

EVALUATION OF PARAMETERS AFFECTING THE COLLOIDAL
DESTABILIZATION OF SPENT VEGETABLE TANNIN LIQUOR

by

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1. INTRODUCTION

One of the more challenging problems confronting the water pollution control field is presented by the tanning industry. Tannery wastes are varied and complex in nature. They are characterized by high values of biochemical oxygen demand, chemical oxygen demand, total solids, suspended solids, volatile solids, and color. The odor of tannery wastes is particularly obnoxious and persists on both clothing and equipment. In considering wastewater treatment for tanneries, it should be recognized that the leather industry has been placed in a relatively unfavorable economic position on the one hand by the development of the synthetic chemical industry and on the other hand by the increased emphasis on water pollution control. Because of this position methods for successful treatment of these wastes must be developed which can be accomplished at a minimum cost if they are to be implemented.

The tannery waste treatment problem is complicated by the fact that tanning wastes vary widely from process to process and even from plant to plant where identical processes are used. These variations are due mainly to the individuality of the tanner which has prompted the observation that tanning remains a combination of art and science. This diversity is particularly true in tanneries using the

vegetable tanning process for the manufacture of sole leather. The three processes presently used are vegetable, alum and chrome tanning.

Optimal treatment of spent chrome tan liquor is accomplished by mixing this waste with effluent from the beam house. This process is not applicable to spent vegetable tan liquor and initial segregation of this wastewater stream is typical. The purpose of this investigation was to develop a satisfactory method of chemical pretreatment of spent vegetable tan liquor. This waste stream is primarily responsible for the color associated with vegetable tanning wastes and also contributes a high percentage of the organic matter as measured by BOD or COD in the factory effluent. An effective means of chemical pretreatment would substantially reduce the color and decrease the organic matter loading on a subsequent biological process unit.

II. LITERATURE REVIEW

Perhaps the oldest technological art of man is the processing of skins and hides to produce leather goods and furs. By the time of literate history textiles were the primary form of clothing, and this particular use of leather was already in descent. The leather industry was highly developed at that time, and natural tanning processes remain substantially the same today as then. Early tanneries were located on water courses, and because of the unpleasant odors associated with tannery operations and because of social custom the tanners congregated in their own districts. (68) Rudolf describes the tanning industry as an operation derived from "prehistoric times with wastes of Neolithic characteristics." (28, 91)

Modern Leather Production

The production of leather consists of 10 major processing steps. These steps are in process order: 1) storage and trimming, 2) washing and soaking, 3) green fleshing, 4) unhairing and lime fleshing, 5) lime splitting, 6) bating, 7) pickling, 8) degreasing, 9) tanning, and 10) finishing. (106) A typical flow diagram for a vegetable tanning process is shown in Figure 1. (29) Steps one through five are known as beamhouse operations; steps six through nine are termed tanhouse operations. Eye (31) lists characteristics and

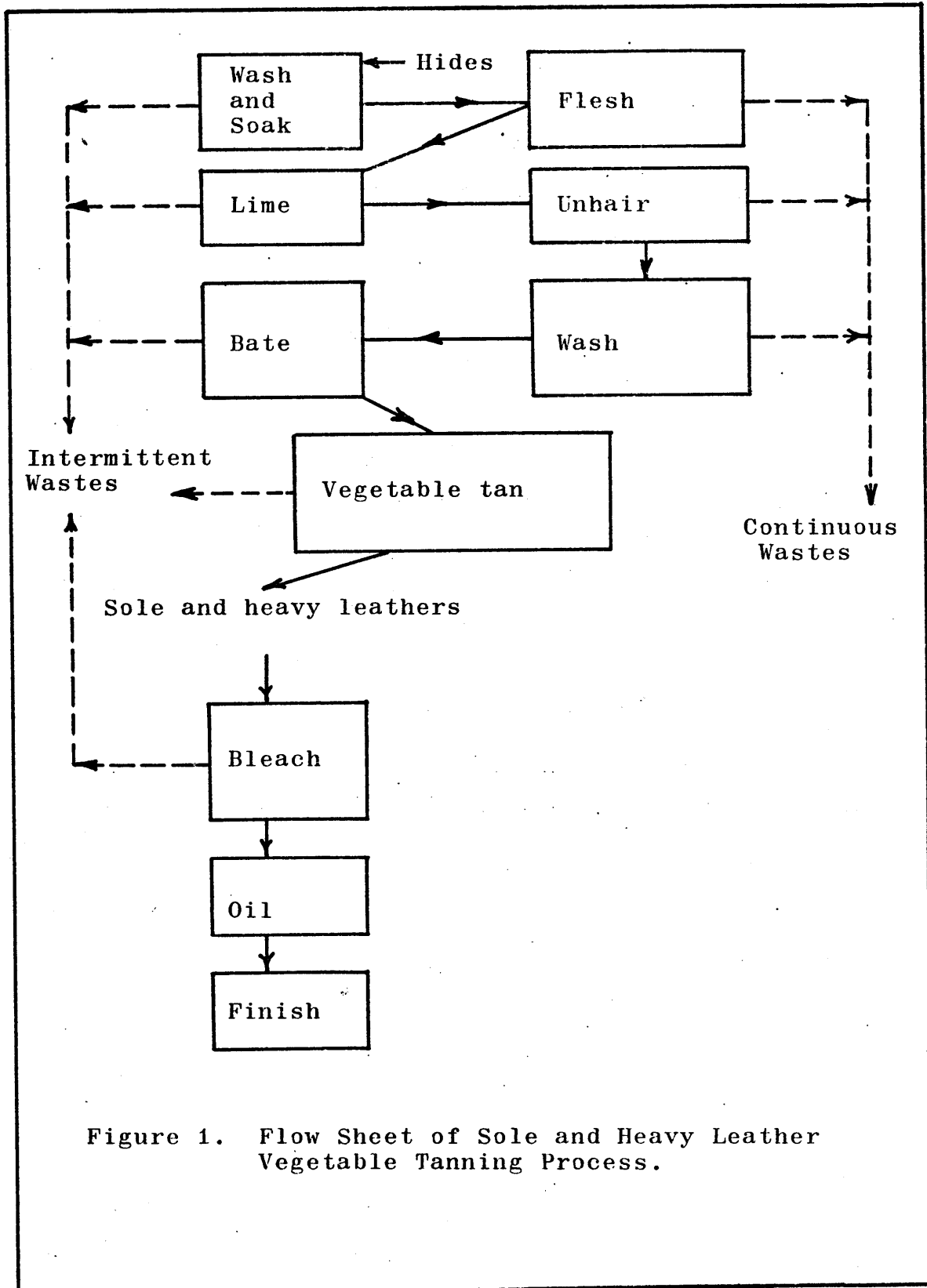


Figure 1. Flow Sheet of Sole and Heavy Leather Vegetable Tanning Process.

quantities of waste flows of a tannery in a summary paper.

Typically, treatment of a hide converts readily putrescible material into leather, a tough, durable substance which will not putrefy for hundreds of years even when wet. (106) All of the various steps prior to the tanning operation are simply preparative to this key process.

Vegetable Tanning Process

Processing prior to the tanning operation removes all fatty and epidermal material from the hide, leaving only the corium (protein collagen, $C_{102}H_{149}N_{31}O_{38}$). (29) In the tanning process the tannin substance combines with the corium protein to form an insoluble resistant compound. (39, 134) Many naturally occurring substances are able to accomplish this step, and this ability defines the word tannin. Tannins are classified as being either hydrolyzable (pyrogallol group) or condensed (catechol group). Basic work by Fischer and Bergmann led to the synthesis of a compound similar to Chinese nutgall tannin, a typical hydrolyzable tannin. This substance, pentadigalloylglucose, has the structure: (39, 134)

Condensed tannins yield a green-black color; hydrolyzable tannins produce a blue-black color. (39)

The stoichiometry of the tanning reaction is not clear, but there is general agreement that the most common protein group, the keto-imide link, is able to interact and bond with the tannin molecule. (40) In McLaughlin and Theis' (74) book a number of theories of tannin collagen interaction are listed. However, Gustavson (41) emphasizes that "the fixation of vegetable tannins by multipointal hydrogen bonding of the phenolic hydrogen atoms on some reactive groups of the protein is the type of mechanism . . . which is favored at this time."

In the physical tanning process it is not desirable for a high concentration of tanning solution to come in contact with raw hides. The rate of combination of the tannin with the skin of the hide would be much more rapid than the rate of diffusion, resulting in a permanent distortion of the hide. (135) To prevent this occurrence the hides and tan liquor are moved countercurrent to one another, with fresh hides coming in contact with weak tannin solutions which have a low tannin-nontannin ratio. The process may take up to one month.

Leather Processing Wastes

Two major wastes are produced in leather production:

1) the waste from the unhairing process in the beam house and 2) the spent tannin liquor. The beam house waste is alkaline, milky colored, sulfide laden, and contains about one-half of the plant waste volume. The spent tannin liquor is only about five per cent of the plant waste volume, but is both highly concentrated and colored. (106) The deep brown color is particularly objectionable in its inhibition of recreational water uses. In Table I the ranges of the tannin waste indices are listed. (3) The effects on the New River of wastes from leather processing plants in Southwestern Virginia have been studied by two chemical engineering students, Sentz (93) and Johnson (48).

Treatment of Spent Vegetable Tannin Liquor

Because of the unique nature of the vegetable tannin liquor, waste segregation and individual treatment is desirable. (107) The summary review paper by Eye (33) lists research accomplished in the treatment of tannery wastes. Indicated in this publication are the four treatment methods generally used.

Mixing With Domestic Sewage

Many researchers have investigated combined treatment of domestic and tannery wastes. The purpose of these investigations has been to define the maximum tannery waste-domestic waste ratio which still results in satisfactory

TABLE I. REPORTED RESULTS OF SPENT VEGETABLE TAN LIQUOR

LOCATION	KENTUCKY	WEST VIRGINIA	VIRGINIA	VIRGINIA
INVESTIGATOR	TOMLINSON, ET AL.	EYE & ALDOUS	KING, ET AL.	BARKLEY, ET AL.
REFERENCE	(103)	(32)	(54)	THIS STUDY
TOTAL SOLIDS	76,600 mg/l	21,825 mg/l	37,750 mg/l	28,000 mg/l (RANGE 26-32,000)
VOLATILE SOLIDS	24,000 mg/l	--	16,000 mg/l	21,000 mg/l (RANGE 19,500-24,000)
SUSPENDED SOLIDS	1,840 mg/l	--	2,640 mg/l	3,000 mg/l
BOD ₅	--	4,390 mg/l	25,600 mg/l	--
COD	51,600 mg/l	--	38,500 mg/l	32,000 mg/l
pH	5.0	3.4	5.2	5.2
TANNIN CONCENTRATION	--	--	--	10,700 mg/l

biological treatment using the trickling filter or activated sludge processes. Consensus conclusions are that hair and fleshings must be removed by pretreatment and that the maximum flow of the tannery waste be no more than 30 per cent of the total waste flow. (54) It is generally true, however, that this method of treatment is not available to many tanneries due to overloaded municipal facilities or the remote location of the tannery.

Mixing with Alum Tanning Solution

Large tanneries often have several tanning processes operating simultaneously. Tomlinson (104) has described treatment of the spent vegetable tannin waste by mixing with the spent alum tanning waste at the Caldwell Lace Leather Company. In this study the volume ratio of vegetable to alum wastes was varied from nine to one through one to one. Significant reductions in color and solids concentration were obtained using the one to one ratio. However, long settling times of up to 18 hours were required to obtain desirable sludge densities.

Biological Treatment

The primary advantage of biological treatment of tannery waste is the large reduction of BOD. Eye and Aldous (32) studied aerobic-anaerobic biological treatment in a stratified lagoon, with the two zones separated by slotted

baffles. Feed was introduced into the anaerobic region and withdrawn at the surface of the aerobic zone. Using an eight day detention time and neutralized feed, BOD reductions of 85 per cent were obtained. Poor color removal was observed.

Parker (80, 81) has also investigated biological treatment and reported on the kinetics of spent vegetable tannin liquor decomposition in an aerobic system. In his latest study Parker (81) observed BOD reductions of up to 90 per cent. Color removals of 90 to 95 per cent were indicated, but color standards were not obtainable, and it is unclear how the values were determined. Also, very large sludge volumes resulted following dilution and treatment with lime wastewaters, being equivalent to the initial volume of the tannin waste.

Foreign researchers have also been active, particularly in India. Tharbaraj, et al. (101) obtained greater than 90 per cent BOD reductions using an aerobic biological system. Chakrabarty (18) also indicated good BOD reductions using the activated sludge process with an acclimated seed. Color removal, however, was not significant.

Chemical Treatment

The spent vegetable tannin waste is colloidal. For this reason several chemical treatment processes have been tested. Toyoda, et al. (105) found that ferric chloride

was an effective coagulant and could be used over a large pH range. Later investigators have specifically attempted to improve color removal which was generally lacking in biological processes. Tomlinson, et al. (104) used massive doses of activated carbon and obtained almost no color removal. They observed that color intensity was a direct function of pH. In a more recent paper Tomlinson (103) observed color removal using a long chain synthetic cationic polyelectrolyte as a coagulant on a laboratory prepared colloidal tannin solution. As the pH was decreased, increased color removal was noted. This work is of doubtful practical value because: 1) the waste must be returned to a higher pH before discharge to the receiving water, and 2) results from a spent and unspent tannin solution may not be similar.

Edwards (27) and King, et al. (54) have investigated the chemical treatment of tannin waste using alum as a primary coagulant and a cationic polyelectrolyte as a secondary coagulant. In this work, the quantitative nature of the investigation was secondary to the basic purpose of determining the feasibility of the process. These researchers also tested biological processes in conjunction with chemical treatment, observing color removal up to 80 per cent. King (55) concluded that "little color removal may be anticipated in a purely biological process." In a later work King (57) observed that the advantage of using both

chemical and biological steps in a colored colloidal waste was that the chemical phase attacked the color problem, the biological phase the removal of organic material.

Nature of Colloids

Naturally occurring colloidal material is generally negatively charged. Positive metal ions have long been used as primary coagulants, and, in accordance with the Schulze-Hardy rule, multivalent ions have proven more effective than monovalent ions. Thus, ferric and aluminum ions were observed in early times to be efficient coagulants. Calcium, with its lower charge is less effective, but being cheaper, has also been used. In order to develop a satisfactory theory of coagulation an understanding of the nature of colloids is essential.

Colloid Structure

In the colloidal state, the suspended substance will have particles in the size range from 10^{-7} to 10^{-4} cm. (126) Colloidal particles move toward an electrode in an electrical field, indicating that the particles are charged. Colloidal particles may exhibit either positive or negative charge. This movement of the particles is termed electrophoresis. (110) As in ionic solutions, a sol (a colloidal suspension of solid particles in a liquid) does not have a net electric charge.

Electrical Double Layer. Colloidal charge compensation is best explained through the model of the electrical double layer. The double layer consists of the charged particle and an equal ionic charge formed by ions in the surrounding liquid near the surface of the particle. (121)

Two methods are suggested by van Olphen (110) for the acquisition of the surface charge: 1) crystal imperfections and 2) preferential adsorption of specific charged ions on the colloid surface. Verwey and Overbeek (121) list only the latter reason. These explanations are apropos to a hydrophobic system in which the solvent is not greatly attracted to the colloid surface. In lyophilic systems the solvent molecule sheath lends added stability to the colloid.

The double layer charges on a specific colloidal system are, of course, repulsive in nature. While there may be a Boltzmann type of distribution, a stable system will be either positively or negatively charged. As one colloidal particle approaches another, repulsive forces, due to their similar charge, keep them from coagulating. This type of colloid stability was recognized by Guoy (37) and Chapman (19). A diagram of the diffuse double layer as they depicted it is shown in Figure 2. (111) Verwey and Overbeek (120) gave the following equation describing the repulsive potential between double layers of spherical particles:

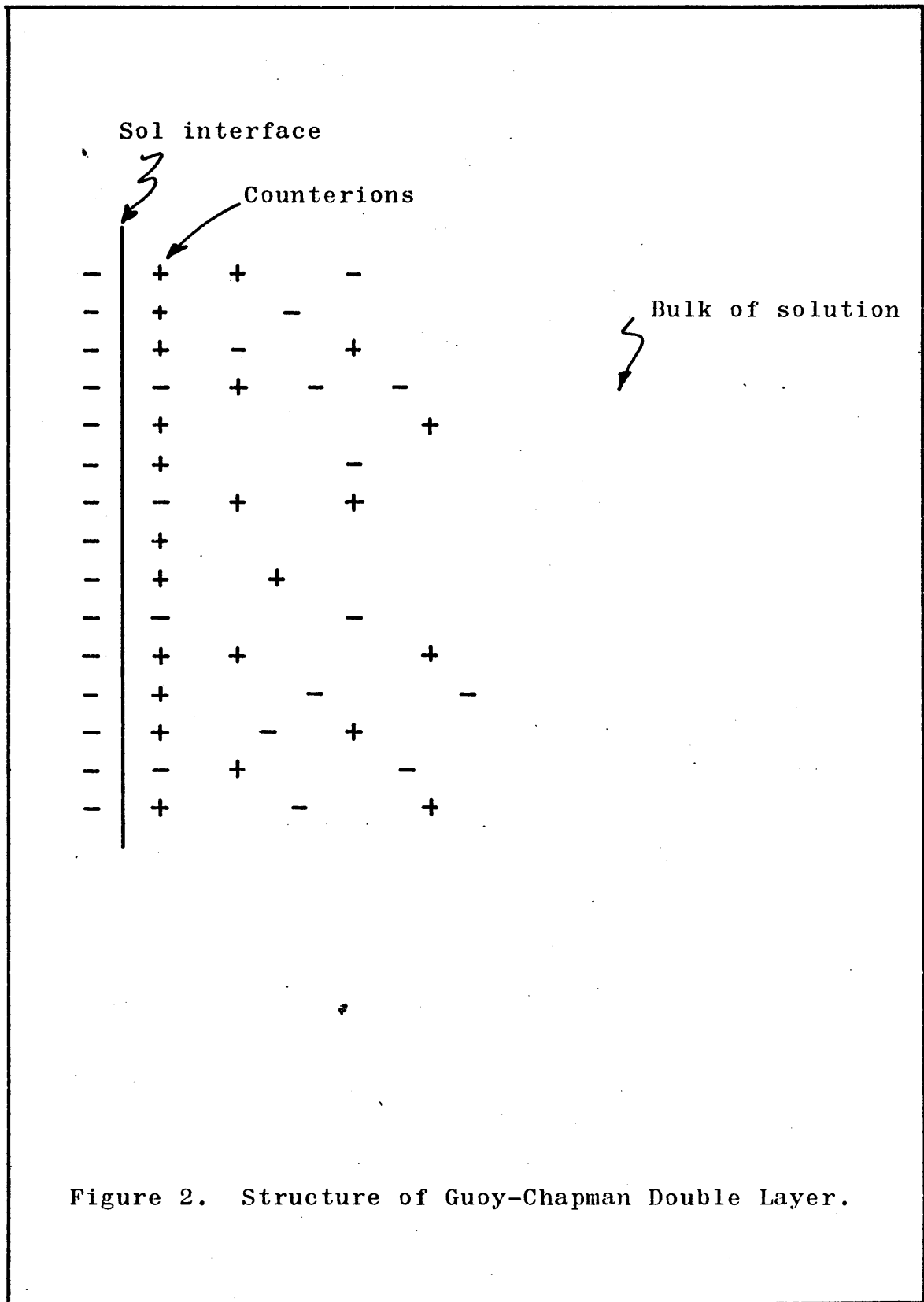


Figure 2. Structure of Guoy-Chapman Double Layer.

$$V_R = \Psi_a \frac{Da^2}{r} \exp [-K(r-2a)] \quad (1)$$

where

D = dielectric constant of solvent

m = ionic concentration

e = electronic charge

Z = valency of the ions

h = Boltzmann constant

T = temperature, °K

Ψ_a = surface potential

a = particle diameter

r = distance from the particle center

$$1/K = (DkT/8\pi me^2 Z^2)^{\frac{1}{2}}$$

Attractive Forces Between Sol Particles. In order to achieve coagulation, there must be attractive forces between sol particles. London described the weak, non-polar Van der Waals attractive forces acting between all particles from a quantum mechanical viewpoint in 1932. (122) Shortly thereafter Hamaker (123, 43) described both attractive and repulsive forces for two particles. It might seem that the Van der Waals forces would be insignificant and thus not have an appreciable effect on the stability of a colloidal system. However, this attractive force between atoms is additive; thus, for systems with large numbers of atoms per sol particle, the force becomes significant. (112) A graphical

representation of repulsive and attractive energy as a function of particle separation is given in Figure 3. (75, 112) By summing the repulsion and attraction curves, net attraction occurs only at very small particle separations with high electrolyte concentration. Hamaker's (43) equation describing sol particle attraction is:

$$V_A = -A/6 \left\{ \left[\frac{4a^2(r^2 - 2a^2)}{r^2(r^2 - 4a^2)} \right] + \ln \left(\frac{r^2 - 4a^2}{r^2} \right) \right\} \quad (2)$$

where: a = radius of particle

r = distance between center of particles

A = Hamaker constant ($\sim 10^{-12}$ ergs)

Following the work of Hamaker, many investigators attempted mathematical refinements to improve his model. Chief among this group were Derjaguin and Landau (20) and Verwey and Overbeek (120). These two pairs of researchers, working independently during the last World War, made similar evaluations and arrived at much the same mathematical developments.

Development of Zeta Potential--Stern Model

The Guoy-Chapman model of the electrical double layer has a serious defect in that the finite dimensions of the ions in solution were assumed to be zero. In dilute solutions this assumption is permissible; however, it leads to

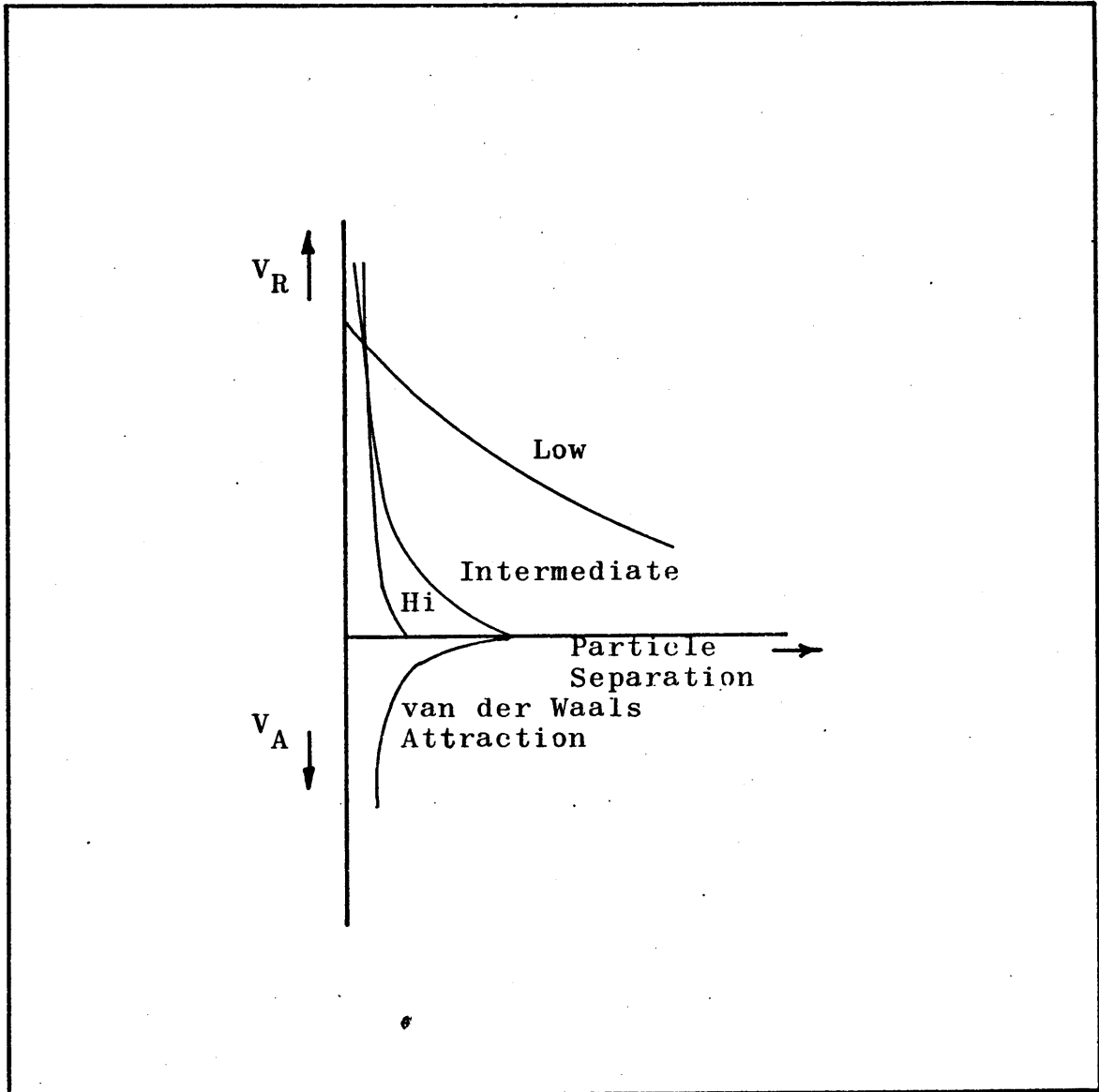


Figure 3. Repulsive and Attractive Energy as a Function of Particle Separation at Three Electrolyte Concentrations.

absurd predictions for counter ion concentration in concentrated solutions. (124) An early attempt to create a more realistic double-layer model was made by Stern (97) when he assumed that the position of closest approach of a counter-ion to the charged sol surface was limited by the size of the ion. (114) In this description the counter ion charge is separated from the surface charge by some thickness, δ , in which there exists no charge. Thus, a molecular condenser exists between the counter-ion charge and the sol surface charge. In this region the potential drops linearly, but in the diffuse region (Guoy-Chapman) the potential drop is exponential. A graph showing the potential function of a sol particle as seen by Stern is shown in Figure 4. (1) The effect of potential causing ions is also shown. In this picture the Stern layer is assumed to be immobile. At some point away from the sol particle surface and at least at the limit of the Stern layer there exists a shear layer where relative movement of counter-ions and the sol particle exists. The potential at this shear layer is known as the zeta potential.

Several authors (115, 125, 127) emphasize the difficulty from both practical and theoretical viewpoints in working with zeta potential. For example Verwey and Overbeek (125) stated in 1948, "there are practically no cases standing the test of even moderate criticism in which

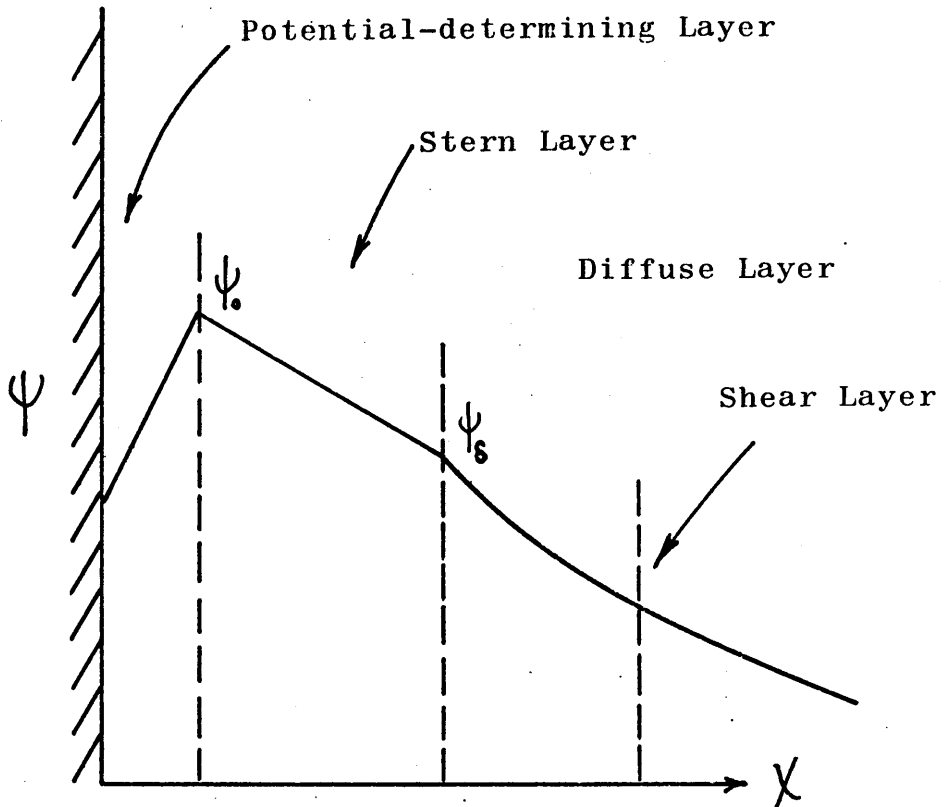


Figure 4. Variation of Potential with Distance Where the Potential Determining Layer is Distinct from the Solid Surface.

determinations of zeta potential for one system with different methods give concordant results." Vold, (127) publishing in 1964, took a somewhat less critical, but still negative viewpoint. van Olphen (115) stated that it was not surprising that a relation exists between colloidal stability and the magnitude of the zeta potential. He then further stated, "because of its ill-defined character, the zeta potential is not a useful quantitative criterion of stability." Clearly there is a wide breach of opinion on the usefulness of zeta potential. Colloidal theoreticians avoid its use; practicing colloidal chemists, such as Rid-dick, rely on it as the fundamental parameter.

Zeta potential is calculated indirectly by measuring the electrophoretic velocity and applying the following equation developed from the work of Smoluchowski and Helmholtz: (22, 95, 128, 129)

$$v = \frac{\epsilon D X}{4\pi\eta} \quad (3)$$

where: v = electrophoretic velocity

D = dielectric constant

X = applied potential gradient

η = viscosity of the liquid phase

Colloidal Stability

All sols are unstable, and thus it is perhaps unfortunate that it is common to describe some as being stable.

"Stable" and "unstable" sols differ only in their rate of coagulation. It is customary to describe the coagulation process by the term flocculation time (time for half of the sol particles to disappear). Thus coagulation is assumed to be similar to a second order chemical reaction. (11)

The basic concepts in the kinetics of flocculation were set forth by von Smoluchowski. (131, 132) He first considered rapid coagulation and developed the equation for coagulation time:

$$T = \frac{1}{4\pi D_1 R v_0} \quad (4)$$

where: D_1 = diffusion constant

R = distance of interaction

v_0 = initial number of particles.

By substituting the definition of the diffusion coefficient he obtained, for room temperature:

$$T \approx \frac{2 \times 10^{11}}{v_0} \quad (5)$$

Thus, Smoluchowski showed that the time of coagulation for a rapidly coagulating system was inversely proportional only to the number of sol particles. Overbeek verified the correctness of this conclusion in a later summary text. (58) The approach taken by Smoluchowski in this development was that every bimolecular sol collision resulted in coagulation.

It is not surprising then that in his effort to describe slow coagulation he added only a fractional factor, α , which converted total collisions to collisions resulting in successful agglomeration. He obtained an expression similarly to equation (4):

$$T = \frac{1}{4\pi D_1 R v_0 \alpha} \quad (6)$$

Using this approach all coagulation-time curves should be interchangeable by manipulation of the time scale. Regrettably, there was no theory relating α with double layer potential, concentration of electrolyte, or valence of electrolyte.

Another fundamental approach for slow coagulation, more applicable to the double layer theory, was developed by Fuchs (59). In this work Fuchs assumed that there was an energy barrier to coagulation similar to the activation of a chemical reaction. As coagulation proceeded fewer and fewer highly energetic sol particles remained; thus, coagulation must slow down. In rapid coagulation this energy barrier was either very low or non-existent, allowing coagulation to go to completion. This concept lent itself very well to the double layer theory of colloidal structure.

Verwey and Overbeek (61, 120) used this approach in reconciling the Schulze-Hardy rule with their theory and

evaluations of colloidal stability. They pointed out graphically that addition of electrolytes lowered the potential of the sol particle; the greater the positive ion charge, the greater the lowering of the charge of the sol particle. Verwey and Overbeek believed, as part of their theory, that this lowering is caused by addition of more ions to the Stern layer and with it compaction of the double layer. This sol potential lowering from Fuchs' viewpoint (with Verwey and Overbeek's agreement) caused a decrease in the energy barrier separating the colloids and resulted in coagulation. Verwey and Overbeek (62, 120) showed that:

$$C = 8 \times 10^{-22} \frac{\gamma^4}{A^2 Z^6} \quad (7)$$

where: C = flocculation value

γ = surface tension

A = van der Waals constant

Z = valence of ion

Thus, flocculation effectiveness of monovalent, divalent and trivalent ions were predicted to be in the ratio of 100:1.6:0.13, values which are in reasonable agreement with experimental evidence. (62)

Mechanistic Theories of Coagulation

The accepted theory of colloid structure and stability is termed the D-L-V-O theory from the initials of the

authors. (20, 120) Verwey and Overbeek also explained the mechanism of colloidal coagulation, as noted in the previous paragraphs. However, there are several competing viewpoints, overlapping explanations, and semantical differences prevalent in the literature which need clarification.

Chemical Theory

Duclaux and Pauli (61), among others, proposed that flocculation was the result of formation of an insoluble salt or, in a modified form, as the result of formation of a non-ionized compound in the double layer. The chemical theory also stated that the primary charge of colloid particles arises from the ionization of complex ionogenic groups present on the surface of the dispersed particles. (98) The weakness of the theory is in the similarity of coagulating ability of ions of the same charge.

Adsorption Theory

Freundlich, et al. (36, 61) proposed that discharge of the sol particle resulting from preferential adsorption of the flocculating ions caused coagulation. This was disproved by experiment evidence.

Physical Theory

This theory was developed over a forty year period by Guoy, Chapman, Fuchs, Stern, Hamaker, Verwey, Overbeek, Derjaguin, and Landau and has been considered in detail. It

emphasizes counter-ion adsorption, reduction of zeta potential, and compaction of the double layer in the coagulative process.

Perikinetic and Orthokinetic Flocculation

These terms describe two different phases of coagulation in accordance with the physical theory. (25, 60) Perikinetic flocculation occurs when repulsive forces between sol particles can be overcome by the Brownian movement of the particles. Perikinetic flocculation has been described as consisting of four phases: 1) hydrolysis of coagulant, 2) spontaneous crystal growth, 3) precipitation of particles, and 4) agglomeration. (53) Orthokinetic flocculation is flocculation caused by systematic movement (velocity gradients). Insufficient energy is present for Brownian movement to overcome repulsion potential between sol particles; this mixing energy must be supplied for rapid coagulation. (60)

Flocculation and Coagulation

van Olphen (109) stated that these two terms are normally used interchangeably. LaMer (63, 64, 65, 98) has chosen to differentiate between them. He defined coagulation as processes which affect a reduction of the total potential energy of interaction between the double layers of two similar particles. Flocculation was defined as processes which enmesh the colloidal particles in a three dimensional floc network

by the formation of chemical bridges. While this distinction seems to be useful, regrettably for the case of hydrolyzed metallic ions, the mechanism is not entirely clear. Destabilization of a hydrophobic colloid by the addition of an indifferent electrolyte is clearly coagulation. Destabilization of a negatively charged dispersion by an anionic polyelectrolyte is an example of flocculation.

As can be seen, the term perikinetic flocculation is comparable to LaMer's term coagulation while orthokinetic flocculation is more like LaMer's term flocculation. Because of the wide use of trivalent hydrolyzed metal ions in coagulation processes this topic will be considered in more detail.

Sweep Floc

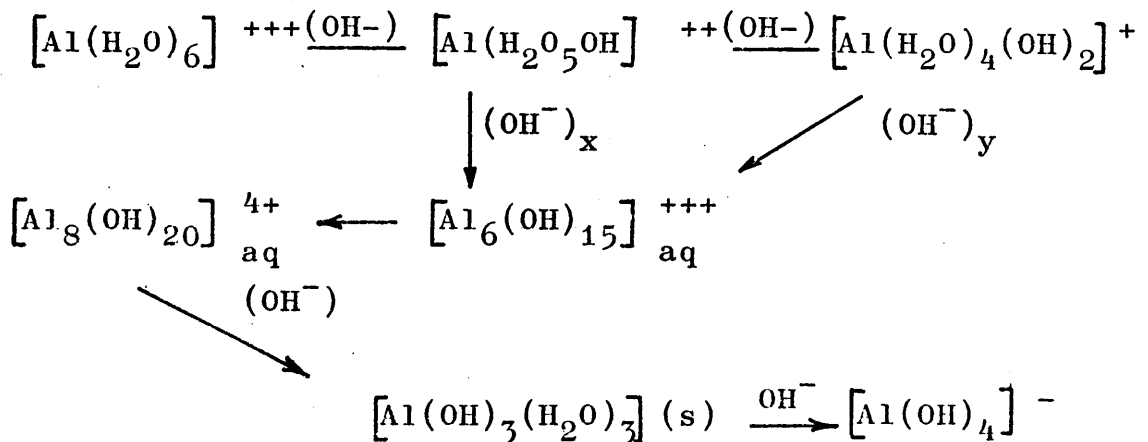
Stumm (98) has described colloidal destabilization occurring close to, but not exceeding the so-called critical stabilization concentration, as being an area in which the hydrolyzed metal ion acted as "sweep floc." In this region the sol particle concentration is very low, as most has already been destabilized. Floc formation is large with extension bridging. Stumm thus described this range of coagulant floc as being comparable to the sawdust used by a floor sweeper to collect dust. Hence, he coined the word sweep floc.

Hydrolyzed Metal Ions

The two most important hydrolyzed metal ions are the ferric and aluminum ions. The following conclusions have been made from previous work concerning hydrolyzed metal ions. (98) 1) Hydrolyzed metal ions are generally more efficient in destabilizing colloidal particles than unhydrolyzed ions. 2) Hydrolysis of metal ions can be interpreted as progressive replacement of coordinated water molecules by hydroxide groups. 3) Simple hydrolysis species can condense and form polynuclear hydroxo complexes, particularly when the metal hydroxide is oversaturated. 4) Polynuclear hydrolysis products may therefore occur as soluble kinetic intermediates in the transition to the precipitation of the metal hydroxide.

Aluminum Ions

The hypothetical conversion of the trivalent aluminum ion to the aluminate ion is postulated as follows. (99)



Matijevic (71) agreed with at least part of this hypothesis as he concluded from his own work that hydrolysis of the aluminum ion in the pH range four to seven leads to the formation of a soluble polynuclear tetravalent aluminum complex. He postulated the structure $[\text{Al}_8(\text{OH})_{20}]^{4+}$ as the most likely formula of the complex.

It was known that the pH of an aluminum ion solution decreased with age and that aged solutions gave different coagulation characteristics than unaged solution. For a given metal ion concentration the pH is the most important factor determining which particular polymeric species predominates. Thus, the pH of the medium is of primary importance in establishing the mean charge of the hydrolysis products and of the rate of coagulation. (99) Matijevic (72) substantiated this opinion in a later paper in which he stated that coagulation and sol particle charge reversal are functions of metal ion concentration and pH.

Figure 5 shows a graph of the pH-solubility curve for aluminum hydroxide. As can be seen in this figure, the hydroxide is least soluble at about pH 6. (99) On this graph the different species of the aluminum ion existing at various pH levels are listed. This compilation by A. P. Black (14) lists the range of existence of $[\text{Al}_8(\text{OH})_{20}]^{4+}$ as from pH 4 to 6, thus, differing from Matijevic's 4 to 7.

In studying coagulation using aluminum as the coagulating counter-ion Stumm noted that as the coagulant dosage

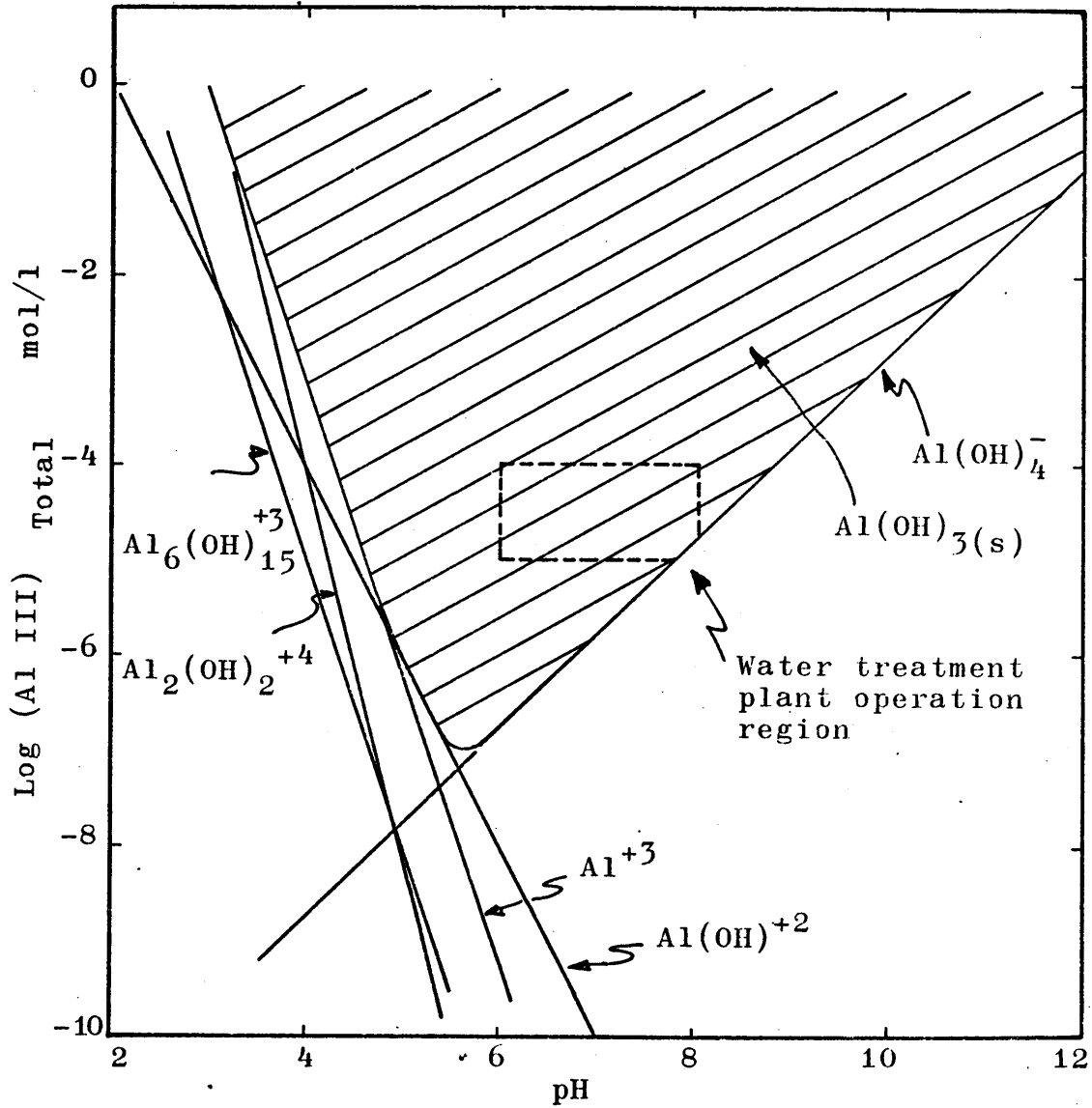


Figure 5. Solubility of Aluminum Hydroxide as a Function of pH.

increased there was always some critical value beyond which coagulation was produced. This value was defined as the critical coagulation concentration. Matijevic (69, 70) described several methods of determining the c.c.c. value. Then, as coagulant concentration increased, increased turbidity, or restabilization of the coagulated sol particles, was observed. This value was defined as the critical stabilization concentration, c.s.c. Thus, between these two concentrations coagulation was observed. As the coagulating counter-ion concentration was increased the negative charge on the sol particle gradually decreased until coagulation was possible. Further concentration increases of the counter-ion eventually caused sol particle charge reversal by forced adsorption and subsequent colloidal restabilization. Matijevic (73) observed that zeta potential did not attain the same constant value at the critical coagulation concentration. Therefore, it was felt that zeta potential alone was not sufficient criterion for stability. Matijevic believed that turbidity determinations were more effective in evaluating coagulation with the hydrolyzed aluminum ion.

T. M. Riddick (87) has studied industrial applications of the aluminum ion over a long consulting career. He believed that pure aluminum oxides were of little value for forming floc on account of the resulting floc fragility, which reflected their low degree of polymerization and a

lack of chemical or mechanical interlocking. Alum (or pure, hydrated aluminum sulfate) produced hydrous aluminum oxides which formed the basic unit of a tough floc. He believed that the following steps occurred when alum was added to water: 1) Hydrous aluminum oxides were instantly formed with a resulting drop in pH. 2) Polymers or gels consisting of aligned polymers (in the range of a few hundred angstroms) were instantly adsorbed on the first available and acceptable colloid. Thus, the colloid was literally coated with coagulant. 3) If, at the moment of hydration formation, a colloid was not immediately available, the polymers underwent further buildup on other floc. 4) In order to obtain good floc-colloid contact it was necessary to have violent agitation when the alum was added. The period of rapid mixing was critical as excessive shearing of the newly formed metallic polymer would result in inefficient coagulation. 5) The smaller the size of the floc, the better was the colloid removal. This latter observation is particularly cogent as many applied colloid chemists seem to feel that "the bigger the floc, the better the removal." Both theory and practice would seem to dispute this viewpoint.

Ferric Ions

The ferric is the second of the most commonly used hydrolyzing metallic ions. Generally, it has not found as wide use as has alum. Edwards (27) compared the use of

alum with the ferric ion in earlier work on the chemical treatment of tan liquor wastes and found the alum to be superior. Matijevic (71) has studied the hydrolysis of the ferric ion very extensively, but due to Edwards' lack of success, it will not be covered in this review.

Recalling that one of the problems with tannin waste is color removal, it is not encouraging to note that Stumm (98) and Black (10) report that many reactions between tannins and similar substances with ferric ions have yielded intensively colored solutions. Hem (45) has studied both natural and synthetically prepared tannin solutions in their reaction with ferric ions to produce color. Benoit (4, 5) reports that due to the stabilizing soluble complex formed by tannin and iron in soil, iron is able to migrate readily in soil systems. These reports and more all point to the inadvisability of adding ferric ion to a tannin system. The only disagreement with this logic is presented by Hommon (46) in which he describes the chemical treatment of tannin waste with ferrous sulphate to produce a waste with the consistency of weak tea. In this treatment, however, the waste was diluted to seven times its initial volume.

Stumm and O'Melia (98) have concluded that the colloid destabilizing ability of the ferric ion is similar to that of the aluminum ion in that it acts by both coagulation

and flocculation and that process efficiency is dependent on concentration and pH.

Polymeric Flocculants

The incorporation of ionic substituents in a polymeric chain produces substances which have the properties of both polymers and electrolytes. Flory (35) reported that the configuration of the polyelectrolyte molecule in a dilute solution may be magnified by electrostatic repulsion between charged portions of its own structure. A possible configuration is shown in Figure 6. This swelling results in high viscosity, even in dilute solutions. Other evidence of the ionic nature of the polyelectrolytes is seen in the high conductivity and heats of solution of these substances. The charge on the primary chain can be either positive or negative and thus these substances are designated as cationic or anionic polyelectrolytes, respectively.

Cationic Polyelectrolytes

When cationic polymers come into contact with a polar solvent the inorganic anion dissociates. The concentration gradient results in diffusion or migration of the anion away from the polyelectrolyte chain. The result of the anion migration is that the polymer chain becomes positively charged, thus making further anion migration more difficult. Steady state is eventually reached. Inorganic cation

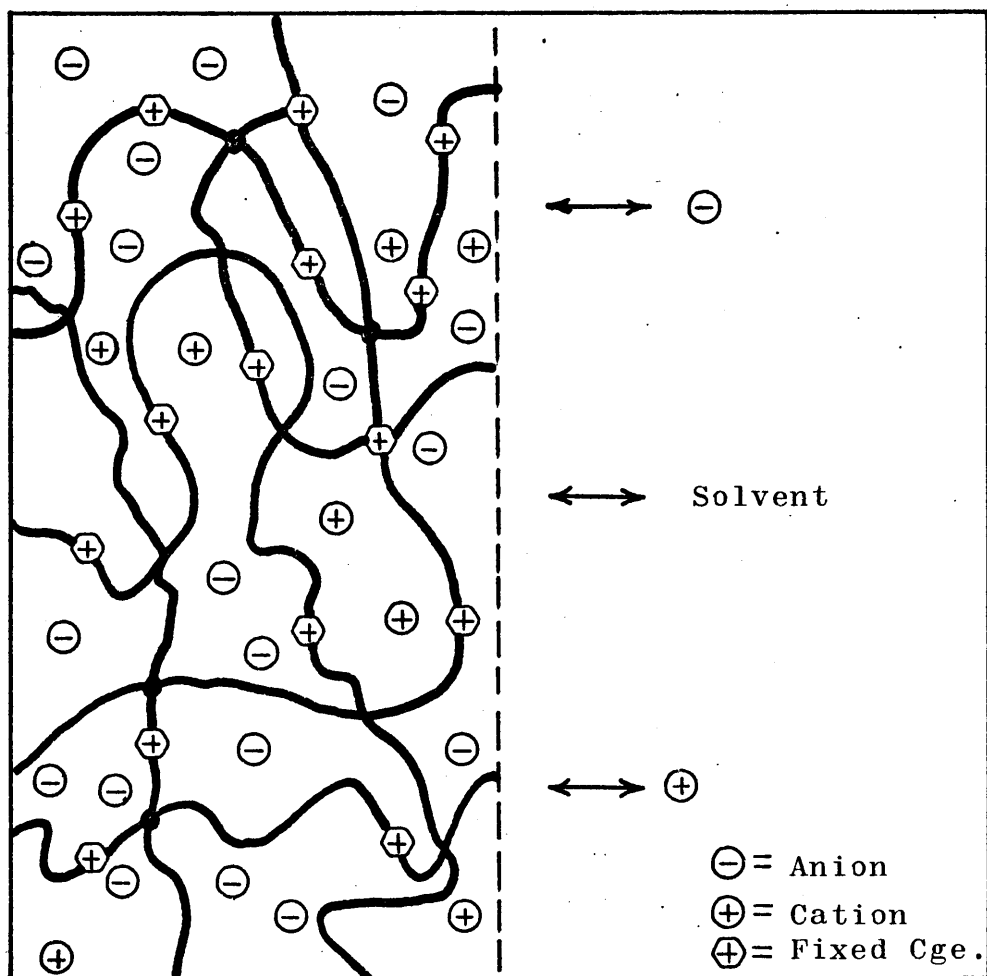
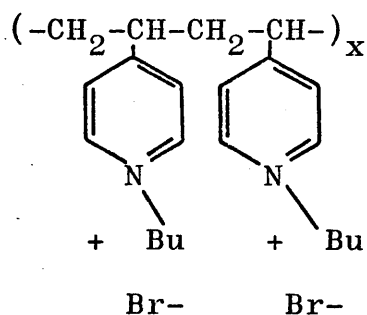


Figure 6. Swollen Ionic Gel in Equilibrium with Electrolyte Solution.

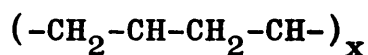
counter-migration will only occur if this ion is introduced from extra system sources. Thus, the very high osmotic pressure following ionization will result, at equilibrium, in a highly charged polyelectrolyte. An example of a cationic polyelectrolyte would be a substituted amino group or an organic salt. Flory (34) gives the following example.



In a coagulation system the positively charged polyelectrolyte would be used to destabilize negatively charged colloidal sol particles.

Anionic Polyelectrolytes

The ionization and equilibration of the anionic polyelectrolyte acts similarly to the cationic polyelectrolyte, excepting the reversal of charges. The anionic polyelectrolyte may be used to destabilize a positively charged colloidal system. An example of this type of polyelectrolyte is illustrated. (35)



Nonionic Polymers

Nonionic polymers are macromolecules with different polar functional groups distributed along the polymer chain resulting in no net charge on the polymer. (118) Examples are polysaccharides and synthetic polyoxyethylene. At present little is understood about the mechanism of interaction between sol particles and the polymer. It is known that they are absorbed on the sol particle surface, but how the adsorption affects ion distribution in the Stern and Gouy layers is not known. (118)

Flocculation Mechanisms of Polyelectrolytes

One of the advantages of polyelectrolytes is that they are effective in very low concentration. Typically, industrial recommendations are a maximum of five milligrams per liter. (76) The reason for this was given by van Olphen. (116) If the polyelectrolyte content of a hydrophobic sol ranges from a few tenths to several percent, the salt tolerance of the hydrophobic soli is increased. The oppositely charged salt ions are attracted to the polymer "membrane" and greater stability is given to the sol particles. van Olphen (116) also suggested that "the polyelectrolytes

envelop the hydrophobic sol particles and lend them the special characteristics of the hydrophilic sols, i.e., their stability and high salt resistance." This protective action is independent of the sign of the charges of the hydrophobic and hydrophilic colloid. When the concentration of the polyelectrolyte is very low, however, the sol is apparently sensitized towards flocculation by addition of salt particles. van Olphen (117) suggests that the polyion is now adsorbed on several different sol particles and in this manner forms a series of interlocking bridges, thus prompting flocculation. He further states that in the absence of salt, polyion adsorption does not occur. "A certain amount of salt must be present to establish particle bridging by simultaneous adsorption on different sol particles." (117) This viewpoint is reinforced by the realization that salt addition reduces interparticle distance and increases the possibility of dual adsorption. van Olphen states that the addition of the polyelectrolyte before the salt increases the possibility that the polyelectrolyte ions will become adsorbed on sol particles. This theory is particularly interesting in light of the fact that work published by practicing chemists and engineering consultants has recommended the reverse order. (8, 23, 27, 89)

In more recent work Walles (133) postulated three separate mechanisms for coagulation by organic water-soluble polymers. The first method was termed charge effect neutralization in which the effective charge of the sol particle was reduced by double layer reduction. In this method, flocculent molecular weight has little bearing. Polymer bridging was the second method. The flocculent polyelectrolyte interferes with the free movement of the particle, either by adsorption of a number of particles on a polymer network or by formation of a long bridge between two particles. Flocculent molecular weight is of critical importance. The third mechanism postulated was mutual dehydration. Hydrophilic colloids or true solutions are flocculated by non-ionic polymers. Chemical reaction or complex formation results in a non-soluble product with flocculent molecular weight being important.

Ries (90) agreed with the first two mechanisms postulated by Walles, and he indicated that the determination of their relative importance is highly controversial and probably not possible at this time.

Applied Polyelectrolyte Research

Birkner and Edzwald (8) have studied the treatment of raw water with both alum and polyelectrolytes to remove colloidal material. They concluded that these coagulants were successful, but stressed the idea that costs were high.

The concentrations recommended were very low, 1.5 mg/l polyelectrolyte and 20 mg/l alum. In a later work these same authors (7) studied the destabilization of a clay colloidal system from an equilibrium viewpoint. Adsorption of the long chain polyelectrolyte was assumed, and Langmuir adsorption graphs were prepared using various counter-ions. Superior polymer adsorption (and subsequent colloidal destabilization) was observed when the monovalent counter-ion was present. It was also found that there was a critical polymer concentration either above or below which the degree of destabilization decreased.

Probably the two most prolific authors on practical application of chemical coagulation of colloidal material and the influence of polyelectrolytes are T. M. Riddick and A. P. Black. T. M. Riddick described in a series of articles and a book (85 - 89) his increasing involvement with the basic control factors involving colloidal stability. In an early article (85) he stated that color and objectionable taste could only be effectively removed in a water treatment plant by the use of a cationic polyelectrolyte. In a sequential article (86) he argued that the most effective method of determining colloidal destabilization is by measuring the zeta potential. This concept was certainly not novel as Burton (17) had noted the necessity of zero zeta potential in working with gold sols in 1906 and

1909. Riddick suggested that colloidal destabilization can be accomplished more completely by simultaneous addition of an inorganic coagulant and a polyelectrolyte. Prior to this time coagulation was normally accomplished by a single coagulant with the quantities being determined by jar testing. Jar testing involved visual estimation of the best flocculation quality for various coagulant dosages. Riddick stated that good flocculation producing dosages were still too electronegative to obtain effective colloid removal. Thus, the visual observation of a floc would tell little concerning the key stability parameter--the colloidal surface charge. Proper coagulant dosages not only cause floc formulation but also reduce surface colloid charge to near zero. At these conditions gentle agitation will cause colloidal collisions; and, there being no charge repulsion, coagulation will then occur.

Riddick listed three stages of flocculation: 1) rapid mixing and microfloc formation, 2) colloid gathering, and 3) agglomeration. The degree of agitation was noted to be important. There must be sufficient velocity gradients to cause bumping, but low enough velocity levels to prevent floc destruction. Riddick suggested that thick wire screens serve more efficiently than solid paddles in producing the proper velocity gradient conditions. For poorly settling flocs he recommended the addition of weighing agents such as barium sulfate or calcite.

A. P. Black (16) has also reported on the use of zeta potential as the primary control parameter in removal of colloidal organic color. In this work he used alum alone as a coagulating agent, but stressed the importance of zero zeta potential rather than floc appearance. In later efforts Black, et al. (11) described the effectiveness of organic polyelectrolytes in destabilizing very dilute colloidal clay suspensions. He also found that a log-log relationship existed between the suspended concentration of silica and polyelectrolyte concentration. In these investigations there was either a need or an attempt to measure coagulation by some numerical, indirect variable.

In other work Black, et al. (12) investigated the flocculation of kaolinite by an anionic polyelectrolyte. The kaolinite was negatively charged and it was necessary to add calcium to reduce interparticle repulsion before flocculation occurred. This work was particularly interesting as negatively charged polyelectrolytes were used to coagulate initially negatively charged colloidal particles.

Teot and Daniels (100), in a paper that was published after the experimental work of this research was completed, made the following conclusions. Anionic sewage colloids were not significantly flocculated by anionic polyelectrolytes in the absence of multivalent cations. The cation alone, in sufficient concentration, will coagulate the

sewage colloid. However, in the presence of an anionic polyelectrolyte a lower concentration of multivalent cation will accomplish the same degree of coagulation. Teot in this same investigation tested the order of adding cation and polyelectrolyte and found that the order was dependent on the system being tested. When a synthetic colloidal system (latex) was used, the order was either unimportant or slightly favored the addition of the polyelectrolyte first. In a natural colloidal system (sewage), however, there was a definite advantage in adding the cation first. Teot stated that it was not possible to prove or disprove any particular mechanism of flocculation with information presently available.

In his most recent published work, Birkner (7) has studied flocculation of colloidal clay suspensions with nonionic polymers. Again it was determined that combined use of cations and polymers provided superior performance to either coagulant alone. He further noted that there was some optimum polymer concentration resulting in minimum colloidal turbidity. On clay sols of 60 mg/l, the optimum coagulating polymer concentration was less than one mg/l.

Dixon, et al. (21) also noted this restabilizing capability of the polymers, but noted a limiting value of 10 mg/l polymer concentration when working with bacterial systems. Successful flocculation of bacterial systems of

concentrations ranging from 50 to 2700 mg/l was obtained with cationic polyelectrolytes.

LaMer and Smellie (66) have successfully flocculated negatively charged clay-type particles using a negatively charged polyelectrolyte. These investigators emphasized that they achieved better results with the polyelectrolyte alone than with a metallic cation. They pointed out that zeta potential as a measure of colloidal destabilization would not have been appropriate in this work.

Independent Variables Affecting Colloidal Stability

There are many variables affecting coagulation efficiency. The purpose of this section is to briefly discuss these factors. In accordance with an evaluation of the literature reviewed, they are described in an approximate order of importance.

Inorganic Ion

Clearly, the most important variable affecting colloidal stability is the inorganic ion. As emphasized in this review, for the negatively charged sol, a multivalent ion is most effective in destabilization. Thus, charge, type, and concentration of the ion all affect sol stability.

pH

The structure and charge of hydrolyzable metallic

cations is dependent on the pH. Therefore, sol stability will be affected by pH. Stumm and Morgan (98) recommended that pH be held constant in any systematic coagulation investigation. These investigators believe that the best procedure for coagulation testing makes use of an automatic titrator, using sodium hydroxide as the titrant. It was pointed out that addition of a hydrolyzable cation decreases the pH in its reaction with available alkalinity. Riddick (89) also supported this viewpoint, but suggested that potassium hydroxide will have less effect on sol stability than sodium hydroxide, therefore providing more constant conditions for varying cation concentrations.

There is some disagreement among investigators as to the best pH range for alum coagulation, but the differences are small. Black and Willems (16) recommended a range of pH from 5.2 to 6.7 as being satisfactory, but later Black and Chen (14) specified a pH of 5.6. Rebhun (82) found that a pH range of 5.6 to 6.2 produced optimum flocculation.

LaMer and Smellie (66) noted that the structure (coiled or threadlike) of polyelectrolytes was a function of pH as observed by the change in viscosity with pH. They remarked that it was not surprising that pH thus affects molecular bridging and the flocculation power of a polyelectrolyte.

Polymer

The charge, or lack of it, and concentration of the

polymer affect colloidal stability. More difficult to evaluate perhaps is the synergistic effect of the different possible combinations of metallic ion and polymer.

Time Lag Between Inorganic Ion and Polymer

There is obvious disagreement among previous investigators on the time variable. This is emphasized from two viewpoints. First, there is no general agreement on the order of addition of the polymer and the inorganic ion. Secondly, no specific time lag is normally stated in the literature. There is either a simple statement on the order of addition or an indefinite recommendation of "several minutes" or "some time after." (8, 23)

Salt Concentration of Colloid System

As noted by both van Olphen (108) and Riddick (89), the salt concentration of a colloidal system affects the double layer structure and potential. Any dilution with distilled water of a colloidal system in order to achieve some common initial solids concentration causes some error. This is because the salt concentration and the colloid-salt concentration ratio changes. The only proper dilution must be accomplished with the salt solution separated centrifugally from the colloid system.

Method of Mixing

Jar testing procedure is discussed in detail in the procedure section, but it would seem reasonable that the manner of contacting the colloid system with the flocculent will be of considerable importance in resulting destabilization. LaMer and Smellie (66) have stated that in order to obtain reproducible flocculation it was necessary to carry detailed systematic studies of the effects of order of mixing and the intensity and length of agitation.

Age of Hydrolyzed Metallic Ion

Riddick has noted repeatedly in his papers the importance of contacting fresh alum with the colloid system. Many investigators apparently prepare cation-water solutions which are used for indefinite periods. Floc formation in the absence of the colloid system to be treated is less efficient in the destabilization process.

Temperature

Temperature should be held constant to insure reproducibility of results.

Dependent Variables Used to Measure Coagulation

Many different variables have been used in the literature to characterize and evaluate coagulation processes. They are listed in the order of frequency encountered in the literature.

Turbidity

Early work by Smoluchowski led to the use of optical density as a function of time to measure the rate of flocculation. It was theorized that as flocculation proceeded the number of particles would decrease, less light would be scattered or absorbed, and the optical density would decrease. Dole (22) has pointed out that this basic concept has severe limitations. Floccs form in complex shapes and light scattering properties vary with floc size. Also, the flocculating system has a memory of previous or prior shear history. Thus, two systems with previous differing shear histories but with otherwise identical characteristics do not produce the same turbidity results even though given the same coagulation treatment. For these reasons, investigators accept the fact that it is unlikely that they will be able to reproduce one another's turbidity results. However, for a given test sequence turbidity data is easily obtainable and readily analyzed.

Turbidity is an optical property of a sample which causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. Two types of turbidity measurements are presently used and are termed nephelometry and absorptometry. In nephelometry the light scattered by colloidal particles at right angles to the incident light is measured. The advantages of this

type of turbidity measurement is that it is sensitive to very low colloidal concentrations and does not record color as turbidity. (42) The principal disadvantages are that the turbidity response curve is bell-shaped, giving the same turbidity reading for two different concentrations, and that data are affected by stray light. The reason for the former phenomenon is that at low colloidal concentrations, there is little light scattering due to the low number of colloid particles. At higher colloidal concentrations there is much greater light absorption, and, consequently, much less light available to be scattered. Less error is involved in using the rising portion of the bell-shaped curve.

Absorptometry is the measurement of light passed through colloidal sample in straight lines parallel to incident light. This type of measurement is identical to spectrophometric methods. The principal advantage of this type of turbidity reading is that there is no upper limit to colloid concentration as with nephelometry. The main disadvantages are that this measurement is insensitive to low turbidity and that color is measured as turbidity.

Zeta Potential

Despite sharp controversy as to its relevance to flocculation either zeta potential or electrophoretic mobility is consistently reported in the literature. Zeta potential is as close as a researcher can get to a direct measurement

of colloidal stability. All other measurements are indirect and therefore subject to other independent variables not related to coagulation. Unfortunately, electrophoresis equipment is expensive, and data are difficult to obtain.

Filtration and Refiltration Time

LaMer in many articles (64, 77, 94) has put forth the concept that coagulation is only successful when it has produced a precipitate which was easily settleable and filterable. He believed that cross linking and hydrolysis increased as filtration time decreased. However, during filtration the filter cake developed, thus changing cake porosity and thickness, both filtration time variables. Thus, the best method is to determine the time of refiltration of the filtrate through the already formed filter cake. It has been determined that the minimum refiltration time falls within the limits of the critical coagulation concentration and the critical stabilization concentration. Only when refiltration is too long is the less accurate filtration time recommended.

Settling Rates

The use of settling rates to measure coagulation has as its basis the same viewpoint that led to the development of refiltration time; namely, that coagulation is successful only when the precipitate is easily removed. Basically the

settling rate is determined by following the change of the height of the solid-liquid interface with time. (24) Graphical results show zones of settling, transition, and compression. (24)

Colloidal Titration

Kawamura, et al., (48 - 52) have described a method of determining null zeta potential using a titration technique. Oppositely charged colloids are used to neutralize the charge on the sample colloid. The reaction is reversible, allowing back titration. A major advantage of this method is elimination of expensive electrophoretic equipment.

Specific Resistivity

An involved graphical calculation is necessary to obtain this parameter describing the resistance of a filter cake to liquid flow. (2) This parameter has to some extent been replaced by filtration and refiltration time.

Solids Concentrations

Any number of different parameters describing reductions of solids concentrations in the clarified phase as compared to the original colloidal suspension are possible. Examples include total solids, volatile suspended solids, and selected chemical component concentrations.

Summary

Destabilizing chemical treatment of colloidal systems has been investigated with increasing thoroughness in recent years. This type of treatment appears applicable to the colloidal spent vegetable tannin waste, and indeed qualitative and limited quantitative work has been completed. There remain many unanswered problems concerning the critical, independent parameters affecting destabilization, the coagulant-tannin waste ratio, the best aluminum-polyelectrolyte system, and the best response to measure colloidal concentration. This investigation will attack these problems.

III. MATERIALS AND METHODS

The following sections contain information related to experimental materials, equipment, and methods.

Experimental Materials

The following paragraphs contain a list of the materials used in this investigation.

Aluminum Sulfate. $(Al_2(SO_4)_3 \cdot 18H_2O)$ crystal, Fisher certified reagent, (Fisher). Used as a primary coagulant.

Anionic Polyelectrolytes. Nalcolyte 672, 674, 675 coagulant polymer (Nalco). Used as a coagulant aid.

Buffer Salt, pH 4.01. (Potassium Biphthalate), dry, Fisher certified reagent, (Fisher). Used in preparing constant pH solution for standardizing pH meter.

Buffer Salt, pH 6.86. (Potassium Phosphate-Monobasic Disodium Phosphate), dry, Fisher certified reagent, (Fisher). Used in preparing constant pH solution for standardizing pH meter.

Buffer Salt, pH 10.4. (Tris (Hydroxymethyl) Amino Methane), dry, Fisher certified reagent, (Fisher). Used in preparing constant pH solution for standardizing pH meter.

Cationic Polyelectrolytes. Nalcolyte 603, 605, 607, 610, 632, 634 polymer (Nalco). Used as a coagulant aid.

Mercuric Sulfate. (HgSO_4), Fisher certified reagent, (Fisher). Used to eliminate interferences due to chlorides in the tannin waste in the Technicon Auto-Analyzer Chemical Oxygen Demand analysis.

Mercury, Metal. Distilled, technical grade, technical reagent, (Fisher). Used as working fluid in U-tube manometer.

Molybdophosphoric Acid. ($20\text{MoO}_3 \cdot 2\text{H}_3\text{PO}_4 \cdot 48\text{H}_2\text{O}$), powder, analytical grade, (Fisher). Used as a component in tannin reagent.

Nonionic Polymer. Nalcolyte 670 coagulant polymer, (Nalco). Used as a coagulant aid.

Phosphoric Acid. (H_3PO_4), 85%, liquid, (Fisher). Used to prepare tannin reagent.

Potassium Dichromate. ($\text{K}_2\text{Cr}_2\text{O}_7$), fine crystal, ACS certified reagent, (Fisher). Used as oxidant in the Technicon Auto-Analyzer C.O.D. analysis.

Potassium Hydroxide. (KOH), pellets, ACS certified reagent, (Fisher). Used to control pH in jar testing.

Silver Sulfate. (Ag_2SO_4), powder, ACS certified reagent, (Fisher). Used as catalyst in oxidation reaction in the Technicon Auto-Analyzer C.O.D. analysis.

Sodium Carbonate. (Na_2CO_3 and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), anhydrous and crystal, respectively, ACS certified reagents. Used in the tannin determination analysis.

Sodium Tungstate Dihydrate. ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), ACS certified reagent, (Fisher). Used to prepare tannin reagent.

Spent Vegetable Tannin Waste. Mixed protein, tannin composition, three per cent colloidal suspension-solution. Obtained from Leas-McVitty Corporation, Pearisburg, Va. Used as the colloidal waste material.

Sulfamic Acid. ($\text{NH}_2\text{SO}_3\text{H}$), Fisher certified reagent, (Fisher). Used to eliminate interference due to nitrates in the Technicon Auto-Analyzer C.O.D. analysis.

Sulfuric Acid. (H_2SO_4), Technical grade, 66 Baume, (Fisher). Used to digest waste tannin liquor in Technicon Auto-Analyzer C.O.D. analysis.

Experimental Equipment

The following paragraphs contain a list of the equipment used in this investigation.

Auto-Analyzer, Technicon. (Technicon). Used to determine chemical oxygen demand.

Analytical Balance. Accuracy 0.0001 grams, (Sartorius), used for determining weights accurately.

Barrel, Plastic. Thirty gallon (obtained from Chemical Engineering Dept., V.P.I.). Used to store waste in chemistry cold room.

Beakers. 50, 100, 250, 500 ml, Pyrex brand glass (Corning). Used in various laboratory tests.

Bottles. Plastic, 20 liter, (Nalge). Used to store tannin waste.

Burettes. 25, 50 ml, (Fisher). Used for preparing exact concentration and for titrations.

Condensers. Water, 24/40 ground glass joint, Pyrex brand glass, (Corning). Used to prepare tannin reagent.

Dessicators. (Fisher). Used to cool gravimetric samples under dry conditions following oven and furnace heating.

Evaporating Dishes. Coors Porcelain, capacity 90 ml, (Fisher). Used in gravimetric testing.

Flasks, Boiling. One liter, 24/40 ground glass joint, Pyrex brand glass, (Corning). Used to prepare tannin reagent.

Flasks, Volumetric. 100, 250, 500, 1000 ml, (Fisher). Used to prepare exact solution concentrations in standardization and tannin analysis.

Filtration Apparatus. 300 ml funnel with ground glass or teflon sealing surface, spring action holding clamp, ground glass or teflon coated base with neoprene stopper, and one liter filtering flask, (Millipore). Used in analytical tests to determine suspended solids, filtration times, and refiltration times.

Filter. Cellulose and fiber glass, 47 mm diameter, (Millipore). Used as filters in all filtration work.

Furnace, Electric Muffle. Six hundred degree centigrade temperature, (Precision). Used to volatilize all organic material to determine volatile and fixed solids concentrations.

Graduated Cylinders. 25 and 50 ml, Pyrex brand glass, (Corning). Used for liquid volume measurement and for filtration rate determinations.

Graduated Cylinders. One liter, Pyrex brand glass, (Corning). Used for subsidence testing.

Jars, Square. Double strength 1/8 inch plate glass, dimensions approximately 4 x 4 x 5 inches, volume about 1.25 liters, made by author. Used as container in jar testing.

Mixer, Electric. One horsepower, (Lightning). Used to mix stored waste to insure homogeneity of stored colloidal waste samples.

Mixer, Magnetic. Capable of heating, (Corning). Used to prepare solutions.

Nephelometer. (Hach). Used to determine turbidity by light scattering.

Oven, Drying. Adjustable to constant 102°C, (Precision). Used to vaporize water and volatile organics.

pH Meter. (Corning). Used to measure pH during jar testing.

Pipettes. 1, 2, 5, 10, 50 ml capacity, Pyrex brand, (Corning). Used to obtain samples during jar testing.

Pump, Vacuum. Welch Dist-0-Pump with motor, single stage, vented exhaust, vacuum limit 15 microns, (Welch). Used to control pressure drop during filtration.

Pipet Filler. (Fisher). Used to fill pipettes.

Shaker. Laboratory bottle shaker, 115 v, 60 cycles, (Eberbach). Used to prepare solutions of polyelectrolytes.

Spectrophotometer. Spec-20, (Bausch and Lomb). Used in tannin and turbidity tests.

Spectrophotometer. Model B-4, (Beckman). Used in initial tannin analysis experimentation.

Steam Bath. Eight variable sized openings, stainless steel, electrically heated, 220 volts, 2000 watts, (Fisher). Used to evaporate most of water before placing evaporating dishes in drying oven.

Stopwatch. Graduated in 1/5 second, jeweled movement, non-magnetic, (Fisher). Used to measure timed operations and analyses.

Stirrer, Multiple. Water analysis, 6-unit, complete with stirrer floc illuminator and base, (Phipps and Bird). Used to produce low velocity gradients in jar testing.

Stirrer, Variable Speed. One-tenth horsepower, 110 V A.C., (Fisher). Used to obtain various velocity gradients during rapid mixing period of jar testing.

Timer-Timeswitch. Eight inch dial, (Fisher). Used to measure operations where less accuracy was required.

Weighing Dishes. Aluminum, weight about 1.5 grams, 60 mm diameter, (Fisher). Used for weighing on analytical balance.

Experimental Methods

The overall purpose of this investigation was to develop a chemical method for treating spent vegetable tannin liquor. To accomplish this objective the effects of selected independent variables on the stability of the colloidal waste material were quantitatively analyzed. A discussion of the major experiments involved in the research is given in this section.

Experiment One: Characterization of Waste

Initial laboratory work centered around characterization and measurement of variation of the spent vegetable tannin liquor. Using total solids, total volatile solids, and total fixed solids as the basic responses, fresh batches of tannin waste were obtained at the same time daily for a ten day period and then analyzed. Duplicate or triplicate samples, depending on laboratory convenience, were taken and the analytical work listed above was performed starting at the same time daily. All solids tests were run in accordance with Standard Methods (96) with minor modifications.

Experiment Two: Deterioration of Tannin Waste and Storing Procedures

Selected batches of waste were tested beyond the first day in order to determine the degree of deterioration as the waste aged. The same test responses used above were performed daily for a seven day period. The first test series was made using room temperature storage facilities. A second series of tests was performed while storing the waste at twenty degrees centigrade. A third and final series of tests was completed while using the cold room storage facilities in the chemistry building, in which the temperature is maintained near zero degrees centigrade.

Also, mixing equipment and procedures were tested to insure waste homogeneity when sampling stored tannin waste. The final method chosen resulted in excess of one hundred gallons of tannin waste being stored in the cold room in the Davidson Hall, V.P.I. A lighting mixer stirred the wastes in the 30 gallon tank for thirty minutes prior to siphoning a two day supply of twenty liters. After removal of the 20 liters from the tank, this quantity was immediately replaced from smaller containers located in the cold room. In this manner tannin waste removed bi-daily was assured to remain uniform.

Selection of Independent Variables to be Tested

As seen in the literature review section on variables affecting colloidal stability, there were a large number of factors which had a possible effect on destabilizing colloids. From Edwards' (27) prior research, aluminum was chosen as the metallic cation to be used as a primary coagulant. The test variable was alum concentration.

Current research had indicated the suitability of using polyelectrolytes in conjunction with the aluminum. From literature surveyed prior to the beginning of experimental work, it appeared that cationic polyelectrolytes would be most suitable for destabilizing a negatively charged colloidal system. It was tentatively decided to test ten different polyelectrolytes. And, in order to consider all charge types, six cationic, three anionic, and one nonionic polyelectrolytes were selected. Two test variables were, therefore, introduced, charge type (qualitative) and polyelectrolyte concentration (quantitative).

The pH of a solution affects the efficiency of a coagulation process. However, because of the necessity to limit the number of independent variables and because pH and effective aluminum ion concentration are interrelated, it was decided to hold pH constant at 6.0 during first stage polyelectrolyte testing. In the final, expanded testing a pH range from 5.0 to 7.0 was tested, covering the most effective pH range for aluminum.

The literature showed that researchers were least confident in their procedure in describing the best time lag between aluminum and polyelectrolyte addition. This was the final independent variable chosen, and the remaining possible variables were either maintained constant (e.g., jar test procedure, concentration of waste) or assumed constant (e.g., quality of waste, temperature).

Experimental Design

It was decided to test each of the polyelectrolyte types separately, thus necessitating ten separate tests involving the three remaining independent variables, aluminum concentration, polyelectrolyte concentration, and time lag. It was felt that a minimum of five levels across the range of each variable was desirable; thus, a total of five cubed, or 125, tests would be required if every possible variable combination were performed. As each test had from two to ten separate response variables (dependent variables) the number of tests involved would require reduction of the number of polyelectrolytes tested. (If each of the ten polyelectrolytes had ten responses, the total number of tests would have been 12,500, an impossibly high number).

For these reasons, Dr. R. H. Myers, Department of Statistics, suggested an experimental design which would reduce the number of tests from 125 to 20. The data obtained from these tests could then be used to produce a

regression equation using the BMD regression program at the V.P.I. computing center. Graphical interpretation would then be possible.

The value range of the variables was more difficult to select. For aluminum the range of zero to 3000 mg/l was chosen initially, but preliminary testing indicated that a range of zero to 6000 mg/l was preferable, allowing maximum colloid destabilization to be obtained. The maximum recommended concentration of some polyelectrolytes was fifty mg/l. So that the time lag variable would always have a real value the minimum polyelectrolyte concentration chosen was 2 mg/l, resulting in a range of two to 50 mg/l. The range for the time lag between the aluminum and the polyelectrolyte was minus 0.811 to plus 3.189 minutes. This range allowed the polyelectrolyte to be added before, at the same time, and following the aluminum addition. After the range was chosen for each variable, the levels were determined for the particular experimental design, and were assigned code values. This coding and the form of the resulting regression equation is illustrated in Table II. Table III gives the experimental design of the 20 component sub-tests for the testing of a given polyelectrolyte.

At the time experimental work was begun and completed there was no reported use of regression equation analysis to predict coagulant dosages. Recently, however, Otts and

TABLE II. REGRESSION EQUATION WITH INDEPENDENT VARIABLES AND THEIR CODE-VALUE RANGE

Regression Equation:

$$Y = B_0 + B_1X_1 + B_{11}X_1^2 + B_2X_2 + B_{22}X_2^2 + B_3X_3 + B_{33}X_3^2 + B_{12}X_1X_2 + B_{13}X_{13} + B_{23}X_2X_3$$

Coding of Independent Variables:

Code Value, Dimensionless	+1.682	+1	0	-1	-1.682
Aluminum Conc., X ₁ , mg/l	6000	4784	3000	1216	0
Polyelectrolyte Conc., X ₂ , mg/l	50	40.3	26	11.7	2
Time Polyelectrolyte Added After Alum., minutes	3.2	2.4	1.2	0	-0.81

TABLE III. EXPERIMENTAL DESIGN TEST SEQUENCE USING
CODED VARIABLE VALUES

<u>Subtest No.</u>	<u>Aluminum, X_1</u>	<u>Polyelectrolyte, X_2</u>	<u>Time, X_3</u>
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	+1
4	-1	-1	+1
5	+1	+1	-1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1
9	-1.682	0	0
10	+1.682	0	0
11	0	-1.682	0
12	0	+1.682	0
13	0	0	-1.682
14	0	0	+1.682
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

Chicca (78) have used regression analysis to predict the alum dosage in treatment for a potable water supply. The work was successful in that a dependent response variable, turbidity, was related to alum concentration in a computer generated regression equation.

Experiment Three: Gravimetric Mass Balance

Because of the author's particular technical background it was believed that a gravimetric measurement, though tedious, might prove an accurate method of determining the efficiency of the various coagulant systems. For this reason a mass balance was made on the treated waste by measuring total, total volatile, and total fixed solids of mixed, clarified, and concentrated portions of waste following a typical coagulant treatment. In addition the same data was obtained for the suspended solids test sequence. From this experiment the reliability of gravimetric methods in measuring mass balances before and after subsidence was assessed, and the particular gravimetric method which showed the greater per cent change following coagulant treatment was determined.

Experiment Four: Selection and Comparison of Dependent Variables

Initial testing was undertaken to determine the most accurate response variable. Ten tests were performed on the

tannin waste using the same independent variable values and Nalcolyte polyelectrolyte 605 as the coagulant aid. The following dependent responses were measured: light scattering turbidity, light transmission turbidity, COD, total volatile solids, volatile suspended solids, filtration time, refiltration time, substance volume and rate, and tannin concentration. It had been hoped to measure zeta potential as a response variable, but the waste system and obsolete electrophoretic mobility equipment proved cantankerous. The responses were thus limited to those previously listed. The data obtained from these tests were analyzed according to range and standard deviation.

Experiment Five: Selection of Procedures for Determining Dependent Variables

In the following sections the specific laboratory procedures used to obtain the different response variables are described or referenced.

Chemical Oxygen Demand. C.O.D. determinations were performed using the Technicon Auto-Analyzer. Specific operation directions for this equipment are listed in the operating manual accompanying the Auto-Analyzer. Generally, the chemical reagents oxidize and digest the oxidizable material supplied by the waste. During the oxidation, depletion of the oxidizing agent reduces the amount of color of the solution.

This change in color is measured by a colorimeter. A standard curve was obtained using glucose concentrations of known C.O.D. From this standard curve the C.O.D. of the waste was determined. A flow diagram of the Auto-Analyzer is shown in Figure 7. (30)

Filtration Time. Filtration time is the elapsed time between the pouring of the sample onto a filter and the appearance of the first dry spot on the filter cake in the suspended solids test. The procedure for this test is given in more detail in the discussion of the suspended solids test. The basis for the filtration time response is given by LaMer, et al. (67, 94)

Light Scattering Turbidity. This turbidity response was made on a Hach nephelometer. A plastic cylinder was supplied to calibrate the instrument in Jackson Turbidity Units (J.T.U.) following a 15 minute warm up period. The undiluted samples were poured into empty, unscarred glass cylinders to at least a minimum depth and placed in the instrument. The glass cylinders were then covered to prevent stray light interference, and the J.T.U. reading was made.

Light Transmission Turbidity. The Bausch and Lomb Spectronic Twenty colorimeter was used to determine light transmission turbidity. Specific operating instructions for this instrument can be found in the operating manual. The general

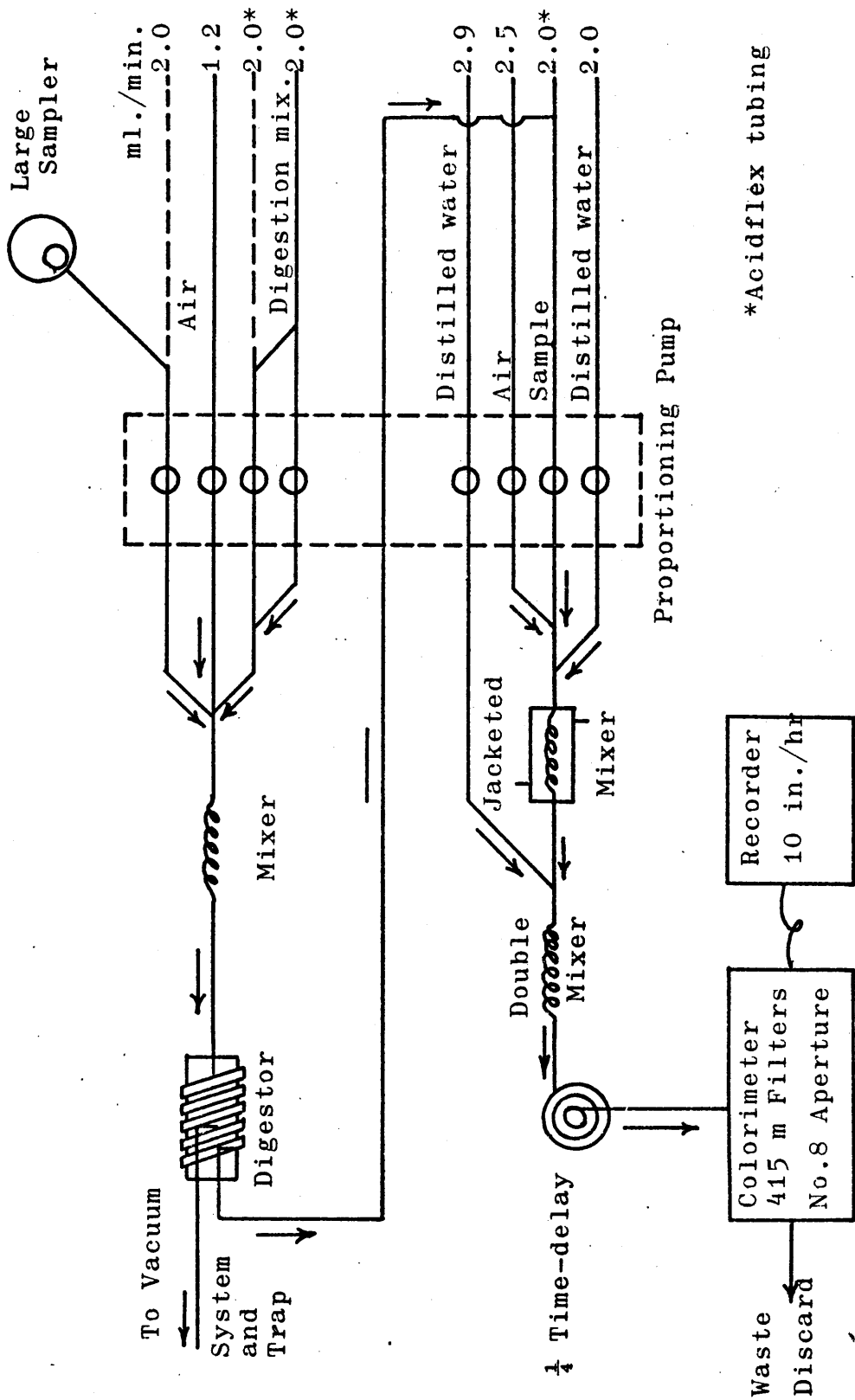


Figure 7. Flow Diagram of Auto-Analyzer for Chemical Oxygen Demand Determination.

procedure was as follows: 1) one milliliter of the clarified portion of the treated waste was diluted with distilled water to 10 milliliters, 2) the sample's per cent light transmission was determined at a wave length of 700 millimicrons. It should be noted that this wave length was not the dominant wave length as described in Standard Methods for the Examination of Water and Wastewater. (96) Another test performed on the Spectronic Twenty was tannin determination, and this test required operation at 700 millimicrons. Operation of the instrument above 675 millimicrons requires a different light photometer than below this wave length. For accuracy and ease of operation it was decided to utilize the wave length of the tannin determination, the more accurate of the two tests. Dilution of the tannin waste was necessary to obtain an initial per cent light transmission of other than zero.

Refiltration Time. The experimental apparatus for the volatile suspended solids test can be modified so that the filtrate can be collected. The time that 10 milliliters of this filtrate takes to refilter through the already formed filter cake is termed refiltration time. LaMer, et al. (67), (94) have described the theory and modified procedures for refiltration time.

Subsidence Volume and Rate. Following the completion of the mixing and stirring sequence in the jar test procedure, the entire mixture was poured into one liter graduated cylinders. The level of the interface between the clarified and concentrated phase was measured at a regular, staggered time sequence for the next 18 hours. The level of this interface at 18 hours was termed the subsidence volume. The rate of change of the interface with time over the initial constant period was termed the subsidence rate. These procedures, in amended form, are described by Eckenfelder (24), and also in Standard Methods (96) under the title of settleable solids.

Tannin Concentration. Tannin concentrations were determined in accordance with the procedure described in Standard Methods (96). The instrument used was the Bausch and Lomb Spectronic Twenty. The method described required very weak solutions, necessitating the dilution of both treated and untreated waste prior to analysis. Initial work in this area was two fold. First different concentrations of pure tannic acid were prepared in an attempt to establish a Beer's Law type relationship. As the author consistently failed to weaken the solutions to a sufficiently dilute condition, this undertaking was overly time consuming. Secondly, testing was done on raw tannin waste to determine the necessary extent of dilution. This level was found to be 1 to 1000.

The dilution was accomplished in two stages. One ml of waste was diluted to 10 ml in a 10 ml graduated cylinder. After inversion mixing, one ml was withdrawn with a one ml pipette and diluted to 100 ml in a volumetric flask. Following the determination of the proper dilution range, tests were made to insure that no interference by non-tannins was observed. This procedure was accomplished by preparing various dilutions in the proper range, doing tannin determinations, and then graphically evaluating Beer's Law relevance.

Berks, et al. (6) have described the critical sections of the tannin determination procedure. It was stated that the amount of tannin reagent was not critical to the accuracy of the analysis, but that both the amount of sodium carbonate and the time interval between addition of sodium carbonate and making the spectrophometric transmission reading were very important.

The final pre-testing related to tannin determination was standardization of the absorption cells using cobalt chloride solutions to measure correction factors for the individual cells. This procedure is described in the spectrophotometer manual.

Total Volatile Solids. Total solids, total volatile solids and total fixed solids are all determined in the same analytical test. Following settling of the treated waste

for 18 hours a 10 ml sample of the clarified portion was placed in a weighed, dry 90 ml evaporating dish. The evaporating dishes were weighed on an analytical balance, evaporated on a steam bath for 90 minutes, and placed in a 103°C oven for a minimum of three hours and usually overnight. Following removal from the oven, cooling, and reweighing the evaporating dish, it was placed in a muffle furnace at 600°C. The minimum of residence time in the furnace was three hours. Cooling and weighing produced data allowing the calculation of total volatile solids. This procedure has been modified for a specific application from the more general directions given in Standard Methods (96).

Volatile Suspended Solids. Suspended solids tests were performed using Millipore filtration equipment and fiberglass filters rather than the Gooch crucibles and asbestos filters recommended by Standard Methods (96). The total suspended solids tests performed using Millipore equipment are described generally in their methods manual. Specifically, a 25 ml sample was filtered under a constant vacuum of 60 cm of mercury through a 47 mm diameter, 35 micron pore size, fiberglass, millipore filter. After completion of filtration, the filter and filter cake were placed in aluminum weighing dishes. Then, using the same technique as was employed in total volatile solids procedure,

the aluminum dishes were 1) weighed on an analytical balance, 2) placed in a 103°C oven for a minimum of three hours, 3) cooled in a dessicator and reweighed, 4) placed in the muffle furnace for a minimum of three hours and 5) cooled in a dessicator and weighed on the analytical balance. From these data the total suspended solids, volatile suspended solids, and the fixed suspended solids were determined.

Jar Testing Procedure

There is no standard jar test procedure. Sawyer and McCarty (92), Birkner and Edzwald (7, 8), Black and Chen (14), Black et al. (13), Eckenfelder (25), Edwards (27), and Hannah et al. (44) all describe coagulation jar testing procedures, and while the methods are similar, they are not the same. The procedures have been modified to suit the individual investigator's system, equipment, requirements (such as constant pH), or prejudice (square versus round jars). The author's procedure is a modification of the previously mentioned investigators' methods and is identical to none of them.

Once the author had familiarized himself with the necessary laboratory techniques, a maximum of 10 jar tests were started on a given day. A particular run extended in its analytical phase over a three day period. Two separate apparatus arrangements were used for the rapid and slow mixing phases of jar testing procedure. The liquid waste

containers were square jars with a total volume in excess of 1200 ml. The rapid-mix apparatus is shown in Figure 8. The jars were filled with one liter of waste and the stirring rod of the variable speed stirrer, the pH electrodes, and the graduated cylinder for pH control were placed in correct proximity as shown. The initial stirring rate was set at 100 RPM and the pH was adjusted to the desired level (normally 6.0) using concentrated potassium hydroxide. The correct dosage of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was added in the fine crystal solid state and the resulting pH drop was corrected by rapid addition of KOH. The concentration of the KOH was such that rarely was more than 10 ml of the solution necessary. This volume variation was neglected in calculating concentrations.

Rapid mixing was continued for exactly one minute and the speed was then reduced to the minimum possible with the stirrer, about 35 RPM, for the time lag required by the experimental design. At this time the stirrer speed was increased to 100 RPM again and the polyelectrolyte concurrently added. The concentration of the solution was prepared so that a 100 to 1 dilution would always produce the concentration desired in the waste. The polyelectrolyte was discharged from a 10 ml pipette at a constant flow rate using a pipette filler for a period of 30 seconds. Rapid mixing was continued for an additional 30 seconds.

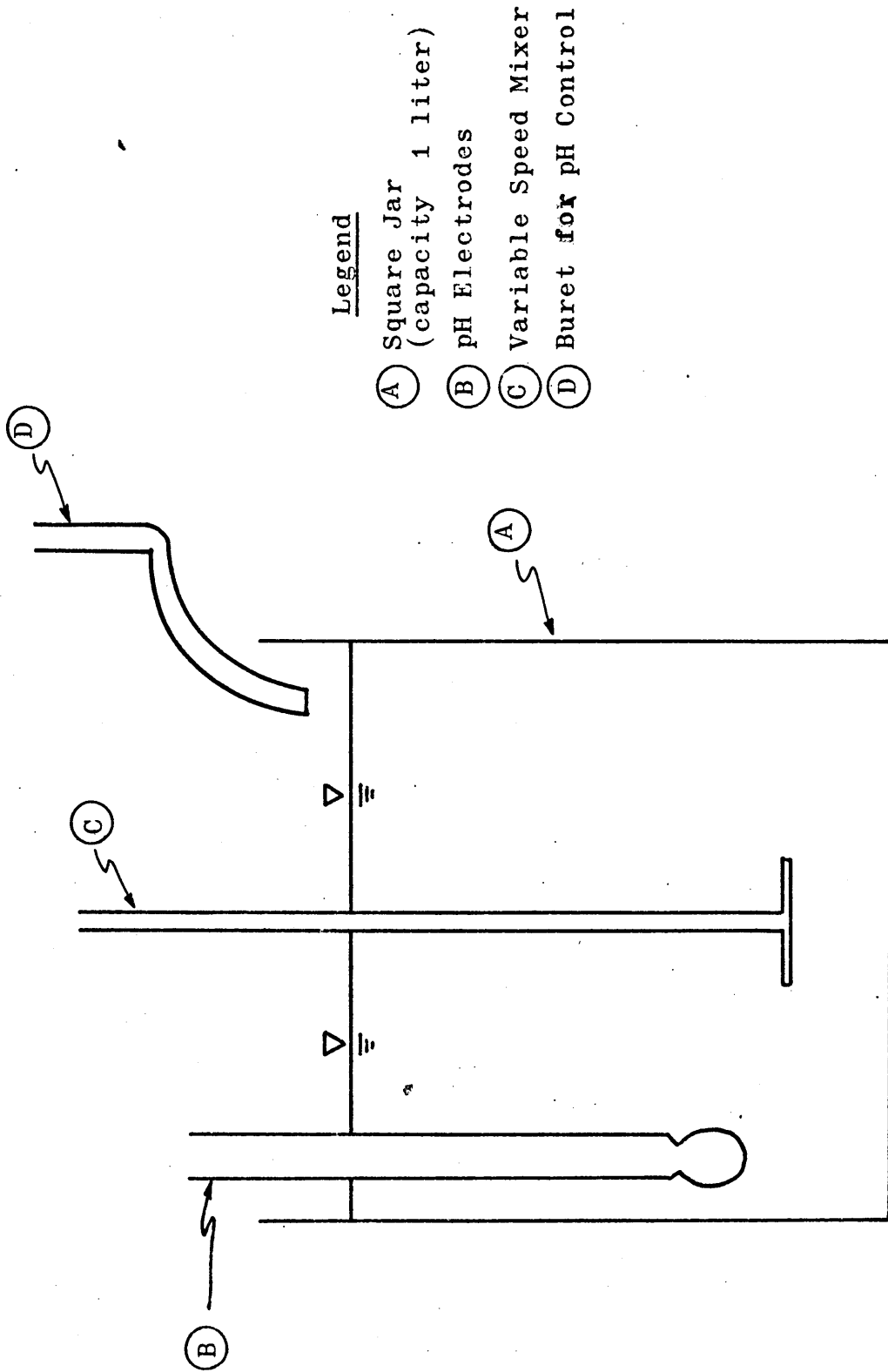


Figure 8. Schematic Diagram of Jar Test Apparatus.

The square jar was then removed from the rapid mix stirrer and placed on the Phipps and Bird multiple stirrer. Here stirring was continued at 30 RPM for a period of 20 minutes. After removal of the first jar to the multiple stirrer a second test was begun, and the procedure was repeated. The timing on each of the 10 separate jar tests was recorded individually. After the stirring periods were completed the contents of the square jars were poured into one liter graduated cylinders and allowed to settle for a period of 18 hours. This period was chosen because of the slow rate of subsidence of the heavy phase-clarified phase interface and because of the convenience of this period in beginning the second day's analytical work. All analytical work was performed on the clarified section with samples being taken $1\frac{1}{2}$ inches beneath the surface.

Some applied chemists use physical appearance as a measure of coagulation efficiency; however, the author did not use this index. Nonetheless, any unusual clarity obtained during or at the completion of mixing was noted and special attention was paid to the results of these tests.

The pH meter was used to measure and control the pH during jar testing. It was standardized daily with buffer solutions of approximately pH 4, 7, and 10. Considerable fouling of the electrodes was observed and this problem was remedied with cleansing solutions of concentrated HCl.

Anionic polyelectrolytes, in particular, were difficult to prepare in the high concentrations necessary for particular subtest requirements. This was overcome finally by use of volumetric flasks (3/4 filled) and alternate use of thermomix (heating and stirring) equipment and the laboratory shaker (violent mixing). Some preparations required 24 hours.

Experiment Six: Polyelectrolyte Testing and Evaluation

Using the jar test and the experimental design described in the previous sections regression equations were obtained for each of the 10 polyelectrolyte system. The coefficients of the polyelectrolyte variable, B_2 and B_{22} (Table II) were compared and the polyelectrolyte showing the highest removal value was chosen for further testing in connection with a new variable, pH. In addition, the accuracy of the various dependent variables was evaluated by comparing these variables with the reduction of total volatile solids using results compiled in testing the aluminum-polyelectrolyte systems. Also, the effect on removal efficiency of each of the three independent variables for each alum-polyelectrolyte system was evaluated and depicted graphically.

Experiment Seven: Expanded Testing Procedure for pH Evaluation

Following selection of the best polyelectrolyte a new

experimental design was developed to evaluate an additional independent variable, pH. This design and coding is shown in Tables IV and V. A regression equation was developed from the data acquired using this experimental design, and graphical evaluation of this equation in a manner similar to that described previously allowed interpretation of the effect of the individual independent variables.

It may be noted that the time lag variable range was doubled from the previous experimental design. This increase in range was based on results of initial coagulation testing with the 10 polyelectrolytes and will be discussed fully in the data and results section.

TABLE IV. EXPANDED REGRESSION EQUATION WITH INDEPENDENT VARIABLES
AND THEIR CODE VALUE RANGE

Regression Equation:

$$\begin{aligned}
 Y = & B_0 + B_1X_1 + B_{11}X_1^2 + B_2X_2 + B_{22}X_2^2 + B_3X_3 + B_{33}X_3^2 + B_4X_4 \\
 & + B_{44}X_4^2 + B_{12}X_1X_2 + B_{13}X_1X_3 + B_{14}X_1X_4 + B_{23}X_2X_3 + B_{24}X_2X_4 \\
 & + B_{34}X_3X_4
 \end{aligned}$$

Coding of Independent Variables:

	+2	+1	0	-1	-2
Aluminum Conc., X ₁ , mg/l	6010	4510	3010	1510	10
Polyelectrolyte Conc., X ₂ , mg/l	50	38	26	14	2
Time Lag between Aluminum and Polyelectrolyte, X ₃ , seconds	6.0	4.5	3.0	1.5	0
pH, X ₄ , Dimensionless	7.0	6.5	6.0	5.5	5.0

TABLE V. EXPANDED EXPERIMENTAL DESIGN FOR pH EVALUATION

<u>Subtest No.</u>	<u>Aluminum, X_1</u>	<u>Poly., X_2</u>	<u>Time Lag, X_3</u>	<u>pH, X_4</u>
1	-1	-1	-1	-1
1A	-1	-1	-1	-1
2	+1	-1	-1	-1
2A	+1	-1	-1	-1
3	-1	+1	-1	-1
3A	-1	+1	-1	-1
4	-1	-1	+1	-1
4A	-1	-1	+1	-1
5	-1	-1	-1	+1
5A	-1	-1	-1	+1
6	+1	+1	+1	-1
6A	+1	+1	+1	-1
7	+1	+1	-1	+1
7A	+1	+1	-1	+1
8	+1	-1	+1	+1
8A	+1	-1	+1	+1
9	-1	+1	+1	+1
9A	-1	+1	+1	+1
10	+1	+1	+1	+1
10A	+1	+1	+1	+1
11	+1	+1	-1	-1
11A	+1	+1	-1	-1
12	+1	-1	+1	-1
12A	+1	-1	+1	-1
13	-1	-1	+1	+1
13A	-1	-1	+1	+1
14	-1	+1	+1	-1
14A	-1	+1	+1	-1
15	+1	-1	-1	+1
15A	+1	-1	-1	+1
16	-1	+1	-1	+1
16A	-1	+1	-1	+1
17	-2	0	0	0
18	+2	0	0	0
19	0	-2	0	0
20	0	+2	0	0
21	0	0	-2	0
22	0	0	+2	0
23	0	0	0	-2
24	0	0	0	+2
25 - 30	0	0	0	0

IV. EXPERIMENTAL DATA AND RESULTS

The experimental data and results for this investigation are presented in the succeeding sections.

Experiment One - Characterization of Waste

The data and results for the characterization of the tannin waste are shown in Table VI. The results of this experiment showed an average total solids concentration of 30,151 mg/l with an average total volatile solids content of 20,815 mg/l. The range experienced for the total solids concentration was, excluding data on 6-6-69, from 28,320 to 32,360, a variation of 4,040 mg/l or about 13 per cent. Since the experimental design required constant tannin waste concentration, it was concluded that this variation was too large and could not be accepted. Subsequent testing showed these variation values were higher than normally obtained in a sequential three month period. While total volatile solids remained relatively constant at 21,000 mg/l, total solids dropped to about 28,000 mg/l.

It was noted that the very high concentrations obtained on 6-6-69 had a distinctly different color from the normal milky brown waste color. Such waste batches were thereafter avoided.

TABLE VI. RESULTS OF EXPERIMENT ONE: CHARACTERIZATION OF THE TANNIN WASTE

<u>Date Sampled</u> month-day-year	<u>Total Solids</u> mg/l	<u>Volatile Solids</u> mg/l	<u>Fixed Solids</u> mg/l	<u>Appearance</u> color
5-28-69	31,853	22,769	9,084	Milky brown
5-30-69	32,005	22,570	9,435	Milky brown
6- 2-69	32,360	22,970	9,390	Milky brown
6- 3-69	29,730	20,380	9,350	Milky brown
6- 4-69	29,710	20,220	9,490	Milky brown
6- 5-69	30,060	20,080	9,980	Milky brown
6- 6-69	38,880	28,030	10,850	Clear brown
6- 7-69	28,680	21,030	7,650	Milky brown
6- 8-69	28,645	20,530	8,115	Milky brown
6-10-69	28,320	18,790	9,530	Milky brown
Average	31,024	21,737	9,287	
Avg. excluding 6- 6-69	30,151	21,038	9,113	
7-1 to 10-30	28,000	21,000	7,000	Milky brown

Experiment Two - Deterioration of Tannin Waste
During Storage

The purpose of this experiment was to determine the rate of deterioration of the tannin waste during storage. Three batches of waste were tested over a one week period at room temperature, 20°C, and approximately zero °C, using solids concentration as the response. The results are shown in Table VII. In Figure 9, the change in volatile solids with time is shown for each of the three temperatures. While the variation was not identical at 20°C and room temperature, there is consistency in that the volatile solids decreased significantly with a tannin waste age of either two or three days. Further, the appearance of the waste underwent a striking change at roughly the same time. Floating white curds began to appear in the waste containers and eventually covered the surface of the waste. On the other hand, storage at near 0°C prevented significant change as shown in Figure 9. The variation at this temperature is believed to be due to error in the analytical technique alone.

The results obtained in Experiments One and Two required that a single large batch of vegetable tannin waste be collected at one time, stored at about 0°C, and used for the major polyelectrolyte experimental sequence. This procedure was followed for the larger portion of the tests as an excess of 100 gallons of waste was stored in the chemistry department cold room.

TABLE VII. RESULTS OF EXPERIMENT TWO - DETERIORATION OF TANNIN WASTE

Age of Tannin Waste Day	Room Temperature Test			20° Test			Near 0° Test		
	volatile solids mg/l	fixed solids mg/l	total solids mg/l	volatile solids mg/l	fixed solids mg/l	total solids mg/l	volatile solids mg/l	fixed solids mg/l	total solids mg/l
0	22,769	9,084	31,853	22,970	9,390	32,360	18,790	9,550	28,320
1	23,195	9,215	32,410	22,858	9,452	32,310	18,943	9,569	28,512
2	23,657	8,661	32,318	22,513	9,457	31,970	19,042	9,550	28,592
3	22,994	9,162	32,156	22,414	9,601	32,005	18,854	9,562	28,416
4	22,746	9,050	31,796	21,511	9,520	31,031	18,872	9,978	28,850
5	22,496	8,874	31,370	20,873	9,471	30,344	18,927	9,430	28,357
6	21,845	8,740	30,585	20,402	9,500	29,902	19,232	9,487	28,719

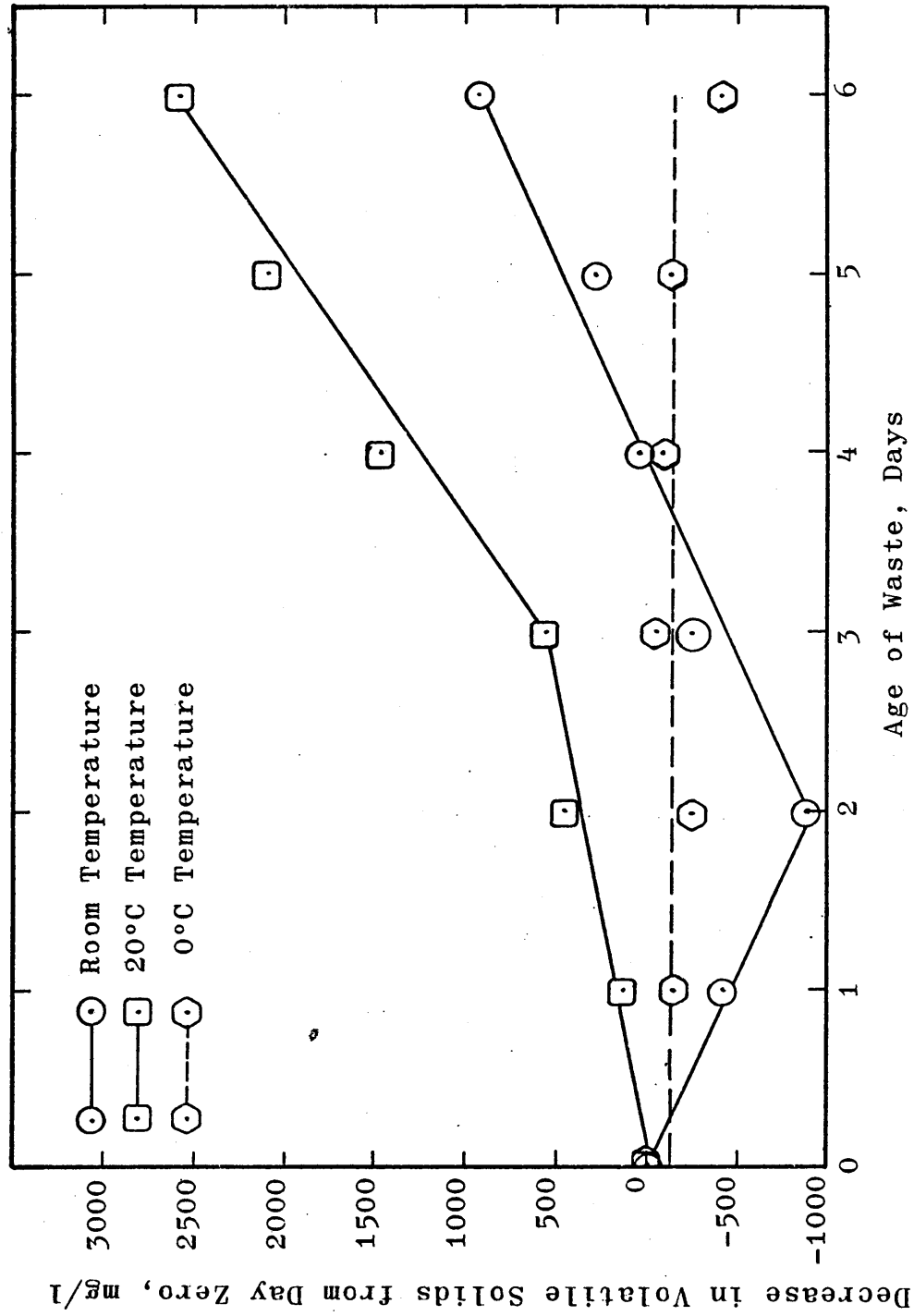


Figure 9. Deterioration of Waste With Time.

The remaining testing in this experiment was concerned with the determination of a sampling procedure from the stored waste that would insure sample uniformity. The final procedure adopted is described in the previous chapter.

Experiment Three - Gravimetric Mass Balance

The purpose of this experiment was to determine the gravimetric index most responsive to change following coagulant treatment. From the results in Table VIII it was concluded that for the solids analysis either the reduction in volatile solids in the clarified portion or the increase in volatile solids in the concentrated portion would be responsive indices to coagulant treatment. Because of the fact that the concentrated portion concentration is a function of time while the clarified portion concentration remains constant, the analysis involving the concentrated portion was rejected. The suspended solids analysis showed much greater percentage changes but were inherently less accurate due to the smaller weights considered and the more involved experimental procedure. Once again the superior index was the reduction of the volatile suspended solids. Fixed solids were not considered as this index is a measure of quantity of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ added.

There were several interesting relationships noted in the results in Table VIII. In terms of a mass balance it

TABLE VIII. RESULTS OF EXPERIMENT THREE - GRAVIMETRIC MASS BALANCE

	Untreated Waste Conc.	% Chg.	Mixed Treated Waste Conc.	% Chg.	Clarified Portion Conc.	% Chg.	Concentrated Portion Conc.	% Chg.
Volatile Solids, mg/l	19,480	-	19,470	0	15,920	-18.3	23,005	+18.1
Fixed Solids, mg/l	10,020	-	12,740	+26.7	12,420	+24.0	12,785	+27.6
Total Solids, mg/l	29,500	-	32,210	+9.1	28,340	-3.9	35,790	+21.3
Volatile Sus. Solids, mg/l	5,190	-	7,333	+41.3	2,790	-46.2	10,220	+96.9
Fixed Sus. Solids, mg/l	420	-	1,655	+294.0	450	+7.1	1,750	+316.7
Total Sus. Solids, mg/l	5,610	-	8,985	+60.2	2,340	+5.8	11,970	+113.4

was seen that the average of the total solids in the clarified and concentrated portions equaled the total solids of the mixed state, 32,065 versus 32,210 mg/l, respectively. This correlation was excellent and expected, as the samples were taken when the concentrated phase had settled to exactly half of the initial volume. No such relationship was found in the suspended solids calculations, indicating the decreased reliability.

The increase and constancy of fixed solids in all samples was significant. The increase was clearly due to the addition of the $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. Further, the constancy of the various fixed solids indicated that this salt was in part either suspended or dissolved and had not precipitated with the destabilized colloidal substances. However, this material was not largely suspended as the fixed suspended solids data indicated. There was essentially no increase in fixed suspended solids from the untreated tannin waste to the clarified portion of the treated waste. This result meant that substantially all of the hydrolyzed metallic ion in the clarified portion was passing through the filter cake and was therefore dissolved in solution.

Related Gravimetric Testing

In the gravimetric analysis development there were a number of related, relatively less important tests that were performed to assure the accuracy of the overall

procedure. On this basis the following decisions were made. 1) Fiber glass Millipore filters were adopted for suspended solids testing because cellulose filters tended to burst into flame in the muffle furnace, scattering filter cake and giving poor results. 2) The sample size of 10 ml for the total solids testing was chosen since the 50 ml size recommended by Standard Methods did not take into consideration the high waste concentration and excessively long drying time. 3) Minimum drying times for solids testing were determined for the steam bath, oven, furnace, and dessicator. 4) Twenty ml suspended solids samples were found to give reasonable filtration times at a vacuum of 60 cm of Hg.

Experiment Four: Accuracy of Dependent Variables

The purpose of this test was to determine which of the dependent variables could be determined with the greatest accuracy. The results are shown in Table IX.

In comparing the coefficients of variation, σ/\bar{x} , of each of the dependent variables it was evident that the most accurate responses were reduction in volatile solids and the spectrophometric tannin concentration. Because the spectrophotometer was used by several other students regularly and because the photometric tube was also changed periodically, it was decided to use the per cent reduction of volatile solids as the primary response. The other

TABLE IX. RESULTS OF EXPERIMENT FOUR - ACCURACY OF DEPENDENT VARIABLE

Test No.	Red. Vol. Solids, %	Red. Vol. Sus. Vol., %	Lt. Scat Turb, JTU	Lt. Trans. Turb, %	Red. COD, %	Filtration Time, min.	Subsid. Vol. %	% Trans. Tannin
1	42.00	49.59	355	60.0	40.0	13.4	48.0	63.0
2	42.39	51.62	325	59.0	44.7	12.5	49.0	63.5
3	42.24	52.17	365	50.0	43.8	14.1	48.5	62.8
4	43.41	51.63	350	55.5	42.4	13.4	45.0	62.4
5	42.97	49.50	343	63.5	43.1	14.8	45.0	63.0
6	41.12	43.90	340	57.0	42.6	15.5	45.0	62.5
7	42.73	48.72	355	54.5	41.8	12.5	60.0	62.7
8	42.24	44.29	345	64.0	44.2	11.9	42.0	64.9
9	41.97	49.21	353	55.0	44.1	13.7	41.0	62.9
10	42.84	52.32	360	58.5	42.5	14.2	48.0	63.6
Avg. \bar{x}	42.39	49.29	349	57.7	42.9	13.6	46.2	62.8
Std. Dev. σ	0.015	.062	.033	.074	.031	.111	.116	.013
Coef. Var. σ/\bar{x}	.638	3.03	11.58	4.26	1.33	1.51	5.36	.803
Acc. Ranking	1-2	5	3-4	6	3-4	7	8	1-2

dependent variables were also tested, but only to compare their accuracy and linearity with the primary response. All regression equation development and, thus, independent parameter evaluation was based on the primary response.

Experiment Five - Calibration of Dependent Response Procedures

Calibrations developed for use in the dependent response procedures are described in the following paragraphs.

Experiment 5-1: Chemical Oxygen Demand

Chemical oxygen demand analyses were performed on the Technicon Auto-Analyzer. The use of this equipment required a calibration curve of light transmittance versus the known chemical oxygen demand of prepared glucose solutions. The results of this test are shown in Figure 10. Use of this curve allowed direct COD measurement of all tannin waste samples. It was necessary to dilute the waste to four per cent solutions in order to duplicate the light transmittance of the glucose samples. Untreated vegetable tannin waste had a chemical oxygen demand of approximately 38,000 mg/l.

Experiment 5-2: Refiltration Time

Attempts to measure refiltration time met with failure. The sample size for the suspended solids test was based on obtaining a sufficiently large filter cake weight to provide reasonable accuracy. Regrettably, this resulted in filtration time ranging up to one hour. Refiltration tests ran

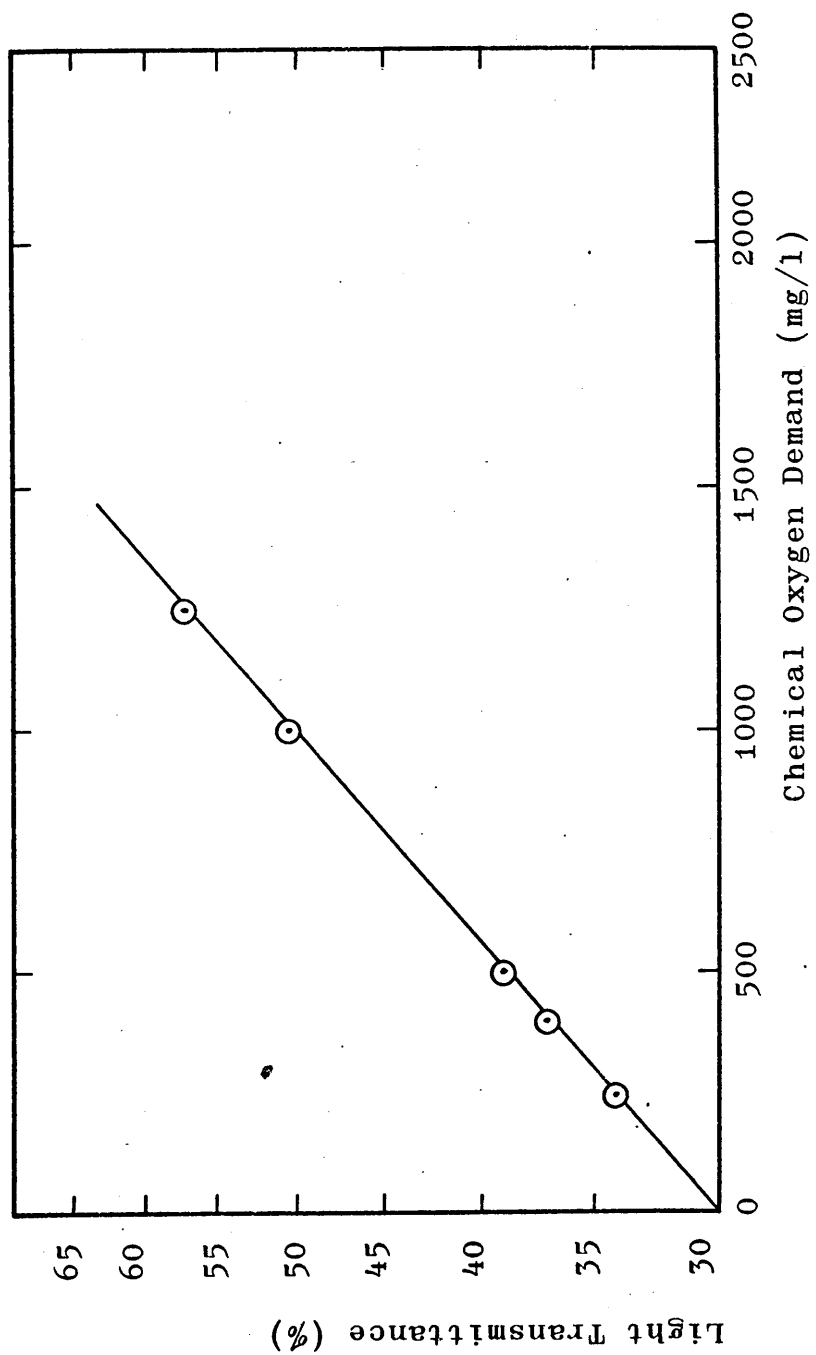


Figure 10. Calibration Curve for Chemical Oxygen Demand.

for a period of 12 hours without completion. During this time filtrate evaporation had to occur as the filtration was performed under 60 cm of Hg. The evaporation would have had a serious effect on accuracy. For these reasons attempts to measure refiltration times were discontinued, and filtration time was substituted.

Experiment 5-3: Tannin Concentration

Tannin concentration determinations was the most accurate of eight response parameters measured in this investigation. The concentrations of tannin in the waste were reported as mg/l of tannic acid, the standardizing tannin. This standardization curve is reported in Figure 11. Beer's Law is obeyed over the range pictured, but fails at concentrations greater than 12 mg/l. As the color problem associated with vegetable tannin waste was due to the tannin concentration, all color removal values were based on tannin concentration reductions. The untreated tannin waste had a tannin concentration equivalent to 10,700 mg/l of tannic acid.

Experiment Six - Polyelectrolyte Evaluation

This experiment had three distinct purposes: 1) comparison of the relationship of all dependent responses with the most accurate dependent response, per cent reduction in volatile solids over the maximum destabilization range,

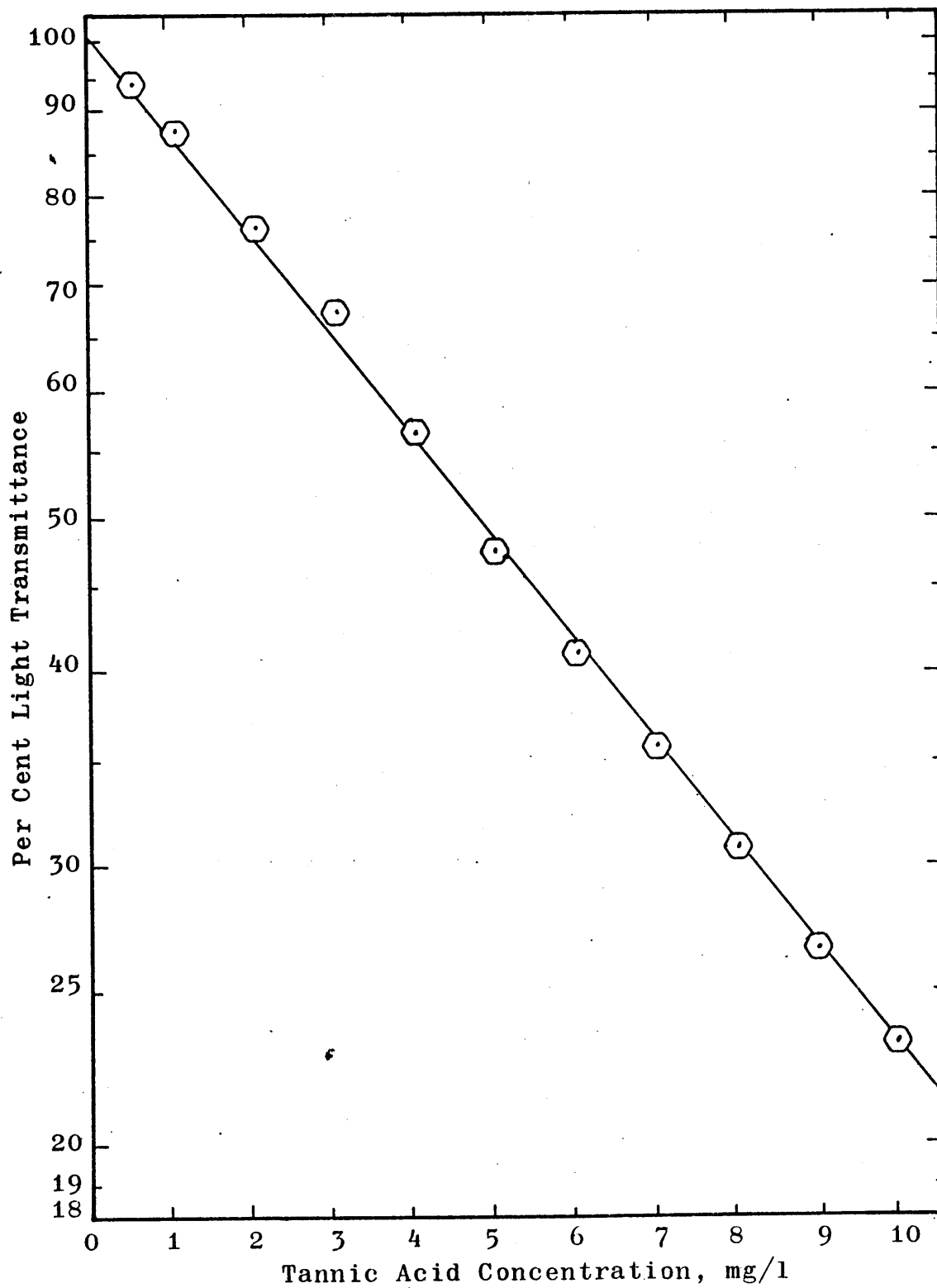


Figure 11. Standardization Curve for Tannin Concentration.

2) evaluation of the importance of each of the three independent variables on waste treatment, and 3) selection of the best polyelectrolyte-alum system for further testing. All of these purposes were accomplished using the data acquired from the experimentally designed jar test sequences.

Dependent Variable - Volatile Solids Reduction Relationship

The data used in obtaining these comparisons came from selected tests of the 10 alum-polyelectrolyte systems, depending on which subsidiary dependent variable was measured beside the primary response. The data for the 10 coagulant system tests are contained in Tables XIII to XXII located in Appendix A. The results of these comparisons are shown in Figures 12 to 15. As seen in these figures, there was a functional linear relationship between all of the response parameters and the per cent reduction in total volatile solids. However, it is clear that most of these parameters have a relatively large spread from this linear correlation and, thus, their use as an analytical response variable would be generally unreliable. As predicted in Experiment Four, the tannin and COD determinations in Figures 14 and 15 appeared to give the best linearity. Thus, it was believed that these two responses would produce the same type of regression equation and response curve as the per cent reduction in volatile solids did. This expectation was confirmed by obtaining a regression equation using tannin concentration as the primary response.

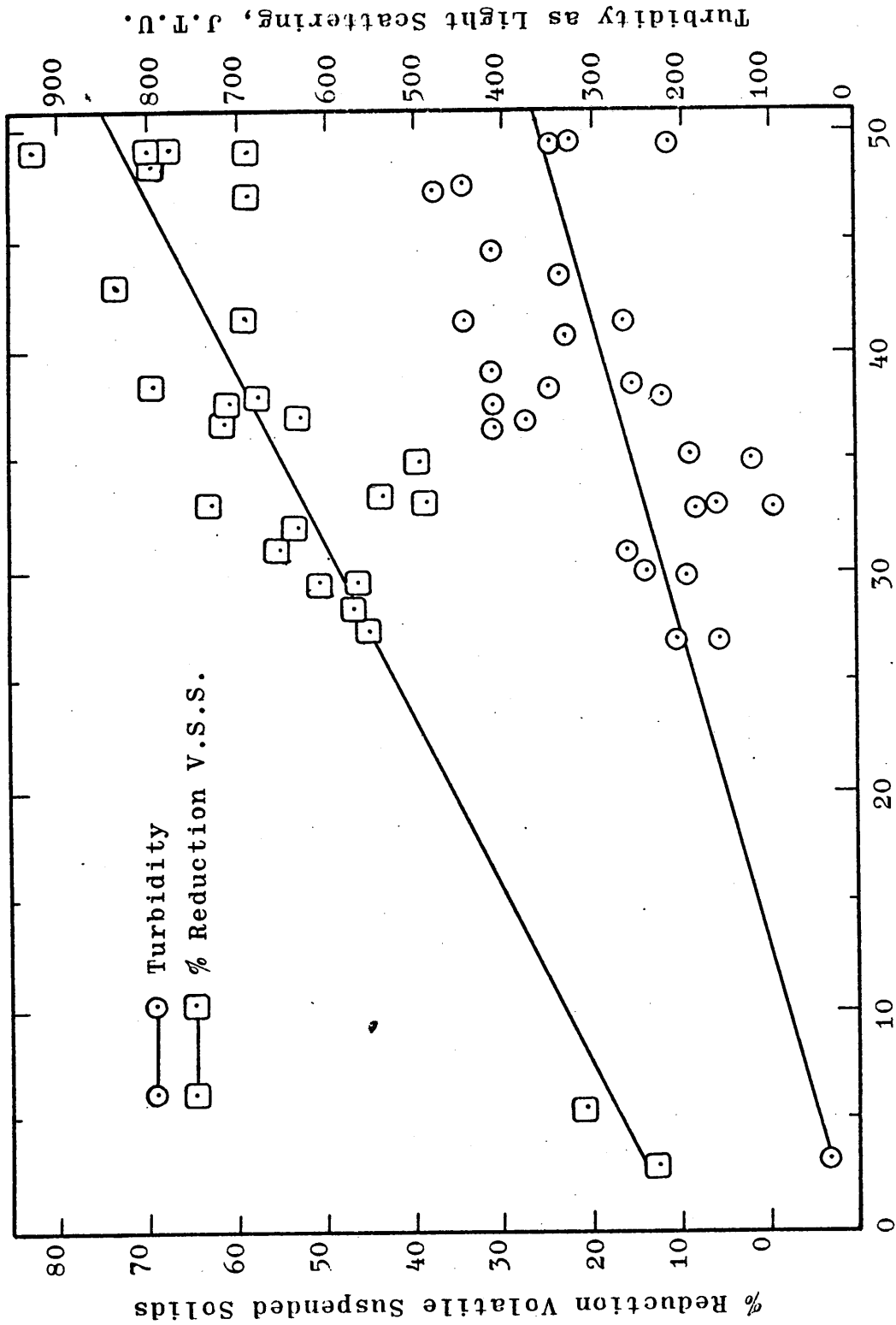


Figure 12. Relationship Between Response Parameters Total Volatile Solids, Volatile Suspended Solids, and Turbidity as Light Scattering.

Turbidity as Light Scattering, J.T.U.

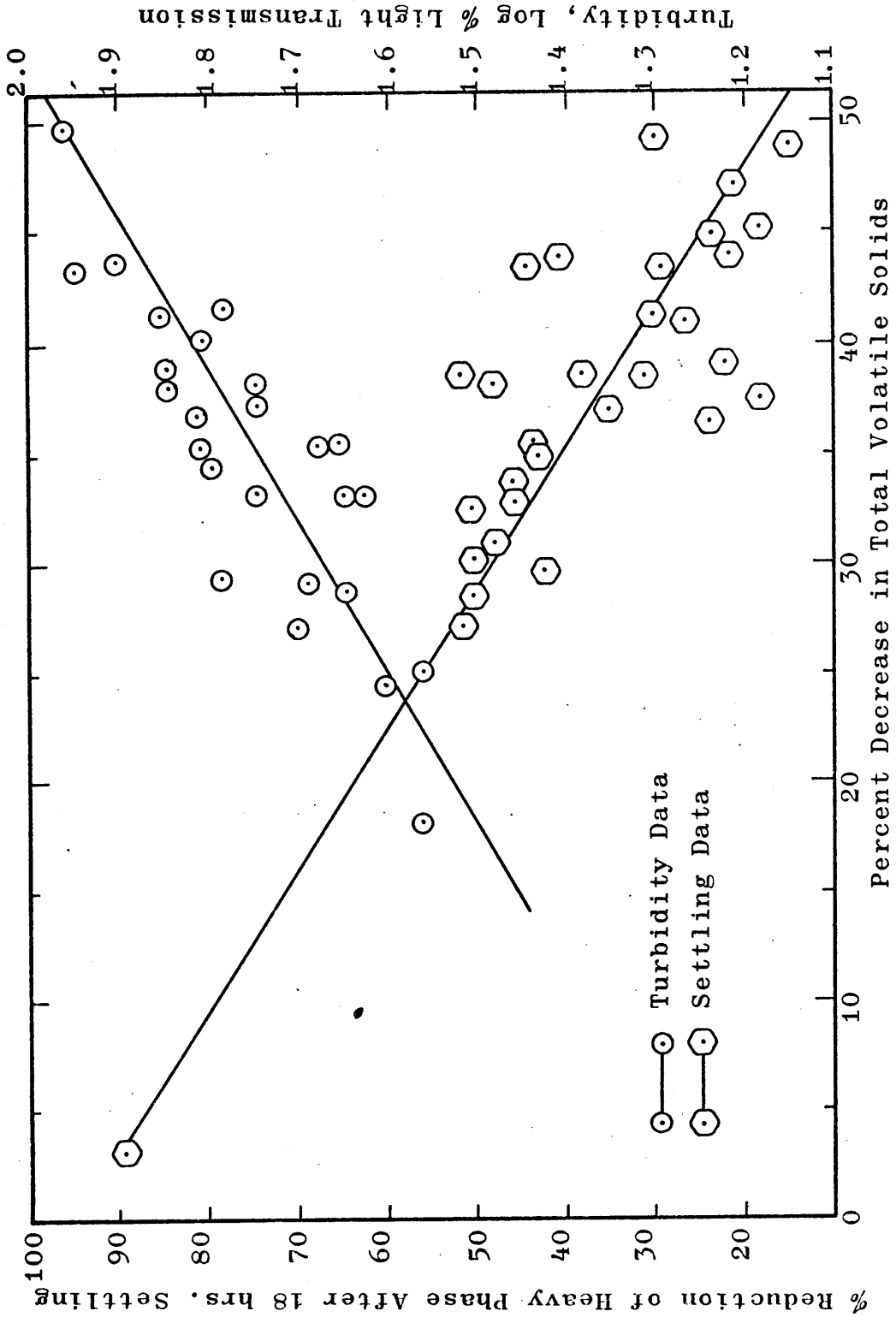


Figure 13. Relationship Between Response Parameters Total Volatile Solids, Settled Volume, and Turbidity as Light Transmission

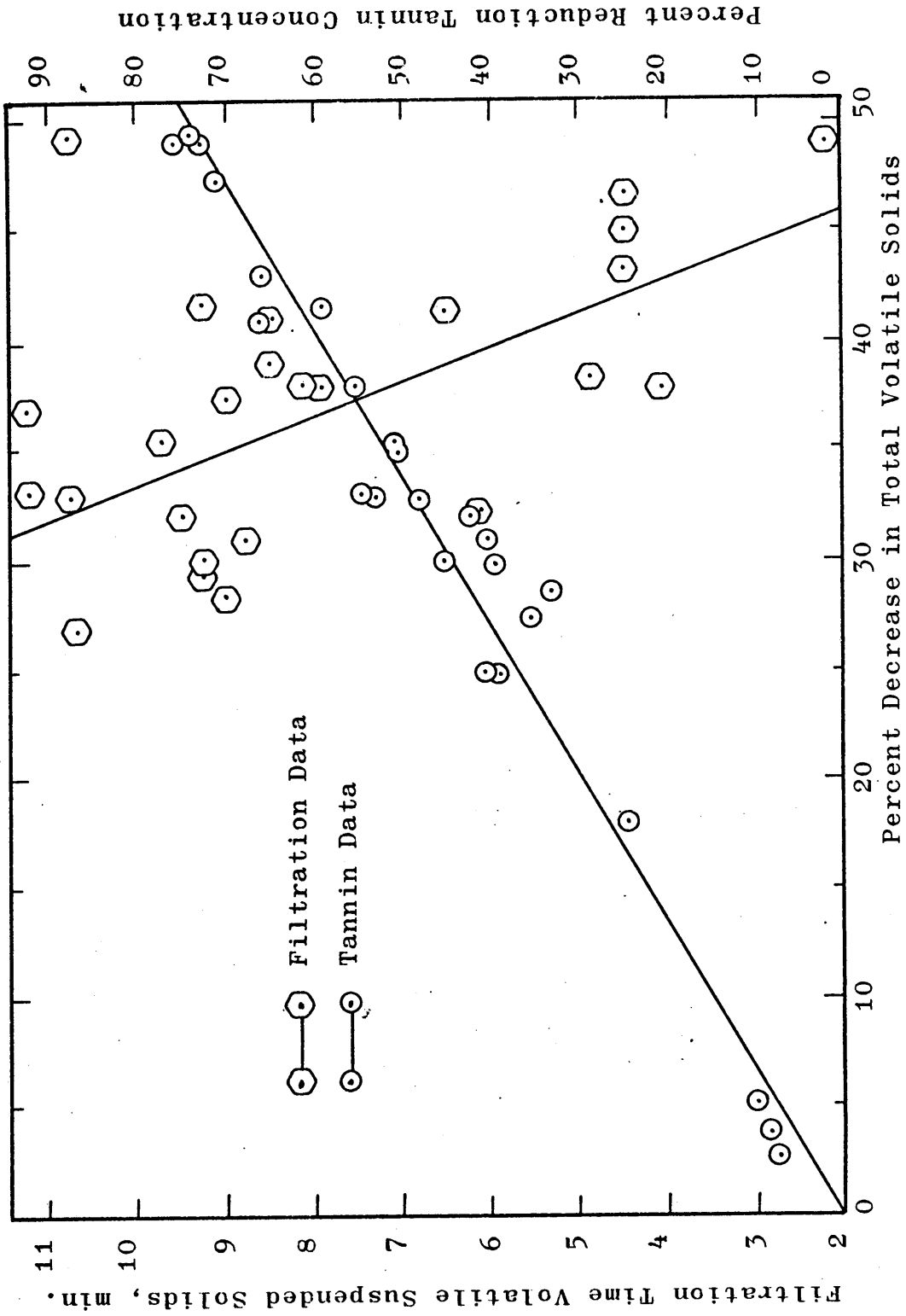


Figure 14. Relationship Between Response Parameters Total Volatile Solids, Filtration Time, and Tannin Reduction.

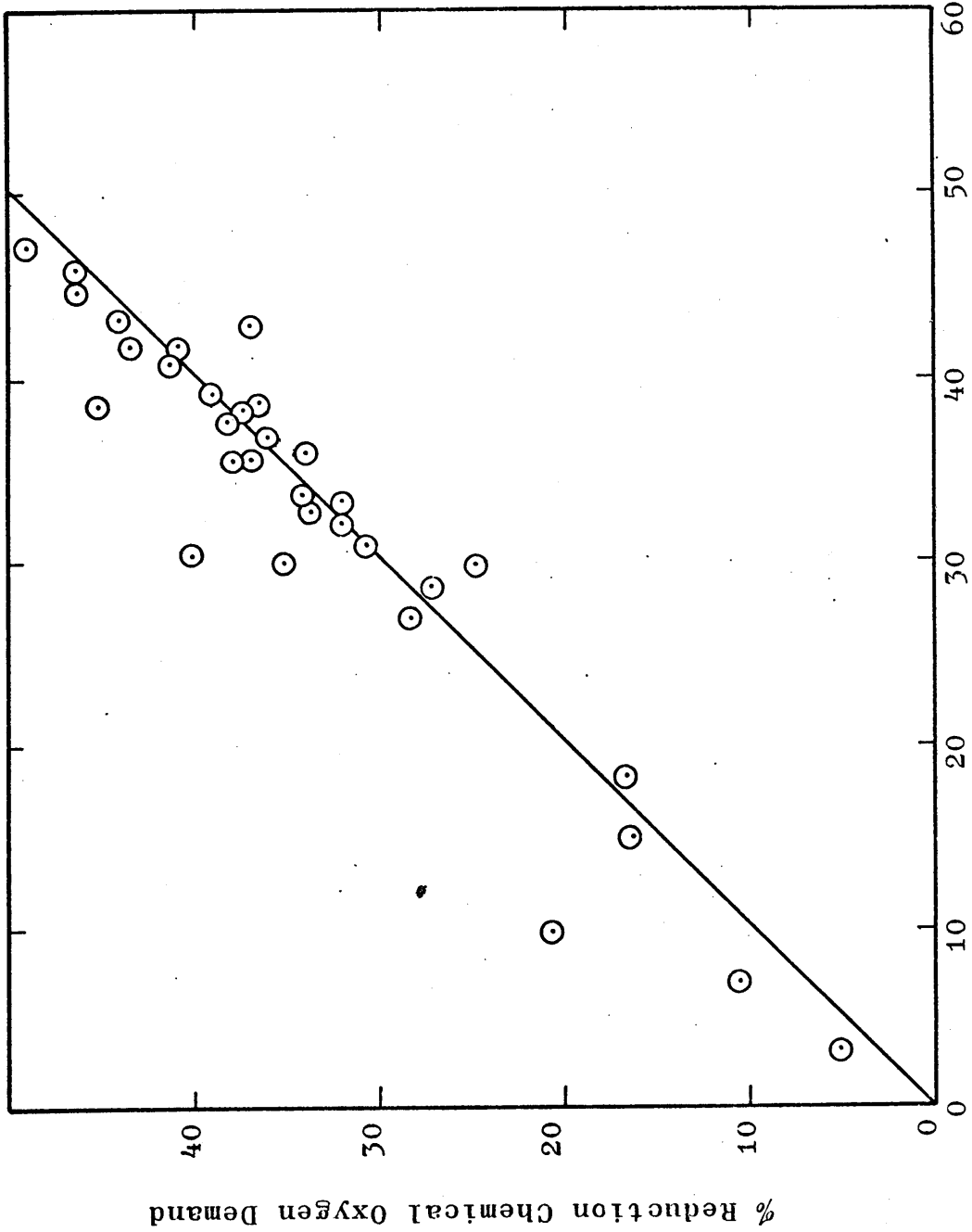


Figure 15. Relationship Between Response Parameters, Total Volatile Solids and Reduction (%) Chemical Oxygen Demand.

Evaluation of Independent Variables

The data used to generate the regression equations describing the alum-polyelectrolyte systems are contained in Tables XIII to XXII of Appendix A. The regression coefficients of Experiments 6A, 6B, and 6C were reported separately from 6D to 6J since the range of the aluminum sulfate concentrations in the former experiments was from zero to 3000 mg/l, half of the value chosen for the final experimental design. However, this difference did not prevent graphical comparison of the different polyelectrolyte systems on the same graph. Regression equation coefficient results are presented in Tables X and XI for 6A to 6C and 6D to 6J, respectively. These coefficient values are for the coded form of the regression equation and are not applicable to an equation using absolute time and concentration values. The regression equations were developed using the primary response variable, percent reduction in total volatile solids. The form of this equation was previously described in Table II. As was seen, the equation used first and second order terms for each independent variable as well as cross products terms between variables. In Table II the coefficients of each of these variable terms were tabulated. In observing the results in Tables X and XI it was seen that the first order alum coefficient was about 10 times larger than the best first order polyelectrolyte coefficient. It was also noted

TABLE X. REGRESSION EQUATION COEFFICIENT RESULTS FOR CODED VARIABLES

IN EXPERIMENTS 6A to 6C

Poly. No. Type and Exp. No.	Constant	Alum		Poly.		Time		Interaction		
	b_0	b_1	b_{11}	b_2	b_{22}	b_3	b_{33}	b_{12}	b_{13}	b_{23}
605 Cat. Exp. 6A	32.1	10.1	-3.96	.75	-1.63	-.77	1.04	.59	-2.10	-.25
654 Cat. Exp. 6B	35.8	9.6	-3.98	.30	.42	-.38	.44	.30	1.22	-.05
605 Cat. Exp. 6C	33.5	10.1	-3.3	.06	.64	-.66	1.38	.30	-.02	.32

Note: For experiments 6A to 6C, only, the following preliminary coding was used:

Coded Variable	+1.682	+1	0	-1	-1.682
Aluminum Conc., mg/l	3000	2392	1500	608	0

Polyelectrolyte and time coding are the same as described in Tables II and III.

TABLE XI. REGRESSION EQUATION COEFFICIENT RESULTS FOR CODED VARIABLES

IN EXPERIMENTS 6D to 6J

Poly.No. Type and Exp. No.	Constant b_0	Alum		Poly.		Time		Interaction		
		b_1	b_{11}	b_2	b_{22}	b_3	b_{33}	b_{12}	b_{13}	b_{23}
632 Cat. Exp. 6D	42.0	8.13	-4.38	-1.88	1.36	-2.53	.809	+1.49	.828	-1.23
610 Cat. Exp. 6J	42.2	10.8	-5.32	.35	-2.72	-.52	.339	+.355	.675	-.18
607 Cat. Exp. 6F	42.2	9.73	-4.36	-.26	1.13	-.493	1.02	+.563	1.10	-.71
670 Nonion. Exp. 6E	44.2	10.99	-5.53	.36	-1.80	-.535	.761	+.125	-.450	-.75
675 Anionic Exp. 6G	45.8	10.82	-5.72	.57	2.2	1.02	.418	-1.84	-.838	.84
672 Anionic Exp. 6H	42.3	9.79	-4.58	.92	2.14	1.19	1.18	-.49	-.49	1.44
674 Anionic Exp. 6I	42.6	11.45	-3.80	.52	-1.39	.24	.898	1.18	.433	0.60

Coded variable and variable concentration relationship listed in Tables II and III.

that all of the alum coefficients were about the same, indicating that alum had roughly the same effect on coagulation regardless of polyelectrolyte type or concentration or variation in the time of addition. There was no apparent consistency in the polyelectrolyte coefficients. The remaining consistency observed was in the time variable. The first order coefficient was negative for cationic polymers and positive for anionic polymers.

The evaluation of experiments involving one independent variable is accomplished with no difficulty. When two independent variables are evaluated, graphical presentations involve three dimensional figures and are difficult to grasp mentally. Experiments involving three or more independent variables, as in this investigation, cannot be graphed simultaneously with the dependent response because four or more dimensions are required. Added to this complexity is the fact that this investigation was experimentally designed with an inherent accuracy greater at the center of the design and smaller at its limits. It is possible to hold two variables constant and plot the third variable against the response variable, typically at zero concentration of the two remaining constant variables. This procedure was not followed because of lesser accuracy obtained at the limits of the experimental variable ranges. Instead the variables not being compared were held constant at the center of the

experimental design, zero code value. Thus, the effects of the variation of the independent variables as they acted in concert with constant values of the remaining two variables were observed.

In Figure 16 the effect of the aluminum sulfate concentration on volatile solids removal is plotted for three cationic polyelectrolytes, Nalco 603, 605, and 634. From this figure it was not clear that the maximum removal was obtained at the aluminum sulfate limit of 3,000 mg/l. For this reason the variable range was doubled to 6,000 mg/l and a new, final experimental design was developed for the polyelectrolyte evaluation testing. It was planned to later retest these polyelectrolytes using the new design. Subsequent results showed anionic polymer superiority, rendering this work unnecessary.

In Figure 17 the effect of alum concentration on total volatile solids removal is illustrated for each of seven polyelectrolytes, Nalco 632, 610, 607, 670, 675, 672, and 674. Polyelectrolyte concentration and time interval were once again held constant at the center of the experimental design, the most accurate position. It was noted that the results obtained in Figure 16 were almost identical to that obtained in Figure 17 over the same variable range. Removal of volatile solids increased linearly through an alum concentration of 3000 mg/l, then tended to level off to a

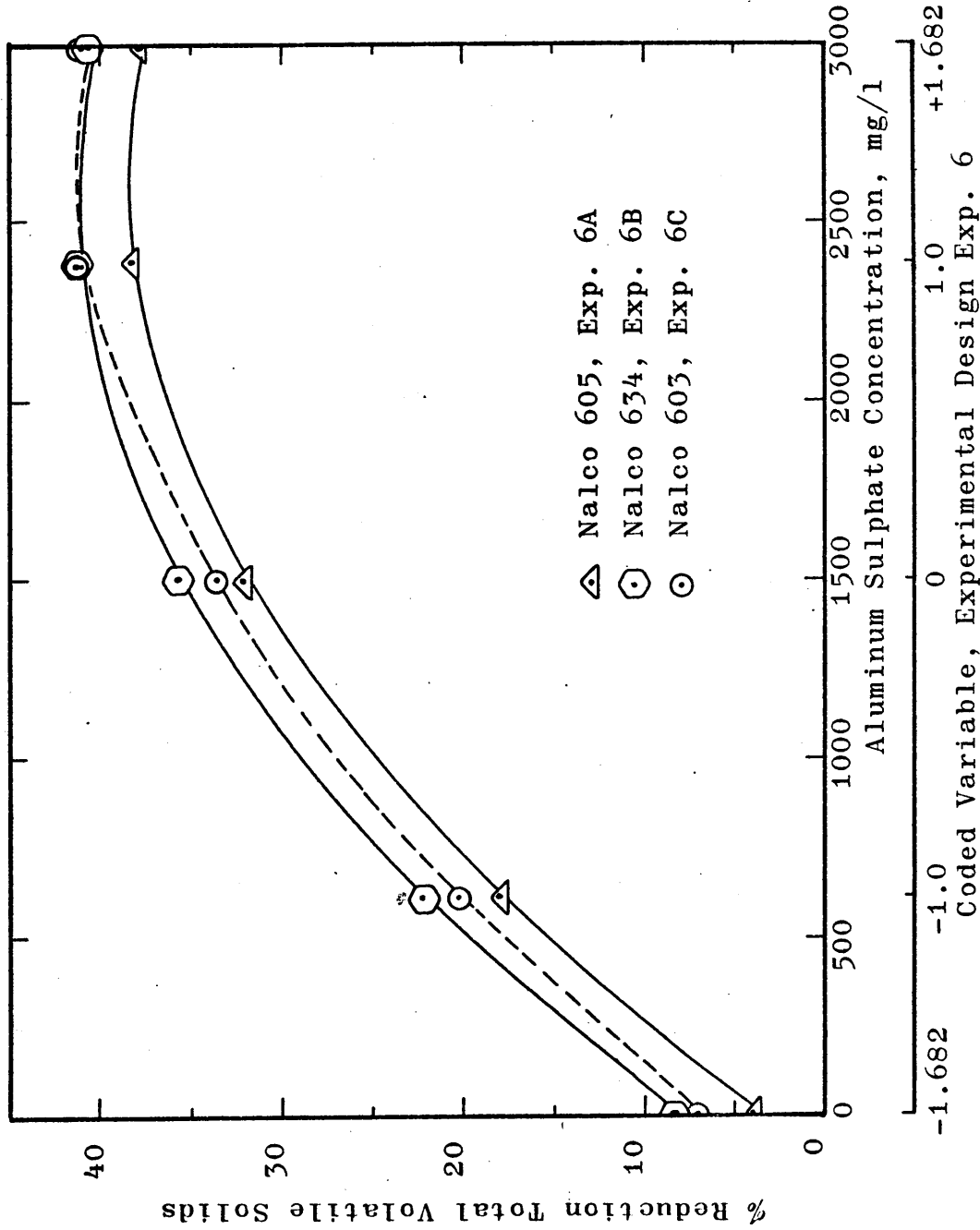


Figure 16. Variation of Volatile Solids with Aluminum Sulphate Concentration, Exp. 6A, 6B, 6C.

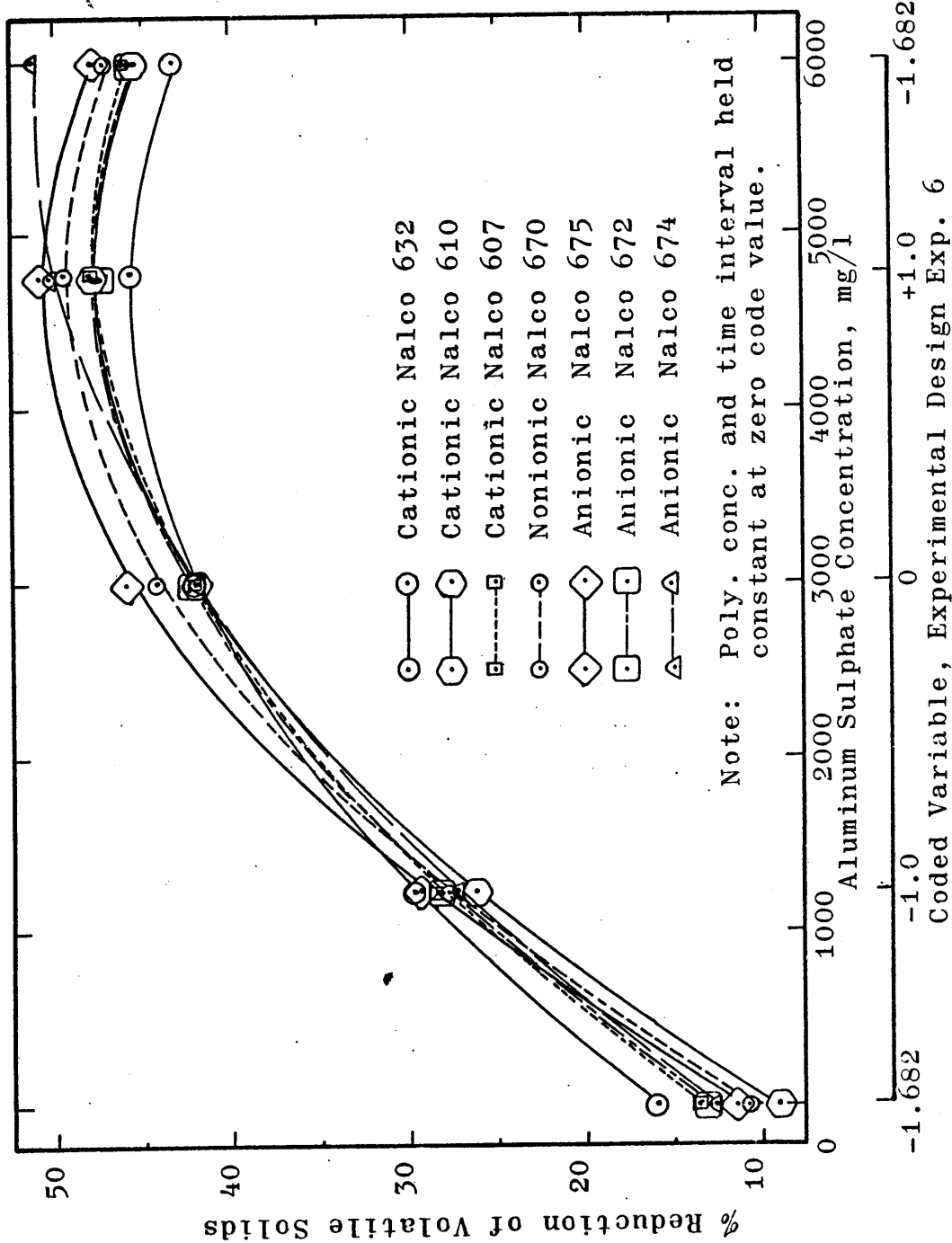


Figure 17. Variation of Volatile Solids with Aluminum Sulphate Concentration, Experiments 6D to 6J.

maximum volatile solids removal of about 50 percent at around 4,500 mg/l alum. While the general trend was the same for all of the alum-polyelectrolyte systems, some significant differences did appear. The differences were more easily seen when averages of the three types of polyelectrolytes, anionic, cationic, and nonionic, were depicted, as in Figure 18. Particularly at low and high alum concentrations a difference in the percent removal of volatile solid was noted with the anionic-alum systems appearing to be more efficient.

In studying the remaining two independent variables, alum concentration was held constant at 3,000 mg/l, the minimum concentration of maximum removal efficiency, and the more accurate constant concentration. In Figures 19 and 20, the percent reduction in total volatile solids is depicted as a function of polyelectrolyte concentration. The remaining independent variables, alum concentration and time interval, were held constant at 3,000 mg/l and 1.2 minutes, respectively. The polyelectrolytes behaved uniquely as illustrated in Figure 19. However, there was a comparable trend between the two best cationic and anionic polymers and this feature is shown in Figure 20. As seen, increasing anionic polyelectrolyte concentration first decreased, then increased substantially the amount of reduction in total volatile solids. For the cationic polyelectrolytes, the

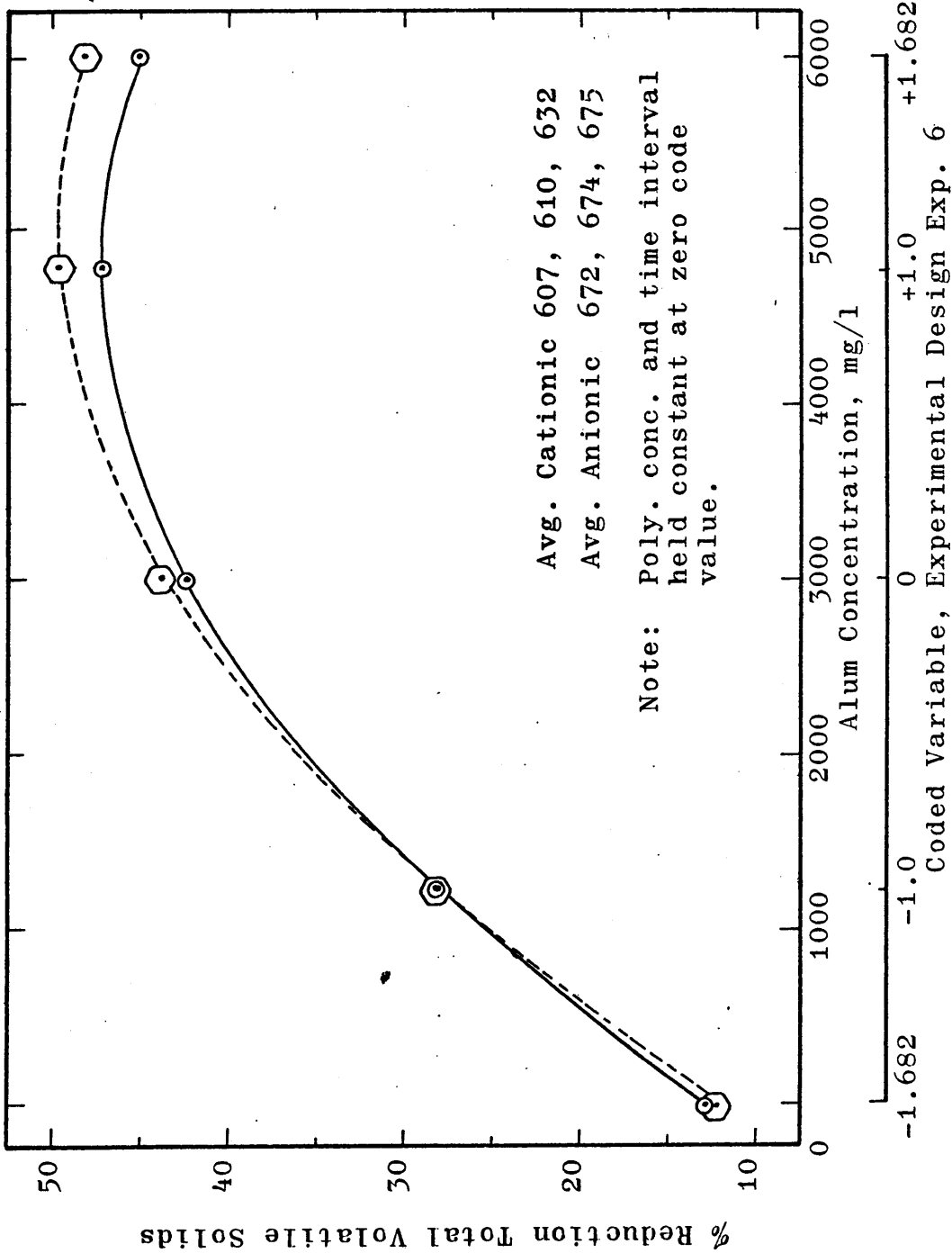


Figure 18. Variation of % Reduction of Total Volatile Solids with Aluminum Concentration for Polyelectrolyte Type.

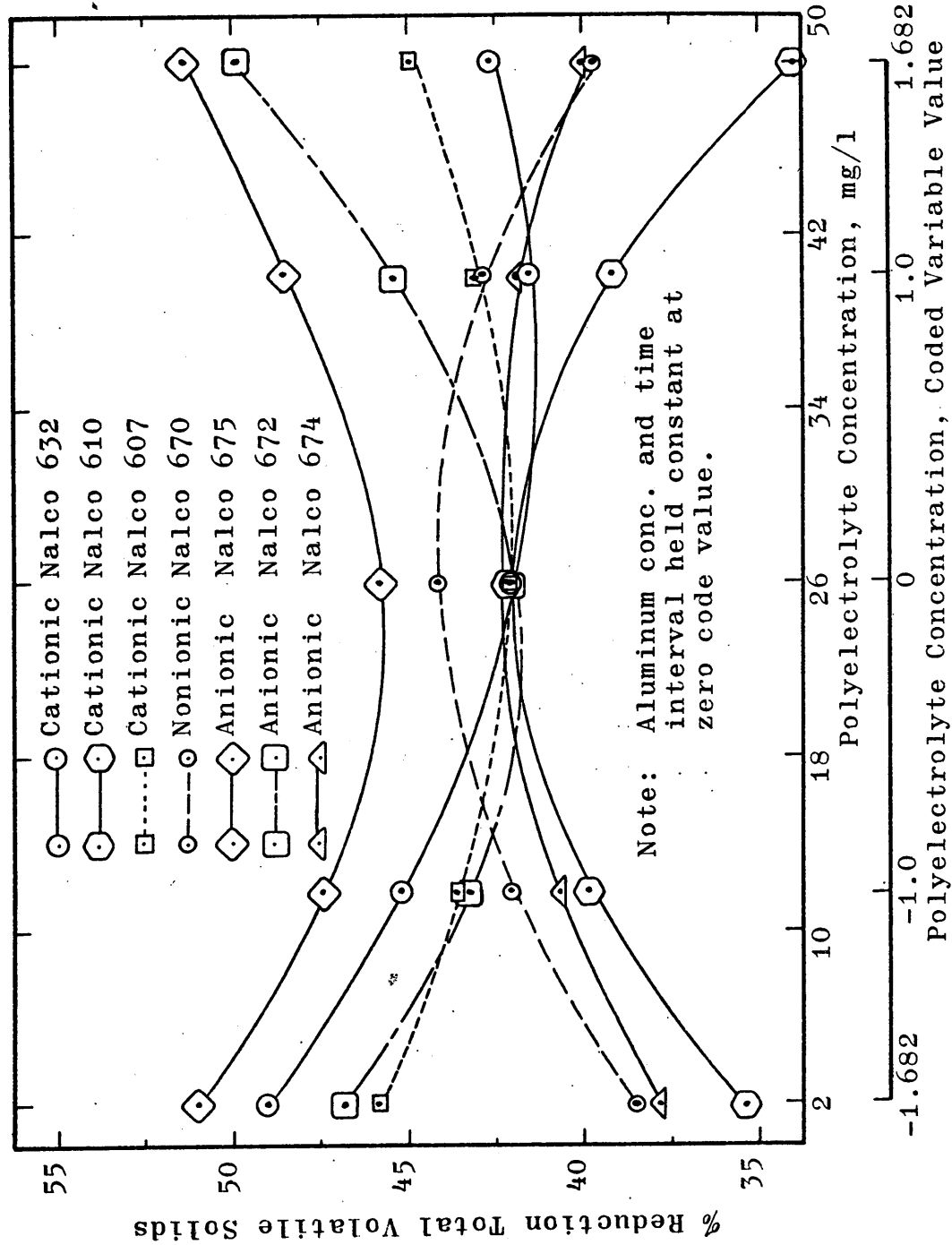


Figure 19. Variation of % Reduction of Total Volatile Solids with Polyelectrolyte Concentration, Experiments 6D to 6J.

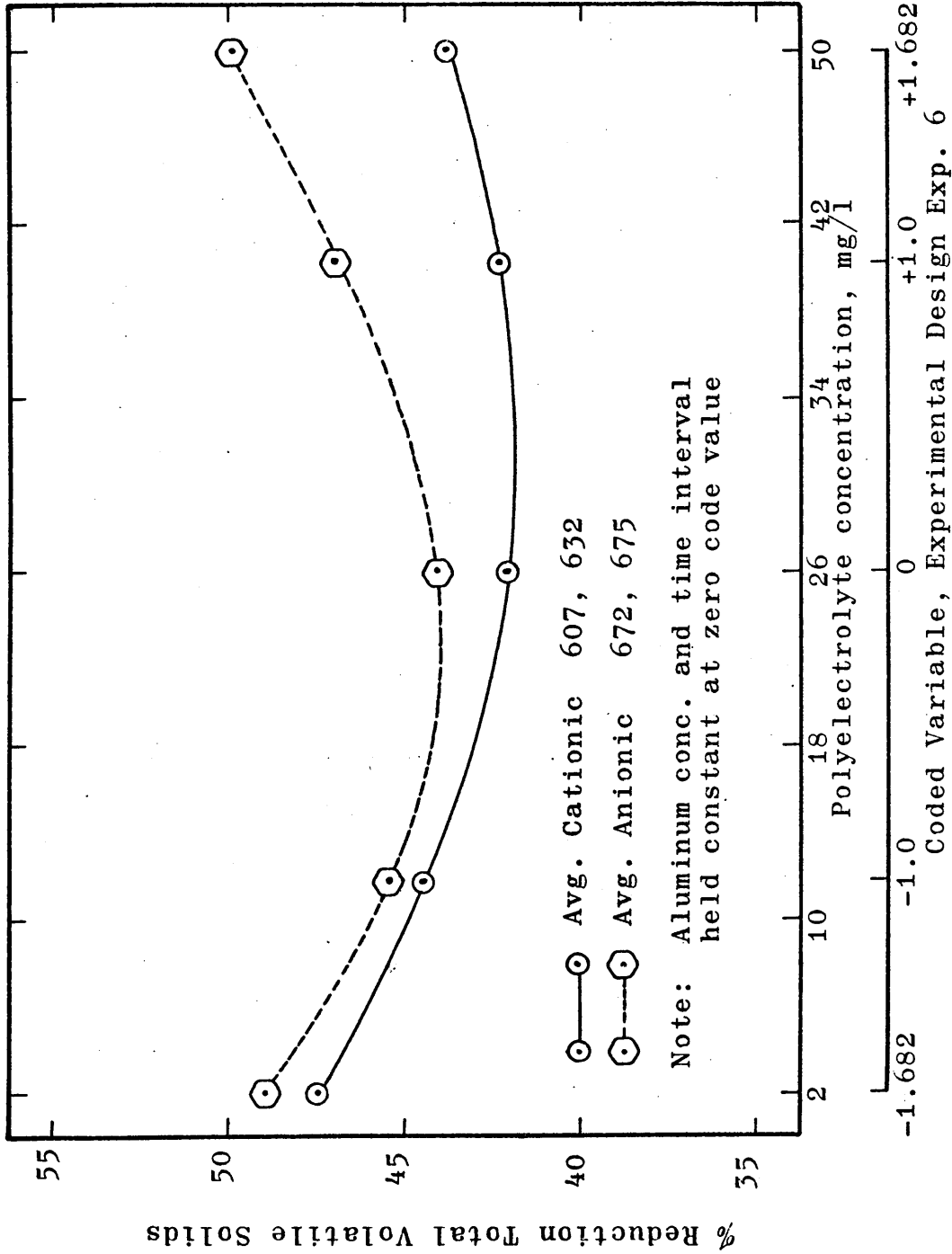


Figure 20. Variation of % Reduction of Total Volatile Solids with Poly. Conc. for Average of Best Poly. Type.

best removals were obtained at low concentrations. Nalco 675, an anionic polymer, clearly appears in Figure 19 to be the best polyelectrolyte for this application.

The final independent variable analyzed was the time interval between addition of alum and polyelectrolyte. Graphs of the time interval versus percent reduction in total volatile solids are shown in Figures 21 and 22. In Figure 21, graphs for each polymer are shown. While each polyelectrolyte system appeared to be unique, there was, in fact, consistency in the noted variation. Increasing cationic polyelectrolyte time intervals brought about a decrease in percent removals. With an anionic polyelectrolyte, there was an increase in removal efficiency as the time interval increased. These trends were more clearly seen when the average of the two anionic and cationic polyelectrolytes were taken as depicted in Figure 22.

The final graphical presentation in this section, Figure 23, illustrated the removal efficiency with alum concentration for various concentrations of the best polyelectrolyte tested, the anionic Nalco 675. The time interval was held constant at its maximum effective value of 3.2 minutes. From these curves it was observed that a combination of either relatively low alum concentration (3,000 mg/l) and high polyelectrolyte concentration (50 mg/l) or relatively high alum concentration (5,000 mg/l) and low alum

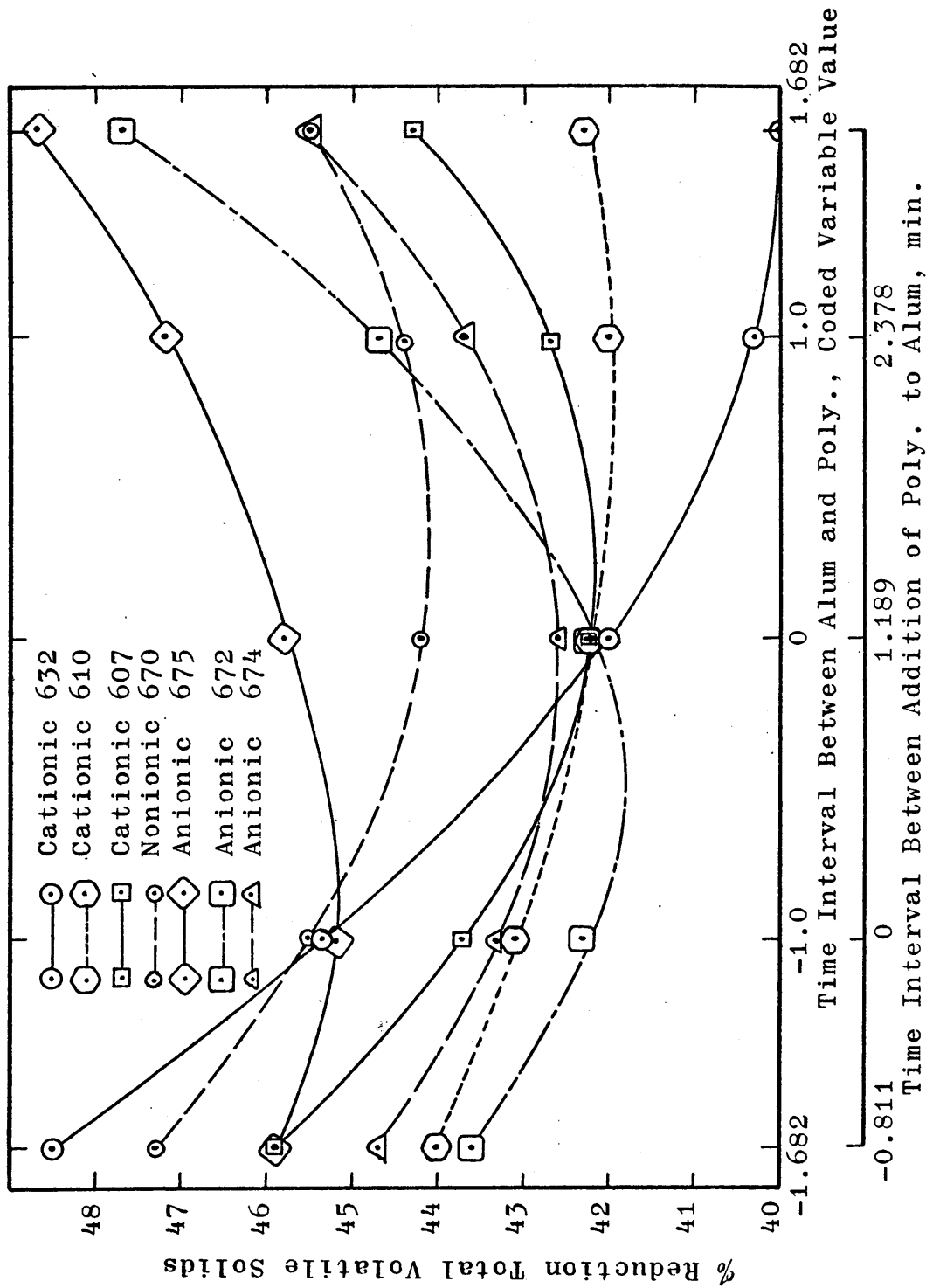


Figure 21. Variation of % Reduction of Total Volatile Solids with Time Interval for Experiments 6D to 6J.

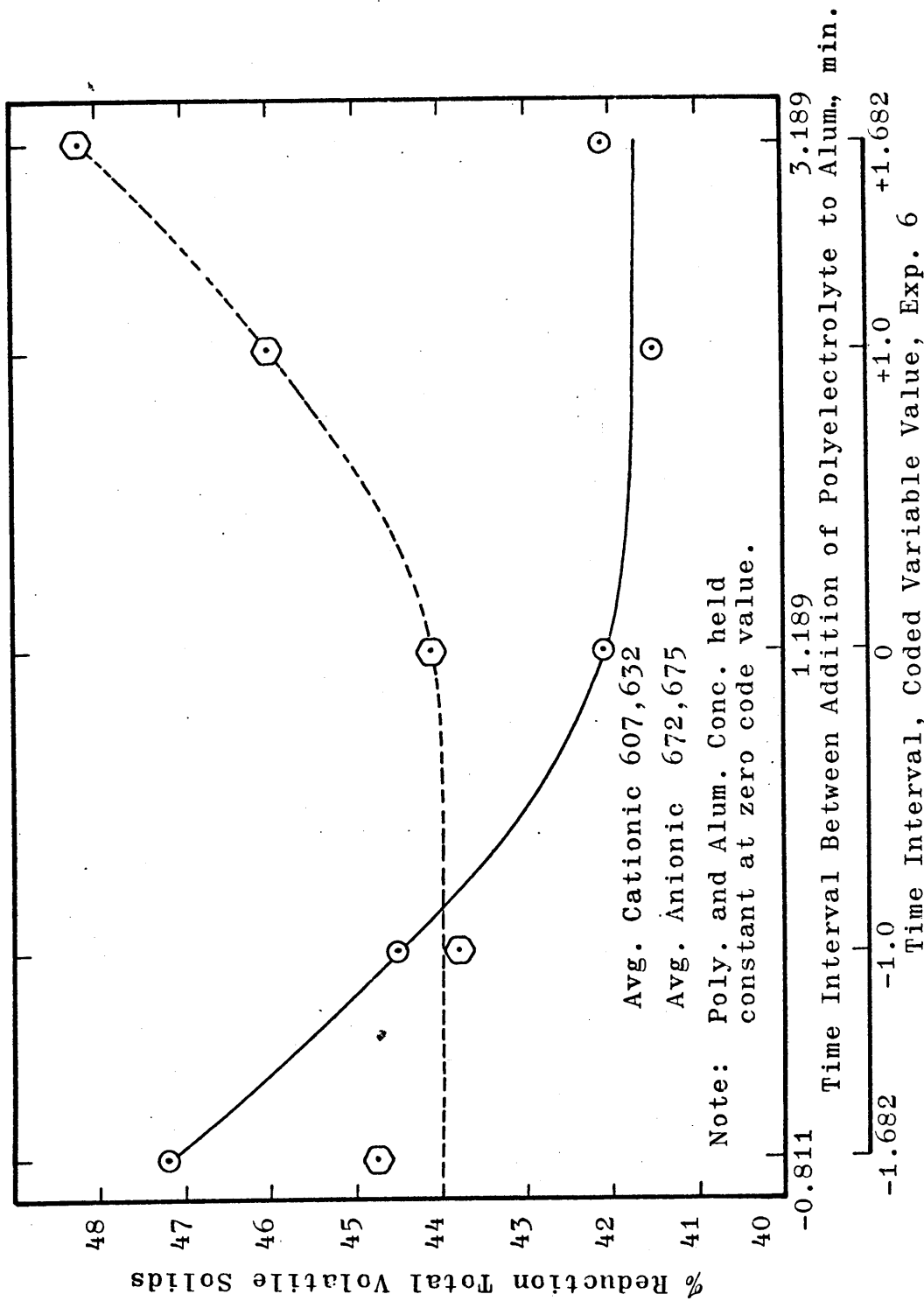


Figure 22. Variation of % Reduction of Total Volatile Solids with Time Interval for Best Polyelectrolyte Type.

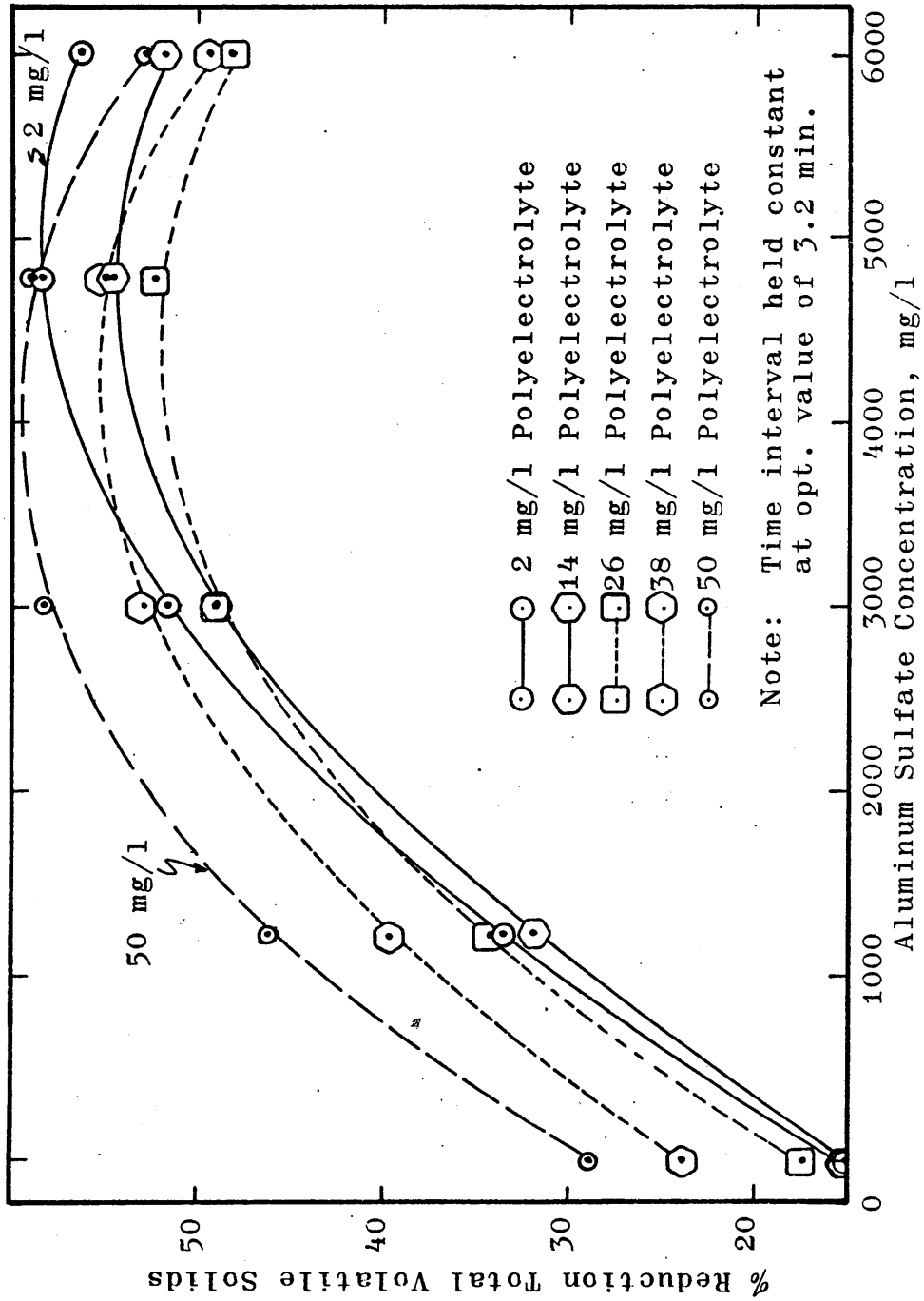


Figure 23. Variation of Volatile Solids with Aluminum Sulfate Concentration for Specific Concentrations of Anionic Polyelectrolyte (Nalco 675), Experiment 6-G.

concentration (2 mg/l) yielded the best removal efficiencies. Nearly 60 percent reduction in total volatile solids was projected for either of these system combinations.

Selection of the Best Polyelectrolyte - Aluminum System

From the data in Tables X and XI it was noted that the anionic polyelectrolytes Nalcolyte 672 and 675 had the highest coefficients for the polyelectrolyte variable, X_2 and X_2^2 . Strictly on the analysis of these coefficients Nalcolyte 672 would have been selected as the superior polyelectrolyte. However, as discussed previously, the variables were studied from a system viewpoint using the regression equation, and Nalcolyte 675 had a superior system constant, b_0 , to Nalcolyte 672. This superiority is clearly seen in Figure 19, where the reduction of volatile solids is substantially better for Nalcolyte 675 than for all other polyelectrolyte systems. For this reason the extended testing, including pH variation, was accomplished using Nalcolyte 675.

Experiment Seven: pH Evaluation in Expanded Test

The purpose of this experiment was to evaluate pH as an independent parameter for the best performing polyelectrolyte and to confirm the earlier results for the other independent variables. The data and response results for this experiment are contained in Table XXIII of Appendix A. The regression coefficients obtained from this data are presented

in Table XII. In comparing these coefficients with data presented earlier in Table XI discrepancies were noted. These value differences were not due to differing experimental results, but were due rather to a larger coding range for the same absolute dimensional parameter ranges. These differences were unimportant when results were compared graphically, but were troublesome in attempting numerical correlation. To overcome these difficulties each independent parameter was graphed using the same techniques employed previously in Experiment Six. Results are shown in Figures 24 to 27. The results from Experiment Six were included for comparison where possible.

Aluminum and Polyelectrolyte Concentration Variables

The variation of per cent reduction of volatile solids with aluminum and polyelectrolyte concentrations are shown in Figures 24 and 25, respectively. The results were very similar to the previous work, as expected.

Time Interval Variable

In Experiment Six the results with anionic polymers indicated that an increased time interval between aluminum sulfate and polyelectrolyte addition resulted in greater colloidal destabilization. For this reason the time interval tested was increased to six minutes in expectation that an upper limit for time interval could be established. As

TABLE XII. REGRESSION COEFFICIENTS FOR EXPERIMENT SEVEN,
EXTENDED TEST FOR pH

<u>Variable Name (if applicable)</u>	<u>Coefficient Symbol</u>	<u>Coefficient Value</u>
Equation Constant	b_0	44.71
Aluminum Conc., X_1	b_1	7.59
Aluminum Conc., X_1^2	b_{11}	-3.57
Poly. Conc., X_2	b_2	1.35
Poly. Conc., X_2^2	b_{22}	1.77
Time Interval, X_3	b_3	0.51
Time Interval, X_3^2	b_{33}	0.88
pH, X_4	b_4	1.82
pH, X_4^2	b_{44}	0.26
Interaction, X_1X_2	b_{12}	-0.87
Interaction, X_1X_3	b_{13}	-0.35
Interaction, X_1X_4	b_{14}	-0.93
Interaction, X_2X_3	b_{23}	0.69
Interaction, X_2X_4	b_{24}	-0.28
Interaction, X_3X_4	b_{34}	-0.01

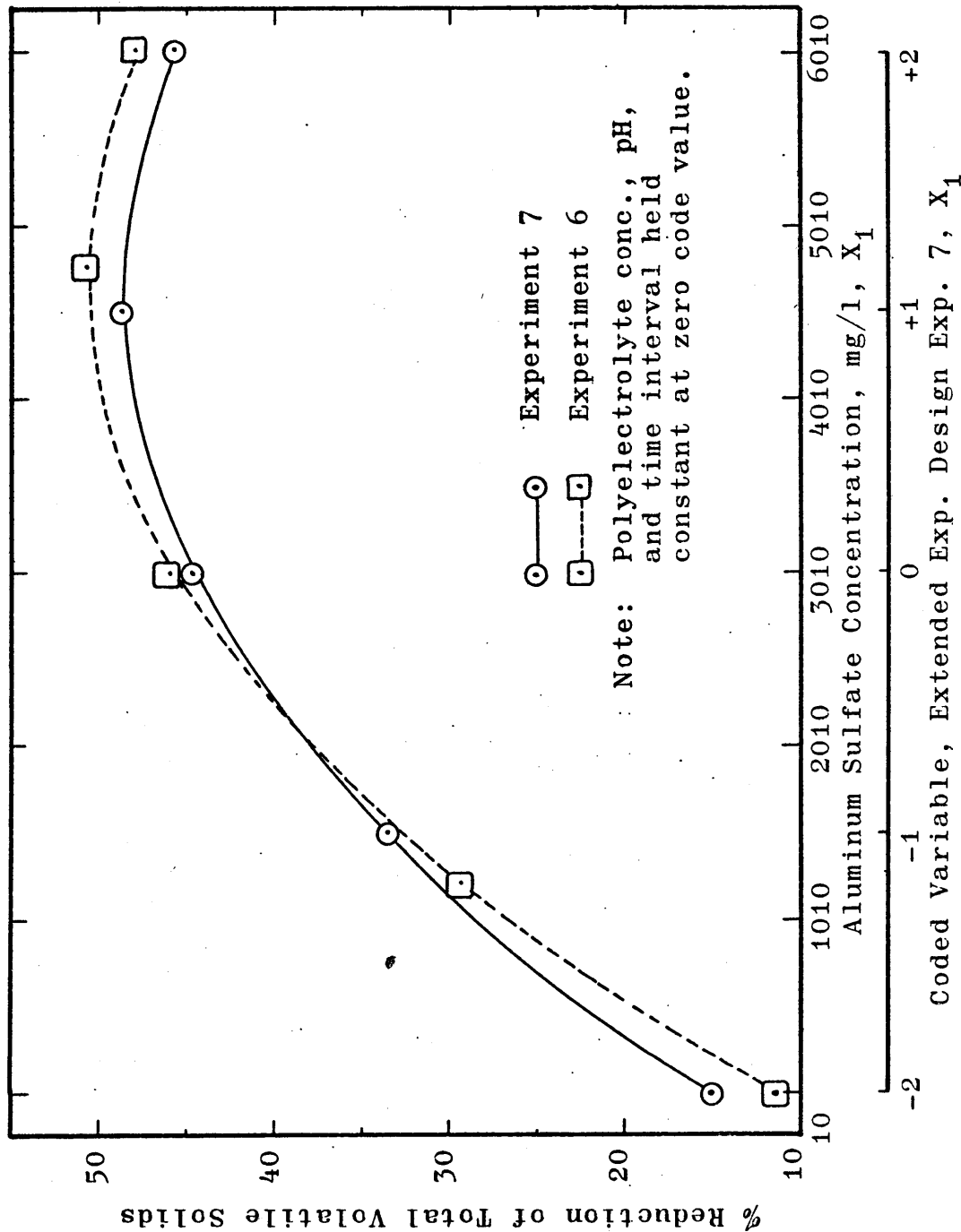


Figure 24. Variation of Volatile Solids with Aluminum Sulfate Concentration for Nalco 675.

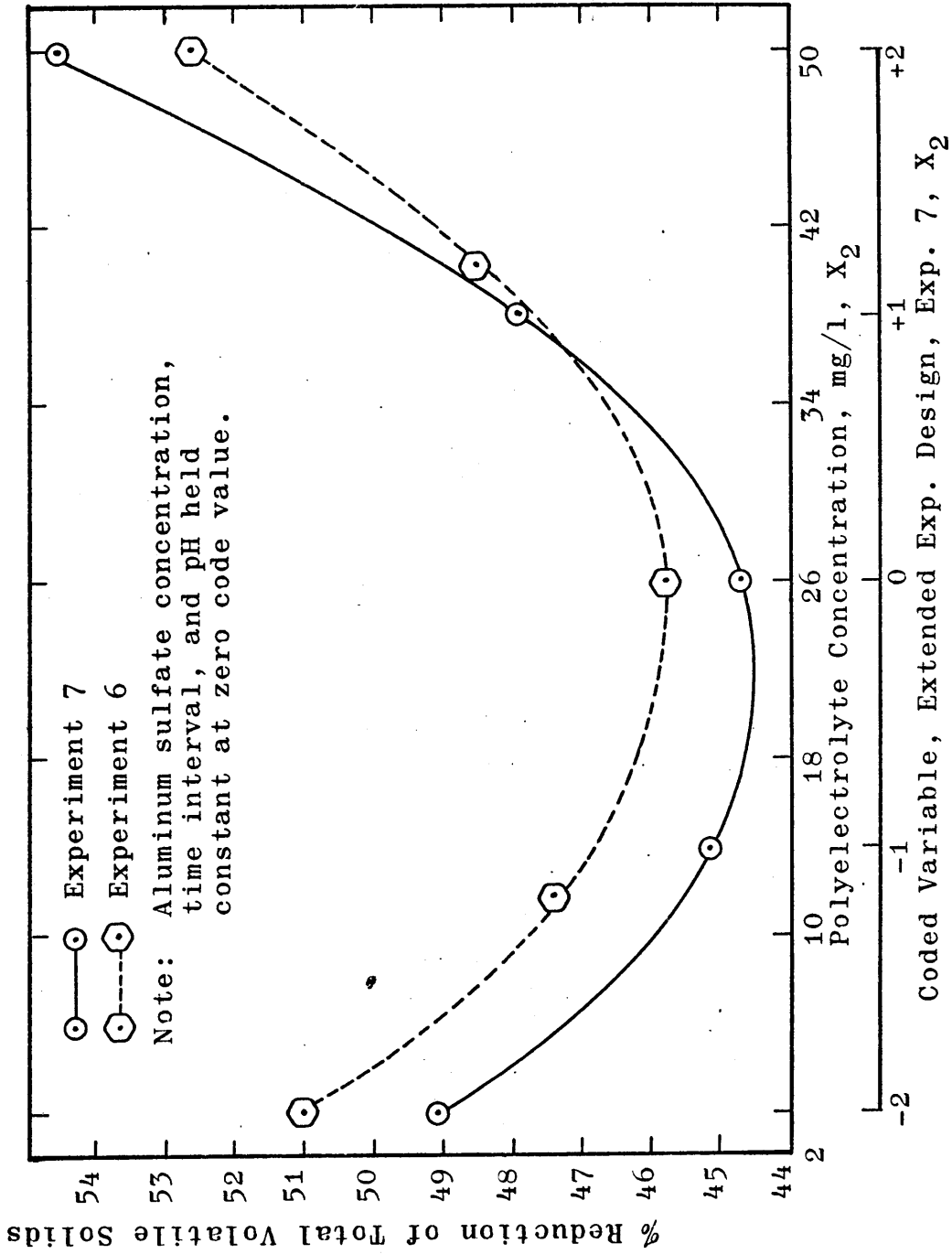


Figure 25. Variation of Volatile Solids with Polyelectrolyte Concentration for Nalco 675.

seen in Figure 26 this upper limit was still not defined; maximum removal is achieved at the six minute interval.

pH Variable

The relationship between colloid destabilization and pH in the presence of coagulants is graphically illustrated in Figure 27. The best destabilization results were obtained at pH 7, also near the upper limit of the experimental design.

Overall Parameter Evaluation

In Figure 28 the per cent reduction of volatile solids was studied as a function of alum concentration for specified polyelectrolyte concentration in a family of curves. Time interval and pH were held constant at their maximum destabilization values of 6 minutes and 7.0, respectively.

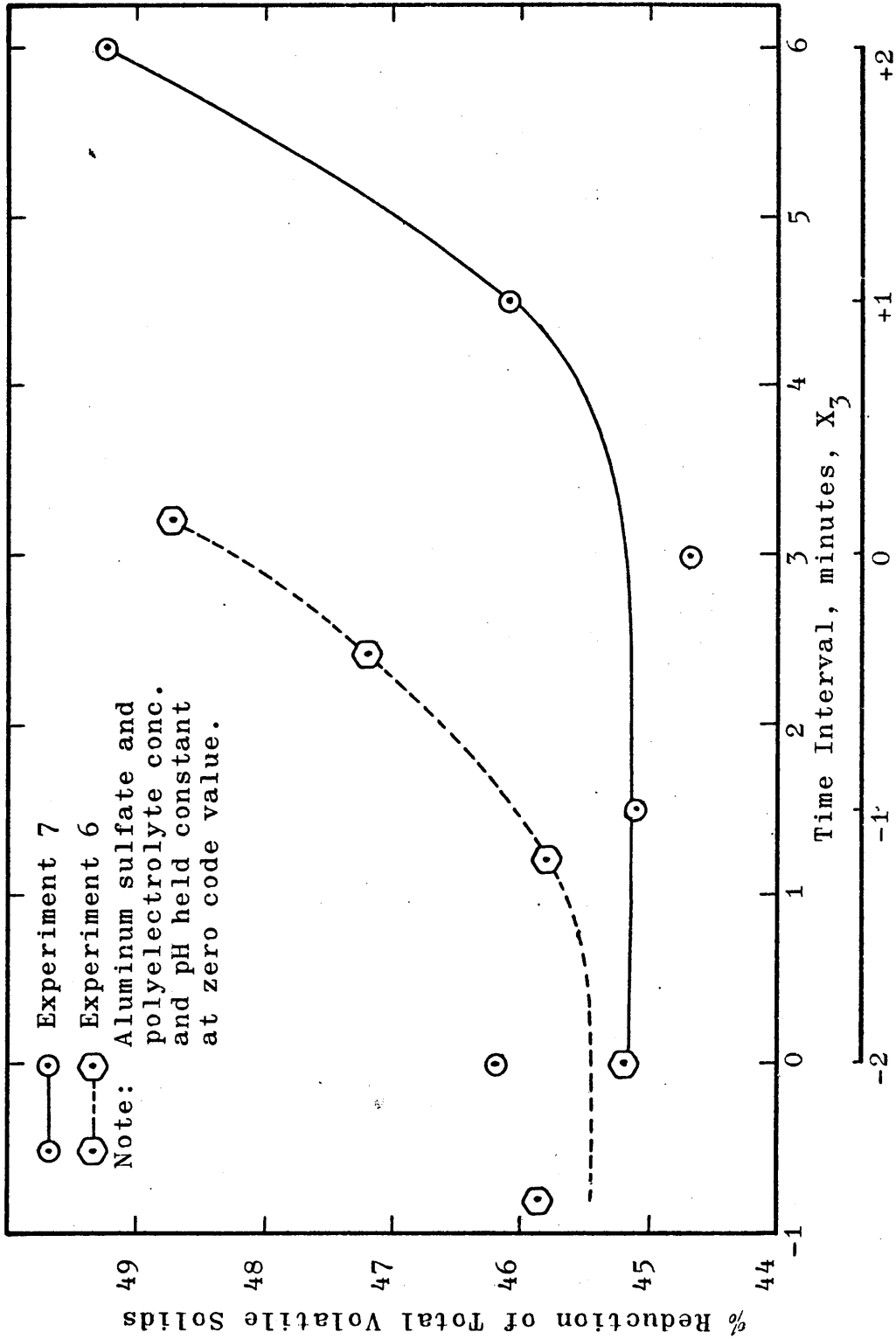


Figure 26. Variation of Volatile Solids with Time Interval for Nalco 675.

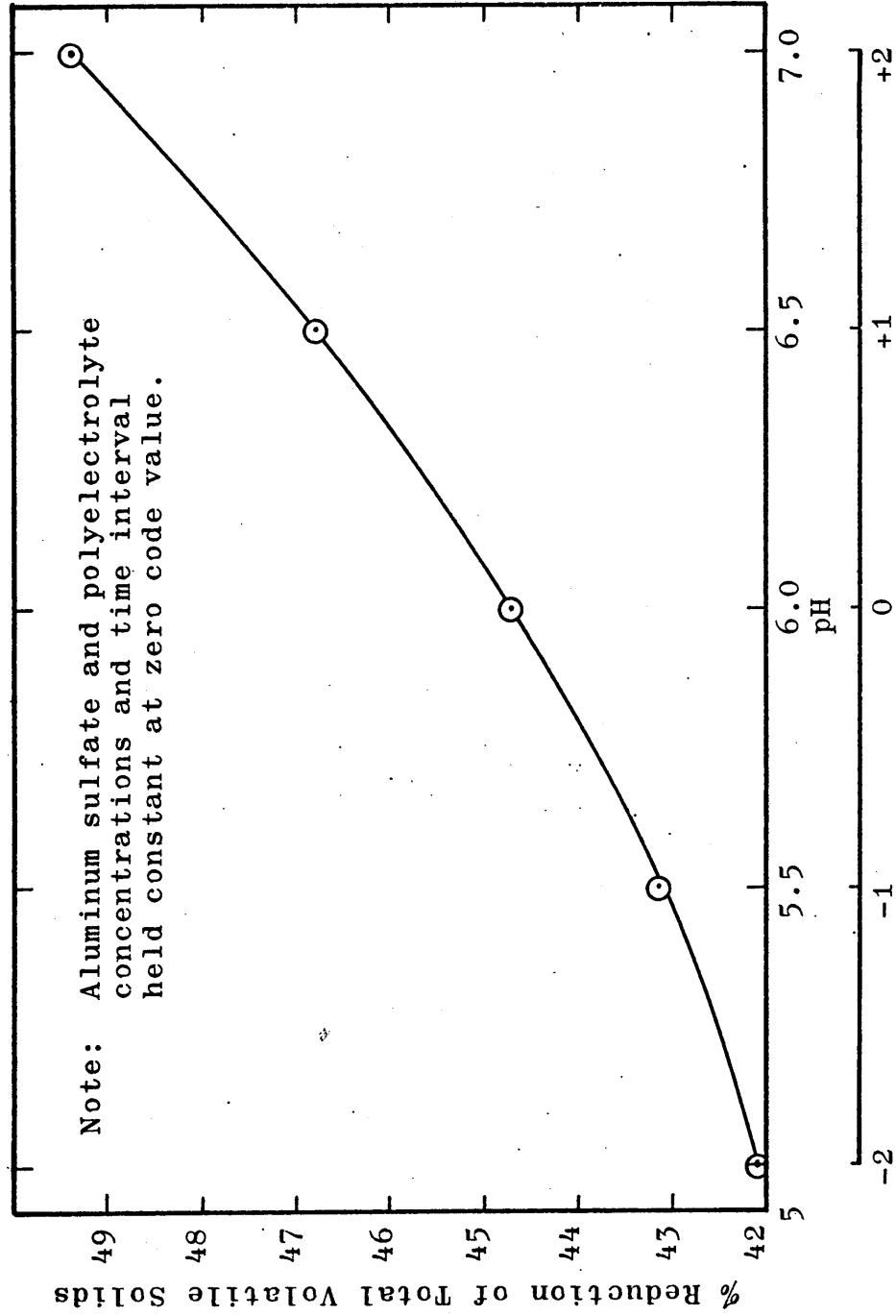


Figure 27. Variation of Volatile Solids with pH for Nalco 675.

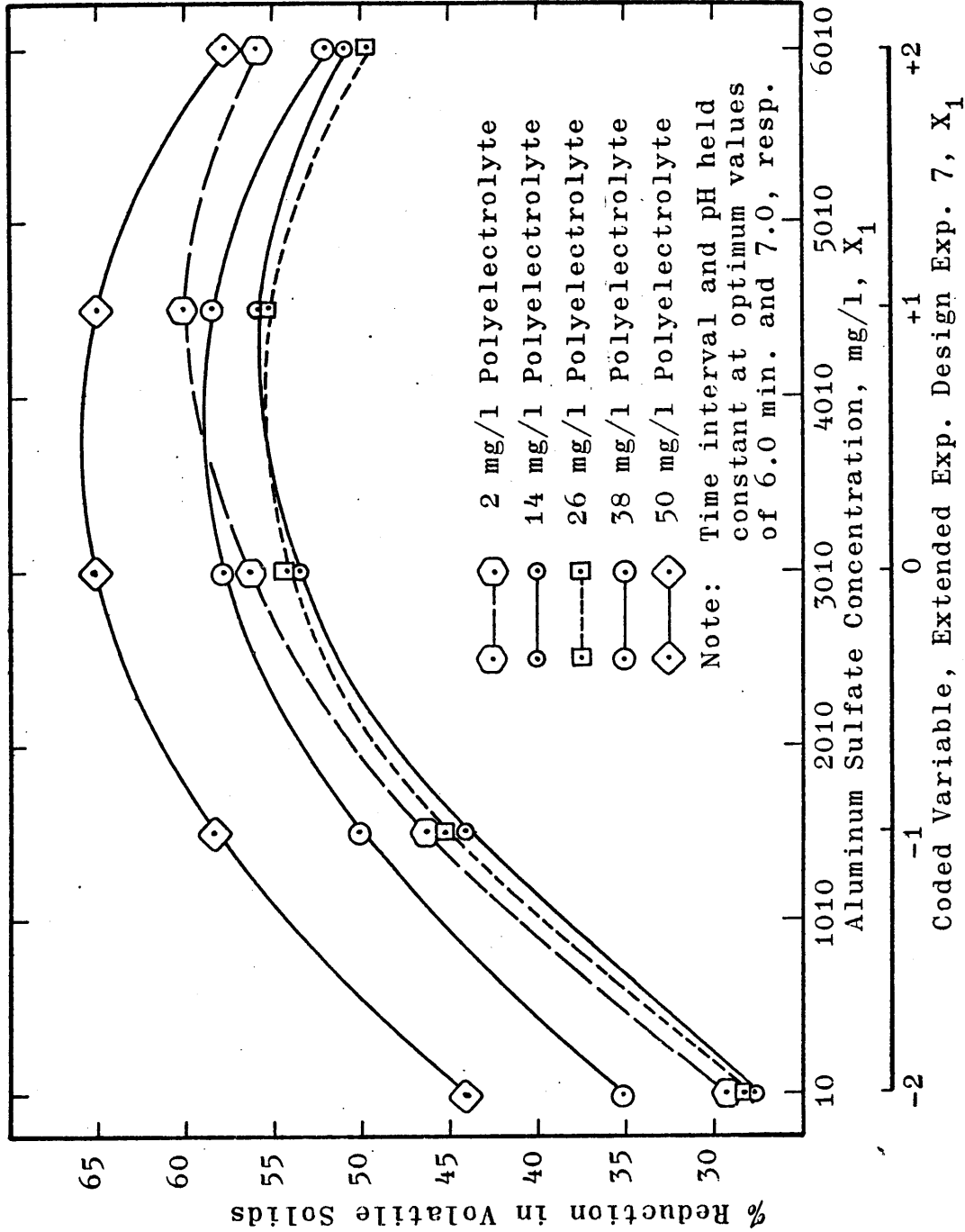


Figure 28. Variation of Volatile Solids with $Al_2(SO_4)_3$ Concentration at Specific Nalco 675 Concs., Exp. 7.

V. DISCUSSION OF RESULTS

The following sections contain a discussion of the results of this investigation.

Nature of Spent Vegetable Tannin Liquor

In reviewing the literature on the treatment of spent vegetable tannin liquor it was immediately evident that individual investigators were unable to insure the constancy of the quality of the vegetable tannin waste. This situation led to disclaimers of applicability of the data and results from one plant to another and thus to a serious impairment of the significance of a given investigation. The large concentration variations of the tannin waste reported in other works were also observed in this investigation. The tannin solutions at the plant in Pearisburg were prepared from weighed mixtures of quebracho barks, and as the percent of tannin varied considerably in concentration for bark even from the same tree, it was probable that the tannin concentration of bark mixtures varied considerably. Tannin concentration measurements at Pearisburg were made with a hydrometer device termed a barkometer, and, since the extracting liquid was well waters of varying solids concentrations, some tannin concentration deviation was expected. The tannin barks were obtained from numerous locations and could be expected to vary in substance.

Finally, operator error in an old, poorly lighted and inadequately equipped plant was to be expected, at least occasionally. The remaining factor affecting the tannin liquor waste was the raw hides. Both the nature of the cowhide and its treatment prior to tanning affected tannin absorption. Combinations of some or all of these reasons led to about a 10 per cent day-to-day variation in the total solids concentration of tannin waste, as noted in Experiment One. This level of variation was prohibitive in attempting to achieve reproducible results. From a practical, long-term treatment viewpoint, the apparent variation of average total solids was critical. The total solids concentration average decreased from a level of 30,000 mg/l to 28,000 mg/l over a four month period. One year earlier, Edwards had reported levels of 38,000 mg/l.

In other characterization tests it was learned that a given sample of the tannin waste decreased considerably in volatile solids concentration after a period of two to three days at temperatures of 20 and 25°C. This change in volatile solids concentration was likely due to microbial action, and was graphically presented in Figure 9. Stability was achieved by cooling the waste to temperatures near 0°C. At this temperature the bacterial activity was reduced, preventing waste deterioration.

From both the chemical process and microbial action viewpoints a single massive sample and cold storage were required to obtain a waste of constant parameters. In other words, the only successful method of consistently procuring an unchanging waste was to have a sufficiently large volume of waste from which smaller test samples could be taken. This technique was followed, but even then stringent mixing procedures were necessary to secure the desired waste quality. Through this approach an experimental design using absolute parameter dimensions rather than parameter-waste ratios was possible. This technique made possible a methodical laboratory approach, with reproducible results. Previous work was limited by inherent error in waste condition to rough estimations of gross independent variables, with variables of lesser importance then being impossible to study.

Gravimetric Relationship of Treated Waste

Gravimetric work was undertaken early in the experimental phase of the investigation, primarily to determine the best gravimetric index to measure colloidal destabilization. This work was accomplished. The total volatile solids was determined to be superior to the other possible gravimetric indices from the standpoint of both accuracy and experimental ease. In this work three systems of treated waste were evaluated for both total and suspended

solids concentrations. These three systems were the completely mixed waste, the clarified portion and the settled sludge. Data obtained in Experiment Three showed that much of the $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ added was remaining in the dissolved state. Of a 1500 mg/l dosage about 40 per cent was found in the clarified section of the treated waste; the remaining 60 per cent was coagulated with the destabilized colloid.

While the precipitated aluminum had probably taken the form of a flocculant aluminum oxide prior to precipitation, this structure seemed an unlikely species for the portion remaining in the clarified section. As the fixed suspended solids concentration for the clarified section of treated waste did not change from the raw waste value of around 450 mg/l, it was evident that the aluminum ion was not being trapped on the filter cake, but was passing through the porous cake structure. This movement would not seem mechanically reasonable for a flocculant structure as described by Riddick and Matijevec in the literature. These observations were obtained from experiments designed for other purposes, but in retrospect were important in providing insight into the behavior of the aluminum ion in solution.

Response Variable Evaluation

There were two phases of testing the response variables. In the first phase repeated testing on the same treated waste allowed calculation of the coefficient of variation. As

listed in Table IX this index permitted comparison of the accuracy of the various dependent variables. As noted earlier the per cent reduction of total volatile solids was selected as the primary response, but others would have been possible choices with little or no loss of accuracy.

During the testing of the 10 aluminum-polyelectrolyte systems the second phase of the response variable evaluation was accomplished. Besides the primary response at least one additional response was measured. The additional responses were then compared with the primary response in a series of graphs, Figures 12 to 15. While the curves approximating the data were drawn linearly, the values of the slopes were not usually one.

Color Removal

It was seen in Figure 14 that the tannin concentration removal was more rapid than the reduction of the total volatile solids. At 50 per cent reduction of total volatile solids a corresponding 75 per cent reduction in tannin concentration was obtained. From a color treatment standpoint this relationship was critical and fortuitous. As described in the literature review the purpose of chemical waste treatment is often directed at color removal; biological treatment at organic solids reduction. While chemical treatment in this investigation generally only removed around half of the total volatile solids it was much more

successful in color removal and would therefore be applicable to a combined chemical-biological sequential treatment system.

Chemical Oxygen Demand

The value of the slope of the chemical oxygen demand-per cent reduction of volatile solids curve was about one. This meant that the volatile solids did not change as to their oxidation requirements as a function of extent of removal from solution. While this seemed normal at first glance, the more rapid removal of the tannin compounds with total volatile solid removal meant that the composition of the total volatile solids was changing. Thus, it would not have been unexpected to have noted a change in the chemical oxygen demand as the total volatile solids concentration decreased.

Settled Volume and Filtration Time

There were two curves with negative slopes, those describing settled volume and filtration time, and they were illustrated in Figures 13 and 14, respectively. LaMer's theoretical prediction on filtration time using polyelectrolytes was applicable to these tests. Filtration of the clarified phase was more rapid as volatile solids removal increased. As there was less suspended solid material to be filtered the filter cakes were thinner, resistance less,

and filtration time shorter. The polyelectrolyte molecule remaining in the clarified section tended to prevent cake compression by maintaining a porous structure of stable channels. The decrease in volume reduction as the volatile solids increased was straightforward: as more of the volatile solids precipitated a greater coagulated volume was acquired.

Turbidity

The transmission turbidity data taken in this investigation was simply not accurate enough, as was evident in the data in Table IX and from the graph in Figure 13. In Figure 12 turbidity as light scattering was presented, and this data correlation was also very poor. However, there was one strong advantage to the light scattering data, that being its facility of operation. No dilution was necessary and the data was taken immediately. The instrument used was an expensive Hach nephelometer; Black and Birkner have reported more satisfactory results using the more sophisticated Brice-Phoenix Light Scattering Photometer, Universal Series 2000. Future turbidity data acquisition is recommended with an instrument of equivalent caliber.

Independent Variable Evaluation

A discussion of four independent variables studied in this investigation follows.

Aluminum Sulfate Concentration

The reduction of total volatile solids showed an expected relationship with aluminum sulfate concentration and was illustrated in Figure 17 for the different aluminum sulfate-polyelectrolyte systems. Figure 18, a graphical presentation of the average results of the individual polyelectrolyte types was easier to follow. Beyond some critical value of aluminum sulfate concentration, additional aluminum sulfate was searching for smaller and smaller quantities of colloidal waste material. The result was, of course, a decrease in the marginal efficiency of organic matter removal with increasing alum concentration. It was evident in Figure 18 that the slope of the curve remained relatively constant up to 3,000 mg/l; beyond this value increasingly smaller amounts of volatile solids were removed for constant aluminum sulfate concentration intervals. Thus, the maximum removal efficiency occurred at an aluminum sulfate concentration of 3,000 mg/l. As the initial total volatile solids concentration is 21,000 mg/l, the optimum total volatile solid-aluminum sulfate ratio was 7 to 1. The slight dip in volatile solids reduction beyond an aluminum sulfate concentration of 4,800 mg/l may be due to entrance to the re-stabilization zone described by Teot and others. In comparing the relative importance of the independent variables it was obvious from Figures 18, 20, 22, and 27 that the

aluminum sulfate concentration was the most important. This variable affected the per cent reduction in volatile solids over the maximum 50 per cent range. The maximum effect of any of the other independent variables was over a range of about 10 per cent reduction in volatile solids.

Polyelectrolyte Concentration and Type

The behavior of the system in terms of the polyelectrolyte concentration and its effect on colloidal destabilization is more difficult to explain. The various polyelectrolytes manifested an individual behavior pattern, as was illustrated in Figure 19. In these curves there was no consistency between curve shape and polyelectrolyte type. However, in collation of the two best performers of each polyelectrolyte type in Figure 20, the anionic type was superior in performance to the cationic type. Maximum colloidal destabilization was attained at highest polyelectrolyte concentrations, but the decreasing reduction of volatile solids at the central aluminum concentration was not understood. This performance was later repeated in the extended testing sequence as shown in Figure 25. The superior performance of these anionic polyelectrolytes was surprising in that it had been expected that the cationic polyelectrolytes with their positive charges would be more effective in destabilizing the negatively charged colloidal particles. In the design of the experiment six cationic polyelectrolytes were tested

while only three anionic polyelectrolytes were evaluated. The reasons for this anionic superiority will be considered later in the mechanism section.

Time Interval

The data for the differing aluminum sulfate-polyelectrolyte systems was consistent according to polyelectrolyte type. As was evident in Figures 21 and 22 there was severe deterioration of the ability of the cationic polyelectrolyte to destabilize a colloidal system when it was added after the aluminum sulfate. When the cationic polyelectrolyte was added prior to aluminum sulfate it was about five per cent more effective in reducing the volatile solids than when added afterwards. This phenomenon was qualitatively true for all cationic polyelectrolytes. The opposite effect was noted for anionic polyelectrolytes; the longer the delay in adding the polyelectrolyte the better the per cent reduction in volatile solids. In fact, consideration of Figure 22 made it clear that the anionic polyelectrolyte really had no effect in helping or hindering colloidal destabilization until after at least a 1.2 minute time interval. As the polyelectrolyte chosen for the extended test sequence was an anionic polyelectrolyte the final experimental design doubled the time interval to be investigated to a six minute range (0 to 6 minutes). Unfortunately, as seen in Figure 27, this range was still

not sufficient as the maximum volatile solids removal was attained at the longest time interval.

It was interesting to note that the magnitude of the removal of volatile solids due to the time interval was around five per cent, the same value as attained by the polyelectrolyte concentration. It was equally important, therefore, to choose the proper time of polyelectrolyte addition as well as the proper concentration. Previous investigators who tested various polyelectrolytes in conjunction with aluminum sulfate at a constant time interval were certainly not obtaining an accurate estimation of the true effectiveness of their polyelectrolytes.

pH

The results obtained for the pH variable were presented in Figure 27. It was noted that volatile solids removal increased as pH increased from 5 to 7. These results were limited to an anionic polyelectrolyte-aluminum sulfate system which precluded definite proof as to whether the aluminum or polyelectrolyte substances were most affected by the pH. However, in the region between pH 5 and 7 the hydrolyzed metallic state of the aluminum ion is the same, $Al_8(OH)_{20}^{4+}$, and previous investigators have described decreasing effectiveness as the pH increases above the range 5.6 to 6.0. It is believed that the increased effectiveness observed in this experiment was partially due to changing

polyelectrolyte structure with increasing hydroxyl ion concentration. With a negatively charged anionic polyelectrolyte, increased hydroxyl ion migration into the polyelectrolyte membrane would cause a more strictured polyelectrolyte conformation. This increased, more open rigidity would lead to a more effective net for holding the hydrolyzed aluminum ion flocs in position.

Another consideration was the manner of pH control. As the aluminum sulfate was introduced to the tannin waste, hydrolyzation occurred and the pH attempted to drop. This drop was prevented and the pH maintained constant at a predetermined value by the addition of a concentrated solution of potassium hydroxide. The higher the required value of constant pH, the greater the quantity of the potassium hydroxide that was added. The maximum quantity added was around six grams, and, while the potassium ion has a charge of only plus one, this large positive ion concentration undoubtedly helped in destabilizing the colloidal waste.

Optimum Values of Independent Variables for Colloidal Destabilization-Economic Considerations

The final experiment was undertaken to establish the best values for treating the colloidal tanning waste. The best values for the time interval and pH were between three and six minutes and seven, respectively. The aluminum

sulfate-polyelectrolyte concentration combinations were examined in Figure 28 for the best polyelectrolyte, Nalco-lyte 675. The greatest removal, 65 per cent volatile solids reduction, occurred at an aluminum sulfate concentration of 3010 mg/l and a polyelectrolyte concentration of 50 mg/l. It was interesting to note that 60 per cent removal was obtainable using the lowest polyelectrolyte concentration of 2 mg/l and an aluminum sulfate concentration of 4510 mg/l. The much higher aluminum sulfate concentration made this concentration combination unfavorable economically. At lower treatment levels, 56 per cent reduction in volatile solids was obtainable using 2 mg/l polyelectrolyte and 3010 mg/l aluminum sulfate. At these conditions there was 8.5 per cent less removal but only four per cent of the polyelectrolyte used at 50 mg/l levels was required. As the polyelectrolyte is expensive, \$1.00/pound, these latter values of 2 mg/l polyelectrolyte and 3010 mg/l aluminum sulfate probably represented the best compromise of degree of treatment and expense. It must be remembered that chemical treatment is generally succeeded by biological treatment which is capable of less expensively processing marginally removable colloidal matter. The major purpose of chemical treatment is color removal. Extrapolation of the curve in Figure 15 estimated 85 per cent reduction of color as measured by tannin concentration at 56 per cent

reduction in volatile solids. The removal of the remaining 15 per cent color would require the much higher 50 mg/l polyelectrolyte concentration, and would, therefore, be very expensive indeed.

Theoretical Consideration of Polyelectrolyte Mechanism

There were three significant facts upon which to base a comparison of the mechanisms of anionic and cationic polyelectrolytes. 1) The anionic polyelectrolytes gave superior performance to the cationic polyelectrolytes when the other independent variables were held constant. 2) Anionic polyelectrolytes were only efficient in destabilization when added after the aluminum sulfate. 3) Cationic polyelectrolytes were only efficient in destabilization when added before the aluminum sulfate.

It would definitely appear that entirely different mechanisms are functional as a result of the anionic and cationic polymer additions. The negatively charged anionic polyelectrolytes largely form molecular bridges between positively charged hydrolyzed aluminum floc particles bringing about a larger, more dense floc which enhances agglomeration of the colloidal material in the waste and results in a floc that is rapidly removed by sedimentation. Bridging is an effective mechanism in situations where the polymer is added after the aluminum ion has been allowed to form insoluble hydrous oxides. The time of addition of anionic

polyelectrolyte is clearly critical in the colloidal destabilization process. Sufficient time must be allowed for the formation of aluminum hydrous oxide floc and for the subsequent colloidal flocculation. Only then should the anionic polyelectrolyte be added to form the larger, quicker settling particles by bridging. Earlier addition of the polyelectrolyte results in premature bridging with resulting loss of destabilizing power of the aluminum ion. Unfortunately, this time interval is probably a function of several factors, for example, rate of mixing, aluminum concentration, waste concentration and others, and is therefore difficult to pinpoint. A positive fact is that it should not make much difference if the polyelectrolyte is added later than the least possible time interval.

As noted, the cationic polymer gave optimum results when added prior to the aluminum sulfate. The mechanism responsible for this effect is probably electrostatic neutralization of the negative charge associated with the colloidal matter in the wastewater. As both components of a cationic polymer-aluminum ion system have the same charge, removal efficiency will be greatest for polyelectrolyte addition while the negatively charged colloidal concentration is still high, that is, before the competing aluminum ion is added. If the cationic polymer is added after the aluminum sulfate, it is apparently doing little more than what

additional aluminum ion could accomplish. The physical appearance of the destabilized colloidal waste for cationic polyelectrolytes at different time intervals was very striking. When the cationic polyelectrolyte was added prior to the aluminum sulfate, dark brown coagulated masses were quickly evident; later addition of aluminum sulfate produced a different, lighter brown precipitate. When added simultaneously, the two coagulants were obviously in competition as they produced two different types of precipitates. There was less evidence of the precipitate produced by cationic polyelectrolyte than in the previous test. When the cationic polyelectrolyte was added following the aluminum sulfate there was no indication of any cationic polyelectrolyte induced destabilization. In summary, all results suggested that aluminum ion-cationic polyelectrolyte system was one of rivalry between two components.

The material presented in the previous two paragraphs is the prevailing mechanistic theory applied to this investigation in a manner suggested by the data and results. Another exposition can be made concerning the anionic polyelectrolyte-aluminum ion system. The synergism of the system is clear. Anionic polyelectrolytes, alone, are incapable of destabilizing colloidal wastewater. In conjunction with the aluminum ion, colloidal removal is more efficient than with the aluminum ion alone. A physical picture of the

bridged aluminum floc would be similar to that of a net, or a three dimensional net with openings offset. At high polyelectrolyte concentrations the negative charge should become more significant than just from a bridging viewpoint. It is known that addition of negatively charged particles to a negatively charged colloidal system further stabilizes the system through electrostatic repulsion. Similarly the highly charged negative polyelectrolytes should repel the negatively charged colloidal particles, even if the polyelectrolytes are partially neutralized in the net structure. The polyelectrolyte-colloid electrostatic repulsion will reflect the sol particles closer to the aluminum ion. This has the effect of increasing the counter ion concentration in the sol particle atmosphere and reducing the double layer. The same result may be considered from another viewpoint. In the reflection of the ion away from the polyelectrolyte surface, the effective volume available to the sol particles is reduced, and the effective counter ion concentration thus increases. This leads to increased colloidal destabilization. Bridging, provable by electron and microscopy and indicated by results of the investigation, is of obvious importance in explaining the mechanism of coagulation in this work. It does seem reasonable that the nature of bridging should at high polyelectrolyte concentration lead to related destabilization phenomena.

Jar Testing Procedure

Coagulation testing is not always comparable because there is no standard jar test procedure. Containers, mixing speeds and time lengths, coagulant form (solid or solution), type of stirrer, and other factors are not standard. There is a need to establish such a procedure. Testing of given variables could then be undertaken, introducing planned deviations from the standard procedures, and reported as such. Comparison of similar colloidal experimentation would then be much more valid.

Limitations of the Investigation

Theoretical considerations made in this investigation were hampered by the limitations imposed by any applied research problem. The natural waste system was ever varying and impossible to reproduce synthetically. The tannin waste had a high salt concentration, and pH control caused variance in ion concentration. For these reasons the time interval variable should be retested using a synthetic, reproducible colloidal system such as the Minusil colloid described by LaMer and his coworkers.

Massive aluminum ion concentrations make the study of other independent variables very difficult. Further investigations of aluminum-polyelectrolyte systems should incorporate lower aluminum concentrations.

VI. CONCLUSIONS

The principal conclusions drawn from this work are as follows.

1. Total volatile solids, tannin, and COD removal are suitable response parameters for spent tan liquor waste coagulation testing.
2. Color removals from spent tan liquor wastes approaching 90 per cent are possible using an aluminum ion-polyelectrolyte chemical coagulation system.
3. A seven to one total volatile solid-aluminum sulfate ratio gives maximum removal efficiency of total volatile solids.
4. Anionic polyelectrolytes give better volatile solids removal results than cationic polyelectrolytes when used in conjunction with aluminum sulfate.
5. The best polyelectrolyte tested was a long chain anionic polymer, Nalcolyte 675.
6. The optimum time interval between addition of alum and anionic polyelectrolyte is a minimum of three to six minutes, and anionic polyelectrolytes are ineffective when added prior to or simultaneously with the aluminum ion.

7. Cationic polyelectrolytes give best performance when added prior to the alum.
8. The optimum pH for the aluminum-anionic polyelectrolyte system was 7.
9. The major mechanism of destabilization of the anionic polyelectrolyte was bridging of the aluminum ion floc.
10. The method developed in this investigation was successfully applied to the treatment of spent vegetable tannin liquor.

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VIII. APPENDIX

APPENDIX A

Included in this Appendix are the data from Experiments 6A through 6J and 7. In the data headings response No. 1 is the per cent reduction in total volatile solids; response No. 2 is the per cent light transmission for tannin concentration; response No. 3 is the per cent reduction of C.O.D., response No. 4 is the per cent reduction in volatile suspended solids; response No. 5 is the settled volume of the concentrated phase after 18 hours; response No. 6 is the filtration time for the volatile suspended solids test; response No. 7 is the per cent light transmission due to turbidity; and response No. 8 is the light scattering measured in JTU. The independent variable conditions for each test in the Experiment were presented earlier in Tables II, III, IV, and V.

TABLE XIII. DATA FOR EXPERIMENT 6A, CATIONIC NALCOLYTE 605

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 2</u>	<u>Resp. No. 3</u>	<u>Resp. No. 5</u>	<u>Resp. No. 6</u>	<u>Resp. No. 7</u>
1	9.61	35.8	21.1	210	17.0	9.0
2	40.73	42.5	35.8	665	21.0	55.3
3	18.44	40.8	17.2	155	41.0	37.3
4	21.26	40.0	18.3	170	42.0	34.0
5	35.30	57.0	32.1	295	85.0	36.0
6	32.07	27.5	30.3	725	60.0	7.0
7	17.18	43.0	17.2	113	85.0	12.0
8	37.52	57.0	31.2	360	43.0	49.5
9	5.12	30.5	4.2	0	3.5	12.7
10	39.74	56.5	37.2	450	2.5	37.0
11	27.40	51.2	28.5	467	65.0	24.8
12	30.66	45.0	24.3	310	3.5	28.0
13	37.08	32.5	33.8	770	23.0	23.0
14	36.13	30.3	31.7	690	35.0	19.9
15	38.42	33.0	35.2	715	35.0	22.2
16	31.87	51.5	27.3	452	65.0	30.0
17	27.34	50.9	29.2	435	80.0	30.7
18	18.28	25.0	16.6	260	26.0	56.7
19	46.03	52.0	42.9	445	65.0	24.8
20	30.28	50.8	23.2	210	65.0	31.3

TABLE XIV. DATA FOR EXPERIMENT 6B, CATIONIC NALCOLYTE 634

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 2</u>	<u>Resp. No. 4</u>	<u>Resp. No. 5</u>	<u>Resp. No. 6</u>	<u>Resp. No. 7</u>
1	24.50	37.5	29.8	300	13.0	40.0
2	38.78	52.7	58.2	440	11.5	42.5
3	25.62	34.1	33.2	310	12.0	40.3
4	24.84	37.5	47.8	285	11.0	35.8
5	39.45	52.8	47.8	440	12.5	47.2
6	42.33	57.5	60.4	450	18.0	51.3
7	24.06	38.3	47.8	305	15.5	40.3
8	44.47	58.8	61.3	540	9.0	64.2
9	4.92	25.3	21.0	1	6.0	12.0
10	43.40	53.3	59.8	410	14.0	39.2
11	36.34	46.2	70.8	400	11.5	41.2
12	36.92	47.0	70.9	430	18.0	44.2
13	37.31	46.5	60.4	405	11.0	48.0
14	36.09	43.5	62.5	375	12.0	37.7
15	36.60	45.0	70.2	385	14.0	40.7
16	34.00	48.3	42.1	415	14.0	48.3
17	35.61	49.3	58.4	385	12.5	50.0
18	36.00	44.5	59.7	370	12.0	42.5
19	37.12	46.0	60.3	388	10.5	43.5
20	35.70	45.5	40.0	382	13.5	44.0

TABLE XV. DATA FOR EXPERIMENT 6C, CATIONIC NALCOLYTE 603

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 5</u>
1	24.1	300
2	41.9	462
3	23.8	300
4	24.6	310
5	42.5	460
6	42.0	440
7	25.3	280
8	44.2	420
9	7.0	0
10	45.9	420
11	35.5	370
12	34.1	350
13	38.7	447
14	35.1	370
15	33.9	390
16	36.0	375
17	34.1	395
18	32.0	390
19	33.0	380
20	32.0	403

TABLE XVI. DATA FOR EXPERIMENT 6D, CATIONIC NALCOLYTE 632

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 5</u>
1	33.33	378
2	45.39	615
3	34.54	435
4	37.16	415
5	49.41	580
6	49.36	515
7	30.28	355
8	51.63	550
9	5.11	8
10	49.75	550
11	44.18	470
12	43.16	470
13	40.82	490
14	43.36	490
15	39.72	480
16	42.48	490
17	41.56	485
18	45.00	450
19	41.61	450
10	42.44	450

TABLE XVII. DATA FOR EXPERIMENT 6E, NONIONIC NALCOLYTE 670

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 2</u>	<u>Resp. No. 7</u>
1	29.1	48.0	60.5
2	48.2	70.8	88.2
3	30.7	45.8	48.0
4	30.6	40.5	61.5
5	48.2	73.0	88.5
6	45.8	69.0	76.0
7	27.1	27.1	49.3
8	44.9	68.0	63.0
9	4.0	30.0	14.5
10	51.9	71.2	73.0
11	36.2	49.5	56.0
12	40.8	62.3	66.5
13	45.6	61.7	45.6
14	45.9	63.3	45.9
15	44.2	63.0	44.2
16	45.9	63.5	45.9
17	41.0	62.8	41.0
18	45.5	62.4	45.5
19	44.6	62.5	44.6
20	44.2	63.0	44.2

TABLE XVIII. DATA FOR EXPERIMENT 6F, CATIONIC NALCOLYTE 607

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 7</u>
1	33.90	42.3
2	48.34	48.0
3	37.12	58.5
4	33.22	44.5
5	49.85	79.5
6	52.59	83.3
7	34.15	42.0
8	50.73	71.0
9	5.51	9.0
10	46.98	66.0
11	43.95	62.0
12	39.61	51.0
13	43.90	59.2
14	39.02	64.0
15	42.00	60.0
16	42.39	59.0
17	42.24	50.0
18	43.41	55.5
19	42.97	63.5
20	41.12	57.0

TABLE XIX. DATA FOR EXPERIMENT 6G, ANIONIC NALCOLYTE 675

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 8</u>
1	34.7	263
2	54.2	225
3	37.4	265
4	34.9	217
5	51.8	375
6	53.3	218
7	43.2	258
8	52.0	210
9	0.3	14
10	51.8	207
11	48.3	462
12	48.6	313
13	40.8	212
14	46.0	215
15	47.3	218
16	44.2	218
17	45.1	225
18	48.7	218
19	45.3	217
20	45.2	222

TABLE XX. DATA FOR EXPERIMENT 6H, ANIONIC NALCOLYTE 672

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 4</u>
1	35.4	51.08
2	51.9	68.97
3	34.4	55.01
4	31.4	44.17
5	51.2	58.54
6	48.2	56.37
7	38.4	49.73
8	51.0	66.53
9	5.9	20.46
10	48.1	64.50
11	44.7	47.97
12	47.4	64.50
13	39.6	46.48
14	47.0	61.65
15	41.9	49.59
16	42.4	51.62
17	40.3	52.17
18	43.3	51.63
19	43.7	49.50
20	43.1	43.90

TABLE XXI. DATA FOR EXPERIMENT 6I, ANIONIC NALCOLYTE 674

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 8</u>
1	28.7	230
2	45.1	340
3	28.2	208
4	27.0	198
5	48.7	410
6	44.5	353
7	25.9	135
8	48.7	361
9	4.4	73
10	51.5	320
11	38.2	225
12	38.9	285
13	42.6	300
14	47.4	350
15	45.6	355
16	42.2	365
17	44.1	355
18	43.3	343
19	39.9	340
20	40.5	355

TABLE XXII. DATA FOR EXPERIMENT 6J, CATIONIC NALCOLYTE 610

<u>Test No.</u>	<u>Resp. No. 1</u>	<u>Resp. No. 6</u>
1	27.6	12.5
2	42.2	4.5
3	25.4	13.5
4	25.8	10.5
5	45.8	5.0
6	42.0	10.0
7	27.3	14.0
8	40.6	11.0
9	2.4	6.6
10	52.0	5.3
11	33.5	12.0
12	35.5	8.3
13	43.8	12.3
14	42.6	13.0
15	43.4	13.4
16	39.7	12.5
17	44.3	14.1
18	41.5	13.4
19	44.8	14.8
20	39.8	15.5

TABLE XXIII. DATA FOR EXPERIMENT 7, EXTENDED PARAMETER

EXPERIMENT USING ANIONIC NALCO 675

Test No.	Resp. No. 1	Resp. No. 2	Resp. No. 3	Resp. No. 4	Resp. No. 5	Resp. No. 6	Resp. No. 7	Resp. No. 8
1	29.9	45.0	25.1	46.6	475	9.3	49.0	235
1A	27.7	42.5	27.3	45.4	370	10.7	51.0	155
2	44.8	56.8	43.8	57.4	660	4.5	53.8	415
2A	43.5	66.2	45.2	72.9	605	4.5	81.5	335
3	31.0	46.0	24.7	56.5	420	8.8	56.2	260
3A	32.2	47.0	31.2	53.0	370	9.5	63.5	190
4	28.5	41.1	39.0	47.3	400	9.0	44.9	200
4A	29.8	48.0	28.5	51.3	395	9.3	60.5	190
5	35.4	52.0	33.7	39.2	458	9.8	45.5	182
5A	35.7	53.0	35.8	92.8	460	11.5	48.0	115
6	47.7	64.1	45.2	63.2	653	2.7	61.9	505
6A	46.8	63.1	45.3	63.2	690	4.5	67.5	350
7	48.3	66.0	49.1	69.9	565	8.5	69.3	540
7A	46.6	70.5	48.2	64.8	620	12.4	76.0	340
8	47.1	66.5	48.1	57.9	640	10.5	60.3	470
8A	49.3	70.0	46.4	58.2	625	14.9	70.7	342
9	41.8	57.3	37.0	58.7	452	6.5	60.5	268
9A	43.0	64.0	41.3	88.7	490	0.3	89.4	28
10	49.3	71.0	48.5	62.4	578	11.0	73.1	480
10A	49.2	71.5	47.9	71.1	620	6.5	81.5	340
11	46.5	64.3	44.2	64.3	620	4.5	69.0	475
11A	49.7	71.0	48.2	82.9	650	2.3	90.5	210
12	44.1	64.2	39.8	61.8	675	4.5	63.9	450
12A	45.8	62.0	37.3	55.1	720	6.3	59.5	300
13	33.2	53.9	32.1	38.5	440	10.8	44.3	154
13A	33.6	55.0	33.5	44.1	435	11.3	43.3	82
14	38.5	50.0	37.2	69.0	378	4.8	71.0	250
14A	32.9	50.0	24.2	62.6	400	6.2	66.0	170
15	47.5	68.2	43.2	57.8	670	13.3	66.0	440
15A	49.4	71.5	38.1	67.6	600	10.7	79.7	320
16	38.1	55.9	38.4	57.6	422	7.8	56.8	220
16A	37.2	55.5	39.2	60.3	402	7.9	60.2	210
17	3.3	33.5	5.2	13.8	10	6.3	11.3	30
18	48.8	71.7	48.2	69.7	750	4.2	77.0	550
19	41.8	59.2	40.1	44.1	495	11.3	50.0	273
20	42.1	58.9	38.2	61.6	530	6.8	58.3	404
21	41.59	67.0	38.2	69.0	740	6.3	82.3	390
22	43.21	67.2	39.9	64.6	605	5.5	71.3	470
23	38.15	61.0	39.9	63.2	520	4.1	71.0	375
24	41.69	71.3	39.0	65.9	600	9.3	78.5	440
25	36.9	65.0	38.2	52.9	540	5.4	56.4	370
26	37.8	67.0	32.2	60.2	717	9.0	70.5	410
27	36.4	78.3	38.4	61.2	665	7.4	68.4	410
28	39.1	66.0	38.2	61.3	680	8.5	73.0	410
29	40.8	64.3	38.2	61.5	635	8.5	66.3	325
30	40.2	66.5	38.1	63.9	585	8.2	70.0	342

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EVALUATION OF PARAMETERS AFFECTING THE COLLOIDAL
DESTABILIZATION OF SPENT VEGETABLE TANNIN LIQUOR

by

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Abstract

The overall objective of this investigation was to develop a chemical method for treating spent vegetable tannin liquor. Vegetable tannin wastes are plagued by a multitude of undesirable characteristics, principal of which is a color problem. Historically, chemical coagulation processes have been successful in reducing color associated with industrial wastes.

The coagulants tested were aluminum sulfate and polyelectrolytes. In addition, the pH and the time interval between aluminum ion and polyelectrolyte addition were studied. Considerable difficulty was encountered in obtaining a waste product of uniform characteristics over an extended period. This problem was solved by storing a large quantity of waste of typical properties at temperatures near zero degrees centigrade.

The most important variable affecting the treatment of the tannin waste was the aluminum sulfate concentration. Maximum destabilization efficiency was achieved at 3,000 mg/l and a waste volatile solids to aluminum sulfate ratio

of seven. Anionic polyelectrolytes, used in conjunction with the aluminum sulfate, gave superior performance to aluminum ion-cationic polyelectrolyte systems. The cationic polyelectrolytes were most efficient when added prior to the aluminum sulfate, the anionic polyelectrolytes most efficient when added afterwards. The suggested mechanism for the anionic polyelectrolyte was chemical bridging between aluminum ion flocs followed by rapid settling. For cationic polyelectrolytes, charge neutralization of sol particles in competition with the aluminum ion was evident. The optimum pH was seven with a range of 5 to 7 being tested. For the best polyelectrolyte tested, anionic Nalcolyte 675, the use of optimum conditions produced reductions of volatile solids of 65 per cent. At these reduction levels upwards of 90 per cent color removal, as measured by tannin concentration, was achieved. For Nalcolyte 675 the maximum treatment was observed using 50 mg/l of polyelectrolyte, but satisfactory performance of 56 per cent volatile solids reductions was attained through the use of 2 mg/l polyelectrolyte.

The investigation was successful in defining economically feasible conditions for chemical treatment which was effective in color removal. Subsequent biological treatment would be required for adequate organic matter reduction.