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THE SCHULZE-HARDY LAW AND THE HOFMEISTER SERIES
OF IONS IN COAGULATIONS OF STARCH-TITANIUM
DIOXIDE WHITE WATER

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A thesis submitted to the
Faculty of the Department of Paper Technology
in partial fulfillment
of the
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ABSTRACT: In recent years the problem of pollution has gained more importance in the pulp and paper industries due to the pressures applied by the State and Federal Governments. One of the areas in which the industry has been weak is the coagulation of starch-titanium white water. The problem is largely due to the stabilizing power of the modified starches used in the industry today. These starches peptize the pigment which is present in the white water and form a highly stable colloidal system.

The coagulating rules set down in the Schulze-Hardy Law and the Hofmeister Series state that the higher the valence on either a cation or an anion in solution, the greater the coagulating power. This is due to the neutralizing of the zeta potential associated with each colloidal particle. However, it has been shown in the following work that for the highly sheared system of Pearl starch and titanium dioxide that a combination of Mg^{+2} and SO_4^{-2} ions have a greater coagulating power than Al^{+3} and SO_4^{-2} . This has been attributed to an unexplained reaction between the Mg^{+2} ions and the peptized titanium particle which favors the formation of larger flocculated particles.

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LITERATURE REVIEW: In recent years State and Federal Governments have been playing an ever increasing role in the concern over stream improvement. With the increasing controls on industries, the paper industry has had to re-evaluate its economics and efficiencies in water treatment. In many cases a paper mill has found that it has just not been economically possible to clean up its effluent to a high degree. This has been especially true in mills where starch has been introduced into the white water system. Starch has been used for many years in the paper industry to improve the physical qualities of the sheet. Even if starch is not introduced into the system originally, it may enter because of its presence in depulped broke. It has been found that the cost of treating white water with any amount of starch is considerably higher than the cost when no starch is present (1). As little as ten parts of oxidized starch per one million parts of water can reduce the settling rate of a typical paper making white water.

It was found by Wilhelm (2) that different types of modified starch had varying degrees of effect on the colloidal stability of a starch-titanium white water. The colloidal stability depended upon three factors: (a) type of oxidized group on the starch, (b) molecular size of starch, and (c) amount of shear introduced on the system during preparation. The presence of carboxyl groups on the starch and a minimum molecular size was found to be necessary for stable pigment dispersions. Thus in order of decreasing colloidal stability, the effectiveness of the following types of starches are:

hypochlorite-oxidized, hydroxyethylated, acetylated, dialdehyde, and enzyme converted (2).

The high shear which is necessary to produce these highly stable white water conditions is introduced into the white water system by the many centrifugal pumps, refiners, and screens which are located throughout the papermaking process. This high shear action, which is simulated in the laboratory by high shear mixing in a Waring Blendor, changes the white water from a relatively non-stable pigment dispersion to a highly stable pigment-starch colloid. During this high energy phase the individual pigment particles are surrounded by a thin layer of charged starch molecules, thus forming a highly stable hydrophilic colloid. The effectiveness of a peptizer in improving the stability of a dispersion can be measured by the increase in the flocculation value (3). The difference in the settling rate of a dispersion depends upon the size and shape of the particles and upon the difference in density of the particle and the liquid. Since in a natural environment a system tends to lower its free energy, there is a spontaneous tendency for the reduction of surface area of the particles. The irregular surfaces of the particles tend to become more regular (3).

With the formation of a peptized system, an electrokinetic variable is brought into the function of coagulation. Charges can be created by the absorption of specific ions on the particle surface. This charge which is set up by the adsorbed ions is respon-

sible for the ion layer and the zeta potential theory. The double ion layer is formed as the negatively charged particle attracts the positively charged ions in solution. This layer of positively charged ion is the inner layer of ions. As one moves farther away from the surface of the particle the density of the oppositely charge ions becomes less and less and more negatively charged ions are found, i. e., this is the diffuse ion layer. A theoretical sketch of this is shown in Figure 1.

It is the undefined surface between the inner layer and the double layer where the zeta potential is measured (3, 4, 5, 6, 7). Zeta potential is described as "the electrokinetic potential in the double layer interface between a particle which moves in an electric field and the surrounding liquid" (3). It has been theorized that the zeta potential developed is responsible for the high degree of stability of colloidal systems. Because of the similar charges developed around each colloidal particle there is a mutual repulsion between them so that they do not conglomerate and settle. One can easily visualize that if the zeta potential was effectively reduced to zero the stability would also decrease to such an extent that the colloid could precipitate of its own accord. This can be done, it is theorized, if the distance between the particles will become smaller than the radius of attraction, and thus the particles will conglomerate and settle.

The process of precipitation may be carried out by two methods, i. e., aging and coagulation. The term "aging" relates to a spon-

taneous change in a colloid with time. With aging comes an increase in particle size. The controlling factor in this process is Brownian movement and is thus dependent upon temperature (5). The aggregation rate is also dependent upon particle shape, with rod shaped particles aging is faster than with spherical particles due to their larger sphere of attraction.

Coagulation " is the process in which coagulating chemicals are added to water to bring about agglomeration or aggregation of the suspension or color particles into larger masses which settle more readily than the colloidal particles. The coagulation process includes addition of chemicals to the water, rapid mix in which the initial reaction and floc formation take place, and slow mix in which the floc is conditioned for settling" (8). It is theorized that the addition of the coagulant reduces the zeta potential of the colloid due to the presence of the positive ions in the coagulant. In the addition of coagulant one must be careful in the dosage used, for the system will pass through three zones. The first is when the colloid is sufficiently neutralized by the positive ions in the coagulant, thus flocculation occurs. The second zone is when an excess of anions from the coagulant is absorbed onto the colloidal particle and the system obtains a positive charge and is stable. As more coagulant is added the positive charge is partially neutralized by the cations of the coagulant and partial flocculation occurs (5). When the electrolyte concentration is such that each

particle collision results in aggregation the flocculation rate is said to be fast.

It is easily seen that if the coagulation rate is dependent upon neutralizing the zeta potential on the colloidal particle, the size of the charge which is related to the anion is very important. The relation between the coagulation power of various anions and their charge is called the Schulze-Hardy Law, the similar relation with the cations is the Hofmeister Series.

The Schulze-Hardy Law states that the divalent anions have approximately eighty times the coagulating power of the monovalent salts. The trivalent salts are much stronger than the divalent by approximately ten to one thousand times (3, 4, 5). The Hofmeister Series states that coagulating power also depends upon the structure and the size of the ions. These variables affect the interaction with the colloidal particles and their hydration in water. This interaction determines how they are attracted to the charged surfaces. Those ions which have to approach closer before being electrokinetically attracted have lower flocculating powers. The Hofmeister series is as follows (5):

In declining flocculating power

1. sulfate
2. citrate
3. tartrate
4. acetate

5. chloride
6. nitrate
7. bromide
8. iodide
9. thiocynate

The above rules have been accepted for many years for the coagulation of sols. However, if one can relate streaming current to zeta potential in such a way that zero streaming current is equal to zero zeta potential there is a discrepancy between these rules for starch-titanium systems. It has been shown (9) that reducing the streaming current to zero in a system having no extraneous ions that coagulation will not readily occur. Because of this work, an interest developed and it was theorized that in this system perhaps the other rules of coagulation did not follow. This could be due to the extremely large starch molecules or unknown reactions which were taking place in the system. This area of the Schulze-Hardy Law and the Hofmeister Series in starch-titanium white water will be further explored in this thesis.

EXPERIMENTAL PROCEDURE: In order to evaluate the coagulating power of anions and cations in starch-titanium white waters a standard procedure was formed. All experiments at this time used Staley pearl starch as a peptizing medium for the titanium. Pearl starch was used as it has been shown in production work that a pearl starch has less of a colloidal stabilizing power than does a modified starch. After obtaining a Kalamazoo City water analysis (see Table I), it was decided to use deionized water of 200,000 ohm resistance or higher throughout the experimental work in order to eliminate any interference in the work by the extraneous ions present in tap water.

Stock solutions of the coagulants to be used were made up at a concentration of twenty-five milligrams per milliliter based on the weight of the positive ion. These solutions were later peptized into the white water at the required dosages.

The starch was cooked at 5 percent solids in a double boiler under constant mixing. The temperature of the starch was maintained at 190 degrees Fahrenheit for one hour to ensure the proper cooking of the starch. After cooking, water was added to compensate for the evaporation which occurred during cooking so that the solids were again five percent. A stock starch solution was made up by diluting half of the cooked starch to a one percent solution. This solution was then kept at one hundred degrees Fahrenheit in a constant temperature bath until it was used. However, starch was cooked daily so that degraded starch was not used in any of the experimental work.

White water was made up by shearing 0.5 grams of titanium dioxide in a Waring Blendor with 0.5 liters of water at "mix" speed for three minutes. After this period of time, the starch dosage was added and shearing was continued for another three minutes in order to produce a thorough peptization. Starch was added at 0, 75, 150 and 200 mg./ml. Dilution to one liter took place after shearing was completed.

The starch-titanium white water was then split into four portions of 250 ml. each and placed under rapid mix (100 r. p. m.) on a gang mixer. The coagulant was introduced from the stock solution under these conditions at 0, 50, 150 and 250 mg./ml. Rapid mix continued for one minute after the introduction of the coagulant, after which a two minute low mix (40 r. p. m.) floc formation period took place. This standard white water was then allowed to stand and settle at a constant temperature of one hundred degrees Fahrenheit. Jackson Turbidity readings were taken on the supernatant liquid after settling at 0, 1, 3 hours.

CONCLUSIONS: So that one can have some relationship between Jackson Turbidity and the concentrations of a pigment dispersion, these two variables were plotted against each other in Figures II and III for a titanium dioxide and a clay slurry. By the use of Figure I the Jackson Turbidity reported throughout this report may be related to the concentration of the titanium left in the supernatant liquid after settling of the white water. One must remember that the graphs can be used only under the conditions stated in the experimental procedure for a change in pigment or the amount of shear administered to the particle will affect the Jackson Turbidity. The dependence of the pigment on turbidity can be seen comparing Figure I and Figure II. Here in equal concentrations of titanium and clay slurry the clay turbidity is approximately half of the turbidity for the titanium slurry. This can be explained because of the differences in the indexes of refraction of the two pigments. The amount of shearing given the pigment will determine the final size of the suspended particle. With a better dispersed slurry the particles are of a smaller size, thus with more particles present the settling power of a specific weight of pigment will increase, creating an increase in turbidity with increased shear. The small amounts of starch introduced into the system showed little effect on turbidity for it was distributed evenly over all of the pigment particles from the high shear action of the Waring Blendor.

Looking at Tables II through IV, one can see that the stability of the peptized dispersion with no coagulant increased with the

increase in starch concentration. This is also shown by looking at the three tables and noting that the lowest turbidities are found with the 75 mg./ml. starch concentration. Thus, this low starch concentration was the easiest for the coagulant to floc. This held true for all of the coagulants evaluated. The most interesting data obtained is that of $\text{Al}_2(\text{SO}_4)_3$ and the MgSO_4 . According to the Hofmeister Series and the Schulze-Hardy Law the $\text{Al}_2(\text{SO}_4)_3$ should have many times more the coagulating power than MgSO_4 . However, in all the observed instances the magnesium sulfate coagulated the starch-titanium quicker than the aluminium sulfate. Thus, for the system under study the Schulze-Hardy Law apparently did not hold true. The reason for this discrepancy is theorized to be due to perhaps some unknown reaction between the colloidal particles and ion in solution. In some manner the magnesium ion is more effective in drawing the colloidal particle with its thin layer of starch covering together. Thus the formation of a larger floc which tends to settle faster.

In the case with 75 mg./ml. of starch this floc formation was very rapid (it occurred during the slow mix) for at zero time the turbidity was down to 1500 J. U. because of the larger floc formation. This occurred only at the low concentration due to the higher stability of the other starch concentrations.

The other compounds evaluated did not show enough coagulating power to be considered effective.

RECOMMENDATIONS: Because of the trend shown, further work should be conducted over that possible in this study to compare the effectiveness of $MgSO_4$ to $Al_2(SO_4)_3$ as coagulants in white water systems. Work should be done to see the effect of the presence of other ions on these coagulants. These ions should be introduced to a real white water system through the use of tap water and other additives. The presence of fiber may also affect the coagulating power; however, it could have a beneficial effect if the white water would be "sweetened" with a small percentage of long fiber stock. This would tend to give the titanium a greater chance to form larger particles and become enmeshed in the fiber network as it settles. The use of certain polyelectrolytes may also aid the inorganics in the coagulation of the stubborn starch white water. However, these are expensive and very selective and sensitive to changes in white water make-up.

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Figure 1.
Diagram of Zero Potential

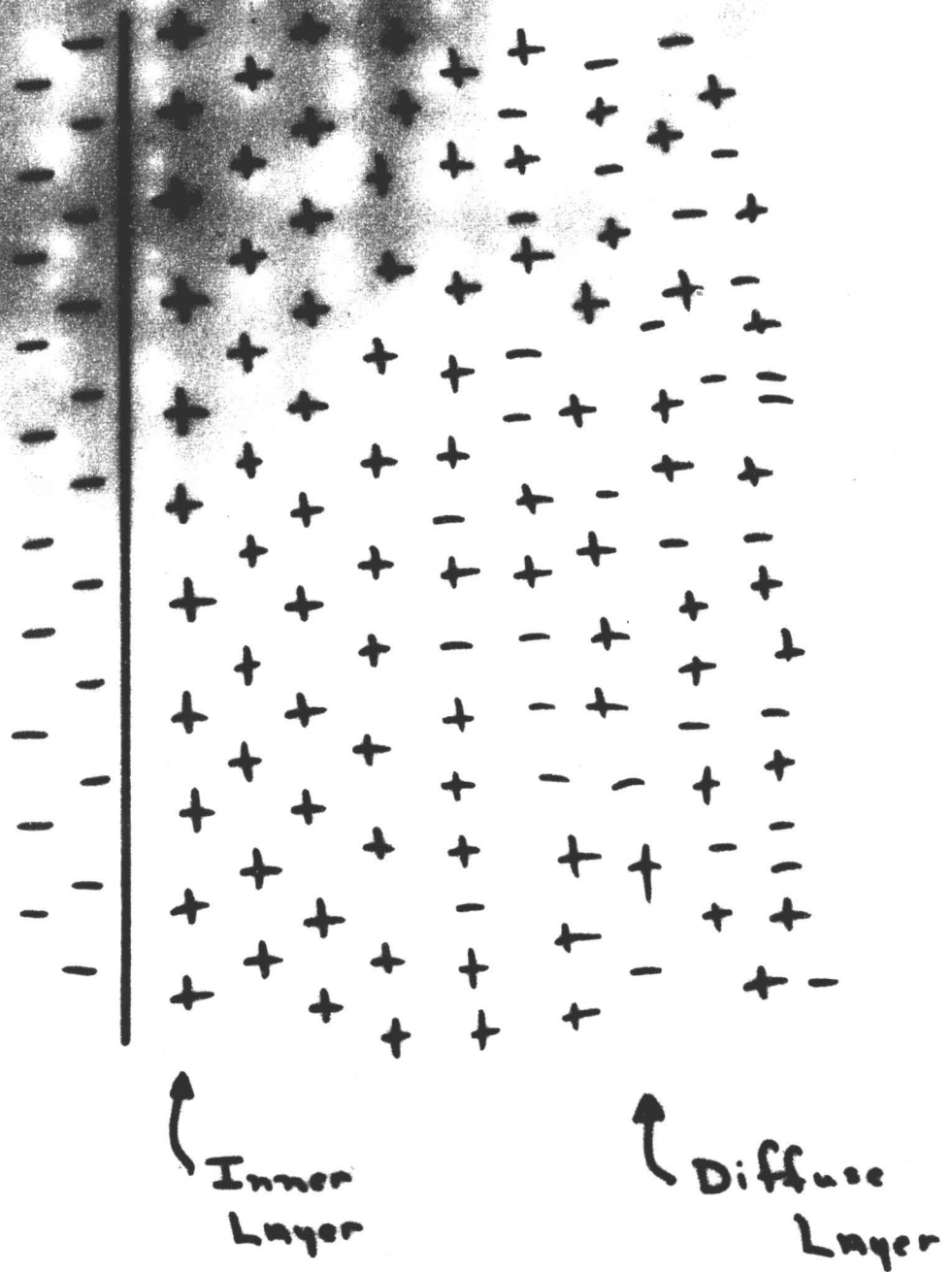
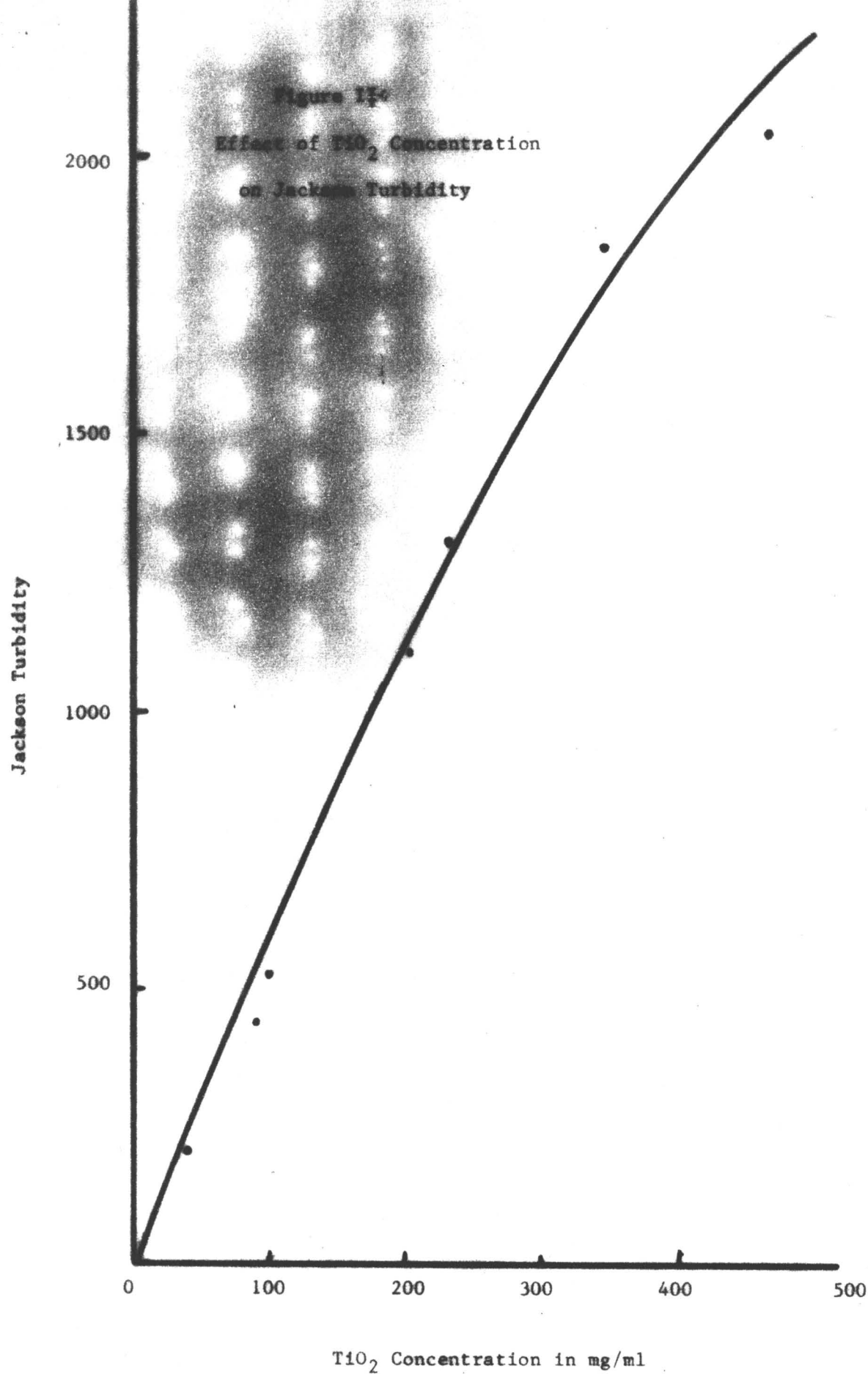


Figure 11a
Effect of TiO_2 Concentration
on Jackson Turbidity



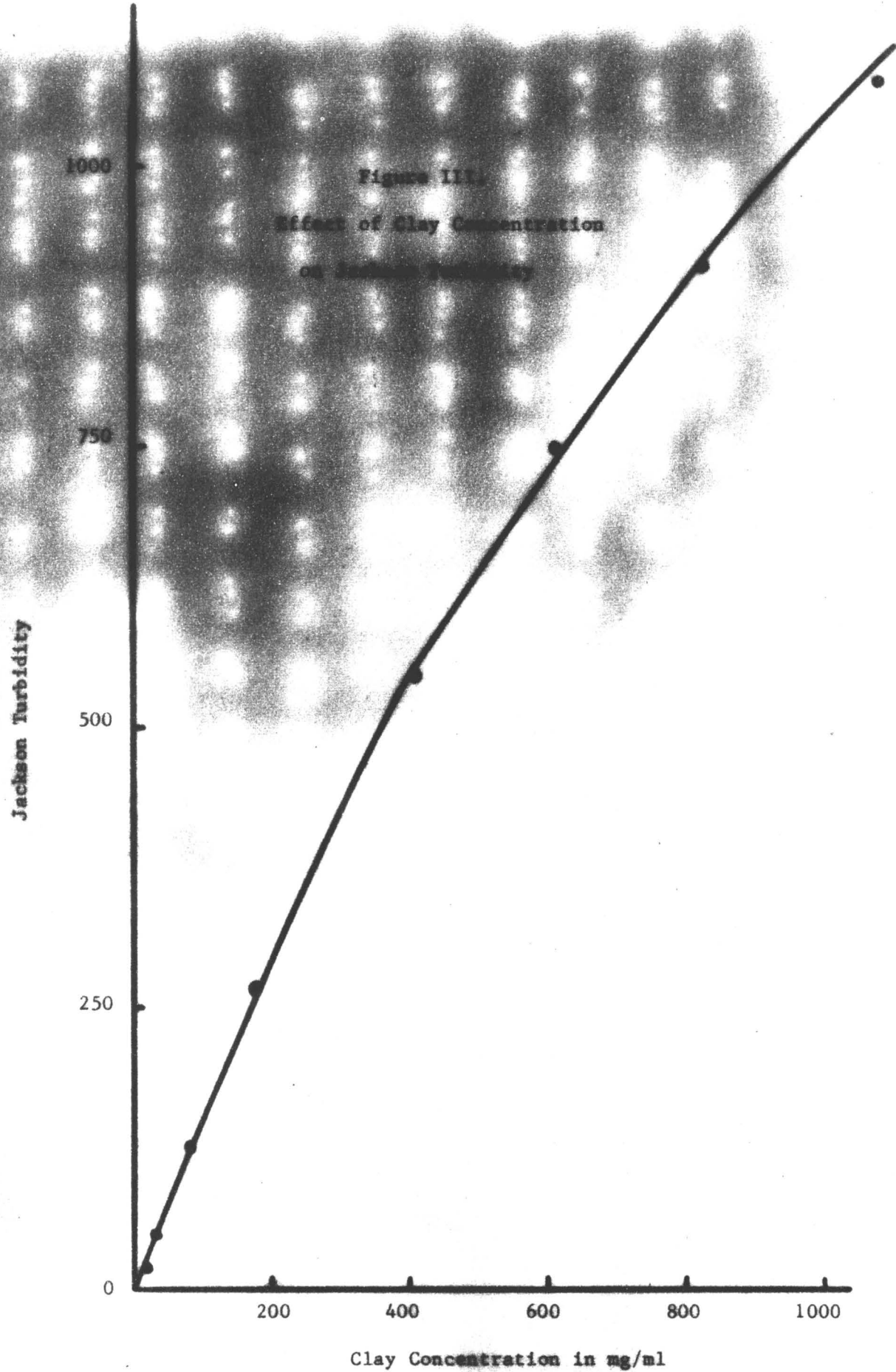


Table I.

Kalamazoo City Water Analysis

	<u>ppm</u>
Total Solids	277-590
Fe_2O_3	5.6-20
Ca^{++}	60-120
Mg^{++}	22-34
$\text{Mn}+\&\text{K}^+$	2-12
Cl^-	2-18
SO_4^{--}	12-139
HCO_3	274-350
CO_3	-----
F	-----
CaCO_3 (hardness)	225-425
pH	7.3-7.9
Cl (added)	0.75
F (added)	1.0

Table II.

Starch Conc.- 75mg/ml

<u>Coag. Dose</u>	<u>Time-hr.</u>	<u>Al₂(SO₄)₃</u>	<u>MgSO₄</u>	<u>AlCl₃</u>	<u>MgCl₂</u>	<u>ZnCl</u>
0	0	2500	2500	2550	2500	2500
	1	2400	2350	2400	2400	2400
	3	2200	2150	2100	2100	2150
50	0	2500	1500	2300	2300	2300
	1	1700	1400	2100	2200	2200
	3	1400	1100	2100	2000	2000
150	0	2500	1500	2300	2400	2500
	1	1300	1100	2200	2100	2000
	3	1300	950	2000	1700	1800
250	0	2500	1500	2400	2400	2400
	1	1800	1100	2300	2300	2400
	3	1700	700	2200	2200	2250

Table III.

Starch Conc.- 150mg/ml

<u>Coag. Dose</u>	<u>Time-hr.</u>	<u>Al₂(SO₄)₃</u>	<u>MgSO₄</u>	<u>AlCl₃</u>	<u>MgCl₂</u>	<u>ZnCl</u>
0	0	2500	3000	2500	2500	2450
	1	2200	2500	2400	2200	2500
	3	2000	2500	2350	2200	2300
50	0	2500	2200	2100	2500	2500
	1	1800	1700	2000	2200	2300
	3	1800	1300	1900	2200	2200
150	0	2300	2200	2100	2500	2500
	1	2000	1700	2100	2200	2300
	3	1800	1300	1900	2200	2200
250	0	2200	2200	2500	2500	2500
	1	1900	1600	2300	2100	2300
	3	1900	1400	2100	1900	2200

Table IV.

Starch Conc. -200mg/ml

<u>Coag. Dose</u>	<u>Time-hr.</u>	<u>Al₂(SO₄)₃</u>	<u>MgSO₄</u>	<u>AlCl₃</u>	<u>MgCl₂</u>	<u>ZnCl</u>
0	0	2500	2500	2450	2500	2550
	1	2400	2450	2300	2300	2400
	3	2400	2400	2300	2200	2300
50	0	2300	2500	2500	2500	2600
	1	2000	1700	2400	2200	2400
	3	1700	1500	2200	2000	2300
150	0	2300	2500	2500	2500	2500
	1	2000	1600	2300	2200	2300
	3	1800	1400	2200	2000	2200
250	0	2300	2500	2500 ²⁵⁰	2500	2500
	1	1900	1600	2200	2200	2250
	3	1900	1500	2100	2000	2100