TIME PARAMETER EVALUATION IN DUAL FLOCCULANT DESTABILIZATION

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REPRODUCIBILITY EVALUATION OF THE FLOCCULATION OF A SYNTHETIC LATEX COLLOIDAL SYSTEM

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PREFACE

In this completion report there are two separate sections describing related research efforts. The separate investigations were completed by Messrs. Bryan Duff and Shen-Chih Wu, respectively, both in conjunction with William A. Barkley. The work by Duff preceded that of Wu with some overlap of experimental work. Both of these investigations dealt with destabilization testing of a synthetic latex colloidal suspension. However, the research objectives - time effects and reproducibility of destabilization - were very different. The conclusions of each section consequently did not consider the conclusions of the other. Added at the end of the second section is a joint conclusions statement prepared by considering the work of both sections of this report.

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ABSTRACT

This research was conducted to obtain an optimum time differential between the addition of dual flocculants aluminum sulfate and polyelectrolytes, to a colloidal suspension. This work was carried out on a synthetic colloidal suspension, latex, which was used in order to achieve the best available reproducibility. Both cationic and anionic polyelectrolytes were examined in conjunction with aluminum sulfate (alum). To simplify tests, pH, ionic strength, and temperature were held constant. The dependent parameters for destabilization measurement were turbidity, total solids, zeta potential, and Al^{3+} concentration. Various alum concentrations, polyelectrolyte concentrations, and time intervals were examined.

This work led to many conclusions. For the cationic polyelectrolyte, the optimum time for addition was dependent upon amount of alum used, but the cationic polyelectrolyte should always be added after the alum. The optimum time for the anionic polyelectrolyte was five minutes after alum had been added to the system. The latex suspension gave reproducible results during the testing period. The use of zeta potential measurements along with the turbidity and total solids, proved useful in evaluating what happened in the suspension. Turbidity by itself could be misleading.

This investigation showed that the time difference between the addition of primary and secondary flocculants affects the efficiency of coagulation in a synthetic colloidal system. This conclusion is probably at least qualitatively valid for real colloidal systems. Water treatment plants should attempt to evaluate this time factor to improve water treatment without additional chemical cost.

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NOMENCLATURE

K^+	Potassium ion	Ca^{++}	Calcium ion
Al^{3+}	Aluminum ion	Na	Sodium
KOH	Potassium Hydroxide	NaOH	Sodium Hydroxide
HCl	Hydrochloric Acid	$CaCl_2$	Calcium Chloride
$Al(OH)_3$	Aluminum Hydroxide	H_2SO_4	Sulfuric Acid
K_2SO_4	Potassium Sulfate	Alum.	Aluminum Sulfate
$CH_2 = CH_2$	Ethene	$Al_x(OH)_y$	Aluminum Hydroxide
$-CH_2CH_2$	Repeating Ethyl Group		
ppm.	parts per million	ppb	parts per billion
rpm.	revolutions per minute	mg/l.	milligrams per liter
mv	millivolts	ml.	milliliters
° C.	Centigrade temperature	Å	Angstroms
mg/ml.	milligram per milliliter		
FTU.	Formazin Turbidity Unit	JTU	Jackson Turbidity Unit
TS	Total Solids	VS.	Volatile Solids
M.	Molar Solution	N	Normality
PE	polyelectrolyte	ZP.	zeta potential
DDL.	diffuse double layer	DP.	degree of polymerization
vs.	versus		

INTRODUCTION

In potable water treatment systems, the problems of turbidity, odor and taste are often encountered. These effects can result from clay and from organic and inorganic particles that are present in the water. Through sedimentation and filtration most particles above one micron in size can be removed. Those particles below one micron in size stay in suspension and cannot economically be removed by sedimentation and filtration.

Sedimentation of the small particles is prevented because of two factors: (a) the small size, which effects the settling velocity, and (b) repulsive electrical charges between particles which prevent coagulation and more rapid settling. These small particles have been described as being colloidal particles. This is because of (a) the particle's size, (b) the particle's ability of scattering light (Tyndall Effect) causing turbidity, and (c) the ability of the particles to adsorb ions because of their electrical charge.

The processes of coagulation and flocculation are used to overcome these effects. Through the addition of coagulating agents the electrical charge is completely or partially neutralized. Then, by mixing the particles together, they form larger particles which can settle out in sedimentation basins. Aluminum sulfate (alum) and ferric chloride have been used as coagulating agents. These chemicals, when dissolved in water, form various radicals which will be attracted to the colloidal surface and help reduce the repulsive charge. After this process, slow mixing forces the particles to stick together, thus becoming large enough to settle out.

In recent years, multi-chained molecules called polyelectrolytes, or polymers, have been introduced as coagulating agents. These polyelectrolytes have been used with and without alum and have been positively, negatively, and neutrally charged. It has been found when polyelectrolytes and alum are used together, that the required alum dosage is smaller than when alum is used by itself. This effect cuts down on the cost of chemicals used, making for cheaper plant operation.

Various studies have been done showing the effect of coagulating agents on the colloid's repulsive charge, and trying to find the optimum dosage for a given turbidity. In this study the charge of a synthetic, reproducible colloidal system, as measured by zeta potential, will be studied. The main objective of this study is to determine if an optimum time exists between the addition of alum coagulant and the addition of a polyelectrolyte. By measuring the zeta potential for the colloidal particles, an optimum time could give more efficient turbidity, odor and taste removal, and may decrease the amount of coagulants needed.

LITERATURE REVIEW

Colloidal particles have been shown to be responsible for color, taste and objectionable odor in potable water (1, 2). Riddick (1) states that tastes and odors come from the decomposition of organic colloids which release gases. Because of the colloids' extremely small size, it is hard for them to be removed by a sedimentation basin. Uneconomically long times would be required for sedimentation.

Nature of Colloids

In water systems, most colloids are negatively charged (3). The colloid can be either organic or inorganic in nature (4). The negative charge of the colloids is neutralized in a water suspension by the addition of positive ions. The solution always maintains a net charge of zero: the charge of the bulk of the solution balances the opposing charge of the colloidal particles.

Colloidal structure. Colloids have been described as being approximately one micron or smaller in size (5). By applying an electrical field to a colloidal suspension, it can be seen through the movement of individual colloidal particles that the colloids have an electrical charge. This charge can be either positive or negative. The movement of colloids under an electrical field is called electrophoresis (3).

There are two forces that act on the colloidal particles in solution (3). The first one is the van der Waals Force of Attraction. The second force is one of repulsion because of the similar charge existing between colloidal particles. When oppositely charged ions exist in solution, these ions will collect around the colloid particles. These ions form an electrical layer (diffuse double layer) around the colloidal particle.

Diffuse double layer (DDL). There are thought to be two sources of the electric charge in the colloid. These sources are: (a) interlattice substitution (called isomorphic substitution) of differently charged ions, and (b) specific ion adsorption on the colloid surface (3). The ions in solution will collect around the colloidal particle depending upon colloidal particle charge, valence and size of ions, concentration of ions, suspension medium, and temperature (3). An idealized picture of this arrangement is shown in Figure 1.

Attempts to visualize the concentration of cations around a negatively charged particle were done by Gouy and Chapman. These men determined equations that gave the relationship between electrostatic potential and distances away from the colloid surface. A figure of cation concentration versus distance from the surface is shown in Figure 2 (3).

As shown in Figure 2 from the Gouy-Chapman idea, as the distance to the surface decreases, the concentration increases exponentially. This exponential increase in cations leads to an overestimation of cations close to the surface of the colloid (3). Also, it

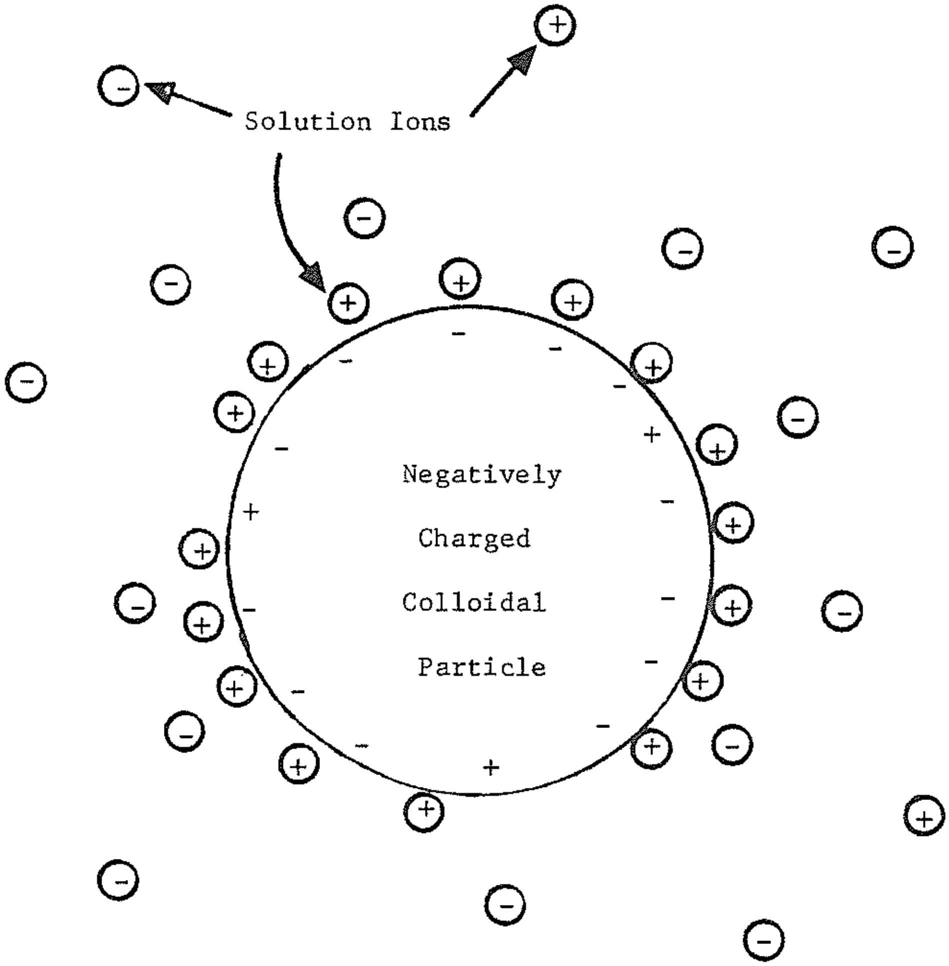

Figure 1

Collection of Ions on
a Colloidal Particle

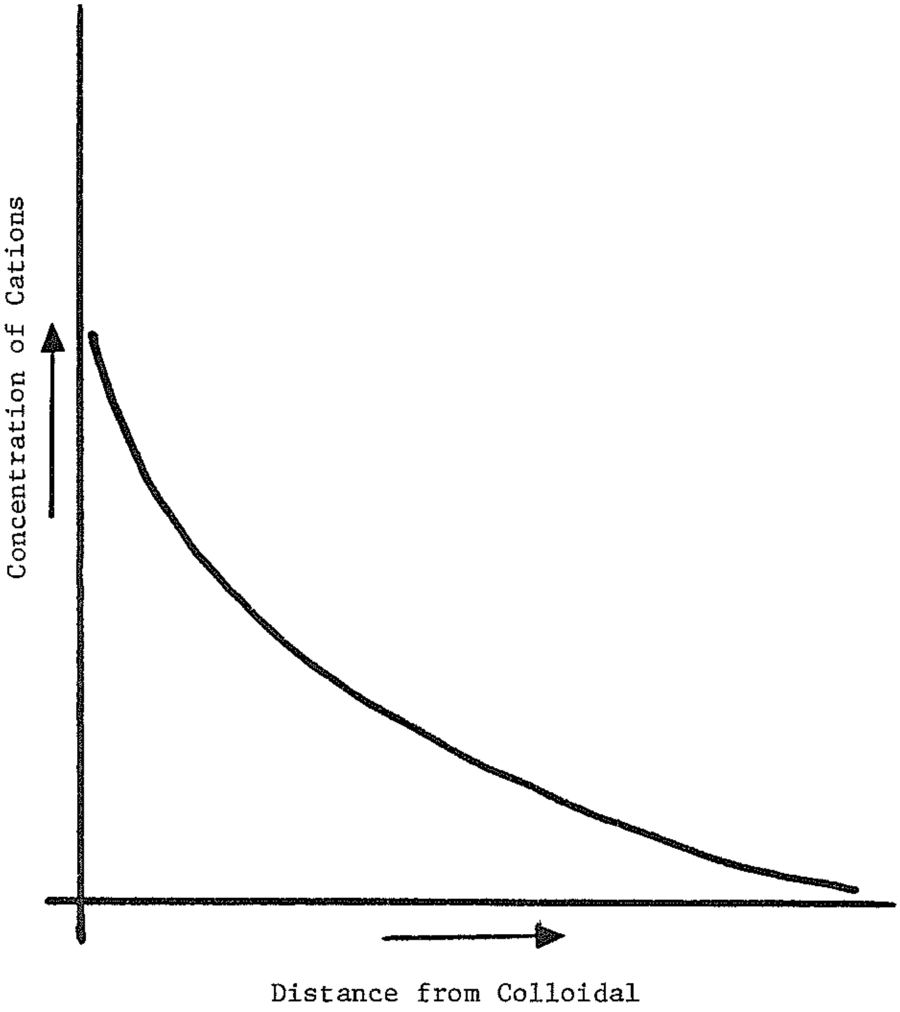

Figure 2

Ion Distribution from Gouy-Chapman Model should be realized that an ion can only get so close to the surface because of its finite size. These two problems in the Gouy-Chapman Theory led to a look at the ions in the outer layer. The ions that do get close to the colloid surface are dependent upon two variables. First, the ion's valence, and second, the ionic size. As a cation approaches a colloidal surface, the main body of the positive charge is located roughly in the middle of the cation. The cation tries to get as close to the negative colloid surface as possible. It is held back by its own outer shell and any waters of hydration that it may have. Thus, an ion must try to shed part of its waters of hydration to get closer to the colloidal surface. Larger ions have smaller hydration energies than smaller ions. In turn, it is easier for larger ions to lose their waters of hydration than smaller ions. For example, two ions, K (potassium) and Na (sodium), can have the same valence (+1) but different ionic radii, K = 1.33Å and Na = .95Å. The K ion, being larger, can shed its waters of hydration easier than the Na ion and approach closer to the colloidal surface.

More important than size, though, is the ionic valence. An ion with a larger positive valence is going to be attracted more to a negative colloid than one with a small positive valence. For example, sodium and calcium (Ca) both have approximately the same ionic size, but have different valences, Na (+1) and Ca (+2). Because of this, the Ca ion will be attracted easier than the Na ion if they were competing for the same site.

Work in these two areas was done by Stern. Stern proposed that the finite size of the ions surrounding the colloidal particle leads to a "condenser" effect of the first layer of particles (3). This condenser effect is brought about because there would be space between the colloidal surface and the centers of the first layer of counter ions. This space was described by Stern as being a "molecular condenser." In this area the charge potential drops linearly. This area is described as the "Stern Layer." After a certain distance out, the Gouy-Chapman Distribution would begin. These two layers, the Stern Layer and the Gouy-Chapman Layer have been called the Diffuse Double Layer (DDL). Figure 3 shows the DDL potential distribution.

This DDL then is what keeps the particles apart. If two particles were approaching one another because of van der Waals Force of Attraction, similar DDLs would cause repulsion. Colloids in suspension in this state are called stabilized (2). Thus, to have the van der Waals Forces effective, the DDL must be small enough to allow the particles to approach each other, and then the van der Waals Force would take over and bring the particles together. This state is called a destabilized state.

Destabilization of colloids. As stated, compression of the DDL can cause destabilization. Two factors can cause the compression (6). First, increasing the concentration of the bulk solution ion can cause compression. Second, increasing the valence of the bulk solution ion can cause compression.

In potable water treatment systems, alum and ferric chloride are used as destabilization colloids. Increasing concentrations of these ions which have a high valence (+3) helps to compress the DDL.

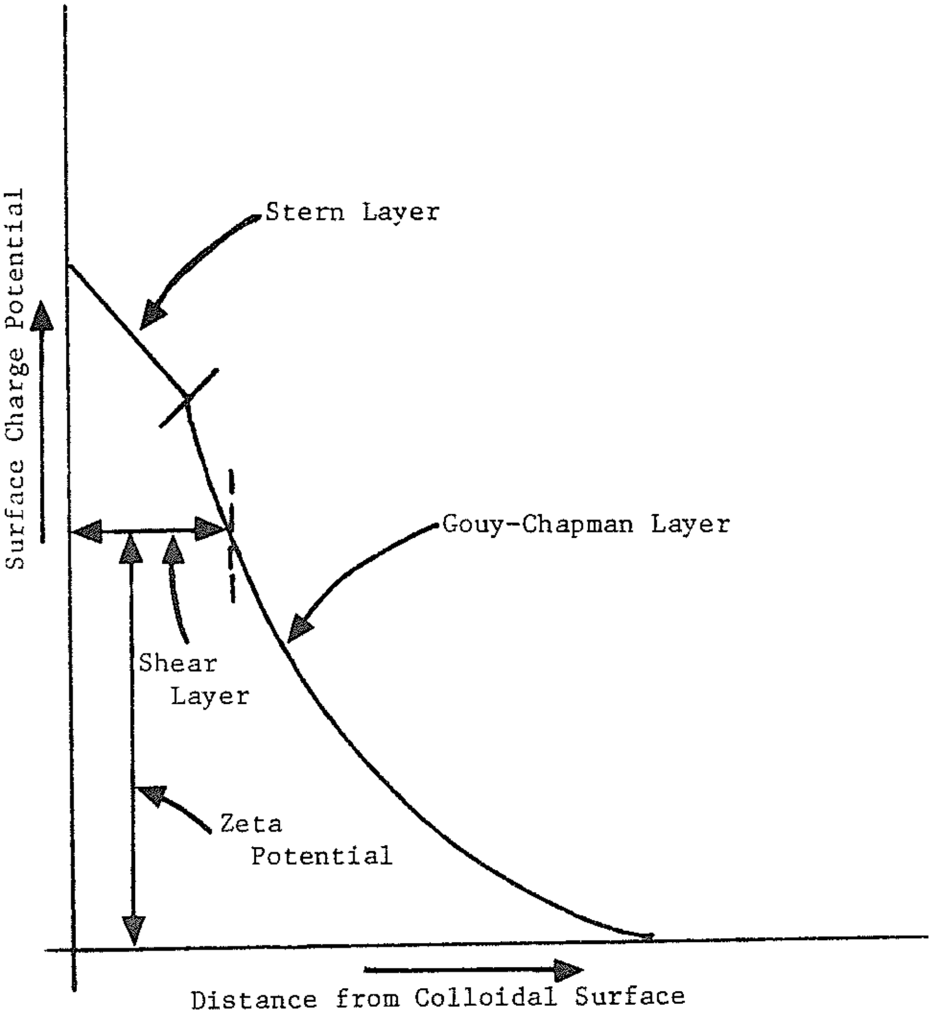

Figure 3

Potential Distribution for Diffused Double Layer

Aluminum Sulfate

Aluminum sulfate (alum) along with ferric chloride are used as coagulating agents. Aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$) hydrolyzes very quickly in a water solution (7). The Al^{3+} ion goes through a stepwise conversion to $Al_x(OH)_y$ depending upon the pH of the solution (7). Ions or molecules that bond to a central metal atom are defined as ligands (8). In this case, the OH^- is the ligand. Figure 4 shows the conversion of the aluminum positive ion into the negative ion (7).

Distribution diagrams of the aluminum species versus (vs.) pH are shown in Figures 5 and 6 (9). Examination of the diagram shows that below pH = 4.5, that the Al^{3+} ion is the dominating ion. Above pH = 8.0, $Al(OH)_3$ as the dominating species. The authors (9) point out that this disagrees with previous work (7, 9, 10). Sullivan and Singley (9) state that they used mononuclear species only. They say that if other negative charged particles are present, these may compete with OH^- and alter composition to form polynuclear complexes.

As should be realized by Figures 4, 5 and 6, the pH of the medium is of primary importance (7). The pH determines what complexes will form and thus, which ones will go to the colloidal particle. This determines how much coagulation can be accomplished by the aluminum sulfate at a certain pH. The best coagulation has been found to occur around a pH of 4.4 to 7.6 (11). $Al_x(OH)_y$ species forms a gelatinous floc which enmeshes around the colloidal particles (12). As stated in the Introduction section, polyelectrolytes are also used as coagulating agents.

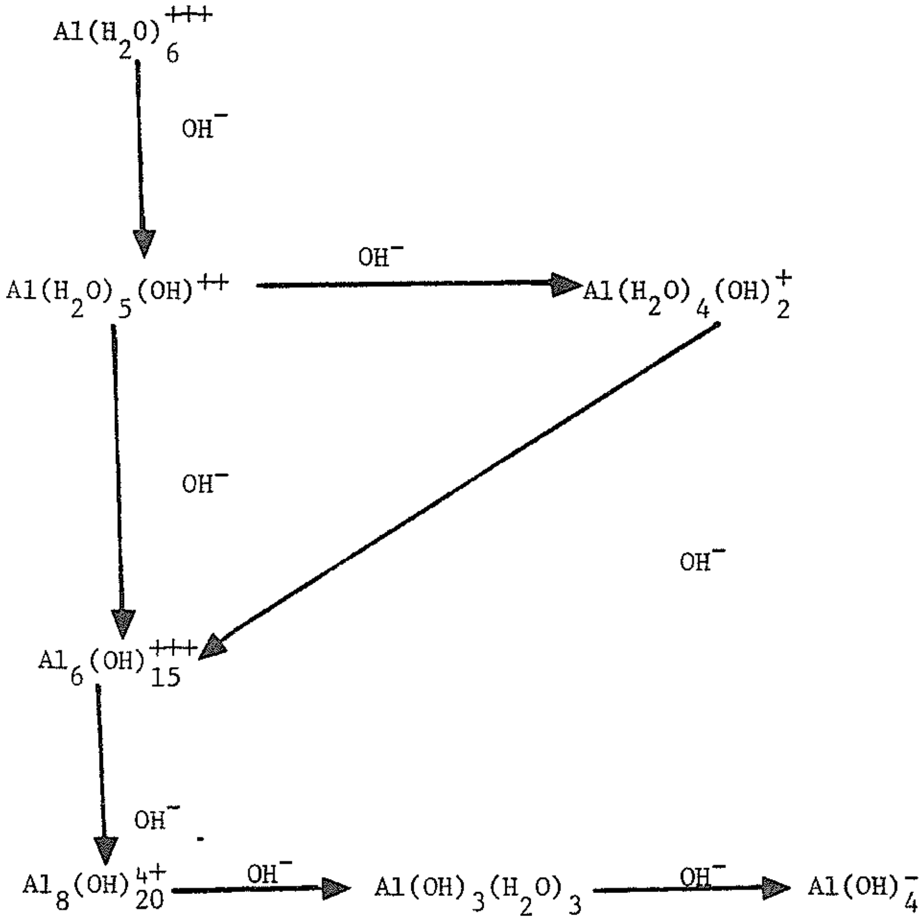

Figure 4

Conversion of Aluminum Ion

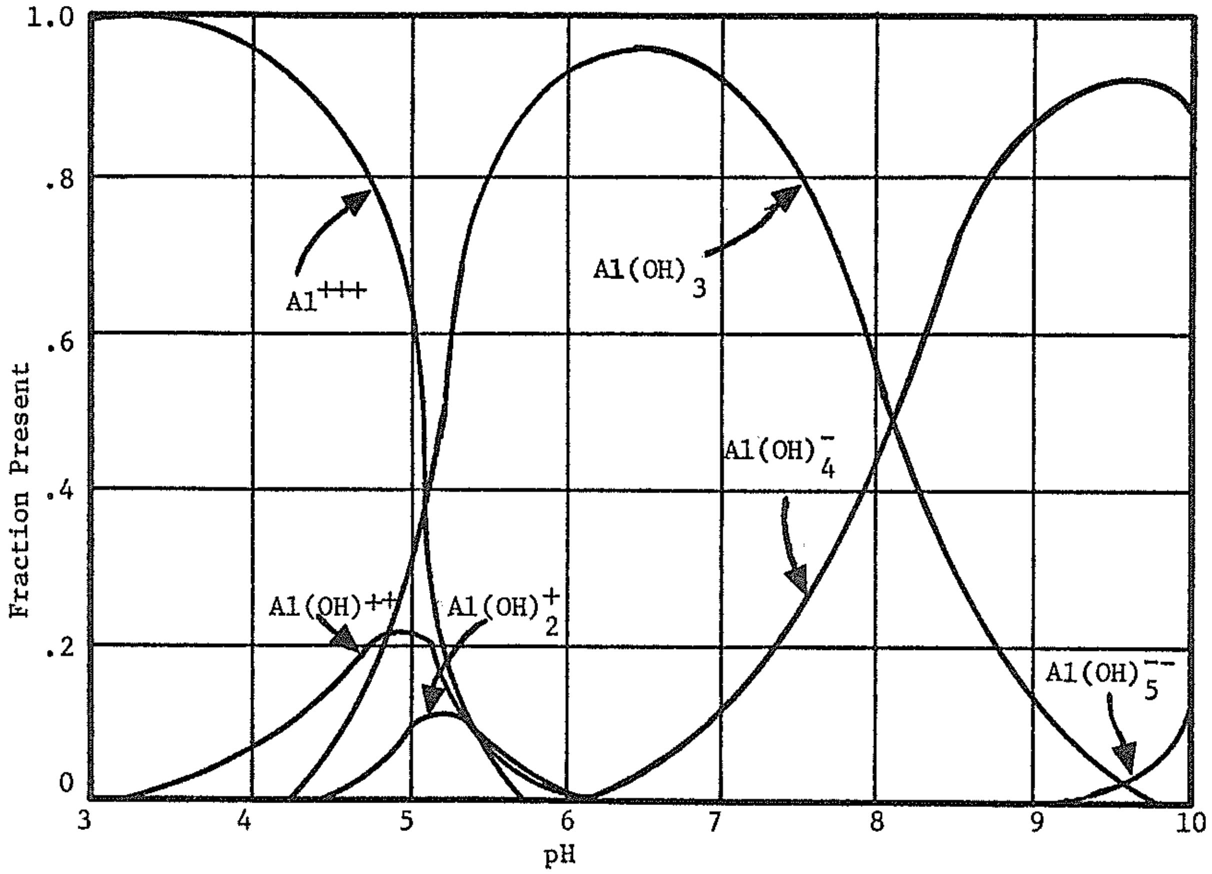

Figure 5

Aluminum Species vs. pH

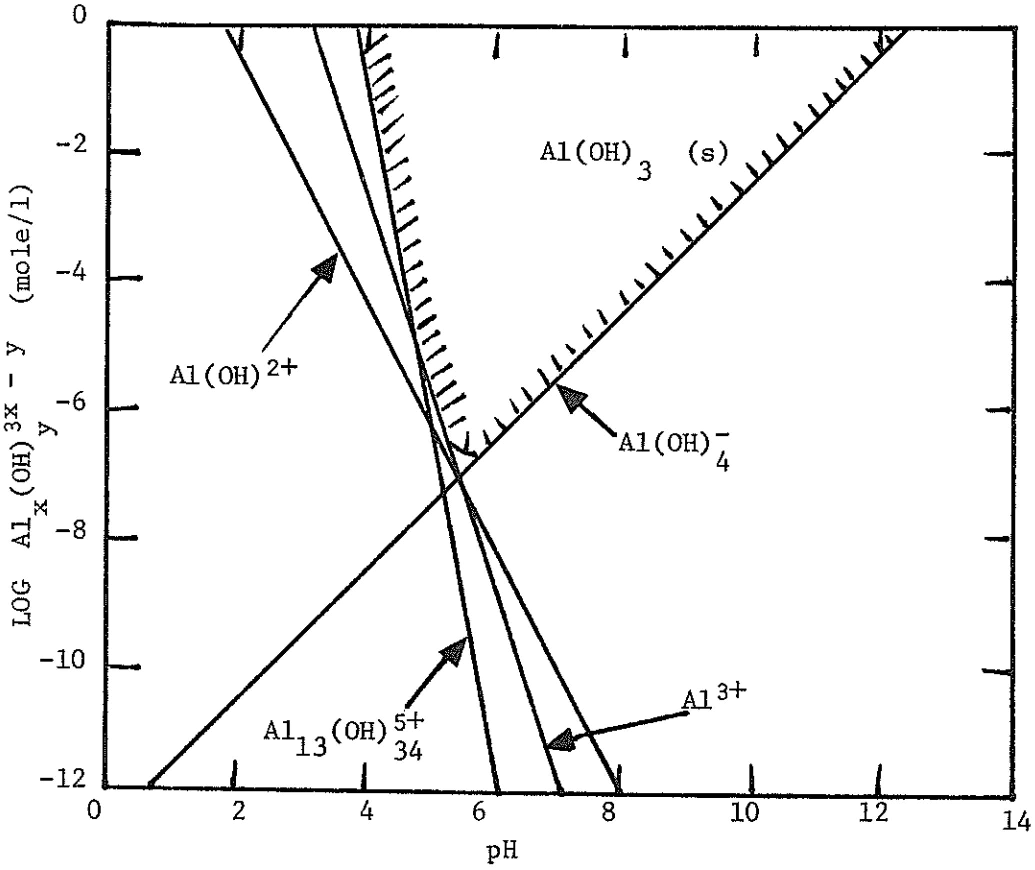

Figure 6

Aluminum Solubility

Polyelectrolytes

In recent years the use of polyelectrolytes has been introduced in water and waste water treatment. As the name describes ("poly" - Greek for many), polyelectrolytes would describe a "many-ionic state" molecule (13). Polyelectrolytes are a type of polymer and have the same characteristics as polymers.

Among other methods of classification, polymers can be classified into two types, biological and non-biological. Polymers are defined as being large molecules built up through repetition of smaller chemical units (14). This repetition can be either linear (like a chain), or branched, which can form 3-dimensional networks. The repeating small chemical unit is like a monomer. The monomer is the starting material of which the polymer is formed. An example of this is in the polymer, polyethelene:

Monomer	Repeating Unit	
$CH_2 = CH_2$	$-CH_2CH_2$	(14).

The length of the polymer is dependent upon the amount of repeating units, and is called the degree of polymerization (DP). To determine the molecular weight of a polymer the DP is multiplied times the molecular weight of the repeating unit. Often molecular weights of polymers can be over 1,000,000. Polymers that are made up of repeating ionic groups are called polyelectrolytes (14).

Polyelectrolytes can be cationic, anionic, or nonionic. Combinations of different polyelectrolytes and polyelectrolytes with inorganic coagulating agents, alum or ferric chloride, have been used in coagulation processes. Black and Vilaret (15) point out that nonionic polymers by themselves have no effect, but when they are added with calcium chloride ($CaCl_2$) coagulation can occur. Meyers and Ries (2) show that by using first cationic and then nonionic polyelectrolytes, there is a great reduction of zeta potential (ZP) and subsequent flocculation.

When a polyelectrolyte is used that has an opposite charge than the colloid, charge neutralization may be the dominant factor in flocculation (16). Use of the higher weight polymers is thought to bring two different mechanisms into act. The first of these is charge neutralization and the second one is the bridging mechanism (16).

Bridging Mechanisms

In the Gouy-Chapman Theory, the chemical forces are neglected and only electrostatic forces are considered for the DDL (17). Stumm and O'Melia (17) point out that for polyelectrolytes, chemical adsorption may occur. This may account for the fact that Kleber (18) states that the apparent charge density of polyelectrolytes is dependent upon the nature of the colloidal particles and the soluble ions present. But it should be noted that Kleber's (18) ideas may also be due to electrostatic forces. Stumm and O'Melia (17) go on to point out that chemical adsorption of a counter-ion, in this case a polyelectrolyte, may decrease stability. Bridging would occur because the polyelectrolytes molecule could adsorb onto two or more colloidal particles. Figure 7 shows a picture of this concept. Other authors (16, 17, 18, 19) have shown evidence of the bridging idea also.

Stumm and O'Melia (17) point out that the best bridging occurs when the polyelectrolytes are adsorbed to just part of the

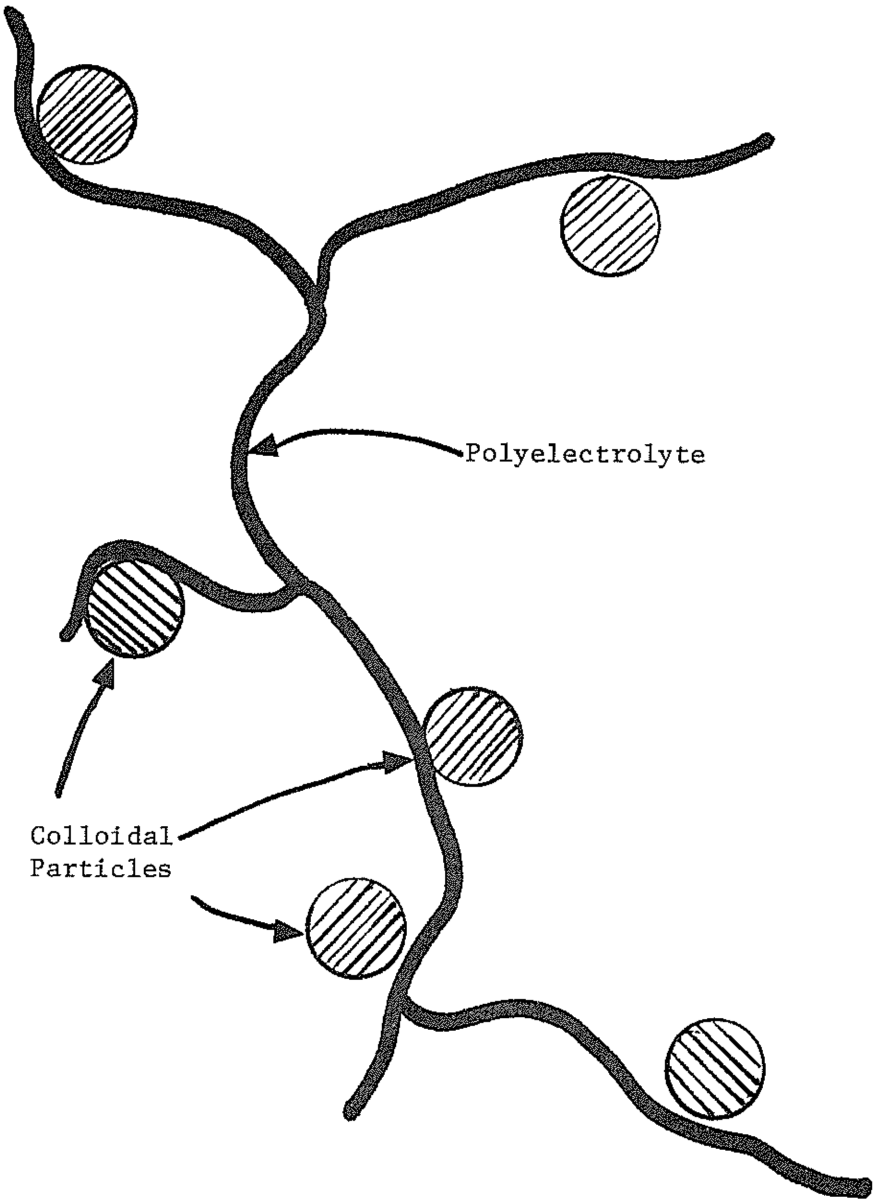

Figure 7

Bridging Mechanism of Polyelectrolyte

adsorption sites on the colloid. Increased dosage of the polyelectrolyte could fill all of the sites and could stabilize the colloidal particles again (5, 16, 17, 20).

To measure the stability of colloidal particles, people have used the relative charge of the particle as a measurement. One way of measuring the "relative charge" is through the use of zeta potential.

Zeta Potential

In Figure 3, it is illustrated that a lot of the ions in the Stern Layer and some in the Gouy-Chapman Layer are held very tightly to the colloidal particle. As the particle moves, these ions will move with it. At some point out from the particle, a "shearing plane" is found between the colloidal particle and its tightly held ions and the other ions in the Gouy-Chapman Layer and the bulk solution. This shearing plane is some distance from the colloidal surface but usually is in the Stern Layer. The potential at this shearing plane is called the zeta potential (ZP)(4).

The relative importance of ZP on colloidal stability is an area of much discussion and debate. Lamer and Smellie (21) point out that by the addition of negatively charged polyelectrolytes to a negatively charged clay, flocculation occurs, which is against the idea of ZP. They also point out that in 1948, Verwey and Overbeek stated that the electrostatic part of the thermodynamic potential ψ controls stability and not the ZP. Other authors have pointed out that other factors in the solution may control the ZP. Hall (22) points out that unless the pH is controlled, measurement of ZP may be irrelevant. Hall (22) says that if pH is controlled at a constant pH, then ZP may be a standard for colloidal stability. Lyklema and Overbeek (23) state that ZP may be dependent upon concentration and the nature of the polyelectrolytes.

From these points of view, there are other authors who state that ZP is relevant to colloidal stability. Friend and Kitchener (24) point out that adding a flocculant effects ZP in two ways. First, it moves the ZP out of the plane of shear. Second, flocculant addition brings more charge into the inner region (Stern Layer) of the DDL. This article points out, also, that some Russian research shows that too high a ZP can prevent flocculation. Electrophoretic mobility, which is related to ZP, has been shown to decrease with increasing polyelectrolyte dosage (20). One of the most outspoken users of ZP in water quality is T. M. Riddick (1). Riddick (1), the inventor of the "Zeta-meter," has used ZP control in the design of water treatment plants (2). Riddick feels that ZP values of -15mv to +4 mv will give good removal of colloids (2). Riddick also feels that if the ZP is kept at a slight (+) value, there will be a greater adsorption of colloids through mutual attraction. It can be seen that the opinion of the relevance of ZP varies greatly. Colloidal chemists seem to ignore it and practicing engineers (including sanitary engineers) use it regularly.

EXPERIMENTAL PROCEDURE

Design of Experiment

In the design of this research, a synthetic colloidal suspension was used in order to achieve more reproducible results. In either kind of suspension, synthetic or natural, the following independent parameters can be tested: pH, ionic strength, alum concentration, polyelectrolyte concentration, temperature, and time between the addition of alum and polyelectrolyte. Possible dependent parameters include turbidity, zeta potential, suspended solids, and aluminum concentration.

Past researchers have used many different synthetic suspensions. Kaolin (20, 22, 25), bentonite (10), Min-u-sil (15, 26), and latex (2, 16, 19, 27, 28) have all been used in colloidal research. The material used should have a narrow size distribution with particles approximately the same size and a well dispersed, stabilized medium with no apparent natural settling over a period of time. The turbidity of suspensions of latex, kaolin, and Min-u-sil were measured with changing time and concentration. Figure 8 is turbidity versus concentration and Figure 9 is turbidity versus time. As Figure 8 shows, all suspensions show an apparent linear relationship with concentration versus turbidity. This linear relationship indicated that all of the suspensions had a narrow size distribution. However, Figure 9 shows different results for stability. A well dispersed suspension would show no turbidity changes versus time and have a horizontal line. This is true because

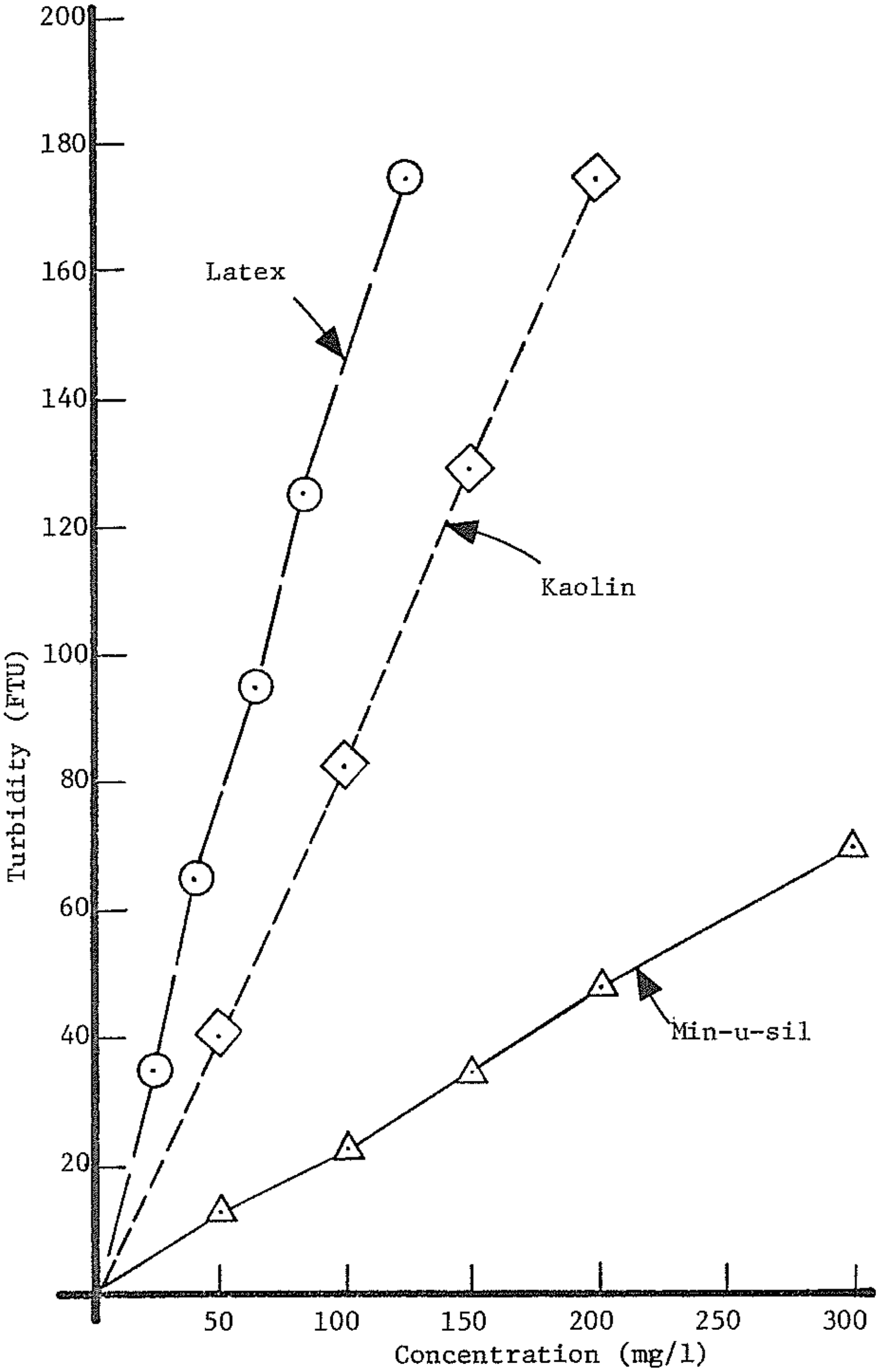

Figure 8

Turbidity vs. Concentration

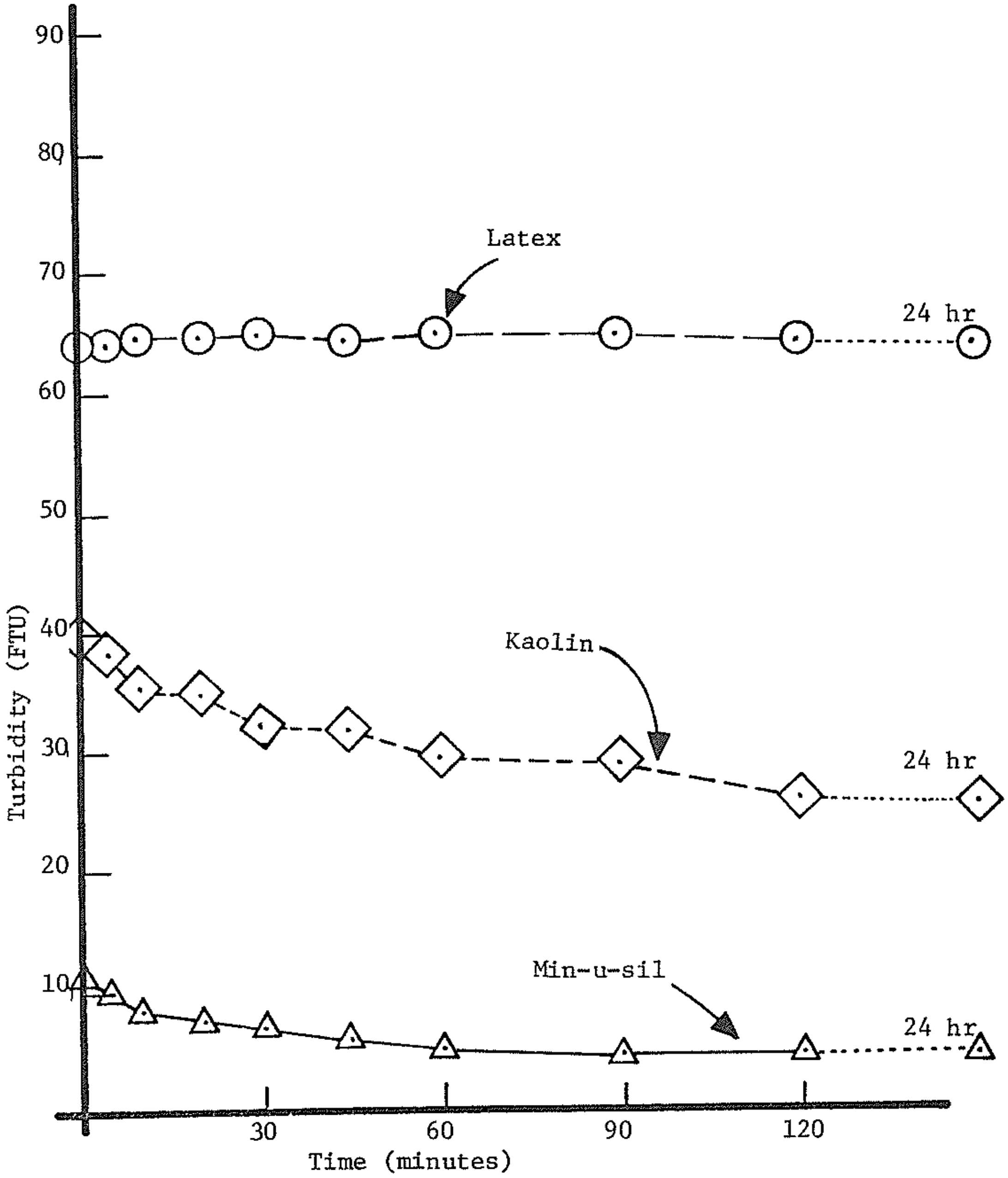

Figure 9

Turbidity vs. Time

there would be no settlement of particles which would decrease turbidity in the upper levels of the suspension. The latex showed this characteristic. The kaolin and Min-u-sil showed a decrease in turbidity, indicating particle settlement in the upper levels. Because the latex exhibited both of the characteristics required, it was used as the synthetic suspension. Use of latex did cause some problems. Emulsifiers on the latex caused problems in getting reproducible results. These emulsifiers may be removed through two processes, dialysis and ion-exchange resins (29). Ion-exchange resins were used because of lesser time requirements. Resins take only 2 or 3 days for purification, while dialysis can take up to 160 days (29). The ion-exchange procedure is given in the procedure section.

As previously stated, there are at least six possible independent parameters. In planning an experimental design, all possible combinations should be considered. Thus, given a latex concentration and polyelectrolyte type, and looking at three different values of the independent parameters, there would be 6^3 or 216 possible combinations. If five different polyelectrolyte types were looked at, there would be 5 x 216 or 1080 tests run. To reduce the number of tests, certain parameters were held constant. The constant parameters selected were pH, ionic strength, and temperature. This left three parameters, polyelectrolyte concentration, alum concentration and time between additions, to be varied in the first phase of testing. Preliminary testing of concentrations showed that three levels of polyelectrolyte and alum concentrations would cover the needed range. Three levels of time intervals were chosen to give 3^3 or 27 tests to perform for each combination of polyelectrolyte and alum. It was thought that these 27 tests could be reduced thru a statistical analysis. Discussion of this was held with Dr. Urquhart (30), Statistics Department of the Department of Agriculture at New Mexico State University. Dr. Urquhart felt because of the possibility of synergistic effects between alum and the polyelectrolyte that all 27 tests should be run. Thus, if synergistic effects are possible, the should show up in the tests. From this, the experimental design of 27 tests was decided upon. The design would use constant pH, ionic strength and temperature. There would be three alum concentrations, three polyelectrolyte concentrations and three different time intervals for each polyelectrolyte tested. The testing sequence for the 27 tests was determined by use of a random numbers table. All initial tests took place at a latex concentration of 120 parts per million (ppm) and two different polyelectrolyte types were examined.

Laboratory Procedure

The laboratory procedure is described in four parts. First, the procedure for the constant independent parameters is given. Second is the procedure for the variable independent parameters. Third is the testing procedure for the dependent parameters. Last, the process procedures for the latex resin preparation and the jar testing procedure are given.

Constant independent parameters.

The pH, ionic strength, and temperature were held constant.

pH and ionic strength. Addition of aluminum sulfate to a solution will cause a drop in the pH of the solution. This is because aluminum sulfate is made from a weak base, $AL(OH)_3$, and a strong acid, H_2SO_4. Since the pH is to be maintained constant, KOH is added to bring the pH up to 6.0. Varying the alum concentration added to a solution varies the amount that the pH drops and the amount of KOH needed for a constant pH. This situation gives varying amounts of K^+ ions in solution and, thus, different ionic strengths. To compensate for this, K_2SO_4 is added to keep the K^+ at constant levels. Given below is the procedure used for constant pH and ionic strength.

1. From experimental tests for ionic strength a maximum of 5 ml of 0.01 M K^+ ion was used for the cationic polyelectrolyte and a maximum value of 12 ml of 0.01 M K^+ ion was used for the anionic polyelectrolyte.

2. The required amount of alum was added and the pH was measured.

3. The needed amount of 0.01 M KOH to raise pH to 6.0 was added and the amount was recorded.

4. From chemistry, for every two moles of KOH added, one mole of K_2SO_4 is formed. Therefore, one mole of K_2SO_4 should be added for every two moles of KOH needed. Therefore, for the cationic polyelectrolyte, Step 3 was subtracted from 5 ml. For the anionic polyelectrolyte, Step 3 was subtracted from 12 ml.

5. The amounts obtained in Step 4 as 0.005 M K_2SO_4 were added to the suspension. These two amounts from Step 3 and Step 5 give a constant amount of 0.01 M K^+ for each polyelectrolyte type. Complete dissociation is assumed because of the low dilution K^+ concentration.

Temperature. The testing was done in an air conditioned laboratory. Because of this, the temperature was maintained relatively constant between 20 to 24° C.

Variable independent parameters. The independent parameters studied included time interval, alum concentration and polyelectrolyte concentration.

Time interval. The time interval was considered as the time between the addition of the alum solution and the polyelectrolyte solution. The time interval was considered relative to the alum solution. There were three intervals considered in initial testing for cationic polyelectrolyte, -5, 0 and +7 minutes and for anionic polyelectrolyte, -5, 0 and +5 minutes. In the expanded testing, amplified time intervals of -5, -4, -2, 0, +2, +4, and +5 minutes were examined. The intervals were measured by use of a timer.

Aluminum sulfate (alum) concentration. The aluminum sulfate solution was 0.001 M $Al_2(SO_4)_3$ solution. The solution was made with distilled water and reagent grade J. T. Baker chemicals. Solution amounts were measured out by use of pipets. Alum concentrations added were 1, 3 and 5 ml of 0.001 M alum for the cationic polyelectrolyte. For the anionic polyelectrolyte, 5, 10 and 15 ml per liter of latex suspension were used.

Polyelectrolyte concentration. The polyelectrolyte solutions were made according to polyelectrolyte weight. Solutions were made to a given concentration that was approximately the same mg/ml of the alum solution. These solutions were pipetted out by use of a 1 ml graduated pipet in 0.7, 0.85 and 1.0 ml amounts per liter of latex suspension.

<u>Dependent parameters</u>. The dependent parameters used to evaluate the experiments were turbidity, zeta potential, solids, and Al^{3+} concentrations.

Turbidity. Turbidity measurements were performed with a Hach Model 2100A Laboratory Turbidimeter. This turbidimeter is a light-scattering device and has a range of 0.1 FTU to 1000 FTUs. FTU (Formazin Turbidity Unit) is the same measurement as the commonly used JTU (Jackson Turbidity Unit). The procedure for calibration and testing was done according to the Instruction Manual for Hach Laboratory Turbidimeter (31). After turbidity measurements were taken, the sample was used for zeta potential measurements.

Zeta potential. The ZP measurements were done using the "Zeta-Meter" (Zeta-Meter, Inc.) developed by T.M. Riddick and Associates. Sample preparation and ZP measurements were done according to the "Zeta-Meter" manual (32). The ZP values were taken from the monograph on page 70 of the manual (32) for ease of calculations. For all measurements, the 8X lens was employed and voltages used were 133, 200 and 300 volts. These voltages were used so that the time of travel of the colloidal particles between scale divisions ranged from 2.4 to 4.0 seconds, which was recommended in the manual (32). The number of colloidal particles tracked was between seven and ten.

Solids analysis. The solids tests run included tests for total (TS), volatile (VS), and fixed (FS) solids. Suspension samples of 50 ml were placed in evaporating dishes. The samples were first placed in a 103° C oven for 24 hours, desiccator for 24 hours and then weighed. Secondly, the samples were then placed in a 600° C muffle oven for 30 minutes, desiccator for 24 hours and weighed again. After subtracting the dish weight, the first weight was the total solids, the second weight was fixed solids, and the difference between the two was volatile solids. The dishes were cleaned and then dried sequentially in the 600° C muffle oven, 103° oven for 24 hours and then the desiccator for 24 hours before each use. The 24 hours drying period was used to assure a constant weight for the dishes.

Al^{3+} concentrations. Aluminum concentrations were run using the Perkin-Elmer 403 Atomic Adsorption Spectrophotometer, which belonged to the Agronomy Department of New Mexico State University. The sample was pipeted from the clarified portion of the suspension.

Process procedure. The process procedures that are given are for latex preparation and jar testing.

Latex preparation. Removal of the emulsifiers on the latex particles was accomplished by use of mixed bed ion-exchange resins. This resin method was developed by H.J. Van den Hul and J.W. Vanderhoff (29). The resins used were the Dowex 1-X4 Quaternary Ammonium resin and the Dowex 50W-X4 Sulfonic resin. These resins may be purchased in bulk from the Dow Chemical Company or for research purposes from the Bio-Rad Company of Richmond, California.

The resins were first rinsed to remove any contaminants that might have been present in the resin. The following steps were used for the rinsing.

1. 454 grams of Dowex 1-X4 was weighed out.
2. This resin was placed in a two-liter pear-shaped separatory funnel.
3. The resin was washed sequentially by elution with 3 N NaOH,

hot distilled water, methanol, cold distilled water, 3 N HCl, hot distilled water, methanol, and cold distilled water.

4. This cycle was repeated three more times.

5. 454 grams of Dowex 50W-X4 was weighed out and rinsed by Steps 2, 3, and 4.

6. After rinsing, the Dowex 1-X4 was converted to the hydrogen form by slow washing with 3 N NaOH and rinsed with distilled water

7. The Dowex 50-X4 was converted to the chloride form by washing with 3 N HCl, but this step was done shortly before usage.

8. The resins were then mixed together and rinsed twice with distilled water.

After resin preparation, 500 ml of 4% latex suspension was added to the resins. Dr. Vanderhoff (33) stated that latex solutions up to 40% (by weight) may be used. After initial mixing of latex and the resins, the mixture was stirred for two hours using a paddle stirrer. The initial procedure gave a five parts resin to one part latex suspension for the amounts needed. Dr. Vanderhoff (33) stated that this ratio was needed to insure complete exchange of the emulsifier. Experience has shown that this ratio was too high (mixing was poor), and the ratio of 910 grams to 500 ml latex or 2:1 was used successfully.

After mixing was finished, the latex-resin mixture was placed in a Buchner funnel with a plastic fiber filter and vacuum attachment. The plastic fiber filter was used to prevent absorbance of the latex suspension into the filter material. The latex-resin mixture was rinsed with 2.5 liters of distilled water in 100 ml "shots" to help was the latex suspension away from the resin. The suspension was vacuumed thru the filter and into a flask. Finally, a total solids analysis was run on the final suspension to determine the concentration of the "rinsed" latex suspension.

Jar testing. Although much work has been done using jar tests, no standard procedure has been developed. The procedure used was one developed by Barkley (5). The jar testing, because of the interval involved, was split into two parts, sample preparation and jar testing.

Sample testing consisted initially of latex sample preparation. Latex samples were prepared by placing 18 ml of 0.56% latex suspension (concentration of "rinsed" latex) in a one-liter volumetric flask and filling with distilled water. The sample was then placed in a one liter beaker. Secondly, polyelectrolyte or alum solution was added depending upon time sequence for a particular test. If alum was added, the pH and ionic strength corrections were made at that time. After the initial coagulant addition, the sample was placed on a counter rotating mixer and mixed at 50 rpm. This mixing continued for the required time interval and then the second coagulant was added. After the second coagulant was added, Barkley's jar testing procedure was followed.

The jar testing procedure consisted of a one minute rapid mix at 100 rpm and a 20 minute slow mix at 30 rpm on a Phipps and Bird six-paddle stirrer. After the mixing, the sample was removed and allowed to settle for two minutes. Then samples for zeta potential, turbidity, solids analysis, and aluminum concentration were taken from one inch below the surface in the center of the beaker with a 50 ml pipet.

PRESENTATION OF RESULTS

Given in this section are the results of the tests. These results are presented in the sequence that they were experimentally completed. The results are presented in four sections. First is the dependent parameter measurement of the pure latex suspension. Second is the destabilization by individual coagulants. Third is the preliminary testing. Fourth and last, is the expanded testing of the cationic polyelectrolyte.

Pure Latex Suspension

Tests were run on a pure latex suspension at constant pH and ionic strength. The following dependent parameters were recorded: turbidity, total solids, and zeta potential. The results are shown in Table 1.

Table 1

Pure Latex Suspension

Turbidity	Total Solids	Zeta Potential
150 FTU	120 ppm	-33 mv

Destabilization by Individual Coagulants

These tests were run to determine the concentration range necessary to achieve the desired magnitude of change in the dependent parameters. The tests were made using the coagulants selected for the main tests, alum, cationic polyelectrolyte, and anionic polyelectrolyte. Most of these tests were run on an uncontrolled pH and ionic strength latex suspension. The destabilization was measured by use of the zeta potential parameter.

Alum. The results of the alum destabilization are shown in Table 2. The alum concentration was 0.001 M and the amounts were diluted into one liter latex suspensions.

Table 2

Alum Destabilization Tests

Alum,	ml	0	4	5	7	10
	ppm	0	2.45	3.07	4.29	6.13
ZP	mv	-33	-19	-21	-14	- 3

According to Riddick (1), optimum destabilization occurs at a ZP of -5 to +5 mv. Because of this, 0.001 M alum volumes between 1.0 and 5.0 ml were selected. It was felt that these concentrations, in addition to satisfactory amounts of cationic polyelectrolyte, would bring the ZP into the optimum range.

Further tests were run on alum concentrations. These tests gave dependent parameter "standard" values for latex removal by alum only. These values were used to compare removal by alum versus removal by alum and polyelectrolyte together. These tests were run at a constant pH and ionic strength. The standard values for turbidity, total solids and ZP are given in Table 3.

Table 3

Standard Values for Alum Destabilization

Alum,	ml	1	3	5	10	15
	ppm	0.61	1.84	3.07	6.14	9.21
Turbidity,	FTU	150	160	88	110	115
Total solids,	ppm	120	108	58	60	60
ZP,	mv	- 42	- 46	-19	- 3	+ 11

Cationic polyelectrolyte. The cationic polyelectrolyte used was Nalco #607. Concentrations were put into one liter suspensions. The results of the cationic polyelectrolyte destabilization tests are shown in Table 4. Since these concentrations were to be used in conjunction with alum, volumes between 0.7 and 1.0 ml were selected.

Table 4

Cationic Polyelectrolyte Destabilization

Cationic PE,	ml	0.5	0.7	0.85	1.0	1.1	1.5
	ppm	0.58	0.81	0.99	1.16	1.28	1.74
ZP,	mv	-32	-33	-26	-8	+6	+11

Anionic polyelectrolyte. The anionic polyelectrolyte used was the Nalco #8173. Anionic polyelectrolyte tests were run after the preliminary testing with the alum and the cationic polyelectrolyte. The same concentrations of alum and polyelectrolyte were tried and the ZPs were extremely negative and all more negative than -20 mv. Since this was out of the ZP range suggested by Riddick (1), volumes of 5 ml and 15 ml alum (0.001 M) were tried with 1.0 ml and 5.0 ml anionic polyelectrolyte. These tests were run at constant pH and ionic strength, and the polyelectrolyte was added five minutes after the alum. The results are shown in Table 5.

Table 5

Anionic Polyelectrolyte Destabilization

Alum,	ml	5	15
	ppm	3.07	9.21
Anionic PE,	ml	5	1
	ppm	0.1	0.02
ZP,	mv	-27	+20

Since these ZP values ranged from -27 to +20 mv, alum volumes between 5 and 15 ml were selected, with anionic polyelectrolyte volumes between 1 to 5 ml.

Preliminary Testing

The preliminary testing was carried out in two parts. First, the alum and cationic polyelectrolyte were used. Second, the alum and anionic polyelectrolyte were used. In these tests, three time intervals, three alum concentrations, and three polyelectrolyte concentrations were evaluated while temperature, pH and ionic strength were held constant. The dependent parameters examined were turbidity, total solids and ZP. Preliminary testing was used to give an indication of how reasonable the arbitrarily chosen time intervals were. Graphical presentations were thought to be the best way to present the results (34). In the graphical presentation, the dependent parameters (turbidity, total solids, and ZP) are shown versus relative time with different constant polyelectrolyte concentrations on the same graph.

Alum and cationic polyelectrolyte. The results are shown in Table 6. These results are graphed and arranged for turbidity, total solids and ZP. The standard values from Table 3 are also included on the figures for comparison.

Table 6

Turbidity, Total Solids and ZP Cationic-Alum
Preliminary Test Results

	Relative Time (min)								
	-5			0			+7		
	Alum (ml)			Alum (ml)			Alum (ml)		
PE	1	3	5	1	3	5	1	3	5
(ml)	Turbidity (FTU)								
.7	245	240	325	440	68	340	236	230	16
.85	280	285	310	400	35	410	80	55	10
1.0	280	220	260	420	330	370	315	200	7.2
	Total solids (ppm)								
.7	94	86	86	104	24	104	110	70	8
.85	110	84	86	112	28	104	110	36	8
1.0	86	66	78	106	80	98	106	64	8
	ZP (mv)								
.7	-35	+23	+11	-33	-4	+ 7	-43	-12	+23
.85	-21	+ 5.5	+13	-33	-6	+13	-42	+ 3	+23
1.0	- 8	+11	+13	-16	+4	+12	-34	+ 6	+24

Turbidity. Figure 10 shows the turbidity results versus relative time for 1, 3 and 5 ml of alum. It was seen that varying the amounts of cationic polyelectrolyte did not effect the "average trend" of the lines, excluding certain points. This lead to "trend curves" which were developed for the average of the polyelectrolyte values at a certain time. Figure 11 is the turbidity trend for the cationic-alum preliminary test. The trend curves show all three alum concentrations on the same graph. Points omitted in the averaging were: 3 ml alum-0 minutes-1.0 ml PE, and 1 ml alum-+7 minutes-.85 ml PE.

Total solids. Figure 12 shows total solids versus relative time for the 1, 3 and 5 ml alum amounts. The total solids trend for cationic-alum preliminary test is given in Figure 13. The point omitted in averaging was at 3 ml alum-0 minutes-1.0 ml PE.

Zeta potential. Figure 14 shows ZP versus relative time for 1, 3 and 5 ml alum amounts. The ZP trend for cationic-alum preliminary test is given in Figure 15. No points were excluded.

Alum and anionic polyelectrolyte. These results are shown in Table 7. These results are graphed and arranged for turbidity, total solids and ZP. Included also are the standard values from Table 3.

Turbidity. Figure 16 shows the turbidity versus relative time for 5, 10 and 15 ml alum amounts. The turbidity trend for anionic-alum preliminary test is given in Figure 17. The point omitted in averaging was at 5 ml alum-0 minutes-5 ml PE.

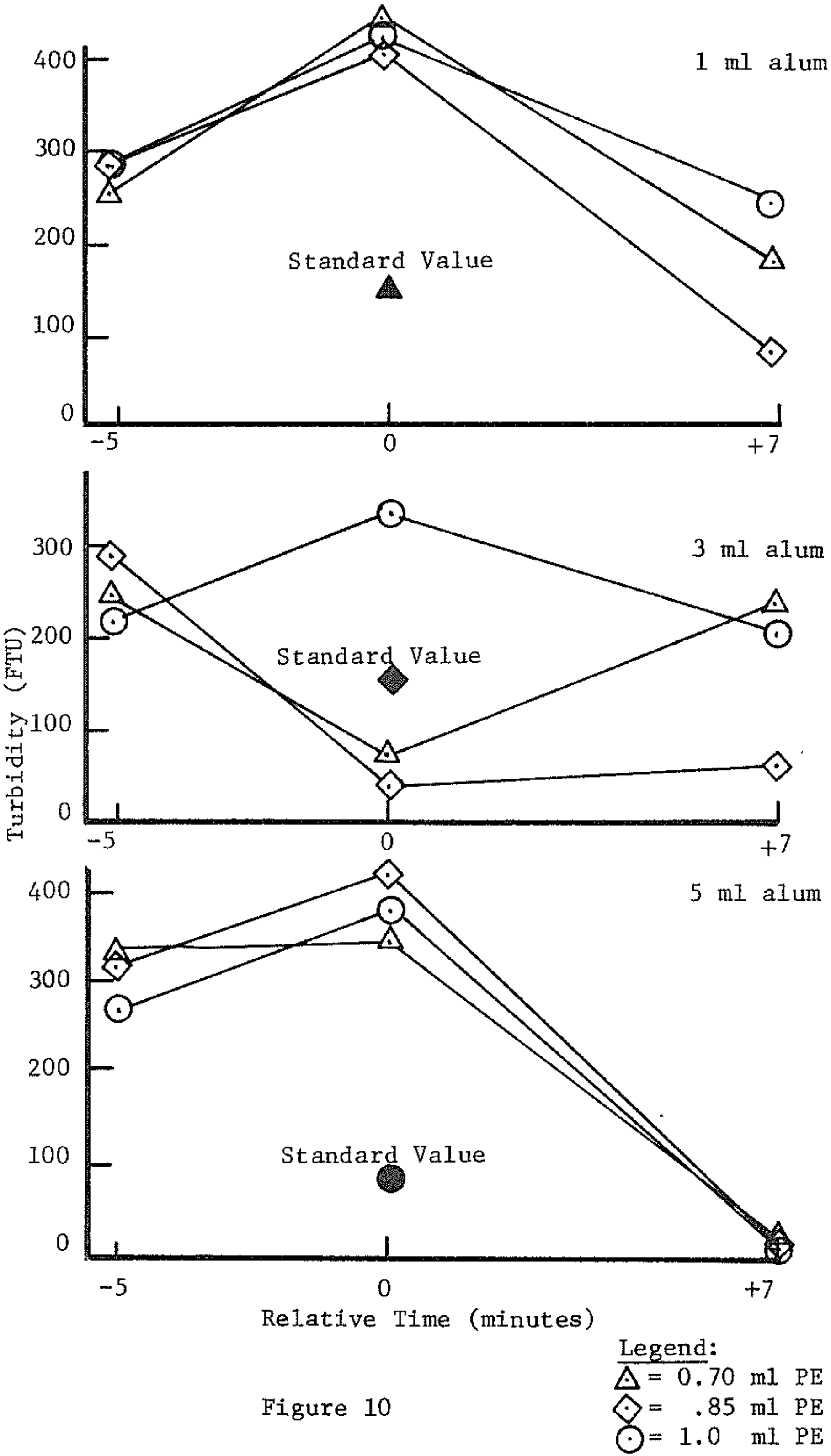

Figure 10

Turbidity vs. Relative Time for
Cationic Preliminary Test

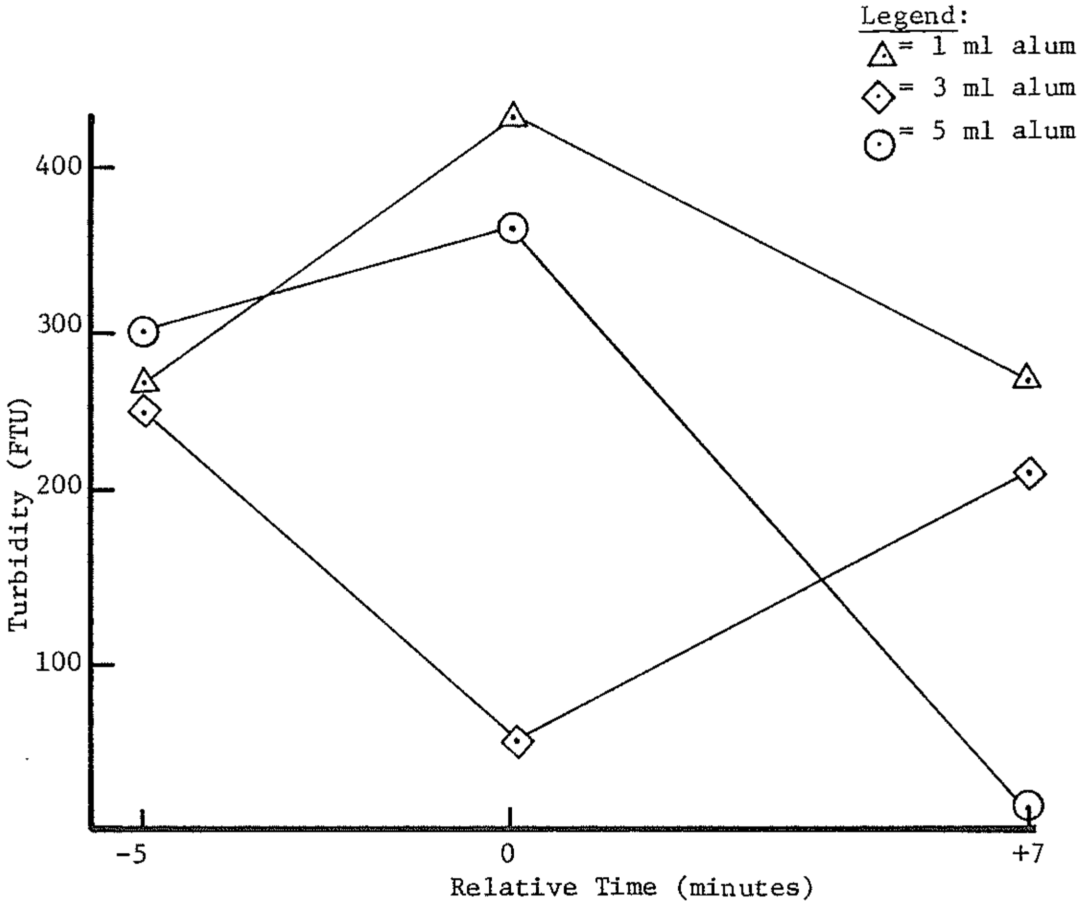

Figure 11

Turbidity Trend for Cationic-Alum
Preliminary Test

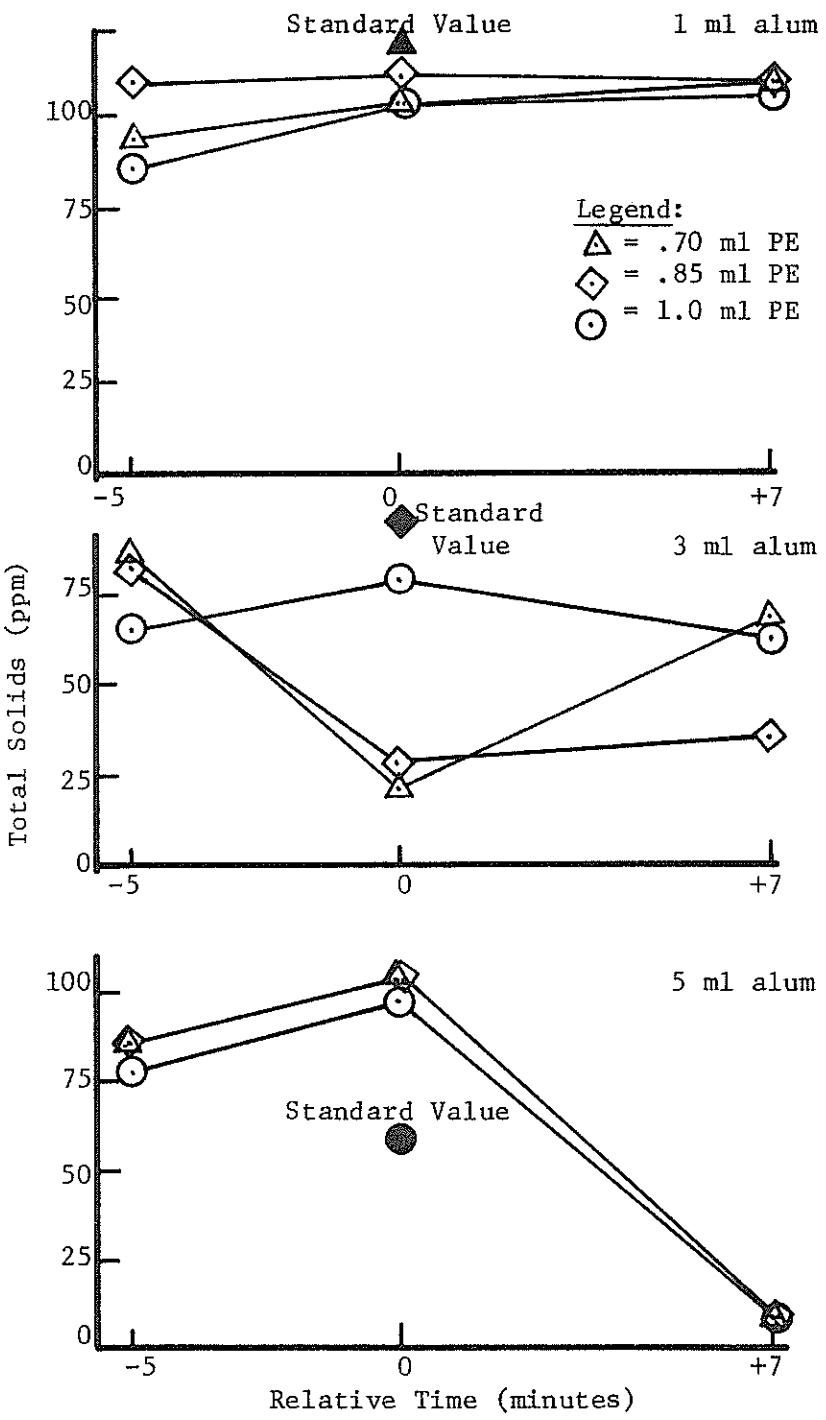

Figure 12

Total Solids vs. Relative Time - Cationic Preliminary Test

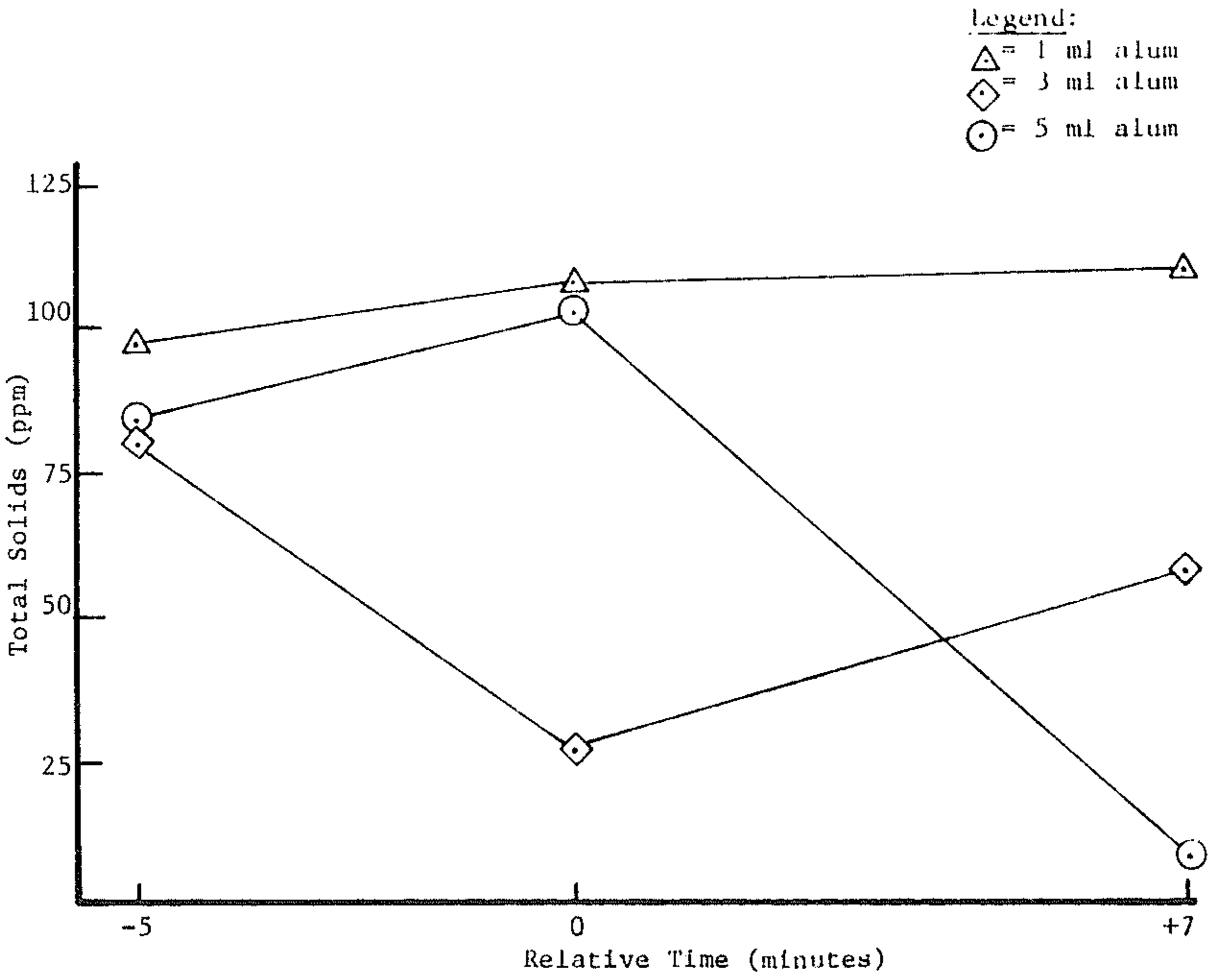

Figure 13

Total Solids Trend for Cationic-Alum
Preliminary Test

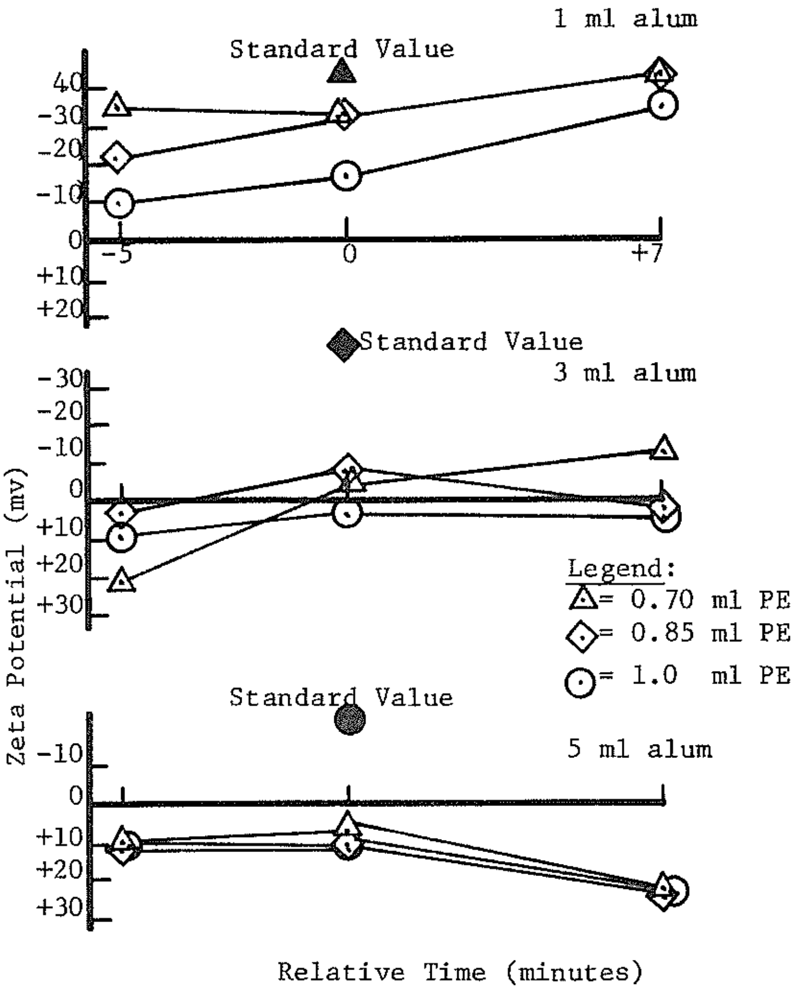

Figure 14

Zeta Potential vs. Relative Time for
Cationic Preliminary Test

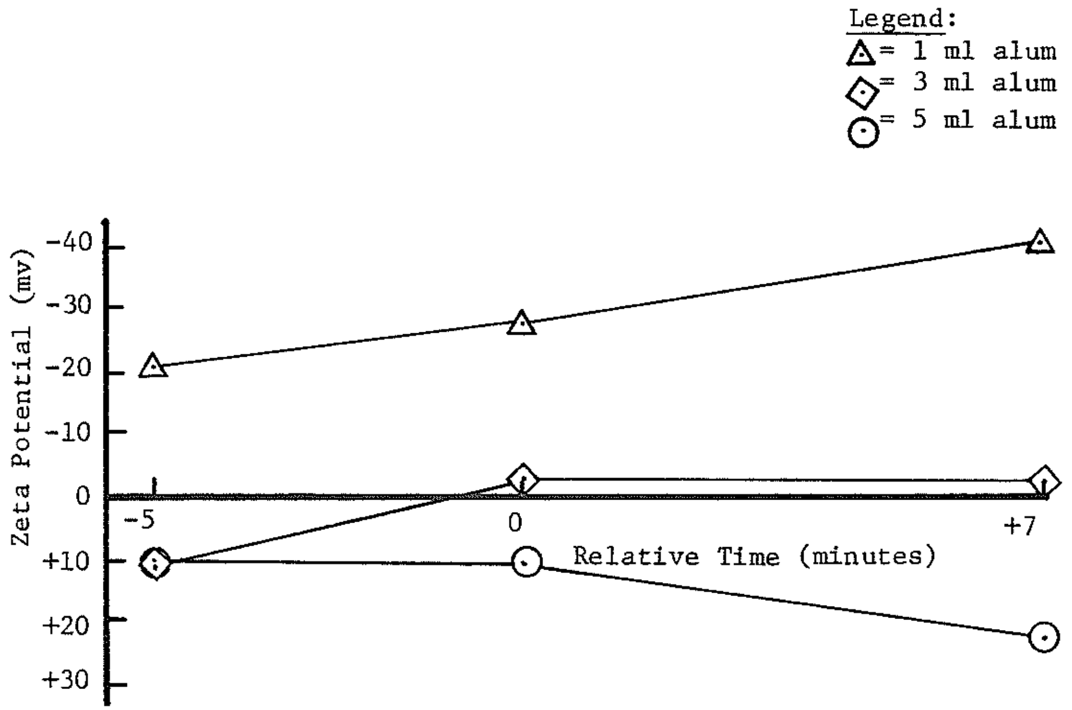

Figure 15

Zeta Potential Trend for
Cationic-Alum Preliminary Test

Table 7

Turbidity, Total Solids and ZP Anionic-Alum
Preliminary Test Results

	Relative Time (min)								
	-5			0			+5		
	Alum (ml)			Alum (ml)			Alum (ml)		
PE	5	10	15	5	10	15	5	10	15
(ml)	Turbidity (FTU)								
1	48	420	115	39	135	80	6.3	18	85
3	90	320	245	42	150	200	5.5	8.2	77
5	150	290	90	420	57	195	25	52	55
	Total solids (ppm)								
1	24	126	62	20	42	44	20	8	38
3	30	100	86	22	44	66	20	8	28
5	50	94	42	110	22	72	2	22	32
	ZP (mv)								
1	-27	+12	+17	-16	- 9.5	+17	-21	-19	+20
3	-34	0	+20	-25	- 4	+17	-25	-20	-
5	-23	+ 2	+20	-22	-20	+16	-27	-34	0

Total solids. Figure 18 shows total solids versus relative time for 5, 10, and 15 ml alum amounts. Figure 19 is the total solids trend for anionic-alum preliminary test. The point excluded was the same as in the turbidity trend.

Zeta potential. Figure 20 shows the ZP versus relative time for 5, 10, and 15 ml alum amounts. The ZP trend for anionic-alum preliminary test is shown in Figure 21. The point omitted for averaging was at 15 ml alum-+7 minutes-5 ml PE.

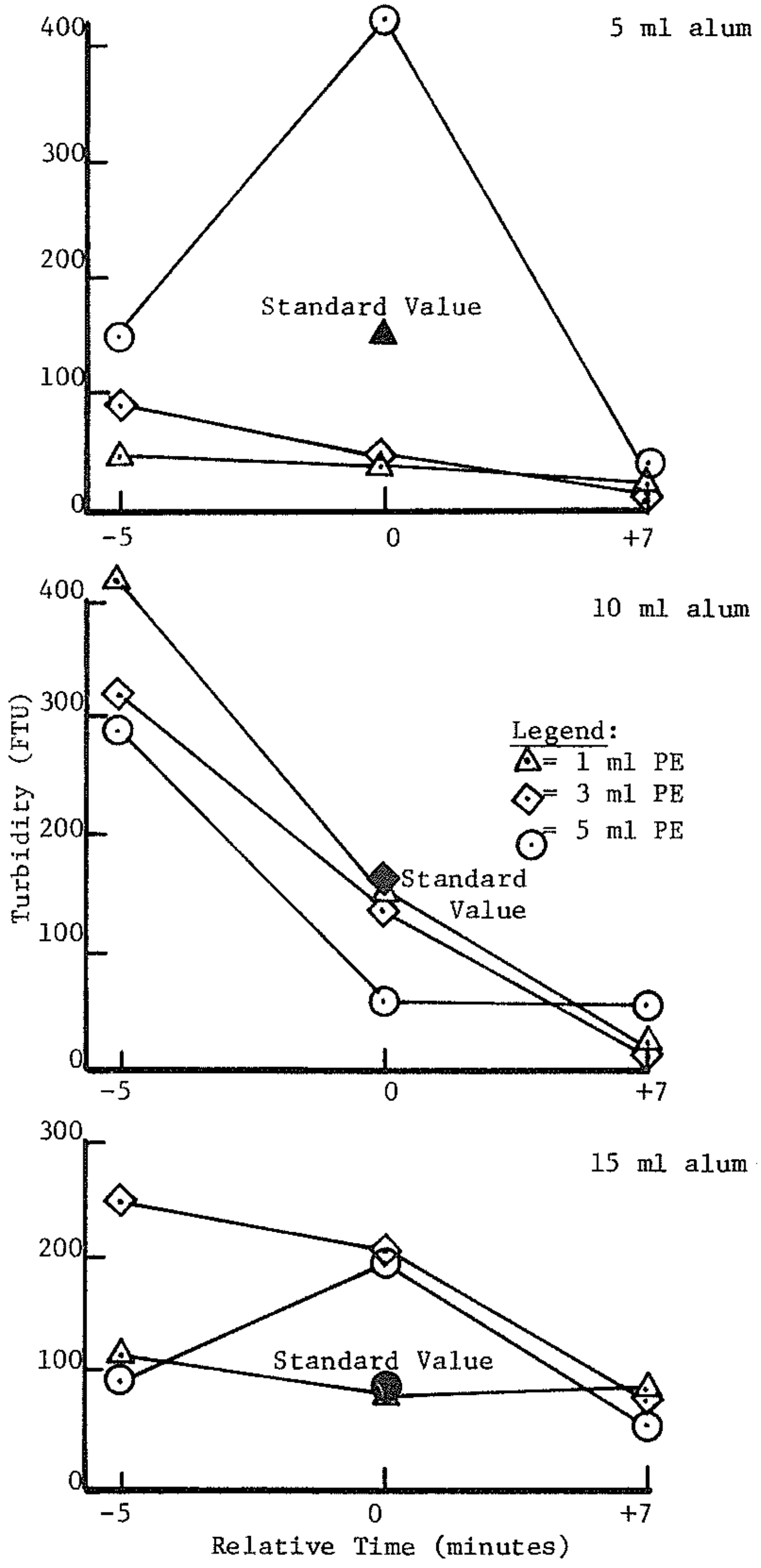

Figure 16

Turbidity vs. Relative Time for
Anionic Preliminary Test

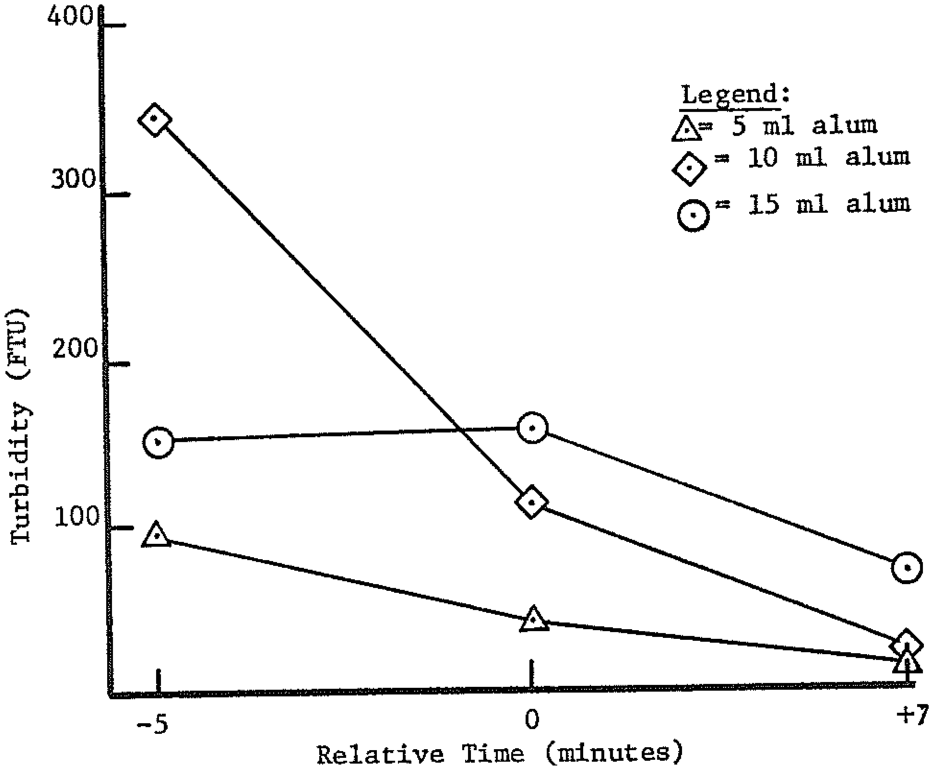

Figure 17

Turbidity Trend for Anionic-Alum
Preliminary Test

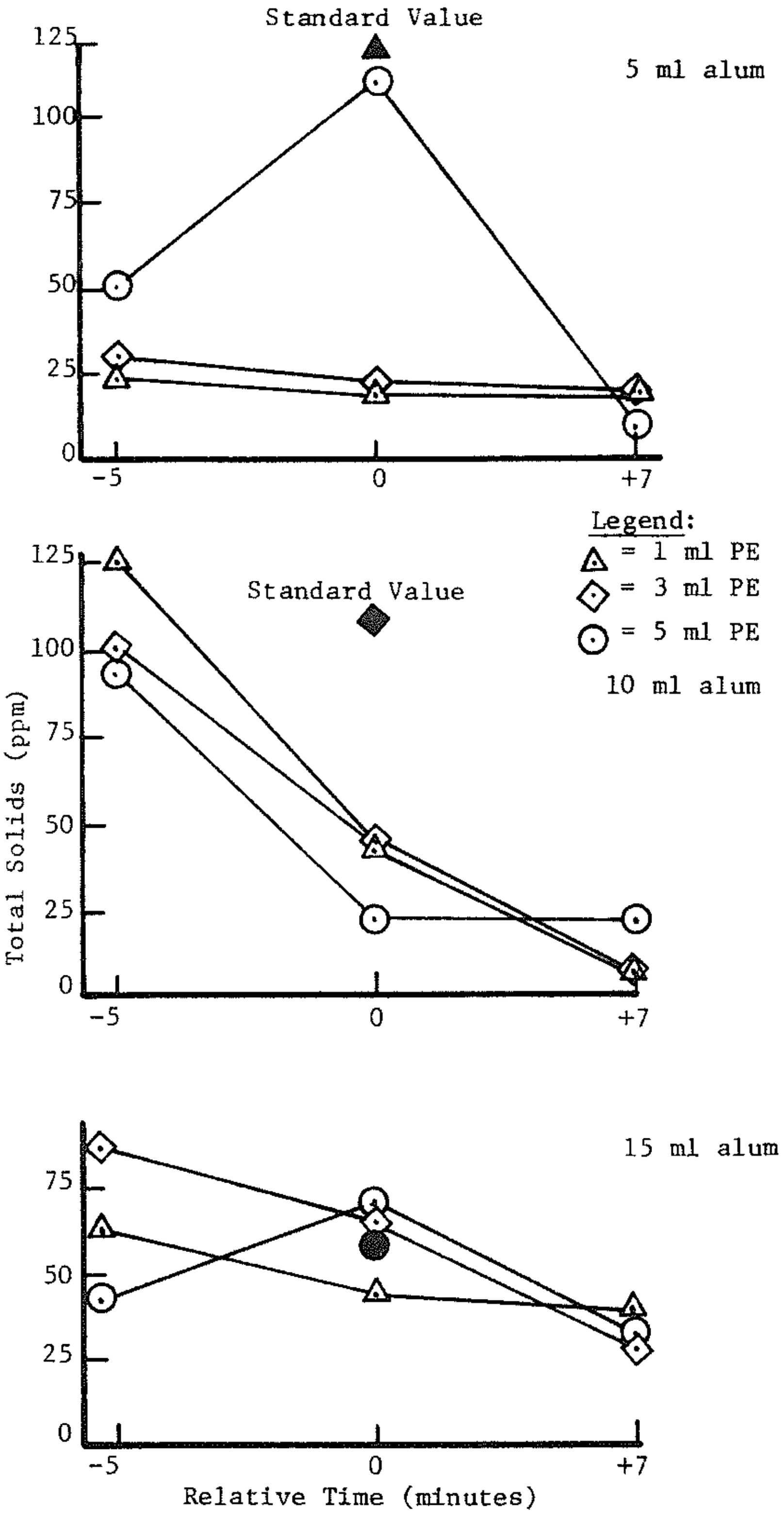

Figure 18

Total Solids vs. Relative Time for
Anionic Preliminary Test

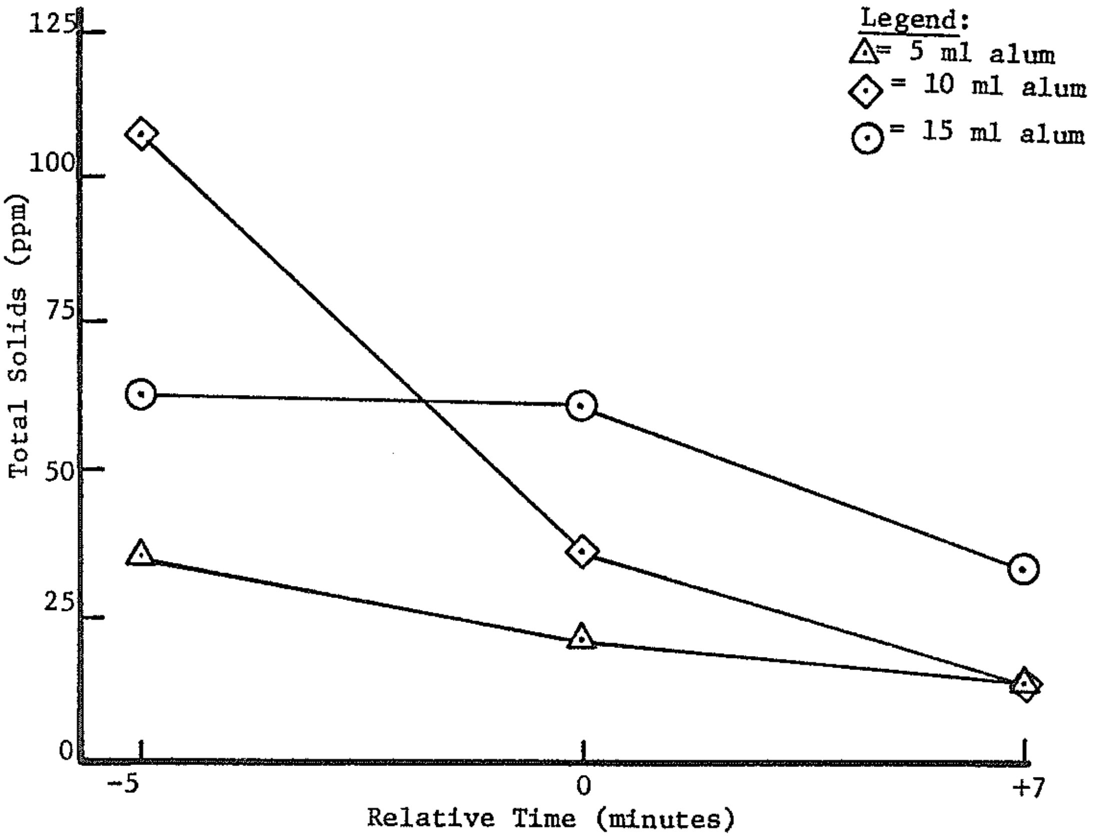

Figure 19

Total Solids Trend for Anionic-Alum
Preliminary Test

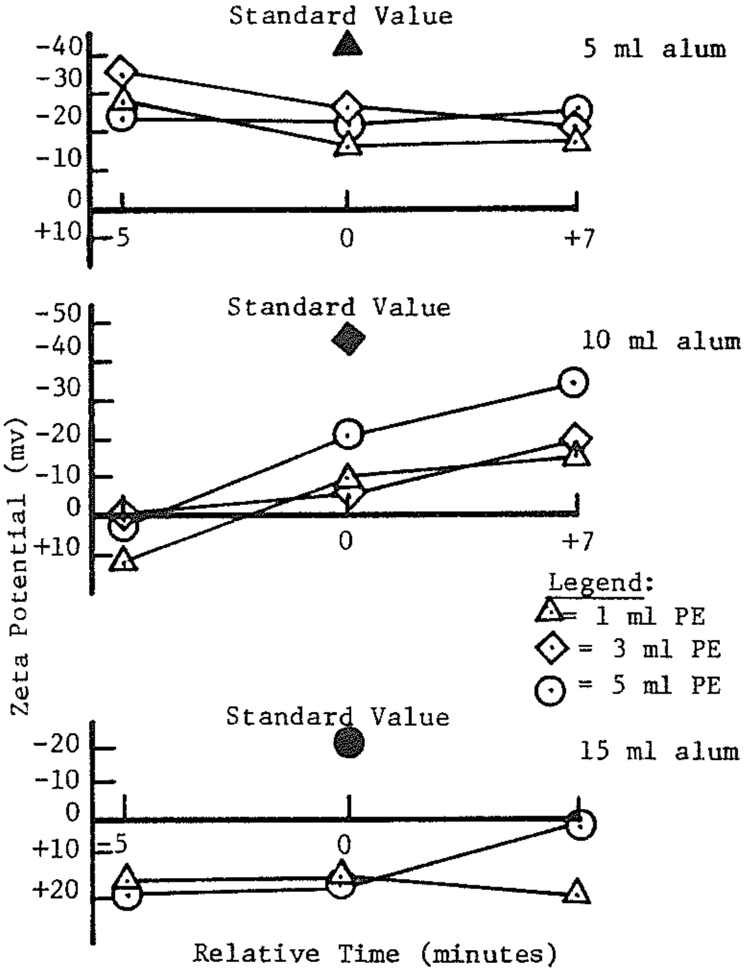

Figure 20

Zeta Potential vs. Relative Time for
Anionic Preliminary Test

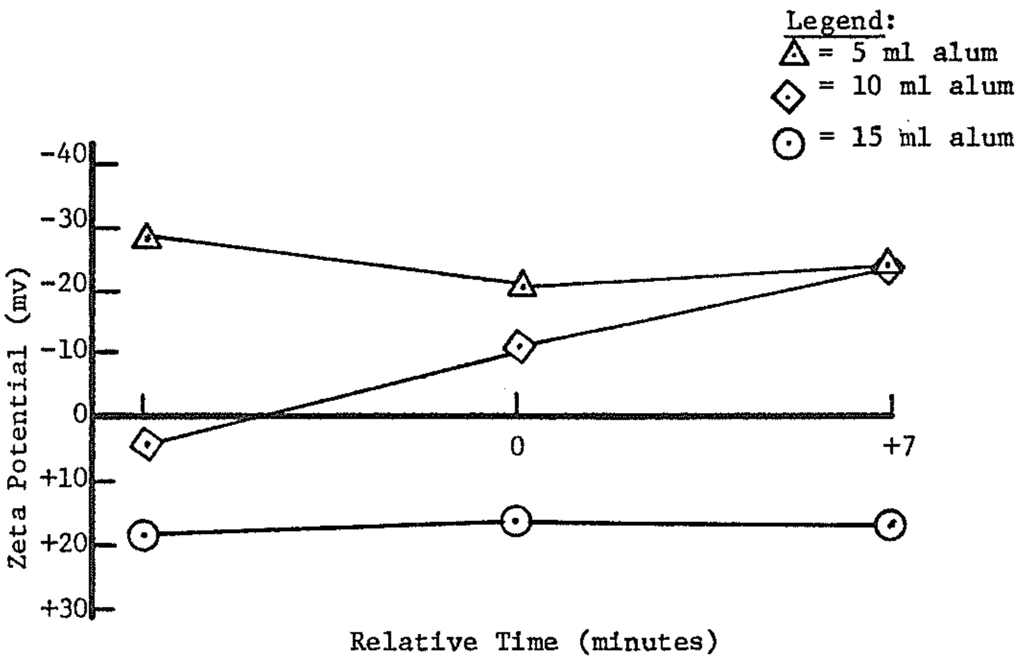

Figure 21

Zeta Potential Trend Curve for Anionic-Alum Preliminary Test

Cationic-Alum Expanded Test

Examination of the preliminary test for cationic polyelectrolyte lead to expanded testing of the cationic polyelectrolyte. The purpose of the expanded testing was to look at intermediate time intervals for the same polyelectrolyte concentrations and alum concentrations. The expanded time intervals "smoothed" out the curves and gave a better idea of what was happening and also checked reproducibility of tests. The expanded intervals were -5, -4, -2, 0, +2, +4, and +5 minutes. The results of the expanded tests are shown in Table 8. The dependent parameters were examined in two ways: first, a correlation between dependent parameters was attempted, and second, graphical presentations were made similarly to the preliminary tests.

Correlation between dependent parameters. Six different correlations were studied: (a) correlation between turbidity and total solids, (b) correlation between turbidity and zeta potential, (c) correlation between total solids and zeta potential, (d) correlation between Al^{3+} concentration and turbidity, (e) correlation between Al^{3+} concentration and total solids, and (f) % Al^{3+} removal and zeta potential.

Turbidity vs. total solids. Figure 22 shows turbidity versus total solids. Also shown in the pure latex suspension value from Table 1.

Turbidity vs. zeta potential. Figure 23 shows turbidity versus zeta potential. Again, the pure latex suspension value from Table 1 is shown.

Table 8

Turbidity, Total Solids, ZP, Al^{3+} Concentration, and % Al^{3+} Removal Cationic-Alum Expanded Test

	Relative Time (min)																				
	-5			-4			-2			0			+2			+4			+5		
	Alum (ml)			Alum (ml)			Alum (ml)			Alum (ml)			Alum (ml)			Alum (ml)			Alum (ml)		
PE	1	3	5	1	3	5	1	3	5	1	3	5	1	3	5	1	3	5	1	3	5
(ml)	Turbidity (FTU)																				
.7	280	48	290	200	275	275	300	50	215	250	125	185	260	83	170	215	56	20	260	100	24
.85	300	88	98	285	43	165	280	40	320	265	38	315	330	69	100	230	70	33	250	58	9.5
1.0	275	97	295	240	90	270	320	51	320	400	55	125	155	280	120	215	53	39	290	63	10
	Total Solids (ppm)																				
.7	72	16	40	96	98	74	66	4	66	112	50	28	112	36	48	108	10	10	110	36	12
.85	84	10	78	78	16	56	96	26	76	116	14	78	108	28	8	120	28	32	98	8	18
1.0	78	14	84	50	30	76	88	20	88	78	20	52	124	112	34	110	14	8	98	18	8
	ZP (mv)																				
.7	-23	0	+13	-37	-27	+11	-22	+11	-3	-34	-23	+14	-37	-11	+11	-43	-18	+16	-36	-19	+21
.85	-24	0	-10	-28	- 8	+10	-22	-13	+7	-44	-13	+ 5	-25	- 8	+20	-40	-17	+20	-45	- 9	+18
1.0	-18	+14	+13	-17	+ 6	+ 6	-15	+ 9	+8	-15	- 9	+ 4	-44	+14	+16	-35	- 5	+13	-33	- 7	+19
	Al^{3+} Concentration (ppb)																				
.7	100	14	45	25	12	34	30	40	100	25	44	227	0	50	96	24	15	50	12	0	24
.85	20	46	70	26	108	14	46	110	0	30	24	0	-	0	24	85	24	46	12	0	20
1.0	110	28	47	46	140	76	24	0	27	63	80	20	28	35	36	15	0	36	80	90	36
	% Al^{3+} Removal (%)																				
.7	-	91	83	54	93	87	44	75	63	54	73	16	100	69	96	54	91	81	78	100	91
.85	63	72	74	52	33	95	15	32	100	44	85	100	-	100	91	47	85	83	78	100	93
1.0	-	83	83	15	14	72	56	100	90	-17	51	93	28	78	87	74	100	87	48	44	87

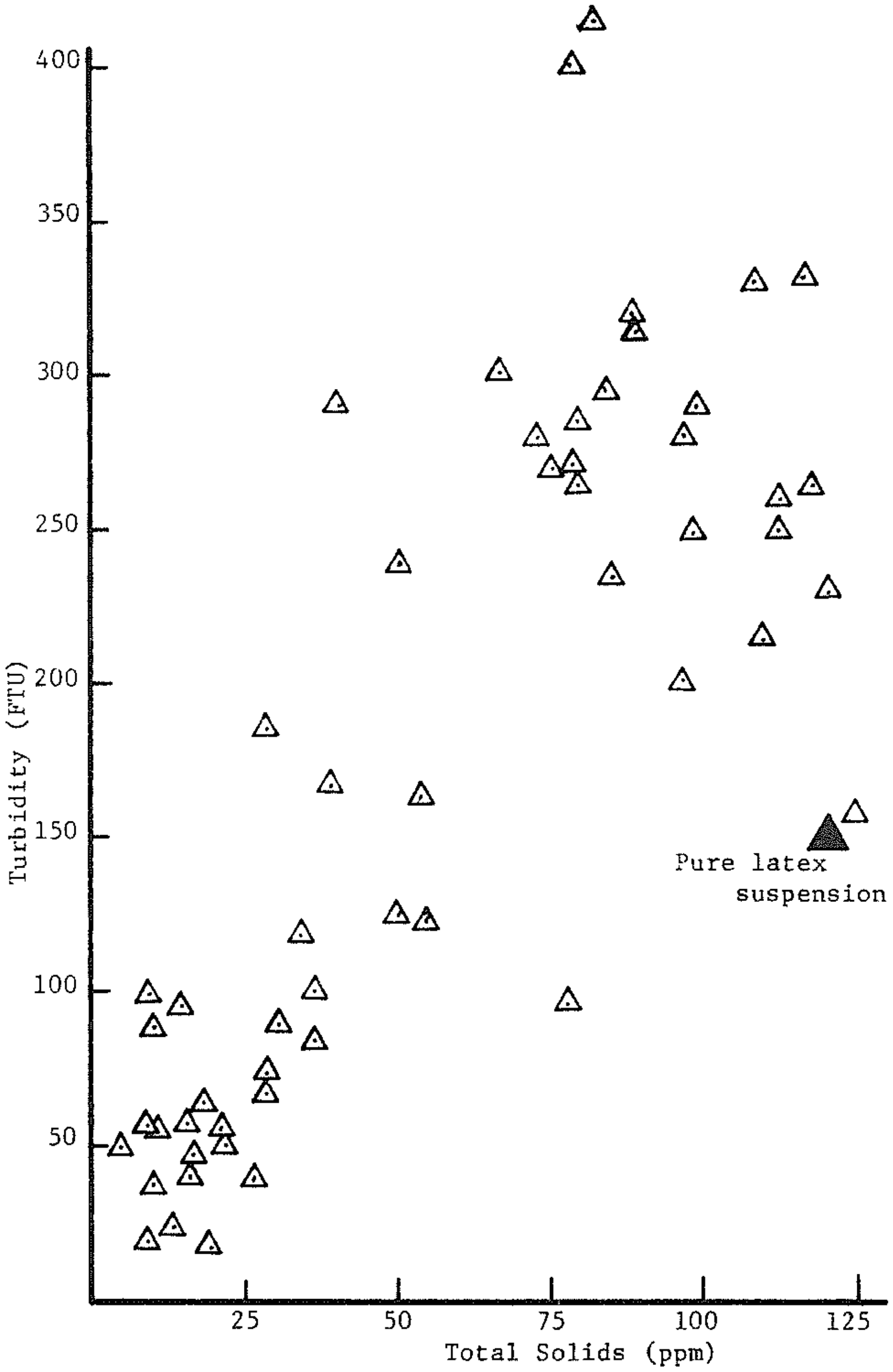

Figure 22

Turbidity vs. Total Solids

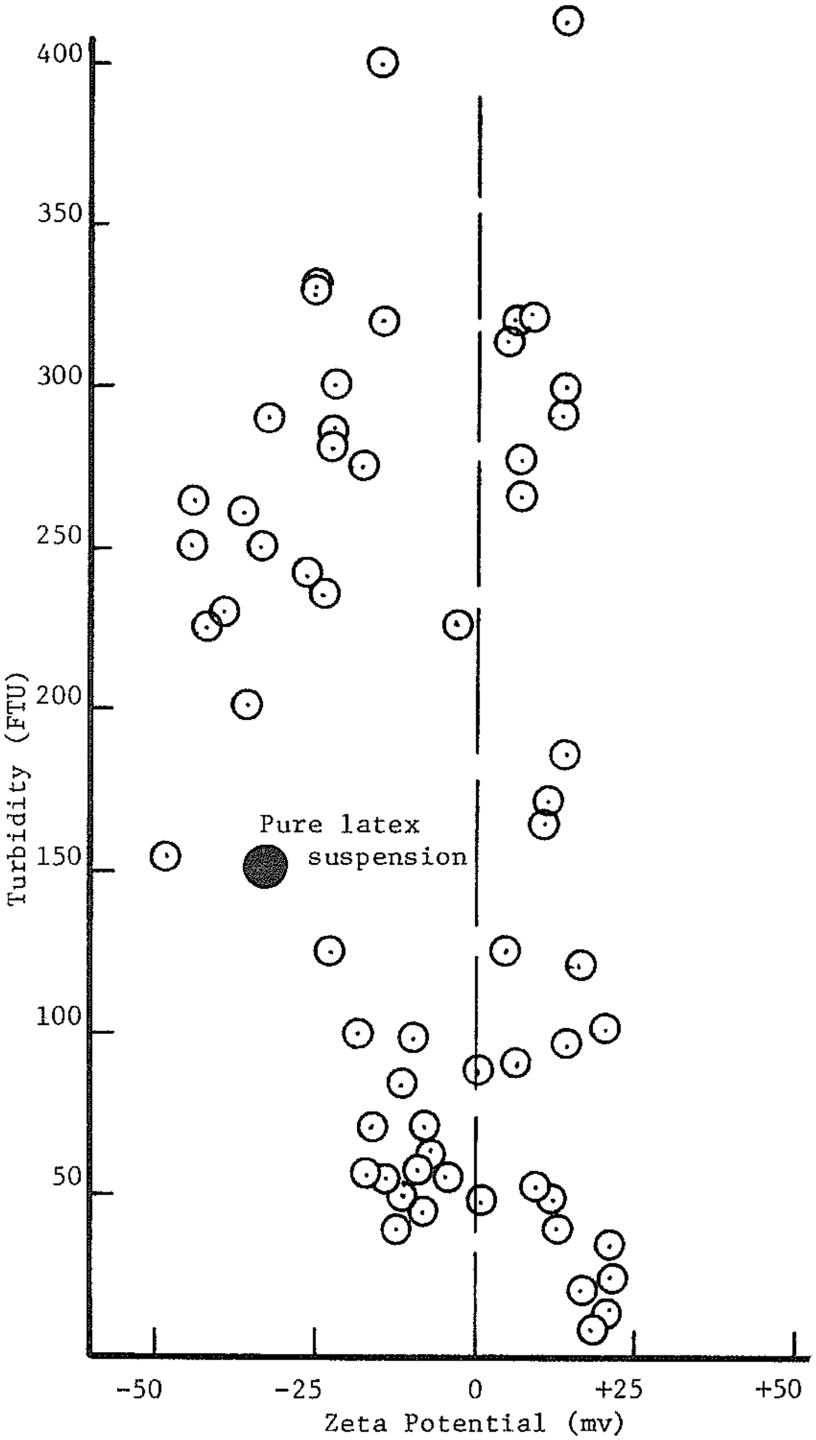

Figure 23

Turbidity vs. Zeta Potential

Total solids vs. zeta potential. Figure 24 shows total solids versus zeta potential. Again, the pure latex suspension value from Table 1 is shown. It can be seen that a zeta potential more negative than -20 mv gave a high total solids amount.

Al^{3+} concentration vs. turbidity. Figure 25 shows the Al^{3+} concentration versus turbidity.

Al^{3+} concentration vs. total solids. Figure 26 shows the Al^{3+} concentration versus total solids.

% Al^{3+} removal vs. zeta potential. For determining % Al^{3+} removal the following formula was used:

$$\% \ \text{Al}^{3+} \text{ removal} = \frac{(\text{Al}^{3+} \text{ in suspension originally}) - (\text{Al}^{3+} \text{ in suspension finally})}{\text{Al}^{3+} \text{ in suspension originally}} \times 100$$

Amounts for Al^{3+} in suspension originally were determined for volumes of 0.001 M alum put into one liter suspensions and are given in Table 9.

Table 9

Al^{3+} Values from Added Alum Amounts

Alum Amount (ml)	Al^{3+} in suspension (ppb)
1	54
3	162
5	270

The present removals were calculated and are listed in Table 8. Figure 27 shows the % Al^{3+} removal versus total solids, with negative values omitted as bad data points.

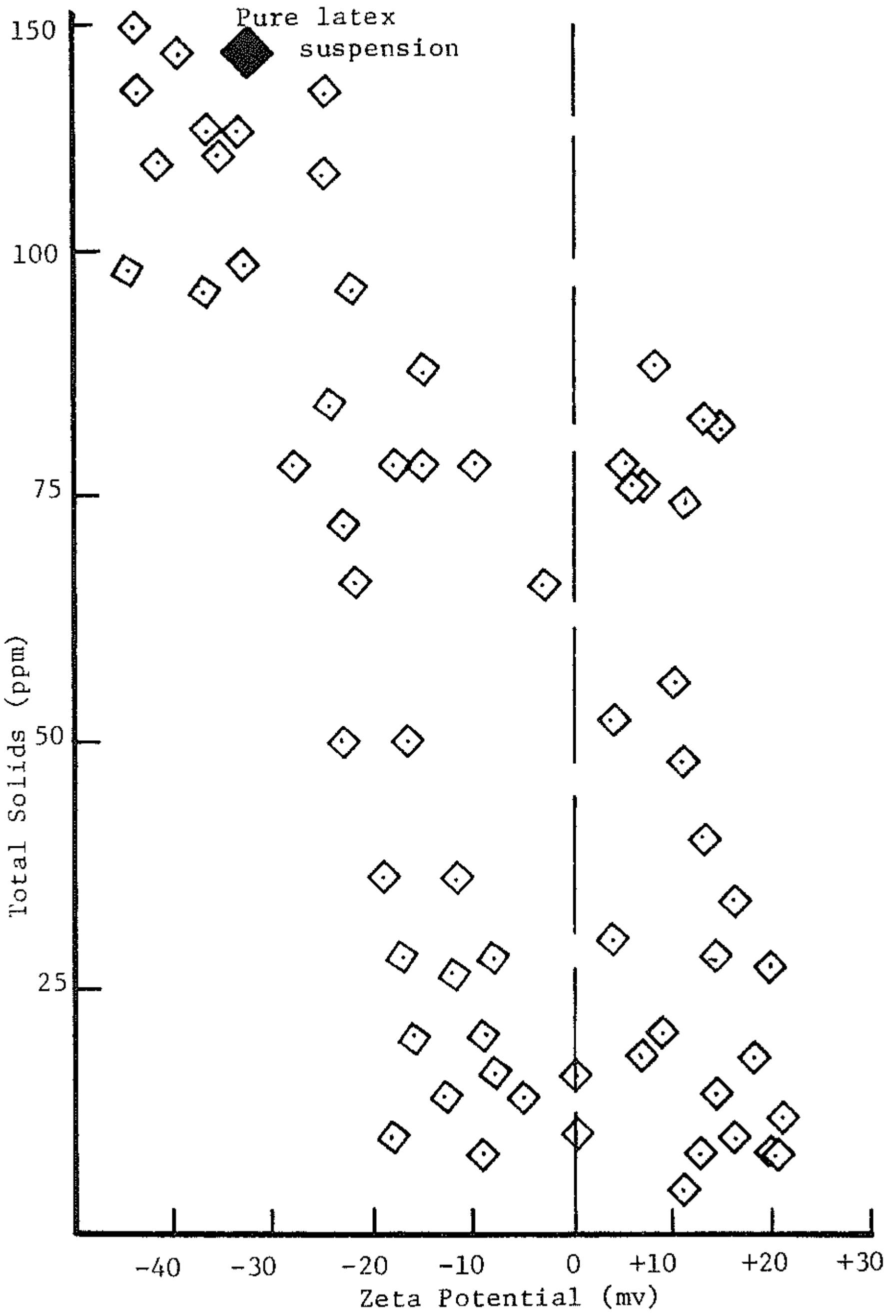

Figure 24

Total Solids vs. Zeta Potential

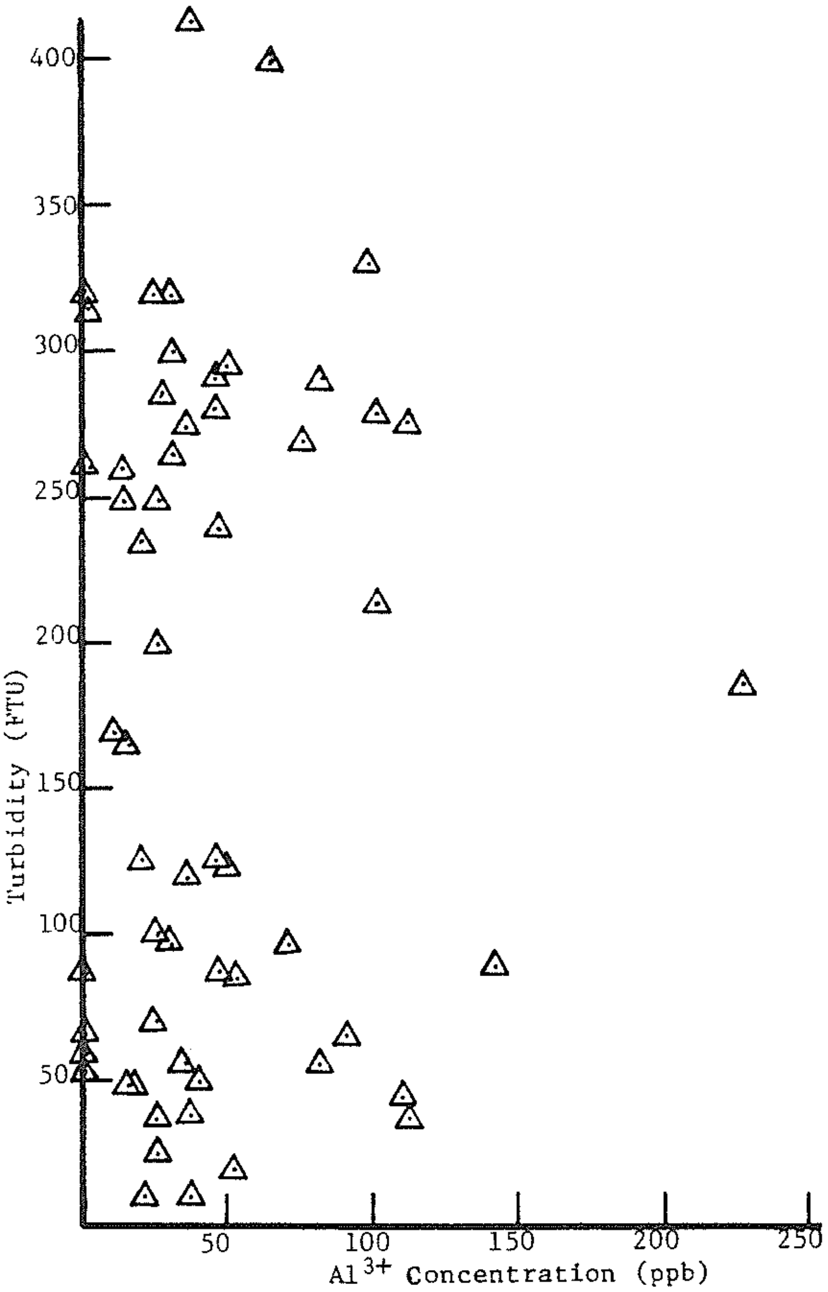

Figure 25

Turbidity vs. Al^{3+} Concentration

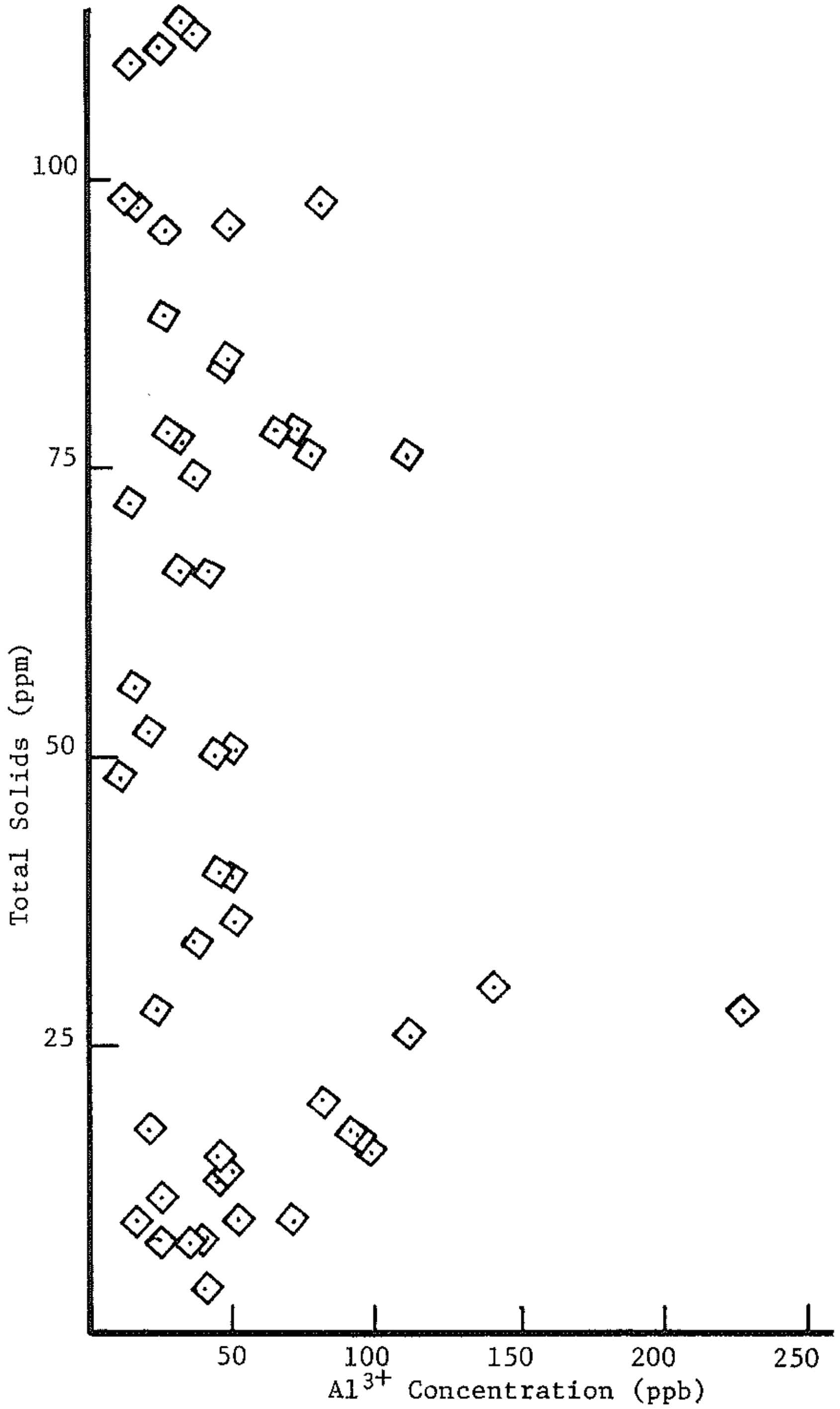

Figure 26

Total Solids vs. Al^{3+} Concentration

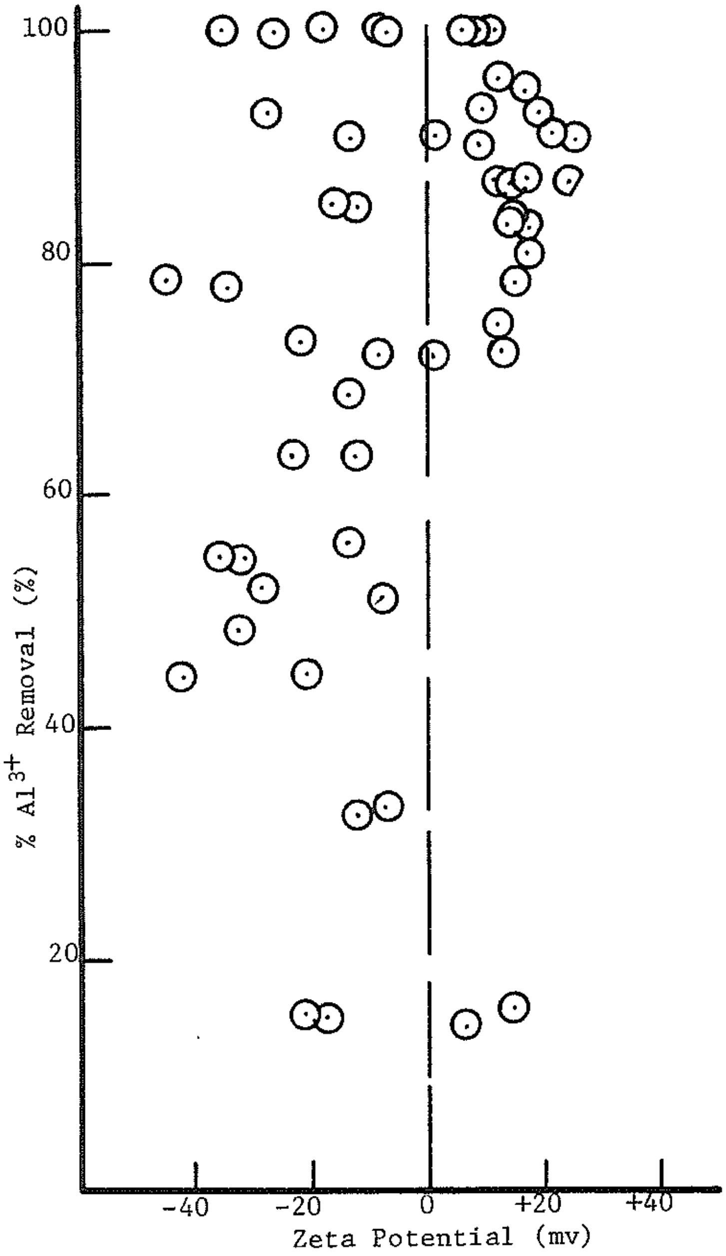

Figure 27

% Al^{3+} Removal vs. Zeta Potential

Dependent parameter vs. relative time. The graphical presentation for expanded tests was just like the preliminary tests. Three dependent parameters were evaluated: turbidity, total solids and zeta potential. Included also were standard values from Table 3.

In order to more easily visualize the variations of total solids as a function of time and alum concentration, Appendix Figure 34, a three dimensional response graph, is presented in the Appendix.

Turbidity. Figure 28 shows turbidity versus relative time for the 1, 3 and 5 ml alum amounts. The turbidity trend for cationic-alum expanded test is shown in Figure 29. Four points were omitted in the averaging: at 1 ml alum--0 minutes-1.0 ml PE, at 3 ml alum--4 minutes-.70 ml PE, at 3 ml alum-+2 minutes-1.0 ml PE, and at 5 ml alum--5 minutes-1.0 ml PE.

Total solids. Figure 30 shows total solids versus relative time for the 1, 3 and 5 ml alum amounts. The total solids trend for cationic-alum expanded tests is shown in Figure 31. Two points were omitted in the averaging: at 3 ml alum--4 minutes-.70 ml PE, and at 3 ml alum-+2 minutes-1.0 ml PE.

Zeta potential. Figure 32 shows ZP vs. relative time for 1, 3 and 5 ml alum amounts. Given in Figure 33 is the ZP trend for cationic-alum expanded test. No points were omitted in the averaging.

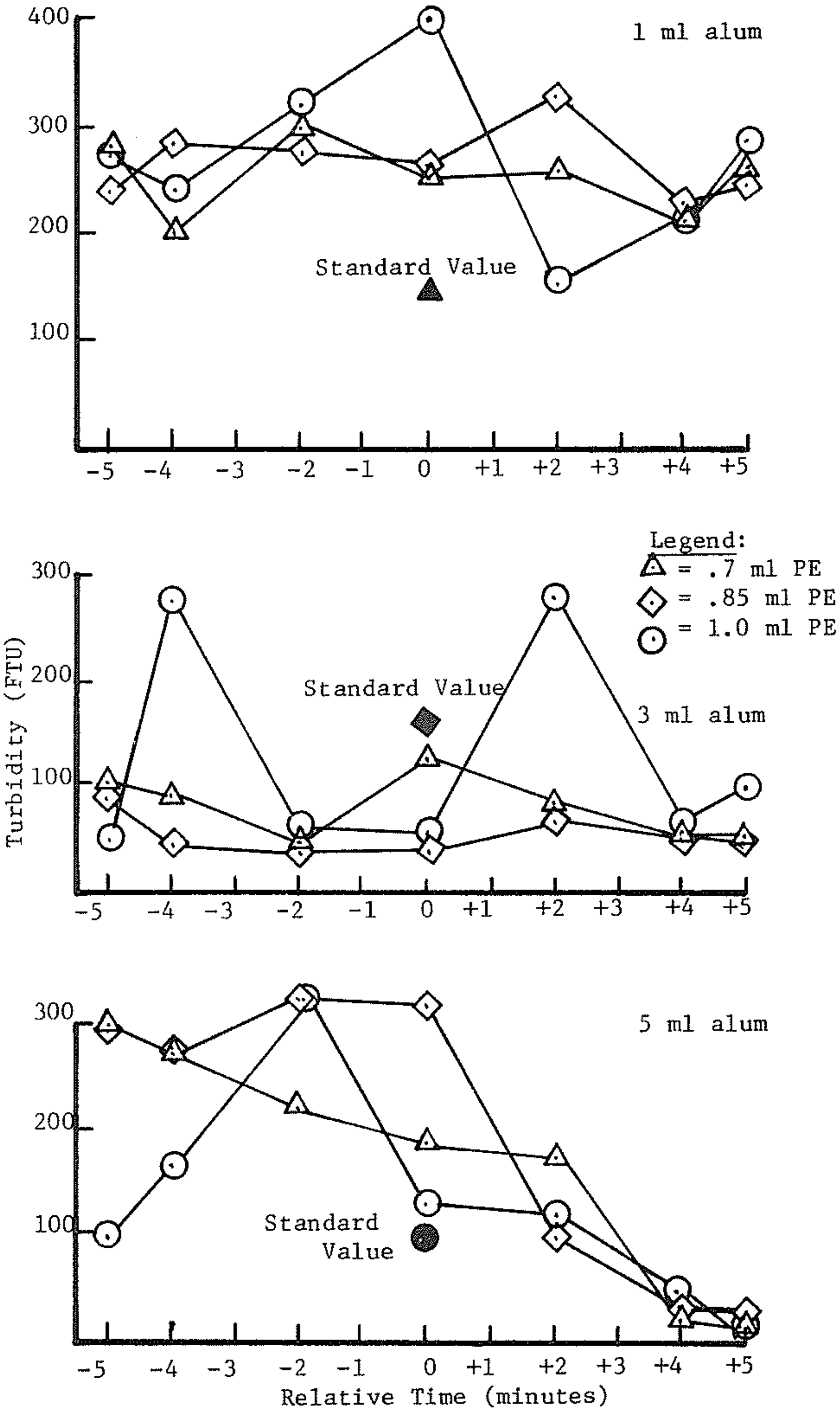

Figure 28

Turbidity vs. Relative Time for
Cationic Expanded Test

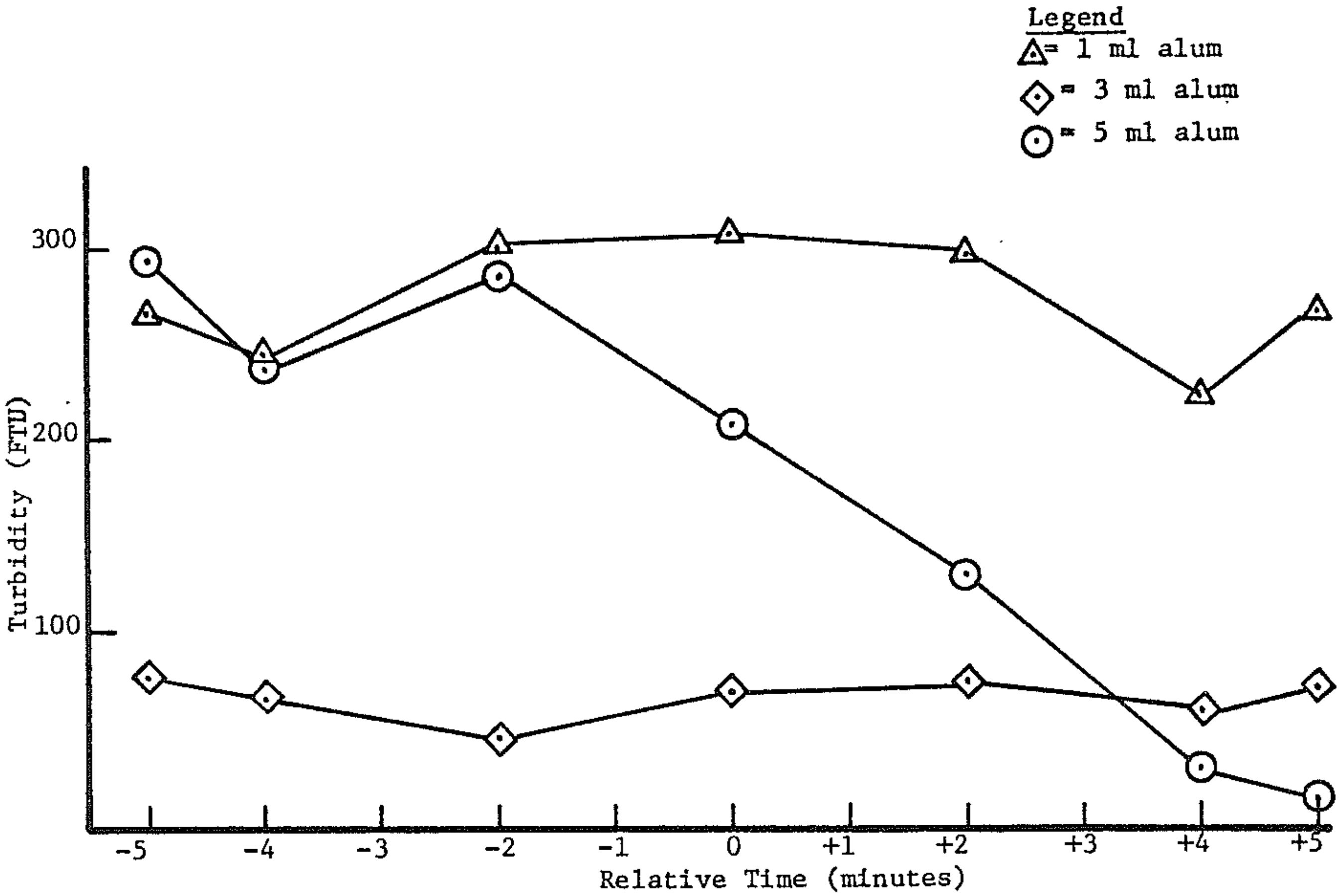

Figure 29

Turbidity Trend Curve for Cationic-Alum Expanded Test

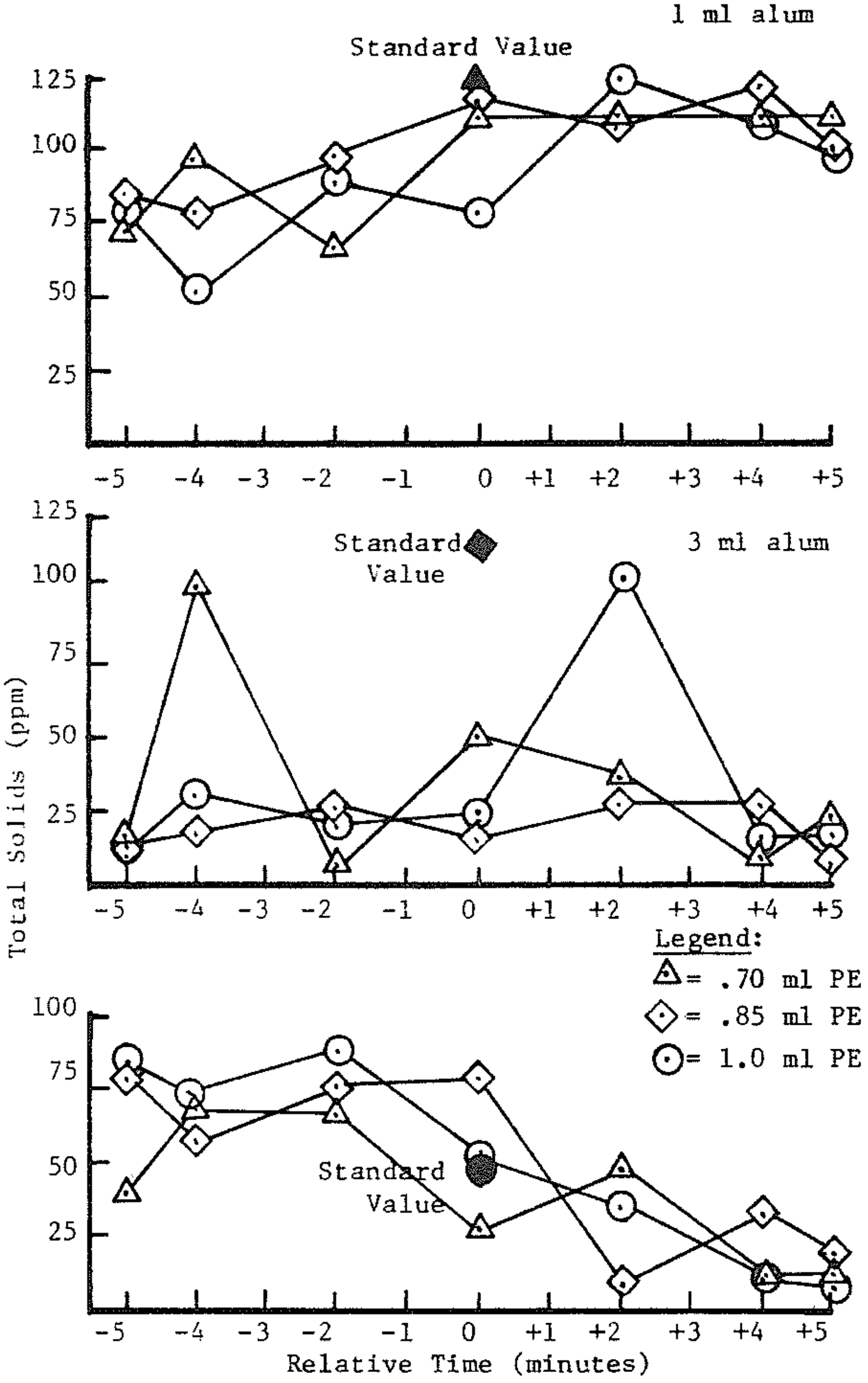

Figure 30

Total Solids vs. Relative Time for
Cationic Expanded Test

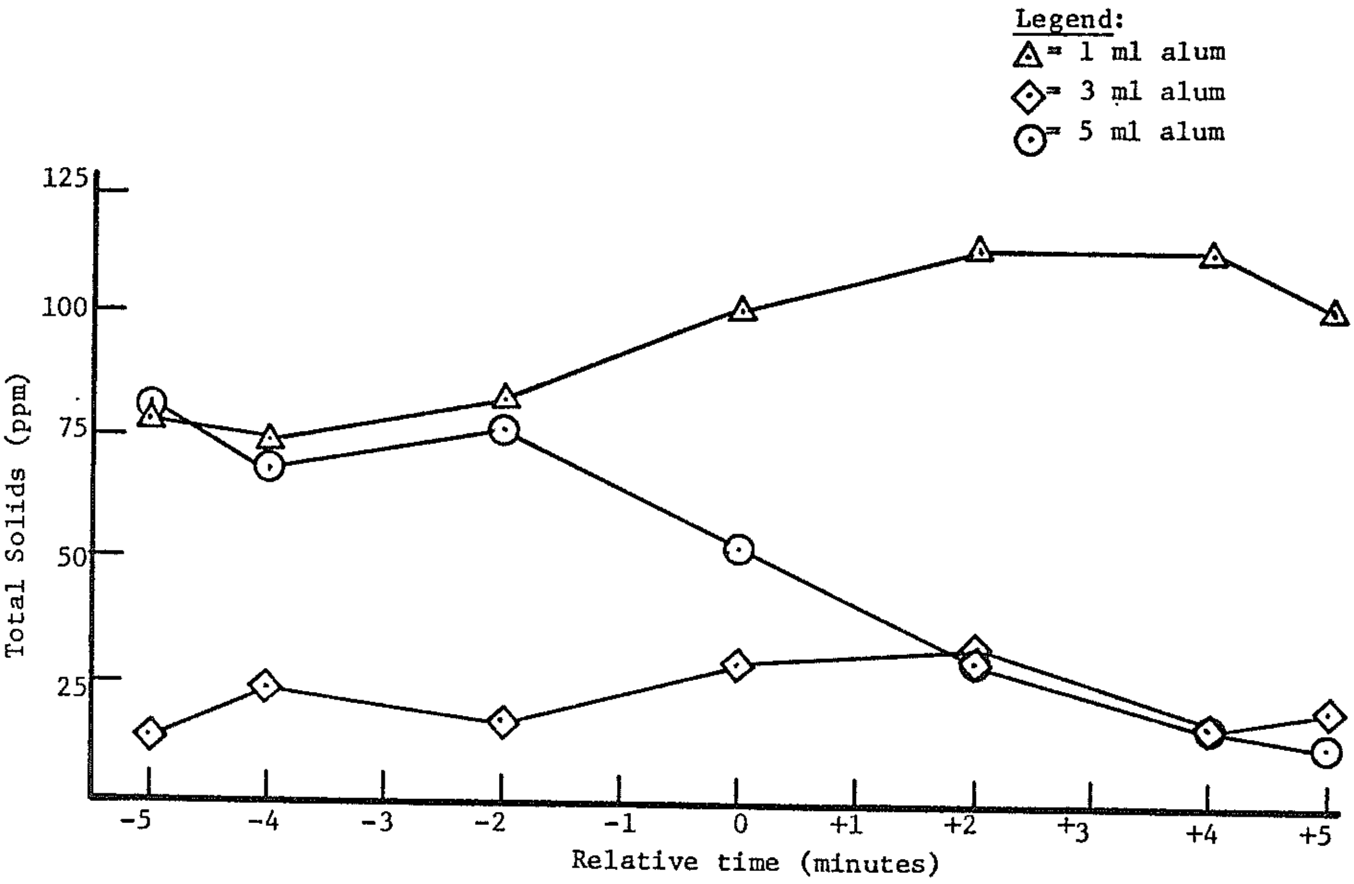

Figure 31

Total Solids Trend Curve for Cationic-Alum Expanded Test

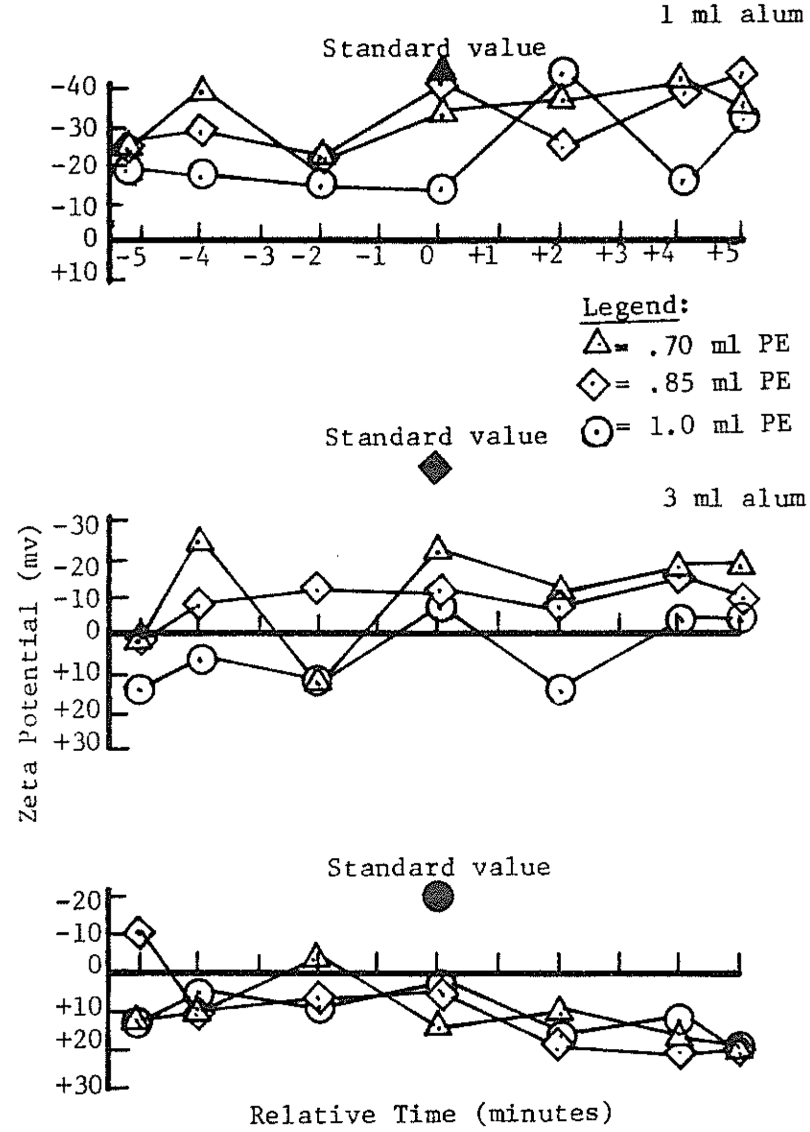

Figure 32

Zeta Potential vs. Relative Time for Cationic Expanded Test

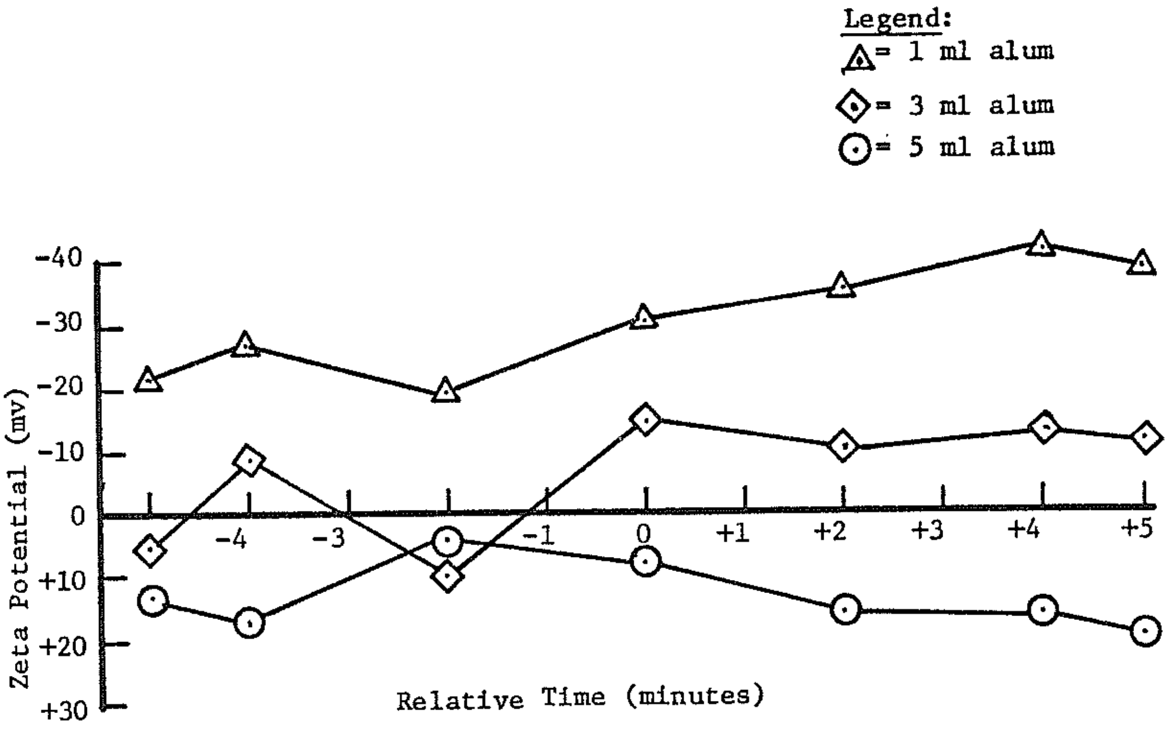

Figure 33

Zeta Potential Trend Curve for Cationic-Alum Expanded Test

DISCUSSION OF RESULTS

The discussion of the results was broken into three sections. First is a general discussion of the initial work of the investigation. Second is the discussion of the preliminary tests. Lastly is the discussion of the cationic-alum expanded test. Within the discussion, reference to "standard values" is made. These standard values refer to use of alum as a coagulant by itself and these values are found in Table 3 and on certain figures.

Initial Testing

In the initial work the material discussed pertains to both the preliminary and expanded testing. These areas include pH and ionic strength, parameter ranges, reproducibility, testing procedure and the selection of a colloidal suspension.

pH and ionic strength.

Although a standard procedure was developed for maintaining constant pH and ionic strength, some problems were encountered. The maximum volumes of K^+ solution which were set for cationic and anionic polyelectrolytes were exceeded at times because the pH of the distilled water varied from a pH of 5.0 to 5.5. Thus for a few tests (10 of 117), the ionic strength was greater than the maximum value. It was felt that this would not effect results significantly and thus no correction was made for these tests. From the Schultz-Hardy Rule, the coagulating power of the K^+ ion is 0.01 of the Al^{3+} ion. In further testing, the K^+ volumes should be increased to

15 ml for cationic polyelectrolyte and 20 ml for anionic polyelectrolyte.

Parameter ranges. As brought out in the Presentation of Results section, ranges for the alum and polyelectrolytes were decided upon by examination of zeta potentials. Examination of the Tables 6, 7 and 8 showed the ranges to be adequate. The ranges were adequate because the zeta potentials ranged from -45 to +20 mv which covered the range given by Riddick (1) for good coagulation. The time range was arbitrarily selected. Examination of the results showed that the time intervals gave the intended trends ranging from little coagulation to good coagulation.

Reproducibility. The latex suspension was chosen in order to achieve the best possible reproducibility of results. Reproducibility was desired in the following areas: zeta potential, total solids, turbidity, and between identical tests made at different times.

Zeta potential. Operator familiarization with the "Zeta-Meter" for a month and a half lead to reproducible results. Familiarization included various concentrations of latex suspension, different applied voltages, and various polyelectrolyte concentrations. It was felt that zeta potential measurements were reproducible within ± 3 mv.

Total solids. The total solids tests were conducted after much experimentation with drying and heating times. The main problem was obtaining a constant initial weight for the evaporating dishes. Thru a series of tests, the heating and drying times given in the

Procedure were determined. It is felt that the total solids were reproducible within ± 6 ppm.

Turbidity. Turbidity measurements were the least reproducible of the dependent parameters because of the sensitivity of the light-scattering measurer. The same identical tests showed that the turbidity would vary from 5 to 30%. Although there was smaller reproducibility, the trend was the same. Therefore, the trend that was found in the turbidity measurements was the same as the total solids trends.

Identical test reproducibility. As brought out in the presentation of the results, the one purpose of the expanded tests was to check the reproducibility of the preliminary tests. It was felt that this was accomplished from examination of Tables 6 and 8 and in the figures. Although dependent results of identical tests did not match exactly, considering the accuracy of the tests (turbidity and total solids) the results were considered reproducible.

Testing procedure. The testing of this latex was very involved. Controlling of pH and ionic strength, measuring alum and polyelectrolyte volumes, and adding flocculants at specific times, all added to the complexity of this testing procedure. Over the entire investigation's duration, familiarization of testing reduced the time for an individual test and increased results' accuracy. Although familiarization was obtained, the complexity of the tests did not decrease, and it is likely normal experimental error was observed.

Selection of colloidal suspension. As previously discussed, a latex suspension was selected as the synthetic colloidal suspension. Because of the latex's narrow size distribution and particle stability, it was felt that the latex would give reproducible results. As already discussed, the latex needed to be cleaned of emulsifiers by use of a mixed-bed of ion-exchange resins. Slight modifications to the published procedure were used and the procedure used is described in the Procedure section. The time for latex preparation was five to seven days. Although the latex preparation contained many steps and rinsings, no problems were encountered with the procedure. Because of the reproducibility achieved with this suspension, it was felt that the latex suspension was a good suspension to use for colloidal research. The time involved in cleaning the latex was worth the reproducibility that was achieved.

Preliminary Tests

Discussion of the preliminary tests is broken into two parts. The first part is discussion of the alum and cationic polyelectrolyte test and the second part is the alum and anionic polyelectrolyte test. These preliminary tests resulted in further expanded tests to help "smooth" out the curves and to check the reproducibility of the tests.

Alum and cationic polyelectrolyte.

In this work the positively charged cationic polyelectrolyte was used in conjunction with alum.

Turbidity. In examination of Figure 10 for the 1 ml alum amount, it can be seen that the turbidity increased greatly over the standard value. Also, it did not drop below the standard value as time of polyelectrolyte addition became positive. It was felt that this was because addition of the alum was enough to form some $Al_x(OH)_y$ mesh around the latex particles, but not enough for coagulation to begin. Also the polyelectrolyte amounts were enough to cause some particle destabilization and interparticle bridging. The $Al_x(OH)_y$ mesh and bridging were enough to increase the light scattering of the suspension and thus increase the turbidity of the suspension.

Examination of the 3 ml alum amount showed a definite drop in turbidity as compared to the standard value, as time increased between the addition of alum and polyelectrolyte. Enough $Al_x(OH)_y$ mesh was formed to cause coagulation, and the polyelectrolyte acted as a coagulant aid by particle destabilization and bridging. This was because the results show lower values for alum and polyelectrolyte than just for alum alone.

At the 5 ml alum amount, the trend began like the 1 ml amount. At negative relative times, the formation of $Al_x(OH)_y$ mesh and particle bridging caused a large increase in turbidity, as compared to the standard value of alum by itself. This was caused by the polyelectrolyte acting with latex first, through destabilization and bridging, causing an increase in turbidity. The polyelectrolyte also reacted with the alum as it was put in the suspension. This reaction of polyelectrolyte and alum would not allow the coagulants to act on the entire latex suspension. As the polyelectrolyte was put in after the alum, it reacted with the mesh and latex particles. This caused an increase in removal based upon turbidity.

Figure 11 showed these trends all in one figure. From the comparison of these trends and their respective standard values, it was seen that the combination of 3 ml of alum and the cationic polyelectrolyte average of 0.85 ml (average of .7, 185 and 1.0 ml) gave a good removal at anytime. A slightly better removal was obtained by allowing 5 ml alum to mix five minutes by itself, then adding the same amount of polyelectrolyte.

Total solids. From Figure 12, it was seen that the trends were similar to the turbidity results. At the 1 ml alum amount, the addition of the alum and polyelectrolyte did not change the total solids as much as the time of addition changed. This strengthened the idea that there was not enough $Al_x(OH)_y$ mesh, destabilization or bridging to cause much coagulation. Some removal was noted since the values were slightly lower than the standard value. At the 3 ml alum amount there was a definite drop in total solids concentration as time was increased. This strengthened the belief that the increase in alum increased the mesh around the particles and that destabilization and bridging then caused coagulation. The 5 ml alum amount reflects the same trend as indicated in the turbidity results. Figure 13 showed these trends and the same conclusions were drawn as in the turbidity results. The use of 3 ml alum amount and polyelectrolyte gave good removal at any time. The 5 ml alum amount gave slightly better removal after a longer alum mixing time.

Zeta potential. For 1 ml alum amount, it was seen that the ZP stayed negative and between -15 and -40 mv. This was outside the range indicated by Riddick (1) for good coagulation and flocculation. This also showed that there was not enough $Al_x(OH)_y$ mesh, destabilization or bridging to decrease the negative potential of the latex particles so they could come together. For the 3 ml alum amount, the ZP ranged from -10 to +20 mv, with most values between -5 and +8 mv. These values are within Riddick's (1) range and show good removal as indicated by turbidity and total solids results. At the 5 ml alum amount the ZPs are all positive. At the minus times this would indicate that there was a charge reversal and a positive charge kept the latex apart. As time increased, the cationic polyelectrolyte acted as a coagulant aid and caused coagulation at later times. Figure 15 shows these trends all together. From this data it was concluded that a ZP between -10 to +10 mv gave best removal based on turbidity and total solids for a cationic polyelectrolyte. Comparison to the standard values shows that by increasing the alum amounts the ZP goes from negative to positive values.

Alum and anionic polyelectrolyte test. The discussion of these results follows the presentation format. First, the turbidity, second the total solids, and last the ZP are presented.

Turbidity. Examination of Figure 16 for 5 ml alum shows good turbidity removal compared with the standard value. The removal increases as time for alum mixing is increased. Since 5 ml alum was used there was enough $Al_x(OH)_y$ mesh for coagulation. The polyelectrolyte acted as a coagulant aid since removal with alum and polyelectrolyte was better than just alum alone. Particle destabilization was possible if the $Al_x(OH)_y$ mesh around the latex particle had enough positive charge to attract the negatively charged polyelectrolyte.

The polyelectrolyte acted mostly as a bridging mechanism between the particles.

For 10 ml alum amount, the negative times showed an increase in turbidity. This increase was caused by the polyelectrolyte acting with the latex particles and then with the alum as already discussed for the cationic polyelectrolyte. A dramatic drop in turbidity was noticed at 0 minutes and at +5 minutes. This indicated that the anionic polyelectrolyte worked better if applied after the alum.

The 15 ml alum showed a slight turbidity removal at a positive time as compared to the standard value. Because of this, it was felt that at 15 ml alum there was a restabilization of the latex particles to a positive charge caused by $Al_x(OH)_y$ mesh and the anionic polyelectrolyte worked by particle destabilization and particle bridging.

Figure 17 showed these trends in one figure. From this it was calculated than an amount of 5 ml alum and a polyelectrolyte amount of 3 ml at a +5 minutes was best for turbidity removal. It should be noted that the concentration of anionic polyelectrolyte is 1/16 of that used for the cationic polyelectrolyte.

Total solids. Figure 18 shows the same trends for total solids as was found in Figure 16 for turbidity. For 5 ml alum, the time interval did not make a great difference in total solids removal and the polyelectrolyte acted as a coagulant aid. The 10 ml alum showed the polyelectrolyte reaction with the latex before alum addition and then reacting with the alum. These values dropped down again at 0 and +5 minutes. The 15 ml alum showed the restabilization of the latex at minus time and a slight increase in removal at plus time. Figure 19 showed these trends and the same conclusions were drawn. It was noted that the total solids removal for 5 and 10 ml alum was the same at +5 minutes. For economical considerations, the 5 ml alum amount and anionic polyelectrolyte would be used.

Zeta potential. In Figure 20 for 1 ml, the ZP trend is -30 to -15 mv. This is outside the range given by Riddick (1) for good coagulation and flocculation. Since good removal was noted at the 5 ml alum amount, the polyelectrolyte acted by the bridging mechanism. This is shown by the 5 ml alum standard value having a negative charge with little removal. By adding a negatively charged polyelectrolyte, the charge did not change but the removal was greatly increased. This indicated that particle destabilization did not occur but particle bridging did. For the 10 ml alum, the ZP started positive (+10) and went negatively. The positive values resulted at a minus time indicating that the polyelectrolyte acted with the alum afterwards, causing high turbidity and total solids, but left enough alum in solution to give a positive charge to the suspension. The final negative value at +5 minutes was the same as for the 5 ml alum amount. At 15 ml alum, particle charge reversal is indicated by the positive ZP. Figure 21 shows the trends together and shows that increasing the alum amounts caused an increase positively in the ZP.

Cationic-Alum Expanded Tests

The discussion of the expanded tests was broken into four parts. First was discussion of the correlations, second was discussion of graphical presentations, third was a general discussion of individual items, and fourth is the discussion of optimum times.

Correlation between dependent parameters. Since there were six correlations examined, they were discussed separately.

Turbidity vs. total solids. Figure 22 shows a poor correlation between turbidity and total solids. The reason for this is that the addition of 1.0 ppm alum could change the total solids by 0.95% (1/120 x 100, Table 1) but could change the turbidity by up to 100 to 170% (see Figure 28, 0.0 minutes). This great change in turbidity resulted from formation of $Al_x(OH)_y$ mesh which effected the light scattering ability of the suspension. It should be noted that a pure homogenous suspension of latex, with no alum, gave a good correlation (Figure 8). But, as alum and the polyelectrolyte were added, the $Al_x(OH)_y$ mesh and particle bridging caused different size particles to form, which could effect the turbidity. Because of this, it was concluded that total solids analysis gave a better idea of the amount of destabilization occurring in the suspension.

Turbidity vs. zeta potential. From Figure 23 there does not seem to be any correlation between turbidity and zeta potential. Again it can be seen that alum and polyelectrolyte additions caused increases in the turbidity above the pure latex suspension. These changes had both positive and negative zeta potentials.

Total solids vs. zeta potential. In Figure 24 there is no apparent correlation, but there was a trend between ZP and total solids. This trend was that a ZP more negative than -20 mv gave a relatively high total solids compared to total solids below -20 mv. This figure also strengthened the use of total solids as a measurement of destabilization. It was seen that the zeta potential changed greatly (-45 to +20 mv) compared to the pure latex suspension's ZP. Although there was this change, none of the total solids are greater than the original as in the turbidity results.

Al^{3+} concentrations vs. turbidity. Examination of Figure 25 showed no apparent correlation between Al^{3+} concentrations and turbidity.

Al^{3+} concentrations vs. total solids. In Figure 26 there did not seem to be any apparent correlation between total solids and Al^{+} concentration.

% Al^{3+} removal vs. zeta potential. From Figure 27, no apparent correlation between % Al^{3+} removal and zeta potential was seen.

Dependent parameters vs. relative time. In the graphical presentations three areas were discussed: turbidity, total solids and zeta potential.

Turbidity. In Figure 28, for the 1 ml alum amount the trend and results for the expanded tests were close to those shown in Figure 10 for the preliminary test of the cationic polyelectrolyte. Because of this, the reaction of the alum and the cationic polyelectrolyte were assumed to be the same in the expanded test as in the preliminary tests. It was concluded that not enough alum was added to induce coagulation.

For the 3 ml alum amount, comparison between expanded and preliminary tests showed good reproducibility, except at -5 minutes. The reason for this discrepancy was thought to be because of the "age of the latex stock suspension. It was felt that the charge on the latex became more positive as the suspension sat on the shelf for the testing period of three months. If so, a small amount of alum would cause the ZP to approach optimum range and coagulation could occur. Thus a decrease in turbidity would happen as shown in Figure 28 at -5 minutes. This idea was disproven since ZP measurements before and after the three-month testing period were the same (-33 mv). Because of this, the reason for the discrepancy is not known. The two points omitted from the trend curve were run again and found to be the same. Thus, the reason for these two "humps" is not known. Further work in these areas may be needed.

For the 5 ml alum amount, the expanded and preliminary tests are good. The high turbidities at minus times indicate the same reaction of the polyelectrolyte with the latex then with the alum. As the time increases, turbidity removal increases and finally becomes optimum at +5 minutes. The low value at -5 minutes was duplicated and found to be the same. The reason for this point of discrepancy was not known and left unanswered. The trend curve in Figure 29 shows the same results and the same conclusions were drawn as in the preliminary test.

Total solids. Figure 30, for the expanded total solids, showed good comparison with Figure 12 for the preliminary test. Because of this, the same conclusions for the separate alum amounts and the trend curve, Figure 31, were drawn. The omitted points again gave reproducible results and the reason for their deviation was not known.

Zeta potential. Figure 33 for the expanded tests compared very well with the preliminary tests, Figure 14. The 1 ml alum value had negative ZPs. The 3 ml values had ZPs between -20 to +15 mv. Finally, the 5 ml alum values were all positive. The same conclusions were drawn for the expanded test as those in the preliminary test.

Individual discussion. The purpose of the individual discussion is to include certain areas not previously covered and to reemphasize certain points of the results. Areas discussed are: omitted points, regression analysis and Al^{3+} concentrations.

Omitted points. In showing the results the trends were described by averaging all polyelectrolyte concentrations. Some points did not show these trends. As brought out in the discussion, the reason for the discrepancy of these data points was not known. Unique, reproducible synergistic phenomena occurring between specific alum and polyelectrolyte concentrations at defined time differences may have caused the trend discrepencies. Further work in these areas should be done.

Regression analysis. The data from the expanded tests were looked at for a possible regression analysis. An experimental statistician felt that a regression analysis was not applicable. It was believed that the graphs showed a good representation of the results and regression analysis would not give any better understanding.

Al^{3+} concentrations. It was hoped that both Al^{3+} concentrations and % Al^{3+} removal would prove to be good indicators of how much colloidal destabilization had occurred. This removal would be evaluated by showing how much Al^{3+} was removed by the $Al_x(OH)_y$ mesh on the latex particles during coagulation. This expectation was not substantiated by the results. For example, from Figure 27, a high % Al^{3+} removal could have a range of zeta potentials from -45 to +25 mv. This did not correspond to the results from the two other tests of turbidity and total solids.

Part of the reason for the poor correlation of Al^{3+} concentrations was because of the collection of samples. As the samples were collected, flocculated latex in the collected sample would stick to the sides of the sample bottle. When the Al^{3+} analysis was made, the sample did not include the floculated latex. Because of this, the sample readings were low and may have shown no Al^{3+}, when, in fact, considerable Al^{3+} was in suspension at the time of sampling. Thus, it was felt that the Al^{3+} concentrations were lower than they would have been if the flocculated latex had been properly distributed. Further work in this area is needed with the possibility of immediate sampling and analysis procedure.

Optimum time. As pointed out in the Introduction section, the main objective of this research was to determine an optimum time difference between addition of the alum and polyelectrolytes. In practice today, the time between addition of the alum and polyelectrolyte is not regulated. The El Paso Water Treatment Plant is an example of this. At the plant there is a channel carrying water from the primary sedimentation basins to the coagulating and secondary settling basins. In this channel, alum is added (at times, lime is also added) and then 30 feet downstream, the polyelectrolyte is added. The combined mixture then goes to a rapid mix, then slow mix, followed by sedimentation. The polyelectrolyte is not used all of the time, but this is the procedure when it is used. In this plant, no optimum time difference is set for the polyelectrolyte addition since it is added at a time difference based upon the flow rate of the water at that time. It is believed that a determination of an optimum time difference could help in removal.

As brought out in the discussion, both the 3 ml and the 5 ml alum volumes gave good removal with a cationic polyelectrolyte. It was shown that the cationic polyelectrolyte acted as a good coagulant aid for the 3 ml alum amount at all time differences. This was done by comparison of the standard value of removal with the 3 ml alum and polyelectrolyte removal. For the 5 ml alum amount, the polyelectrolyte did not act as a coagulant aid until the +4 and +5 minutes time differences. Until this time, the polyelectrolyte acted against coagulation. Because the 3 ml alum amount showed a good removal at any time of polyelectrolyte addition, it was concluded that the 3 ml alum plus the polyelectrolyte gave the more economical approach than the 5 ml alum. It was concluded that the polyelectrolyte should be added 5 minutes after the alum. The reason for adding the polyelectrolyte then is that it acts as a "safety catch" if a little bit more alum than necessary is added. In some plants the philosophy of a "little bit more won't hurt" is followed. If a little bit extra (5 ml) is used instead of

3 ml, there is a good removal in any case, if polyelectrolyte is added at +5 minutes. If the "little bit extra" practice is to be followed, it is felt that the polyelectrolyte must be added at +5 minutes. Clearly water treatment facilities which use dual flocculant systems should evaluate, through jar testing, the optimum time differential between the addition of the flocculants. This work has shown substantial differences in flocculation efficiency for the same concentrations of primary and secondary flocculants added at varying time differentials. This means that water treatment plants should be able to achieve improved water treatment quality through improved operating procedures at no additional costs.

Regretably this work only indicates the potential for this opportunity. It is unlikely that the specific time recommendations made for these flocculants and a synthetic latex will be apropos for practical operations. However, the optimum time differential for each specific application of a given real colloidal system and the locally used flocculants should be readily determinable through standard jar testing.

SUMMARY AND CONCLUSIONS

In this research, the study of dual flocculants on a synthetic colloidal system was examined. The time of addition of the two flocculants was examined for optimization. Controlling certain independent parameters was done to eliminate the effect of those variables whose importance was believed to be of little consequence. The examination of a cationic polyelectrolyte by preliminary and expanded testing was accomplished, and preliminary testing of the anionic polyelectrolyte was also done. The following conclusions were made based upon the results:

1. Turbidity by itself is not a good basis for judging the amount of destabilization.
2. Total solids were a good basis for judging the amount of destabilization.
3. ZP used along with turbidity and total solids were useful in determining if charge reversal, particle destabilization, or particle bridging was taking place.
4. The latex suspension gave good reproducibility over a testing period of three months.
5. From preliminary testing and expanded testing, best removal by cationic polyelectrolyte was achieved by using 3 ml alum (1.84 ppm) in combination with 0.85 ml (1.0 ppm) polyelectrolyte at a time interval of +5 minutes between the two flocculants with the alum added first.
6. From preliminary testing, best removal for an anionic

polyelectrolyte was achieved by using 5 ml alum (3.07 ppm) in combination with 3 ml (.06 ppm) polyelectrolyte at a time interval of +5 minutes between the two flocculants with the alum added first.

7. Al^{3+} concentrations or % Al^{3+} removals did not give good correlation with other dependent parameters.
8. The best "general optimum" time was to add the polyelectrolyte after the alum. By adding afterwards, the polyelectrolyte seemed to act as a bridging mechanism for the colloidal particles.
9. There appears to an opportunity in optimizing the time differential between the addition of dual coagulants to improve the quality of water in water treatment facilities without increasing cost.

RECOMMENDATIONS

Based upon the research done, the following recommendations were made.

1. Do expanded testing for anionic polyelectrolyte to check the conclusions made.
2. Do retesting around the omitted data points when they were extremely random to check out the discrepancies and possible causes.
3. Increase the range of cationic polyelectrolyte testing to five or six values and decrease alum to 2, 3 and 4 ml.
4. Work further with Al^{3+} concentrations to obtain a procedure that gives a better correlation with turbidity and total solids results.
5. Expand the work to include testing of real, rather than synthetic, colloidal suspensions.

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APPENDIX

Three Dimensional Response Figure

On the following page is presented Figure 34, Three Dimensional Response Surface of Total Solids as a Function of Time and Alum Concentration. This figure is used to permit better visualization of the response of colloidal solids concentration to variation in time and alum concentration. The polyelectrolyte concentration is maintained at a constant value of 1 mg/l. As was observed in a series of two dimensional figures earlier, the now effect alum concentration at a negative time value is 3 mg/l. As the time is increased to a positive value both the 3 and 5 mg/l alum concentrations become effective in colloidal destabilization.

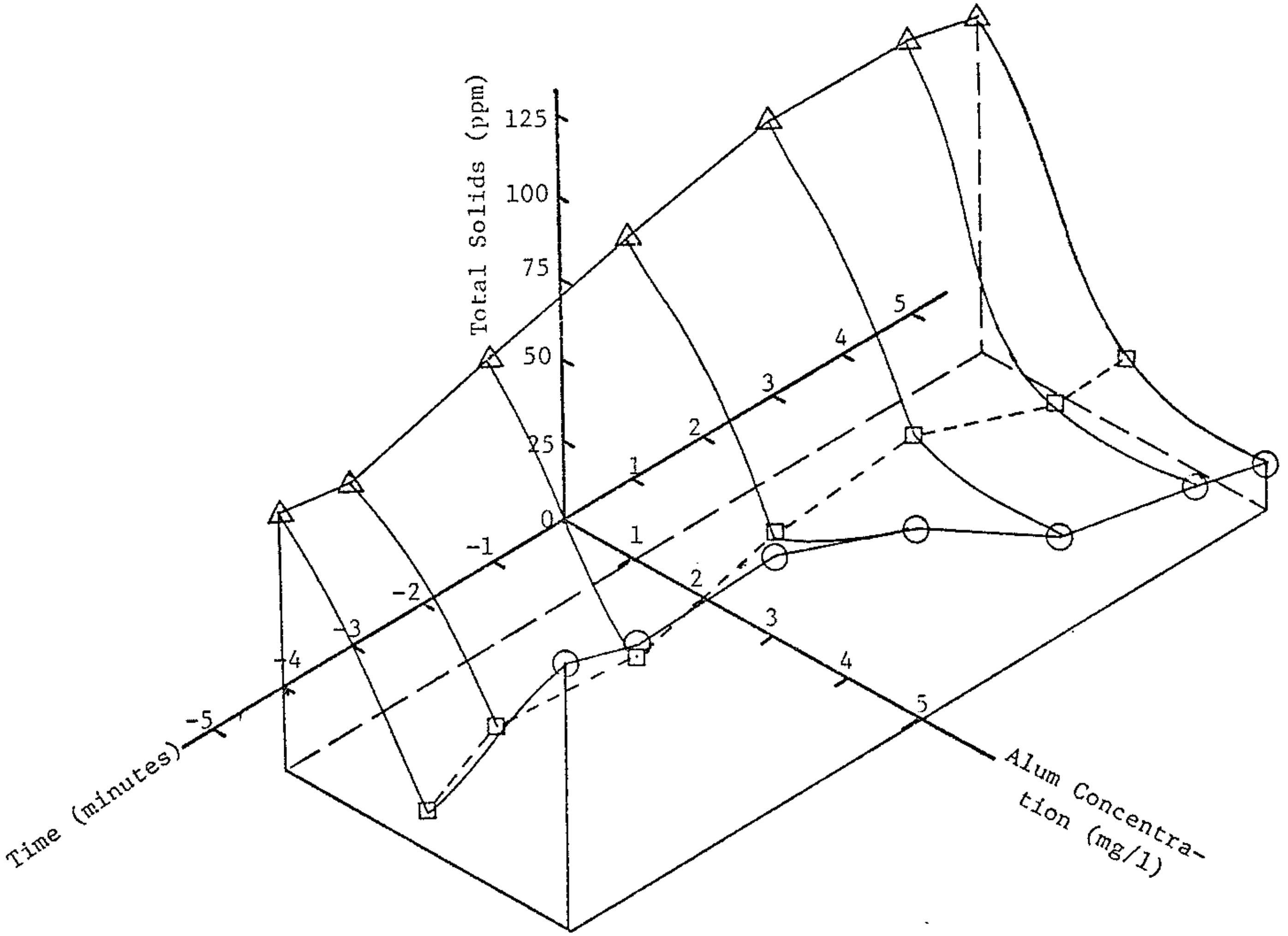

Figure 34

Three Dimensional Response Surface of Total Solids as a Function of Time and Alum Concentration

REPRODUCIBILITY EVALUATION OF THE FLOCCULATION OF A SYNTHETIC LATEX COLLOIDAL SYSTEM

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ABSTRACT

This research investigated the reproducibility of a series of jar tests on colloidal destabilization and the performance of the specific coagulants, alum and cationic polyelectrolyte. A synthetic latex suspension, which was conditioned by a thoroughly purified mixed-bed ion-exchange resin, was used as a model colloidal suspension. The experiment was conducted in 10 different test conditions based upon pH, cationic strength, alum, and cationic polyelectrolyte destabilization. Each test condition was repeated 14 times and a total of 140 test results was obtained.

Three dependent variables (zeta potential, total solids and turbidity) were used to express the destabilization of colloidal suspension. After the laboratory work was finished, the results of the three dependent variables were evaluated by statistical analysis.

It was found in this experiment that alum performed better in colloidal destabilization than the cationic polyelectrolyte did. It was also found that when alum and cationic polyelectrolyte were used jointly as primary coagulants, the most reproducible result was obtained. The effects of pH and cationic strength adjustment on the performance of the coagulants were discussed and the correlations between the three dependent variables were also evaluated.

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NOMENCLATURE

Al^{+++}	Aluminum ion
$Al(OH)_3$	Aluminum Hydroxide
Alum.	Aluminum Sulfate
Å	Angstroms
DP.	Degree of Polymerization
FTU	Formazin Turbidity Unit
gm.	Gram
HCl	Hydrochloric Acid
H_2SO_4	Sulfuric Acid
K^+	Potassium ion
KOH	Potassium Hydroxide
K_2SO_4	Potassium Sulfate
M	Molarity
mg/l.	Milligrams per liter
ml.	Milliliters
mv.	Millivolts
μ	10^{-6} of a meter
N	Normality
n	Any number, 1, 2, 3, etc.
NaOH.	Sodium Hydroxide
ppm	Parts per million
rpm	Revolutions per minute

TS	Total Solids
Turb.	Turbidity
X	Symbol referring to zeta potential
Y	Symbol referring to total solids
Z	Symbol referring to turbidity
$\bar{X}$	Average of zeta potential
$\bar{Y}$	Average of total solids
$\bar{Z}$	Average of turbidity
σ_X	Standard deviation of zeta potential
σ_Y	Standard deviation of total solids
σ_Z	Standard deviation of turbidity
$\sigma_X/\bar{X}$	Coefficient of variation of zeta potential
$\sigma_Y/\bar{Y}$	Coefficient of variation of total solids
$\sigma_Z/\bar{Z}$	Coefficient of variation of turbidity
S_X^2	Variance of zeta potential
S_Y^2	Variance of total solids
S_Z^2	Variance of turbidity
γ_{XY}	Correlation coefficient between zeta potential and total solids
γ_{YZ}	Correlation coefficient between total solids and turbidity
γ_{ZX}	Correlation coefficient between turbidity and total solids
ZP	Zeta potential

INTRODUCTION

In water and wastewater treatment, destabilization of colloidal particles (coagulation) is one of the most important processes a sanitary engineer might encounter. In biological treatment almost all of the organic substances in a wastewater can ultimately be removed through the aggregation of the microorganisms. There is still some amount of organic substance, comprised of a high percentage of colloidal matter, which passes through the biological treatment process. The rapid expansion of industry which produces a tremendous amount of synthetic matter gives rise to problems in the conventional wastewater treatment. For these reasons, coagulation has been attracting more and more attention as an advanced wastewater treatment method during the past two decades.

Aluminum and ferric salts have been well-known as effective coagulants, but recently developed, high molecular weight polyelectrolytes have also been shown to be effective in coagulation. Some reports have indicated that the usage of polyelectrolytes is even more superior than alum and ferric salt. However, the conventional coagulants, like alum, still have importance in wastewater treatment and have not yet been supplanted by polyelectrolytes.

Previous investigations have indicated that the coagulation process is affected by many factors, such as pH, ionic strength, alkalinity, temperature, coagulants, colloidal concentration, mixing and detention time. All of these factors contribute to the complexity of the coagulation process. For this reason many of those who work with coagulation consider it to be an art rather than a science.

PURPOSE

The purpose of this research was to evaluate the reproducibility of colloidal destabilization caused by alum and a cationic polyelectrolyte, both alone and jointly, and both with and without pH and ionic concentration control.

In addition, in order to determine the most convenient and most accurate measurement of colloidal destabilization, three dependent variables (zeta potential, total solids, and turbidity) were used and the results were compared.

LITERATURE REVIEW

In natural or polluted raw water, the pollutants consist of soluble and insoluble materials. Insoluble material can be divided into two fractions: (a) a coarse fraction with particle diameter between 1 mm and 1 μ and (b) a fine (colloidal) fraction with particle diameter between 1 μ and 10 Å (20). The removal of the coarse or larger than coarse particles can be accomplished by simple sedimentation, optionally aided by conventional alum coagulation. Colloidal particles are too small to settle by gravitational force alone and will sometimes interfere with purification processes that include ion-exchange, dialysis or adsorption (8, 33). Also, colloidal suspensions may cause turbidity and tend to adsorb objectionable taste and odor components, thus becoming a tremendous problem in potable and wastewater purification.

Colloidal Properties

The most important property of colloidal particles is the surface charge potential. In natural water systems, almost all the colloidal contaminants, both organic and inorganic, have a negative charge (24). Due to their charge potential, the particles tend to move in an electrical field. This movement is called "electrophoresis" (14, 30). The velocity of the particles in an electrical field is proportional to the voltage applied to that field and the electrical charge of those particles (24).

The second important property of colloids is the significant increase in the ratio of the surface area to the mass as the particle size decreases (4). If two colloidal suspensions have the same mass, the total surface area of a suspension which consists of smaller particles is much larger than that of a suspension of larger particles. When this ratio is low, the mass effects, such as sedimentation, predominate; when the ratio is high, the electrical charges of the colloidal particles predominate.

The third important property of colloidal particles is their dispersing effect on a light beam passed through a solution. This is the so-called "Tyndall effect" (14, 30). Based on this effect, a light scattering technique was developed for evaluating the concentration of the colloidal particles (9).

The Stability of Colloidal Suspensions

Some colloidal suspensions will aggregate slowly and some will not. Like chemical kinetics this property is not theoretically based, but must be ascertained experimentally. The rate of aggregation depends upon the stability of colloidal particles. There are several factors which affect the stability of colloids. One of these factors is the degree to which the colloidal particles are able to adsorb water and form a layer of bound water. "Hydrophilic" (water loving) colloids are surrounded by layers of bound water and "Hydrophobic" (water hating) colloids are not (2). Theoretically, hydrophobic colloids are never stable (16).

There are other physical factors which prevent colloidal particles from gathering together. Riddick (23) states:

There are three natural methods for creating and maintaining a colloidal system in a dispersed state. These methods are (a) mutual replusion due to high zeta potential, (b) adsorption of a small lyophilic colloid onto a larger lyophobic colloid, thereby encasing the colloid in an adherent aqueous film, and (c) adsorption of a nonionic polymer on the colloid to provide steric hindrance.

The mutual repulsion is due to the colloidal particles' electrical potential which have been studied extensively for nearly one century by Helmholtz, Gouy, Stern, Grahame, Chapman (cited by Adamson (1) and Mysels (18)), Verwey and Overbeck (31), Derjaguin and Landau (6), and others. A diffused double layer theory has been derived by combining their ideas and has gained general acceptance.

The Diffused Double Layer Theory

Any charged colloidal particle is surrounded by layers of accumulated counter-ions which are attracted by the charged particle. The concentration of these counter-ions is highest near the surface of the particles and decreases exponentially with an increase in distance away from the surface of the particles. Those ions with the same sign as the particles are repelled from the surface of the particles into the bulk of the solution. A diffused double layer, a Stern and a Gouy-Chapman layer, is then formed as shown in Figure 1 (17).

The different concentrations of the counter-ions in this diffused layer results in a net potential which, under stable colloidal conditions, will force the two particles away from each other. There is an opposing force, termed "van der Walls" forces, which competes with the repulsive forces. The difference between these two forces (net repulsion) is called the "energy barrier."

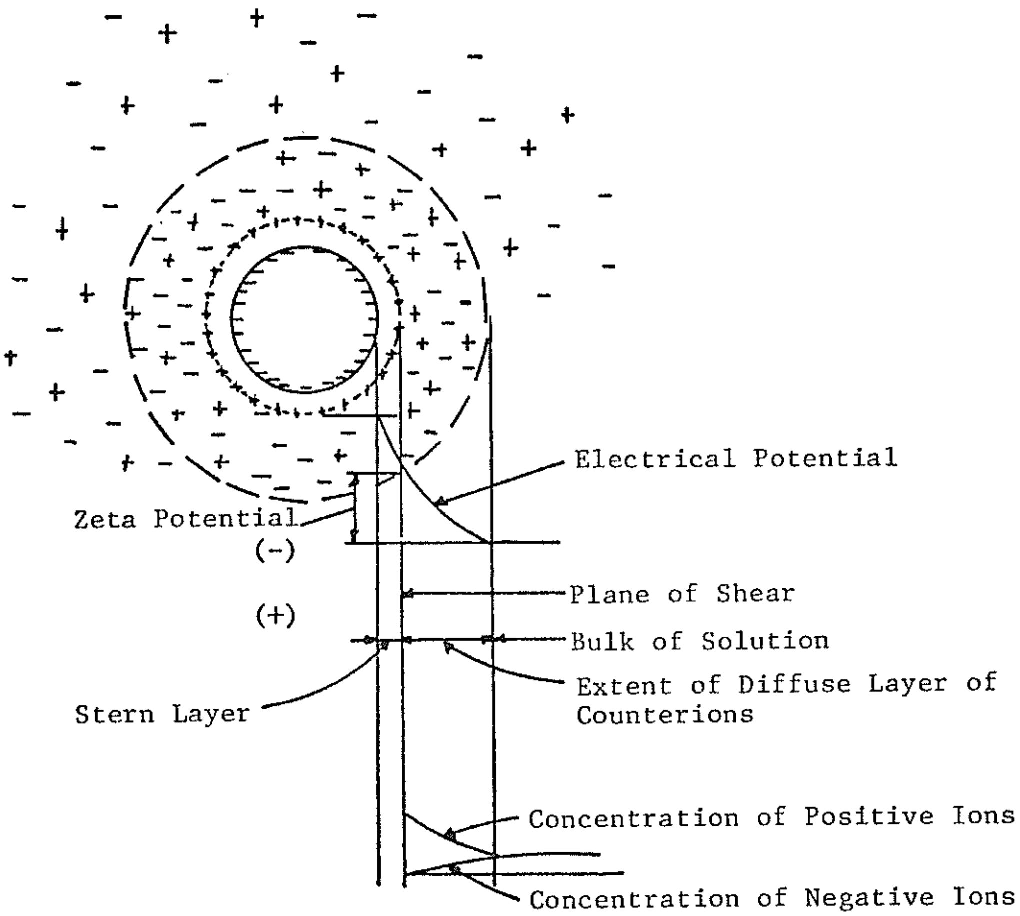


Figure 1. Concept of Zeta Potential (17)

The thickness of diffused double layer and the value of energy barrier are reduced when the ionic strength in the solution increases as shown in Figure 2 (33). Under these conditions more counterions move into the double layer.

Zeta potential. When a particle moves in an electrical field it drags a cloud of ions with it. The potential at the surface of the cloud (called plane of shear) is called the zeta potential. This was illustrated in Figure 1 (17).

Measurement of zeta potential. For the purpose of measuring the zeta potential, Riddick (22) has developed a "Zeta-Meter" which consists mainly of a microscope, a power unit, and an electrophoresis cell (as shown in Figure 3). When a voltage is applied across the cell, colloidal particles will move and cause an electro-endosmotic return flow in the tube as shown in Figure 3. In order to measure the velocity of the colloidal particle, special care must be taken in focusing and counting the colloidal particles at the point where the endosmotic liquid flow is zero. Therefore, the measurement of the zeta potential with a "Zeta-Meter" is, no doubt, a technique requiring considerable skill.

Previous research (14) has indicated that measurements with this device were not very reproducible. Kace (14) explained:

> The zeta potential is not a well defined quantity because of the difficulties in locating the exact position of the shear plane experimentally and because of the deformation in the shear plane that occurs during the experimental measurement.

However, zeta potential measurement has been used in designing

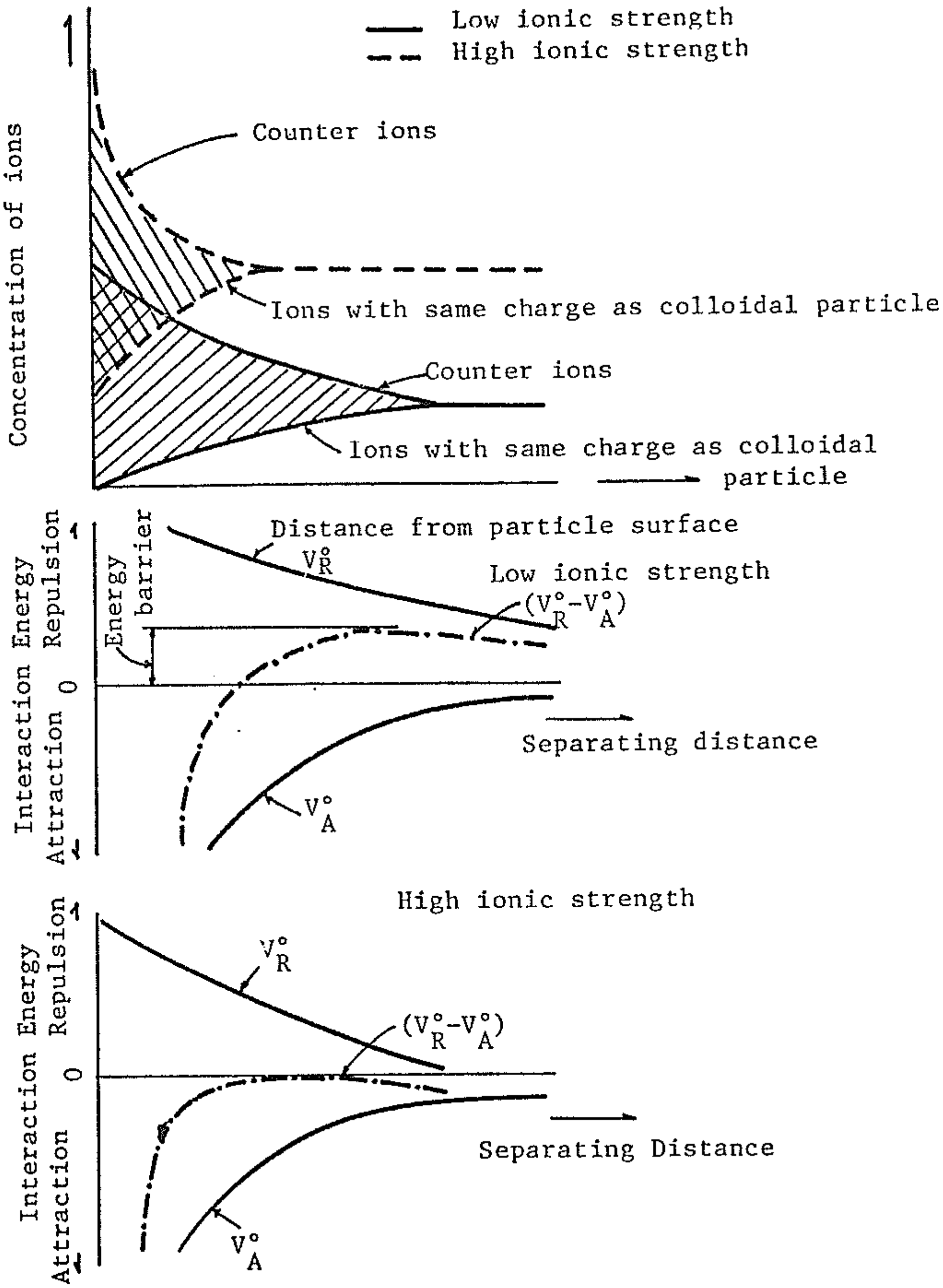
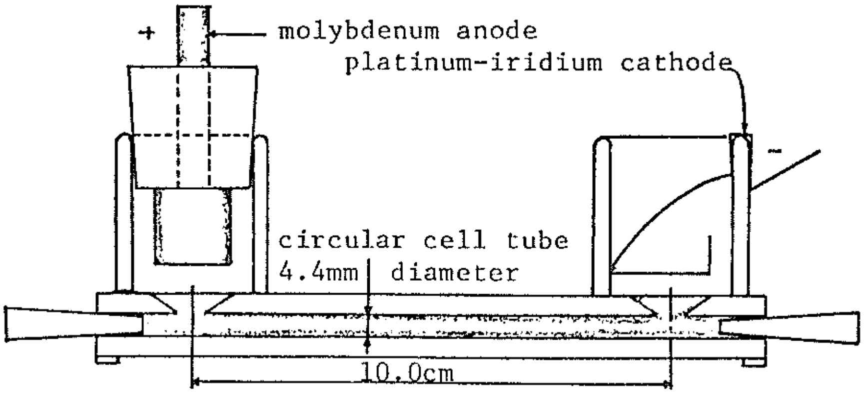


Figure 2. The Electric Double Layer, The Electric Potential, and The Interaction Energy of a Colloidal System (33)



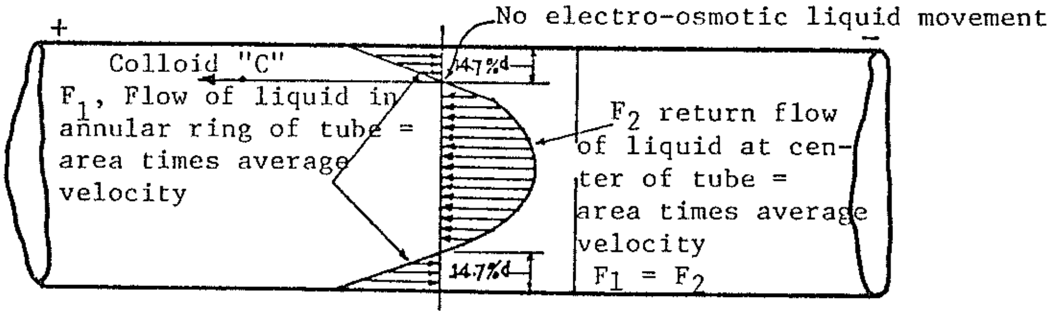


Figure 3. Plan at Mid-Depth of Zeta Meter Cell Tube

and operating a water treatment plant and has been reported to be useful in controlling the optimum coagulant dosage (16, 21). Though zeta potential measurement is not an accurate method for measuring the colloidal destabilization, it is still a very useful method in interpreting the coagulation phenomena.

Destabilization of Colloids

In order for destabilization of colloidal particles to occur, it is necessary to reduce the energy barrier between the particles; in other words, it is necessary to reduce the electrical potential (or zeta potential) of the colloidal particles. As soon as the energy barrier is reduced to the extent that van der Waals' attractive forces can overcome the repulsive forces, aggregation takes place.

O'Melia (cited by Weber (3)) detailed four possible mechanisms responsible for colloidal destabilization: (a) compression of diffused layer, (b) adsorption to produce charge neutralization, (c) enmeshment in a precipitate, and (d) adsorption to permit interparticle bridging.

In order to accomplish colloidal destabilization of a stable suspension, it is usually necessary to add some amount of inorganic electrolyte and/or a charged polymer which has a high molecular weight.

In any of the cases of colloidal destabilization, combinations of these mechanisms may take place (19). For example, in alum destabilization, either adsorption or compression of the diffused layer may be present (19). Different kinds of coagulants have different ways of achieving the destabilization of colloids depending upon their charge, their molecular weight, and the pH of the colloidal suspension (19, 32, 33). But many authors have already proven that the adsorption mechanism plays a more important role in most cases of water treatment (16, 19, 24).

Flocculation. In order to allow the destabilized colloidal particles to stick to each other and finally to form flocs large enough to settle out, it is necessary to agitate the colloidal suspension continuously. Riddick (20) divided the flocculation process into three distinct stages: (a) the rapid mix and microfloc stage, (b) the colloidal gathering stage, and (c) the agglomerating stage.

In the rapid mix and microfloc stage, an agitation of high velocity gradient should be applied to induce the rapid and uniform dispersion of the coagulant. The detention time is usually very short. Griffith and Williams (10) stated that turbidity removal was not improved by rapid mix detention periods greater than five seconds. They also suggested that dilution of alum solutions will induce the dispersion of the alum and improve its efficiency in the coagulation process. Normally, however, the detention time lasts for a few minutes, depending upon the flow rate and capacity of the flocculation basin. The purpose of this stage is to produce tough microflocs which have a zeta potential close to zero.

In the colloid gathering stage, the destabilized colloidal suspensions are usually stirred slowly to provide maximum chances of impingement between the colloidal particles and the growing flocs (20). The velocity gradient should not be so high to produce a shear force that breaks down the flocs. It is important to maintain a small floc size (about 0.5 to 1 mm) in this stage to maximize the total surface area of flocs (21). The detention time for optimum turbidity removals are about 30 to 35 minutes. It was found that turbidity removals became poorer when detention times were over 40 minutes (10).

The agglomerating stage starts whenever a polymer of long chain and/or high molecular weight is introduced into the flocculating suspension. The long chain of the polymers serves as a bridge to combine the flocs and let them agglomerate to larger flocs which can settle rapidly. The polymers used in this stage are called coagulant aids. The coagulant aids usually have molecular weights in the range of 500,000 to 1,000,000 or more (20).

Obviously, the degree of agitation and flocculation time are important factors which will influence the flocculation process. But there are some other important factors which cannot be ignored; these factors are listed below.

pH. Riddick (21) stated that "the stability of aluminum hydroxide is markedly affected by pH, with a definite isoelectric point." In fact, alum has different predominant species at different pH values. This had been proven later by Black and Chen (3) and Sullivan and Singley (26). In early 1975, Gupta, Bhattacharjya and Dutta (11) presented some curves of zeta potential versus pH which showed that when the pH is raised, the zeta potential shifted to higher negative values.

Characteristics of colloidal suspension. As stated before, the size of the particles affects the surface area of the colloidal suspension which, in turn, will influence the optimum dosage of coagulant to be used (33). Also the number of particles will influence the rate of flocculation and the density of the flocs, and, thus, will influence the settling velocity (4).

Temperature. Heller and de Lander (12) found that an increase in temperature results in a large increase in the rate of flocculation.

Alkalinity. Alkalinity will increase the buffer capacity of the water and maintain the pH at the same level when aluminum and iron salt are added (33).

Destabilization by Alum

Alum has been used as a clarifying agent since the earliest water treatment times. Its mechanism in the hydrolysis process was not well known until the last two decades when some reports of the research on the chemical structure of the hydrolysis products were published. In 1967, Black and Chen (3) described the behavior of hydrolysis of alum species on kaolinite clay destabilization at different pH values. Some previous reports proposed that the predominant species in the region below pH 4 is Al^{+++}; in the pH range roughly from 6 to 8, it is $Al(OH)_3$; in the region above pH 8, it is $Al(OH)_4^-$; while in the region between pH 4 and pH 6, one or more of the hydrolyzed aluminum polynuclear multivalent cations such as $Al_6(OH)_{15}^{3+}$, $Al_8(OH)_{20}^{4+}$, $Al_7(OH)_{17}^{4+}$, or $Al_{13}(OH)_{34}^{5+}$ are the dominant species. A hypothetical model of the hydrolysis process has been proposed by Stumm (cited by Metcalf & Eddy, (17)) as shown in Figure 4. Black and Chen (3) believed that when Al^{+++} is the predominant species, the destabilization is fulfilled by

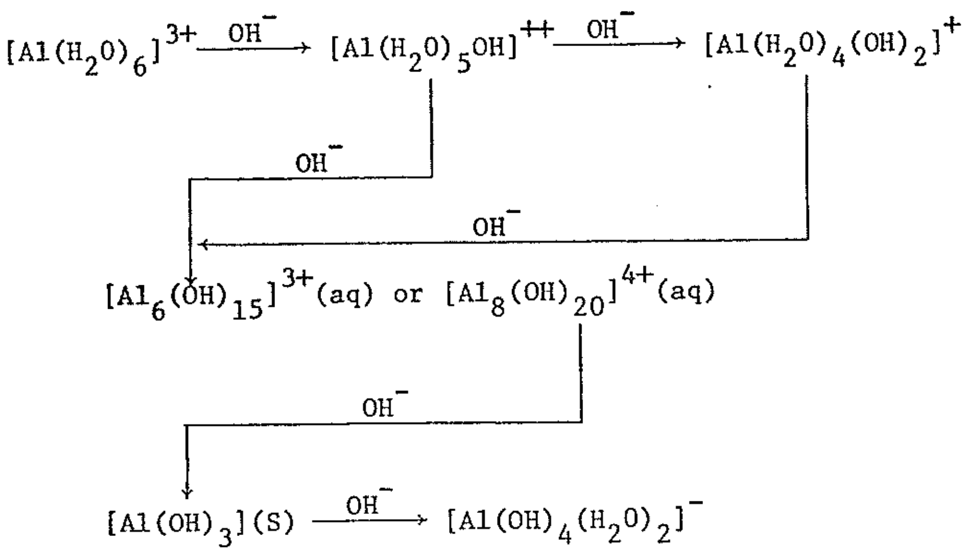


Figure 4. Hypothetical Hydrolysis Reactions of Al^{+++} (17)

the compression of electrical double layer of the colloidal particles; when polymeric multivalent aluminum ions are predominant, the destabilization mechanism is the adsorption of the multivalent polymers on the colloidal particles; when $Al(OH)_3$ precipitate forms, the mechanism is the enmeshment of the colloidal particles on the $Al(OH)_3$ "sweep flocs."

Since different hydrolysis alum products are formed at different pH values it is clear that as pH varies different mechanisms will apply in colloidal destabilization. Thus the shear effects will not be the same, and, because the hydrolysis reaction is a stepwise process (17), the effectiveness of alum will vary with time.

Polyelectrolyte and Polyelectrolyte Destabilization

Natural organic polymers have long been used for water purification (27). But the use of synthetic polymers with high molecular weight is a relatively new achievement in the water industry. Synthetic polymers can have high molecular weights of up to and greater than 1,000,000. Those polymers which contain repeating units of electrical charges or ionizable groups are called polyelectrolytes and may be either cationic or anionic, depending on the type of charge on the polymer chain. There are also polymers containing both ionizable groups which are called nonionic polymers.

The main function of polymers in the flocculation process is in a bridging mechanism because of their long chain structures. Ries and Meyers (24) have obtained some micrographs of polymeric flocculation by using electron-microscope techniques which strongly suggest the bridging mechanism of the polymer flocculants. Almost all of the polymers are used as coagulant aids. But in those cases where the suspended particles carry an opposite charge, cationic or anionic polyelectrolytes can become a primary coagulant, functioning both as a charge neutralizer or as a floc bridger (15).

It has been reported that polyelectrolytes are much more effective than inorganic aluminum or iron salts (15) due to the long polymer lengths and the number of charged sites along the polymer chains. It has also been reported that polyelectrolytes are superior to inorganic salts for such reasons as: (a) the small amounts needed, (b) the formation of large, stable, low-density flocs, (c) insensitivity to and little effect on pH, (d) ease of dewatering of sludge, and (e) filterability of flocs (21). Polyelectrolytes also have drawbacks such as: (a) narrow range of optimum dosage and ease of restabilization of colloidal suspension because of charge reversal (21), and (b) shorter destabilization time and, therefore, the requirement of additional mixing.

Cationic polyelectrolytes and alum can also be used together as dual primary coagulants. Better results in reducing the tendency of redispersion (21) and reducing the alum dosage by applying alum and cationic polyelectrolyte together have been reported (15). In this case, attention should be noted in the determination of the time of the addition of the polyelectrolyte. The optimum addition time of polyelectrolyte may vary for each suspension; it may be added any time before or several minutes after the addition of alum (5).

EXPERIMENTAL APPARATUS, DESIGN AND PROCEDURE

General Outline

This research was conducted using a synthetic latex colloidal suspension to perform a series of jar tests in which alum and polyelectrolyte were used as coagulants. During the jar tests, temperature, paddle speed, rapid mixing time, and flocculation time were kept constant. Ionic strength, pH, and coagulant dosage were also controlled at specific levels, depending upon the test being performed. After the jar tests, samples were allowed to settle and the turbidity, zeta potential, and total solids of the samples were measured.

A total of 140 tests with 10 different sets of conditions were performed and were subjected to statistical analysis in order to evaluate the reproducibility of the tests.

Apparatus

The following apparatus were used in this investigation.

1. Laboratory stirrer: a Phipps and Bird six-paddle stirrer was used for jar testing.
2. Turbidity meter: a Hach Model 2100A laboratory turbidimeter was used for turbidity measurement.
3. Zeta meter: a "Zeta Meter" developed by Riddick (22) was used for zeta potential measurement.
4. Analytical balance: a Mettler Model H51 Analytical Balance was used for making total solids analyses.

5. Oven: a W. H. Curtin oven was used for drying samples in evaporating dishes.

Design of Experiment

In order to obtain relationships between three dependent variables (zeta potential, total solids, and turbidity) and to evaluate the reproducibility of the results, ten tests were designed based on four independent variables (pH, alum destabilization, cationic polyelectrolyte destabilization, and ionic strength). The ten tests are listed below.

Test 1. Colloidal System Preparation

Test 2. Colloidal System Destabilization by Alum

Test 3. Colloidal System Destabilization by Polyelectrolyte

Test 4. Colloidal System Destabilization by Alum with pH control

Test 5. Colloidal System Destabilization by Polyelectrolyte with pH Control

Test 6. Colloidal System Destabilization by Alum with pH and Ionic Strength Control

Test 7. Colloidal System destabilization by Polyelectrolyte with pH and Ionic Strength Control

Test 8. Colloidal System Destabilization by Alum and Polyelectrolyte

Test 9. Colloidal System Destabilization by Alum and Polyelectrolyte with pH Control

Test 10. Colloidal System Destabilization by Alum and Polyelectrolyte with pH and Ionic Strength Control

These 10 different tests were repeated 14 times, using a random order within each set of 10 tests.

Ionic Strength and pH Control

Previous research had shown that the coagulating capability of aluminum hydroxide was markedly affected by pH. Superior performance was generally obtained in the pH range of about 4.5 to 7.2 (21). Duff (7) in his research controlled the pH at 6.0 and the potassium ion concentration at constant levels. Duff's method in controlling pH and $[K^+]$ was adopted in this experiment.

Laboratory Procedure

The laboratory procedure used in this investigation can best be described by division into eight steps.

Colloidal suspension preparation (Step I). This procedure followed the method developed by Vanderhoff and van den Hul (29). By this method, a mono-disperse, latex suspension with well characterized surface was prepared. This latex suspension was clean, stable, and was considered a model colloidal suspension. This method had two steps: (a) conditioning of commercial ion-exchange resins, and (b) the ion-exchange process. In the first step, one pound of Dowex 50W-X4 sulfonic acid resin and one pound of Dowex 1-X4 quaternary ammonium resin were eluted sequentially in a pear-shaped separatory funnel with 3N NaOH hot distilled water, methanol, cold distilled water, 3N HCL, hot distilled water, methanol and cold distilled water. This cycle was repeated four times. In the last cycle, the Dowex 50W resin was converted to hydrogen form by the slow elution with an excess of 3N HCl, while Dowex 1 was converted to the hydroxide form with 3N NaOH. Dowex 1 resin was converted only shortly before use; it was stored in chloride form. The resins were then rinsed copiously with distilled water and mixed under agitation. In the ion-exchange process, a 4.17 weight percent latex suspension was mixed with resins in the ratio of 1:2. They were agitated on a platform shaker for two hours. After the ion-exchange process was finished, the latex suspension was then washed from the resin bed through a Büchner funnel with a plastic filter and a vacuum attachment. It was finally diluted to about 0.56 weight percent concentration.

Alum solution preparation (Step II). A 1.71 gm of powder reagent grade J. T. Baker $Al_2(SO_4)_3 \cdot nH_2O$ (Alum) was weighed and put in a 500 ml volumetric flask and filled with distilled water. After the alum powder was dissolved homogenously in the distilled water, 100 ml of the alum solution was drawn out with a 100 ml pipet, placed in a 1000 ml volumetric flask and diluted to one liter with distilled water. The diluted alum solution was then shaken well and was ready for coagulation tests. This alum coagulating solution was prepared daily. Atomic absorption analysis of five samples of the coagulating solution resulted in an average concentration of 39.9 mg/l Al^{+++}.

Polyelectrolyte solution preparation (Step III). This process followed the Nalco "Instant Liquid Polymer Test Solution Preparation" (13) procedure. It was prepared daily. The polymer used was Nalco 607 liquid cationic polyelectrolyte. The procedure was as follows.

Preparation of activator solution. A 1.85% Nalco Activator solution was made by adding 1 ml of activator to 53 ml of distilled water. The solution was mixed with a stirring rod or shaken briefly.

Mixing. The small sample of Nalco 607 liquid polymer was shaken for several seconds until product uniformity was achieved (no viscous material on the botton).

Dilution and activation. Two ml of 1.85% Nalco Activator solution was added to 196 ml of distilled water while mixing with a magnetic stirrer. Then two ml of Nalco 607 liquid polymer were added and mixed for 15 minutes.

Aging. After 15 minutes of mixing, 20 ml of the mixed 1% polyelectrolyte solution was drawn out by pipet and diluted with 180 ml of distilled water. The concentration was 0.1%.

KOH and K_2SO_4 solution preparation (Step IV). A 0.01M KOH solution was prepared for pH adjustment. The 0.005M K_2SO_4 solution was prepared for $[K^+]$ cationic strength adjustment. Both solutions were made with reagent grade J. T. Baker chemicals.

Determination of optimal dosages of alum and polyelectrolyte (Step V). Before running the main series of tests, several preliminary jar tests were run to determine the optimal coagulant dosages based upon the zeta potential values of the samples. It was found that zeta potential approached zero when (a) 10 ml of alum solution alone, (b) 2.3 ml of polyelectrolyte solution alone, or (c) 6 ml of alum solution and 0.65 ml of polyelectrolyte jointly were added to one liter of diluted latex suspension in the coagulation process. The pH and ionic strength were not adjusted during these determinations.

Jar test (Step VI). The 18 ml of 0.56% latex suspension were pipeted into a 1000 ml volumetric flask and diluted with distilled water to 1000 ml. The sample was then poured into a one liter beaker and moved to the gang stirrer where agitation of the sample at 100 rpm was accomplished. Then a definite amount of alum or polyelectrolyte or both were injected into the beaker by a pipet just above the gang stirrer (about one inch below the surface of the sample). The purpose of injecting, instead of pouring, coagulant into the suspension was to induce the rapid dispersal of the coagulant (20).

After the first coagulant (usually alum, but it could be polyelectrolyte if it was the only coagulant to be used) was added, pH and ionic strength were adjusted immediately. In those cases where a second coagulant (always polyelectrolyte) was required, it was added one minute after the first coagulant (alum) was added. The 100 rpm rapid mix was continued for two minutes, then followed by 30 minutes of slow mix at 30 rpm. After the mixing, the sample was removed and allowed to settle for 20 minutes. Then a sufficient amount of sample was taken from a point one inch below the surface for the purpose of measuring zeta potential, turbidity, and total solids.

Turbidity and zeta potential measurement (Step VII). The turbidity was measured by a Hach turbidity meter. The zeta potential was measured by a "Zeta-Meter" (22). When the zeta potential was measured, the 8X lens and a 300-volt electrode potential were used. Usually two samples were taken from each beaker for zeta potential measurement. In each sample, 5 to 10 particles were tracked. Then the values of zeta potential were calculated from the Zeta-Meter manual (22) and the average of the two samples was taken as the zeta potential of the colloidal suspension being tested.

Total solids analysis (Step VIII). A 50 ml sample was taken from each beaker and placed in an evaporating dish. The sample was put in a 103° C oven for 24 hours, desiccated for 24 hours, and then weighed. The total solids was calculated by subtracting the empty dish weight from the final weight.

RESULTS AND DISCUSSION

In this section are located the experimental results and discussion of those results. In the initial part of this section the general coagulation results, the performance of the coagulants, and the correlation of the dependent variables are presented. In the final part of this section the statistical evaluations on significance and reproducibility are presented. Because some of the data, for example, average results of dependent variables, are relevant to the discussion of both sections, these data will be duplicated as needed in each section.

The experimental work, which consisted of the analytical determination of the three dependent variables on each of the 140 tests were performed in such a manner as to permit proper statistical evaluation. The 140 tests were not performed in a completely random fashion. In each block of the ten basic tests, there was random ordering. Then when that block was complete the second block of the ten basic tests was performed in a random fashion. This procedure was followed until the replications of each of the 14 blocks were completed. This approach allowed statistical evaluation of the differences between blocks or an evaluation of the time of duration of the 140 tests on the experimental results. The values of the dependent test variables, zeta potential, total solids, and turbidity, obtained from the 140 individual jar tests are listed in Table 1. For each of the 10 test conditions, the 14 repeated tests are listed in the order in which they were performed.

Table 1. Zeta Potential, Total Solids and Turbidity Values of the Dependent Tests 1 through 10

No.	Z.P. (mv)	T.S. (mg/l)	Turb. (FTU)	No.	Z.P. (mv)	T.S. (mg/l)	Turb. (FTU)
		Test 1				Test 2	
1	-31.5	94.4	131	1	- 1.1	12	17.2
2	-31	89.2	131	2	- 7.1	14.4	29.7
3	-29	89	131	3	- 3.3	8	19.2
4	-27.6	91.6	131	4	- 4.4	11.6	25.5
5	-30.5	84.6	115.5	5	- 1.9	7.8	16.1
6	-32.8	88.6	115.5	6	- 0.9	8.2	15
7	-29.8	81.6	123	7	- 2.7	8.8	20.3
8	-31.6	83.4	115.5	8	- 4.8	3.2	19.2
9	-30.8	85.6	150	9	- 2.1	7.2	17.2
10	-31.5	78.2	150	10	- 2.8	11.6	17
11	-33.1	93.8	150	11	- 3.5	16.8	17
12	-30.5	89	145	12	- 4.1	11.6	21.5
13	-28.9	84.2	150	13	- 4.2	13.6	19
14	-28.6	89	140	14	+ 5.1	7.2	20
		Test 3				Test 4	
1	- 2.6	16.2	21.3	1	-12.5	18.8	24.4
2	- 3.4	8.6	17.2	2	-15.2	16.0	18.2
3	- 6.2	16.2	19.2	3	-13.0	12.0	16.1
4	- 5.3	13.8	19.2	4	-13.4	12.8	14.0
5	+10.6	85.0	168.5	5	-13.8	12.4	16.1
6	- 1.0	9.6	18.2	6	-15.7	15.4	19.2
7	- 6.8	6.0	18.2	7	-11.0	22	14.0
8	- 2.6	13.8	18.1	8	-12.2	17.4	13.0
9	- 9.3	51.0	140.0	9	-11.7	8.4	14.0
10	- 4.1	5.2	17.2	10	-12.4	9.0	14.0
11	- 4.9	20.0	16.0	11	-15.8	13.0	11.0
12	- 6.8	11.2	17.5	12	-24.0	21.2	36.5
13	- 4.3	12.4	15.0	13	-28.0	29.8	54.0
14	- 9.0	11.2	13.0	14	-10.2	10.4	12.0
		Test 5				Test 6	
1	-14.0	60.0	115.5	1	- 7.7	28.8	15.1
2	-18.9	38.2	62.2	2	-13.0	34.6	15.1
3	-13.8	37.2	83.5	3	-12.5	25.4	15.1
4	-17.2	35.2	84.7	4	-16.1	19.0	18.2
5	-15.9	77.2	156.0	5	-16.7	28.4	20.3
6	-17.6	31.4	82.2	6	-21.2	19.2	25.5
7	-19.8	73.2	168.5	7	-15.2	20.4	16.1
8	-18.9	30.0	78.6	8	-22.7	35.8	22.0
9	-18.5	49.0	120.0	9	-16.3	21.8	16.5
10	-21.1	66.8	165.0	10	-13.7	17.2	14.0
11	-20.2	30.8	88.5	11	-16.5	30.0	14.0
12	-22.2	53.4	140.0	12	-23.7	34.4	38.0
13	-23.0	74.8	180.0	13	-16.3	23.8	26.0
14	-21.2	43.6	54.0	14	-12.8	18.4	21.0

Table 1. (Continued)

No.	Z.P. (mv)	T.S. (mg/1)	Turb. (FTU)	No.	Z.P. (mv)	T.S. (mg/1)	Turb. (FTU)
		Test 7				Test 8	
1	-17.3	57.4	84.7	1	+ 3.7	20.4	18.2
2	-37	83.8	114	2	0	5.2	16.5
3	-17.8	35.8	36	3	- 1.3	5.8	16.0
4	-20.0	51	99	4	+ 3.0	16.2	17.16
5	-21	84.9	148.5	5	+ 0.9	5.6	16.1
6	-19.8	40.2	66.8	6	+ 0.2	12	14
7	-22.8	78.6	148.5	7	- 2.5	5.2	17.2
8	-22.7	76.2	150	8	- 3.3	14.6	18.1
9	-23.6	55.6	100	9	+ 1.2	8.8	12.5
10	-24.2	55	125	10	+ 1.1	11	15
11	-23	53.8	93	11	- 0.4	16	13
12	-25.9	86.6	170	12	+ 1.8	7.4	13
13	-27.6	88	180	13	- 0.35	10	15
14	-27.1	78.4	145	14	+ 6.1	1	13
		Test 9				Test 10	
1	- 5.2	14.8	18.2	1	-14.4	26	17.15
2	- 8.8	14.6	16.5	2	-17.8	25.6	18.2
3	-15.1	12.0	27.6	3	-15.5	28	29.7
4	-20.5	27.2	45.7	4	-17.5	20.8	20.3
5	-10.9	20	16.1	5	-19.4	33.8	49
6	-12.1	11	16.1	6	-17.4	17	19.2
7	-15.8	13.2	35	7	-24	47.6	55
8	-16.8	22	48	8	-20	29	31
9	-13.1	15	23.4	9	-26	56.2	96
10	-16.2	18.6	20.3	10	-21.3	26.6	21.5
11	-21.7	42.6	68	11	-23.1	32	33.5
12	-20.2	32.6	47	12	-23.7	36.4	43
13	-19.4	32.8	58	13	-21.7	33.2	54
14	-22.2	45.2	85	14	-19.5	33.4	33.5

Coagulant Performance Evaluation

Average values of zeta potential ($\bar{X}$), total solids ($\bar{Y}$) and turbidity ($\bar{Z}$) were calculated and are listed in Table 2. The performance of alum, polyelectrolyte and their combination in the coagulation tests are described in the following sections.

Alum. The results of Test 2 showed that with a satisfactory dosage, zeta potential could be brought to -2.7 mv through the use of alum alone. This value was in the the range of rapid agglomeration with gentle mechanical agitation (± 5 mv) (21). The average values of total solids and turbidity also showed that alum performed very well in coagulation.

Polyelectrolyte. The results of Test 3 showed that when a cationic polyelectrolyte was used alone as a coagulant, low zeta potential could be obtained, but the results of total tolids and turbidity were not as good as that obtained by alum coagulation.

Alum and polyelectrolyte. The results of Test 8 showed that when a proper combination of alum and polyelectrolyte were used together as coagulants, the best overall performance was obtained for the test conditions imposed.

Alum with pH control. The results of Test 6 showed that the addition of KOH for pH control drastically shifted the zeta potential to about -15 mv while the turbidity remained relatively constant. The value of total solids increased from 10.14 mg/l to 15.61 mg/l. When pH control was used the results of the total solids and turbidity showed

Table 2. Average Value of Zeta Potential, Total Solids and Turbidity for the Dependent Tests 1 through 10

Test	Test Description	$\bar{X}$ of Z.P. (mv)	$\bar{Y}$ of T.S. (mg/l)	$\bar{Z}$ of Turb. (FTU)	KOH added for pH control (mg/l)*	K_2SO_4 added for ionic strength control (mg/l)*
1	Latex suspension	-30.51	87.30	134.17		
2	Alum	- 2.7	10.14	19.56		
3	P.E.	- 3.97	20.01	37.04		
4	Alum, pH→6	-14.92	15.61	19.75	4.00	
5	P.E., pH→6	-18.73	50.05	115.62	2.26	
6	Alum, pH→6, $[K^+]$**	-16.02	25.51	19.77	4.12	11.01
7	P.E., pH→6, $[K^+]$**	-23.55	66.41	118.60	2.24	13.92
8	Alum + P.E.	+ 0.72	9.94	15.34		
9	Alum + P.E., pH→6	-15.57	22.97	37.49	3.41	
10	Alum + P.E., pH→6, $[K^+]$**	-20.09	31.82	37.15	3.70	11.66

*Approximate value (values were not measured for each of the 14 replications of each test)
**Cationic strength adjustment

that the alum performed equally well as in the tests without pH control, this occurring despite the higher zeta potential obtained with pH control.

Alum with pH and cationic strength control. As happened in the case of alum with pH control, the addition of K_2SO_4 for cationic strength adjustment slightly shifted the zeta potential to higher negative values, but the performance of alum in coagulation was as good as that in Test 4.

Polyelectrolyte with pH control. The results of Test 5 showed that the addition of KOH for pH control gave rise to a significant change in zeta potential as well as in total solids and turbidity. Comparing the results obtained in Test 3, the low total solids and turbidity removal revealed that the performance of polyelectrolyte was drastically reduced by the addition of KOH.

Polyelectrolyte with pH and cationic strength control. The results of Test 7 showed that the addition of K_2SO_4 for cationic strength adjustment also slightly shifted the zeta potential to higher negative values and reduced the total solids and turbidity removal. However, the degree of change was not as large as was observed in Test 4 with pH adjustment.

Alum and polyelectrolyte destabilization with pH control. As in Test 5, the results of Test 9 once again showed the effect of pH adjustment on the colloidal destabilization capability of the polyelectrolyte. Obviously, the total solids and turbidity removal was reduced at these conditions, and it was felt that the change was due to the deterioration of the performance of polyelectrolyte.

Alum and polyelectrolyte destabilization with pH and cationic strength control. The results of Test 10 showed that zeta potential was slightly shifted to higher negative values by the addition of K_2SO_4 while turbidity remained about the same. The value of total solids was a little higher than that obtained in Test 9.

From the above discussion, the effect of pH and cationic strength adjustment on coagulant performance can be summarized by the following three statements:

1. the addition of KOH for pH control significantly shifted the zeta potential to higher negative values;
2. the turbidity results showed that pH adjustment did not substantially depress the performance of alum, but it significantly reduced the performance of polyelectrolyte (compare Tests 2 and 4 with Tests 3 and 5); and
3. the addition of K_2SO_4 for cationic strength adjustment also slightly shifted the zeta potential to higher negative values but did not significantly reduce the performance of alum and polyelectrolyte (compare Tests 4 and 6 with Tests 5 and 7).

Evaluation of the Dependent Variables

The results of colloidal destabilization testing can be expressed by turbidity, total solids or zeta potential. The results of the three dependent variables are discussed in the following paragraphs based upon their average values as listed in Table 2. The approximate amount of

KOH and K_2SO_4 added in colloidal suspension were also calculated and are listed in Table 2.

Turbidity and total solids. From the results shown in Table 2, it was felt that the variation in total solids and turbidity followed the same trend. This is verified and discussed later in the correlation of dependent variables' section. There were some cases where turbidity remained constant with slight changes in total solids. It is believed that this difference in total solids at constant turbidity was due to the addition of pH and ionic concentration reagents. For example, the turbidity remained constant in Tests 2 and 4; in the same tests, the total solids increased 5.47 mg/l. However, 4.0 mg/l of KOH was added in Test 4. Similar results were obtained in Tests 4 and 6, Tests 5 and 7, and Tests 9 and 10. It was felt that a volatile solid analysis might give more consistent results as this analysis would measure only the latex remaining in suspension. The addition of pH or ionic concentration reagents would not affect the volatile solids analysis.

Zeta potential. The zeta potential results indicated that zeta potential did not have linear correlation with total solids and turbidity. For example, pH and ionic strength adjustment shifted the zeta potential to higher negative values (see Tests 2, 4 and 6), while the turbidity remained about the same value. The zeta potential responded differently to different kinds of coagulants and their combinations. For example, Test 6 and Test 9 had the same zeta potential value but their turbidity values were significantly different. For alum destabilization, values of zeta potential less than 15 showed good results. But for the polyelectrolyte, only zeta potential near zero values obtained fair results (Test 3).

Summary. It was concluded that turbidity was the best index to measure colloidal destabilization. It provided rapid measurements and was an accurate index of the total solids remaining in suspension. Zeta potential results only provided a rough picture of colloidal destabilization. Total solids was a good measurement of colloidal destabilization, but was time-consuming and suffered from interference with KOH and K_2SO_4.

Correlation between Zeta Potential, Total Solids and Turbidity

Correlation between zeta potential and turbidity. The graphical correlations of zeta potential, total solids and turbidity are presented in Figures 5, 6 and 7. The curves were not modeled but drawn by eye. In Figure 5 the data from all the tests for zeta potential versus turbidity were plotted. It seemed not to be a simple curve but one having its lowest points between zeta potential -10 mv to 0, and having a rough "U" shape. In order to find out if there were some differences between alum and polyelectrolyte destabilization, three curves were plotted with combined data: (a) alum destabilization as shown in Figure 6 (from Tests 1, 2, 4, and 6), (b) polyelectrolyte destabilization as shown in Figure 7 (from Tests 1, 3, 5, and 7), and (c) destabilization by alum and polyelectrolyte together as shown in Figure 8 (from Tests 1, 8, 9, and 10).

When alum was used alone as a coagulant, turbidity dropped to

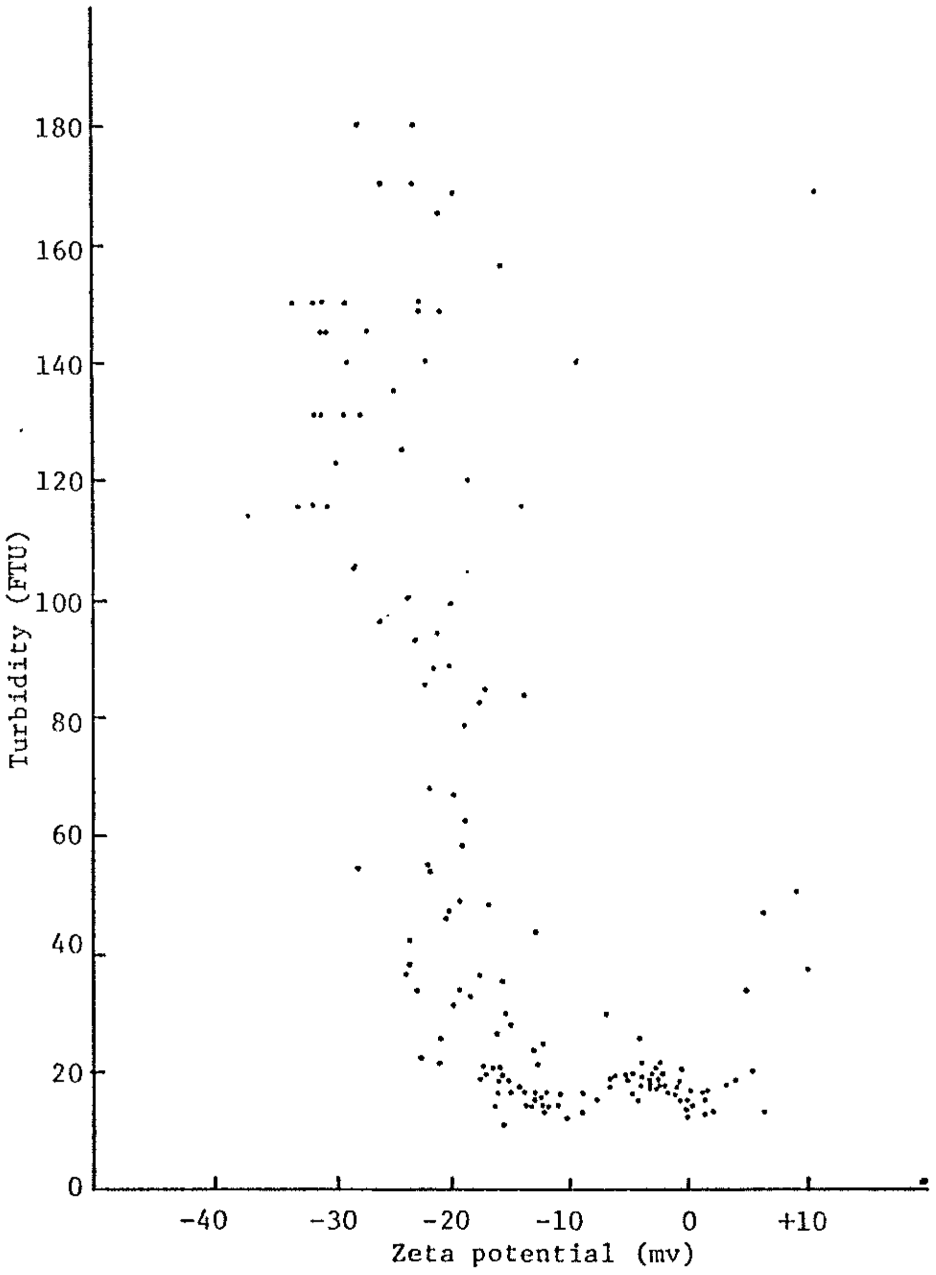


Figure 5. Relationship between Zeta Potential and Turbidity (All Data)

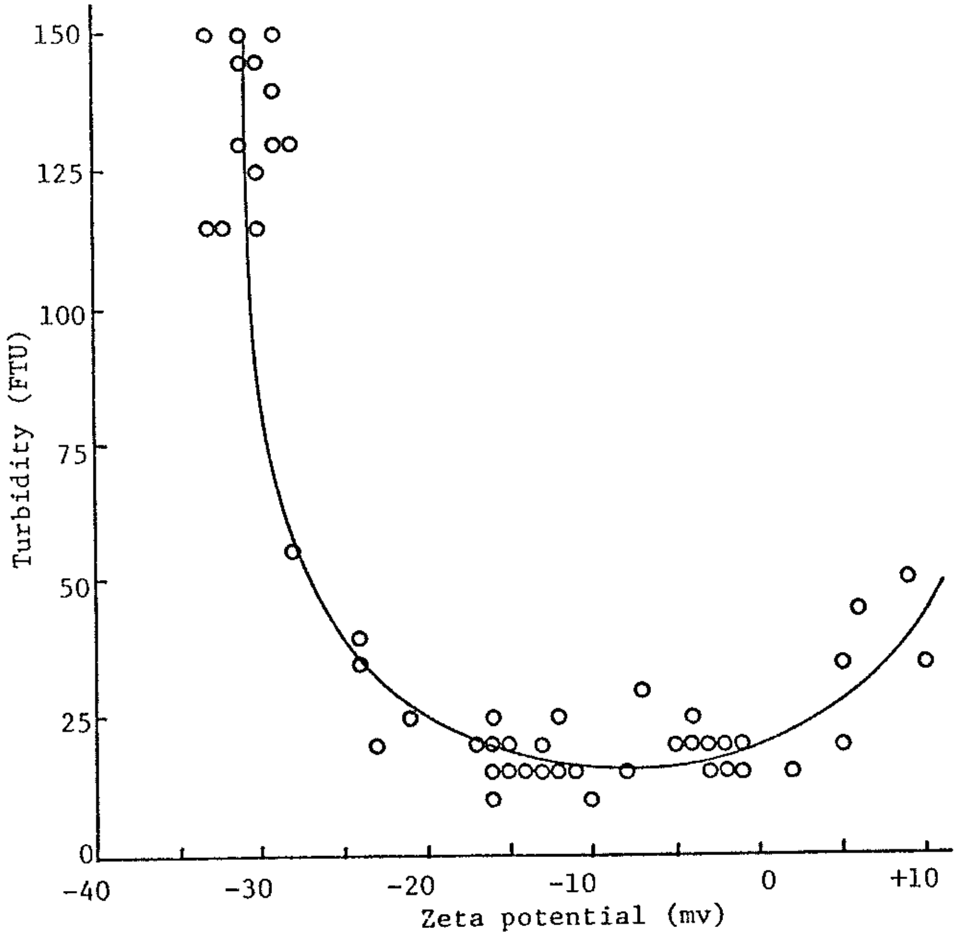


Figure 6. Relationship between Zeta Potential and Turbidity (Alum Destabilization)

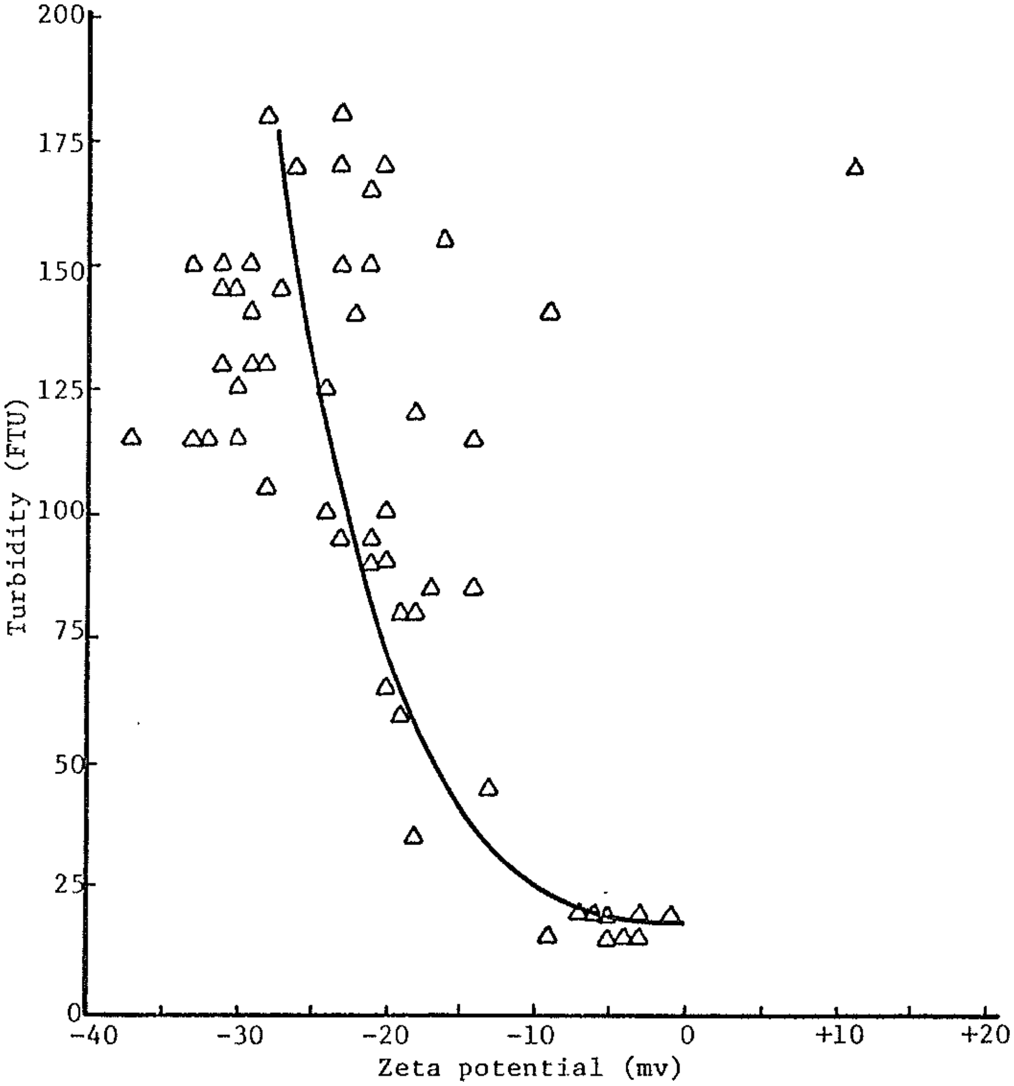


Figure 7. Relationship between Zeta Potential and Turbidity (Cationic Polyelectrolyte Destabilization)

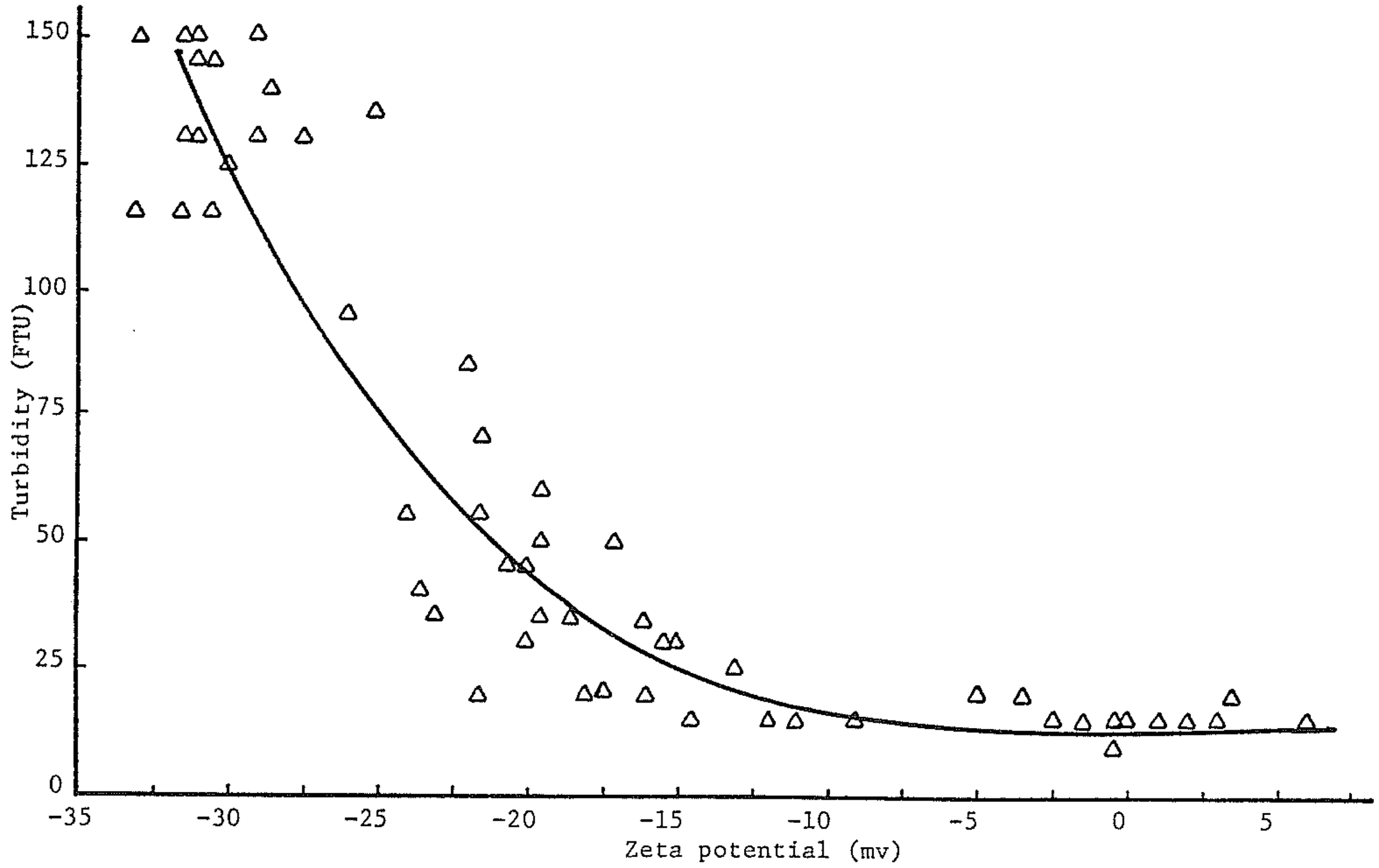


Figure 8. Relationship between Zeta Potential and Turbidity (Destabilization by Alum and Cationic Polyelectrolyte)

the lowest point at a zeta potential range of -18 to 0 mv, as shown in Figure 6. Values out of this range showed rapidly increasing turbidity values. Thus, there was a critical range of zeta potential values which allowed satisfactory alum destabilization. Figure 7 showed that when polyelectrolyte was used alone, turbidity dropped to its lowest point at a zeta potential of around -5 mv. It is believed that the curve would go up rapidly if there were enough data available. The minimum value of zeta potential satisfactory for adequate destabilization was around -10 mv; the critical range for satisfactory polyelectrolyte destabilization was smaller than when alum was used. Figure 8 showed that when both alum and polyelectrolyte were used, turbidity dropped to 13 FTU at a zeta potential of about -15 mv and kept the same low value to a zeta potential equal to +5 mv. From this curve, it was clearly seen that there was a wider range of better turbidity removal for dual coagulant usage. Use of the polyelectrolyte and alum combination seemed to provide a safety margin to the user, as a greater variation in coagulant concentrations could be experienced while still providing adequate destabilization. This fact is important--the use of the polyelectrolyte is not just providing superior performance, it is providing a broader operational latitude which gives satisfactory performance. Obviously, the destabilization using alum and polyelectrolyte jointly as coagulants was somewhat different from the tests where they were used alone.

Correlation between zeta potential and total solids. Figure 9 shows the relationship of zeta potential versus total solids using data

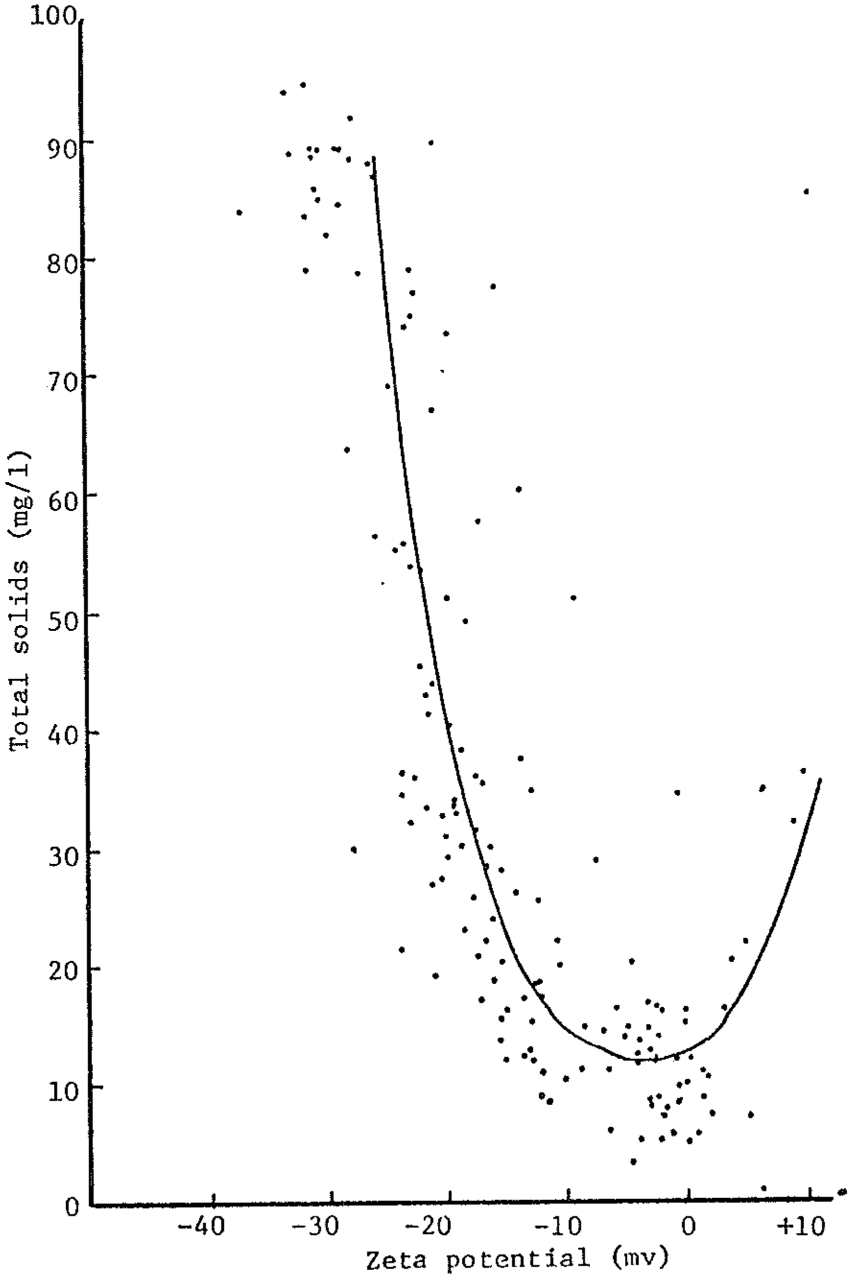


Figure 9. Relationship between Zeta Potential and Total Solids (All Data)

for all 140 tests. The shape of the curve was generally the same as the zeta potential versus turbidity curve. It was noted that the total solids concentration obtained its lowest values in the zeta potential range of -10 to +5 mv. With zeta potential there was a critical value or a small critical range beyond which satisfactory colloidal destabilization did not occur.

Correlation between turbidity and total solids. Figure 10 shows the relationship between turbidity and total solids. It was clear that there was a strong linear relationship between these two variables. Unlike the nonlinear zeta potential versus turbidity or total solids relationships, the linear turbidity and total solids relationship was predictable. The turbidity was a measurement of the light scattered perpendicularly from the suspended particles. It was reasonable to assume that in the dilute region the greater the number of particles existing the greater would be the turbidity. Therefore, the relationship should be directly proportional.

Statistical Analysis for the Correlation between Zeta Potential, Total Solids and Turbidity

In order to understand more deeply the correlation between these three variables, the correlation coefficients between the zeta potential, total solids, and turbidity (γ_{XY}, γ_{YZ}, γ_{ZX}) in each test condition were calculated and are listed in Table 3. The results of the correlation coefficients for each test as shown in Table 3 were, in fact, of no practical value and were actually only a statistical curiosity. Under perfect reproducibility, the 14 replicated results for a given

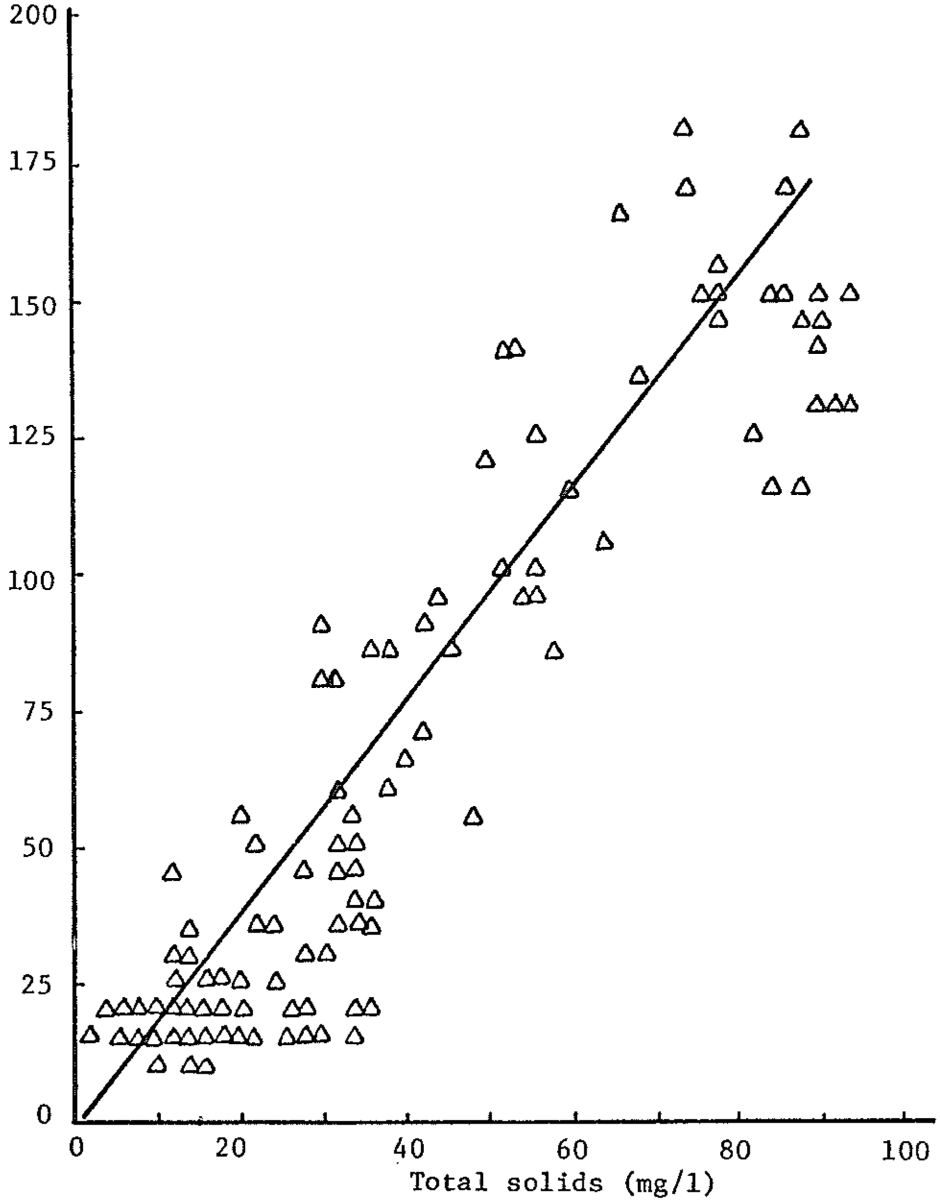


Figure 10. Relationship between Total Solids and Turbidity

Table 3. Variance, Correlation Coefficients, Standard Deviation, and Coefficient of Variation of Variables Zeta Potential (X), Total Solids (Y) and Turbidity (Z)

Test	$\bar{X}$	$\bar{Y}$	$\bar{Z}$	S_X^2	S_Y^2	S_Z^2	γ_{XY}	γ_{YZ}	γ_{ZX}	σ_X	σ_Y	σ_X	$\sigma_X/\bar{X}$	$\sigma_Y/\bar{Y}$	$\sigma_Z/\bar{Z}$
1	-30.51	87.30	134.17	2.35	19.67	168.88	-0.05	0.033	0.076	1.53	4.43	12.99	-0.05	0.05	0.1
2	- 2.70	10.14	19.56	7.11	11.81	15.07	-0.35	0.28	-0.46	2.66	3.43	3.78	-0.99	0.35	0.21
3	- 3.97	20.01	37.04	21.62	439.83	2,322.2	0.63	0.96	0.5	4.64	20.97	48.18	-1.22	1.09	1.35
4	-14.92	15.61	19.75	23.56	31.99	129.93	-0.72	0.81	-0.92	4.85	5.65	11.39	-0.34	0.38	0.6
5	-18.73	50.05	115.62	7.41	283.25	1,439.67	-0.18	0.93	-0.38	2.72	16.83	37.94	-0.15	0.35	0.34
6	-16.02	25.51	19.77	17.03	39.39	40.67	-0.27	0.24	-0.72	4.12	6.27	6.37	-0.27	0.26	0.33
7	-23.55	66.51	118.6	23.05	317.25	1,570.4	-0.6	0.9	-0.47	4.80	17.81	39.62	-0.21	0.28	0.35
8	0.72	9.94	15.34	5.6	27.21	3.69	-0.034	0.334	-0.303	2.36	5.21	1.91	3.41	0.54	0.13
9	-15.57	22.97	37.49	24.1	119.64	443.06	-0.78	0.914	-0.845	4.90	10.93	21.04	-0.33	0.49	0.58
10	-20.09	31.82	37.15	10.7	95.44	425.57	-0.78	0.92	-0.175	3.27	9.76	20.62	-0.17	0.32	0.58
Average													0.46*	0.45**	0.5**

*Does not include Tests 1, 2 and 8

**Does not include Test 1

test would be a single point and have a correlation coefficient of zero. Thus, the tests showed "good" correlation for a specific test only when that test had substantial scatter--consequently resulting in a range of values. In order to properly evaluate the correlation of any two of the dependent variables, it was necessary to look at the data for several, or, best, of all the tests. This was done and the data are listed in Table 4.

Table 4. Correlation Coefficients between Zeta Potential (X), Total Solids (Y) and Turbidity (Z)

Data	γ_{XY}	γ_{YZ}	γ_{ZX}
All	-0.75	0.93	-0.64
$-15 \leq$ zeta potential ≤ 0	-0.45	0.85	-0.26
$-30 \leq$ zeta potential ≤ -15	-0.79	0.89	-0.61

<u>Statistical analysis for the correlation between zeta potential versus total solids</u>. The results of correlation coefficient in Table 3 showed that there was no consistant linear relationship between these two variables. Whenever the variance of zeta potential was small, the correlation coefficient for a particular test was small. When the variance was large, then a trend was more likely and the correlation coefficients increased. A further analysis was made by dividing all the data into two groups depending on their zeta potential. Group 1 was greater than a zeta potential of -15 mv; Group 2 was smaller. The results in Table 4 showed that when zeta potential ranged from -15 mv to -33 mv, γ_{XY} is -0.79; this meant that there was a fair linear relationship between these two variables. But when the zeta potential ranged

from 0 to -15 mv, there was not any linear relationship. It is felt that there seemed to be a breaking point at a zeta potential value of about -15 mv above which the turbidity decreased very rapidly and below which the turbidity decreased very slowly as zeta potential moved toward zero.

Statistical analysis for the correlation between zeta potential versus turbidity. The correlation coefficient, γ_{ZX}, listed in Table 3 showed that there was no linear relationship between these two variables except in Tests 4 and 9, when the zeta potential variance was relatively high. Further analysis was followed by calculating the γ_{ZX} for all the data, for data with zeta potential ranging from -15 to -33 mv, and for data with zeta potential ranging from 0 to -15 mv (shown in Table 4). Again it was shown that there was no linear relationship between these two variables.

Statistical analysis for correlation between total solids versus turbidity. The correlation coefficient, γ_{YZ}, listed in Table 3 showed that there was a strong linear relationship between those two variables. It is felt that when the variance of these variables were low (Tests 1, 2, 6, and 8), their correlation coefficients, γ_{YZ}, were low too. In those situations when variance was low, their data fell into a small range which could not show the existence of a linear relationship. Further analysis was followed by putting all the data together and calculating the correlation coefficient, γ_{YZ} (Table 4). The result was $\gamma_{YZ} = 0.93$ which revealed again that there was a strong linear relationship between turbidity and total solids. Breaking the data into zeta potential values greater and smaller than -15 mv also resulted in high correlation coefficients.

Reproducibility of the Tests

In order to evaluate the reproducibility of each of the coagulation tests, the variance, the standard deviation, and the coefficient of variation of the three dependent variables were calculated and listed in Table 3. The variance and coefficient of variation of each dependent variable for each test were plotted in Figures 11 and 12, respectively.

The reproducibility of tests evaluated by zeta potential. From Table 3 and Figure 11, it was seen that the variances of the zeta potential were lower than those of the total solids and turbidity. This does not necessarily mean that measurements of zeta potential were more reproducible than those of the other two variables; this evaluation is more properly done with the coefficient of variation. The variance of zeta potential was useful in comparing the results of zeta potential for the 10 tests. Of the 10 test conditions, Tests 2 and 8 had the lowest values of zeta potential. This result showed that the alum destabilized tests without pH and ionic concentration control were the most reproducible when zeta potential was the dependent variable.

The reproducibility of tests evaluated by total solids. From Table 3 and Figure 11, it was again seen that the variance of the tests in which alum was used as a coagulant without pH and ionic concentration control were lower than all other tests. When using total solids as the dependent variable, it was shown that alum coagulation had more

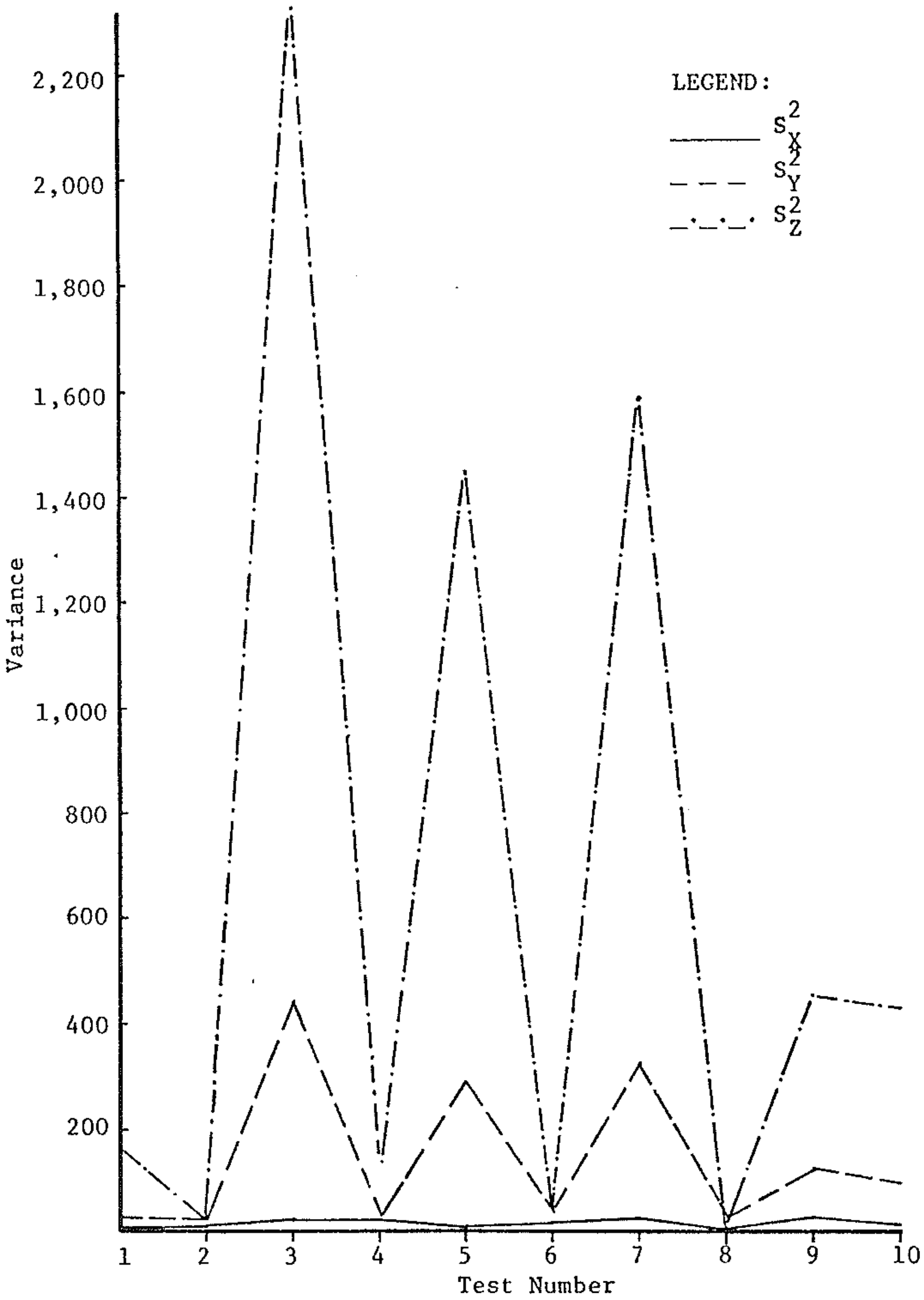


Figure 11. Changes of Variance in Zeta Potential (S_X^2), Total Solids (S_Y^2) and Turbidity (S_Z^2)

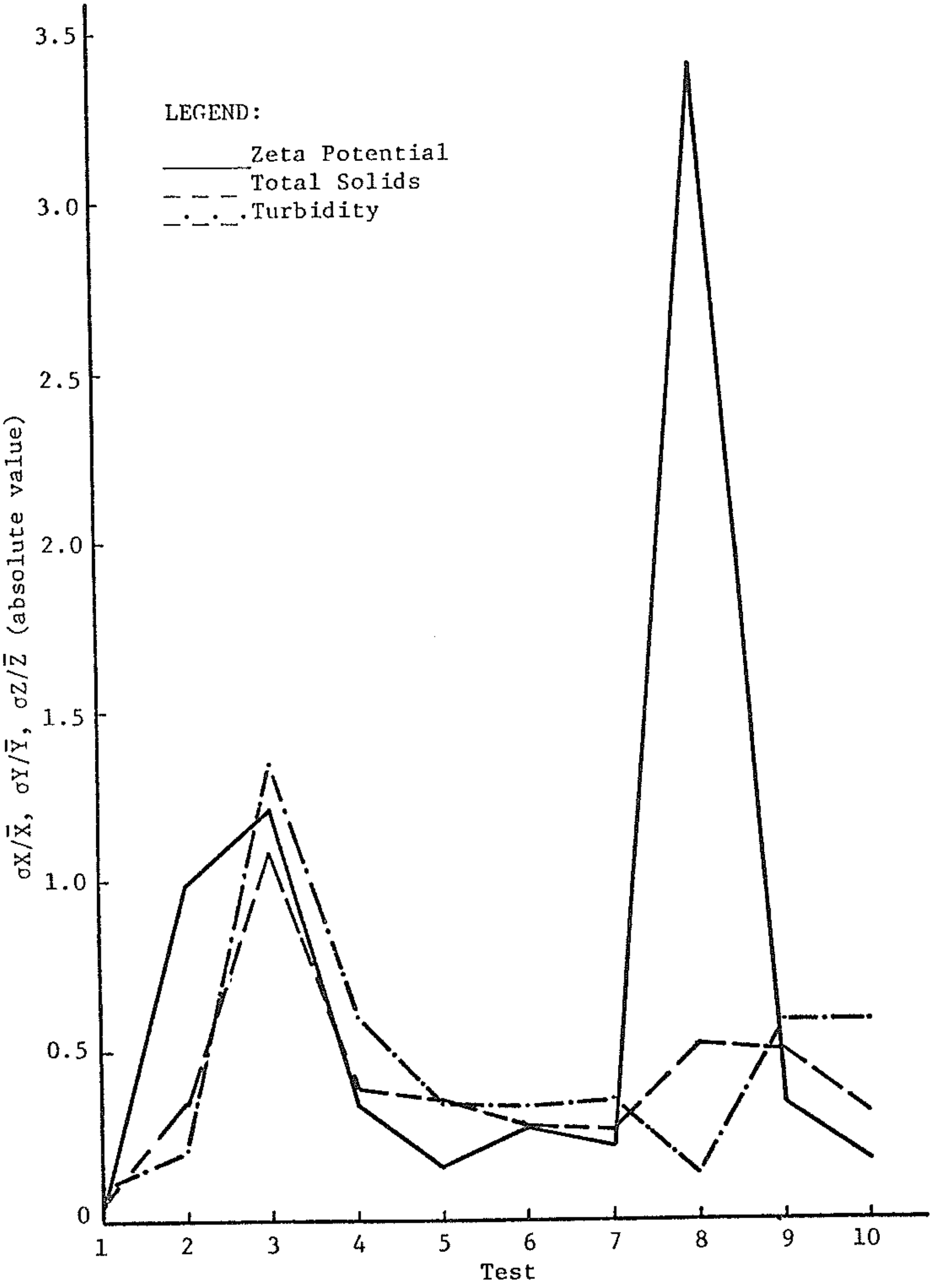


Figure 12. Changes of Coefficient of Variance of Zeta Potential, Total Solids, and Turbidity in the Different Tests

reproducible results than polyelectrolyte coagulation. It was further shown that pH and ionic concentration control decreased reproducibility.

The reproducibility of tests evaluated by turbidity. Table 3 and Figure 11 showed that the variance of turbidity followed the same trend as total solids and zeta potential. Again, it strongly revealed that alum coagulation obtained more reproducible results than polyelectrolyte coagulation. The value of variance of turbidity in Test 8, together with those of total solids and zeta potential in the same test, showed that when alum and polyelectrolyte were used jointly, the most reproducible result was obtained.

Coefficient of Variation Results

Analysis of the coefficient of variation results permits evaluation of the relative reproducibility of the three dependent variables. From Table 3, it was seen that the coefficients of variation for the three dependent variables were all of roughly the same value for all the tests and were particularly close together for a specific test. It was noted that for Tests 2 and 8 (the most reproducible tests as measured by variance) that turbidity had the lowest coefficient of variation. This indicates that turbidity would be the dependent variable of choice in well destabilized tests. However, the average coefficient of variation of each of the three dependent variables for the coagulation tests (Tests 2 through 9) was very nearly the same: 0.46, 0.46 and 0.50 for zeta potential, total solids, and turbidity, respectively. This last calculation excluded the data point for Tests 2 and 8 for zeta potential. This was due to an inherent weakness in the index. As the average of any variable comes close to zero, the coefficient of variation becomes unreasonably large and does not measure accurately the "percentage of deviation." It was known from the variance in Table 3 that the most reproducible results for zeta potential in the coagulation tests was Test 8. Because the average of the zeta potential was 0.72 for Test 8, the coefficient of variation for Test 8 was the highest of all tests. This index must be used with caution.

Time Effect

During the one and half months of experimental work, there was a concern that some sources of time dependent error might influence the result. There was a need to determine if the dependent variables of zeta potential, total solids and turbidity changed with time. In order to evaluate the presence of time effect throughout this experiment and to find out the sources of error, the experiment was conducted in a randomized complete block design (25) with results shown in Tables 5, 6 and 7 for zeta potential, total solids, and turbidity, respectively. It was designed with 14 different times as blocks; within each block the 10 different tests were conducted in a random order. The F values were calculated following the statistical text (25) and are listed in Table 8. Three curves of block mean versus time were also plotted in Figure 13.

The results in Table 8 showed that the variables were time dependent. Specifically it was determined that: (a) for zeta potential, the level was 99.5%, (b) for total solids, the level was 95%, and (c) for turbidity, the level was 99%. Figure 13 also shows the evidence of the time effect

Table 5. Randomized Complete Block for Zeta Potential

Block	Test										Block Totals	
	1	2	3	4	5	6	7	8	9	10	A*	B**
1	315	11	26	125	140	77	173	- 37	52	144	1,026	195,914
2	310	71	34	152	189	130	370	0	88	178	1,522	354,350
3	290	33	62	130	138	125	178	13	151	155	1,275	219,281
4	276	44	53	134	172	161	200	- 30	205	175	1,390	267,932
5	305	19	-106	138	159	167	210	- 9	109	194	1,186	270,534
6	328	9	10	157	176	212	198	- 2	121	174	1,383	292,459
7	298	27	68	110	198	152	228	25	158	240	1,504	303,738
8	316	48	26	122	189	227	227	33	168	200	1,556	325,812
9	308	21	93	117	185	163	236	- 12	131	260	1,502	319,038
10	315	28	41	124	211	137	242	- 11	162	213	1,462	310,654
11	331	35	49	158	202	165	230	4	217	231	1,622	359,546
12	305	41	68	240	222	237	259	- 18	202	237	1,793	426,761
13	289	42	43	280	230	163	276	3.5	194	217	1,737.5	405,916.25
14	286	- 51	90	102	212	128	271	- 61	222	195	1,394	382,700
TTA†	4,272	378	557	2,089	2,623	2,244	3,298	-101.5	2,180	2,813	20,352.5	4,380,635.25
TTB††	1,306,862	20,158	52,425	344,695	501,809	383,526	809,188	8,575.25	373,202	580,195		

*A is $X_{.j}$

**B is $\sum_{i} X_{ij}^{2}$

†TTA is Total Treatment A: $X_{i.}$

††TTB is Total Treatment B: $\sum_{j} X_{ij}^{2}$

Table 6. Randomized Complete Block for Total Solids

	Test										Block Totals	
Block	1	2	3	4	5	6	7	8	9	10	A*	B**
1	944	120	162	188	600	288	574	204	148	260	3,488	1,870,664
2	892	144	86	160	382	346	838	52	146	256	3,302	1,906,836
3	890	80	162	120	372	254	358	58	120	280	2,694	1,266,372
4	916	116	138	128	352	190	510	162	272	208	2,992	1,451,536
5	846	78	850	124	772	284	894	56	200	338	4,442	3,092,932
6	886	82	96	154	314	192	402	120	110	170	2,526	1,177,116
7	816	88	60	220	732	204	786	52	132	476	3,566	2,167,540
8	834	32	138	174	300	358	762	146	220	290	3,254	1,698,524
9	856	72	510	84	490	218	556	88	150	562	3,586	1,947,924
10	782	116	52	90	668	172	550	110	186	266	2,992	1,531,544
11	938	168	200	130	308	300	538	160	426	320	3,488	1,748,752
12	890	116	112	212	534	344	866	74	326	364	3,838	2,260,740
13	842	136	124	298	748	238	880	100	328	332	4,026	2,449,996
14	890	72	112	104	436	184	784	10	452	334	3,378	1,197,212
TTA†	12,222	1,420	2,802	2,186	7,008	3,572	9,298	1,392	3,216	4,456	47,572	26,545,688
TTB††	10,697,348	160,568	1,176,556	386,116	3,904,560	966,520	6,619,356	176,504	906,264	1,551,896		

*A is $Y_{\cdot j}$

**B is $\sum_i Y_{ij}^2$

†TTA is Total Treatment A: $Y_{i\cdot}$

††TTB is Total Treatment B: $\sum_i Y_{ij}^2$

Table 7. Randomized Complete Block for Turbidity

Block	Test										Block Totals	
	1	2	3	4	5	6	7	8	9	10	A*	B*
1	131	17.2	21.3	24.4	115.5	15.1	84.7	18.2	18.2	17.2	462.3	40,206.56
2	131	29.7	17.2	18.2	62.2	15.1	114	16.5	16.5	18.2	438.6	36,638.76
3	131	19.2	19.2	16.1	83.5	15.1	36	16	27.6	29.7	393.4	28,553.6
4	131	25.5	19.2	14	84.7	18.2	39	17.2	45.7	20.3	474.8	38,478.64
5	115.5	16.1	168.5	16.1	156	20.3	148.5	16.1	16.1	49	722.2	91,970.68
6	115.5	15	18.2	19.2	82.2	25.5	66.8	14	16.1	19.2	391.7	26,958.31
7	123	20.3	18.2	14	168.5	16.1	148.5	17.2	35	55	615.8	71,317.88
8	115.5	19.2	18.1	13	78.6	22	150	18.1	48	31	513.5	46,960.07
9	150	17.2	140	14	120	16.5	100	12.5	23.4	96	689.6	77,183.9
10	150	17	17.2	14	165	14	125	15	203	215	559.	67,426.18
11	150	17	16	11	88.5	14	93	13	68	33.5	504	45,758.5
12	145	21.5	17.5	36.5	140	38	170	13	47	42	670.5	77,211.75
13	150	19	15	54	180	26	180	15	58	54	751	97,983.
14	140	20	13	12	94	21	145	13	85	33.5	576.6	59,131.25
TTA[+]	1,878.5	273.9	518.6	276.5	1,618.7	276.9	1,660.5	214.8	524.9	520.1	7,763.4	805,779.08
TTB[++]	254,418.75	5,558.85	51,721.24	7,279.91	207,311.73	6,046.07	218,932.83	3,347.24	25,882.81	25,279.65		

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[*] A is $Z_{.j}$

[**] B is $\sum_i Z_{ij}^2$

[+] TTA is Total Treatment A: $Z_{i.}$

[++] TTB is Total Treatment B: $\sum_i Z_{ij}^2$

Table 8. Analysis of Variance for Zeta Potential, Total Solids and Turbidity

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	F
Zeta Potential				
Blocks--				
Times	γ-1 = 13	74,319.84	4,178.44	3.36***
Test	γ-1 = 9	1,222,339.48	135,815.49	109.41****
Error	(γ-1)(t-1) = 117	145,231.25	1,241.29	
Total		1,421,890.47		
Total Solids				
Blocks--				
Times	γ-1 = 13	337,370.8	25,951.6	1.89*
Test	γ-1 = 9	8,441,019.14	837,891.01	68.48****
Error	(γ-1)(t-1) = 117	1,602,332.06	13,695.14	
Total	γt-1 = 139			
Turbidity				
Blocks--				
Times	γ-1 = 13	18,758.76	1,442.98	2.31**
Test	γ-1 = 9	283,459.41	31,495.47	50.44****
Error	(γ-1)(t-1) = 117	73,058.3	624.42	
Total	γt-1 = 139			

*Significant level = 5.0%
**Significant level = 1.0%
***Significant level = 0.5%
****Significant level = 0.1%

in that the three curves also generally followed the same increasing trend. Urquhart (28) felt that time effect could reflect a characteristic change of latex suspension during this experiment. Even if the time effect reflected a real change in the latex suspension, the majority of the effect in the results was caused by the tests. The F ratios in Table 8 for tests were much larger than the F ratios for time, clearly reflecting the much greater importance of tests than time. There were also some other sources of errors, like temperature and alkalinity, which might have contributed to the variance of the results.

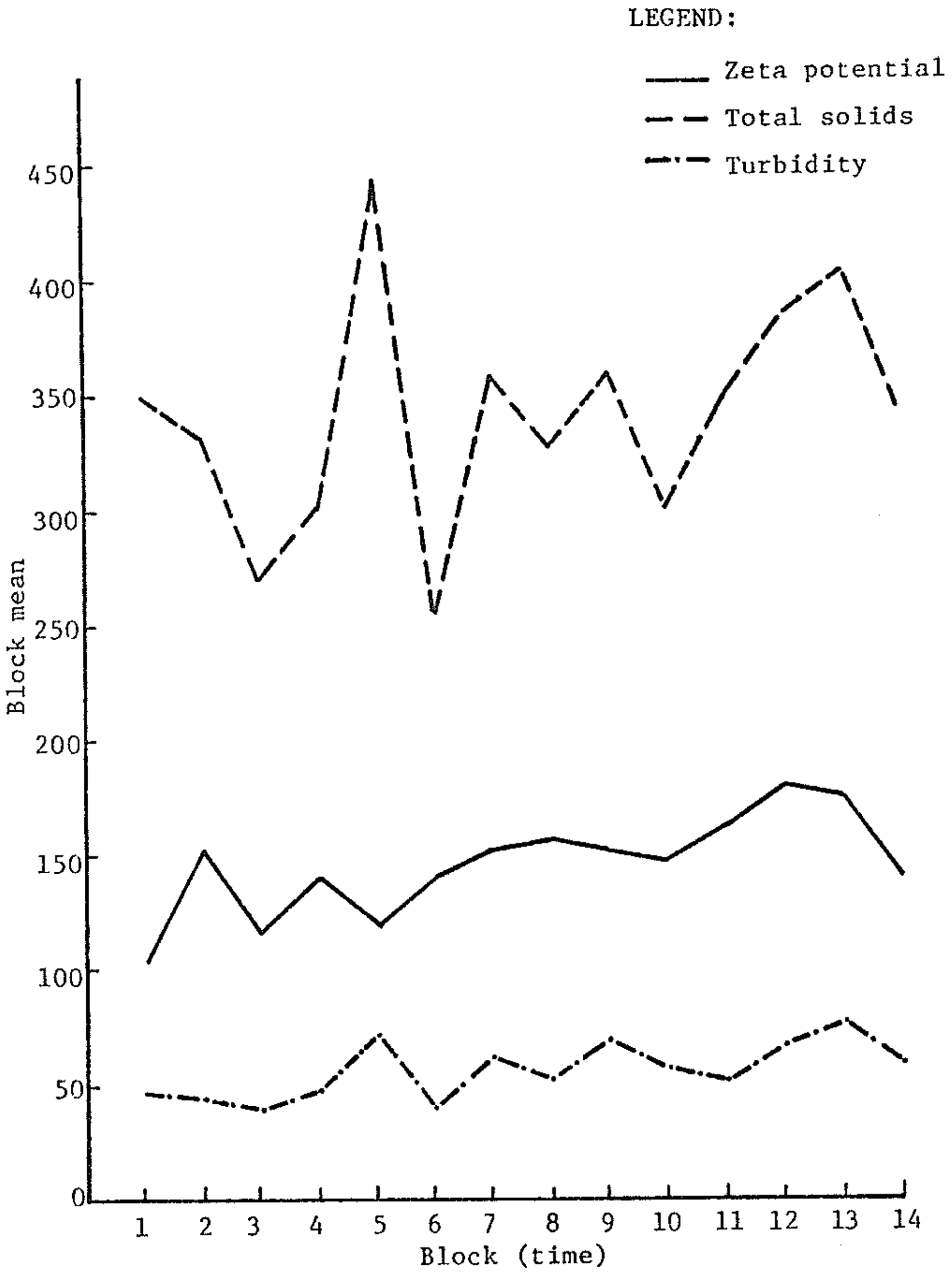

Figure 13. Variance of Block Mean versus Time

CONCLUSIONS

The following conclusions were made based upon the results.

1. The experiment was time-dependent. This dependency was probably due to deterioration of the synthetic colloidal latex suspension.

2. Generally, the farther away the zeta potential shifted from zero, the greater was the variance in a coagulation result.

3. Alum was an effective coagulant. Polyelectrolyte, when used alone as a primary coagulant, was also effective in colloidal destabilization, but did not perform as well as the alum did.

4. The addition of KOH for pH adjustment gave rise to a drastic change in zeta potential of the colloidal particles toward a higher negative value. The performance of alum in colloidal destabilization was not depressed by the addition of the KOH. However, the addition of the KOH reduced the performance of polyelectrolyte substantially.

5. The addition of K_2SO_4 for cationic strength adjustment also slightly shifted the zeta potential to higher negative value and reduced the performance of polyelectrolyte. The effect was not, however, as significant as was the pH adjustment.

6. Control of pH and ionic strength did not appear warranted except in keeping the pH adjusted to a satisfactory value within a wide range.

7. Colloidal destabilization by the alum gave more reproducible

results than destabilization by the polyelectrolyte. When the proper combination of alum and polyelectrolyte was used together as primary coagulants, the most reproducible results and the best overall performance were obtained. The use of polyelectrolytes provided a wider range of zeta potential over which alum and polyelectrolyte were effective as coagulants. As such the polyelectrolyte essentially became a safety factor.

8. There was a strong linear correlation between total solids and turbidity. This was logical since light scattering turbidity evolved from light deflected by colloidal particles.

9. Zeta potential could only give a rough picture of colloidal destabilization. There was a critical range of zeta potential of about -15 to +5 mv within which colloids destabilized satisfactority. Total solids analysis, despite its time consuming procedure, still gave an accurate indication of colloidal destabilization. Turbidity appeared to be the best index to measure the colloidal destabilization; its coefficient of variation was approximately equal to the values for the other variables, and it was much easier to measure.

RECOMMENDATIONS

Based upon the results of the research conducted on the reproducibility of the destabilization of the synthetic latex colloidal suspension, several recommendations are made.

1. It is noted that this series of tests was an idealized as possible through the use of a reproducible synthetic latex colloidal suspension of uniform size particles. It is a logical extension of this work to apply the same experimental procedures to real, variable colloidal suspensions of natural turbid waters and domestic and industrial wastewaters.

2. In future work it is recommended that volatile solids be used as the dependent variable instead of total solids.

3. The advantage of greater effective zeta potential range of colloidal destabilization when using polyelectrolytes should be publicized in the water and wastewater treatment field.

4. It is recommended that the reproducibility of polyelectrolyte to destabilization testing be done as zeta potential values move closer to zero.

5. Synthetic latex preparation must be done at shorter intervals to eliminate the time effect deterioration.

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JOINT CONCLUSIONS STATEMENT

In this statement the results and conclusions of Duff and Wu are considered jointly.

1. Duff concluded that the dependent parameter turbidity was not in itself a good index of the amount of destabilization. Wu's results do not concur with this conclusion. Wu shows clearly that the coefficient of variation of turbidity was at least equal to zeta potential and total solids; it certainly was easier to use in jar tests.
2. Both investigations agreed that dependent variable variation for zeta potential, dissolved solids, and turbidity increased as the zeta potential of the latex increased (either positively or negatively) from zero.
3. Duff noted that the latex suspension gave good reproducibility over the three month test period. We showed that the experiment was time dependent and gave the opinion that this time effect was "probably due to deterioration of the synthetic colloidal latex suspension." It was clear, however, from Wu's Table 8, p. 53, that the experimental effect was much, much greater than the time effect. For this reason Duff probably was unable to observe the time effect.
4. The standard deviation values for turbidity listed by Wu in Table 3, p. 42, which ranged from 1.9 to 48.2 for specific test conditions gave weight to unusual test results obtained by Duff in Figures 29, 31, and 33 on pages 60, 62, and 64 respectively. In those figures Duff showed that the polyelectrolyte could be successfully

added prior to the alum if the proper alum dosage was used.

5. Wu expanded on Duff's dependent variable correlation and better defined the limits of their linear correlation.
6. Both investigators agreed that the use of an alum-polyelectrolyte system gave a "safety factor" in destabilization range which did not exist with either coagulant alone.
7. In general Wu's reproducibility work provided a useful tool to analyze Duff's results.