of flocculation would allow a reduction in the period normally required in standard treatment plant design.

5. In all cases, except two, clarification was improved by the use of polyelectrolytes with alum.

6. Different efficiencies of clarification were obtained by the various polyelectrolytes used. Several reduced turbidity greatly and permitted a considerable reduction in the alum dosage; others produced only a slight improvement in clarification; two types inhibited the growth of the floc with a resultant clarity less than that which would have been obtained by alum alone.

7. On a comparable basis more turbidity was removed at the

lower concentration of alum and polyelectrolytes.

8. The addition of some polyelectrolytes reduced the required dosage of the metal coagulant (alum) appreciably.

9. Increased dosages of the polyelectrolytes had two opposing effects. While the appearance and settleability of floc particules improved the removal of turbidity decreased.

10. Some polyelectrolytes at any dosage produced floc which settled slowly but yielded excellent resultant clarity of the supernatant, while for others, the reverse effect was observed.

11. One cationic polyelectrolyte was much more versatile in that it could be used as a coagulant or a coagulant aid and was much more effective from the standpoint of turbidity removal. It was comparable to anionic and nonionic polyelectrolytes from the standpoint of settling rate.

Suggestions for Further Work

There are three major investigational channels which could be fruitfully pursued in extending this work:

1. In view of the aspect brought out in the discussion, (see pages 71 and 76) it could be ideal to determine if the percentage removal of color and turbidity is proportional to their initial concentrations.

2. An investigation to compare the efficiencies of color and turbidity removal under single and multi-stage operation should be made.

3. An investigation to compare the effect on color and turbidity removal by simultaneous and sequential addition of alum and polyelectrolytes should be made.

Since the application of polyelectrolytes in the water supply and pollution control field is new, many needed investigation could be cited. However the three listed above appear to be the most important extensions of the present work.

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