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Polyelectrolytes in the treatment of wastewaters

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Polyelectrolytes in the treatment of wastewaters

by

Martins Olusola Ogedengbe

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Civil Engineering
Major: Sanitary Engineering

Approved:

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Ames, Iowa

1972

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

The decision to undertake this study is an outgrowth of the fact that the discovery of synthetic organic polyelectrolytes, enthusiastically welcomed and embraced in many water and wastewater treatment operations, has failed to get more than casual interest from domestic wastewater treatment managements. At a time when the effluent-quality demands imposed by ecological and wastewater reuse problems tax the ability of conventional sewage treatment plants, it is inconceivable that sewage treatment operators would ignore these new products without cause. In fact, many of these plants do use polyelectrolytes to condition sludge prior to vacuum filtration, and in many instances substantial improvements have been reported. It appears, therefore, that polyelectrolytes have not been found to perform well as a clarification aid in sewage treatment operations.

The primary sedimentation unit in a conventional sewage treatment plant may remove up to 75 or 80 percent of suspended solids and 35 percent of BOD (Biochemical Oxygen Demand). Figure 1 represents a flow diagram through such a treatment system. The primary unit is purely a sedimentation unit, and the secondary is a biological unit which may be a trickling filter or an activated sludge system. A tertiary unit is not now a regular part of a sewage treatment operation, but may soon be as more and more stringent

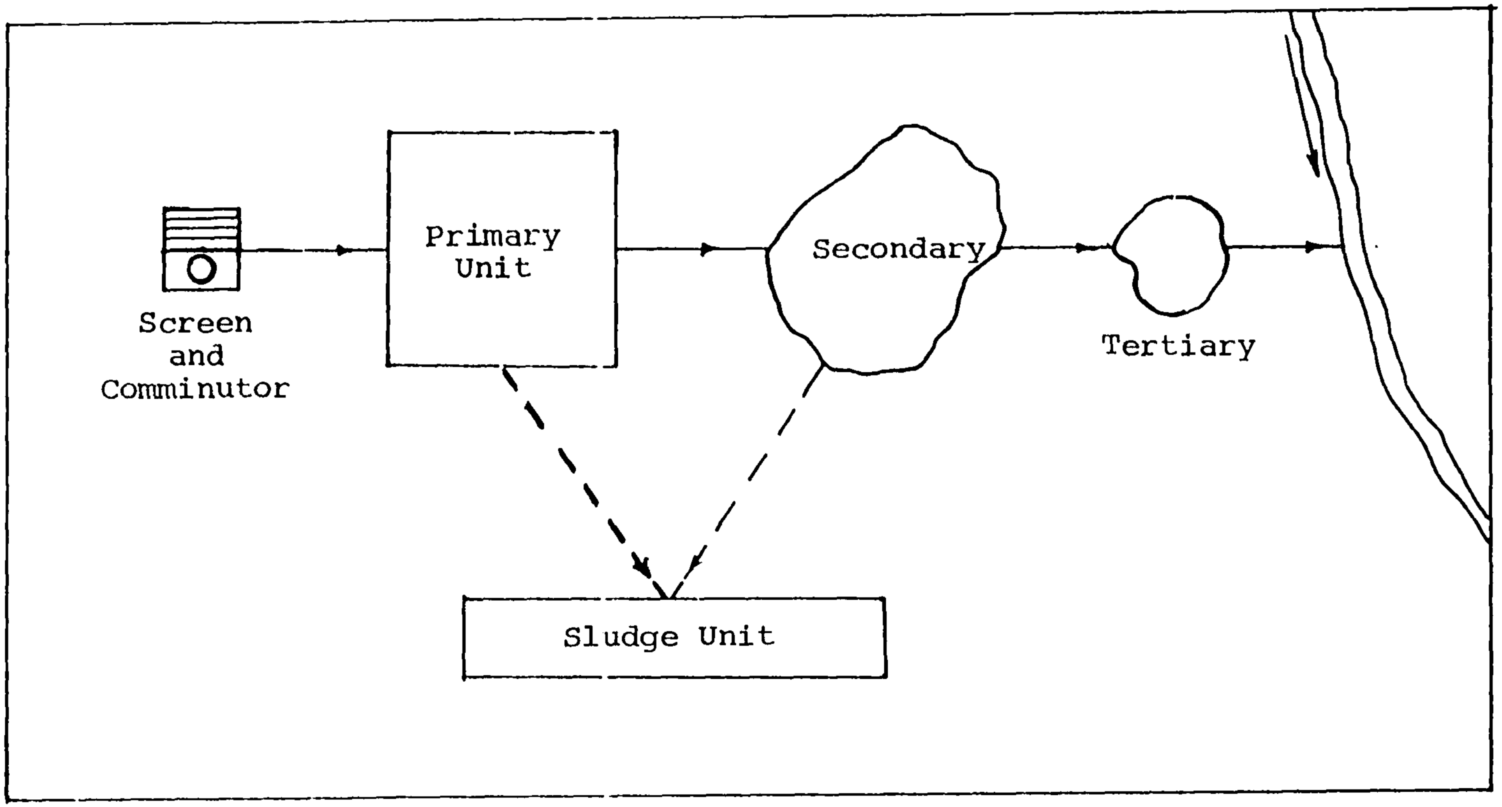


Figure 1. Flow diagram through a wastewater treatment plant

standards of final effluent are being set. Tertiary treatment units currently under study include physico-chemical processes such as reverse osmosis (RO), ultra-filtration, carbon-adsorption units, rapid sand filtration with its various modifications, and so on.

The secondary units (trickling filters or activated sludge units) may increase the BOD removal to 90 percent, when properly operated. The remaining 10 percent or more of BOD coming out of the secondary units could still constitute a substantial pollutional load on a stream, considering that several million gallons per day of such effluent are frequently involved. Some form of additional treatment (possibly but not necessarily a tertiary process) generally seems called for, to further reduce the pollution-potential at the plant.

If some material could be found that would effect a higher removal of suspended solids and BOD in the primary units, the solids load on the secondary units would be reduced. A reduced solids load on a secondary treatment unit should cause a reduction in the air-supply requirement (in the case of an activated sludge system), and, correspondingly, a reduction in power cost. The final effluent of either system could be much improved.

Trivalent salts of iron and aluminum have been used with varying degrees of success to effect some improvement in over-all plant effluent. There is one major set-back in the use of these inorganic salts, however, the resulting sludge-volume is usually great. The new synthetic organic polyelectrolytes, on the other hand, do not create such a sludge-volume problem, partly because much less dosage of these materials need be used, but mainly because polyelectrolytes may actually condition the sludge for vacuum filtration by creating a filter cake structure with sufficient rigidity and porosity to provide passages within the cake for an efficient water egress. In spite of this apparent superiority of polyelectrolytes little use is made of them in sewage treatment processes.

Mixed reactions come forth from plants which use or have tried the materials as to their performance. For example, large-scale tests of polymeric flocculants in primary clarification at Cleveland's 125 mgd Easterly plant (in Ohio) has been reported (3) as having demonstrated a 57 percent reduction of BOD in the first stage, a $3,300 per month savings of aeration power cost--enough to pay 25 percent of the cost of the chemicals used--and a 33 percent reduction in secondary effluent BOD. On the other hand, the report states that cases are known where wastewater treatment officials conclude that although some increased efficiency was achieved in the treatment step the over-all result in secondary effluent quality was not sufficient to justify the cost. Thus, the case for polyelectrolytes in wastewater treatment is not at all clear cut.

A number of reasons could be cited for the failure to obtain predictable results from polyelectrolyte-coagulated wastewaters.

First, far too few studies involving the use of polyelectrolytes with wastewaters have been reported in the coagulation literature. Most coagulation studies have been carried out using inorganic salts on synthetic waters such as, for example, a dispersion of a clay mineral in distilled water. The use of synthetic waters in coagulation research is rational because it provides the researcher with a suspension of known qualities, and facilitates reproducible results which are essential in the understanding of basic mechanisms and in the development of relevant mathematical models. However, if the gap between research and its application is to be narrowed somewhat, studies on synthetic waters should be followed where possible with corresponding studies on real waters or wastewaters.

Second, it appears that many investigators in the coagulation field are frequently too ready to pursue certain aspects of the coagulation phenomenon and completely ignore others purely on the basis of theoretical rationalization. Thus, even though there are no conclusive data to show that intensive rapid mixing is always detrimental, many studies assume that it is. It is too often assumed that intensive mixing would break up the floc as soon as they are formed, and that the only rational purpose of rapid mixing is to disperse the chemicals into the suspension. As a consequence of this attitude, most of the recent studies (5, 27, 45, 59, 60) on the physical aspects of coagulation are concentrated on the problem of slow mixing, or, as it is frequently referred to, flocculation.

It is apparent from the above that research is needed to investigate the performance-potential of polyelectrolytes on real waters and wastewaters, and that investigators should keep an open mind with regard to what is rational and what is not. Furthermore, the tendency towards over-application of theories developed from the use of synthetic waters to real waters must be tempered, so that research may be truly relevant to field applications.

The purpose of this study, in broad terms, is to determine if, and under what conditions, polyelectrolytes would enhance clarification of domestic wastewaters.

The study will be made using the sewage of the city of Ames, and the results can be expected to reflect the peculiarities of this particular wastewater. However, Ames' sewage is considered substantially domestic and of normal strength, and, therefore, the findings would probably withstand the challenge of other domestic wastewaters of normal strength.

II. BACKGROUND ON POLYELECTROLYTES

A. What are Polyelectrolytes?

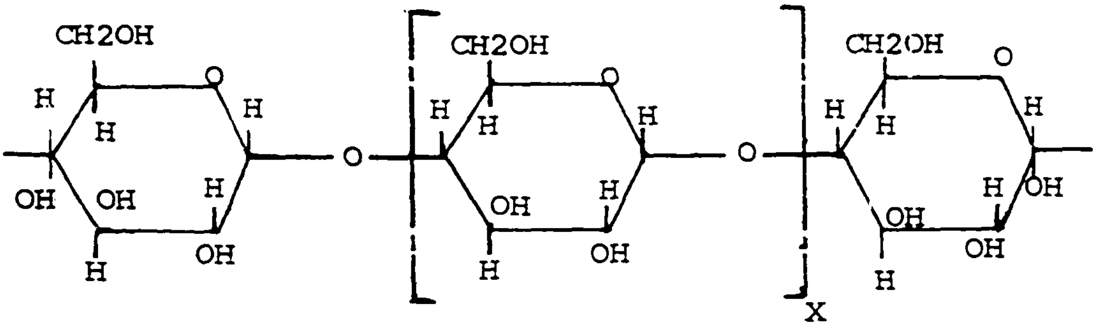
Polyelectrolytes are long chain organic polymers often having molecular weights in excess of one million and are either natural or synthetic in origin. A polymer molecule is defined as a series of repeating chemical units held together by covalent bonds (15, 18, 19). If the repeating units are of the same molecular structure the compound is called a homopolymer. However, if the molecule is formed from more than one type of repeating chemical units it is called a copolymer. The individual repeating units that make up the molecule are called monomer units. The molecular weight of the polymer molecule is, therefore, the sum of the molecular weights of the individual monomer units. The total number of monomer units is referred to as the degree of polymerization.

Natural polymers include starches, gelatin, vegetable gums, and proteins (e.g., egg-white). The ability of such natural polymers to act as coagulant-aids has long been known (18), but the commercially more important types in clarification processes are the synthetic ones, the list of which includes high-molecular-weight polyamines, polyacrylamides, polyalkyleneimines, and polyacrylonitrile.

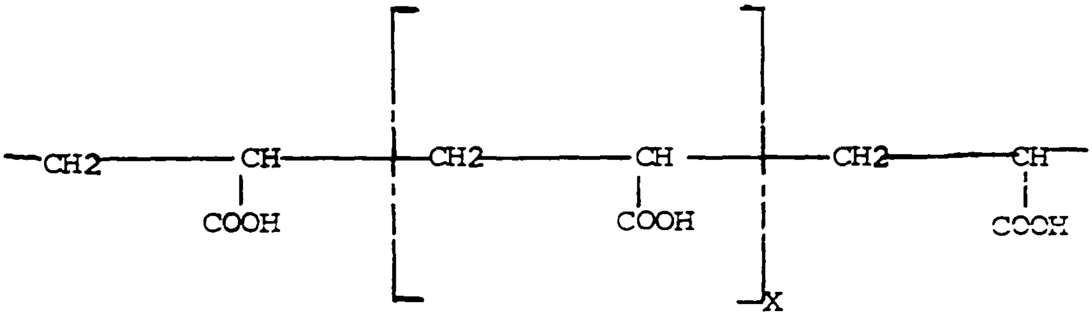
The similarity between a naturally derived polymer such as starch, and a purely synthetic polymer such as polyacrylic acid, exists in the fact that both compounds have repeating units--glucose and acrylic acid respectively--and that each of the recurring units contains ionizable functional groups--hydroxyl in one, and carboxyl in the other (see Figure 2).

The term "polyelectrolyte" was introduced to include those polymers which, by some ion-producing mechanism, can become converted to a polymer molecule having electrical charges along its length. The electrical charges arise from the presence of ionizable functional groups along the polymer chain. Polyelectrolytes are, therefore, polymeric-electrolytes, i.e., having characteristics of both polymers and electrolytes.

When the ionizable groups dissociate, polymer molecules become charged either positively or negatively, depending upon the specific functional groups present. Polymers whose ionizable functional groups have a net positive charge are called <u>cationic</u> polyelectrolytes. Those with a net negative charge are referred to as <u>anionic</u>, and those having an equal amount of positive and negative charges such that the net charge is zero are called nonionic. Figure 3 shows examples of the three types of polyelectrolytes using the structure of polyacrylamides.

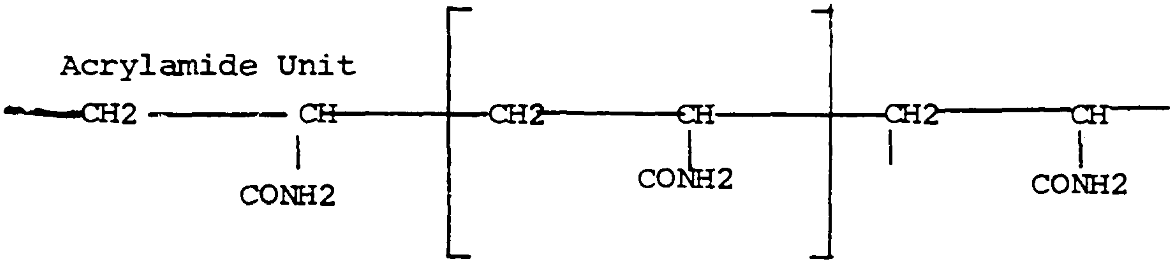


(a) Starch

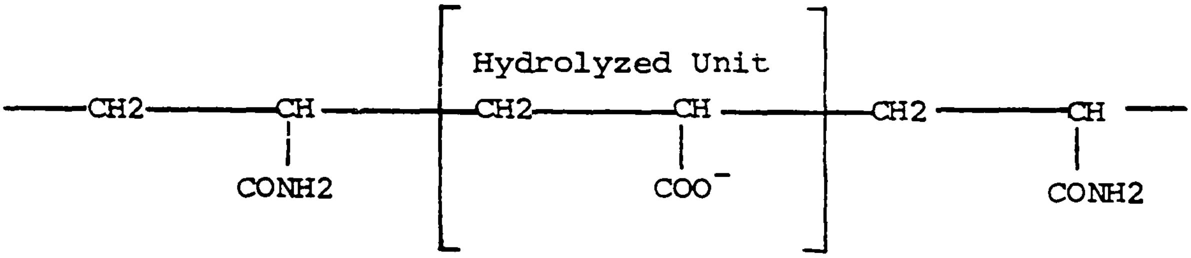


(b) Polyacrylic Acid

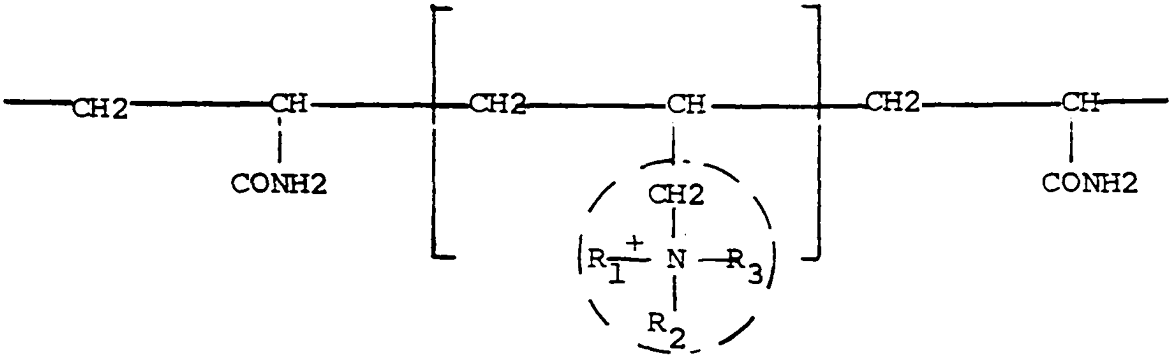
Figure 2. Recurring molecular units of natural and synthetic polymers, (a) shows the structural formula of starch, a natural polymer; and (b) shows that of a synthetic polymer--polyacrylic acid



(a) Nonionic



(b) Anionic



(c) Cationic

Figure 3. Examples of nonionic, anionic and cationic polyelectrolytes, (b) is a partly hydrolyzed polyacrylamide and (c) is a partly substituted quartenary ammonium group (25)

B. Mode and Extent of Polyelectrolyte Utilization

Commercial polyelectrolytes used in the aggregation of suspended matter are water-soluble. They may come in granular forms, in form of powder, or as highly-viscous liquids. All existing polyelectrolytes have a tendency to degrade when stored over a period of time. For a particular product, such a period is usually stated by the manufacturer. In general, the more dilute a polyelectrolyte solution is, the faster the degradation, which probably involves the breaking up of the long chains, resulting in decreasing viscosity. This would account for the fact that these products are supplied in dry or highly viscous liquid forms. The user would then make up dilute solutions as needed, discarding unused portions of such dilute forms after a few days. Most manufacturers of synthetic polyelectrolytes give detailed information about their products to guide the user in the preparation, storage, and mode of application.

The actual mechanism of polyelectrolyte action is discussed in a later section under "Theory of Coagulation". However, it is important in discussing the mode of polyelectrolyte utilization to point out the reason why it is essential to use only very dilute solutions of polyelectrolytes in particle aggregation. Adsorption is one of the many important steps involved in particle aggregation with long chain polymers. This is a process in which the charged sites of a linear polymer molecule are attached (adsorbed) to the surface of a number of particles, forming what is generally referred to as <u>particle-polymer-particle bridges</u> (17, 28, 47, 67), resulting in larger-sized particles which settle faster. Polyelectrolytes are believed to become irreversibly attached to solid particles, therefore, the best effects are achieved by adding it in as large a volume of water as possible, usually about 0.01 to 0.1 percent solution. But even with such dilute solutions localized adsorption can be prevented only by immediate mixing to disperse the polyelectrolyte solution with the suspension-system.

1. Extent of utilization

The use and importance of polyelectrolytes is increasing rapidly. The number of manufacturers producing these materials is likewise increasing. A list of more than thirty polyelectrolyte manufacturers was published in the first "Control Directory" (20) of *Engineering Science and Technology*, October 1968. This represents a fairly rapid growth since it was but 15 years ago that the first trace of synthetic polyelectrolyte was introduced into the market as competitors to conventional inorganic coagulants. Synthetic polyelectrolytes have found considerable applications in the following broad areas:

Process industries

Industrial wastewater treatment

Water treatment

Domestic wastewater treatment.

Specific uses of polyelectrolytes in process industries include clarification of raw sugar juice in the sugar industry; separation of gypsum from wet process phosphoric acid; settling improvement in coal-washer operation; increasing thickener capacity in wet process cement manufacture; separation of clay impurities from hot borax streams; improving the quality of metal deposition in the electrolytic refining or electrowinning of copper and zinc; improvement of thickening operations in uranium processing, and so on.

Many industrial wastewaters also are amenable to treatment with polyelectrolytes. In the ever-increasing fight against river pollution, industries need all the help they can get, and polyelectrolytes are becoming more and more an important factor in the abatement of these pollution problems. It is predicted (3, 4) that polyelectrolytes will make greater inroads in industrial wastewater treatment than in municipal treatment. One possible explanation for this is that the funding of industrial wastewater treatment plants is not subject to the same constraints as municipal plant financing, consequently, industrial waste treatment plant designers are more sensitive to reducing overall treatment plant costs than to whether the saving is in capital investment or operating costs.

In drinking water, or water for use by the beverage and food processing industries, care must be exercised in introducing new chemicals into the treatment processes, unless and until such chemicals have been subjected to tests relating to public health safety. In 1962, the United States Public Health Service (USPHS) published a list of synthetic organic polyelectrolytes which it approved as safe for use in treating water for public consumption (62). An additional list was published in 1967 (63). The combined list is shown in Table 1. In approving these products the USPHS emphasized that its findings bear only on the health aspect of the use of the products and do not constitute endorsement or otherwise indicate effectiveness for the proposed use. The products, says USPHS, may be used in water treatment without adverse physiological effect on those using the water when applied in the concentrations recommended by the manufacturers and provided the products continue to meet the quality specifications furnished by the manufacturers. The specified maximum concentrations allowed for each product in the treatment of water are also shown in Table 1.

In wastewater treatment there is no limitation such as imposed by USPHS in water treatment. The need for similar

Table 1. List of synthetic organic polyelectrolytes approved safe for use in treating water for public consumption (62, 63)

Manufacturer	Product	Max. Conc. Recommended by Mfgr., ppm
Allyn Chemical Co.	Claron	1.5
	Claron #207	2
American Cyanamid Co.	Superfloc 16	1
	Magnifloc 990	1
	Superfloc 20	1
	Magnifloc 971-N	1
	Superfloc 84	1
	Mangifloc 985-N	1
Betz Laboratories, Inc.	Poly-Floc 4D	25
The Burtonite Co.	Burtonite #78	5
Calgon Corporation	Coagulant Aids	
	#2	1
	#7	0.75
	#11	4
	#18	15
	#801	6
	#952	3
	#961	5
	Coagulant Aid 233	≤1
	Coagulant Aid 243	_1
	Coagulant Aid 253	≤1
Commercial Chemical Products, Inc.	Coagulant Aid-Speedifloc #1	10
Dearborn Chemical Co.	Aquafloc 422 Potable	1
The Dow Chemical Co.	Separan NP10 Water Grade	1
	Purifloc N17	1
	Separan AP30	1
	Purifloc A22	1
Drew Chemical Corp.	Drewfloc No. 3 (formerly Alchem Coagu-Aid #261)	3
	Drewfloc 21	5
	Alchem Coagu-Aid 252	5
	Alchem Coagu-Aid 265	1

Table 1 (Continued)

Manufacturer	Product	Max. Conc. Recommended by Mfgr., ppm
Drew Chemical Corp. (Cont.)	Drewfloc 265	1:8 alum
	Drewfloc 1	0:5:10 lime[a]
Electric Chemical Co.	Ecco suspension Catalyzer #146	3.5
Garratt-Callhan	Coagulant Aid 70	≤1
	Coagulant Aid 72	≤1
General Mills, Inc.	SuperCol Guar Gum	≤10
Hercules Powder Co.	Carboxmethylcellulose	1
	Reten A-1	1
	Reten A-5	1
Frank Herzl Corp.	Perfectamyl A5144/2	≤10
Illinois Water Treatment Company	Illco IFA 313	19
Ionac Chemical Co.	Ionac Wisprofloc 20	5
	Ionac Wisprofloc 75	5
Kelco Company	Kelgin W	5
	Kelcosol	5
Key Chemicals, Inc.	Key-Floc-W	25
Metalene Chemical Co.	Metalene Coagulant P-6	5
Nalco Chemical Co.	Nalcolyte #110	5
	Nalco 671	1
Narvon Mines Ltd.	Sink-Floc Z-3 and AZ-3	10
	Sink-Floc Z-4 and AZ-4	10
National Starch and Chemical Corp.	Floc Aid 1038	5
	Flock Aid 1063	5
North American Mogul Products Co.	Mogul CO-982	1.5
	Mogul CO-980	2
	Mogul CO-983	1

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[a] One part of Drewfloc to 8 parts of alum when used simply as an aid in alum coagulation and 0.5 ppm of Drewfloc to 10 ppm of lime when used in connection with lime softening.

Table 1 (Continued)

Manufacturer	Product	Max. Conc. Recommended by Mfgr., ppm
O'Brien Industries, Inc.	O'B-Floc	10
Stein, Hall and Co., Inc.	Hallmark 81	1
	MRL-19	1
	MRL-13	1
	MRL-14	1
	MRL-22A	1
	Jaguar	0.5
W. E. Zimmie, Inc.	Zimmite	1
American Cyanamid Co. 30 Rockefeller Plaza New York, New York	Magnifloc 860A	≤ 1
Imperial Chemical Industries, Limited P.O. Box 7 Winnington, Northwich Cheshire, England	Alfloc 370	0.5
W. A. Scholten's Chemische Fabrieken N.V. Foxhol, Postbus 1 The Netherlands	Wisprofloc P	5
Stein, Hall and Co., Inc. 605 Third Avenue New York, New York 10030	Polyhall M-295	1
Nalco Chemical Co. 6216 West 66th Place Chicago, Illinois 60638	Nalcolyte 671	1

limitations could, conceivably, arise in the future, especially with the increasing trend towards wastewater reuse. The use of polyelectrolytes in wastewater treatment has been mostly in the conditioning of sludge prior to vacuum filtration.

C. Advantages and Disadvantages in Polyelectrolyte Usage

Specific practical benefits frequently cited include the following:

1. The materials are effective in much lower dosages than those required with inorganic flocculants.
2. The resulting sludge is correspondingly smaller.
3. There is achieved a reduced capacity for existing plants and reduced capital costs for new plants through a reduction in size of the sludge-handling and treatment equipment required.
4. More efficient use of valuable land because of reduced area requirements for settling tanks and filters.
5. Performance of separations which had previously been economic impossibilities.

The major disadvantage in the use of polyelectrolytes is their cost. Prices for these specialized polymers often run between one to three dollars per pound, whereas conventional inorganic flocculants are available at literally pennies per pound. Another major disadvantage, which, hopefully, can be eliminated through further research, is that why and how they work is still very little understood. The Edisonian technique (trial and error) is still relied upon to discover whether a given flocculant can make economical improvements in a given liquid-solid separation problem. Furthermore, polyelectrolytes can be difficult and messy to put into solution and to handle.

III. FUNDAMENTALS OF PARTICLE AGGREGATION

A. Colloid and Colloid Stability

1. Description of colloids

A colloidal substance can be viewed as one in a peculiarly fine state of subdivision, as a consequence of which the properties of the surfaces or interfaces play a prominent role. A colloidal system consists of discrete particles that are separated by the dispersion medium. The particles may be aggregates of atoms, molecules or mixed materials that are considered larger than individual atoms or molecules but are small enough to possess properties different from coarse dispersions. Colloidal particles normally range in size from about 1-100 millimicrons (mμ), i.e., in the range of 10-1000 atoms. True solutions of macromolecules are therefore treated as colloids (23, 51 68). Particle shape, surface properties, particle-particle and particle-dispersion medium interactions are all important in giving the suspension its colloidal characteristics. Accordingly, colloids with particle sizes greater than one micron are not uncommon. A dispersion of bacteria in water is a typical example.

Colloidal dispersions may exist in form of solids, liquids, or gases. Eight classes of colloidal dispersions are recognized and are as follows: 1) a dispersion of solid in solid, of which carbon in steel is an example; 2) liquid in solid, e.g., water of crystallization; 3) gas in solid, e.g., hydrogen in various salts; 4) solid in liquid, e.g., colloidal dispersions of metals in water; 5) liquid in liquid, e.g., emulsion of oil in water; 6) gas in liquid, e.g., air in water; 7) solid in gas, e.g., particles in air; and 8) liquid in gas, e.g., clouds (51). Dispersions in classes 4 through 8 are commonly encountered in sanitary engineering practice and are commonly referred to as suspensoids, emulsoids, foams, smokes, and fogs respectively. Suspensoids, emulsoids, and foams are of course the colloidal systems of concern in liquid clarification.

Colloid-sized particles can be produced by grinding coarse materials. Hard-rock drilling and blasting operations generate considerable amounts of such particles. Another source of colloid-sized particles is the reaction of certain ions that react to form insoluble compounds. Under proper conditions, aggregates of molecules result that do not grow into crystals of a size large enough to settle or be filtered out. Other modes of colloidal system formation include dispersions in water of soap, starch, gelatin, protein, clay, etc. This is the class of colloids commonly encountered in domestic wastewater treatment.

2. General properties of colloids

As pointed out earlier, colloidal particles are so small in size that the properties of the surfaces play a prominent role. In other words, the surface area of a colloidal particle is very great in relation to its volume. Some concept of the area-to-volume relationship of colloids can be grasped by considering how the surface area of a cube of one centimeter increases as it is broken down to smaller and smaller cubes. If a cubic centimeter solid could be divided into small particles, each a cube with edge 10 mμ, the total surface area of the resulting 10^{18} cubes would be 600 square meter, or about 1/7 acres. If it could be divided down to cubes of 0.1 mμ a total of 10^{24} such cubes would be formed, giving a total area of about 15 acres (6, 51). With such an enormous surface in contact with the dispersion phase it is understandable that colloidal chemistry is often considered synonymous with surface chemistry.

Most colloidal particles are charged, and particles carrying similar charges will repel one another. The repulsive forces arising from these charges constitute one of the principal causes of the stability of colloids. The principle of electrophoresis--a phenomenon by which particles migrate toward the pole of opposite charge in an electric field--is used extensively to determine the nature of the charge on particles of a colloidal system. This principle is further discussed in a later section under "Measurement of Charge".

Under proper lighting conditions, a bright beam of light passed through a colloidal dispersion produces what is called a Tyndall Cone which results from the reflection of part of the transmitted light by the tiny particles. This phenomenon is due to the fact that colloidal particles, despite their small sizes, have dimensions greater than the average wavelength of white light, and so interfere with the passage of light. Light which strikes them may be reflected. As a result, a beam of light passing through a colloidal dispersion is visible to an observer who is at or near right angles to the beam of light. The phenomenon is commonly referred to as the Tyndall effect, in honor of the English physicist who studied it extensively. The Tyndall-effect-test is often used to prove the presence of a colloid, since true solutions and coarse suspensions do not produce this effect. The Tyndall effect is used as a basis of determining turbidity when the Baylis or St. Louis type of turbidimeter is used.

3. Nature of colloid stability

The stability of any system, including a colloidal system, is understood to mean its ability to maintain its state, and, in particular, full homogeneity throughout its volume. Two forms of colloidal stability are commonly identified, namely those particles whose stability is due mainly to the effects of electric charges carried by the particles, and those whose stability factors stem from hydration. These two classes of colloidal systems are referred to respectively as lyophobic and lyophilic. When the suspending medium is in water, they may be called hydrophobic and hydrophilic, respectively.

Hydrophobic colloids are electrically charged. The charges may be positive or negative, depending upon the nature of the sol. The stability of the system is generally a function of the magnitude of the charge carried, and the yardstick used in determining this stability factor is called zeta potential. This is discussed more fully in a subsequent section. Clay minerals, in general, belong to the class of hydrophobic colloids. Hydrophobic (water-hating) colloids do not interact with the water medium.

Hydrophilic (water-loving) colloids, on the other hand, owe their stability primarily to hydration, or as it is called when the liquid is not necessarily water, "solvation". This stability factor arises from attachment of water molecules to the particle by coordination bonds (68). This hydration effect is the property possessed by some particles to attract relatively large numbers of solvent molecules to their surfaces. The resulting stability arises from the fact that contact between particles is hindered by the solvent "sandwich". Examples of hydrophilic colloids include many products of plant and animal life--soap, soluble starch, proteins, protein-degradation products, synthetic detergents, and so on--which form solutions of macromolecules.

The terms hydrophobic and hydrophilic, introduced at the turn of this century, were used to differentiate aqueous suspensions of markedly differing properties. And although a complete range of intermediate types are known to exist, as Shaw (52) pointed out, these terms are still in common use. The differences between the two systems are briefly enumerated in Table 2.

Since surface charges are involved in colloidal stability (definitely in hydrophobic and, at least, to some extent in hydrophilic dispersions), it is useful to consider the origins of these charges. In a review of the coagulation process, O'melia (44) presented three distinct processes which can produce a charge on a particle. All of the processes depend upon the nature of the solid phase; two of the processes are also dependent upon the composition of the solution. The processes are briefly explained here:

1. A surface charge may arise because of imperfections within the crystal lattice of the particle. Such

Table 2. Basic difference between lyophilic and lyophilic sols (Alexander and Johnson (1))

Lyophobic (solvent-hating)	Lyophilic (solvent-loving)
Only low concentrations of dispersed phase are stable	High concentration of dispersed phase are frequently stable
Very easily precipitated by electrolytes	Unaffected by small amounts of electrolytes
Particles migrate in one direction in an electric field	Particles may migrate in either direction or not at all in an electric field
Unstable on prolonged dialysis due to removal of small amounts of electrolyte necessary for stabilization	Stable to prolonged dialysis
Irreversibly coagulated on desiccation	Residue after desiccation will take up dispersion medium spontaneously
Coagulation gives definite granules	Coagulation gives gel or jelly
Very marked light scattering and Tyndall beam	Usually gives a weak Tyndall beam
Surface tension not affected	Surface tension generally lower than that of the dispersion medium
Viscosity only slightly increased	Viscosity frequently much higher than that of medium
Typical examples are silt, metals, silver chloride etc. in water	Examples are gelatin, proteins, soap, starch etc. in water

imperfections may be due to isomorphic replacement, a process by which an element replaces another in a compound. This mechanism is responsible for a substantial part of the charges on clay minerals. Clays are layer structures. Typically, sheets of SiO4 tetrahedra are cross-linked with sheets of AlO6 octahedra. If an aluminum (Al) atom is substituted for a silicon (Si) atom in the SiO4 lattice, a negatively charged framework results. Similarly if a magnesium (Mg) atom substitutes for an aluminum atom in the aluminum oxide network, a negative charge will also result. That a negative charge would result in both cases of these isomorphic replacement is not difficult to comprehend since, in each of the two cases, an element of a lower valence is being substituted for one with a higher valence, both carrying positive charges. The sign and magnitude of the charge produced by such isomorphic replacements are independent of the characteristics of the aqueous phase. This is a classical example of hydrophobic colloids.

2. The primary charge on a colloidal particle may arise from ionization of chemical groups present at the surface of the particle. Many colloids which occur in nature contain surface groups such as carboxyl, amino, sulfato, hydroxyl groups, which can ionize. The charge on these particles is then dependent on the extent to which these surface groups ionize; particle charge therefore depends

upon the PH of the solution. For example, proteins contain free carboxyl (-COOH) and amino (-NH2) groups. At proper ranges of PH values the carboxyl group may ionize and become negatively charged ($-COO^-$), and the amino group may bind a proton and become positively charged ($-NH3^+$). Thus a protein may carry a positive charge if in acid solutions, the charge arising from the ($-NH3^+$) form; a negative charge if in basic solutions, due to the ($-COO^-$) form; and a net charge of zero somewhere in the neutral pH region, where the negative charge ($-COO^-$) and the positive charge ($-NH3^+$) cancel out. Proteins, unlike clay or silt, interact very nicely with water, forming a macromolecular solution, and so constitutes a classical example of hydrophilic colloids. Thus, whether a hydrophilic colloidal system is charged or not, and what kind of charge is involved--all depends on the pH of the system.

3. As a third possible origin of charge on a colloid, preferential adsorption of certain ions may take place. Such ions are often constituents of the crystal lattice of the solid. For example: Ag^+, and I^- are specifically adsorbed on the surface of AgI sols. The specific adsorption of ions arises from hydrogen bonding, covalent bonding, or van der Waals bonding, and can be augmented by electrostatic attraction.

From the discussion of these three possible origins of colloid charge, the following should be noted:

1. When isomorphic displacement is the mechanism involved, the nature of the solid phase alone is the controlling factor, not the composition or characteristics of the solution, and

2. When the charge arises from either ionization of surface groups or preferential adsorption of certain ions, the sign and magnitude of the charge depends in large part upon the characteristics of the aqueous phase.

B. Criteria for Particle Settleability

1. Elements of Stokes' equation

It is somewhat intuitive that if a substance is heavier (denser) than water, that substance will sink. It is not so obvious however why some substances will not sink in water even though they are denser than water. Many of the suspensions which are included under the term "colloidal solutions" consists of particles with densities many times that of water. Why do these particles not settle out on standing? A logical reaction to this question is that perhaps other factors are also involved; that density alone may not be sufficient to determine if a particle (or substance) will sink when placed in a liquid.

Stokes, in 1845, analyzed the relative motion between a body and a fluid in which the body is placed (56).

According to Stokes, a particle in suspension in a fluid is acted upon by 1) the gravitational force, acting vertically downward due to the weight of the particle, 2) the buoyant force due to the suspending medium, acting vertically upward, and 3) the drag force or resistance to the motion of the particle, due to the viscosity of the fluid. This resistant force is in the direction opposite to that of the motion of the particle. Thus, in the case of a particle falling in a fluid the drag force acts vertically up. When the downward force (gravitational) equals the sum of the upward forces (buoyancy + drag), the net force on the particle would be zero, acceleration is then nil and the particle would move uniformly at the velocity attained. This velocity is referred to in fluid mechanics as the terminal velocity. Figure 4 is a diagramatic summary of the essentials of Stokes'Law.

Equating the gravitational force ($4/3\ \pi r^3 \gamma_s$) to the sum of the buoyant force ($4/3\ \pi r^3 \gamma_w$) and the rather simplified drag force ($6\pi r \mu v$), the resulting equation is:

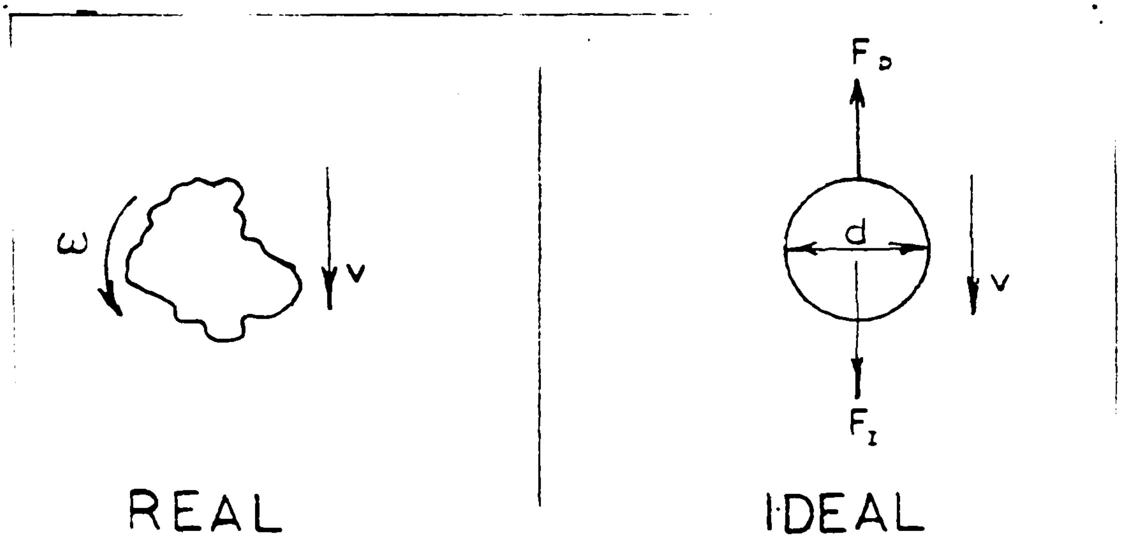
$$4/3\ \pi r^3 \gamma_s + 4/3\ \pi r^3 \gamma_w = 6\pi r \mu v \qquad (1)$$

where

γ_s = specific weight of the particle (spherical),

γ_w = specific weight of fluid.

r = radius of the particle,



$$F_I = (\rho_s - \rho_w) g \left(\frac{\pi d^3}{6} \right)$$

$$F_D = \frac{C_D \rho v^2}{2} \left(\frac{\pi d^2}{4} \right) .$$

$$v = \frac{g d^2 (\rho_s - \rho_w)}{18 \mu}$$

Stokes' Law

Figure 4. Elements of Stoke's equation

μ = viscosity of the fluid,

v = terminal velocity of the particle.

Solving Equation 1 for v and replacing γ by ρg, where ρ is mass density, and g is the gravitational constant, we obtain

$$v = [2r^2/(9\mu)][\rho_s - \rho_w]g \qquad (2)$$

Replacing the radius, r, by the diameter, d, of the particle we obtain the most used form of the equation:

$$v = (d^2/18\mu)(\rho_s - \rho_w)g \quad . \qquad (3)$$

From Equation 3, it can be seen that the basic factors that influence the rate of settling (sedimentation) in a fluid, say water, of a given mass density are the size of the particle, the mass density of the particle, and the viscosity of the liquid. Thus, the larger the particle the faster it will settle in water provided its specific gravity is greater than unity; the greater the specific gravity the faster the particle will settle; and, the lower the viscosity of the liquid the faster it will settle. Viscosity decreases with increasing temperature, therefore a warm liquid will hasten the rate of particle settling in it, than a colder one.

Since the settling velocity varies directly as the square of the diameter, it is apparent that as diameter decreases there is a rapid decrease in the settling rate. Burton (13) presented a table as shown (Table 3) which gives values of the settling velocity for silver particles falling in water, temperature 20°C, $\mu = 0.01$, $\rho_s/\rho_w = 10.5$.

Most colloidal particles of interest in liquid clarification works are not spherical, nor is a "quiescent" settling really quiescent, as will be discussed later in connection with Brownian motion and inter-particle attractive forces, nevertheless, Table 3 does point up the important role the size of a particle can play if it will settle in a liquid, given that its specific gravity is greater than that of the liquid.

2. Instability factors in a colloidal dispersion

Since large particles settle faster than smaller ones, as Stokes' equation indicates, it would be advantageous to bring particles together to form larger masses for the purpose of settling. Surface charges and hydration effects tend to stabilize particles in a colloidal dispersion and prevent them from coming together to form larger masses. Therefore, as a prerequisite to particle aggregation the stability forces must be neutralized or at least reduced. In other words, instability forces must be called into play to counteract the repulsive forces in the system. Two

Table 3. Limiting velocity of fall of silver spheres in water (13)

Radius	Velocity, cm/sec	Time to fall one cm
1 cm	200,000	0.000005 sec
0.1 cm	2,000	0.0005 sec
0.01 cm	20	0.05 sec
0.001 = 10μ	0.2	5.0 sec
0.0001 = 1μ	0.002	500 sec
0.00001 = 100mμ	0.00002	50,000 sec, ca 1/2 day
0.000001 = 10mμ	0.0000002	5,000,000 ca 58 days

broad classes of instability factors may be identified, namely; those artificially imposed in form of chemical conditioning and mixing, and those forces occurring naturally within the system as a result of the specific characteristics of the particles and of the suspending medium. The second class of factors is discussed first.

a. Natural factors The two most important non-artificial factors, otherwise referred to as factors of perikinetic coagulation, are the Brownian Movement and the van der Waals forces of attraction.

The Brownian Movement is the motion imparted to the suspended sol particles because of their impact with invisible, rapidly moving particles of the medium. It is therefore essentially a thermal effect that tends to drive particles closer to each other and may even cause them to penetrate the force fields surrounding each particle. This phenomenon was discovered by the botanist Robert Brown about 1828. Sheludko (53) reports that investigations by Brown, and others such as Smoluchowski (54) and Gouy (26), have established the nature of this unusual motion of particles. As Sheludko reports, these workers indicated that Brownian motion is not a vibration, not a simple progressive movement, but rather a trembling motion. The particles, they say, pursue irregular zig-zag paths in all directions in the space field, as if they were pushed here and there by accidental collisions with molecules of the medium. The maximum diameter of a particle that would show this motion is believed to be about one micron (34), and inspite of their feverish activity the progress of particles subjected to Brownian motion is very slow (34). In water and wastewater treatment the effect of the Brownian motion as a destabilizing force may not be substantial, nevertheless, the motion is recognized as one factor in the destabilization of colloidal dispersions.

It is well known that short-range van der Waals forces of attraction exist between molecules, and are responsible for the existence of the liquid state. Like coulombic forces which result from net charges on particles, the van der Waals forces are also based on electric interactions. However, while coulombic forces may be attractive or repulsive, the van der Waals forces are always attractive, and do not involve net charges. Further, while the coulombic forces decrease with the square of the distance between two particles, the van der Waals forces decrease more rapidly. Burton (13) states that the van der Waals forces is of the form

$$F = \alpha\ 1/d^n \qquad (4)$$

where n has values between 4 and 8 and never 2, and α is a proportionality constant.

The van der Waals forces arise as follows (8, 13, 41, 53):

1. Two molecules with permanent dipoles mutually orientate one another in such a way that, on the average, attraction results.
2. Dipolar molecules induce dipoles in other molecules so that attraction results.
3. Attractive forces are also operative between non-polar molecules, as is evident from the liquefaction of hydrogen, helium, etc. According to McBain (41), these universal attractive forces were first explained by London in 1930 and are due to the polarization of one molecule by fluctuations

in the charge distribution in a second molecule and vice versa.

In short, van der Waals forces (or London-van der Waals forces) involve a deformation of the distribution of positive and negative charges, the so-called polarization, which creates a force of attraction between two molecules that are sufficiently close to each other. The attractive energy between two particles may be computed by integration over all interacting molecular pairs.

b. Artificial forces If the natural instability factors--Brownian and van der Waals forces--were great enough to counteract the instability forces arising from colloidal charges and hydration effects, particles would be free to aggregate to form larger units which would settle in accordance with Stokes' equation. However, the Brownian and van der Waals forces are generally far too inadequate to counteract the stability forces, and must be augmented by artificially-imposed destabilizing forces to effect aggregation and sedimentation.

Artificial destabilization of colloidal dispersions is accomplished by a combination of chemical and physical means. These artificial forces are geared towards altering the hydration and electric forces on the particles in the suspension so as to effect agglomeration or coalescence of particles. This is accomplished by dosing the suspension with suitable chemicals; mixing rapidly to disperse the chemicals uniformly; then mixing slowly to promote agglomeration.

The chemicals commonly used in water, wastewater, and many industrial wastewater clarification processes include salts of aluminum (alum) and iron, as well as some synthetic organic polyelectrolytes. The application of suitable chemicals and the rapid mixing constitute the destabilizing force, while the slow mixing and settling provide opportunity for particle contact and aggregation.

3. Summary of stability and instability forces

In a colloidal dispersion the important stabilizing factors are the electrical repulsive forces arising from the charges carried by the particles in the dispersion; and the hydration forces (referred to as solvation when a liquid other than water is involved), arising from attachment of water molecules to the surface of particles, resulting in the so called water sandwich, prevents particles from coming together. Against these stabilizing forces are the Brownian forces, which are due to impact of the darting molecules of the suspending medium on the dispersed particles, and the van der Waals forces which attract two approaching particles towards each other regardless of whether they are similarly or oppositely charged. Since these natural destabilizing forces are small compared to the stability forces, additional instability forces are artificially imposed in form of chemical addition and physical mixing to promote clarification.

IV. THE COAGULATION PROCESS

A. General Background

Chemical coagulation is sometimes defined as the process of forming flocculant particles in a liquid by the addition of a chemical coagulant; also the removal of colloidal or finely divided suspended matter from the liquid by the floc, and the agglomeration of the flocculated matter. This definition contains most of the essential elements of coagulation. However, most authors seem to prefer to explain rather than define the process. O'melia (43, 44) describes coagulation as a two-step process. First, particles to be aggregated must be able to adhere to each other when brought into contact. This is a destabilization step. Second, these destabilized particles must be transported or brought into contact to effect the formation of larger particles. The steps are thus <u>particle destabilization</u> and <u>particle transport</u>.

The destabilization step is perhaps the more important step since the transport step would be ineffective without it. Once the repulsive forces on particles in a colloidal system have been overcome, the agglomeration can be achieved through Brownian diffusion and van der Waals forces (perikinetic flocculation); by agitation and fluid motion (orthokinetic flocculation), and by differential settling. Thus, the story of coagulation is, in effect, the story of particle destabilization.

B. Principles of Coagulation

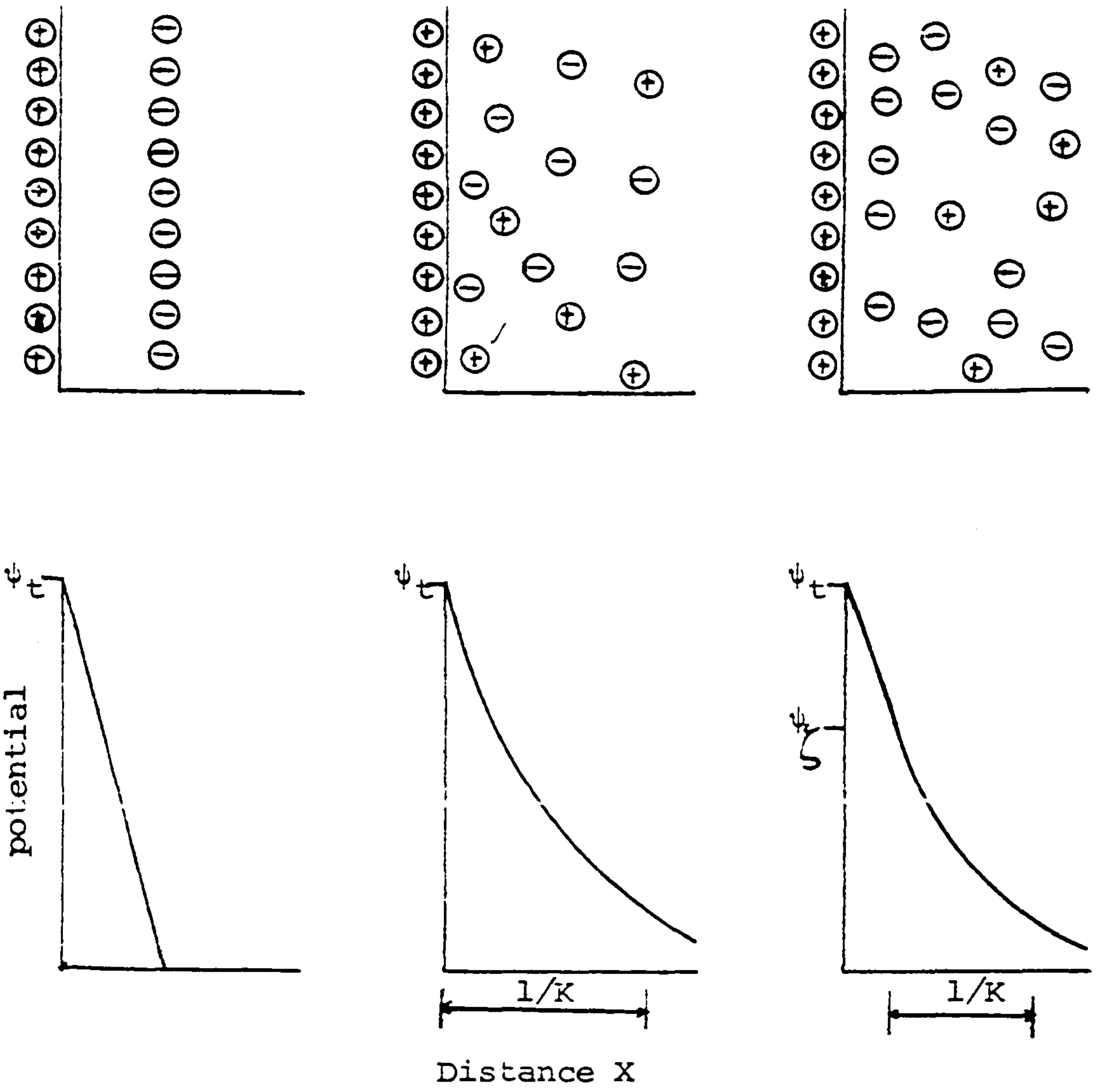
Theories of particle destabilization are based on colloid and surface chemistry. The selection of the type and dosage of coagulant in a coagulation process is based on consideration of particle destabilization. The stability factors in a colloidal system have been discussed in an earlier section. Stability against aggregation is a consequence of repulsive interaction between similarly charged particles and particle-solvent affinity (52). In hydrophobic, and to a lesser degree, in hydrophilic colloidal dispersions the problem of particles with charged environments is of paramount consideration, and has been studied off-an-on for nearly a century. The phenomenon of particles with charged environments is classically referred to as the electrical double layer concept, and is discussed in the following section.

1. The electrical double layer

The theory of the electrical double layer deals with the distribution of counter-ions and co-ions in the locality of a charged surface which is in contact with a polar medium, and hence with the magnitude of the electric potentials which occur in this region.

Bear (8), Delahay (21) and several other authors have reviewed works done by physicists and chemists to focus attention on the problem of charged colloids in a liquid medium. Helmholtz (30) in 1879 advanced an electrokinetic theory of the double layer at a charged plane surface. The particle surface with counter-ions was presumed to behave like a condenser, the charge of the particle forming the inner layer and the counter-ions the outer layer, close to the former as shown in Figure 5a. This original Helmholtz picture of charged particles shows a closely held double layer of charges of opposite sign. Unfortunately, the movement of charged particles in an electric field (electrophoresis) could not be explained by such a picture. Helmholtz's theory therefore was an oversimplified picture and was later improved upon by Gouy (26) and Chapman (16).

Gouy (26) and Chapman (16) later but independently, developed the theory of the diffuse double layer at a plane surface. According to this theory, a stationary layer of ions on the surface of the particle is surrounded by a movable diffuse layer extending out into the solution, with an excess of the counter-ions (counter to the surface charge) in the diffuse layer. The Gouy-Chapman picture (shown in Figure 5b) was found not entirely satisfactory especially when the surface charge is high (41, 68). Stern (55) suggested the existence of a compact layer of counter-ions



(a) (b) (c)

Figure 5. A schematic representation of ion and potential distribution in the double layer according to the theories (a) Helmholtz (30), (b) Gouy (26) Chapman (16), and (c) Stern (55). ψ_t denotes the total potential, ψ_ζ, the zeta potential

firmly attached to the surface by surface forces such as dipole attraction. This layer is usually referred to as the Stern layer. Outside the Stern layer exists the Gouy-Chapman diffuse layer. Thus, in effect, Stern's electrical double layer (Figure 5c) combined the Helmholtz fixed layer and Gouy-Chapman diffuse layer. The ions held in the Stern layer are considered to move with the particle, becoming, in essence, part of the particle. According to the Stern model, a rapid drop in potential occurs between the particle and the stationary layer (i.e., within the Stern layer), and a much more gradual potential drop occurs between the stationary layer and a point in the solution at which electroneutrality exists.

The decay of the repulsion potential from the surface has been expressed as follows (41, 52, 65):

$$\psi = (2kT/Ze)\left[\ln\left(\frac{1 + \gamma\ \exp(-KX)}{1 - \gamma\ \exp(-KX)}\right)\right] \qquad (5)$$

where

$$\gamma = \frac{\exp(Ze\psi_o/2RT) - 1}{\exp(Ze\psi_o/2RT) + 1} \qquad (6)$$

$$K = \left(\frac{8\pi e^2 n_o Z^2}{DkT}\right)^{1/2} \qquad (7)$$

ψ = repulsive potential

k = Boltzmann constant

T = absolute temperature

Z = the valence of a single symmetrical electrolyte

ψ_o = surface potential

e = the charge of an electron

x = distance from the surface

n_o = the bulk concentration of each ion's species

D = dielectric constant of the dispersion medium.

The above expressions are a direct outgrowth of the Boltzmann distribution, to which simplifying assumptions have been applied. The interested reader is referred to treatise by Olphen (42), Shaw (52), and other colloid chemistry books for detailed development. On the assumption that $Ze\psi_o/2RT << 1$ (kT/e = 25.6 millivolts at 25°C), Shaw applied the Debye-Hückel approximation, namely (52):

$$\exp[\frac{Ze\psi_o}{2RT}] \simeq 1 + \frac{Ze\psi_o}{2RT} \qquad (8)$$

and thus simplified Equations 5 and 6 to

$$\psi = \psi_o \exp(-Kx) \quad . \qquad (9)$$

Here K represents the rate of decay of the repulsion potential with distance. The reciprocal of K, i.e., 1/K is defined as the double layer thickness, which denotes the average distance of counter ions from the surface. From Equations 7 and 9 it can be seen that K increases (1/K decreases) with the square root of the electrolyte concentration n_o, and so, adding (more) electrolyte may result in the compression of the diffuse double layer, thus causing the reduction of the effective range of the repulsion potential. The overall potential is called the *chemical* or *Nernst* potential, whereas the lesser potential between the stationary and the solution is called the *zeta* potential.

2. The zeta potential

The Stern layer is a layer of immobile dispersion medium about one molecule thick, around each colloidal particle. As the particle moves, it carries this layer with it. The actual slipping plane, or the shear plane, is therefore at the outside boundary of this layer. The potential at the shear plane is referred to as the zeta potential. It is the zeta potential that makes it possible for the particle to move within a charged electric field.

In colloidal systems where stability is due principally to charges (i.e., hydrophobic colloids), the stability is found to be a function of the magnitude of the zeta potential, ζ, which is defined by the equation:

$$\zeta = 4\pi\delta q/D \qquad (10)$$

where,

q = the charge on the particle

δ = the thickness of the layer around the particle through which the charge difference is effective

D = the dielectric constant of the medium.

The zeta potential is thus a measure both of the charge and of the distance into the solution to which the effect of the charge extends.

3. Measurement of charge

As is evident from Equation 10, the motion of a charged particle in an electric field is independent of its size or shape and dependent mainly on the zeta potential. The measurement of particle mobilities therefore affords a rapid and accurate method of determining the magnitude of zeta potentials. The smaller the zeta potential the better the chance of two similarly charged particles to approach each other. Equation 10 is not a good working equation because the charge q, and the thickness are difficult to determine. Consequently, the concept of electrophoretic mobility is used instead of zeta potential (12, 68). Electrophoretic mobility derives from the principle of electrophoresis. When charged particles are placed in an electric field, the particles migrate toward the pole of opposite charge. The rate of migration is proportional to the potential gradient (zeta potential) in the system. This phenomenon is called electrophoresis (23, 37).

Baumann and Oulman (7) have reviewed the work of Black and his coworkers (11) at the University of Florida, where extensive use of electrophoretic measurements have been made. Basically, a flat glass chamber that can be viewed under a microscope is filled with a suspension and a direct current is applied to the electrodes at each end of the chamber. The particles in the chamber move toward the electrode of opposite charge, and when viewed at the appropriate depth (about 0.2 or 0.8 of the chamber depth), their velocity is not affected by the electro-osmotic flow of water in the chamber (7).

The electrophoretic mobility, M, in microns per second, per volt/cm, is given by the relation (12):

$$M = Xd/(tIRs) \tag{11}$$

where,

d = distance traveled, in microns during a time period, t (in seconds)

I = current in amperes

Rs = specific resistance of the liquid as determined by a conductivity-meter, ohm-cm

X = chamber cross-section, cm^2.

Equation 11 merely gives the magnitude of the electrophoretic mobility. The sign must be determined by observing the movement of the particles and ascertaining what electrode they are moving toward.

Electrophoretic techniques for measuring particle charge are particularly useful when the particles are small enough not to settle out in the electrophoretic chamber (7).

4. Charge neutralization

In colloidal systems where electric charges are the principal cause of stability, neutralization of these charges is necessary in order to destabilize the particles and eventually bring about aggregation and sedimentation. O'melia (43, 44) and other workers (12, 19, 38, 50, 68) have discussed the principles involved in charge neutralization. When two charged particles in a colloidal dispersion approach each other, their diffuse layers interact and repel each other. If no attractive forces are present to overcome this repulsion the particles will not adhere and aggregation does not occur. However, attractive forces, namely, van der Waals forces, plus the Brownian motion, do exist between all materials in such a dispersion, regardless of the type of charge carried by each, as previously discussed. If these attractive forces are stronger than the coulombic repulsion between the similar diffuse layers, attachment could occur if they are brought into contact. Figure 6 is a representation of the repulsive forces, the van der Waals attractive

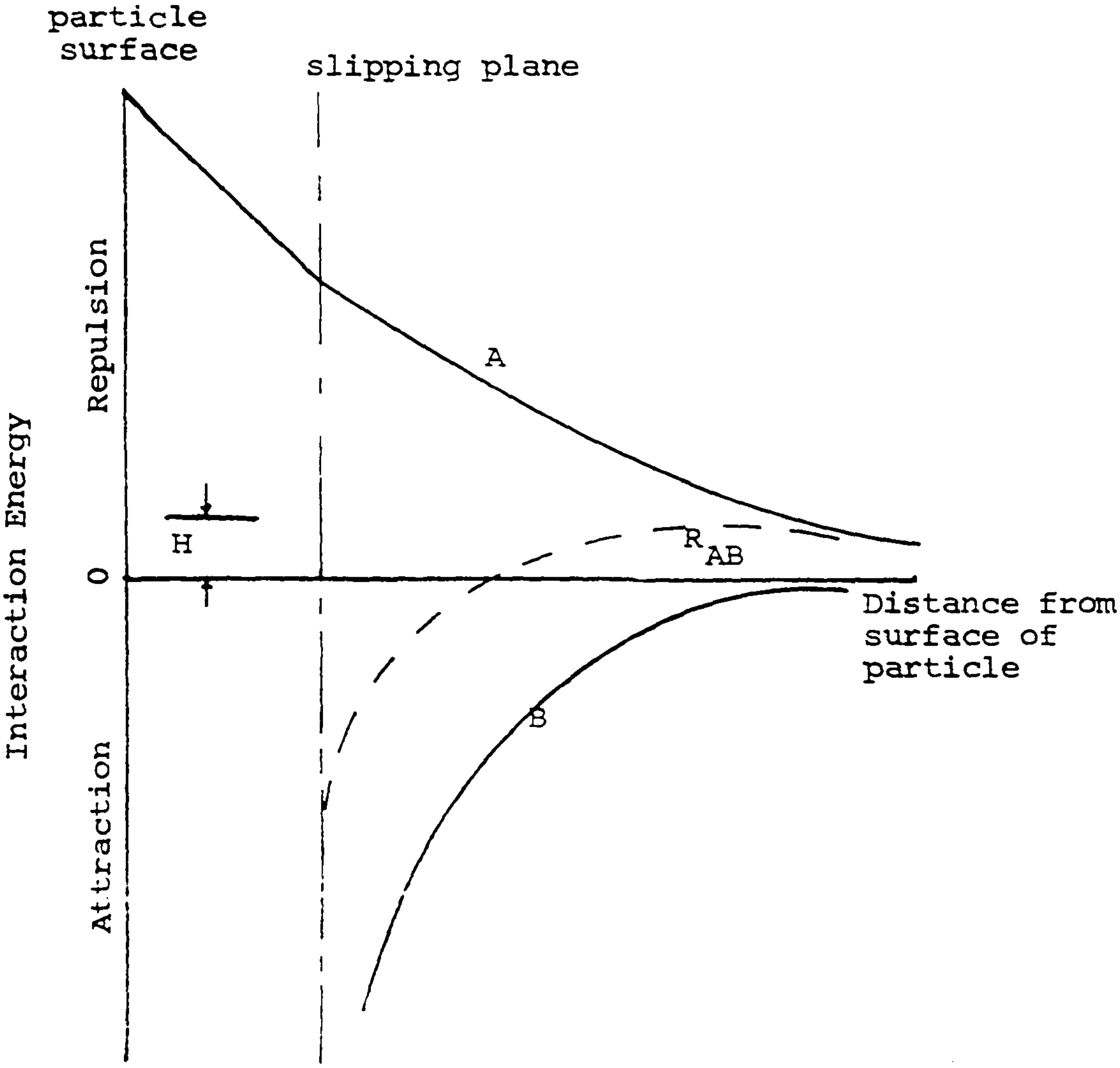


Figure 6. The interaction energy picture. The resultant interaction energy R_{AB} is obtained by algebraic addition of the repulsive energy curve A, and the van der Waals attractive energy curve B. H is the energy barrier that must be overcome to achieve particle destabilization in a hydrophobic colloidal system

forces and the resultant of the two opposing forces. This picture is of course for hydrophobic colloids in which the effect of solvation (hydration) could be neglected. The resultant interaction between colloidal particles of such a system is the sum of the van der Waals forces and the electrostatic forces of the double layer. At distances corresponding approximately to the thickness of the diffuse double layer, repulsive electrostatic forces resulting from the mutual penetration of the diffuse ionic atmospheres may predominate. This may happen when the total, or psi, potential of the interacting particles is high and of the same sign, and when the diffuse double layer is sufficiently thick (38). Under such conditions the <u>energy</u> <u>barrier</u> is formed which can prevent the approach of the particles within a distance at which the attractive forces predominate. Overcoming the energy barrier is what destabilization is about in hydrophobic colloidal systems.

If an indifferent electrolyte (for example, a salt whose ions do not specifically adsorb or otherwise interact with the colloidal particles) is added to the colloidal dispersion, the counter-ions are attracted toward the particle surface and can enter into the diffuse layer. As the concentration of these oppositely charged ions increases in the diffuse layer, the distance over which the primary charge on the particle can exert coulombic effect is reduced. The diffuse layer is thus compressed, and the repulsive interaction between the particles is consequently reduced. If sufficient compression of the diffuse layer occurs the energy barrier may be overcome, and interparticle attachment may be achieved when an opportunity of contact is provided.

One method of destroying hydrophobic colloids is by addition of electrolytes. Salts of monovalent cations, such as sodium chloride (NaCl) can supply the positively charged ions to compress, to some degree, the diffuse layer around a negatively charged particle. Salts having divalent cations do a better job than monovalent, and trivalent cations better still. As reported by several authors (44, 51, 41, 52, 53), based primarily on the observation of Schultz 1882, Hardy formulated the Schultz-Hardy rule in about 1900. The Schultz-Hardy rule states that coagulation is brought about by the ion of opposite charge to that of the colloid, and that the efficacy of the ion increases markedly with its charge, or valence. It was further stated that a bivalent ion is 50-100 times more effective than a monovalent ion, and a trivalent ion, 700-1000 times more effective than a monovalent ion. For example, the concentration of Na^+, Ca^{++}, and Al^{+++} required to coagulate a negatively charged colloid have been observed (44) to vary approximately in the ratio of 1:1/100:1/1000. Experimental and theoretical works by Verwey and Overbeek (64), Derîagin and Landau (22) resulted in a Derîagin-Landau-Verwey-Overbeek (DLVO) theory as reviewed by McBain (41); namely, that destabilization is brought about by the counter-ions and that the efficacy of these ions increases with the sixth power of their charge or valence. Stated another way, the concentration of Na^+, Ca^{++}, and Al^{+++} required to coagulate a negatively charged colloid are in the ratio of $1:1/2^6:1/3^6$, or 1:1/64:1/729. The DLVO model is thus in agreement with the Schultz-Hardy rule.

The two coagulants most widely used in water treatment (and sometimes in wastewater treatment) are aluminum and ferric salts, mostly aluminum sulfate, aluminum chloride, ferric sulfate and ferric chloride. All supply trivalent cations. Inasmuch as it has been shown that, in general, both turbidity and organic color in water are present as negatively charged colloids, the significance and importance of trivalent positive charge becomes immediately apparent.

5. Bridging model

The principle of charge neutralization as discussed in the foregoing section is valid for hydrophobic colloidal systems, systems where stability is due principally to charges carried by the particles. Most surface waters belong in this class. Hydrophilic colloids on the other hand may owe their stability both to the double layer effect and to hydration of the particles of the system. Such a system may remain stable even after charge neutralization has been achieved. Many products of plant and animal life (e.g., soap, soluble starch, proteins) belong to this class of colloids. It stands to reason therefore that domestic wastewaters, and wastewaters from food-processing industries) should contain hydrophilic colloids alone or in addition to hydrophobic colloids. One way to destabilize such a system is to add a fairly large amount of ions to compete for the water of hydration. The effectiveness of a particular type of ions to compete for the water of hydration depends upon its tendency for hydration. For example, Ca^{++} is more effective than K^{+}. This so-called <u>salting-out</u> process needs a high concentration of electrolyte, and may not be practical for water (or wastewater) treatment. Purchas (47) states that the water sheath in hydrophilic colloids can also be removed by the addition of a reagent such as alcohol, with which water combines. Unfortunately, the need to use a concentration of 50 percent or more of alcohol makes this approach uneconomical. Purchas describes another method which involves destruction of hydrogen bonds of the water sheath by adding a reagent which would affect the solid-water interface. Tannin is cited as an example of such a reagent, and is believed to act by adsorbing onto the particles, with the aromatic part of each tannin molecule directed outwards. Again, this tends to be an expensive technique. One method that appears to be practical is the use of natural or synthetic polyelectrolytes. A description of polyelectrolytes has been given in a previous section.

Polymers can act like simple electrolytes in the double layer model if the polymer and the suspended particles are oppositely charged. The most important mode of action is, however, believed to be particle-polymer-particle bridging. Several theoretical and experimental studies have been made, to varying degrees of success, of the bridging model.

Ruehrwein and Ward (50) were the first to propose a polymer bridging mechanism for the stabilization of clay particles. Later, Healy and La Mer (28, 29) and La Mer and Healy (36) developed a mathematical model for the polymer bridging. According to this theory, the polymer molecules attach themselves to the surface of the suspended particles at one or more adsorption sites and part of the chain extends out into the bulk of the solution. When these extended chain segments make contact with vacant adsorption sites on other suspended particles, bridges are formed. The particles are bound into small packets which can grow to a size limited only by the shear gradient imposed by the conditions of agitation in the system and by the amount of polymer initially adsorbed upon the surfaces of the suspended particles. Le Mer and Healy (36) proposed that adsorption of polymer be described by a Langmuir isotherm of the form:

$$\theta/(1 - \theta) = bP \tag{12}$$

where P is the concentration of residual polymer after adsorption, b is the ratio of rate constants for adsorption-desorption of polymer with the solid, and θ is the fraction of the adsorbent surface covered by adsorbed segments.

Equation 12 is actually an outgrowth of the Simha-Frisch-Eirisch (SEF) isotherm for polymer adsorption, neglecting polymer-polymer interactions on the adsorbent surface. The SEF equation is of the form:

$$\theta/\ \beta(1 - \theta)^{\beta} = KP \tag{13}$$

where β is the number of segments per polymer molecule attached to the adsorbent surface, K is a constant, and θ and P are as previously defined. If β is set equal to one, then the SEF equation reduces to the Langmuir form. La Mer and Healy (36) further postulate that if n_o is the number of primary particles in a colloidal dispersion, then the rate of floc formation is given by the relationship:

$$-dn_o/dt = k_1 n_o \theta(1 - \theta) \tag{14}$$

where flocculation occurs between units with a covered surface portion represented by $(n_o\theta)$ and uncovered surface $(n_o(1 - \theta))$, k_1 is the rate constant for floc formation, and, as before, θ is the fraction of a particle surface covered by the adsorbed polymer segments. These equations suggest that the maximum efficiency, in terms of adsorption, would occur when one-half of the particle surface is covered. Deviations from the apparent Langmuirian behavior are noted in the low concentration range. Nevertheless, the process of polymer adsorption is not so different from the Langmuirian process as has been suggested if it is kept in mind that it is the individual segment rather than the whole molecule that competes with solvent molecules for the surface sites.

In a flocculation study using electron microscope, Ries and Meyers (49) presented an electron micrograph of polystyrene latex and a cationic polymeric flocculant, see Figure 7. The authors describe as "striking", the well defined fibers connecting the latex spheres. They further observed, "not only do all of these latex particles appear to be attached to fibers (none is in the open area), but they apparently prefer the thicker portions of the fibers and in many cases the points of branching". This is a rare indication of the concept of particle-polymer-particle bridging.

Coackley and Wilson (17), following the works of La Mer and others, summarized the important conditions under which the bridging theory would work as follows:

1. that extended polymer segments must be available for interparticle bridging;
2. that the segments must be of sufficient length or number, and;
3. that free surface sites must be available.

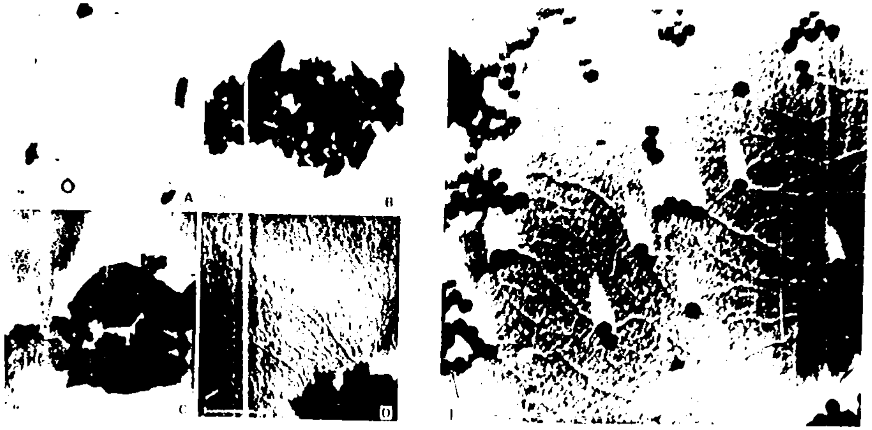


Figure 7. Electron micrographs of colloidal silica and a cationic polymeric flocculant. A-silica blank; B-silica plus flocculant; C-silica plus flocculant (shadowcast); D-silica plus flocculant at higher magnification (shadowcast). Electron micrograph of polystyrene latex and a cationic polymeric flocculant. Markers in all figures indicate 1 micron (49)

There are of course other important factors involved in the process. For example, the entanglement of extended segments of different polymer molecules from the same particle would reduce efficiency. This can happen when too much polymer is added to the system. O'melia (43, 44) made pictures representing reactions that can take place between colloidal particles and polymers, see Figure 8. In this picture, reaction 1 represents the simplest form of the chemical bridging model, which proposes that a polymer molecule can attach itself to the surface of the particle at one or more adsorption sites, with the remainder of the molecule extending into the solution. The extended segments can then interact with vacant adsorption sites on another particle, forming a chemical bridge between them, as in reaction 2A in Figure 8. Failing to find a suitable adsorption site on another particle, the extended segments can eventually adsorb at other sites on the same particle, as in reaction 2B, and the particle may be restabilized. A situation as in reaction 3 could occur when the polymer dosage is excessive, and saturates the available surfaces of the dispersed phase. This condition would produce restabilized particles since no sites are available for the formation of polymer bridges. Finally, reactions 4A and 4B show situations in which a destabilized suspension could be restabilized by excessive violent mixing resulting in the breaking of polymer-particle

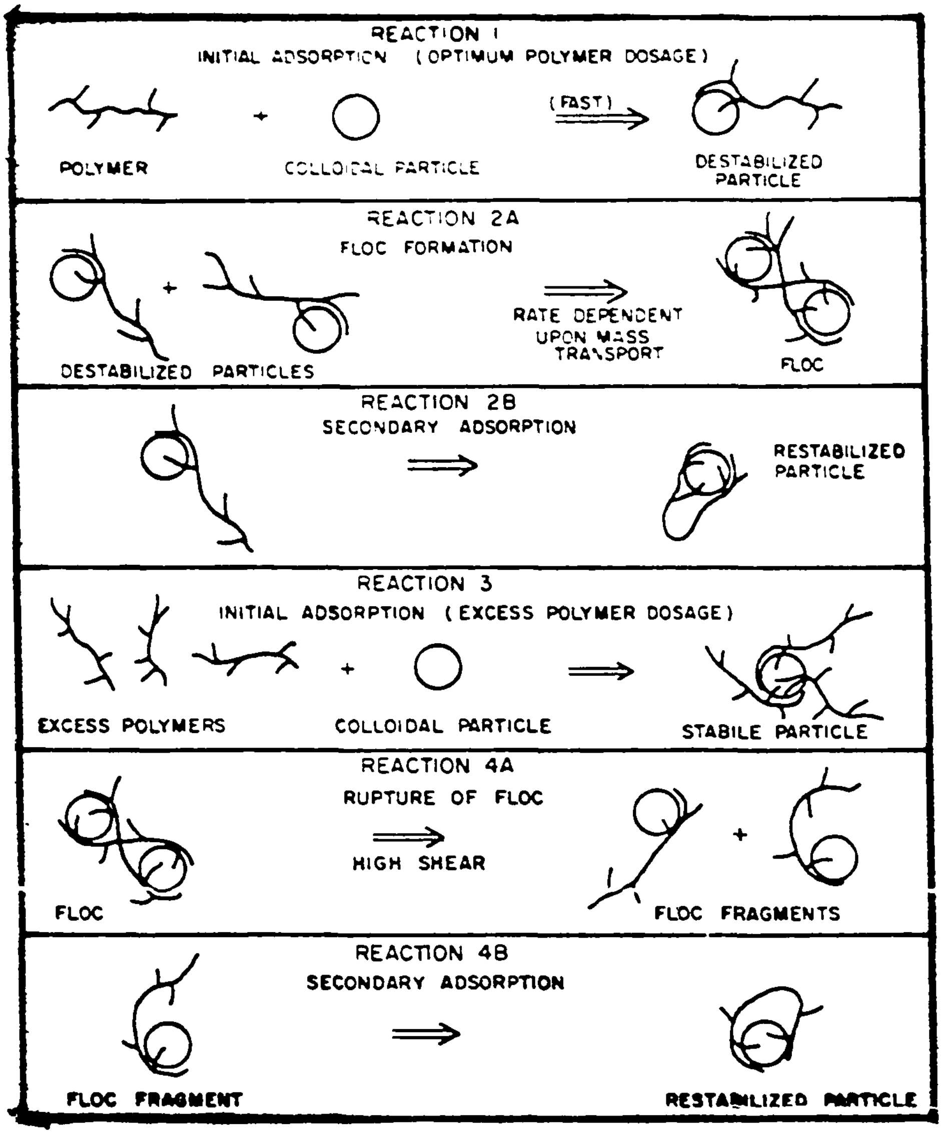


Figure 8. Reactions which can occur with colloidal particles and polymers, as suggested by O'melia (43)

bonds and the folding back of the extended segments onto the surface of the primary particle. The picture, as shown in Figure 8 and explained above, is highly simplified, but it does point up the important ramification of the bridging model, namely, that a direct relationship exists between the available surface area of particles in the dispersion and amount of polymer required to produce optimum destabilization.

C. Summary of the Coagulation Process

Coagulation is a two-step process, namely, the particle destabilization step, and the particle transport step. The colloidal particles are treated chemically to remove or reduce stability factors so that they will adhere if brought into contact, then contact and aggregation are promoted by a combination of factors, namely, the Brownian motion, and the van der Waals forces, and mechanical fluid-motion.

Some colloidal particles are stable as a result of repulsive surface charges, others by a combination of charges and hydration. If charges are the controlling stability factors, then charge-neutralization may result in destabilization. However, if stability is due principally to hydration (as is often the case in hydrophilic systems), charge neutralization may not be useful as a destabilizing force.

The charge carried by particles of a colloidal dispersion can be determined by measuring the zeta potential. In most studies, the electrophoretic mobility is found more practical and used instead of the zeta potential.

To destabilize a dispersion in which repulsive charge is the stabilizing factor, ions of opposite charge are introduced which compress the diffuse double layer and consequently remove or reduce the energy-barrier against interparticle contact. According to the Schultz-Hardy rule, and as confirmed by Verwey and Overbeek (64) and other workers, the higher the valence of the oppositely charged ions, the better the performance in charge neutralization.

For the class of hydrophilic colloids, in which hydration is an important stabilizing factor, polyelectrolytes may be useful as destabilizers. The working-mechanism of polyelectrolytes is explained in terms of particle-polymer-particle bridging. The works of Healy and La Mer (28, 29) are very illuminating in explaining the bridging model. In the simplest form, the bridging theory proposes that a polymer molecule may adsorb to the surface of a colloid at one or more adsorption sites, with the remainder of the molecule extending into the solution, ready to adsorb onto other particles. A bridging together of particles may occur, resulting in larger-sized particles which would settle more readily.

D. Coagulation versus Flocculation

A great deal of controversy has been generated during the last decade over what has been called the indiscriminate use of the words coagulation and flocculation in water and wastewater clarification processes. The two words have been used as though they are synonymous, without a recognition of their major differences in fundamental mechanisms. Purchas (47) contends that an inevitable consequence of this "casual approach" is that the full potential of these powerful techniques frequently remains unexploited.

In raising an objection to the indiscriminate use of the words coagulation and flocculation, La Mer and Healy paraphrased Percy Bridgman and Irving Langmuirs' writings of the 1930's and stated:

> To communicate properly, we must use words that have clear-cut meanings, representing distinguishable basic concepts, which, in turn, must be based upon recognized operations and results, and that a concept for which a distinguishing operation does not exist, either physically or in thought, is meaningless (36, p. 292).

La Mer and Healy (36) then pleaded that the fundamental Latin meanings of these two words be adhered to, in order to correctly identify the mechanisms involved. The word "coagulation" derives from the Latin "coagulare", meaning to drive together. This, according to La Mer and Healy (36) is an appropriate term for the effect of salts on a colloidal dispersion, where the mechanism generally accepted results from a reduction of the repulsive potential of the electric double layer surrounding the individual particles. The word "flocculation", on the other hand, comes from the Latin "flocculare", meaning to form a floc, i.e., a tuft of wool or a highly fibrous structure. This term, La Mer and Healy suggested, should be used for the adsorption of large polymers permitting the formation of particle-polymer-particle bridges.

While many other workers (17, 21, 47) agree that these two words should not be used as though they are synonymous there is little agreement on what the distinction should be. Gregory[1] has pointed out that where cationic polyelectroltyes are concerned, the relative roles of charge neutralization and bridging are not clear-cut, and therefore that differentiation such as suggested by La Mer and Healy (36) cannot be made in practice. Black _et_ _al_. (11) considered the coagulation and flocculation of suspensions with alum to proceed in three stages.

1. a rapid neutralization of the zeta potential of the particle;
2. the formation of positively charged microflocs which can still remove negatively charged particles; and

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[1] Gregory, J., Ames, Iowa. Polyelectrolytes. Private communication. 1970.

3. a step involving the formation of a large well-formed floc similar to that considered by La Mer and Healy (36) to be true flocculation.

This, in effect, is saying that flocculation can be regarded as taking over where coagulation stops--building up larger final particles from aggregates of smaller ones. O'melia (43) on the other hand prefers that the term coagulation be applied to the overall process of particle aggregation, including both the particle destabilization and particle transport while the term flocculation is used to describe only the transport step.

The controversy remains largely unresolved and probably will remain so until a clearer explanation of the specific mechanisms and the relative roles of charge neutralization and particle bridging can be given. Meanwhile, this author will apply the term coagulation to the overall process of particle destabilization, aggregation and sedimentation, while the term flocculation will be reserved for the transport step, including slow mixing and differential settling--a position somewhat similar to O'melia's (43).

V. A REVIEW OF PERTINENT LITERATURE

A. General

Whereas the previous section contains a review of the coagulation process with respect to the principles currently found in chemical coagulation literature, this section is concerned with reviewing specific works that are more directly related to this study.

Most coagulation studies have been concerned with its chemistry. The works of Black (10), Stuum and Morgan (57), Matijevic et al. (40) are among the important studies which deal with multivalent metal salts. Except for the important work of Langelier (37) about half a century ago, little attention had been paid to the physical aspects of coagulation until quite recently.

Chemical coagulation studies have been made, involving the use of Fe^{+++}, Al^{+++}, and also of synthetic organic polymers. In his review of the coagulation process O'melia (43) has pinpointed a fundamental difference that exists between the floc formed from hydrolyzed species of metal ions and synthetic organic polymers, namely; that floc formation in the case of metal salts is brought about when quantities of these salts sufficient to exceed the solubility limit of the metal hydroxides are added to the dispersion; however, in the case of synthetic organic polymers, the species are added directly to the dispersion, pre-formed. It is also generally believed (43, 60) that flocs are stronger in the case of synthetic polymers, and can withstand higher shear arising from mixing, or agitation, or from pumping, than flocs of inorganic salts. Several of these workers agree, further, that if polymer-floc particles are ruptured, the chances of reattachment are much less than for inorganic flocs, in that the extended segments of ruptured polymer bridges tend to fold back and occupy additional sites on the same particle.

Because of the differences between the modes of formation of synthetic polymer flocs and flocs of inorganic salts, rapid mixing tends to be expected to perform two main functions with inorganic salts, and only one function when polyelectrolytes are used. In the former case, rapid mixing is believed to be necessary: (a) to form proper flocs as soon as the inorganic salts enter the dispersion-system, as the speed of the hydroxide formation is fast, and (b) to disperse the flocs uniformly and thus facilitate adsorption reaction between the particles and the flocs. In the case of polyelectrolytes, since the floc-formation takes place prior to entering the dispersion, the only function of rapid mixing is generally considered to be to facilitate adsorption.

For many years the criteria for designing mixing and flocculating facilities for water clarification were based on limiting velocities and theoretical detention times (33). The use of velocity gradient has been included as an important parameter in current practice.

B. Velocity Gradient

Velocity gradient is an expression of the relationship between the rate of power dissipation with respect to time, in a given fluid system, and the viscosity of the fluid. The rate of power dissipation, sometimes referred to as the dissipation function is the work of shear per unit volume of fluid, per unit of time at a point in the fluid-system.

Camp and Stein (14) have provided the basic equation for calculating velocity gradients in the mixing chambers. Hudson and Wolfner (33) condensed these basic equations and presented the following expressions for:

1. Mechanical agitation:

$$G = 425\ (hpw/t)^{1/2}$$

2. Ports and conduits:

$$G = (f/D)^{1/2}\ V^{3/2}$$

3. Baffled chambers:

$$G = 178(H/t)^{1/2}$$

where

hpw = water horse power per million gallon daily flow rate

G = the velocity gradient in fps/sec

t = theoretical detention time, minutes.

D = diameter, in ft

V = velocity in fps

H = headloss in ft of water, and

f = Darcy-Weisbach friction factor, based on roughness factor of 0.00085 ft (33).

In their original work, Camp and Stein (14) had given consideration to the concept of average velocity gradients. The velocity gradients in a fluid system may vary considerably in magnitude from point to point. However, under steady conditions of work input there is a mean velocity gradient which corresponds with the mean value of work input into the system. Camp and Stein (14) designate as ϕ_m, the mean value of work input per unit time, per unit volume. The usable velocity gradient, G_m, referred to as the root-mean square velocity gradient, is defined by the following relationship:

$$G_m = (\phi_m/\mu)^{0.5}$$

where

μ = the viscosity of the suspension.

Dimensionally,

$$\phi_m = FL/TL^3 = FL^{-2}T^{-1}$$

$$\mu = FT/L^2 = FTL^{-2}$$

$$G = (T^{-2})^{1/2} = T^{-1} \quad .$$

Velocity gradient may thus be expressed in units of fps/ft, or simply as sec^{-1}.

The product Gt of G and t is a dimensionless quantity. This product is frequently used as a design parameter in the design of a mixing tank. Walker (66) and other workers (14, 33) state that the most important factors in flocculation are velocity gradient and time, and that too low a velocity gradient would yield floc particles with more trapped water than desirable for best density and subsidence value.

C. Rapid Mix

The function of a rapid mix chamber has been to insure completely homogeneous coagulation. As Hudson (32) and Hudson and Wolfner (33) report, practice in design is, frequently, to use not more than 30 seconds for rapid mixing, with a relatively high-powered mixing-device. The belief, that the sole function of rapid-mixing units is to quickly disperse the chemical, has been so entrenched in the coagulation literature that it has come to be accepted almost as a gospel truth, and so most studies relating to the physical act of mixing have been restricted to the problem of slow mixing, floc break-up and so on. Yet, even as far back as 1921, Langelier (37) had alluded (if indirectly) to the potential usefulness of prolonged mixing. He wrote:

> Most engineers favor the idea that only the slightest agitation possible is desirable after an initial, reasonably thorough mixing of alum with water. This theory is not in accord with any of the experimental data that we have obtained. Our results, checked many times under varying conditions, indicate that prolonged agitation is not only not objectionable, but is highly desirable in increasing the efficiency of the process (37, p. 924).

Data on the effect of prolonged and high-energy mixing are rare in the literature, but the indictment against rapid mixing has not subsided, and has been extended to include situations involving the use of polyelectrolytes as well as inorganic salts. For example, O'melia (43), in a review of the coagulation process states that intense rapid mixing is essential to disperse quickly and evenly the chemicals added in coagulation work involving the use of salts and iron and aluminum. He further states that when synthetic organic polymers are used, an intense rapid mixing may be less important than for the inorganic coagulants.

In their study in which alum was used to coagulate some synthetic silica dispersions having an average particle diameter of 1.1 micron, Tekippe and Ham (60) observed that some form of high rate mixing is desirable, and that such a rapid mix period should be followed by a period of moderate mixing. In the same study, Tekippe and Ham (60) stated that velocity gradient of 140 sec^{-1} or higher, caused floc break-up to occur, and that a 5-minute slow mix period at G = 30 sec^{-1} following the period of high shear did not rebuild the broken particles and so the turbidity removal results were poorer than in the case where lower shear was used. It should be pointed out here that the data from which the conclusions were drawn, the high velocity gradient (G = 140 sec^{-1}) was not instituted at the beginning of the rapid mix period. In fact, the run started with a G of 20 sec^{-1} for 10 minutes, followed by a 5-minute mixing at G = 140 sec^{-1}, then a 5-minute mixing at G = 30, and finally a one-minute period at G = 50 sec^{-1}. It is conceivable, therefore, that if the high shear had been instituted at the beginning of the run, followed by mixing at lower G-values, the turbidity removal migh have been better. Further, as if to reinforce this writer's suspicion on the interpretation of the data, Tekippe and Ham (60) presented in another section of their study, a plot of turbidity versus time of rapid mixing for varying velocity gradients (see Figure 9). The turbidity values, according to Tekippe and Ham (60) were determined from suspensions that were rapid-mixed for the indicated time, and then allowed to settle for 5 minutes. The plots indicate that the higher the G-value the better the turbidity removal, at least, during the first 6 minutes of

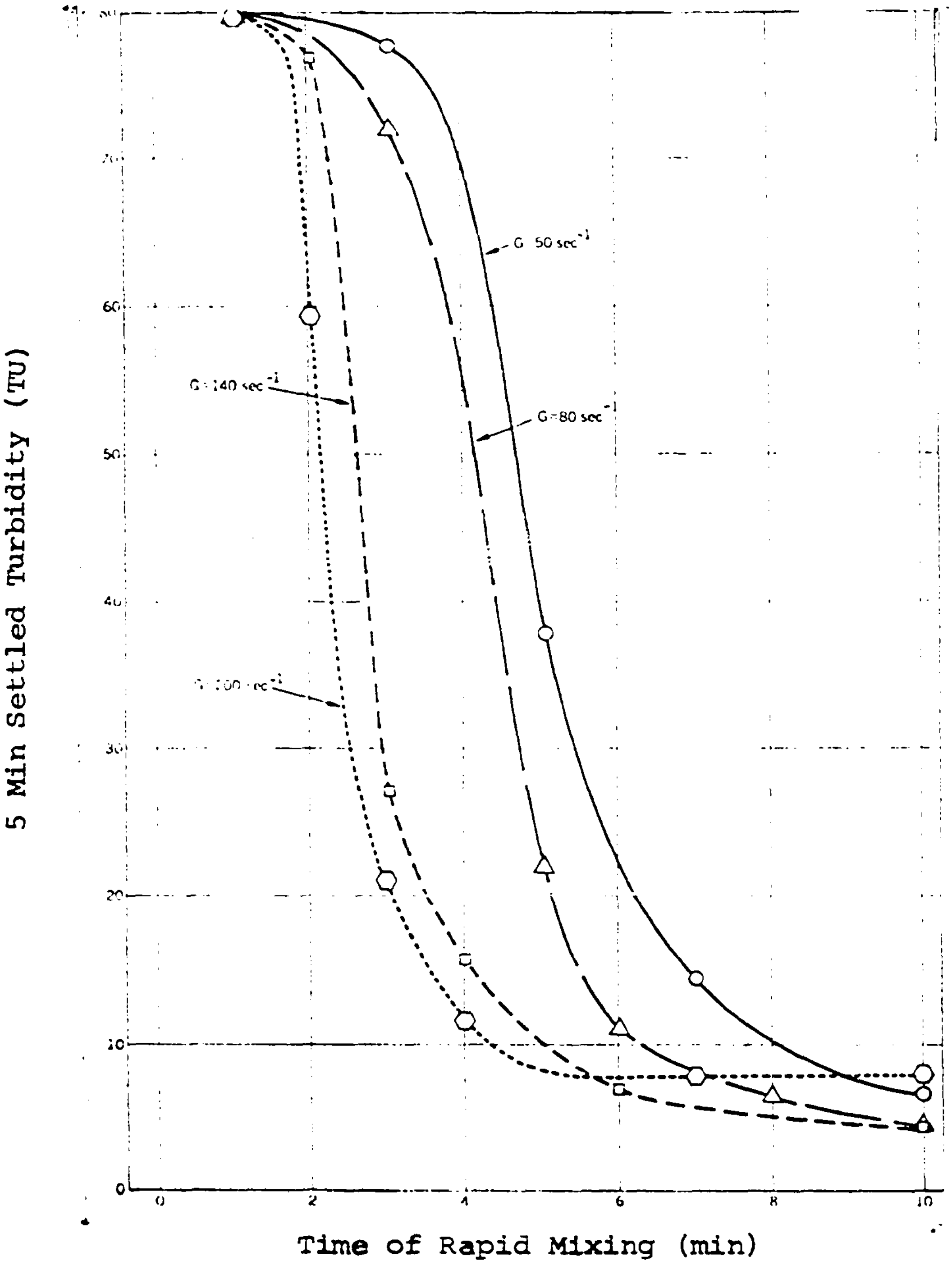

Figure 9. Effect of time of rapid mix on particle-size equilibrium, from Tekippe and Ham (60)

mixing. The velocity gradient values involved are 50, 80, 140, and 200 sec^{-1}. Velocity gradients higher than 200 were not included because, "it was not physically possible to obtain higher values with the available jar tests" (60). The indictment of high-energy mixing does not seem to be sufficiently supported by the data.

Walker (66) states that rapid mixing is a vital part of the coagulation process, but that it often fails to accomplish the desired results. He proceeded to suggest that better mixing can be achieved using "a short contact time and high velocity gradients". This position is not much different from the traditional attitude.

The point that has been made here is that there are no sufficient data in published coagulation studies to support or reject the desirability of high-velocity-gradient and/or extended period of rapid mixing in coagulation works.

D. Slow Mix

Unlike the rapid mix phase, which has received very little attention in coagulation studies, the slow mix phase has attracted many workers (9, 14, 27).

Smoluchowski has been credited with developing the basic mathematical model from which the present theory of flocculation emerged. Expressions were developed for interparticle collision frequencies in perikinetic transport (when collisions occur through Brownian diffusion), and orthokinetic transport. The phenomena were introduced to the civil engineering literature in 1943 by Camp and Stein (14).

The general form of the collision frequency for perikinetic transport and orthokinetic transport may be represented respectively by Equations 15 and 16

perikinetic:

$$b_{ij} = 4\pi(r_i + r_j)n_i n_j D_{ij} \tag{15}$$

orthokinetic:

$$b_{ij} = (4/3)(r_i + r_j)^3 \ n_i n_j \ du/dz \tag{16}$$

in which b_{ij} represents the frequency of collision between i-fold and j-fold particles, r is particle radius, n is particle concentration, D_{ij} is the diffusion constant for the particle in perikinetic transport, and du/dz is the velocity gradient in orthokinetic transport.

Tekippe and Ham (60) redefined and rearranged terms of the expressions in Equations 15 and 16 and came up with an expression for the ratio of orthokinetic to perikinetic transport as follows:

$$(b_{ij})_{ortho}/(b_{ij})_{peri} = \frac{\mu(du/dz)R_{ij}^3}{2kT} \tag{17}$$

where R_{ij} is a replacement for $(r_i + r_j)$, μ is the absolute viscosity of the medium, and k is the Boltzmann's constant (1.38×10^{-16} ergs/degree K). The terms μ, k, and T arise from an expression for the diffusion constant, namely:

$$D_{ij} = 2kT/(3\pi\mu R_{ij}) \tag{18}$$

Tekippe and Ham (60) state that because of the R^3 term in Equation 17, "it is obvious that orthokinetic transport predominates in the aggregation of larger particles". They state further that a one-micron diameter particle flocculated at a velocity gradient of 50 $\sec^{-1}$ would be transported at an orthokinetic rate that is 50,000 times the corresponding perikinetic transport rate. For this reason the orthokinetic transport is considered, by far, the more useful in most practical coagulation works.

In its cleanest form, the Camp and Stein (14) equation characterizing the flocculation process is given by:

$$N = (G/6)N_1N_2(d_1 + d_2)^3 \quad . \tag{19}$$

This equation states the relationship between energy applied to flocculation as described by the velocity gradient, G, and the number of contacts, N, between N_1 particles of size d_1 and N_2 particles of size d_2; and it can be used to study the speed with which small floc particles join to form large floc particles, or the rate at which suspended particles in the raw water are entrapped by the floc particles. In the case of coagulation involving the use of polyelectrolytes, it may be assumed that d_2 represents the average diameter of the matrices formed as a result of initial adsorption of polymer on particles, and d_1 represents average diameter of particles naturally present in the suspension.

Equation 19 has been verified experimentally by Manley and Mason (39) for monodispersed systems and may be considered the basic expression describing orthokinetic flocculation. One important limitation of this equation is that it describes the reaction of only two sizes of particles, a condition that cannot be met in real waters and wastewaters. Work continues to be done, notably by Argaman and Kaufman (5), Harris, Kaufman and Krone (27), and Parker, Kaufman and Jenkins (45) at the University of California in Berkeley directed to improving the basic mathematical model of orthokinetic transport to cater for hetero-dispersed systems and to accommodate the phenomenon of floc breakup in turbulent flocculation processes.

Going back to the basic expression of orthokinetic flocculation (Equation 19), we see that the rate of floc formation is directly proportional to the velocity gradient. It would seem then that the greater the magnitude of the velocity gradient, G, the less should be the time required for floc formation, and consequently, that, for economy in the sizing of flocculation units, the velocity gradient should be as large as practicable. The concept of an infinitely large velocity gradient is not in agreement with any field or experimental experiences in coagulation. It appears that a great deal more factors determine optimum velocity gradients of flocculation than the basic equation suggests. For example, Hudson (32) reports that field studies of velocity gradients indicate that toward the end of the flocculation process, tolerable G-values may be as low as 7 $\sec^{-1}$ for waters in the Piedmont area, and as high as 100 $\sec^{-1}$ for Great Lakes waters. Black et al. (11) working with dilute suspensions of kaolinite clay with polyelectrolytes reports that for the same initial weight concentration of clay, the sample agitated at 200 rpm consistently exhibited a lower residual turbidity than that agitated at 100 rpm. In contrast, Hemenway and Keshavan (31), using kaolinite and illite clay-suspensions with polyelectrolytes, found that turbidity removal increased with an increase in velocity gradient until an optimum value was reached. They added, "no upper limit was reached at which the flocs disintegrated". Their data showed that turbidity removal was better, or at least stayed the same, as velocity gradient was increased. It should be pointed out here that the maximum value of velocity gradient used in the study was 70 $\sec^{-1}$, Hemenway and Keshavan (31) further state that better removals were achieved from the longer of the two flocculation periods (15 and 30 minutes) used. They conclude that, in general, the optimum ranges of velocity gradients for cationic polyelectrolytes were much less than the range recommended for chemical coagulants, meaning that less power input would suffice to achieve a good result in the coagulation involving the use of polyelectrolytes.

The results of these studies show that, in spite of its importance as a fundamental mathematical expression of orthokinetic transport, Equation 19 , in its present form, is incapable of accurately relating rates of flocculation to velocity gradients. It is conceivable that a modification of the equation so as to properly accommodate breakups in floc matrices, and to ease up on the assumptions relating to the heterogeneous nature of suspensions, would provide an acceptable expression of the relationship. Moreover, it is this writer's suspicion that if more attention would be paid to the role of rapid-mixing than is the case at present, the problem of slow mixing might be found to fall into place more readily.

VI. SPECIFIC OBJECTIVES OF STUDY

The broad objective of this study has been stated previously, namely, to determine if polyelectrolytes would work on wastewaters and the conditions under which they work. It was thought, early in the study, that if polyelectrolytes would perform well in coagulating sewage, and do so economically, the following two things might be important:

1. The manner in which the sewage is dosed with the chemical, and,
2. The magnitude of the energy input (in the form of velocity gradient applied during mixing), and the duration of the mixing operations.

La Mer and Healy (36) had developed an equation relating to the rate of floc-formation (Equation 14). According to this equation, the maximum efficiency in flocculation would occur when one-half of primary particle surfaces are covered by polyelectrolyte segments.

Using this relationship, Lyklema[1] in an unpublished work was reported to have proposed and verified, using silver sols, that by dosing a portion (one-half, ideally) of the

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[1] Lyklema, J., Ames, Iowa. Coagulation of silver iodide sols with cationic polyelectrolyte. Private communication. 1970.

colloidal dispersion with polyelectrolyte, and then mixing the dosed and undosed portions, the required polymer dosage to achieve optimum coagulation should be substantially reduced.

This proposition is rational in theory, and, if true, it would lend support to the extended segment concept which is the foundation of the bridging model in polymer-coagulated-dispersions. Conceptually, a relationship between the residual turbidity or suspended solids, of the dispersion, and polymer dosage applied would be somewhat as shown in Figure 10.

The first objective of this study was to investigate this idea, which is being referred to by this writer as "the split-flow-dosing technique", using domestic sewage and selected cationic polyelectrolytes.

The second major objective was to determine the extent to which the coagulation is affected by high energy input during rapid mixing.

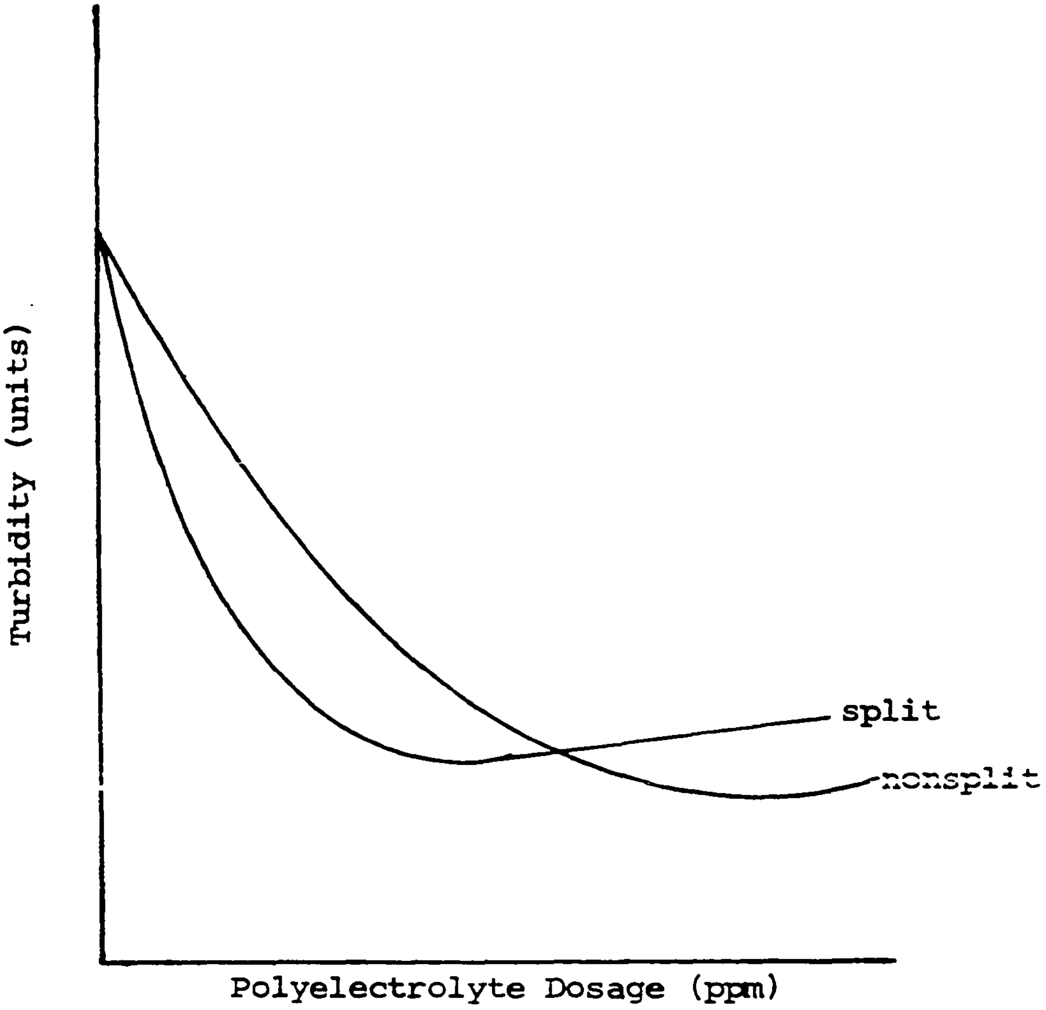

Figure 10. A hypothetical set of curves showing the polyelectrolyte dosages needed (ideally) to reach optimum turbidity removal with the split-flow-dosing technique and the nonsplit

VII. EXPERIMENTAL INVESTIGATIONS

A. Background

Two different forms of experimental investigations were made in this study, and are referred to as phase I and phase II. The first phase is strictly on a laboratory jar-test-scale involving liter-size samples and directed primarily towards accomplishing the first objective of this study, namely; to investigate the influence of split-flow dosing technique on polyelectrolyte-based coagulation of domestic sewage. Phase two, still a batch process like phase one, involved larger sized samples. Ten gallon-samples were used in this phase, to facilitate the use of measurable, high velocity gradients. The principal objective of phase two, therefore, was to investigate the influence of high velocity gradients and time of rapid mix on the coagulation process.

B. Phase I

1. Materials and apparatus

The basic materials needed for this investigation include some cationic polyelectrolytes, notably, Nalco 610, Hercofloc 810 and 814; some feed-grade bentonite clay, represented by Nalco 650; and, of course, sewage, partly from the Boone sewage treatment plant but mainly from the Ames' "Water Pollution Control Plant". Additional materials are involved, complementary to some of the equipment used. These are discussed as the need arises.

The equipment used include the following:

1. a turbidimeter unit, Hach's Model 1860[1]
2. a laboratory pH meter
3. an electrophoresis apparatus
4. a laboratory mixer (or stirrer)
5. a simple laboratory jar-test unit
6. a viscosity measuring device.

Other normal laboratory facilities such as stop watches, glassware, sampling vessels, and so on, were also used as needed during the course of the investigation.

Some of these equipment were not directly needed in carrying out the actual investigations stated in the objectives, but were useful in setting the pace for the study, in terms of narrowing the field of possibilities to manageable proportions. The equipment in question include the viscometer and the electrophoresis apparatus. Their roles are briefly discussed in the following sections.

a. The viscometer   A solution of polyelectrolytes in water is a very viscous liquid because of the high molecular weight of these materials. If a polymer solution

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[1] Product of Hach Chemical Company, Ames, Iowa.

is stored for an extended period of time the molecules can degrade, thus reducing the nominal molecular weight of the material. Correspondingly, the viscosity of the solution decreases.

Most polyelectrolyte manufacturers stipulate that a 0.5 percent stock solution of their products should be useable over a period of a week. It goes without saying that a degraded polymer-solution cannot perform at optimum effectiveness.

Early in the study, the need was recognized to reconcile two conflicting desires. First, because of the relative difficulty of dissolving polymers in water and the length of time the process takes, it would economize time and effort if a large quantity of 0.5 stock solution to last at least a week, could be made. At the same time, since a degrading polymer solution would be an additional source of variability in the coagulation study, it was deemed important that the stock solution be kept only as long as its quality did not substantially change. It was decided therefore to use the viscosity measurement to provide an insight into how long a stock solution should be kept under the prevailing storage conditions of this study.

Using a multi-speed Model RVF of the "Synchro-Lectric Viscometer", viscosity readings were taken over a period of several days on 0.5 and 0.25 percent stock solutions of Nalco 610 and Hercofloc 810 and 814, stored in an air-conditioned environment. All of these materials were supplied in powder form by the manufacturers. Table 4 illustrates a typical observation, showing how the viscosities decrease with time, for the materials tested. These are not absolute values of the viscosity of the material, as evidenced by different speeds of viscosity operations giving different results for the same material.

Non-Newtonian fluids (46) behave this way, and these polyelectrolyte solutions are non-Newtonian. Viscosity is defined as the ratio of shearing-stress to rate of shear, and, for non-Newtonian fluids the rate of shear is a function of the speed of relative motion between layers of the fluid.

The results of this experiment show that viscosity of polymer solutions does indeed decrease very rapidly during storage. Storing the solution in a refrigerator was found to slow down the rate of decrease of the viscosity. Based on these findings it was decided that one percent stock solutions would be made in quantities sufficient to last no longer than 3 to 4 days, and be kept as much as possible in a refrigerator.

b. The electrophoresis apparatus Using the arrangement shown in Figure 11, and adapting the procedures used by Black and Smith (12) at the University of Florida, in several of their experiments, the electrophoretic mobility measurements were made on some preliminary laboratory runs.

Table 4. Viscosity of 0.5 percent and 0.25 percent solutions of Nalco 610 over a period of time, and at different speeds of the viscometer operation

% Stock Solution	Date of measurements	Day	Viscosity Readings in Centipoise (cps)			
			2 rpm	4 rpm	10 rpm	20 rpm
0.5	10-15-71	0	980	770	525	372
0.5	10-18-71	3	760	625	445	324
0.25	10-18-71	0	370	300	215	160
0.25	10-19-71	1	360	300	215	160
0.25	10-20-71	2	340	285	210	156
0.25	10-25-71	7	320	270	195	144
0.25	10-28-71	10	260	220	170	130
0.25	11-11-71	24	40	35	36	38

The purpose was to see if points of zero electrophoretic mobility (described in an earlier section) corresponded with points of optimum polyelectrolyte dosages. The tests were cumbersome and could not be performed routinely during the period of the main investigation. The results obtained during the preliminary investigation were as varied as the sewage. On sewage samples containing some silt or clay (such as from infiltration into the plant following a storm) the optimum dosage of cationic polyelectrolytes may occur

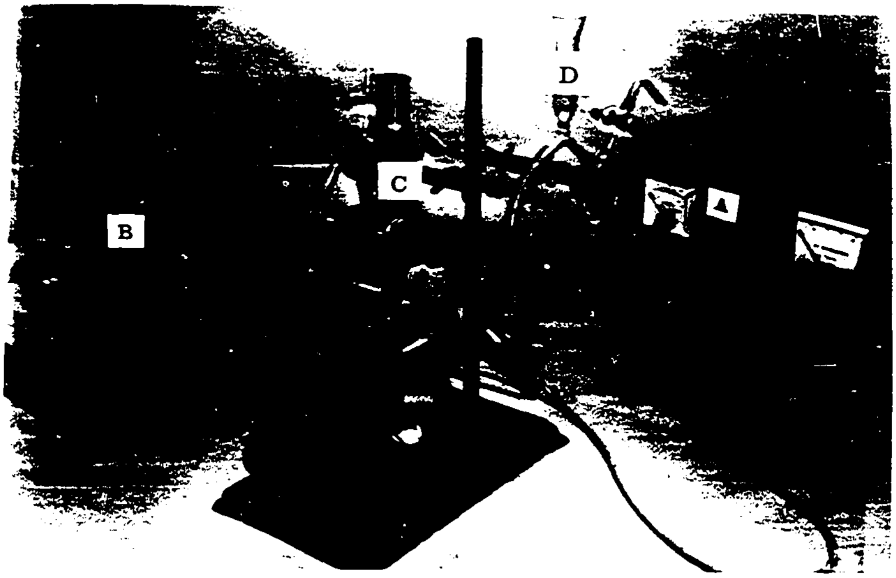

Figure 11. An arrangement for determining electrophoretic mobility. A indicates the direct current source and indicator, B is the source of illuminating light for the cell under the microscope C, and D is the entrance for the sample under study. The exit is hidden behind the microscope in the picture

near the point of charge neutralization. On the other hand, for what might be called a normal domestic sewage, no relationship could be found between optimum dosage (dosage required to produce optimum turbidity removal) and the dosage required to cause charge-neutralization in the dispersion.

2. Sampling and test procedures

During this phase of the study it was necessary to take sewage samples from the sewage plant into the laboratory for the experiment. The flow of sewage into a sewage treatment plant varies both in quantity and strength during a typical day. Figure 12 illustrates the flow variation at the Ames' treatment plant. In order to eliminate variability due to the flow pattern within-day from the investigations, efforts were made to draw the samples at about the same time each day. About 10:30 a.m. was picked, principally because it was convenient.

A one percent stock solution of the cationic polyelectrolyte to be used was made by dissolving 10 grams of the material in a liter of distilled water. This stock solution was kept in the refrigerator when not in use, and was made in such quantities to last 3 to 4 days, after which whatever remained was discarded. From the stock solution of 0.1 percent solution was made by pipetting 10

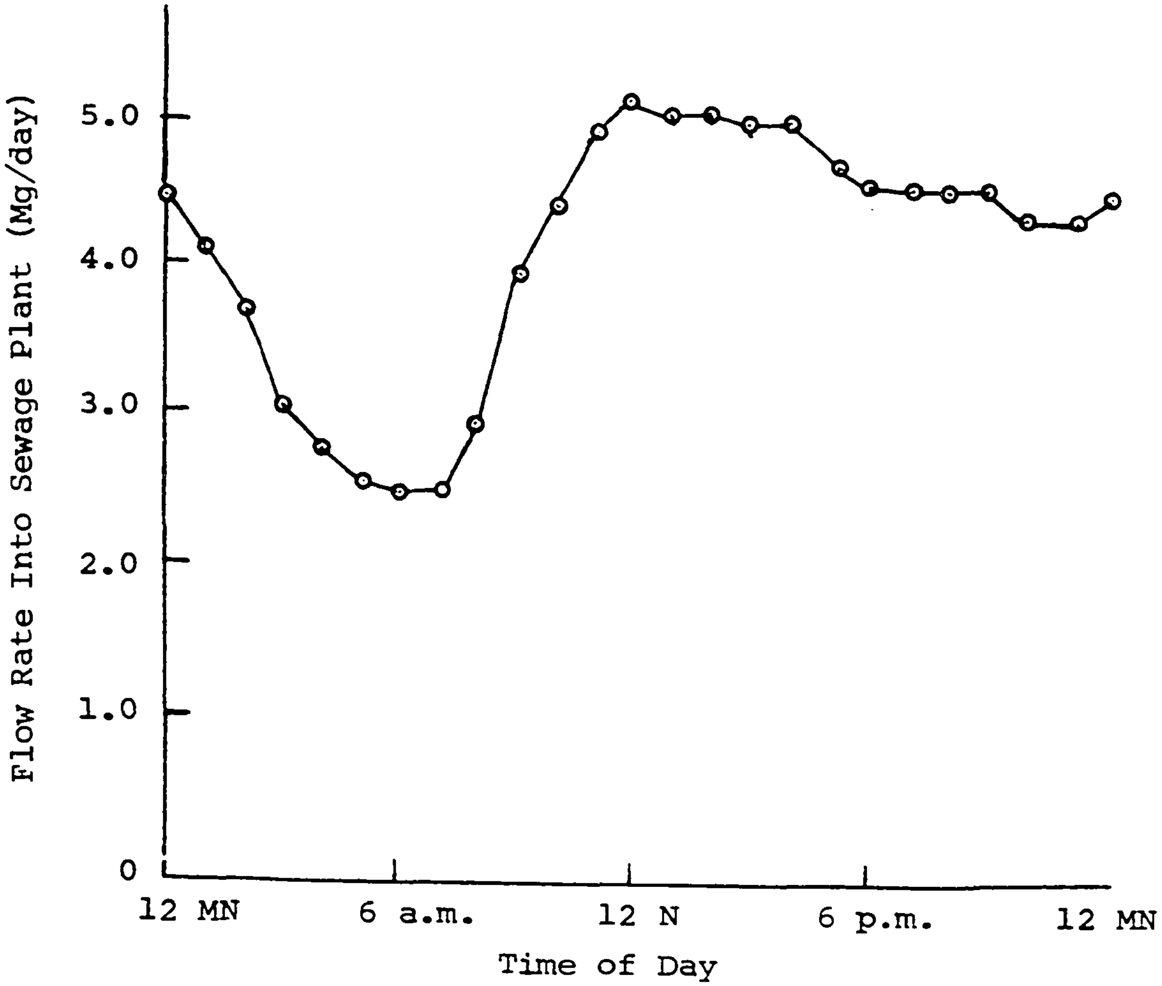

Figure 12. Sewage flow variation at Ames' treatment plant

ml of it into a 100 ml volumetric flask and making it up with distilled water, shaking to mix, to the 100 ml mark. The remnant of 0.1 solutions was discarded after each day's run. A one-ml aliquot of the 0.1 percent solution when dosed into a liter sample of sewage corresponds to a one-mg/l dosage. Appropriate dosages of the polyelectrolyte solution were applied through burettes mounted up for the purpose.

a. Dosing and mixing techniques Operating on the theory that the principal purpose of rapid mixing is to quickly disperse the chemical into the suspension with as little violence as possible, the process of rapid mixing by pouring from beaker to beaker was adopted. First, the desired polyelectrolyte dosage was measured into an empty liter beaker. The sewage sample, contained in another beaker, was poured quickly into one containing the polymer aliquot. The sample was poured back and forth ten times, after which it was subjected to a 10 minute period of slow mixing at 25 rpm blade speed on a common laboratory jar test apparatus such as is shown in Figure 13. The samples were then allowed to settle 30 minutes and the turbidity (and in some cases, the suspended solids) measurements were made and recorded. Turbidity readings were taken by means of Hach's turbidimeter unit, model 1860.

In addition to the beaker-to-beaker mode of mixing, the

MULTIPLE SPINDLE STIRRER

- **For floc formation tests in water treatment plants**

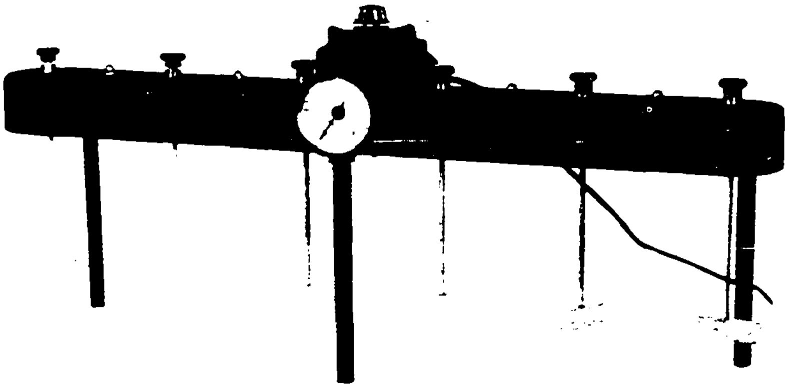

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Figure 13. Multiple stirrer commonly used in jar-tests in coagulation studies (courtesy of Phipps and Bird)

conventional mixing procedures were also used, namely, apply the polymer dosage, rapid mix at 100 rpm for one minute, then slow-mix and settle as before. Preliminary observations indicated that the two techniques were about the same.

For the purpose of investigating the effect of the dosing technique as stated in the objective, arrangements were made to run tests on nonsplit (NS), 75 : 25 split, 50 : 50 split, and 25 : 75 split. The nonsplit represents the conventional method, namely, dose the entire sample, rapid mix, slow mix, and settle. In the case of split (S), however, the sample would be divided into two portions, the portion indicated first is dosed with the polymer and rapid-mixed for one-half of the time (30 seconds, or five beaker-to-beaker pourings), then mixed with the second, undosed, portion and rapid mixed together for the remainder of the rapid mix period. The slow mixing and quiescent settling then follow as usual. Thus, for example, 75 : 25 S means that 75 percent of the liter sample was dosed with the desired amount of polymer, mixed for one-half of the rapid-mix period; then the remaining 25 percent, undosed, is added, and the total volume mixed for the remaining half of the rapid-mix period, and so on. Some tests were performed in which the dosed portion was rapid-mixed, the undosed portion was poured in and the combined volume subjected to slow mix only. Large amounts of floating matter were observed whenever this was done; the performance was obviously poor, and so, subsequent tests were run under conditions in which the combination of the dosed and undosed portions underwent some form of rapid mixing. Another dosing technique, referred to as "Dosed Twice, DT" was used. This involved putting in one-half of the polymer dosage intended, at the beginning of the rapid mix period, and the remaining half at the middle of the rapid-mix period.

b. Randomization In many instances, a complete set of runs involved the use of five dosing techniques, each carried through six different polymer dosages. Thus, a total of 30 individual coagulation operations made up one set of runs. Since the sewage sample for each set of runs had to be drawn at the same time each day, it meant that the coagulation-operations toward the end of the runs were performed on sewage samples that had sat around longer than those used at the beginning of the set. The suspended solids, especially the colloids in such samples could conceivably undergo changes in surface characteristics, if so, this would be a source of variability that could affect performance, and thereby jeopardize the basis for comparison. As it was not possible to prevent some samples from having to sit around longer than others, some other device had to be used to eliminate, or at least reduce the potential for quality variability. A randomization procedure was used for this purpose. A table of random numbers was used to assign the order in which all the combinations of techniques and dosages would be run. Thus, it could be that the 50 : 50 S technique with a dosage of 7.5 mg/l would be run first; nonsplit with a dosage of 2.0 mg/l might be second, and so on. The next set of runs would involve the use of a new set of random numbers.

3. Results and interpretations

Table 5 represents a summary of the data obtained for the raw sewage of the city of Ames coagulated with the polyelectrolyte Nalco 610. The table is made up of eight sets of runs, and each set lists residual turbidity-values for samples coagulated with the cationic polyelectrolyte, for each of the five dosing techniques. Figures 14, 15, and 16 show three of the runs in graphical forms, illustrating the relative efficacies of the five different dosing techniques over the range of one to 15 polymer dosages.

a. Basis for comparison   Even with careful sampling and experimental procedures, the sewage samples used from one set of runs to another could not be expected to be identical. As Table 5 shows, the residual turbidity for any combination of technique and dosage varies widely from day to day, and so, a summary based on averaging the

Table 5. Residual turbidity-values of Ames' raw sewage coagulated with the polyelectrolyte Nalco 610, using the dosing techniques: nonsplit-flow (NS), dosing twice (DT), and split-flow (S)

Nalco 610 Dosage in mg/l		Dosing Techniques				
		Nonsplit (NS)	Dosing Twice (DT)	Split Flow Dose 75% (75:25S)	Split Flow Dose 50% (50:50S)	Split Flow Dose 25% (25:50S)
Run No. 1-06-72[a]						
1.0	Turbidity	43.0	45.0	43.0	43.0	42.0
	Rank	26	30	26	26	25
2.0	Turbidity	41.5	45.0	40.0	40.0	40.0
	Rank	24	26	20	20	20
5.0	Turbidity	38.0	41.0	37.5	34.0	35.0
	Rank	19	23	18	16	17
7.5	Turbidity	30.5	30.5	25.0	25.0	27.5
	Rank	14	14	10	10	13
10.0	Turbidity	23.0	24.5	22.5	22.0	25.0
	Rank	8	9	6	3	10
15.0	Turbidity	20.0	20.0	22.0	22.0	22.5
	Rank	1	1	3	3	6
Run No. 1-07-72[b]						
1.0	Turbidity	46.0	47.5	47.0	45.0	47.5
	Rank	24	27	26	21	27
2.0	Turbidity	47.5	47.5	45.0	46.0	45.5
	Rank	27	27	21	24	23
5.0	Turbidity	42.5	41.5	39.5	35.0	35.0
	Rank	20	19	18	15	15
7.5	Turbidity	34.0	37.5	29.5	32.0	32.0
	Rank	14	17	11	12	12
10.0	Turbidity	24.0	28.0	25.0	22.0	24.0
	Rank	7	10	9	5	7
15.0	Turbidity	23.0	20.0	21.5	20.0	20.0
	Rank	6	1	4	1	1

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[a] Conditions of run: average original unsettled turbidity 53 TU; sewage temp. = 16°C warmed up to 21°C.

[b] Conditions of run: average original unsettled turbidity = 55 TU; sewage temp. = 16°C warmed up to 26°C.

Table 5 (Continued)

Nalco 610 Dosage in mg/l		Dosing Techniques				
		Nonsplit (NS)	Dosing Twice (DT)	Split Flow Dose 75% (75:25S)	Split Flow Dose 50% (50:50S)	Split Flow Dose 25% (25:50S)
Run No. 1-10-72[c]						
1.0	Turbidity	51.0	48.5	45.0	42.0	43.0
	Rank	30	29	26	22	25
2.0	Turbidity	46.0	45.0	42.0	41.0	42.0
	Rank	28	26	22	21	22
5.0	Turbidity	40.0	37.5	35.0	39.0	37.5
	Rank	20	17	16	19	17
7.5	Turbidity	33.0	31.0	27.0	30.0	31.0
	Rank	15	13	11	12	13
10.0	Turbidity	24.0	24.0	24.0	24.0	27.0
	Rank	6	6	6	6	10
15.0	Turbidity	20.0	20.0	18.5	21.0	21.5
	Rank	2	2	1	4	5
Run No. 1-12-72[d]						
1.0	Turbidity	44.0	43.0	40.0	49.0	48.0
	Rank	23	22	19	30	29
2.0	Turbidity	45.5	46.0	47.0	46.0	46.0
	Rank	24	25	28	25	25
5.0	Turbidity	40.0	39.0	37.0	39.0	40.0
	Rank	19	17	16	17	19
7.5	Turbidity	36.0	35.0	33.0	32.0	34.0
	Rank	15	14	11	10	13
10.0	Turbidity	30.5	33.0	28.0	24.0	25.0
	Rank	9	11	8	2	4
15.0	Turbidity	25.0	22.5	25.0	24.0	26.0
	Rank	4	1	4	2	7

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[c] Conditions of run: average of original turbidity = 55 TU; sewage temp. = 18°C.

[d] Conditions of run: average of original turbidity = 58 TU; sewage temp. = 18°C.

Table 5 (Continued)

Nalco 610 Dosage in mg/l		Dosing Techniques				
		Nonsplit (NS)	Dosing Twice (DT)	Split Flow Dose 75% (75:25S)	Split Flow Dose 50% (50:50S)	Split Flow Dose 25% (25:50S)
Run No. 1-17-72[e]						
1.0	Turbidity	56.0	62.0	64.0	59.0	60.0
	Rank	21	29	30	23	24
2.0	Turbidity	61.0	60.0	60.0	53.0	54.0
	Rank	28	24	24	16	17
5.0	Turbidity	60.0	50.0	55.0	54.0	55.0
	Rank	24	12	19	17	19
7.5	Turbidity	56.0	50.0	50.0	49.0	47.0
	Rank	12	12	12	11	9
10.0	Turbidity	43.0	50.0	47.0	44.0	45.0
	Rank	6	12	9	7	8
15.0	Turbidity	38.0	38.0	38.0	39.0	38.0
	Rank	1	1	1	5	1
Run No. 1-18-72[f]						
1.0	Turbidity	50.0	49.5	48.5	45.0	49.5
	Rank	30	28	26	23	28
2.0	Turbidity	47.5	47.0	43.0	44.0	49.0
	Rank	25	24	21	22	27
5.0	Turbidity	39.0	39.0	38.0	35.5	35.0
	Rank	19	19	18	17	16
7.5	Turbidity	32.0	32.5	26.0	32.0	34.0
	Rank	12	14	8	12	15
10.0	Turbidity	25.0	29.0	25.0	27.5	27.0
	Rank	6	11	6	10	9
15.0	Turbidity	21.0	22.5	21.0	24.0	22.5
	Rank	1	3	1	5	3

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[e] Conditions of run: average of original turbidity = 70 TU; sewage temp.

[f] Conditions of run: average of original turbidity = 52 TU; sewage temp.

Table 5 (Continued)

Nalco 610 Dosage in mg/l		Nonsplit (NS)	Dosing Twice (DT)	Split Flow Dose 75% (75:25S)	Split Flow Dose 50% (50:50S)	Split Flow Dose 25% (25:50S)
Run No. 1-19-72[g]						
1.0	Turbidity	39.0	40.0	37.5	40.0	39.0
	Rank	21	27	18	27	21
2.0	Turbidity	42.0	40.0	38.0	39.0	39.5
	Rank	30	27	19	21	26
5.0	Turbidity	38.0	39.0	33.0	39.0	35.0
	Rank	19	21	12	21	15
7.5	Turbidity	34.5	35.0	29.5	31.5	35.0
	Rank	14	15	4	10	15
10.0	Turbidity	31.0	33.0	27.5	27.5	28.5
	Rank	9	12	1	1	3
15.0	Turbidity	30.0	30.0	32.5	30.0	30.0
	Rank	5	5	11	5	5
Run No. 1-20-72[h]						
1.0	Turbidity	44.0	42.5	43.0	40.0	43.0
	Rank	29	25	27	19	27
2.0	Turbidity	40.0	42.5	45.0	35.5	37.0
	Rank	19	25	30	16	17
5.0	Turbidity	40.0	37.0	40.0	40.0	41.0
	Rank	19	17	19	19	25
7.5	Turbidity	33.0	32.0	31.0	33.5	30.0
	Rank	13	12	11	15	8
10.0	Turbidity	30.5	33.0	30.5	26.5	28.0
	Rank	9	13	9	1	6
15.0	Turbidity	28.0	27.5	26.5	26.5	27.5
	Rank	6	4	1	1	4

[g] Conditions of run: average of original turbidity = 54 TU; sewate temp.

[h] Conditions of run: average of original turbidity = 60 TU; sewage temp.

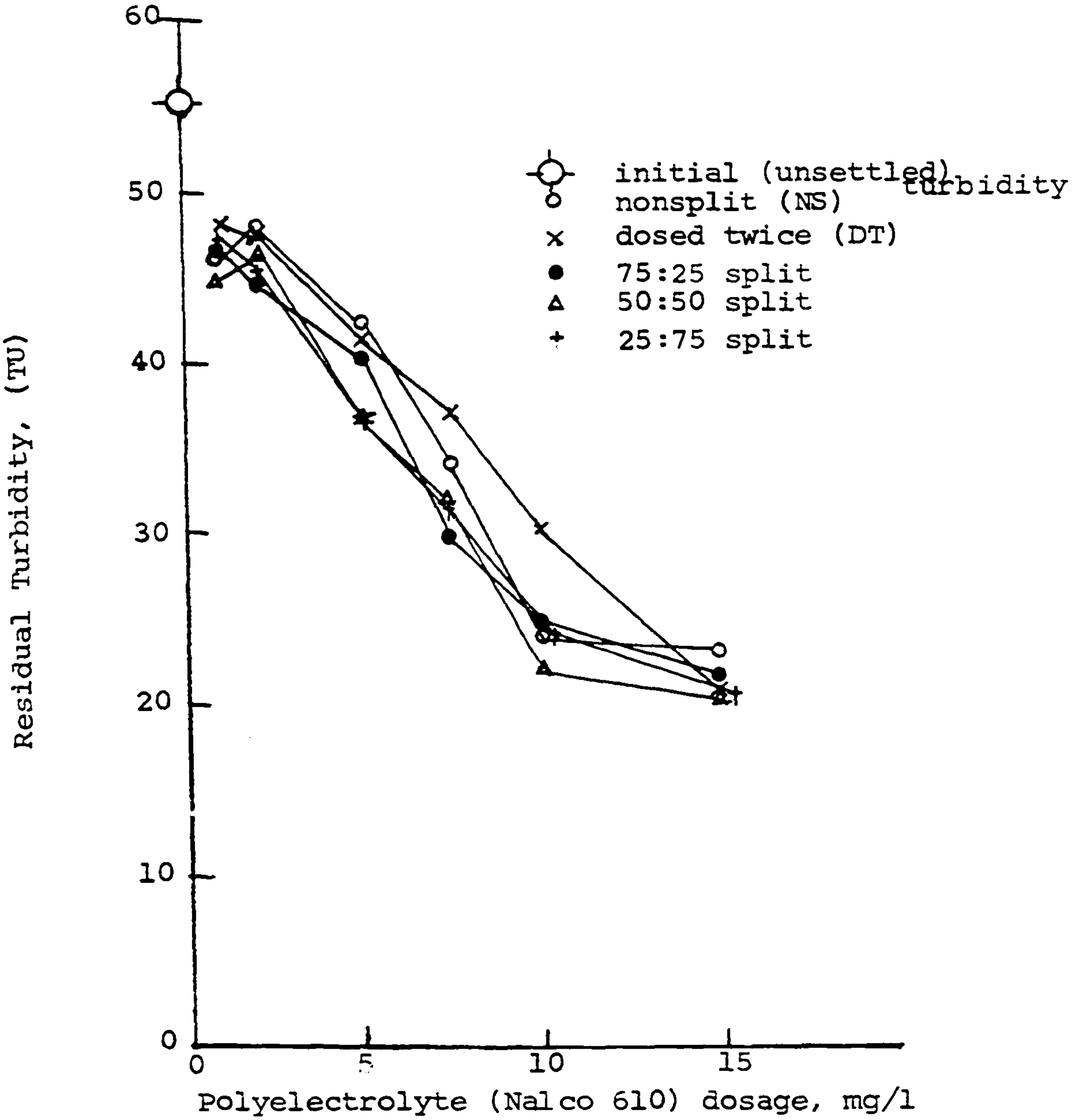

Figure 14. Plots of residual turbidity versus dosage of the polyelectrolyte, Nalco 610, for all five dosing techniques. Run No. 1-07-72, Ames raw sewage

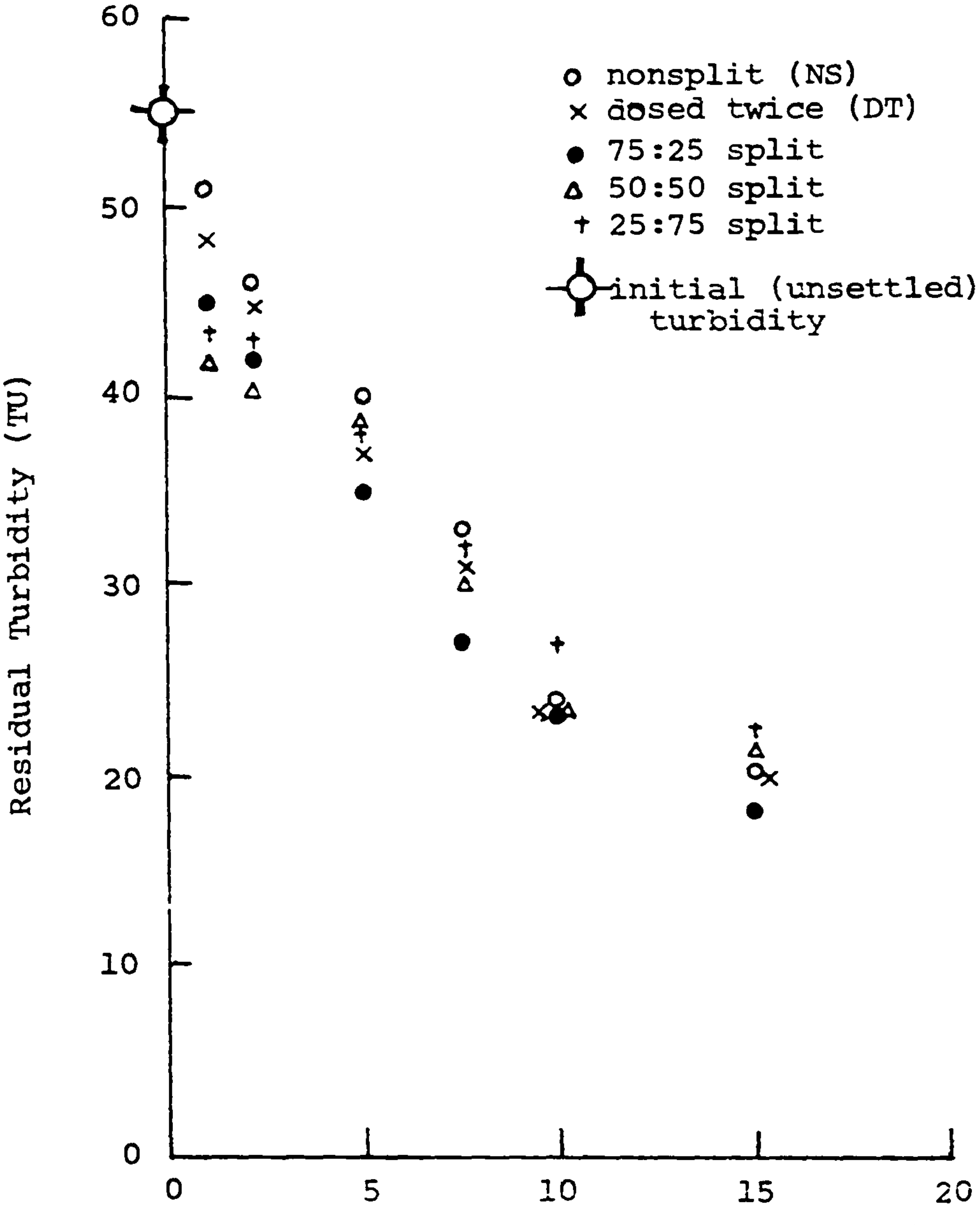

Figure 15. Plots of residual turbidity versus dosage of the polyelectrolyte, Nalco 610, for all five dosing techniques. Run No. 1-10-72, Ames' raw sewage

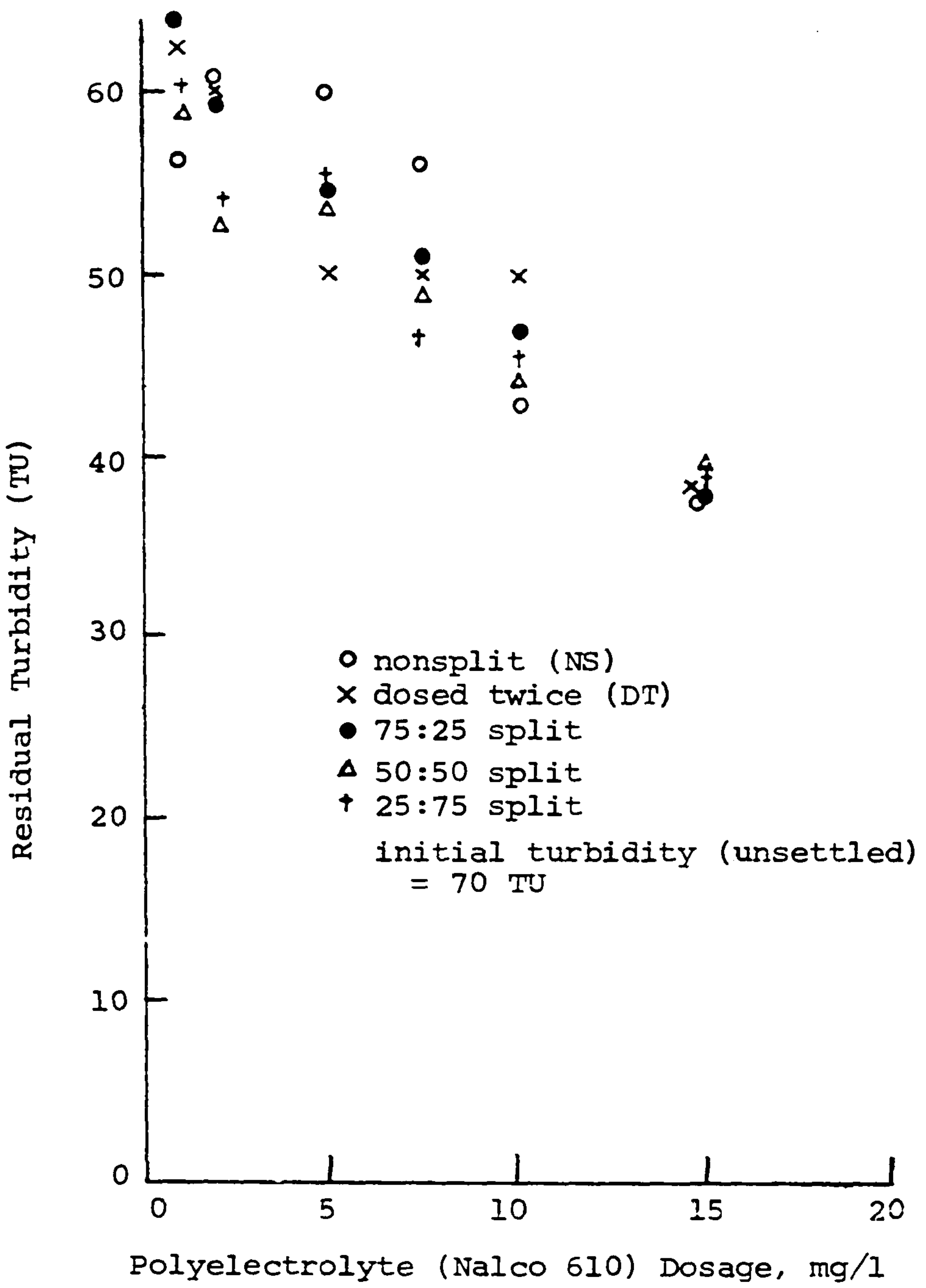

Figure 16. Plots of residual turbidity versus dosage of the polyelectrolyte, Nalco 610, for all five dosing techniques. Run No. 1-17-72, Ames' raw sewage

turbidity results over the sets of runs is not very meaningful, and is therefore not used. Instead, a ranking procedure is applied, as follows: In a given set of runs, that combination of technique and dosage that produced the lowest residual turbidity is ranked number one; the combination resulting in the next higher residual turbidity is assigned number two, and so on, until all 30 individual turbidity-values have been assigned ranks, see Table 5.

Table 6 summarizes the mean rank for each technique-dosage combination over all the sets of runs, and Figure 17 is a graphical illustration of each technique ranks relative to the others at each value of the polyelectrolyte dosage.

The following statements can be made, based on the results presented thus far:

1. At least 10 mg/l of the polyelectrolyte 610 is required to effect maximum removals of turbidity regardless of the dosing-technique used under the present operating conditions. See Figures 14, 15, and 16.
2. At polymer dosages near optimum ($\geq$ 10 mg/l), the 50:50 split technique appears to perform slightly better than the conventional (nonsplit) technique as the ranking illustration (Figure 17) shows.
3. It does not seem important at what confidence

Table 6. Average rank for each combination of dosage and dosing-technique, obtained by summing rank of all 8 runs, and dividing by 8--lower rank is better performance

Nalco 610 Dosage (mg/l)	Average Rank for Each Technique				
	NS	DT	75:25S	50:50S	25:75S
1.0	26	27	25	24	26
2.0	26	26	23	21	22
5.0	20	18	17	18	18
7.5	15	14	10	12	12
10.0	8	11	7	4	7
15.0	3	2	3	3	4

level the 50:50 split method is better than the nonsplit, because;

4. None of the five dosing techniques, even at optimum dosages, reduces turbidity to values below 20 units. In most cases the resulting residual turbidity-values are quite high and vary considerably from one set of runs to another.

The above conclusions were drawn, based on turbidity-removal data only. However, suppose suspended solids removal measurements were made, would the results lead us to reach a different set of conclusions?

In an attempt to answer this question, further

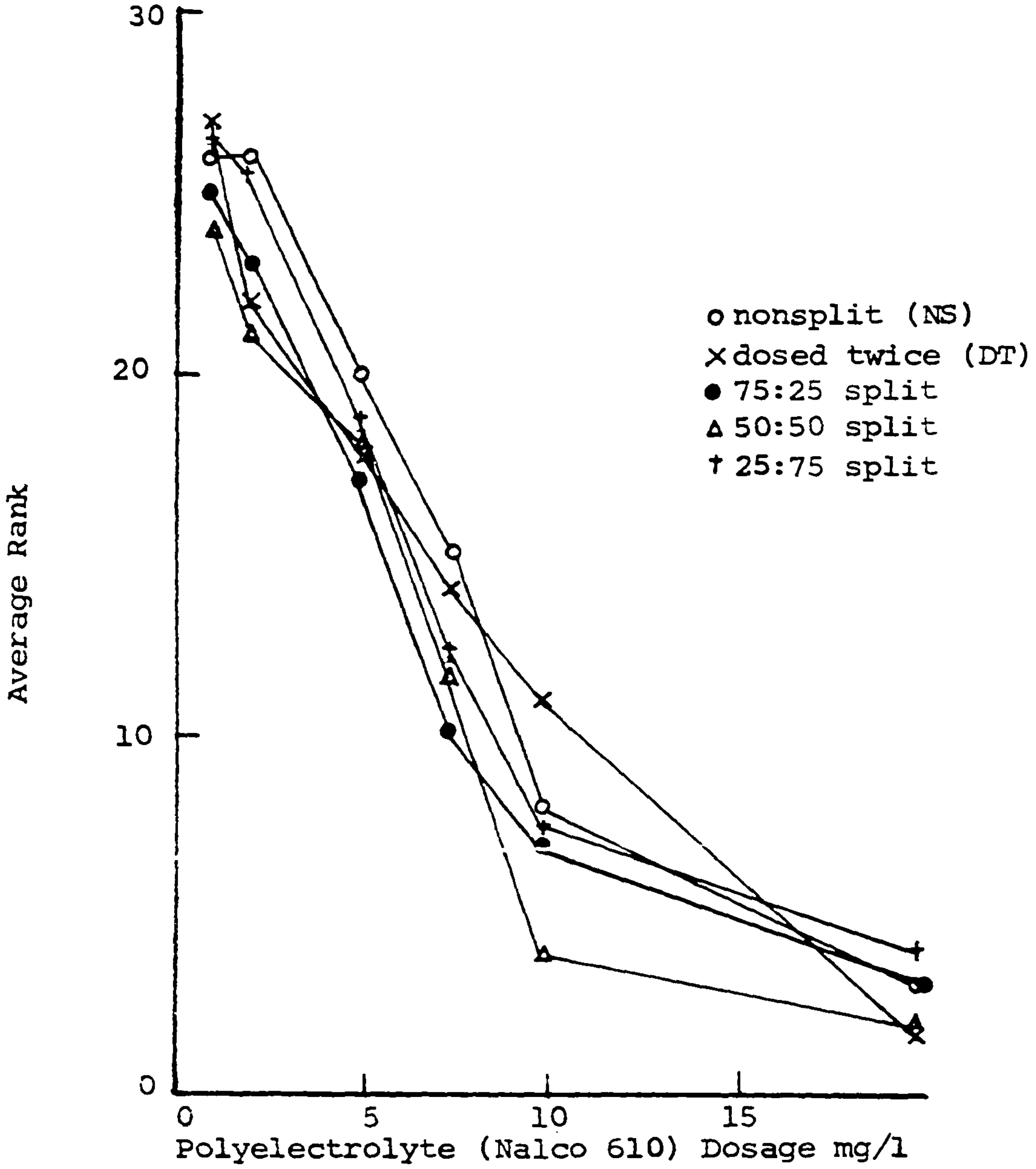

Figure 17. Average rank for dosage and dosing-technique combinations. Lower ranks represent better performance

experimental investigations were carried out, involving determinations of removals of turbidity and suspended solids. This time however the two dosing techniques investigated were the 50:50 split and the nonsplit techniques. Table 7 summarizes the results of two sets of runs, using Ames' raw sewage, and Figures 18 and 19 are the corresponding graphical representations. The removal patterns of suspended solids and turbidity are fairly similar as can be seen in these figures. A set of runs made using sewage samples from the city of Boone, Iowa, gave results summarized in Table 8 and graphed in Figure 20.

Finally, Table 9 and Figure 21 summarize the results of a set of runs on the primary effluent at the Ames' plant. Again, neither the turbidity removals nor the suspended solids show any consistent differences between nonsplit and 50:50 split. Furthermore, the percent suspended solids removal were, in general, below 90 percent, the range being between 60 and 90 percent. This performance cannot be called impressive since ordinary sedimentation of raw sewage can remove up to 70 percent or more of suspended solids. The use of other cationic polyelectrolytes, namely, Hercofloc 810 and 814 did not materially alter the result pattern.

It was beginning to appear that cationic polyelectrolytes simply would not perform well as coagulants for domestic sewage; that perhaps the whole project should be

Table 7. Residual suspended solids and turbidity-values of Ames' raw sewage, coagulated with the polyelectrolyte Nalco 610--a comparison between nonsplit and 50:50 split

Nalco 610 Dosage (mg/l)	Turbidity						Suspended Solids mg/l					
	Nonsplit			50:50 split			Nonsplit			50:50 split		
	Before (ave.)	After	% Rem.	Before (ave.)	After	% Rem.	Before (ave.)	After	% Rem.	Before (ave.)	After	% Rem.
Run No. 2-01-72												
0	70	47	32.9	70	44	37.2	232	65	72.0	232	58	75.0
1	70	46	34.3	70	47	32.9	232	75	67.7	232	79	66.0
2	70	47	32.9	70	50	28.6	242	80	67.0	242	83	65.8
4	70	38	45.7	70	42	40.0	242	77	68.3	242	86	64.5
8	70	34	51.5	70	34	51.5	208	48	77.0	208	49	76.5
16	70	28	60.0	70	33	53.0	208	35	83.2	208	40	80.7
Run No. 2-05-72												
0	70	45	35.7	70	44	37.1	263	52	80.0	263	48	81.6
1	70	43	38.6	70	44	37.1	263	59	77.3	263	54	79.2
2	75	42	44.0	75	40	46.7	255	51	80.0	255	49	81.0
4	75	45	50.0	75	44	41.4	255	43	83.0	255	45	82.3
8	72	39	46.0	72	34	53.0	243	40	83.5	243	30	87.6
16[a]	72	24	66.7	72	20	72.3	243	17	93.0	243	8	96.6

[a] With the 16 mg/l dosage, the 50:50 split sample was rapid-mixed for about 2 1/2 minutes instead of one minute. This is the first indication that some form of extended rapid mixing would be beneficial.

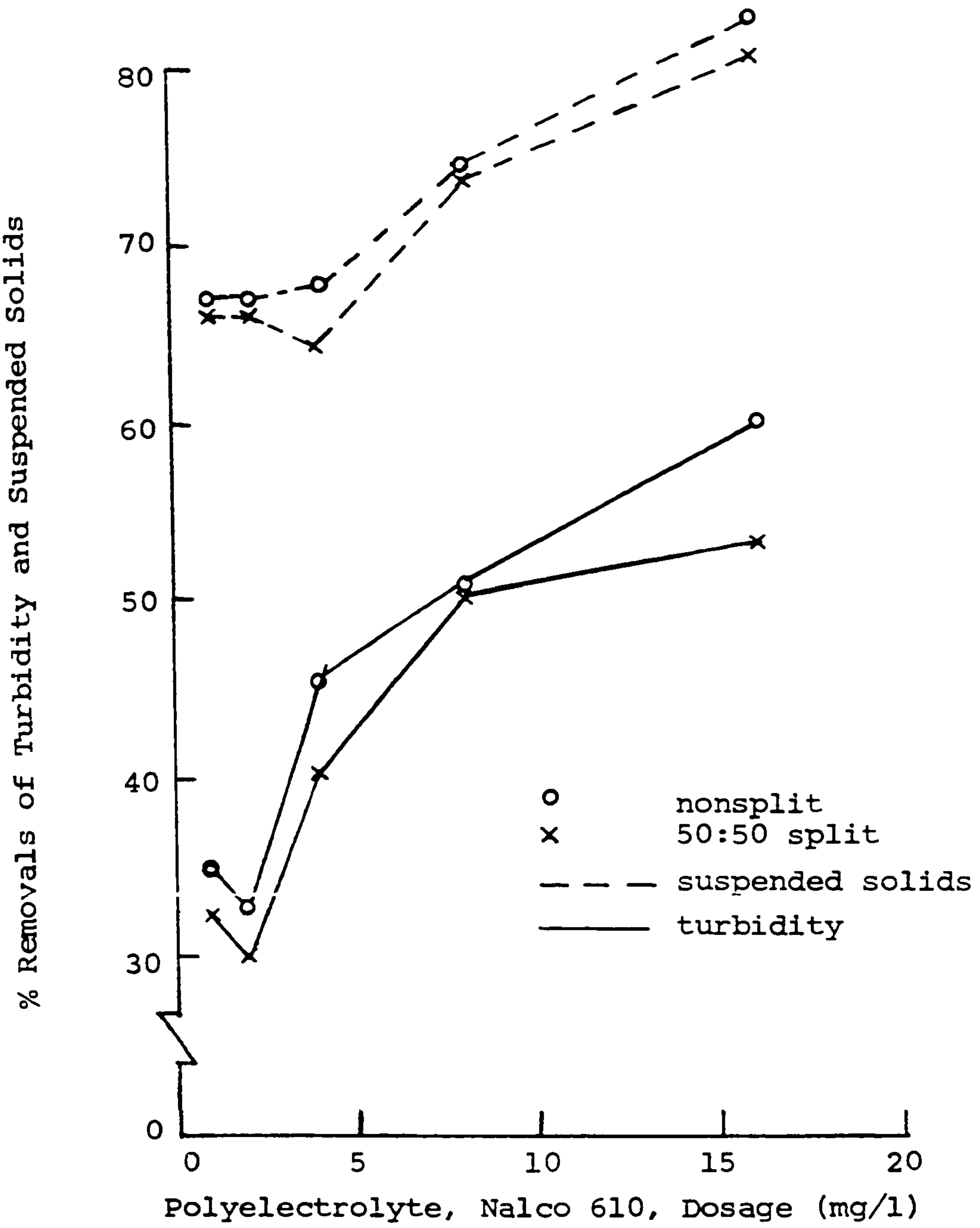

Figure 18. Plots of residual suspended solids and turbidity versus dosage of the polyelectrolyte, Nalco 610, for nonsplit, and 50:50 split. Run No. 2-01-72 Ames' raw sewage

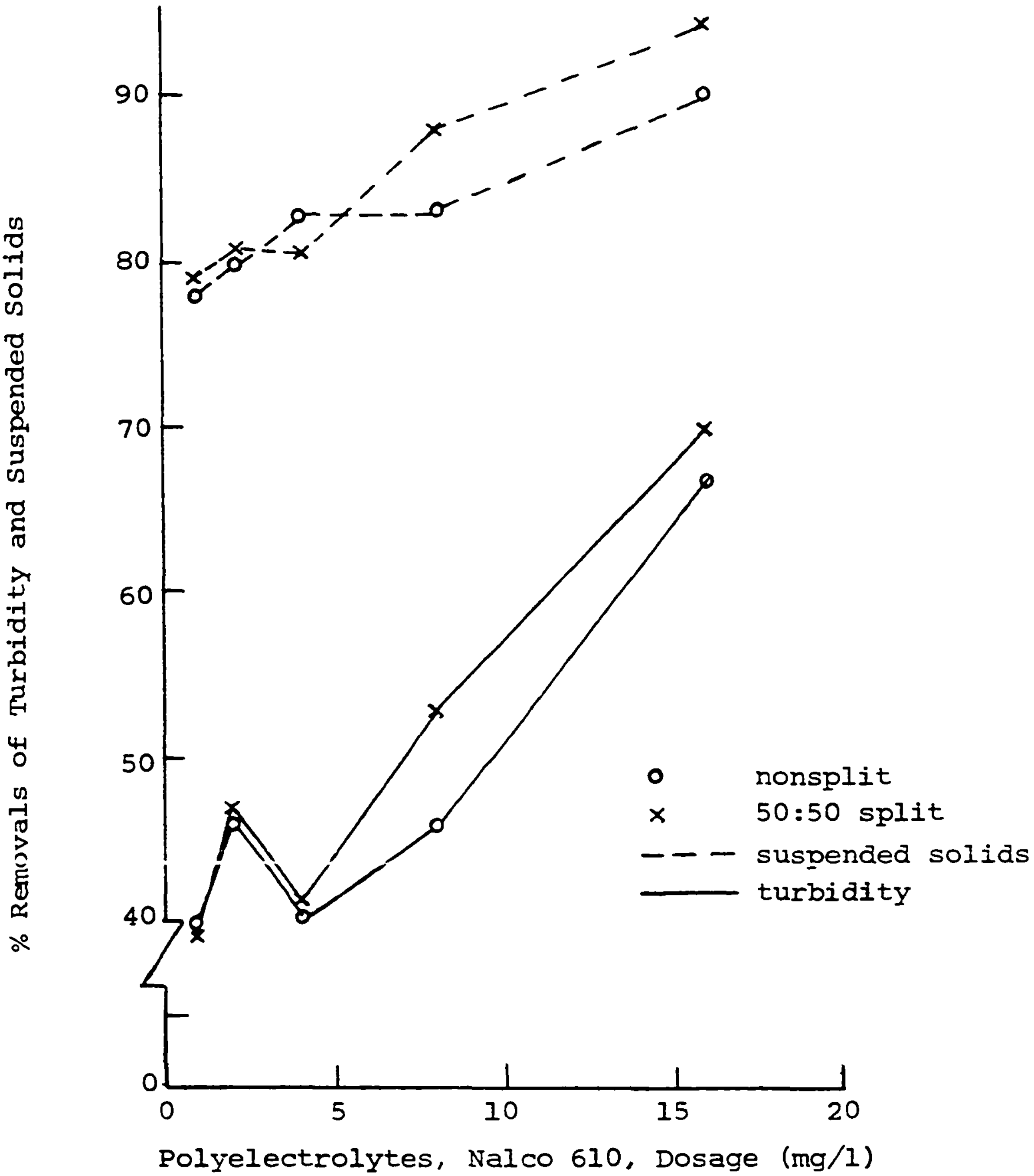

Figure 19. Plots of residual suspended solids and turbidity versus dosages of the polyelectrolyte Nalco 610, for nonsplit and 50:50 split. Run no. 2-05-72, Ames' raw sewage

Table 8. Residual suspended solids and turbidity-values of Boone's raw sewage, coagulated with Nalco 610--a comparison between nonsplit and 50:50 split

Nalco 610 Dosage (mg/l)	Nonsplit			50:50 Split		
	Before (ave.)	After	% Rem.	Before (ave.)	After	% Rem.
Run No. 2-02-72						
			Turbidity			
0	75	65	13.3	75	60	20.0
1	75	50	33.3	75	52	30.6
2	75	50	33.3	75	44	41.4
4	75	27	64.0	75	42	44.0
8	75	27	64.3	75	30	60.0
16	75	25	66.6	75	29	61.3
			Suspended Solids (mg/l)			
0	405	110	73.0	405	100	75.5
1	405	88	78.4	405	102	75.0
2	472	93	80.3	472	86	82.0
4	472	61	87.1	472	115	75.6
8	403	54	86.6	403	60	85.0
16	403	57	85.7	403	60	85.0

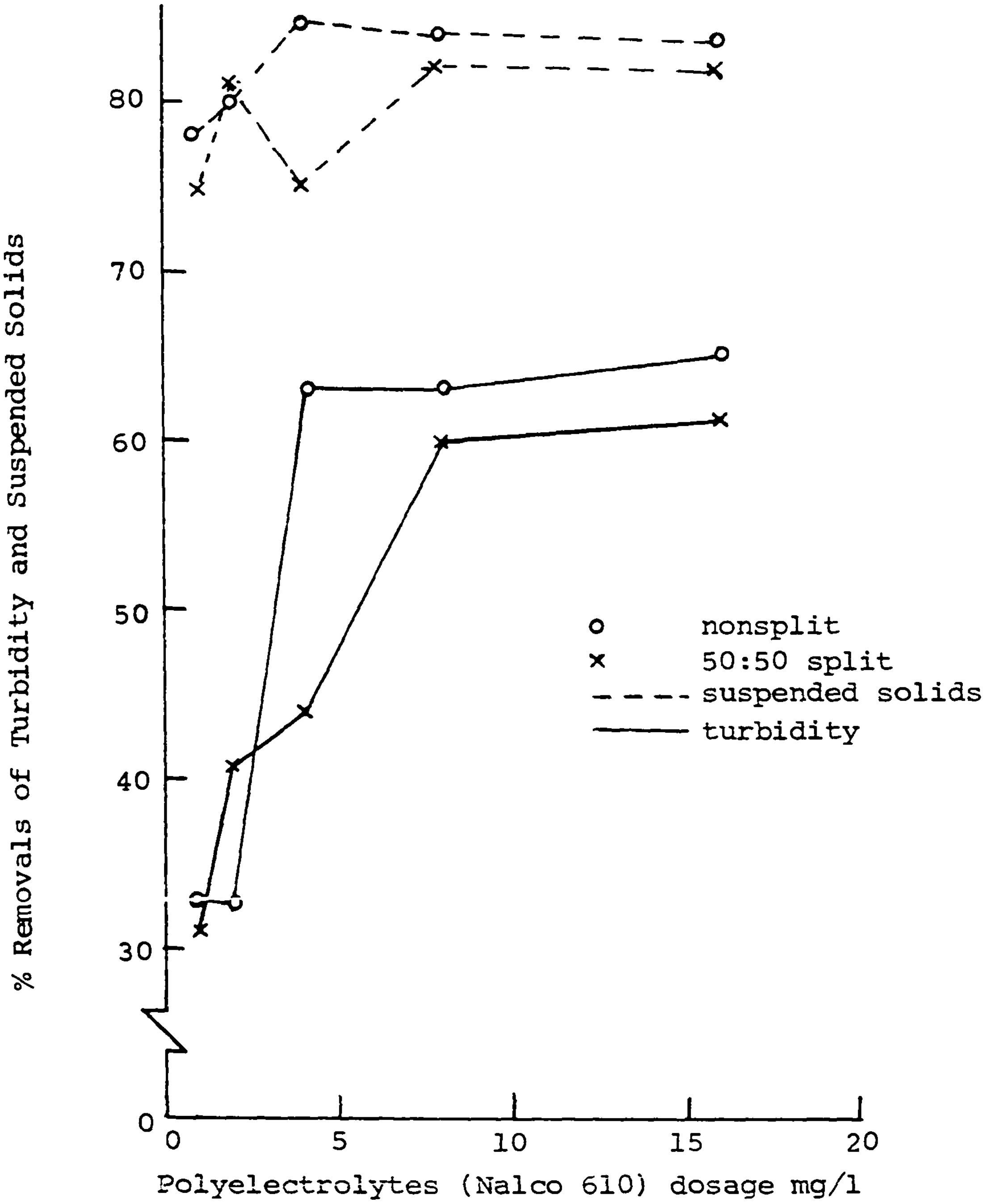

Figure 20. Plots of residual suspended solids and turbidity versus dosage of the polyelectrolyte, Nalco 610, for nonsplit and 50:50 split. Run No. 2-02-72, Boone's raw sewage

Table 9. Residual suspended solids and turbidity-values of Ames primary effluent, coagulated with the polyelectrolyte Nalco 610--a comparison between nonsplit and 50:50 split

Nalco 610 Dosage (mg/l)	Nonsplit			50:50 Split		
	Before (ave.)	After	% Rem.	Before (ave.)	After	% Rem.
Run No. 2-11-72						
			Turbidity			
0	37	26	29.8	27	21	43.4
1	37	23	37.9	37	24	25.2
2	37	24	35.2	37	25	32.4
4	37	23	37.9	37	23	37.9
8	37	21	43.3	37	21	43.3
16	37	--		37	22	40.5
			Suspended Solids (mg/l)			
0	88	43	51.2	88	43	67.0
1	88	42	52.3	88	40	54.5
2	88	43	51.2	88	41	53.3
4	88	40	54.5	88	42	52.3
8	88	35	60.3	88	32	63.6
16	88	30	66.0	88	32	63.6

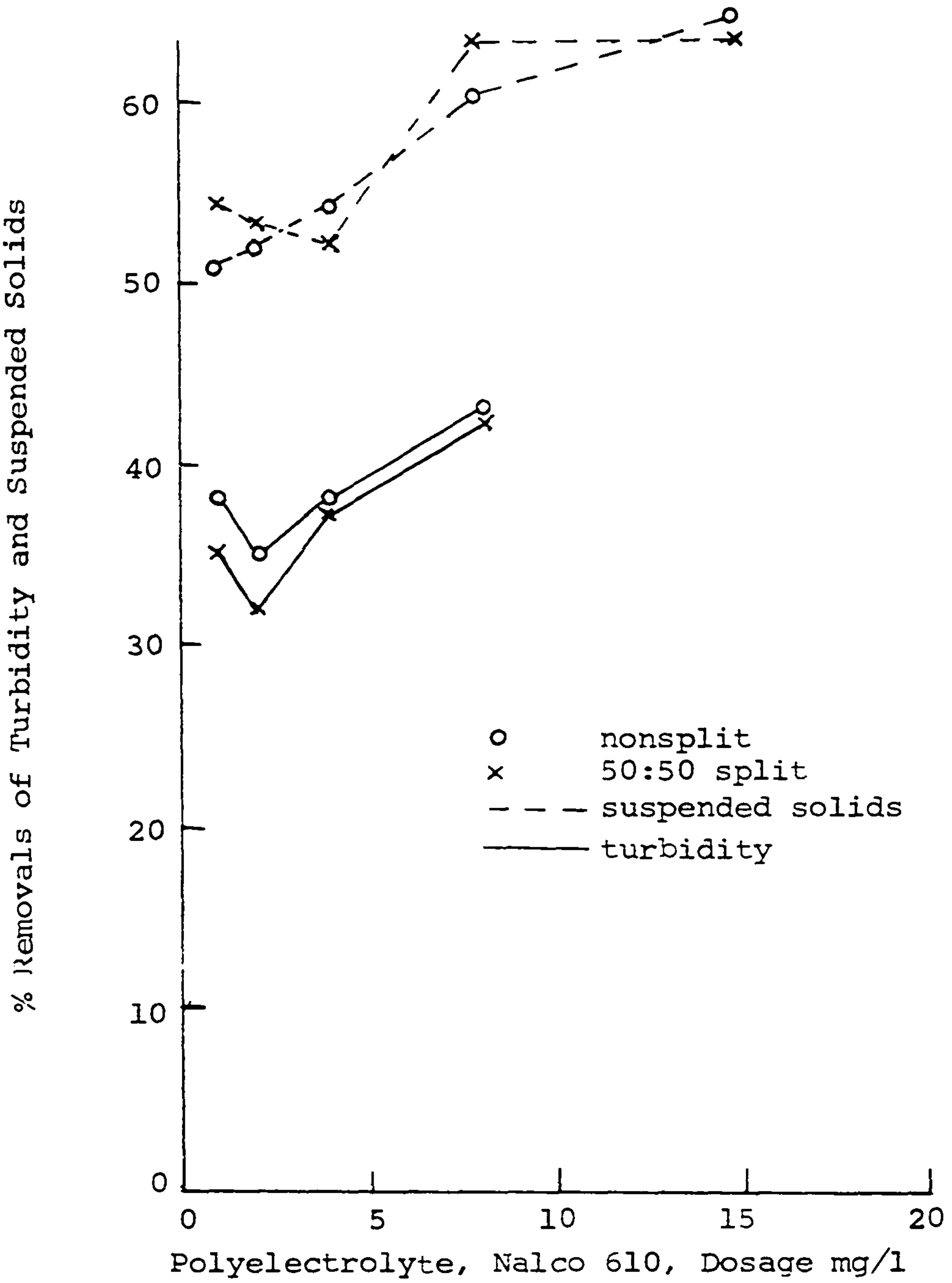

Figure 21. Plots of suspended solids and turbidity removals versus dosage of the polyelectrolyte Nalco 610, for nonsplit and 50:50 split. Run no. 2-11-72, Ames' primary effluent

abandonded to prevent further waste of time along this line of research. However, there was just a little something in the results that gave a little ray of hope. In Run No. 2-05-72, Table 7, as stated in the footnote, one sample rapid mixed at 100 rpm for about 2 1/2 minutes gave results that obviously were a radical improvement from the others in the set. Residual suspended solids went as low as 8 mg/l, a removal of better than 96 percent. It appeared therefore that the second objective of this investigation could be favorably realized, namely to investigate the effect of extended rapid mixing. Furthermore, it was thought that some form of coagulant-aid might be needed to act as a nucleating agent or a weighting material to reduce the amount of floating matter on coagulated samples.

Table 10 summarizes a set of runs on Ames raw sewage involving the use of Nalco 610 and feed-grade Bentonite clay (Nalco 650). One of the runs (identified in the table) was rapid-mixed at undetermined high speed for 4 minutes, then slow-mixed and settled as usual. In general, for a given polyelectrolyte dosage, the higher the clay dosage the better the performance. The sample dosed with 15 mg/l of polyelectrolyte and 10 mg/l clay, and subjected to extensive rapid mixing, reduced residual turbidity from 47 units to 10 and the suspended solids from 450 mg/l to 7 mg/l. This amounts to about 98 percent suspended solids removal.

Table 10. Residual suspended solids and turbidity-values of Ames raw sewage coagulated with the polyelectrolyte, Nalco 610, and Bentonite clay, Nalco 650

Nalco 610 Dosage (mg/l)	Clay Dosage (mg/l)	Turbidity Before (ave.)	Turbidity After	Turbidity % Removal	Suspended Solids Before (ave.)	Suspended Solids After	Suspended Solids % Removal
Run No. 2-16-72		Sample Temp. 17°C					
0	0	47	46	2.1	450	68	84.7
0	0	47	36	23.4	450	43	90.3
0	1	47	37	21.3	450	57	87.4
0	5	47	38	19.2	450	50	88.8
0	10	47	37	21.3	450	49	89.0
0	50	47	35	25.6	450	60	86.7
5	0	47	36	23.4	450	55	87.7
5	1	47	37	21.3	450	57	87.4
5	5	47	37	21.3	450	55	87.7
5	10	47	35	25.6	450	56	87.5
5	50	47	27	42.6	450	41	90.7
1	10	47	37	21.3	450	55	87.7
2	10	47	40	14.9	450	62	86.0
10	10	47	30	36.3	450	43	90.5
15[a]	10	47	10	78.0	450	7	98.3
settle only		47	46	2.1	450	70	84.5

[a] With this is mg/l Nalco 610 and 10 mg/l clay, rapid mixing for about 4 minutes caused turbidity to be removed down to 10 units, and percent suspended solids removal increased to 98 percent. Once again the potential usefulness of extended period of rapid mixing is pointed up.

Table 11 gives the results of runs in which time of rapid mix was varied, and Figure 22 represents the graphical illustration. From this figure it is clear that extended periods of rapid mixing holds good promise. In the runs summarized in this table and the one before it the rapid mixing unit employed was a one-inch curve bladed laboratory mixer. No facilities were immediately available to determine the speed or the velocity gradient of mix. This is the reason why phase II of this study becomes extremely important. In phase II the speed of rotation, the torque input, and consequently, the velocity gradient were determined. Nevertheless, the same speed was used in the run graphed in Figure 22.

Table 12 represents an attempt to still test the dosing-technique theory with extensive rapid mixing. But, as Figure 23 shows, the conventional (nonsplit) method performs at least as well as the 50:50 split method.

4. A capsular summary of phase I results

Based on all the data collected during this phase of the study, the following conclusions can be drawn:

1. The traditional rapid mixing, namely mixing the chemical into the dispersion at about 100 rpm for a short period of one-minute or less will not considerably accomplish good removals of turbidity or suspended solids when a domestic sewage such as that of the city of Ames is coagulated with a

Table 11. Effects of times of rapid mixing on turbidity and suspended solids removal on Ames' raw sewage coagulated with the polyelectrolyte Nalco 610

Description of Run				Turbidity			Suspended Solids mg/l		
Nalco 610 Dosage (mg/l)	Time of Rapid Mix min.	Time of Slow Mix min.	Time Settle min.	Before (ave.)	After	% Rem.	Before (ave.)	After	% Rem.
Run No. 2-17-72			Sample Temperature = $17^{\circ}C$						
0	0	10	30	65	44	32.4	275	52	81.7
0	1	10	30	65	35	46.2	275	35	88.0
0	2	10	30	65	36	44.7	275	40	86.2
0	4	10	30	65	35	46.2	275	37	87.3
0	8	10	30	65	36	44.7	275	33	88.7
5	1	10	30	65	29	55.5	275	26	91.3
5	2	10	30	65	27	58.5	275	22	92.7
5	4	10	30	65	16	75.4	275	6	98.6
5	8	10	30	65	15	77.0	275	13	96.1
10	1	10	30	65	20	69.4	275	10	97.2
10	2	10	30	65	16	75.4	275	2	99.4
10	4	10	30	65	--	--	275	3	99.0
10	8	10	30	65	9	86.3	275	0	99.99+
5	4 split flow	10	30	65	23	64.7	275	19	93.0
10	4 split flow	10	30	65	23	64.7	275	28	90.0

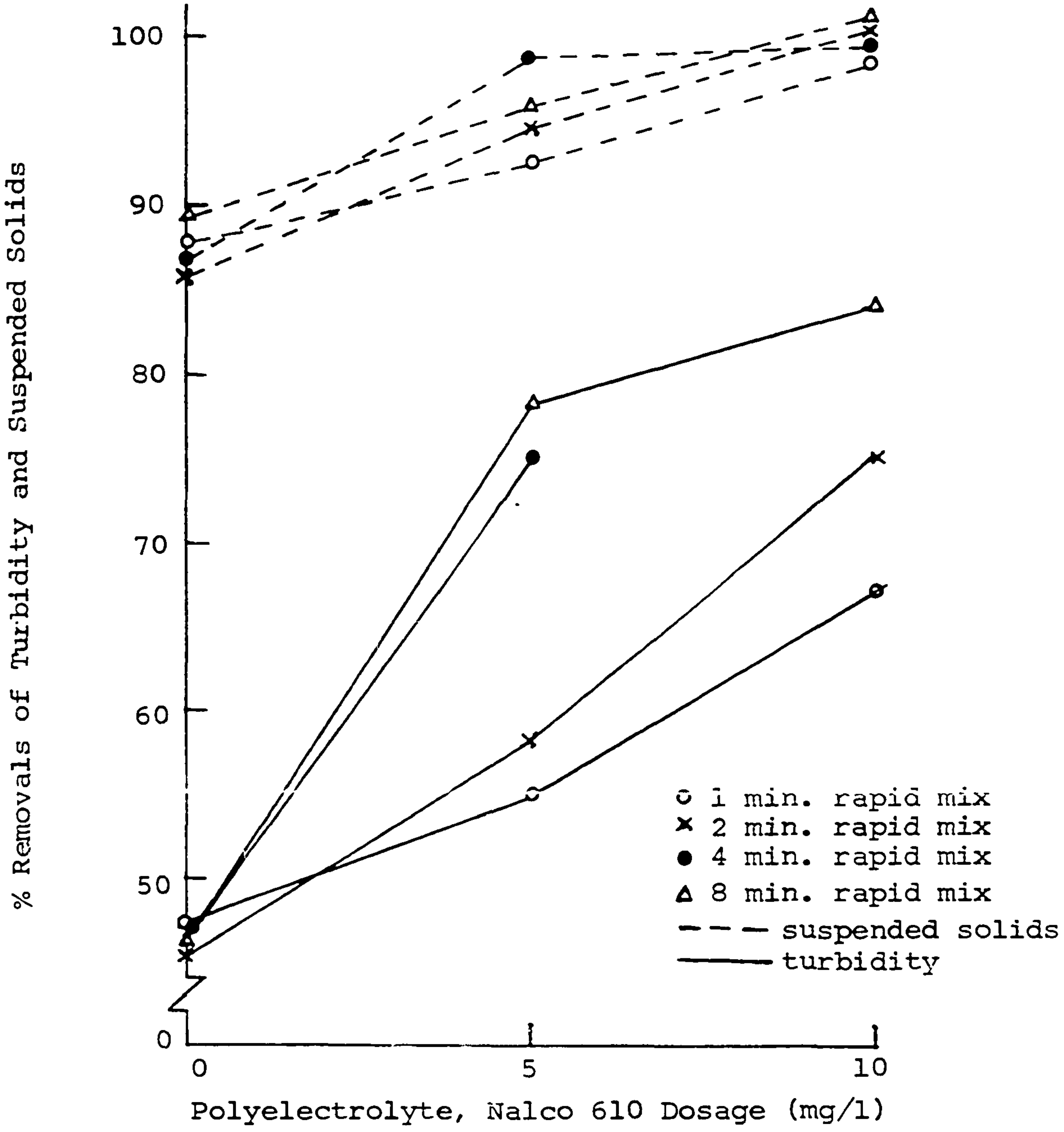

Figure 22. Plots of turbidity and suspended solids removals versus dosage of Nalco 610 for varying times of rapid mix. Run No. 2-17-72, Ames' raw sewage

Table 12. Turbidity and suspended solids removals on Ames' raw sewage for a rapid mix period of 4 minutes and varying dosages of Nalco 610 polyelectrolytes--a comparison between nonsplit and 50:50 split

Description of Run				Turbidity			Suspended Solids mg/l		
Nalco 110 Dosage (mg/l)	Time of Rapid Mix min.	Time of Slow Mix min.	Time Settle min.	Before (ave.)	After	% Rem.	Before (ave.)	After	% Rem.
Run No. 2-18-72			Sample Temperature = 17°C						
0	0	0	30	65	41	37.0	256	60	76.5
0	4	10	30	65	32	50.7	256	39	84.9
1(NS)[a]	4	10	30	65	30	54.0	256	40	84.5
1(S)[a]	4	10	30	65	28	56.0	256	34	86.7
2(NS)	4	10	30	65	22	66.4	256	36	86.0
2(S)	4	10	30	65	20	69.3	256	24	90.7
4(NS)	4	10	30	65	19	70.6	256	15	94.2
4(S)	4	10	30	65	18	72.5	256	19	92.8
8(NS)	4	10	30	65	14	78.5	256	2	99.0
8(S)	4	10	30	65	16	75.5	256	10	96.0
16(NS)	4	10	30	65	19	70.6	256	13	95.0
16(S)	4	10	30	65	21	67.8	256	25	90.2

[a] NS represents nonsplit, and S represents 50:50 split flow.

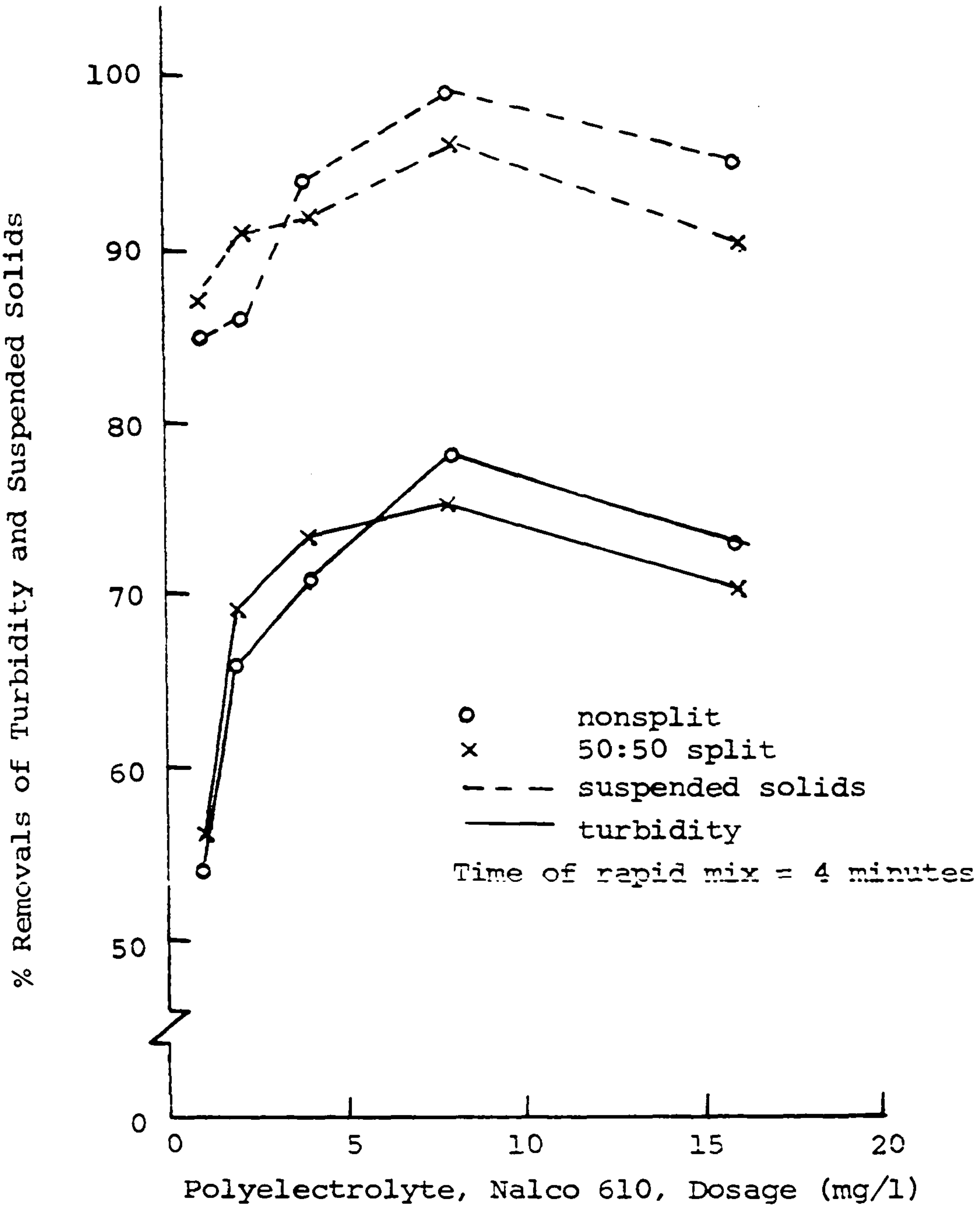

Figure 23. Percent removals versus dosage of Nalco 610 for 4 minutes rapid mix. Run No. 2-18-72, Ames' raw sewage

cationic polyelectrolyte. Nonionic or anionic polyelectroltyes accomplish even less, as preliminary tests indicate.

2. Some form of prolonged high energy rapid mixing appears to hold good promise.
3. It may be necessary to use a nucleating agent, such as bentonite clay, in addition to extensive rapid mixing to improve clarification.
4. The contention that by dosing a portion of the sewage volume and later mixing it with the undosed portion would reduce the dosage of polyelectrolyte required to reach optimum performance is not supported.

C. Experimental Investigations--Phase II

1. Materials

The materials used in this phase of the study are essentially the same as in phase I, namely, polyelectrolytes Nalco 610 and Hercofloc 810; the raw sewage and the primary effluent of Ames' water pollution control plant; Bentonite clay (Nalco 650). In addition, some laboratory-grade aluminum sulfate, and sodium aluminate (Nalco 680) were used as coagulant aids.

2. Apparatus

While the results of phase I pointed up the potential usefulness of high-energy mixing, energy quantities could not be determined. Phase II was intended to overcome this shortcoming. Specifically, facilities were required which would give the desired mixing, with an opportunity to determine the speed of mixing and the torque, from which velocity gradients could be calculated. Accordingly, a Master Servodyne[1] was purchased. With this machine both speed and torque-input in a mixing operation could be read off directly. Furthermore, in order to produce torques of measurable magnitudes, larger volumes of sewage samples were necessary. Fifteen-gallon capacity heavy-duty polyethylene tanks were purchased, suitable for holding at least 10-gallon samples subjected to violent mixing. Other items used during phase I, namely turbidimeter, laboratory jar test equipment, and so on, were also used in this phase of the study.

a. Calibration of the Master Servodyne The Master Servodyne has two dials, one indicating the speed of mixing in rpm, capable of indicating speeds from 0 to 3,000 rpm; the second dial is a torque indicator in millivolts. The procedures and factors for converting millivolts of torque to in-lb were supplied by the manufacturer. It was necessary

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[1] Product of Cole-Parmer Instrument and Equipment Company, Niles, Illinois.

at the initial stage of the study to express velocity gradients in terms of speed (N) and torque (T).

From the relation discussed earlier, namely,

$$G = \left(\frac{2\pi NT}{60V\mu}\right)^{1/2}$$

we obtain

$$NT = \frac{60\mu VG^2}{2\pi} \quad .$$

When

V = 10 gallons or 1.33 ft^3;

viscosity μ at 20°C = $2.1 \times 10^{-5} \frac{\text{lb-sec}}{\text{ft}^2}$.

Based on these conditions, the values of NT corresponding to selected G-values were calculated, and shown in Table 13, where N is expressed in rpm and T is in in-lb. Figure 24 plots speed against torque in millivolts for varying G-values, such that the product of N and the corresponding T for each value gives the value in Table 13. Preliminary tests were then made on a 10-gallon water sample, impeller sizes, to determine torques readings obtained for different speed settings. These were superimposed on Figure 24 as shown in Figure 25. The points of intersection of the two sets of curves give the various combinations of N and T that would give the desired G-values. Thus, to mix at a G-value of 400 sec^{-1}, using the 3.1 inch diameter impeller on a

Table 13. Products of speed, N (rpm) and torque, T (in-lb) corresponding to various velocity gradient values

G, sec^{-1}	NT
1000	3144
800	2016
600	1132
500	785
400	504
200	126
100	31.2
50	7.8
25	1.92

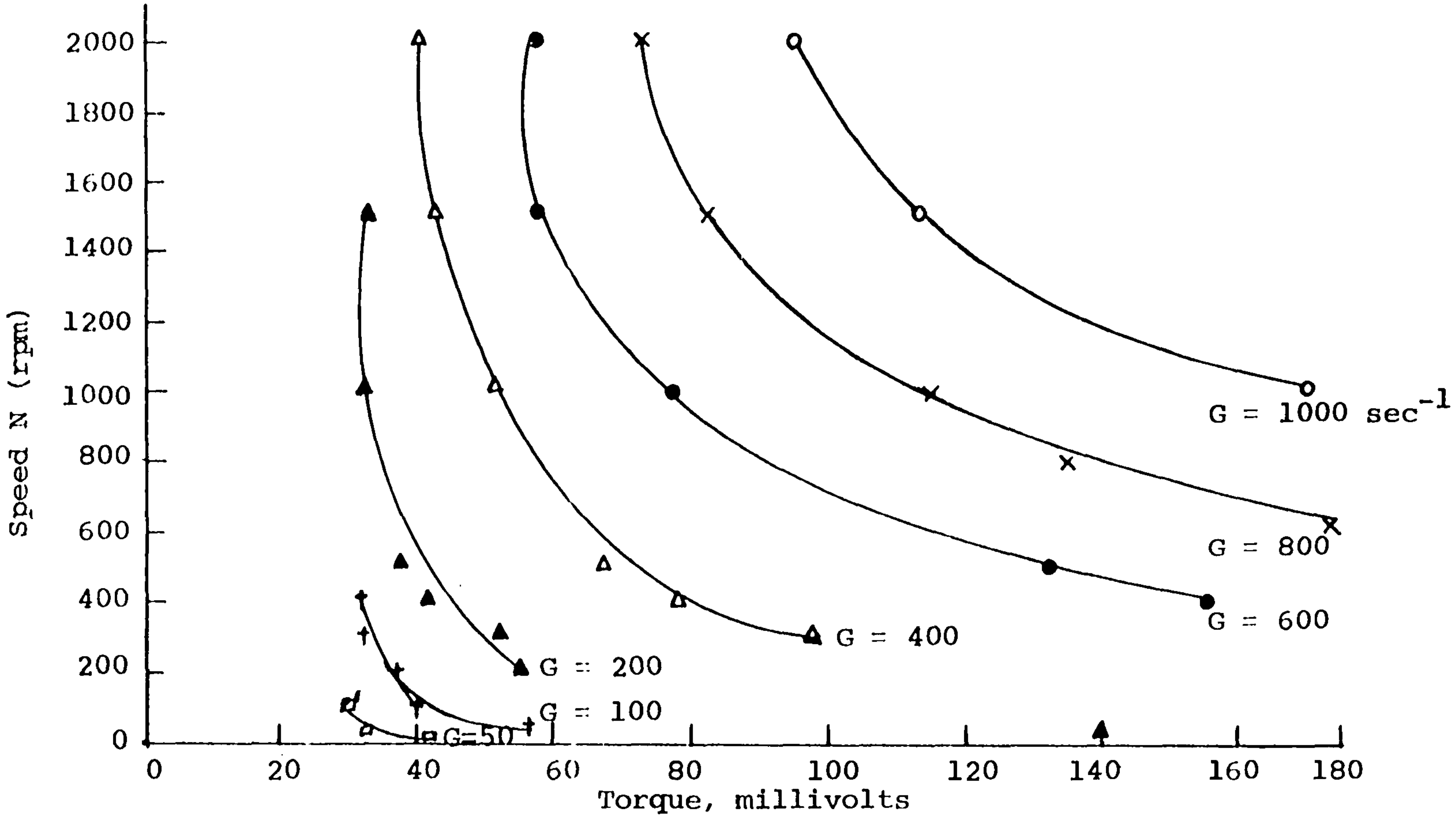

Figure 24. A plot of N (rpm) versus torque (millivolts) for varying velocity gradients

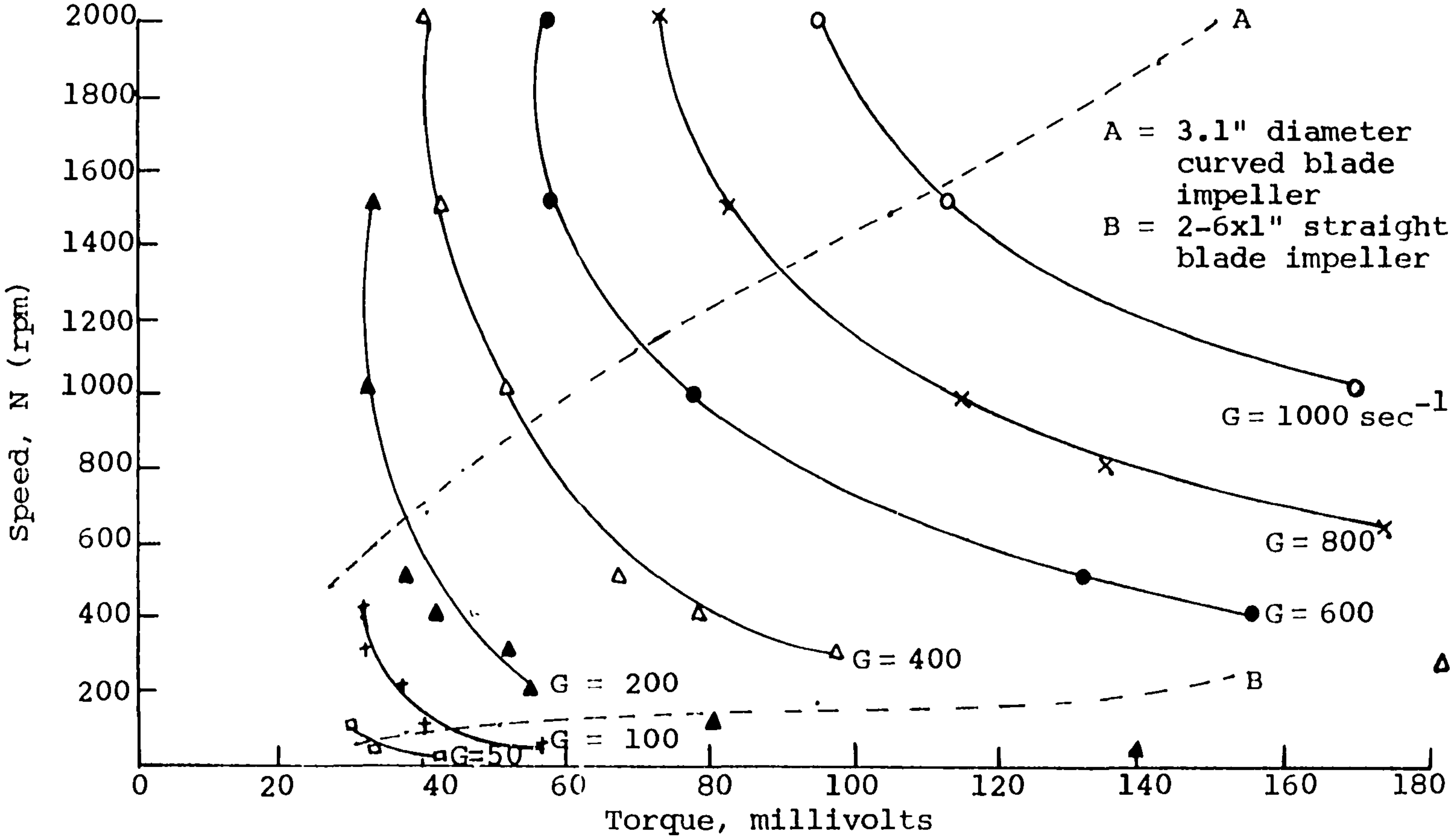

Figure 25. A calibration curve for the Master Servodyne determining N, and T corresponding to different velocity gradients

10-gallon sample, the speed should be set on 960 rpm, and the torque-meter would automatically read about 49 millivolts. The torque-limiter knob on the Master Servodyne could be used to make slight adjustments so that exact torque reading would be achieved, corresponding to the speed for a selected G-value.

3. Sampling procedure

The study was carried out at the sewage plant for two main reasons. First, at the rate of 10 gallons per sample, and several samples per set of runs, the total quantity of sewage required for each set of runs could not be conveniently hauled from the sewage plant to the laboratory; and, second, by working right there at the plant it was possible to keep an eye on the operational and physical conditions at the plant that could affect the quality of samples drawn. For example, the treatment plant management often had to return a one-mgd flow rate of final effluent to the raw pit during periods of low influent flow. Furthermore, whenever sludge from the primary unit was too thin to be sent into the sludge digester, the operators simply returned the thin sludge into the raw pit. Both of these operational conditions could substantially change the quality of the incoming raw sewage. Physical conditions, basically, have to do with the presence or absence of rainfall. During periods of rainfall, the inflow of waste water into the plant could increase (above normal) due to infiltration. Infiltration usually brings in silt and clay, and when this happens, the characteristics of the sewage may become more hydrophobic than hydrophilic. The response of such a wastewater to coagulation could substantially change. By running the test at the sewage plant, it was possible to observe these operational and physical conditions, and exercise some control on the operational aspects when necessary.

As Figure 12 shows, the rate of flow of sewage to the plant varies during the day. The quality of the incoming sewage is known to vary with the quantity. Thus, unless samples are taken at about the same time from day to day, a source of unnecessary variability could be introduced into the coagulation results obtained. To avoid this variability factor as much as possible, samples for a given set of runs were taken all at once, and at the same time every test day. For this phase of the study, samples were drawn at about 2:30 p.m. each test day. This, of course, would mean that some samples would have to sit around longer than others--a possible source of unidentified errors. A process of randomization, such as described in phase I, was used to temper such errors.

4. Test procedures

As in phase I, a 0.1 percent solution of the cationic polyelectrolyte was prepared each day. One ml of this sample dosed into a liter sample would constitute a one mg/l dosage. For the 10-gallon samples used, therefore, 37.8 ml of the solution would be required to achieve a 1 mg/l dosage. Thus for a dosage of 10 mg/l, for instance, 378 ml of the 0.1 percent solution of polyelectroltye was required for a 10-gallon sample.

A 10-gallon sample in the 15-gallon capacity tank was positioned ready for the run, a 3 inch diameter curved blade impeller was affixed to its motor which in turn was connected to the Master Servodyne. The mixing was started with an appropriate combination of speed and torque readings to provide the desired velocity gradient. The suspension was dosed with appropriate materials, namely, cationic polyelectrolytes Nalco 610, or Hercofloc 810. In cases where clay, sodium aluminate or aluminum sulfate was used to aid the coagulation, the coagulant aid was added first, and the polyelectrolyte was added about 5 seconds later.

While the rapid mixing was going on, 500 ml samples were drawn into 600 ml beakers after 2, 4, 8, 16 minutes, etc. Each was immediately subjected to slow mix on the laboratory jar test stirrer at a blade-speed of 25 rpm. Following 10 minutes of slow mixing, the sample was set aside for quiescent settling and turbidity measurements taken after 5, 10, 15, and 30 minutes of settling. Duplicate and sometimes triplicate beaker samples were used whenever practicable and the mean turbidity values were recorded. The results were often the same and very frequently quite close.

In cases where only one single rapid mix period was to be investigated, 3 beaker samples were drawn out for slow mixing and settling at the end of the rapid mixing period. At the same time, the 3 inch impeller blade in the rapid mix tank was quickly replaced by a 2-6 inch x 1 inch blade and the speed and torque settings were reset to provide a 50 sec^{-1} velocity gradient which constituted slow mixing. The turbidity results of the beaker sample and of the tank sample were often quite close.

5. Results and interpretations

Table 14 summarizes the results of 4 sets of runs involving the coagulation of Ames' primary effluent with 10 mg/l dosage of the cationic polyelectrolyte, Nalco 610. Figures 26, 27, and 28 represent graphical illustrations of the relationships between velocity gradients on the one hand and the period of mixing, on the other, as they affect turbidity removal. In Figure 26, the 200 sec^{-1} velocity gradient consistently gave a lower residual turbidity than G-values of 100, 400, and 600 sec^{-1}. Figure 27 shows that G-values of 200, and 400 perform about the same, both better than G-values of 100 and 600. The residual turbidity units were not less than 15 turbidity-units. The results

Table 14. Effects of velocity gradients and time of rapid mixing on turbidity removal for Ames' primary effluent coagulated with the polyelectrolyte Nalco 610

Time of Rapid Run	t_r	2 min.	4 min.	8 min.	16 min.	24 min.	32 min.
G sec^{-1}	Time Settle min.	Turbidity Units					
Run No. 7-18-72[a]							
100	5	34.0	31.5	25.0	25.0	23.0	22.5
	10	34.0	32.0	29.0	22.0	22.5	22.0
	15	29.0	28.5	28.5	24.0	22.5	22.0
	30	29.0	26.0	23.5	20.0	19.5	--
200	5	28.0	28.0	22.5	21.0	22.0	19.0
	10	29.5	27.0	25.0	23.0	20.5	21.0
	15	27.0	24.0	22.0	20.5	18.5	21.5
	30	28.0	25.0	25.0	20.0	19.0	19.0
400	5	25.5	22.5	24.0	22.5	22.5	21.0
	10	25.0	22.5	24.0	22.5	20.0	22.0
	15	24.0	22.5	21.0	22.5	19.0	22.0
	30	24.0	25.0	24.0	20.5	21.0	21.0
600	5	28.0	26.0	25.0	24.0	23.0	22.0
	10	28.0	25.0	22.0	23.0	21.0	23.0
	15	28.0	25.0	23.0	22.0	20.0	21.5
	30	28.0	25.0	23.0	22.0	21.0	21.0
800	5	30.0	28.5	28.0	29.0	28.0	27.0
	10	27.0	27.0	23.0	22.5	22.0	23.0
	15	29.0	25.0	25.0	20.5	21.0	24.0
	30	27.0	26.0	21.0	20.0	20.0	23.0

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[a] Conditions of run: primary effluent; sample temp. = 22°C; used Nalco 610 10 mg/l; slow mix period of 10 minutes following rapid mix; average original turbidity = 50 units.

Table 14 (Continued)

Time of Rapid Run	t_r	2 min.	4 min.	8 min.	16 min.	24 min.	32 min.
G sec^{-1}	Time Settle min.	Turbidity Units					
Run No. 7-20-72[b]							
100	5	31.0	29.5	27.0	25.0	22.5	22.0
	10	30.0	29.5	27.0	24.0	22.5	21.0
	15	30.0	29.0	26.0	24.0	22.0	21.0
	30	29.0	27.5	25.0	23.0	22.0	21.0
200	5	27.0	25.0	23.5	21.0	20.0	20.0
	10	25.5	24.5	24.0	21.0	20.0	19.0
	15	25.5	24.5	22.5	20.5	19.5	19.0
	30	25.0	22.5	21.0	20.5	19.0	18.5
400	5	30.0	27.5	26.0	24.0	22.5	22.0
	10	28.0	26.5	25.0	23.5	23.0	21.0
	15	29.0	26.0	26.0	23.0	22.0	22.0
	30	27.5	27.0	25.0	22.5	21.5	21.0
600	5	30.0	27.0	26.5	24.5	25.0	26.0
	10	28.0	26.0	26.0	24.0	25.0	24.5
	15	27.0	25.5	25.0	24.0	23.0	24.0
	30	26.5	26.0	25.0	24.0	22.5	23.0
Run No. 7-21-72[c]							
100	5	29.0	25.5	23.5	20.5	19.5	19.0
	10	27.5	25.0	23.0	20.0	19.0	18.0
	15	27.5	25.0	23.0	20.0	19.0	18.0
	30	26.0	24.0	22.5	20.0	19.0	19.0
200	5	23.5	22.0	19.5	18.5	16.0	16.0
	10	22.5	21.0	19.5	17.5	16.0	15.5
	15	23.0	20.5	19.5	17.5	16.0	15.0
	30	23.0	20.5	19.5	16.0	16.0	16.0
400	5	22.0	20.0	18.0	16.0	16.0	15.5
	10	22.0	19.5	18.0	16.0	15.5	15.5
	15	22.0	19.5	19.0	missed	15.5	15.5
	30	22.0	20.0	18.0	missed	15.5	15.0

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[b] Conditions of run: primary effluent; sample temperature = 24°C; Nalco 610 10 mg/l; slow mix 10 minutes; average original turbidity = 52 units.

[c] Conditions of run: primary effluent; sample temperature = 25°C; Nalco 610 10 mg/l; slow mix 10 minutes; average original turbidity = 50 units.

Table 14 (Continued)

Time of Rapid Run	t_r	2 min.	4 min.	8 min.	16 min.	24 min	32 min.
G $\sec^{-1}$	Time Settle min.	Turbidity Units					
Run No. 7-21-72[c] (continued)							
600	5	22.0	20.0	20.0	19.0	19.0	20.0
	10	22.0	20.0	20.0	18.5	19.0	18.5
	15	21.0	20.0	19.5	18.5	18.0	18.0
	30	21.5	20.0	19.0	18.5	17.5	17.0
Run No. 7-26-72[d]							
100	5	15.0	12.5	11.5	10.0	9.0	8.5
	10	13.5	12.0	11.0	10.0	9.0	8.5
	15	13.0	12.5	11.5	10.0	9.0	7.5
	30	14.0	12.5	12.0	10.0	9.0	7.5
200	5	15.5	12.5	10.0	8.0	7.0	6.0
	10	14.0	12.0	10.0	8.0	7.0	6.0
	15	14.0	12.0	10.0	8.5	7.0	6.0
	30	13.5	11.0	9.5	8.0	6.5	6.0
400	5	11.0	10.0	7.5	5.5	4.5	3.5
	10	11.0	10.0	7.5	5.5	4.5	3.5
	15	10.5	10.0	7.5	5.5	4.5	3.5
	30	10.5	9.5	7.0	5.5	4.25	3.5
600	5	10.5	8.5	6.0	4.5	3.5	3.0
	10	10.5	8.5	6.0	4.5	3.5	3.0
	15	10.5	9.0	6.0	4.5	3.5	3.0
	30	10.5	9.0	6.0	4.0	3.5	3.0
800	5	10.0	7.5	6.0	4.0	3.5	3.0
	10	10.0	7.5	5.5	4.0	3.5	3.0
	15	10.0	7.5	5.5	4.0	3.5	3.0
	30	10.0	7.5	5.5	3.5	3.25	2.75

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[d] Conditions of run: primary effluent; sample temperature = 22°C; Nalco 610 10 mg/l; slow mix perios 10 minutes; average original turbidity = 68 units; 2 1/2 inches of rainfall the previous night.

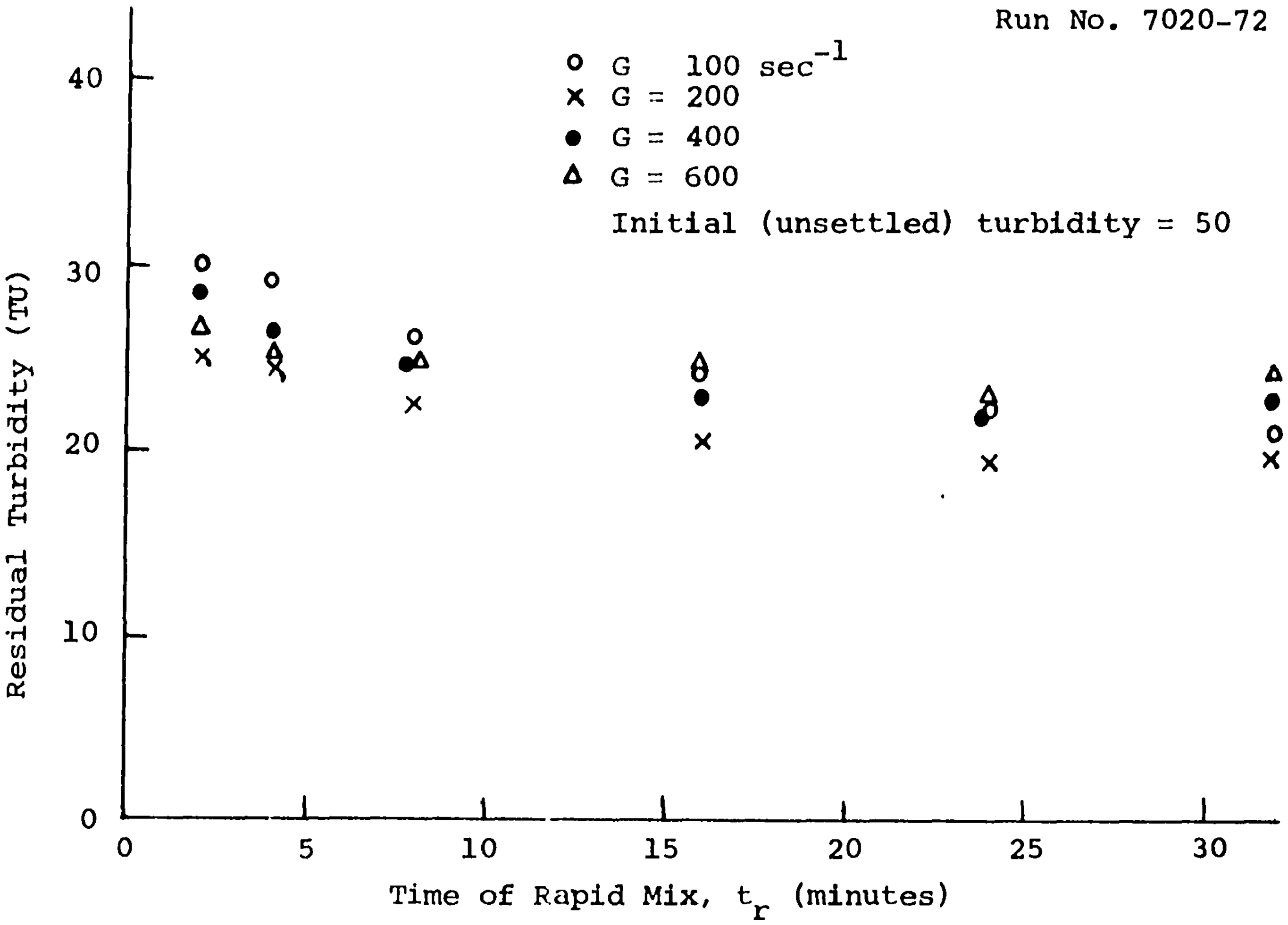

Figure 26. Effects of velocity gradient and time of rapid mix on turbidity removal. Ames primary effluent coagulated with 10 mg/l Nalco 610. Run No. 7-20-72

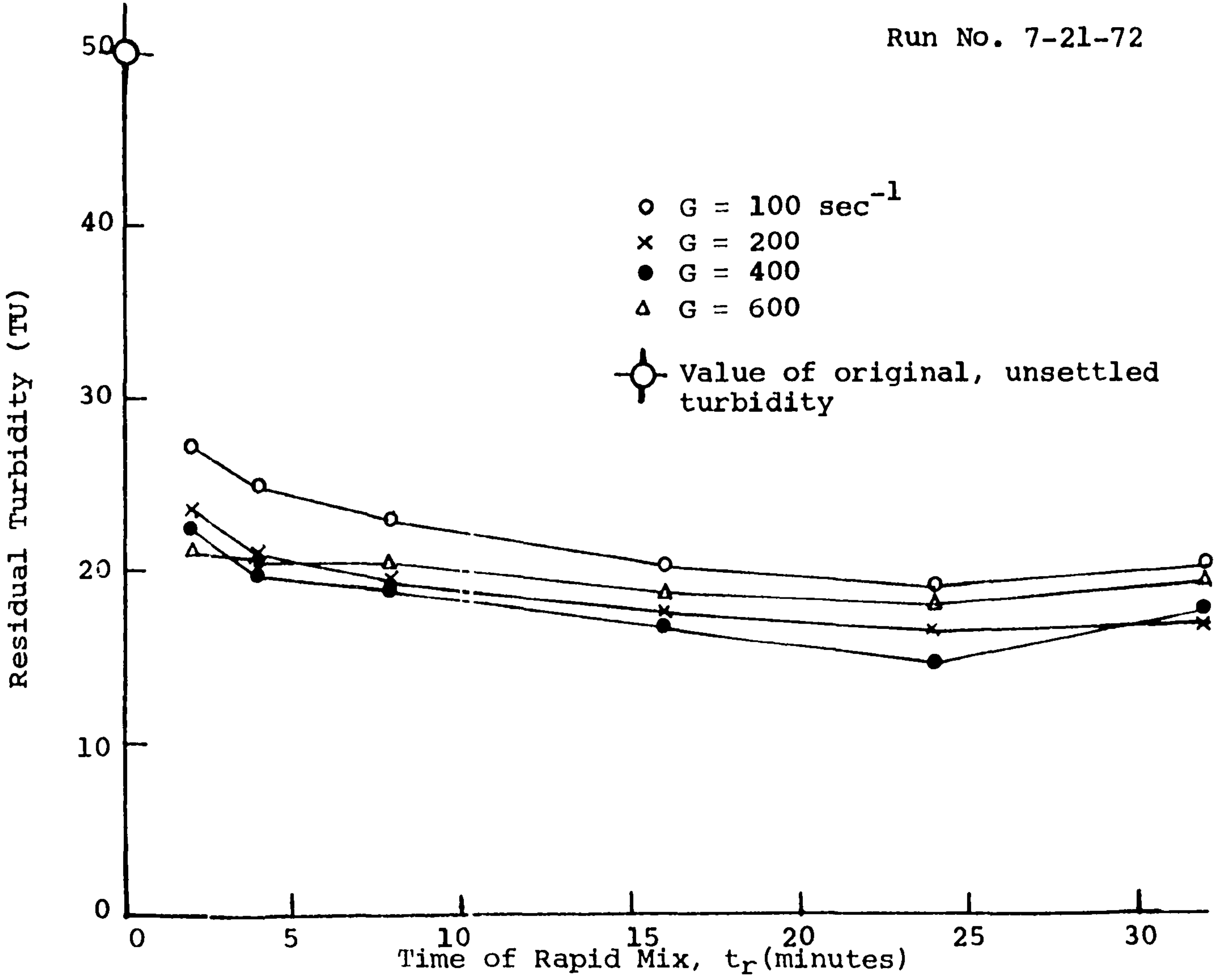

Figure 27. Plots of residual turbidity versus time of rapid mix for Nalco 610 varying G-values. Ames' primary effluent with 10 mg/l, Run No. 7-21-72

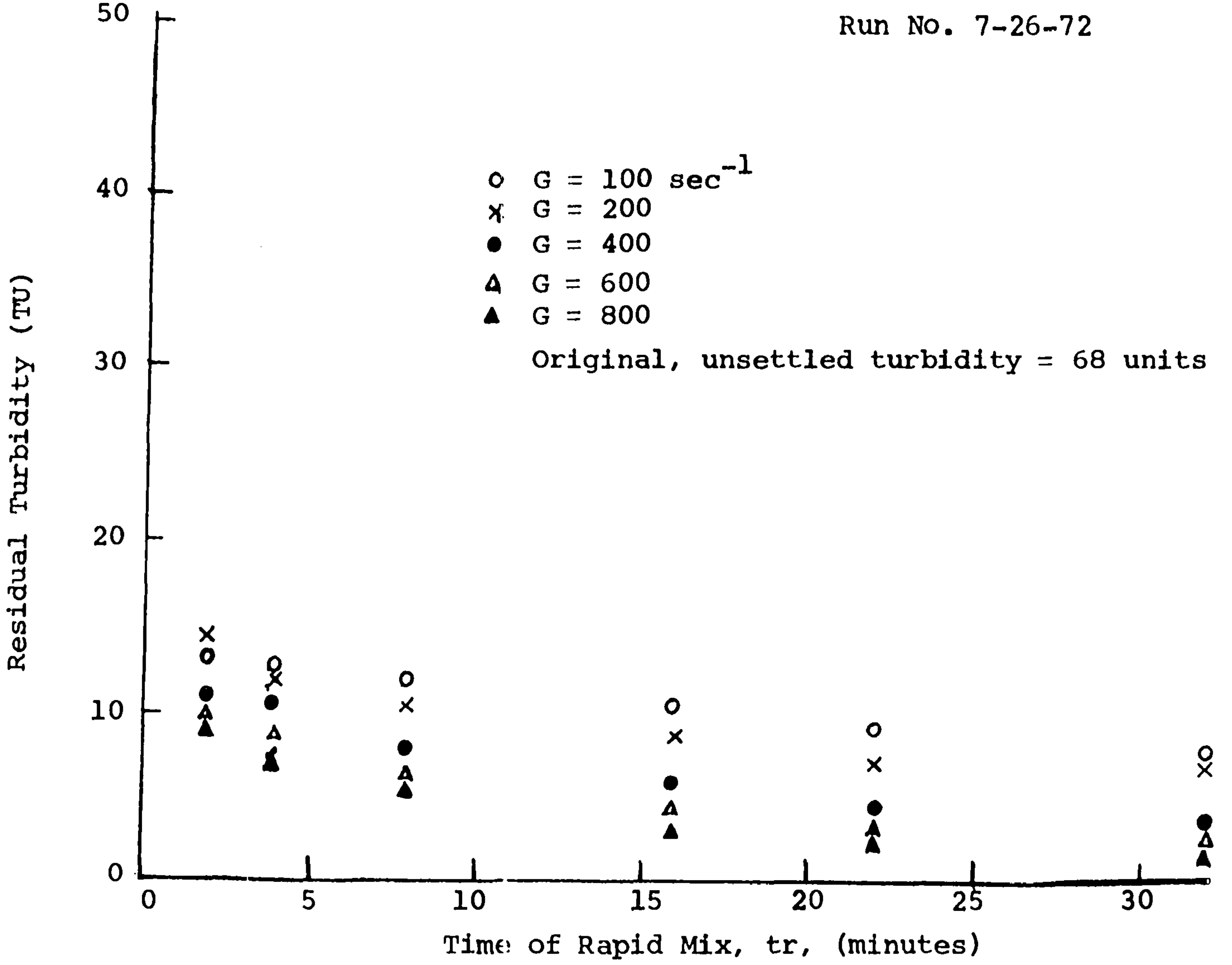

Figure 28. Plots of residual turbidity versus time of rapid mix for varying G-values, Ames' primary effluent with 10 mg/l Nalco 610. Run No. 7-26-72

of run 7-26-72 were dramatically different, however. Here, the best results were produced with highest G-values. In fact, the higher the velocity gradient the better the performance, see Figure 28. Furthermore, turbidity was reduced all the way down to 3 units! What did it? As it happened, there was about 2.5 inches of rain the night before, resulting in infiltration of storm water into the sewage system. Such infiltration waters carry silt and clay, thereby modifying the characteristics of the sewage. The dramatic results of run 7-26-72 must be due to the effect of clay and silt.

If infiltration waters carrying clay and/or silt would improve performance in polyelectrolyte coagulation of sewage, it is possible that by artificially conditioning normal sewage with clay before dosing with the polymer, some consistently low residual turbidities could be achieved. Tables 15 and 16 summarize results of such an undertaking. In run 7-27-72, the velocity gradient was set at 400 sec^{-1}, and clay dosages were varied, the polymer dosage still being 10 mg/l. As shown graphically in Figure 29, the higher the clay dosage from zero to 75 mg/l, the better the turbidity removal. The residual turbidity of the primary effluent was reduced down to a low of 7.5 units from an initial unsettled value of 40 turbidity units. When the clay dosage was held constant at 25 mg/l and the velocity gradients varied, the

Table 15. Effects of clay as a coagulant aid and of time of rapid mixing on turbidity removals for Ames' primary effluent coagulated with Nalco 610 polyelectrolyte

Rapid Mix Time		2 min.	4 min.	8 min.	16 min.	24 min.	32 min.
Clay Dosage	t Settle min.	Turbidity Units					
Run No. 7-27-72[a]							
0.0	55	23.0	21.0	20.0	18.5	19.0	13.0
	10	22.0	21.0	20.0	19.0	17.5	13.0
	15	22.0	20.5	20.0	19.5	17.5	13.0
	30	22.0	20.5	19.5	18.0	17.0	12.5
12.5	5	19.5	18.0	16.5	14.5	14.0	13.5
	10	19.5	18.0	16.0	14.5	13.5	13.5
	15	19.5	17.5	16.0	14.5	14.0	13.0
	30	19.5	17.5	16.0	14.0	13.5	13.0
25	5	15.0	15.0	13.5	12.5	12.0	11.5
	10	15.0	14.5	13.0	12.5	12.0	11.5
	15	15.0	14.5	13.0	12.5	12.0	11.0
	30	15.0	14.5	13.0	12.5	11.5	11.0
50	5	15.0	14.0	13.0	12.0	11.0	10.0
	10	15.0	14.0	12.5	12.0	11.0	10.0
	15	15.0	13.5	12.5	12.0	11.0	10.0
	30	15.0	13.5	12.5	11.5	11.0	10.0
75	5	13.0	12.0	10.5	9.5	8.5	8.0
	10	13.0	12.0	10.5	9.5	8.5	7.5
	15	12.5	12.5	11.0	9.5	8.5	7.5
	30	13.0	12.5	11.0	9.5	8.0	7.5

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[a] Conditions of run: primary effluent; sample temp. = 21°C; Nalco 610 10 mg/l; G for rapid mix 400 sec^{-1}; average original turbidity = 40 units.

Table 15 (Continued)

Rapid Mix Time		2 min.	4 min.	8 min.	16 min.	24 min.	32 min.
G, sec^{-1}	t Settle min.	Turbidity Units					
Run No. 7-28-72[b]							
100	5	20.5	20.0	19.5	16.5	15.5	15.0
	10	20.5	20.0	18.5	16.5	15.5	15.0
	15	20.5	19.5	18.5	16.5	16.0	15.5
	30	19.5	19.0	18.5	16.5	15.0	15.0
200	5	17.0	16.0	15.0	13.5	13.5	12.5
	10	17.0	16.0	15.0	14.0	13.0	13.0
	15	16.5	16.0	15.0	14.0	13.0	13.0
	30	16.0	15.5	14.5	13.5	13.0	13.0
400	5	15.0	15.0	13.5	12.5	12.0	11.5
	10	15.0	14.5	13.0	12.5	12.0	11.5
	15	15.0	14.5	13.0	12.5	12.0	11.0
	30	15.0	14.5	13.0	12.5	11.5	11.0
600	5	14.5	13.0	12.0	10.5	10.5	10.0
	10	14.5	12.5	12.0	10.5	10.5	10.0
	15	14.5	12.5	12.0	11.0	10.5	10.0
	30	14.0	13.0	12.0	11.0	10.0	10.0
800	5	15.0	13.0	12.5	11.5	11.5	12.0
	10	15.0	13.0	12.5	11.5	10.5	11.0
	15	15.0	13.5	12.0	11.0	10.5	10.0
	30	15.0	13.0	12.0	10.5	9.5	9.5
200 no clay	5	22.5	21.0	18.5	17.5	17.0	16.0
	10	22.0	20.0	18.5	17.5	17.0	16.0
	15	21.0	19.5	18.5	17.5	16.5	16.0
	30	21.0	20.0	--	17.0	16.0	15.0

[b] Conditions of run: primary effluent; sample temp. = 21°C; Nalco 610 10 mg/l; clay (Nalco 650) 25 mg/l; average original turbidity 38; slow mix period 10 minutes.

Table 16. Effect of clay as a coagulant-aid, and of time of rapid mixing on turbidity removal for Ames' final effluent coagulated with polyelectrolyte, Nalco 610

Time of Rapid Mix			2 min.	4 min.	8 min.	16 min.	24 min.	32 min.
G	Clay Dosage mg/l	t Settle Clay	Turbidity					
Run No. 7-31-72[a]								
200	0	5	12.5	11.5	12.0	11.5	11.0	11.0
		10	12.0	11.5	11.5	11.5	11.0	11.0
		15	11.5	11.5	11.5	11.5	11.0	11.0
		30	11.0	10.5	11.0	11.0	10.5	10.5
200	25	5	9.50	8.50	8.00	7.50	7.25	7.00
		10	9.00	8.25	8.00	7.50	7.00	7.00
		15	8.50	8.00	8.00	7.50	7.00	7.00
		30	9.00	8.25	7.75	7.50	7.00	7.00
400	25	5	9.00	9.00	7.75	7.50	7.00	6.75
		10	9.00	8.00	8.00	7.25	7.00	6.75
		15	8.75	8.50	8.00	7.50	6.75	6.75
		30	8.50	8.25	8.00	7.50	7.00	6.50
600	25	5	9.00	8.25	6.75	6.25	6.00	6.00
		10	8.50	7.50	7.00	6.00	5.75	6.00
		15	8.50	8.00	7.25	6.50	6.00	5.71
		30	8.50	8.00	7.25	6.00	5.75	5.50
100	25	5	9.50	8.50	8.25	7.50	7.25	6.75
		10	8.50	8.50	8.50	7.50	7.25	6.75
		15	8.50	7.50	8.00	7.50	7.25	6.75
		30	8.25	7.50	7.75	7.25	7.25	6.75

[a] Conditions of run: final effluent; sample temp. = 22°C; Nalco 610 10 mg/l; average original turbidity 12 units; slow mix period 10 minutes.

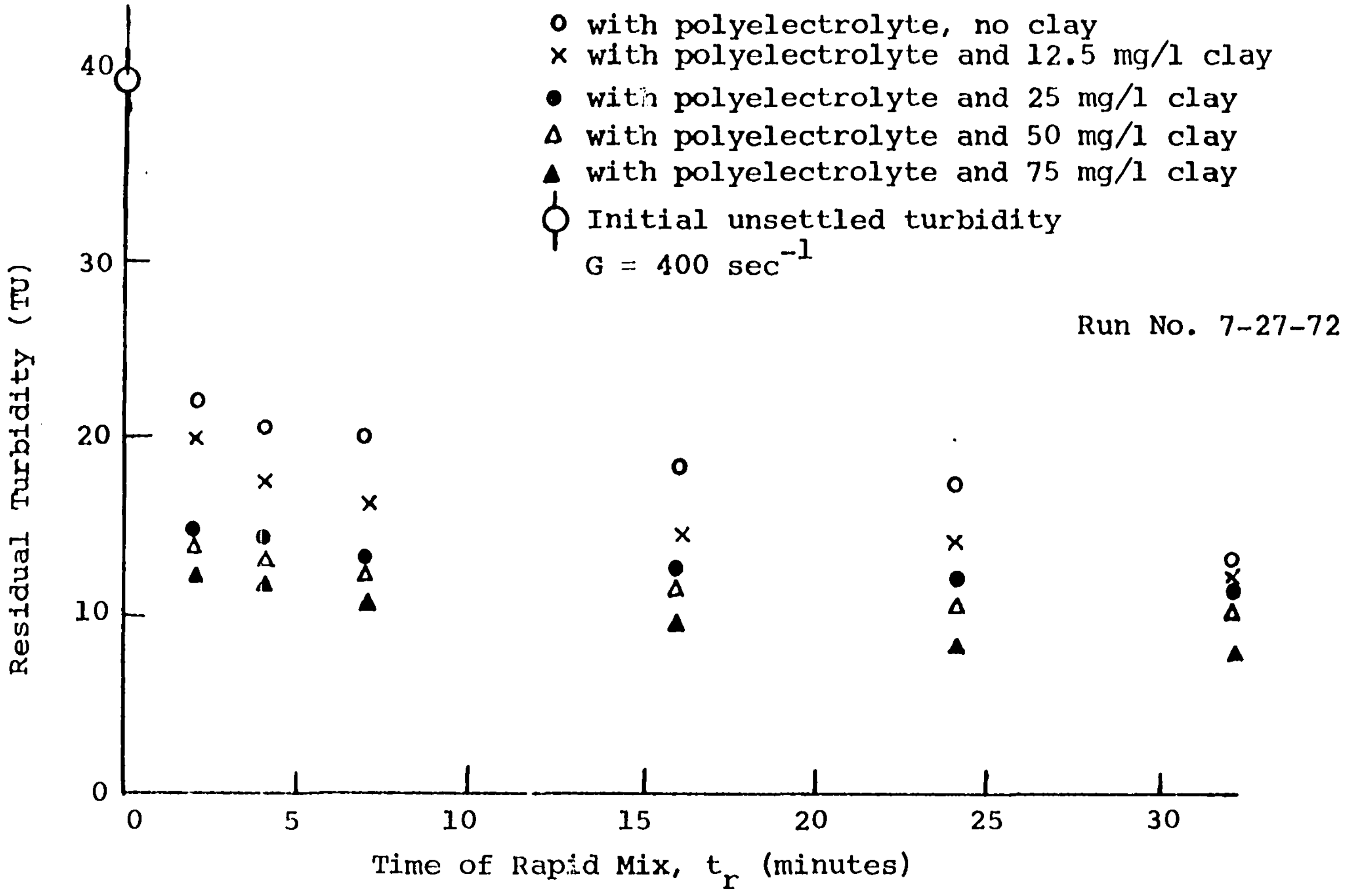

Figure 29. Effects of increasing clay dosage on clarification of Ames' primary effluent coagulated with 10 mg/l Nalco 610. Run No. 7-27-72

results shown in Figure 30 shows that high G-values are desirable. The worst performance was obtained with a G of 200 sec^{-1} when no clay was used. With 25 mg/l of clay used, performances were progressively better with G-values 100, 200, 400, and 600 sec^{-1}. A G-value of 800 sec^{-1} did not improve on the 600 sec^{-1} performance. These same conclusions can be reached in the results of Table 16 involving the coagulation of Ames' final effluent. However, in this case the turbidity was only reduced to 5.5 units from an initial value of 12.

Up to this point then, the results show:

1. For normal sewage primary effluent without clay or silt, dosed with 10 mg/l of the polyelectrolyte Nalco 610 when rapid mixed at a velocity gradient of 200 to 400 sec^{-1}, it resulted in the best turbidity removal.
2. When the sample was naturally or artificially conditioned with clay mineral (Bentonite) the removal effectiveness increased as the velocity gradient increased, although the improvement was no longer substantial after a velocity gradient value of 600 sec^{-1}. The residual turbidity was lower than in case #1 where no clay was involved.
3. With or without clay, and regardless of the G-values used, the longer the time of rapid mix, the better

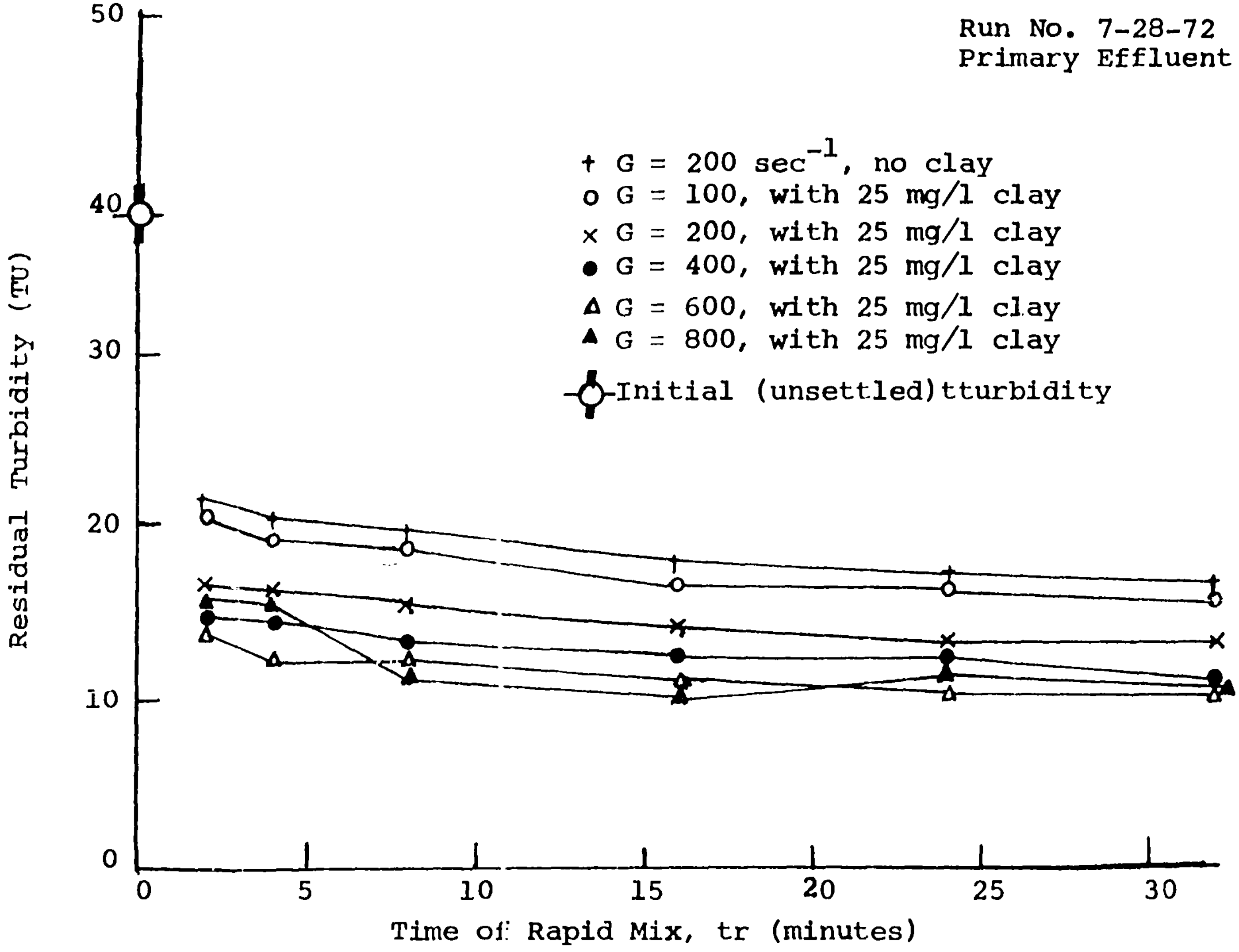

Figure 30. Residual turbidity versus time of rapid mix, for varying G-values. Ames' primary effluent with 10 mg/l Nalco 610 and clay as nucleating agent. Run No. 7-28-72

the removal performance, but the time of rapid mixing need not exceed 16 to 24 minutes.

4. All the results show that settling was essentially over in 10 to 15 minutes.

6. Optimum polymer dosage and dosing technique

Now that the need for an intensive rapid mixing, and for the use of a coagulant aid has been established, the question of the split-flow-dosing technique ought to be reexamined. Furthermore, the optimum polymer dosage established in phase I of this study was about 10 mg/l. The question now is, would the optimum be different when extensive rapid mixing is used?

Table 17 summarizes results of some runs comparing the 50:50 split-flow technique with the nonsplit, for varying dosages of polyelectrolyte, at a fixed G-value of 400 sec^{-1} and with 25 mg/l of clay as a coagulant aid. Figure 31 is a graphical illustration of these results. The optimum polyelectrolyte dosage appears to be around 4 to 5 mg/l, once again, the higher the time of rapid mixing (from 2 to 16 minutes), the better the turbidity removal. The split-flow dosing technique gives the worst result.

Nalco 610 had been used extensively. Would the results be different if another cationic polyelectrolyte were used? Table 18 summarizes the results of treating Ames' raw sewage

Table 17. Split-flow dosing versus nonsplit for Ames' primary effluent coagulated with polyelectrolyte (Nalco 610) and clay using extensive rapid mixing

Time of Rapid Mix		Turbidity Units							
		2 min.	2 min.	4 min.	4 min.	8 min.	8 min.	16 min.	16 min.
Clay Dosage mg/l	Nalco 610 Dosage mg/l								
Run No. 8-01-72[a]									
25	1		19.0		20.0		19.0		18.5
25	2	14.0	19.5	13.0	19.5	11.5	17.5	10.0	15.0
25	4	12.5	17.0	11.5	18.5	10.0	18.0	8.50	16.5
25	8	11.5	16.0	11.0	20.0	10.0	17.0	8.50	16.0
25	16	14.5		14.0		13.0		12.5	
Run No. 8-02-72[b]									
25	2		15.0		15.0		15.0		12.5
25	4	10.5	13.5	10.0	13.0	8.50	14.5	7.00	13.5
25	8	11.5	14.0	9.50	15.5	10.0	15.0	9.00	14.0
25	16	13.0		13.0		12.5		11.5	

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[a] Conditions of run: G = 400 sec^{-1}; primary effluent; sample temp. 21°C; slow mix 10 minutes; settle 15 minutes; average original turbidity 38 units.

[b] Conditions of run: primary effluent; G = 400 sec^{-1}; temperature 22°C; slow mix 10 minutes; settle 15 minutes; average turbidity 35 units.

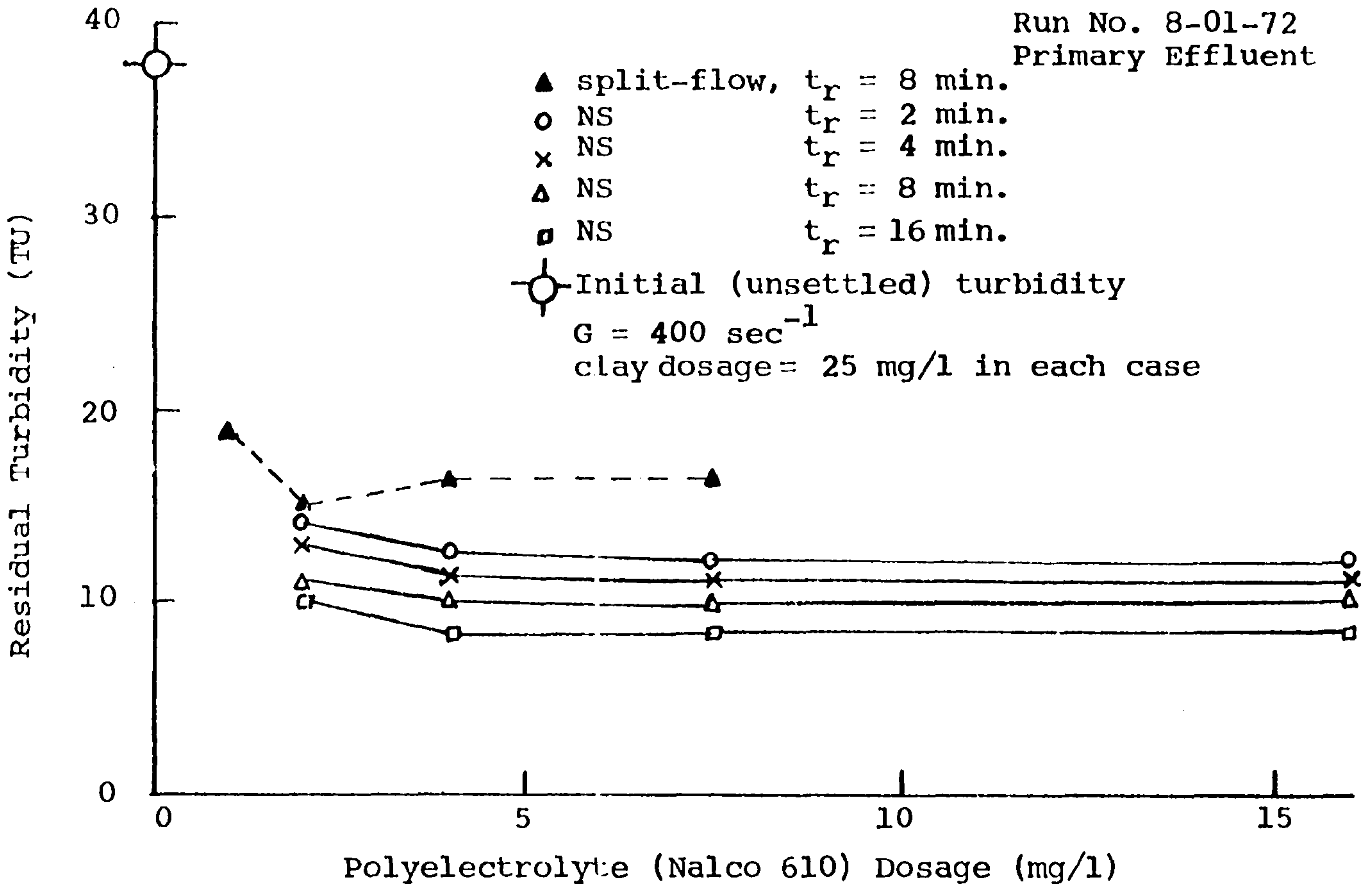

Figure 31. Plots of residual turbidity versus polymer dosage for varying periods of rapid mixing

Table 18. Coagulation of Ames' raw sewage using the polyelectrolyte (Hercofloc 810) with clay, sodium aluminate, or aluminum sulfate as a coagulant aid

Rapid Mix G sec^{-1}	Rapid Mix Time min.	Time Settle min.	Hercofloc 810 Dosage mg/l	Clay Dosage mg/l	Na-Al Dosage mg/l	Alum Dosage mg/l	Turbidity units
Run No. 8-14-72[a]							
500	15 min.	15 min.	2	--	--	--	29.0
			4	--	--	--	20.0
			8	--	--	--	17.5
			16	--	--	--	22.0
			5	25	--	--	14.5
			5	50	--	--	11.0
			5	75	--	--	12.0
			5	--	25	--	9.0
			5	--	50	--	7.5
			5	--	75	--	5.5
Run No. 8-15-72[b]							
500	15 min.	15 min.	5	--	25	--	2.80
			5	--	50	--	2.75
			5	--	75	--	2.35
			10	--	25	--	4.60
			10	--	50	--	4.10
			10	--	75	--	4.50
			5	--	--	25	9.5
			5	--	--	50	3.75
			5	--	--	75	1.25
			5	--	--	--	19.0

[a] Conditions of run: raw sewage; sample temp. 22°C; used Hercofloc 810; slow mix 10 minutes; original turbidity 60 units; settled 2 hours only 37 units.

[b] Conditions of run: raw sewage; temp. 23°C; Hercofloc 810; slow mix 10 minutes; original turbidity 55 units; settled 2 hours only 35 units.

with Hercofloc 810, which preliminary test in phase I had shown to perform more or less similarly. As Figure 32 shows, the optimum dosage is less than 8 mg/l and appears to be around 5 mg/l as is the case with Nalco 610. Using 5 mg/l of Hercofloc 810 together with clay, and then with sodium aluminate, removals are improved, see Figure 33. Again sodium aluminate is a better coagulant-aid than clay. And Figure 34 shows that sodium aluminate and aluminum sulfate perform about the same when about 50 mg/l of each is used with 5 mg/l of Hercofloc 810. It further shows that a dosage of 10 mg/l of the polyelectrolyte does not perform as well as a 5 mg/l dosage.

Table 19 and Figure 35 show that in spite of its usefulness as an aid to cationic polyelectrolyte, sodium aluminate, by itself, does not do a good job of turbidity removal. The figure further reinforces the fact that the aluminate salt is a better coagulant aid than clay. However, where alum salts are used as aids to cationic polymer, the best G-value for rapid mixing should be around 200 sec^{-1} as opposed to the case of clay where higher values of G (about 500 or more) are needed, see Table 20 and Figure 36.

The following statements can now be made about the results of this section:

1. The optimum polymer dosage when extensive mixing is employed is much closer to 5 mg/l than to 10.

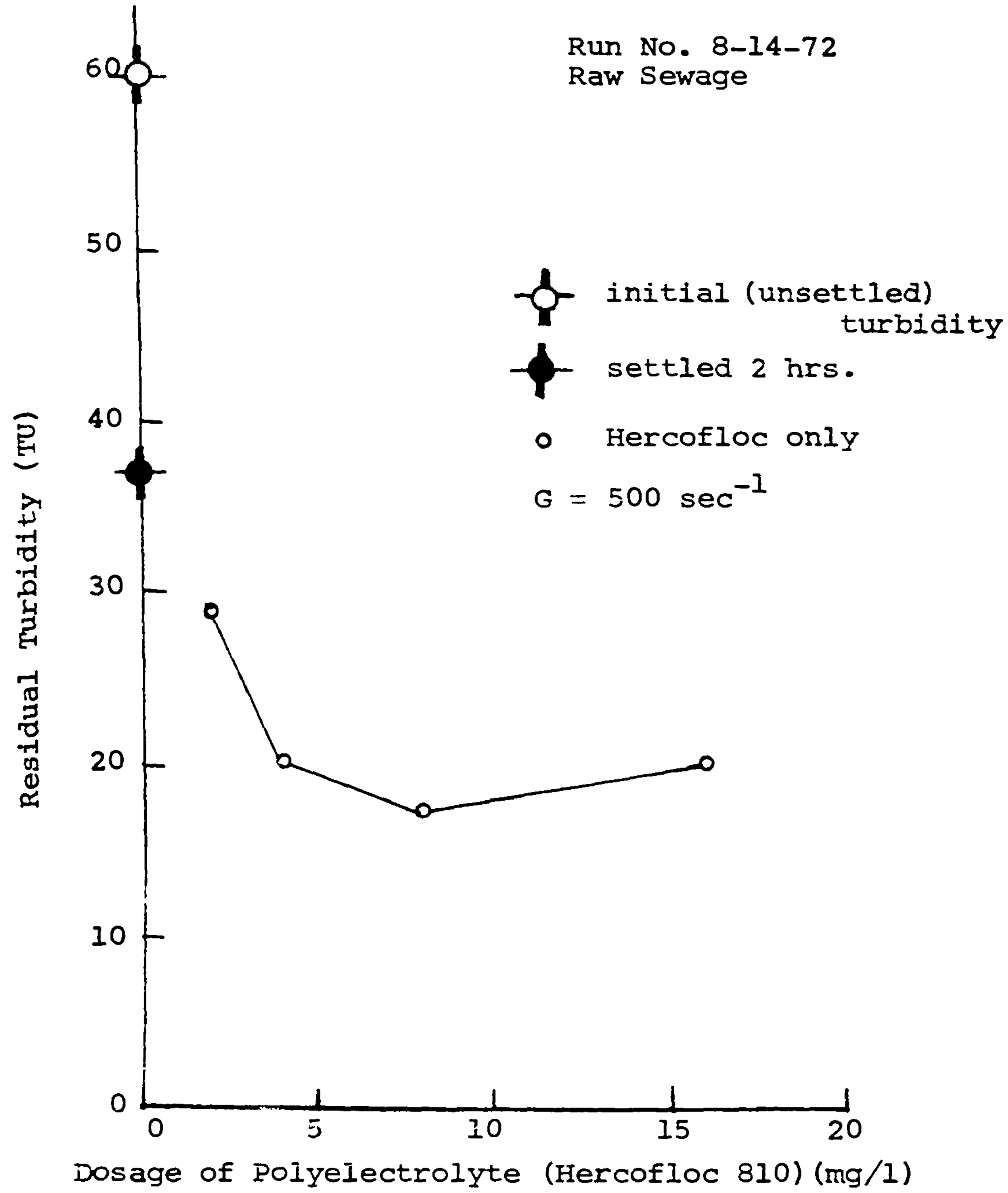

Figure 32. Residual turbidity versus dosage of the polyelectrolyte Hercofloc 810. Ames' raw sewage, Run No. 8-14-72

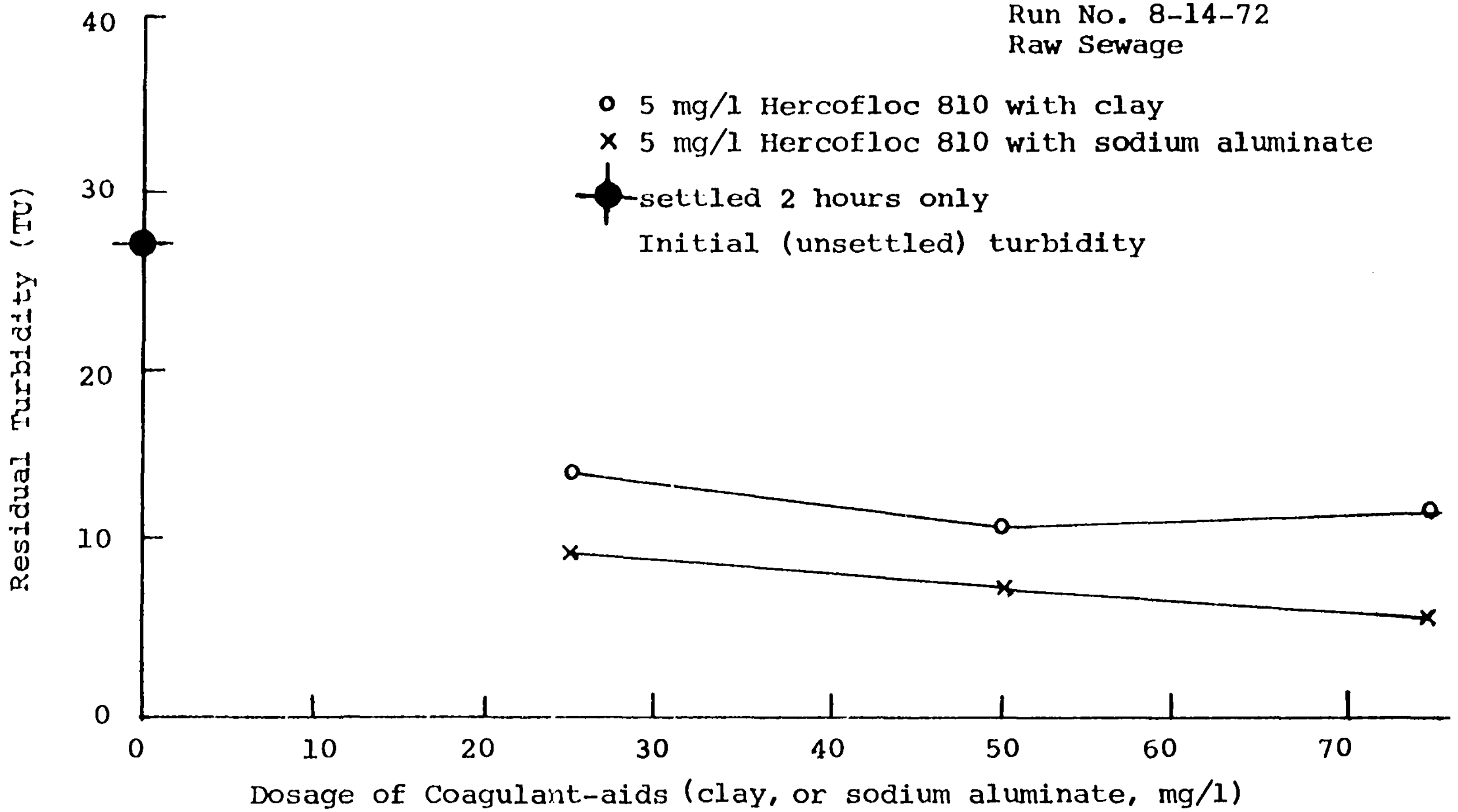

Figure 33. Residual turbidity versus dosages of coagulant-aids. Ames' raw sewage with 5 mg/l Hercofloc 810. Run No. 8-14-72

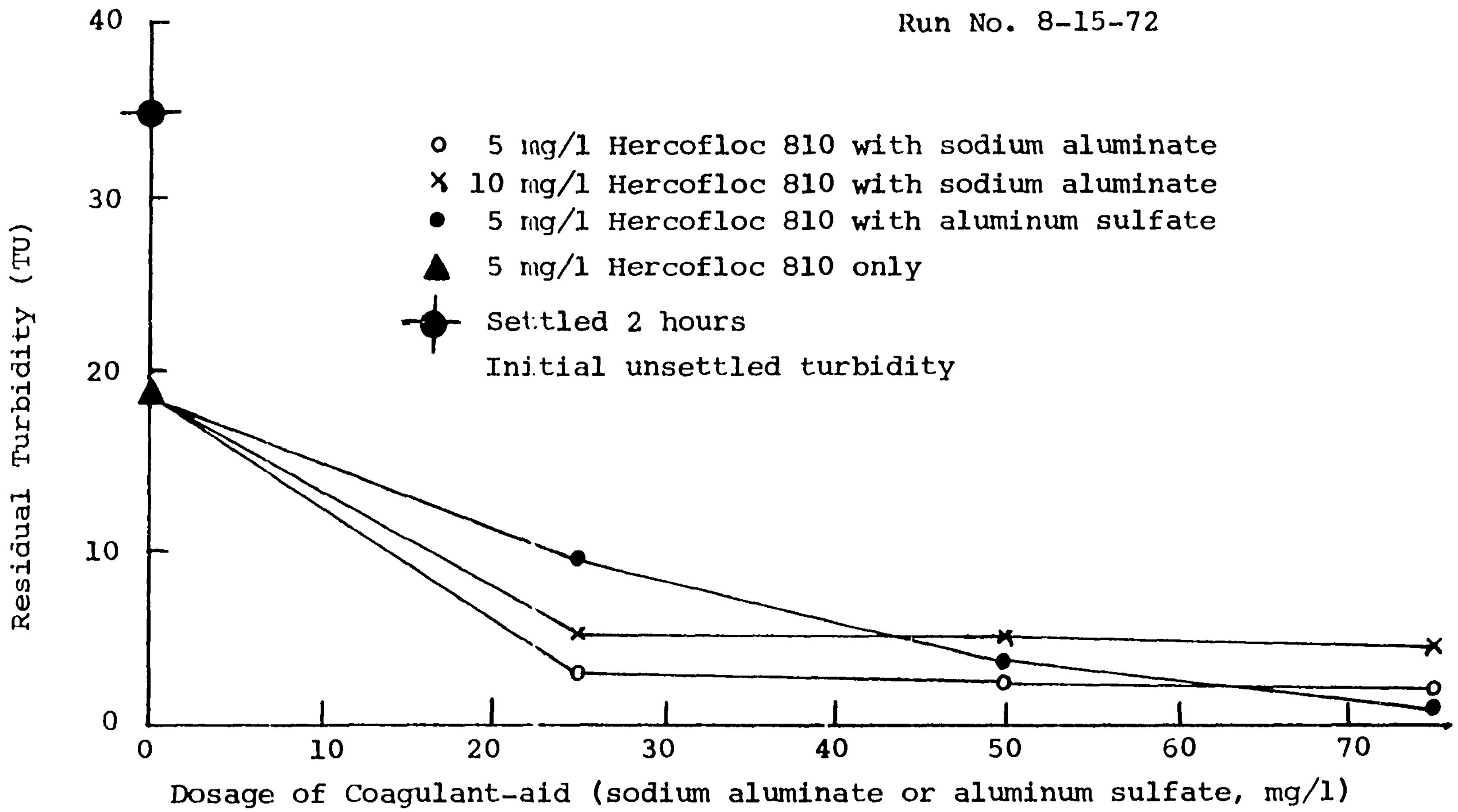

Figure 34. Effects of varying coagulant-aid dosages on turbidity removals. Ames' raw sewage coagulated with Hercofloc 810. Run No. 8-15-72

Table 19. Ames' raw sewage coagulated with polyelectrolyte (Nalco 610) with clay or sodium aluminate as a coagulant-aid

Rapid Mix G sec^{-1}	Rapid Mix Time min.	Time Settle min.	Nalco 610 Dosage mg/l	Clay Dosage mg/l	NaAl Dosage mg/l	Turbidity units
Run No. 8-10-72[a]						
500	15 min.	15 min.	5	25	--	14.0
			5	50	--	10.0
			5	75	--	9.5
			10	25	--	20.0
			10	50	--	18.0
			10	75	--	15.0
			15	25	--	24.0
			15	50	--	20.0
			15	75	--	15.5
Run No. 8-11-72[b]						
500	15 min.	15 min.	--	--	10	30.0
			--	--	20	28.0
			--	--	40	25.0
			--	--	80	17.5
			5	--	0	22.0
			5	--	12.5	15.0
			5	--	25	11.5
			5	--	50	7.0
			5	--	75	9.0
			10	--	25	10.0
			10	--	50	9.0
			10	--	75	10.0
			15	--	25	14.0
			15	--	50	10.5
			15	--	75	10.5

[a] Conditions of run: raw sewage; sample temp. 21°C; used Nalco 610; slow mix 10 minutes; original turbidity 48 units; settled 2 hours, 33 units.

[b] Conditions of run: raw sewage; sample temp. 22°C; used Nalco 610; slow mix 10 minutes; original turbidity 48 units; settled 2 hours, 30 units.

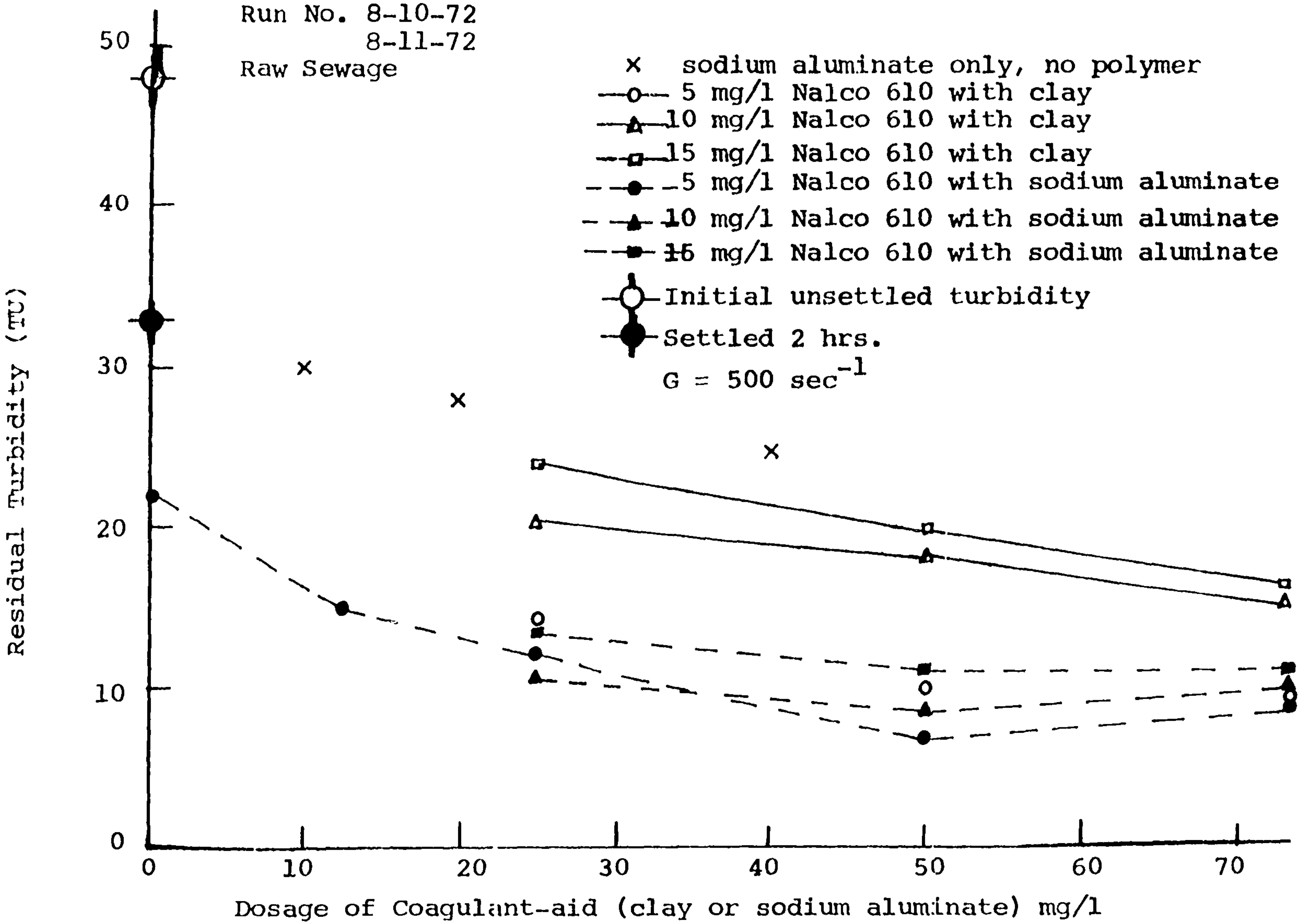

Figure 35. Residual turbidity versus dosage of coagulant-aid (clay or sodium aluminate) Ames' raw sewage with 5 mg/l Nalco 610, Run Nos. 8-10-72, 8-11-72

Table 20. Effects of time of rapid mixing on Ames' raw sewage coagulated at varying G-values

Time of Rapid Mix, Minutes						2	4	8	16	24	32	40	48
G Rapid Mix sec^{-1}	Time Slow Mix min.	Time Settle min.	Nalco 610 Dosage mg/l	Alum Dosage mg/l	Clay Dosage mg/l	Turbidity Units							
Run No. 8-25-72[a]													
100			5	50	--	20.0	18.0	14.5	11.5	9.5	8.5	8.0	7.5
500			5	50	--	15.0	12.5	11.0	10.0	9.5	10.0	11.0	12.0
800	10 min.	15 min.	5	50	--	19.0	16.0	14.5	13.5	14.5	15.5	15.0	15.0
100			5	--	50	35.0	35.0	30.0	26.5	23.5	21.5	20.0	19.5
500			5	--	50	32.5	28.0	23.5	20.5	19.0	19.0	18.0	16.0

[a] Conditions of run: raw sewage; sample temp. 22°C; Nalco 610 used; slow mix 10 minutes; average initial turbidity 70 TU; settled 2 hours 56 TU.

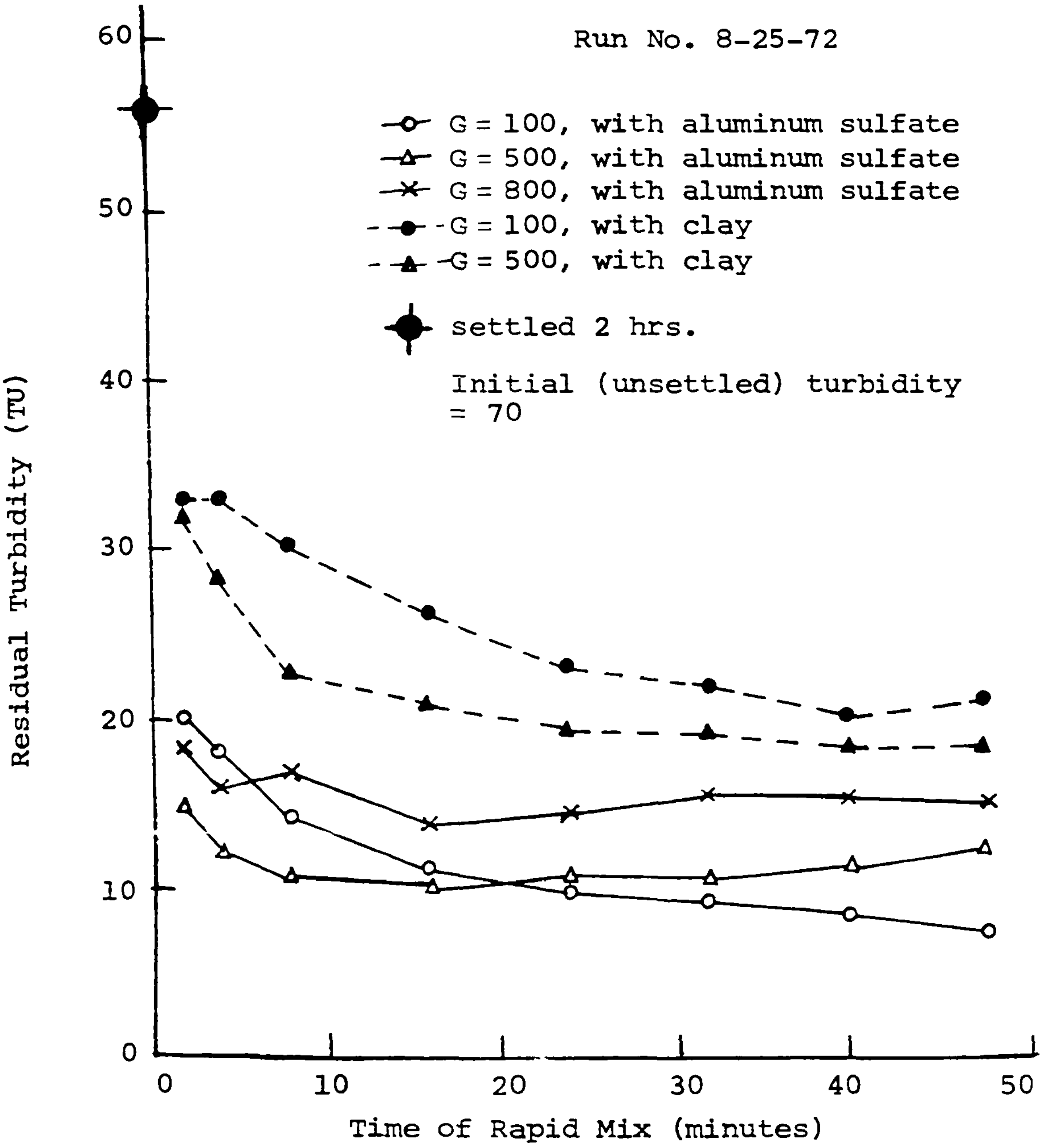

Figure 36. Residual turbidity versus time of rapid mix for varying G-values. Ames' raw sewage with 5 mg/l Nalco 610 with clay or aluminum sulfate as coagulant aid. Run No. 8-25-72

2. The use of a coagulant aid--clay, sodium aluminate, or aluminum sulfate improves turbidity removal.
3. As coagulant aids, sodium aluminate and aluminum sulfate perform about the same, causing better removals than when clay is used, reducing residual turbidity to values much below 10 TU.
4. Twenty-five to 50 mg/l of either the sodium aluminate or aluminum sulfate is about all that is needed to get optimum removals when these materials are used in conjunction with the cationic polyelectrolyte.
5. There is no doubt that coagulation of sewage with cationic polyelectrolytes (especially when a coagulant aid such as clay or aluminum sulfate is used), under extensive rapid mixing, substantially enhances turbidity removal. These plots show turbidities of the raw unsettled wastewater, as well as the turbidities after 2 hours of quiescent settling. The residual turbidities resulting from coagulation all plot substantially below the two hour settling product.

7. The dimensionless quantity Gt

It has been shown conclusively in this study that, for any selected velocity gradient G, the longer the time of rapid mix t, the better the turbidity removal. The product

Gt is often used as a design parameter in designing mixing units. If the dimensionless parameter Gt is to be useful then high G values would effect a turbidity removal in a shorter time than a lower G-value. Specifically, mixing at a G-value of say 400 sec^{-1} for 1 minute should perform about the same as with a G of 100 sec^{-1} for 4 minutes. The results of this study do not support this theory, as can be seen in Tables 22, 23, and 24 and a typical semi-logarithmic plot as shown in Figure 37.

Based on the results of this study, it appears that, while t and G are individually important, their product is not very meaningful as a design parameter. The designer would have to pick a suitable G-value (e.g., about 200 sec^{-1} when an aluminum salt is used in conjunction with a suitable cationic polyelectrolyte, or about 500-600 sec^{-1} when clay is the coagulant aid); and mix for as long a period of time as economy of mixing unit would permit between 5 and 30 minutes, since the longer the time of mixing, the better, in general, the performance.

8. Economics

This study involves a batch, not a continuous-flow process. Therefore, no extensive economic analysis can be made, until a pilot plant study can be made. The optimum dosage picture could change when a continuous flow process

Table 21. The dimensionless quantity Gt corresponding to various G and t values

G, sec^{-1}		100	200	400	500	600	800
Time, t minutes	Time, t seconds	Gt					
2	120	1.2×10^4	2.4×10^4	4.8×10^4	6.0×10^4	7.2×10^4	9.6×10^4
4	240	2.4	4.8	9.6	12.0	14.4	19.2
8	480	4.8	9.6	19.2	24.0	28.8	38.4
15	900	9.0	18.0	36.0	45.0	54.0	72.0
16	960	9.6	19.2	38.4	48.0	57.6	76.8
24	1440	14.4	28.8	57.6	72.0	86.4	115.2
32	1920	19.2	38.4	76.8	96.0	115.2	153.6
40	2400	24.0	48.0	96.0	120.0	144.0	192.0
48	2880	28.8	57.6	115.2	144.0	172.8	230.4

Table 22. Gt-values versus the resulting residual turbidity values, of Run No. 7-21-72

G, sec^{-1}	100	200	400	600
Gt	Residual Turbidity Units			
1.2×10^4	27.5			
2.4	25.0	23.0		
4.8	23.0	20.5	22.0	
7.2				21.0
9.6	20.0	19.5	19.5	
14.4	19.0			20.0
19.2	18.0	17.5	19.0	
28.8		16.0		19.5
38.4		15.0		
57.6			15.5	18.5
76.8			15.5	
86.4				18.0
115.2				18.0

Table 23. Gt-values versus the resulting residual turbidity values, of Run No. 7-28-72

G, sec^{-1}	100	200	200[a]	400	600	800
Gt	Residual Turbidity Units					
1.2×10^4	20.5					
2.4	19.5	16.5	21.0			
4.8	18.5	16.0	19.5	15.0		
7.2					14.5	
9.6	16.5	15.0	18.5	14.5		15.0
14.4	16.0				12.5	
19.2	15.5	14.0	17.5	13.0		13.5
28.8		13.0	16.5		12.0	
36.0						
38.4		13.0	16.0	12.5		12.0
48.0						
54.0						
57.6				12.0	11.0	
72.0						
76.8				11.0		11.0
86.4					10.5	
96.0						
115.2					10.0	10.5
153.6						10.5

[a] No coagulant-aid used for this column.

Table 24. Gt-values versus the resulting residual turbidity values, of Run No. 8-25-72

G, sec^{-1}	With Aluminum Sulfate As Coagulant Aid			With Clay As Coag. Aid	
Gt	100	500	800	100	500
1.2×10^4	20.0			35.0	
2.4	18.0			35.0	
4.8	14.5			30.0	
6.0		15.0			32.5
9.0					
9.6	11.5		19.0	26.5	
12.0		12.5			28.0
14.4	9.5			23.5	
19.2	8.5		16.0	21.5	
24.0	8.0	11.0		20.0	23.5
28.8	7.5			19.5	
38.4		14.5			
48.0		10.0			20.5
72.0		9.5			19.0
76.8			13.5		
96.0		10.0			19.0
115.2			14.5		
120		11.0			18.0
144		12.0			16.0
153.6			15.5		
192.0			15.0		

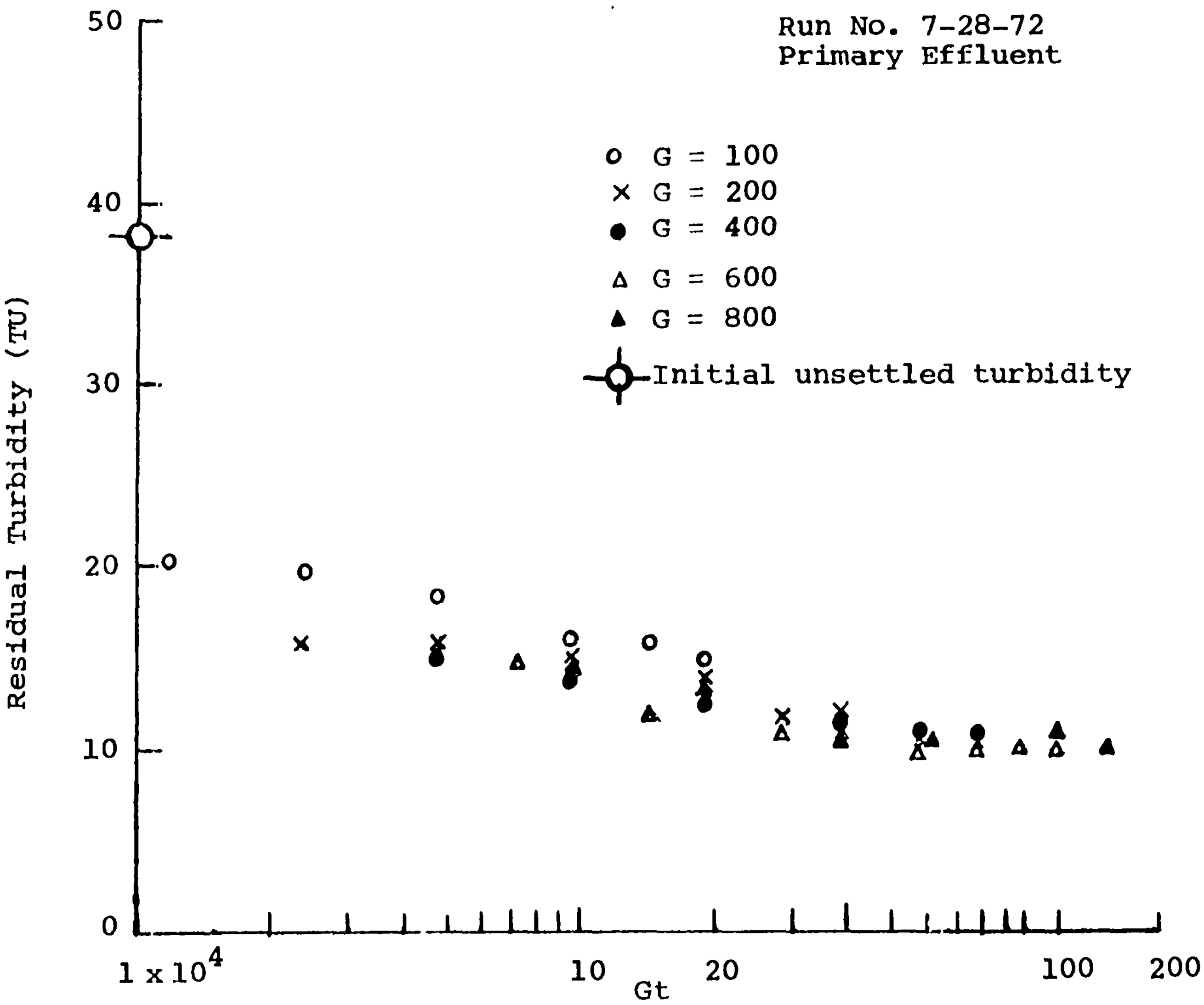

Figure 37. Semilogarithmic plots of residual turbidity versus Gt for varying G-values. Based on Run No. 7-28-72

is used, and a substantial portion of the economy of this process concerns the quantity of polymer and coagulant-aids required to promote a good clarification.

Based on this batch process alone, the following economic analyses (if crude) can be made:

Assuming a dosage of 5 mg/l, it means, 5 lbs of polymer would treat 1 million pounds of sewage.

Since one United States gallon of such a liquid weighs approximately 8.34 pounds, it follows that 5 pounds would treat 1,000,000/8.34 gallons or 41.70 pounds would treat 1 million gallons. Thus 1,000 gallons would require 0.042 pounds. At an average price of about $1.5 per pound (when large quantities of polyelectrolytes are used), this amounts to about 6.3 cents per 1,000 gallons.

Assuming further that 50 mg/l of aluminum sulfate would be used as a coagulant aid, at a cost of 15 cents per pound, another 6.3 cents would be needed. The total chemical cost would be about 13 cents per 1,000 gallons. This is a rather high cost, but perhaps, with further studies, this cost could be drastically reduced.

VIII. SUMMARY AND CONCLUSIONS

Phase I of this study was an attempt to investigate the effects of different dosing-techniques when cationic polyelectrolytes are used to coagulate domestic sewage. The comparison was primarily between split-flow-dosing technique and the nonsplit. The former is a process by which a portion of the sewage sample is dosed and mixed with a designated amount of the polymer, then mixed with the undosed portion, slow mixed and settled; and the nonsplit technique is the conventional method, in which the entire sample is dosed, mixed and settled. The expectation was that if the extended segment theory of polymer coagulation is valid for this process, then some economy in terms of the dosage required to reach optimum turbidity and suspended solids removal could be achieved through the process of split-flow dosing.

The second phase of the study involved the roles of high-energy-input in mixing and the period of mixing in the coagulation of wastewaters using synthetic organic polyelectrolytes that are positively charged (i.e., cationic).

The following conclusions can be drawn from the results of this investigation.

1. The cationic polyelectrolytes (Nalco 610, Hercofloc 810) used will enhance clarification of sewage only if a reasonably high velocity gradient, G, is used in rapid

mixing, and if the rapid mixing period is reasonably long.

2. When the polyelectrolytes are used without any coagulant-aid, a G-value of 100 sec^{-1} is too low. The best values lie between 200 and 400 sec^{-1}.

3. The longer the time of rapid mixing, the better, in general, is the removal performance; although the rapid mix period need not exceed 16 to 24 minutes.

4. When Bentonite clay or an aluminum salt, such as aluminum sulfate or sodium aluminate, is used as a coagulant-aid, the clarification is substantially improved. Of the two classes of coagulant-aids (clay and aluminum salt), the aluminum salt is the better one. About 25 to 50 mg/l of the alum appears to be the optimum. This is a reasonable range for clay also, although no optimum was reached even when 75 mg/l of clay was used.

5. With an aluminum salt as coagulant aid, the optimum velocity gradient is about 200 sec^{-1}, whereas for clay, the best range is between 400 sec^{-1} and 600 sec^{-1}. Again, in either case, the longer the time of rapid mixing the better, provided a period of slow mix at a G-value of about 50 sec^{-1} for about 10 minutes followed rapid mixing.

6. While G and t separately are important, their product, Gt does not appear to be a good design parameter.

7. In general, the results of this study challenges the traditional attitude of workers and investigators in

the coagulation field, with respect to the problem of extended rapid mixing. Based on the findings of this study and as opposed to the traditional attitude, the use of high velocity gradient and extended time of mixing is not detrimental, rather it is desirable. It poses a challenge not only to wastewater managements but to water works officials as well. Hydrophobic suspensions seem to require higher energy of mixing than hydrophilic systems, as exemplified in cases where clay is added to the samples in this study. Since surface waters tend to be more hydrophobic than domestic sewage, it is possible that water coagulation processes could take more violent mixing and give better results than as currently practiced.

IX. RECOMMENDATIONS

It is recommended that a pilot plant study be made as a follow up to this study.

A process involving high energy rapid-mixing of sewage (using polyelectrolytes, with other aids as appropriate) and filtering the clarified effluent through some form of rapid filters is worth investigating.

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