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## COAGULATION IN WASTE

BY

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A THESIS

#### PRESENTED IN PARTIAL FULFILLMENT OF

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#### ABSTRACT

#### COAGULATION IN WASTE WATER TREATMENT

This paper emphasizes a practical approach to the coagulation of domestic waste water. A portion of the paper is a synopsis of current published literature on the subject. Laboratory studies on the coagulation of raw domestic waste waters were conducted to provide the basis of a practical procedure for the evaluation and design of a coagulation process. Studies included the development of a relationship between the B.O.D. and the soluble and solids portion of two waste tests. The jar test was used for the studies on the coagulation process. The final section of the paper outlines the chemical cost factors involved in process selection. APPROVAL OF THESIS

COAGULATION IN WASTE WATER TREATMENT

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FOR

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#### FACULTY COMMITTEE

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#### I. INTRODUCTION

Contamination of natural waters has become a major problem in our society. Much of the contamination is the result of heavy solid loadings, both organic and inorganic, being discharged into the waterways. The self purification capacity of the waterway is often overburdened and serious pollution problems arise. Contaminants are from two major sources -- industrial and domestic waste.

Present treatment methods for domestic waste water consist of primary and secondary treatment processes. Primary treatment consists of the physical separation of about 35 per cent of the solids from the liquid phase by gravity settling. Standard secondary treatment is a biological process which, in combination with primary treatment, results in an overall solids reduction of about 75 to 90 per cent.

The high quantities of waste water being discharged in densely populated areas demand a consistant high degree of solids removal, often in excess of that which can be obtained by standard biological treatment processes. This high degree of solids removal can often be achieved by chemical coagulation in conjunction with other standard treatment processes. Chemical coagulation is a unit process for the removal of colloidal solids from solution. The process consists of the addition of chemicals as slurries, solutions or in the dry form; a rapid mix to quickly disperse the chemicals throughout the solution; flocculation or a slow agitation period to permit floc growth and agglomeration of particles; and separation of solids and liquid phases.

The chemicals normally added consist of:

- A coagulant -- usually the salts of a trivalent metal such as iron and aluminum.
- 2. A control chemical for pH and alkalinity -- usually lime.
- 3. A coagulant aid such as activated silica or a polyelectrolyte.

The type, amount, order and point in the process at which the chemical additions are made are important and are best determined by field measurements.

The aim of chemical treatment is to provide a desired quality effluent at the required plant capacity with the most economical overall operation.

Too little chemical addition will not provide the desired quality. Overfeed of chemicals is a waste -- may result in interference with filtration and may result in undesirable chemical residuals in the plant effluent. If the sludges are to be separately digested, the effect of certain chemical additions must be carefully evaluated. This paper presents a literature review of the chemical coagulation process, laboratory experiments aimed at a practical evaluation of the process, and an evaluation of results with regard to applications in the field. The laboratory work is restricted to two specific domestic waste waters, one containing an appreciable industrial contribution.

#### II. SOLIDS IN WASTE WATER

The quantity of solids in waste water generally represents less than a thousand parts of solids per million parts of water (expressed as milligrams per liter, mg/l). The role these solids play in waste water quality is of extreme importance. A significant amount of biochemical oxygen demand (BOD) is associated with these solids and even the relatively small concentration, when multiplied in the millions of gallons of wastes, often exceeds the natural assimilation capacity of many waterways.

#### Classes of Solids

Solids are classed as either suspended solids or filterable solids. These main classifications are further divided as shown in Figure No. 1. Suspended solids are defined as those retained in a Gouch crucible in accordance with a standard test while those not retained are termed filterable solids. Suspended solids are classified further as settleable solids which will settle in an Imhoff cone. Those which will not settle are termed colloidal. Filterable solids are classified further as dissolved solids or colloidal solids.

All solid classifications may be further described by identifying the organic (volatile) portion and the mineral (fixed) portion.



CLASSIFICATION OF SOLIDS IN WASTE WATER

Standard waste water treatment processes have little effect on the dissolved solids and solid removal is confined to settleable and colloidal solids.

#### Settleable Solids

These "larger than colloidal" solids have a relatively small surface to volume ratio and their density is usually that under the influence of gravity they will tend to settle downward and out of solution. The rate of settling depends on the particle size, weight, shape and on the resistance, or viscosity, of the containing liquid.<sup>9</sup>

#### Colloidal Solids

Colloids may be considered as particles which cannot be separated by the force of gravity alone and can remain in suspension indefinitely.

The range of particle size for the classification of colloids is somewhat arbitrary. In general the range may be considered 1 millimicron or mu (one mu equals onemillionth of a millimeter) to several hundred or a thousand mu. At the upper limit, the particles generally can be separated from solution by physical means and the particles are referred to as suspended solids. Classification based on relative size is shown in Figure No. 2. At the lower end of the colloidal range, dispersed particles consisting of small, simple molecules or ions constitute a solution.



PARTICLE SIZE CLASSIFICATION

The most important physical property of the colloid is its small mass relative to its surface area. The behavior of a colloid is greatly controlled by the nature of its surface properties. Because of their small mass, gravitational effects on colloids are unimportant.

The basic physical and chemical characteristics of colloids are important to the understanding of the factors influencing chemical treatment. The five most important properties of colloids are:

Electrical properties
 Brownian movement
 Adsorption
 Hydration
 Forces of attraction

#### Electrical Properties

All colloids possess electrical charges of varying magnitude referred to as the electrokinetic charge. This charge is acquired on the surface of the colloids as a result of ionization of surface components or preferential adsorption of ions from solution.<sup>17</sup> Particles of similar composition tend to acquire a like charge. The like charges create an electrostatic repulsion between the charged particles stabilizing the dispersion by decreasing the probability of collisions which could affect aggregation of the particles. The particle will migrate (particle mobility or electrophoresis) to an oppositely charged pole. This movement is independent of the particle size or shape and

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dependent on the magnitude of the electrokinetic charge that surrounds a particle (Zeta potential). The Zeta potential is directly proportional to the particle mobility for a given liquid at a constant temperature as given by the following formula:

$$ZP = UV4\pi$$

where:

ZP = Zeta potential (MV millivolts) U = Mobility of the particle (microns/sec/volt/cm) V = Viscosity of suspending liquid D = Dielectric constant of suspending liquid

In practice the mobility (U) is measured in an electrophoresis cell by timing the rate of travel of an individual colloid (microns per second) and measuring the voltage drop between electrodes (volts per centimeter between electrodes). Measurement is made with a proprietary meter or a Briggs microelectrophoresis cell. At 25°C. the Zeta potential is approximately thirteen times the electrophoretic mobility and ranges from -12 to -25 mv in natural waters. Zeta potential is considered by many as the predominant factor affecting stabilization.

If particles are oppositely charged, electrostatic forces will result in an attraction.

#### Brownian Movement

The motion imparted to colloidal particles as a result of their impact with thermally excited molecules of the

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dispersing medium is termed Brownian movement. The action causes collisions of colloidal particles and under the proper conditions can result in aggregation.

#### Adsorption

Colloidal particles have a tendency to concentrate or adsorp other substances at their surfaces. The quantity of substance adsorbed by a given adsorbent depends on the nature of the substance, its concentration, and the temperature.

#### Hydration

The surfaces of some colloids have a strong affinity for water (hydrophilic colloids) and they acquire a shell of water molecules. This shell is bonded to the surface of each particle and shields it from the action of coagulants and contact with other particles.

Colloids with a weak affinity for water (hydrophobic colloids) are not affected by hydration unless a substance is present which has an affinity for both water and the surface of the colloid.

#### Forces of Attraction

Molecular forces between atoms tend to attract. These Van der Waals forces are minute for individual atoms but are additive and significant for a group of atoms. These forces are not considered a dominant colloidal removal mechanism because of the rapid decrease of their effect at distances larger than the molecular diameter of the particles. They may, however, be significant in preventing redispersion of removed particles.

Chemical bonds also hold atoms together with energies many times those of the Van der Waals forces. Hydrogen bonds are of the same order of magnitude as the Van der Waals forces and are of little significance in the direct attachment of colloidal particles, but may be a major force in the attachment of flexible polymer chains to particles.

#### Stability of Colloidal Dispersions

The factors described above may be classed as those promoting solution stability and those tending to separate the matter from solution. The most important factors are listed as follows:

#### Stability Factors

- 1. Electrokinetic charges
- 2. Hydration

Instability Factors

- 1. Brownian movement
- 2. Van der Waals forces

#### Factors which may Affect either Stability or Instability

- Other irons in solution 1.
- 2. Amount of kind of matter present
- 3. pΗ
- 4. Concentration of dissolved solids
- 5. The kind and amount of coagulant
- 6. Order of chemical additions
- Mixing characteristics
- 7.8. Temperature

#### III. COAGULATION

Coagulation is the destabilization and aggregation of a colloidal dispersion to permit particle removal by sedimentation and for filtration. The physical chemistry of coagulation may be considered as:

- 1. The dissociation of the coagulant into positively charged ions which may combine with the negatively charged colloids neutralizing some of the charge on the colloid permitting agglomeration.
- The formation of insoluble complexes (floc) by the reaction of the metal ions with the hydroxide ions (and other available ions such as phosphates, sulfates and chlorides in complex solutions).

The most widely used coagulants for waste water are the salts of iron and aluminum (both supply cations and have positive Zeta potential). Natural and synthetic polyelectrolytes have considerable value as coagulant aids.

#### Aluminum Salts

The most common aluminum salt used for chemical treatment is aluminum sulfate  $(Al_2(SO_4)_3 \cdot 14H_2O)$  marketed dry or in solution as alum. Alum is basic and its zone of best floc formation is at a lower pH than the iron salts. When used at its optimum pH of coagulation, low residual metal is found. Good coagulation is in the pH range of 5.5 to 7.8 with best coagulation at the isoelectric point.

Chemical reactions between the aluminum salts and water (disregarding other ions which may be present) may be written as follows:

$$Al_2(SO_4)_3 \cdot 14H_2O + 6H_2O = 2Al(OH)_3 + 3H_2SO_4$$
  
3Ca(HCO\_3)\_2 + 3H\_2SO\_4 = 3CaSO\_4 + 6CO\_2 + 6H\_2O  
or

 $Al_2(SO_4)_3$   $l^{4}H_2O + 3Ca(HCO_3)_2 \longrightarrow Al(OH)_3$  + 3CaSO<sub>4</sub> + 6CO<sub>2</sub>

#### Iron Salts

Ferric sulfate  $(Fe_2(SO_4)_3 \cdot 2 H_2O)$ , ferric chloride (FeCl<sub>2</sub>), ferrous sulfate (FeSO<sub>4</sub> . 7H<sub>2</sub>O) and chlorinated copperas  $(Fe_2(SO_4)_3 \cdot FeCl)$  are the common iron salts available. The salt used in any particular area is determined by its availability and cost.

Most of the iron salts are highly acidic and pH control is necessary unless sufficient alkalinity is present as a buffer.

Ferric chlorida, ferric sulfate and chlorinated copperas exhibit a dual range of effective pH, one from 4 to 6 and the other from 8 to 10. Copperas has appreciable solubility below pH 8.5 and its use is normally limited to the pH range of 8.5 to 10.5.

Chemical reactions between the iron salts and water (disregarding other ions which may be present) may be written as follows: Ferrous Sulfate (Copperas) FeSO<sub>4</sub> · 7H<sub>2</sub>O  $\longrightarrow$  Fe<sup>++</sup> + SO<sub>4</sub>= Fe<sup>++</sup> + 2 OH<sup>-</sup>  $\longrightarrow$  Fe(OH)<sub>2</sub> 4Fe(OH)<sub>2</sub> + 2H<sub>2</sub>O + O<sub>2</sub>  $\longrightarrow$  4Fe(OH)<sub>3</sub> Ferric Sulfate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 2H<sub>2</sub>O  $\longrightarrow$  Fe<sup>+++</sup> + SO<sub>4</sub>= Fe<sup>+++</sup> + 3OH<sup>-</sup>  $\longrightarrow$  Fe(OH)<sub>3</sub>  $\longrightarrow$  Fe<sub>2</sub>O<sub>3</sub> · xH<sub>2</sub>O Ferric Chloride 2FeCl<sub>3</sub> + 3Ca(OH)<sub>2</sub>  $\longrightarrow$  2Fe(OH)<sub>3</sub> + 3CaCl<sub>3</sub>

Other Coagulants

The following have also shown to be good coagulants:

Lime Sodium Aluminate Aluminum Chloride Chromic Chloride Titanium Tetrachloride

Lime and sodium aluminate have found practical use as coagulants. The remainder are no better than ferric chloride and are of little practical use.

Sodium aluminate has found most of its use in treatment of boiler feed waters. Its use in waste water treatment is discussed in Section VI of this paper.

Lime should be considered in treating waters high in magnesium compounds or in the removal of phosphates.

#### Coagulant Aids

Often the simple addition of iron or aluminum salts does not produce completely satisfactory treatment results, especially in difficult waters. Activated silica and natural and synthetic polyelectrolytes may be added to stimulate floc formation.

#### Activated Silica

Activated silica is a negatively charged colloidal dispersion (sol) formed by the reaction of a dilute solution of sodium silicate with a dilute solution of an acid material of other activant. Activated silica acts to aid in flocculation of the positively charged metallic hydroxide sol formed by the aluminum or iron salts.

#### Polyelectrolytes

Polyelectrolytes are water-soluble high-molecularweight polymers that contain groups capable of being converted to polymer molecules of highly charged irons polymers having ionizable sites).

Polyelectrolytes generally are used in conjunction with common metal coagulants to increase the strength of the floc and to make the floc settle more rapidly. The reasons for their application are to improve clarification, reduce the metal coagulant dose, or to overcome some inadequacy in a plant unit. Polyelectrolytes are grouped in three general classes depending on the sign of the electrical charge as:

- a. Anionic or negatively charged
- b. Cationic or positively charged
- c. Nonionic or no charge

Some polyelectrolytes called polyampholytes can have both positive and negative charges. Among the natural polyelectrolytes used as coagulant aids are starch and starch derivatives, cellulose compounds, polysaccharide gums and proteinaceous materials. An ever growing list of synthetic polyelectrolytes is being developed. Care must be exercised in use of these compounds in sewage treatment because of possible toxicity which may have detrimental effects on bacteriolical treatment processes such as trickling filtration and anaeorbic sludge digestion. Prior to plant scale use of a polyelectrolyte, laboratory or pilot plant testing should be undertaken to evaluate any possible detrimental effect.

#### Effects of Coagulation

Coagulation may be employed to achieve any of the following in waste water treatment:

1. Improved Primary Treatment for Raw Sewage. Coagulation used ahead of gravity settling may be expected to yield suspended solids removals of about 90 per cent as compared to about 35 per cent without coagulation. Where the primary treatment is followed by biological treatment the latter should be designed as a high-rate low solids retention unit. Thus the coagulation-gravity settling first phase of treatment provides high removal of dispersed microorganisms,

suspended, colloidal and macromolecular materials. The biological treatment second phase would be designed essentially for removal of soluble organic matter.

- 2. <u>Effluent Polishing</u>. Coagulation of the effluent of a secondary treatment plant is employed as a tertiary treatment to provide high degree of solids removal.
- 3. <u>Phosphate Removal</u>. Phosphates may be removed from waste water treatment plant effluents by precipitation with iron and aluminum salts.

#### IV. PROCESS EVALUATION AND CONTROL

Many variables are associated with the coagulation process such as coagulant dosage and the effects of coagulant aids, mixing characteristics, other ions present in the waste, pH and order of chemical addition. Cost, effectiveness and control of the process depend on the determination of the proper conditions under which optimum treatment may be obtained. The nature of the solutions being treated precludes reasonable theoretical calculations and only through investigation can quantitative information be obtained applicable to a process for treatment of a given waste. Laboratory studies are the most satisfactory method for obtaining meaningful evaluations if they can be related to plant scale treatment.

Available methods for evaluation and control of coagulation are jar testing, electrophoretic mobility studies, colloidal titration techniques and conductivity measurements.

#### Jar Testing

A standard method for the determination of the amount of coagulant required for good coagulation is the jar test. Apparatus consists of a multipaddle stirring machine. The stirring paddles agitate the water in several adjacent 1or 2-liter beakers. An equal volume of the solution to be treated is placed in each beaker. Different chemical

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dosages are applied to each. After a period of mixing relative to actual or proposed plant conditions, the size and appearance of the floc are observed and the rate of sedimentation of the floc is noted. The factors of floc size, floc appearance and rate of sedimentation are used to decide the most efficient chemical dosage. The determinations from these jar tests are strongly dependent on human factors.

Coagulation studies at the Robert A.Taft Sanitary Engineering Center have led to an improved jar test procedure.<sup>16</sup> In this procedure, dependence on the extent of experience of the operator is reduced. A device permits the simultaneous and rapid sampling from all jars at a predetermined depth for turbidity or other derived measurements. Results are plotted on semi-log paper providing information on the quality of coagulation from the shape of the curves.

#### Electrophoretic Mobility Studies

Electrochemical phenomena are presumed to be involved in the removal of colloids from solutions. The magnitude of the electrical charge surrounding a suspended particle may be determined from particle mobility and may be expressed as the electrophoretic mobility or subsequently calculated as the Zeta potential. Measurement is made using a Briggs cell or a commercially produced

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complete unit (Zeta Meter-product of Zeta-Meter, Inc.). Extensive work using continuous Zeta potential control of the coagulation-sedimentation-filtration process at the Waterford, New York water treatment plant is reported by Riddick.<sup>22</sup> Faust, etc.<sup>13</sup> have studied electromobility values of domestic wastewater by the Briggs Cell technique. Values obtained ranged from -0.55 to -3.75 u/sec/v/cm with an average of -1.73 u/sec/v/cm for 707 observations.

Rock<sup>23</sup> has studies and offers comparisons of the Briggs Cell and Zeta-Meter Cell.

Mobility measurements appear to require skill, experience and considerable time and use of specialized apparatus.

#### Colloidal Titration

Kawamura<sup>17,18,19</sup> has written a number of recent articles on the application of a colloidal titration technique to determine colloidal charge characteristics.

The technique is based on the neutralization of a measured amount of a standard colloidal dispersion. Methyl glycol chitosan (MGC) and polyvinyl alcohol sulfate (PVSK) are used as standard positive and negative colloids.

Information from the titration is used in a manner similar to electrophoretic mobility data. The procedure can

be carried out without the need of specialized equipment. The author points out several limitations and alludes to a complicating factor in the effect of salts on the titration. Such factors are likely to present considerable problems in application of colloidal titration on waste waters.

#### Conductivity Measurement

Coagulant control by the use of conductivity measurements is reported by Babcock and Knowlton.<sup>1</sup> Conductivity measurement is based on electric current measurements through the solution. As a strong acid is neutralized by a strong base the conductance of the solution decreases steadily as the base is added. When neutralization is complete (equivalence point) the conductance increases with continued addition of the base. The equivalence point can be determined from a graphical plot of conductance vs. base added. Similarly in chemical treatment a weak base (alkalinity) can be titrated with a weak acid (alum) and the equivalence point determined.

Tests conducted by the authors showed maximum color removal at the equivalence point on a particular water. There is little in the literature to substantiate the use of conductivity measurements for coagulation control on other than solutions of specific characteristics.

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#### Advantages and Disadvantages

Most of the literature refers to the use of the above methods for coagulation evaluation and control when used for water treatment in which turbidity and color are primary parameters of quality.

There is very little repudiation of the jar test except in its difficulty in application to automatic control. The improved jar test procedure offers a quantitative analysis procedure. The settling characteristics of floc in beakers cannot easily be equated to plant settling; however, in most cases a reasonable relation between jar test and plant results can be obtained.

Electrophoretic mobility studies are being evaluated by an increasing number of researchers. Some report that devices for mobility measurements are reliable and easy to use.<sup>26</sup> There appears to be general agreement that mobility measurements provide useful information for coagulation control but that Zeta potential alone is not a cure-all for coagulation control.<sup>4</sup>,<sup>22</sup>

The application of conductivity measurements for coagulation control has been limited. Experiments have shown that the use of these measurements is confined to selected waters.<sup>16</sup>

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At present there appear to be many limitations on the colloidal titration technique for application to coagulation of waste waters.

#### Summary

Of the control methods described, jar testing and mobility measurements appear to have the widest application to the coagulation of waste waters. Mobility measurements require more specialized equipment and skill than the jar tests and it is doubtful that the operating personnel at many of the waste water treatment plants are qualified to perform such work. The jar test procedures are simple and acknowledged by most as the basic tool in coagulation control. For these reasons the jar test procedure has been selected for further work in this paper.

#### V. LABORATORY STUDIES

#### Purpose

Laboratory studies on several selected waste waters were conducted using jar test procedures. The purposes of the studies were to:

- 1. Substantiate the principles developed in the preceding sections of this paper.
- 2. Observe the mechanics of coagulation on actual waste water samples.
- 3. Develop a practical procedure for the evaluation and design of a coagulation process taking into consideration the many variables involved.

#### B.O.D. - Suspended Solids Relationships

The two common parameters used to evaluate the effidency of a waste water treatment process are Biochemical Oxygen Demand (B.O.D.) and suspended solids removal. A jar testing procedure should therefore be related to these parameters. The standard tests for B.O.D. and suspended solids, however, are too time consuming to be run on each set of jar tests.

B.O.D. is exerted by the volatile (organic) portions of the dissolved and suspended solids in a solution. Coagulation is not expected to significantly affect the dissolved volatile solids but is expected to remove most of the suspended solids. By knowing the effect of suspended solids on the B.O.D. of a particular waste, it would be possible to determine the effect of a coagulation process on B.O.D. removal.

Tests were run on waste water samples to determine the relationship between B.O.D. reduction vs. suspended solids removal. The results of these tests are shown in Table 1 and are plotted on Figures 3 and 4.

Sample	Susper	nded Solids (S.S.)	7-I	Day B.O.D.	(mg/l)	
	mg/l	% Remaining	S.S. + Soluble	Estimated Soluble Portion	Estimated S.S. Portion	
Plant "B" (l-19-68) (Raw Influent)	0 110 170 230	0 50 75 100	102 144 189 225	82 82 82 82 82	20 62 107 143	
Plant "A" (l-27-68) (Raw Influent)	0 50 130 210	0 25 63 100	58 110 138 200	65 65 65 65	45 73 135	
Plant "A" (2-10-68) (Raw Influent)	0 75 150 290	0 25 50 30	85 133 155 248	91 91 91 91	42 64 157	

Table 1

### SUSPENDED SOLIDS - B,O,D, TESTS

Note: The three samples each are 3-hour composites of the plant's influent waste after comminution

FIG. 3



B.O.D. VS SUSPENDED SOLIDS

## B.O.D. VS SUSPENDED SOLIDS



FIG. 4

Figure 3 illustrates the linearity of B.O.D. vs. suspended solids relation for the wastes tested. Figure 4 is a composite of the three tests with the 7-day B.O.D. due to the suspended solids portion of the waste plotted against the actual suspended solids.

#### Conclusions - B.O.D. vs. Suspended Solids Relationships

The tests performed illustrate that the B.O.D. of the waste may be considered as two fractions; that resulting from the soluble portion and that resulting from the suspended solids portion of the substrate. The suspended solids portion accounts for between 55 and 70 per cent of the 7-day B.O.D. It is therefore apparent that removal of suspended solids has a major influence on B.O.D. reduction.

It is apparent that a B.O.D. - solids relationship could be developed for any given waste undergoing coagulation. From this relationship an approximation of B.O.D. reduction could immediately be made from a solids determination rather than waiting the incubation period for a B.O.D. analysis.

#### Coagulation Equipment and Test Procedures

A six-paddle mixer was employed to obtain an initial rapid mix followed by a slow flocculant mix under conditions which could be duplicated for a large number of samples. One liter beakers were selected for use under the mixing apparatus, each containing 500 ml of the waste under test. Tests were run with a three-minute rapid mix at 100 rpm and a five minute flocculant mix at 20 rpm. The coagulant and coagulant aids were dissolved into stock solutions. A determined amount of coagulant was pipetted into each beaker with the stirrer in operation. Where a coagulant aid was used this was added immediately after the coagulant. To keep the mix time of all samples about the same required two persons to make the chemical additions. The samples were then carefully poured into 500 ml graduated cylinders. A seventh cylinder containing an uncoagulated sample and the six samples were lined up against a white background.

Figure 5 shows the form developed and used during the jar tests. The following observations are suggested for use on this form:

#### Floc

O - None P - Pinpoint M - Medium size L - Large VL - Very large

#### Settling

O - None
S - Slowly settling
M - Moderate settling
R - Rapidly settling

				WASTE WATER JAR	TESTS		RUN	е <sub>н</sub> а се
Sample	<u></u>			]	Date	B;	У	
Initial mix at rpm for				minutes. Flo	cculant mix	at	rpm for	minutes
Initia	al pH	Initial	suspend	led solidsmg	/l Initial	volatile	suspended	solids
		<u>, , , , , , , , , , , , , , , , , , , </u>				Settlin	g time	
Jar	Alum mg/l	Aidmg/l	Final pH	Description	5 min.	10 min.	15 min.	30 min.
1				Floc				
2				Floc				
3				Floc Settling Interface, ml Supernatant			· · · · · · · · · · · · · · · · · · ·	
4.				Floc Settling Interface, ml Supernatant				· · · · · · · · · · · · · · · · · · ·
5				Floc Settling Interface, ml Supernatant				
6				Floc Settling Interface, ml Supernatant				

.

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FIG. 5

#### Interface

Indicate the ml level and describe as

- R Ragged
- S Sharp

#### Supernatant

- T Turbid
- F Contains suspended floc
- C Clear

#### Results of Experiment

The results of three series of jar tests performed are shown in Table 2 and are illustrated in Figure Nos. 6 and 8 with cylinders arranged in an ascending order from left to right.

#### Table 2

#### RESULTS OF COAGULATION EXPERIMENTS

			,	Cylin	der N	umber		
Test	Measurement	1	2	3	4	5	б	7
Fig. No. 6	Initial pH	7.3	7.3	7.3	7.3	7.3	7.3	7.3
	Alum Added mg/l	0	250	300	350	400	450	500
	Final pH	7.3	6.2	5.9	5.3	4.9	4.6	4.2
Fig. No. 8	Alum Added mg/l	0	250	250	250	250	250	250
Run "A"	Coagulant Aid*mg/l	0	2	10	15	20	30	40
Run "B"	Alum Added mg/l	0	100	150	200	225	250	275
	Coagulant Aid**mg/l	· 0	0.5	0.5	0.5	0.5	0.5	0.5

\*Anionic polymer "Magnifloc 865-A" American Cyanamid Company \*\*Nonionic polymer "Magnifloc 900-N" American Cyanamid Company



T = O Minute



T = 5 Minutes



T = 30 Minutas



T=IO Minutes



T = 45 Minutes

#### COACHEATION STUDIES

Initi	al mix a	at_100_rp	m for	<u>3</u> minutes. Flo	cculant mix	c at <u>20</u>	rpm for	<u>5</u> min
Initi	al pH <u>7</u>	.3 Initial	suspend	led solids 210 mg	/l Initia	l volatile	suspended	soli
Γ	Ι				*********	Settlin	g time	
Jar	Alum mg/l	Aid mg/l	Final pH	Description	5 min.	10 min.	15 min.	30
				Floc	0	0	0	
2	250	None	6.2	Settling	0	0	V-S	<u>v</u>
				Interface, ml	0	0	5	Į
				Supernatant	T			
				Floc	Р	P-M	P-M	P
3	300	None	5.9	Settling	0	0	V-S	V
			2.2	Interface, ml	0	10	25	2
				Supernatant	Т	Т	Т	
				Floc	M	M	M	
<u> </u>	350	None	53	Settling $$	S	М	М	]]
	500	None		Interface, ml	10	50	45	4
				Supernatant	F	म	С	. '
				Floc	М	M	М	]
5	400	None	4.9	Settling	R	R	R	]
				Interface, ml	50	55	50	4
				Supernatant	F	С	C	
•				Floc	М	M	M	
6	450	None	4.6	Settling	R	R	R	
		None		Interface, ml	65	60	50	4
		•		Supernatant	F	C	С	
				M	М	M	1	
7	500	500 None	4.2	Settling	М	R	R	
				Interface, ml	50	60	50	- 4
				Supernatant	F	C	С	
	l	l	1				·	1

-

## FIG. 8

## RUN A



T=O Minutes



T = 1 Minute



T = 3 Minutes



T=5 Minutes







T = 15 Minutes

The tests shown in Figure No. 6 were performed on a raw waste water using alum as the coagulant. Figure No. 7 shows a completed record of the observations corresponding to this test.

After 5 minutes of settling, the bottom 50 ml of cylinders 4 through 7 contained most of the settled floc and an interface between the supernatant and floc was just starting to form. This interface was sharp after 10 minutes of settling although some flocculated particles remain suspended in the supernatant liquor. After 30 minutes the supernatant in cylinders 4 through 7 was crystal clear and the initial volume of the sludge was reduced by about 50 per cent. It is clear from the photographs that the optimum chemical dosage is between cylinders 3 and 4 (300 to 350 mg/l alum).

It is interesting to note the apparent complete lack of settling taking place in cylinder No. 1. The waste under test is typical of that received at a particular northern New Jersey municipal waste treatment plant. A major contributor (5 to 10 per cent of total flow) to the plant is a fabric finishing and dye plant. The lack of settling without coagulation is thought to be due to a dispersant present in the finishing compounds used at the industrial plant. It is also observed that the amount of sludge in the bottom of the cylinders is about the same for those displaying a clear supernatant even though cylinder No. 7 had almost 50 per cent more coagulant than cylinder No. 4. Subsequent tests on the same waste using coagulant aids and less than 200 mg/l alum yielded approximately the same sludge volume.

The tests shown in Figure No. 8 were performed on the same raw waste as that shown in Figure No. 6 except that alum feed was reduced and coagulant aids used.

The high concentration of polymer in Run "A" produced large, very heavy floc which settled immediately leaving a clear supernatant in about 3 minutes. Feed rates at this magnitude to any significant plant flow are not feasible. Such feed rates at the source of an industrial waste prior to discharge into the municipal system may, however, be feasible due to the very short detention time needed for solids removal.

From Run "A" it was concluded that the alum feed rate could be substantially reduced through the use of a coagulant aid. Further tests run with the anionic polymer used in Run "A" showed an optimum combination of 150 mg/l alum and 0.5 mg/l aid with a 15 minute settling time.

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In Run "B" a nonionic polymer was used. Optimum coagulation was obtained in cylinder No. 4 at 200 mg/l alum and 0.5 mg/l aid.

#### Conclusions

The characteristics of the coagulation process on a certain domestic waste were observed under many varying conditions. During the course of these tests the following were concluded:

- Increasing amounts of coagulant result in a progressive increase from fine floc to large bulky floc.
- 2. A flocculant mix is essential to the formation of other than pinpoint floc which would not settle in a reasonable time period.
- 3. The size of the floc has little effect on the rate of settling.
- 4. Once a condition was obtained which would produce a good settleable floc little was gained in higher coagulant additions. In most cases the higher additions resulted in a faster settling floc, but the decrease in settling time seemed insignificant.
- 5. Once a floc was obtained that would settle in 15 minutes or less, the supernatant had a 90 per cent or greater suspended solid removal.
- 6. The need for pH adjustment to improve coagulation in the ranges of coagulant used in the tests appeared to have only a minor effect on reducing the amount of coagulant. This is due to the fact that the pH range for optimum precipitation of Al<sup>+++</sup> is between pH 5 and pH 7. The pH of the raw waste was consistantly about 7.0 and it took 450 mg/l of alum to reduce the pH to about 5.0.
- 7. The addition of small amounts of polyelectrolytes (less than 1 mg/1) resulted in a major reduction

in the use of alum. The reduction in alum feed rates resulted in the lowering of a chemical feed for neutralization of the supernatant after coagulation.

- 8. Tests on trickling filter effluents proved it to be more difficult to coagulate than the raw water.
- 9. A record keeping procedure is needed to compare one set of jar tests to another. The sample form, Figure No. 5, was developed to serve this purpose as a result of the observations made during the testing for this paper.
- 10. The use of a more analytical procedure than the jar test such as Zeta potential or turbidity measurements seems unnecessary unless coagulant feed is to be controlled automatically on effluent quality.
- 11. The amount of coagulant added to the waste will result in little or no noticeable increase in sludge volume, although its density (weight) certainly is increased. It is suspected that this is true for most wastes. Such a phenomenon is of practical importance in plant operations where the volume of sludge to be pumped or handled is an important consideration. Pumping equipment would need to be suitable for a higher density sludge.

#### VI. PRACTICAL APPLICATION

During the course of conducting the coagulation studies, it became apparent that some practical application knowledge would be of benefit. Although the studies performed for this paper were made using alum as the primary coagulant, there are at least two other choices, namely, ferric sulfate and sodium aluminate. Consideration must also be given to the cost of neutralizing the treated effluent of the coagulation process to meet stream discharge criteria or to prevent interference with following biological treatment process.

#### Primary Coagulant

Alum was chosen for the coagulation studies because of its availability, ease in handling and relative low cost. It is by far the most widely used coagulant today. Alum treatment does not interfere with the operation of following biological process such as anaerobic sludge digestion and activated sludge. Alum does have the following disadvantages:

- 1. May cause ponding if carried over onto a trickling filter process.
- SO4 compounds in the sludge may be reduced to H<sub>2</sub>S in anaerobic sludge digestion process causing severe corrosive problems in gas piping and equipment.
- 3. Use of alum will result in an increase in the total solids (sodium and sulfates) content of plant effluent.

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4. Neutralization may be needed after the coagulation process resulting in higher chemical costs.

Iron compounds have not been widely used as a primary coagulant probably because of color problems and oxidation - reduction reactions which may take place.

Sodium aluminate offers a possible solution to some of the difficulties associated with alum. Sodium aluminate (Na<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>, 62-72% dry, 33-46% liquid) contains nearly two and one half times the amount of aluminum ion on a weight basis (22.5% compared to 9% for dry form, 14.1% compared to 4.4% for liquid form). Thus if coagulation is a function of the metal ions a lesser amount of aluminate would be required. The problems of sulfate compounds do not exist. A 1 per cent solution of dry sodium aluminate has a pH of 11.5 to 12.0. Since a significantly lesser amount of aluminate may be required, pH adjustment may not be required after the coagulation process. The major problems with sodium aluminate are:

- 1. Cost
- 2. Availability
- 3. Viscosity in solution

At present bulk per ton chemical costs including delivery (based on 100 mile delivery for alum and 300 mile delivery for aluminate) in the northeast are as follows:

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	Approximate Delivered Cost Per Ton			
Liquid alum	\$ 25.00			
Dry alum	60.00			
Liquid aluminate	115.00			
Dry aluminate	180.00			

Manufacture of sodium aluminate is limited; however, there is some indication that increased use in the public works field may result in more competitive pricing and improved availability.

Solutions of sodium aluminate are very viscose and present pumping difficulties at temperatures much less than 80°F. unless in dilute solutions.

#### Cost Relationships

Relative costs of coagulants, coagulant aids and neutralizers are of value in selecting jar test combinations. Available cost data have been plotted on Figures 9 and 10 as 1967-68 prices.

It may be seen from these figures that the same cost will result with a reduction of 100 mg/l of alum in lieu of a feed of 3.0 mg/l coagulant aid costing \$1.00 per pound. The value of a coagulant aid is thus apparent especially when the cost of neutralization is taken into consideration.

FIG. 9



FIG. IO



#### Type of Feed

Dry feed systems for the primary coagulants have become outdated. The bulk purchase of liquid alum represents a significant cost saving over that of dry alum. The cost savings are increased when the handling costs of dry chemicals are combined. Alum is normally shipped in 3000-4000 gallon tank trucks and stored at the plant in 5000-6000 gallon fiberglas-epoxy tanks. Feed to the system is through specially constructed metering pumps.

Polyelectrolytes are difficult to put into solution. A dilute solution must be made in a mixing tank and then transferred to a feed tank. Feed again is through metering pumps.

#### Phosphate Removal

Phosphorus removals in excess of 90 per cent may be obtained through coagulation. Thus where coagulation is used, phosphorus removal may be achieved as a side benefit. It has been found that the aluminum ion feed rate for phosphate removal is directly proportional on a weight basis to the phosphate concentration. Thus for domestic sewage (10-20 mg/l P) an alum feed rate of 100-200 mg/l will provide high phosphorus removals.

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