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COAGULATION AND FLOCCULATION OF FLEXOGRAPHIC INK WASHWATERS BY VARIOUS ORGANIC AND INORGANIC POLYMERS

by
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A Thesis Submitted
to Dr. David K. Peterson
in Partial Fulfillment of
the Curriculum Requirements for
the Bachelor of Science Degree

Department of Paper Science and Engineering
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ABSTRACT

A review of flocculation is presented. Included is a discussion concerning the factors controlling pigment and heavy metal removal via flocculation treatment. Also included is a brief background on the regulatory status concerning the heavy metals contained in flexographic inks. A detailed experimental procedure involving the use of jar tests and several industrial polymers is included along with the analyses performed.

It is found that flocculation treatment on flexographic washwaters produces excellent results with respect to clarity and heavy metals removal. In most cases flocculation at an optimum concentration followed by simple gravitational settling resulted in heavy metals removal well within the federal safe drinking water standards. Heavy metal and turbidity removal were proven to have a strict linear relationship to one another with respect to flocculant dosage.

Both the flocculation and settling characteristics of this laboratory study appear to coincide with typical industrial waste treatment practices. The flocculants produced optimum removal of turbidity and heavy metals well within the manufacturers suggested addition range. The gravitational setting of the floc formations was represenative of ranges found in common industrial treatment parameters. Overall, this experiment points favorably to the feasibility of polymer treatment of flexographic washwaters followed by gravitational settling as a treatment application in the flexographic and boxboard industry.

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INTRODUCTION

In recent years, many serious thoughts have been given and many dramatic actions have been instigated in dealing with the enormous water pollution problem. Mainly due to continuous pressure by the State and Federal governments, ink and box manufacturers have become more and more concerned with the elimination of toxic wastes and color from their effluents.

Coagulation and flocculation of both toxic and non-toxic pigments found in flexographic ink washwaters is an inevitable step in the abatement process and its efficiency determines to a great extent the overall effectiveness. In order to gain a more complete knowledge in this area, different polymers and conditions are investigated as to their effect on coagulation and flocculation of flexographic pigments in washwaters.

It is the purpose of this investigation that it will provide helpful insight into some of the industrial design and application considerations when utilizing coagulation and flocculation processes for eliminating flexographic pollutants from discharges.

I. FLEXOGRAPHIC INKS DEFINED

Flexographic inks, generally defined (5), are quick drying, low viscosity inks used in the flexographic printing industry. Flexographic inks are generally based on volatile solvents but can also be water based. The three major portions of the ink are the vehicles, pigments, and dryers. These three portions are mixed thoroughly to provide an equal dispersion of pigments in the vehicle.

The ink's vehicle provides two primary functions. The first is to contain and carry the pigment onto the surface to be printed. The second function is to bind the pigment and provide workability after the ink has dried. A solvent base ink will use an oil or solvent as the primary vehicle. A water base ink contains a binder which is either water soluble or water dispersible. Driers are composed of volatiles which greatly accelerate the drying of printing ink.

Pigments, or colorants, are used to give printing inks their characteristic shades and colors. These substances are finely divided, colloidal in nature, and are insoluble and dispersed in the vehicle rather than dissolved.

There are two primary classifications of pigments used in flexographic printing. One classification deals with organic pigments which are made up of long complicated molecules. These pigments are chiefly synthetic and generated from coal tar derivatives.

The other classification of pigments consist of inorganic compounds of various metals. Usually they are simple chemicals and consist of small molecules such as lead chromate, $PbCrO_4$. Forty per cent of total production in the ink manufacturing industry relies on inks utilizing inorganic pigments.

Toxic Effects and Treatment Objectives

It is the inorganic pigments which generate the hazardous effects and toxicity associated with flexographic washwaters. Inorganic pigments are generally comprised of lead compounds or other heavy metals which are priority pollutants.

Inorganic pigments are rated as "very toxic" by the Environmental Protection Agency (EPA) and dissuades any chronic or acute exposure to these compounds. In addition, the compounds must be disposed of as a toxic solid waste according to the Resource Conservation and Recovery Act (RCRA) (10).

It has been alluded to that the primary objective of treating flexographic washwaters is to remove heavy metals. However, two other secondary objectives remain important: solids removal and color removal. These two objectives may be secondary in nature at the present but as future governmental regulations become more stringent, their importance will grow.

Regulations

Most of the regulation governing flexographic washwaters stems from RCRA. This federal statute was passed by Congress in 1976 and set up broad and general guidelines for establishing a national hazardous waste program. This statute also mandated that the EPA has the authority and responsibility to establish criteria on hazardous wastes.

In December of 1978, it was proposed that criteria for identifying and listing hazardous wastes be established to follow up RCRA. Following that, in August of 1979, additions to RCRA were passed which first suggested flexographic inks as having hazardous wastes.

In the latest move, final interim quidelines and regulations were established in May of 1980. These regulations show criteria for determining which wastes are hazardous and details a system for tracking and monitoring the waste from the point of generation to the point of disposal. Also presented in this regulation, is criteria for the operation of disposal facilities.

The major categories which characterize a hazardous waste are ignitability, corrosivity, reactivity, and toxicity by a specific extraction procedure (EP toxicity). Flexographic wastes are unlikely to be hazardous in the ignitability, corrosivity, and reactivity criteria.

However, three components of flexographic inks are considered hazardous under the EP toxicity category. These three are lead, chromium, and barium and must not exceed specific standards. Concentrations of lead and chromium must not exceed 5 mg/liter in acid leachate (EP) and barium concentration must not exceed 100 mg/liter or the waste must be declared hazardous (10).

Sources and Wastewater Generation

Overall wastewater volumes from flexographic ink manufacturers are small and can be considered insignificant. The largest portion of wastewater comes from printing operations using water base flexographic inks. Water used to clean the presses in between runs becomes contaminated with the inks used. However, even on a large scale operation, such as a corrugated box plant, the wastewater generated rarely exceeds 1000 gal/day (10).

II. COAGULATION AND FLOCCULATION

There are a variety of unit operations currently being used to treat flexographic wastes to meet stringent federal requirements. The operations reportedly in use are evaporation, coagulation, flocculation sedimentation, filtration, ultrafiltration, centrifugation and activated carbon treatment (5). Each of these methods provides a means for sedimentation of the undesired pigments in waste waters which are too small (colloidal) for gravitational settling to be effective. If each of these operations are carried out properly, the supernatant (filtrate) is disposed of as a purified effluent to meet regulation requirements.

Of the methods previously prescribed, coagulation and flocculation seems to be the most popular. It is less energy intensive than most of the other operations and can be conviently carried out in a batch or continuous process. This physical/chemical treatment is not only helpful for removing heavy metals but is also excellent in removing suspended solids.

Coagulation and Flocculation Defined

There are many different interpretations of the terms "coagulation" and "flocculation" to be found in scientific literature. Because of the wide diversity of definitions affixed to them, the terms are sometimes used synonomously.

LaMer (9) describes coagulation as the process by which destabalization of a colloidal solution occurs when the electrical double layer surrounding the colloidal particles is compressed, that is, colloidal aggregation by electrical charge compression. He goes on further to define flocculation as the process of destabilization which comes about by the adsorption of large organic polymers and the subsequent formation of particle-polymer-particle bridges. Both of these definitions describe coagulation and flocculation as two separate modes of particle destabilization. However, it is generally acknowledged that particle aggregation consists of two steps, particle destabilization and particle transport.

LaMer's definitions are applicable when contrasting optimum coagulant dosages for destabilization of various concentrations of colloidal material. However, this paper will apply the definitions used by Weber (3). The term coagulation will be used to describe the total process of particle aggregation, including both particle destabilization and particle transport. Flocculation will be used to describe only the transport step. These definitions conform to their common usage by engineers who are concerned with coagulation and flocculation as a method for treating wastewater.

III. STABILIZATION

Stability of a colloidal system refers to the extent to which small particles remain uniformly distributed throughout the sample. It is the objective of destabilizing the sample through coagulation and flocculation methods in the treatment of flexographic washwaters. Destabilization is essentially the process by which we reduce the naturally occurring repulsive forces of the colloidal system so that aggregation of the particles may take place.

Before the mechanisms of stabilization and destabilization are discussed, a brief summary of the terms and definitions associated with colloidal stability must be presented. Some colloids are stable indefinitely and some are not. Thermodynamically stable colloidal systems are called reversible and examples include soaps, proteins, and starches. Thermodynamically unstable colloidal systems are called irreversible and examples of this type of system include clays and metal oxides. Thermodynamically unstable systems which aggregate slowly are called diuturnal. Other irreversible systems are termed caducous and aggregate rapidly (2).

In treating contaminated water or wastewater, coagulation processes are used to aggregate irreversible colloidal systems. The primary objective of the coagulation process is to transform a diuturnal colloidal system into a caducous one.

The factors that influence colloidal stability have been a source of discussion and research work for many years. However, three stabilizing factors are generally acknowledged as being major contributors: 1) double layer repulsion; 2) short range hydration repulsion; and 3) protective colloid phenomenon. These factors are well summarized in a paper by Burke (4) and are discussed in detail by Hiemenz (1).

Double Layer Repulsion

The physical interpretation of this phenomenon is based on the theory of the electrical double layer, formulated by H. von Helmholtz (11). The electrical double layer consists of a surface charge, usually negative, and a compensating counter-ion charge. The counter-ion charge exists in the bulk of the liquid solution and tends to diffuse away from the surface of the colloidal particle where their concentration decreases. Figure I illustrates the electrical double layer model proposed by Stern (12).

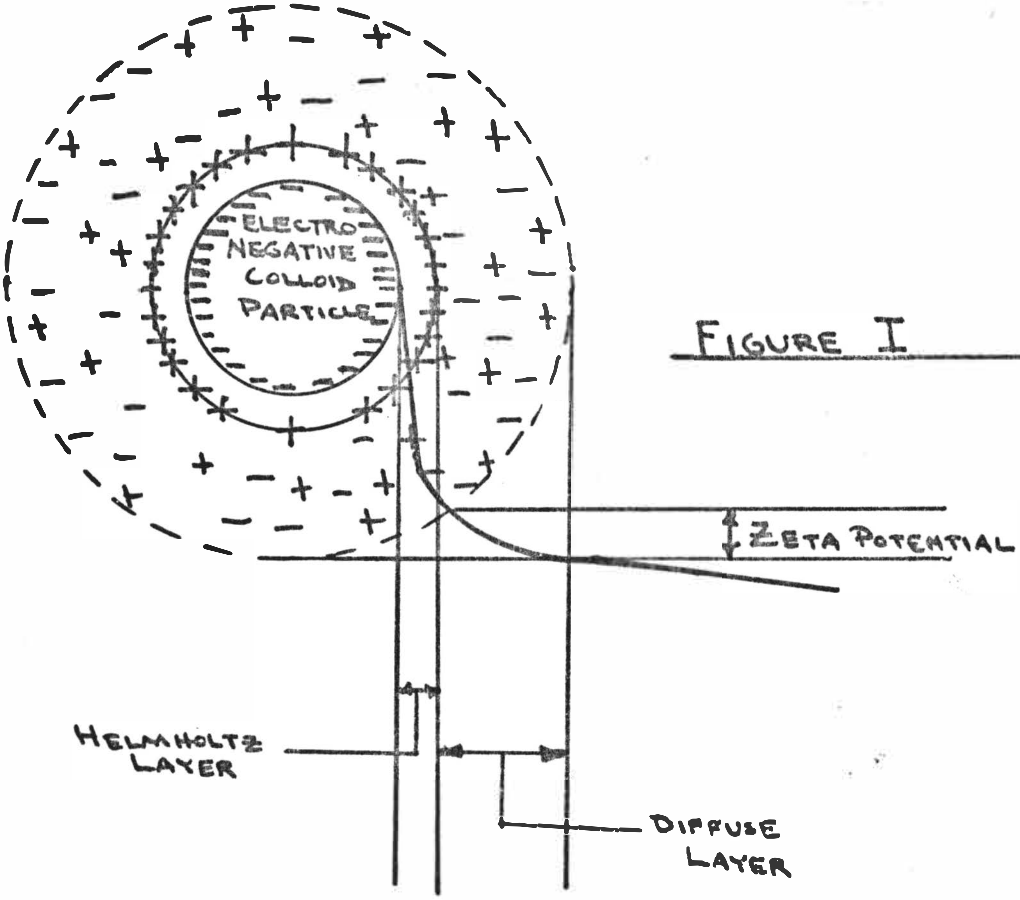
When two particles converge on one another in a suspension, their electrical double layers interfere and a mutual repulsion occurs. This mutual repulsion is generally termed "double-layer" repulsion and is measured by the magnitude of the zeta-potential of the particles.

Zeta potential, or electrokinetic potential, is the potential between the fixed, adsorbed ions on a particle and the ions which remain in solution. Figure II show the relationship between zeta potential and distance from colloidal surface. Essentially, the zeta-potential can be conceived to be the electric potential developed at the interface of the Helmholtz layer and Diffuse layer. Zeta potential is generally measured by micro-electrophoresis in agueous systems. This method allows you to observe and measure the particles movement, potential of the field, particle velocity, and along with the dimensions of the electrophoresis cell permits you to calculate particle mobility and the sign of the charge (16).

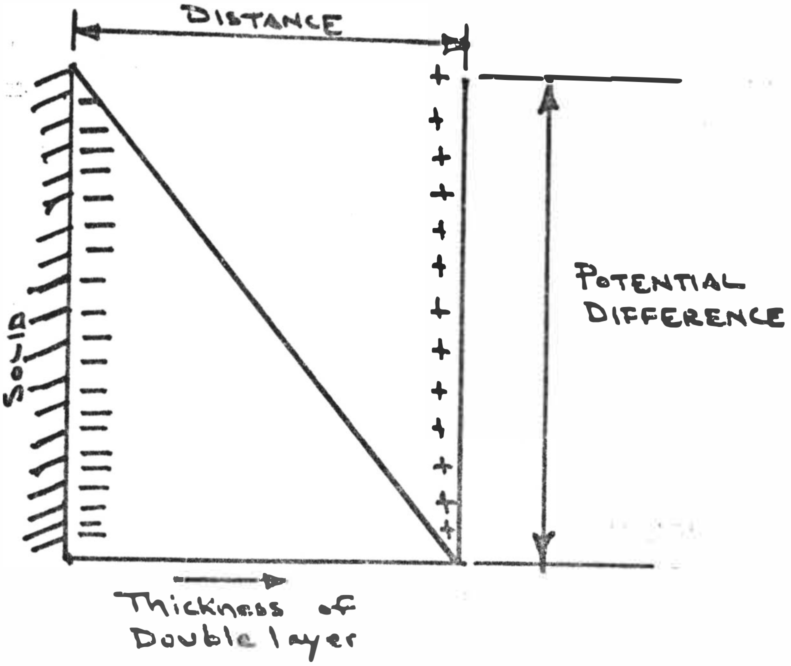
Short Range Hydration Repulsion

The effects of short range hydration repulsion on the stability of irreversible colloids are not well understood. Verwey, and Overbeek (13) were unable to characterize the stability of such systems, basing their models on charge effects alone.

FIGURE I


ELECTRO NEGATIVE COLLOID PARTICLE
ZETA POTENTIAL
HELMHOLTZ LAYER
DIFFUSE LAYER

E II


DISTANCE
SOLID
POTENTIAL DIFFERENCE
Thickness of Double layer

The stabilization in this case is thought to be due to adsorbed water molecules on the particles, to the degree of one or two monolayers. This layer serves to reduce the effective attractive forces (VanderWaals forces) among the particles and therefore prevents aggregation.

Protective Colloid Phenomenon

This stabilizing factor is found in systems where surface-active molecules are found rather than agueous systems. Examples of this system would be in the case of a gelatin on clay or silica.

The stability of a colloidal system based on this phenomenon is due to surface-active molecules preferentially adsorbing onto the particles. This can create a steric hindrance to the close approach necessary for aggregation or gives the surface a new property related to that of the adsorbed particles.

IV. DESTABILIZATION

As discussed earlier, destabilization is essentially the process by which the naturally occurring repulsive forces of the colloidal system are reduced so that aggregation of the particles may take place. Therefore, destabilization can be considered to be the combined effects of coagulation and flocculation or particle aggregation.

It has long been known that different chemical coagulants can bring about the destabilization of colloids in various ways. These chemical additives can function as coagulants or coagulant aids contingent upon the conditions under which they are applied.

Moreover, some coagulants can achieve colloidal destabilization by more than one method. An understanding of how coagulants function is required before proper selection and optimum dosage of these materials can be determined.

As in stability, destabilization of a colloidal system has been a source of much theoritical and research work. However, four distinct mechanisms are accepted as being primarily responsible for colloidal destabilization: 1) double layer compression; 2) adsorption and charge neutralization; 3) enmeshment in a precipitate; and 4) adsorption and interparticle bridging.

Double Layer Compression

The physical interpretation of this phenomenon was developed by Verwey and Overbeek (13) and was based on the effects of indifferent electrolytes on colloidal systems. The interaction of a coagulant species which acts as an indifferent electrolyte is purely electrostatic, that is, ions of similar charge to the primary change of the colloid particle are repelled, and counter-ions are attracted.

Counter-ions effect destabilization by compressing the diffuse layer (Figure I) around the colloidal surface. Addition of high concentrations of an indifferent electrolyte to a colloidal system will result in a high concentration of counter-ions in the diffuse layer. This results in a reduction of the thickness of the diffuse layer as a consequence of the reduced volume needed in the layer to maintain electroneutrality. Therefore, the naturally occurring repulsive forces between similar colloidal particles decreases, and existing inter-particle attractive forces may take over. These attractive forces are attributed to the general VanderWaals forces which exist between all colloidal particles no matter dissimilar their chemical natures are. These forces tend to increase with particle size and decrease with increasing distance tween the particles.

The mechanism proposed by Verwey and Overbeek also supports the empirical Schulze-Hardy rule developed in the early 1900's. This rule states that the destabilization of a colloidal system by an indifferent electrolyte is due to the counter-ion effect and that the effectiveness of the electrolyte as a coagulant increases with charge. It has been proven in research studies that the concentrations of Na^+, Ca^{+2}, and Al^{+3} required to coagulate negatively charged colloidal systems decrease in the same ratio as their charges.

The double layer compression phenomenon is of little interest to those concerned with treatment of water and wastewaters by coagulation methods. Indifferent electrolytes are rarely used in such processes and generally undergo other interactions aside from electrostatic effects. To develop an understanding of how coagulation manifests itself in these systems it is necessary to look at other modes of destabilization.

Adsorption and Charge Neutralization

This phenomenon is an outgrowth of the double layer compression mechanism discussed previously. It grew out of laboratory studies which indicated that it is possible to overdose colloidal dispersions with certain coagulant species which result in restabilization. This restabilization forms a uniformly distributed colloidal system and is accompanied by a charge reversal, that is, the primary charge on the colloidal particle is reversed from negative to positive by the adsorption of excess counter-ions. If electrostatic interactions were the only means by which destabilization occurs, the adsorption of excess counter-ions and subsequent change reversal could not happen. An example of this contrast is the experimental work performed by Tamamushi and Tamaki (14). Their work compared the coagulation effects between sodium ions and a charged organic amine product, dodecylammonium ions ($C_{12}H_{25}NH_3^+$), in a silver iodide sol. Their work showed that sodium ions were effective for coagulation up to concentrations around 10^{-1} moles/liter. However, it was impossible to overdose the colloidal dispersion with sodium ions upon further addition. The organic amine product was effective for coagulation at concerntrations as low as $6x10^{-5}$ moles/liter, but at concentrations at or above $4x10^{-4}$ moles/liter, restabilization occurred accompanied by a charge reversal.

It was determined that the organic amine used in this experiment was responsible for the restabilization and charge reversal of the colloidal system due to its surface active properties. These surface active materials are squeezed out of water onto particle surfaces due to their lack of interaction between the water molecules and the CH_2 groups in the tails of these ions.

It is generally acknowledged that the adsorption and charge neutralization mechanism works on the same principle as that outlined in the experimental work. Charged surface active materials, or coagulants which work similarly, accumulate at particle surfaces and account for the charge neutralization that takes place. This charge neutralization allows the natural attractive forces between colloidal particles become predominant and aggregation occurs.

Enmeshment in a Precipitate

This mechanism of destabilization is purely physical in nature and quite simple. It involves no electrostatic forces nor change of colloid surface properties. The enmeshment mechanism can be considered to be a filtering type of colloid removal and is dependent on the reaction time of a precipitation reaction.

This mechanism works on the basis that colloidal particles will be enmeshed in a precipitate as formed by metal salts, hydroxides, or oxides. Examples of metal salts would include alum ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$) or in the case of hydroxides and oxides, calcium hydroxide ($Ca(OH)_2$) and calcium oxide (CaO). These coagulants must be used in high concentrations in order to effect rapid precipitation. The rate of precipitation is primarily dependent upon the degree of oversaturation of the coagulant (3).

The amount of coagulant needed to produce good removal can generally be reduced however, due to the relationship of most colloids to positively charged precipitates. If the colloidal particles happen to be negatively charged (as they usually are) they will serve as nuclei for the formation of the positively charged precipitates. Therefore, the greater amount of colloidal particles in the sample will reduce the amount of coagulant dosage needed to achieve its removal.

Adsorption and Interparticle Bridging

Bridging is the mechanism by which a long chain polymer forms a connection between two or more particles. To be effective in destabilization, a polymer molecule must have chemical groups which can interact with sites on the surface of the colloidal particles.

According to LaMer and Healy (6), there are two types of bridging which can occur. See Figure III. First, bridging can occur when one end of a polymer chain contacts and is adsorbed upon one particle, while the other end of the chain attaches to another particle. The second method involves bridging through loops and tails. In this mechanism, a long chain polymer adsorbs on the particle surface at various sites along the polymer chain while the remaining, unattached portions of the polymer extend out into the solution ready to form bonds with other available particles.

Bridging requires that the places of attachment at the polymer-particle interface be strong. Britt (15) suggests that the addition of small, highly cationic molecule for preadsorption could provide the right conditions for good bridging and strength. Bridging in this case would be achieved through a long chain, anionic polymer.

LaMer and Healy (6) also discuss the importance of polymer concentration in colloidal systems. Too little polymer will leave available bridging sites unoccupied. Too much polymer will cause coating of the particle surfaces and reduce the available bridging sites. Thus, with no available bridging sites the extended polymer chains will have nowhere to adsorb onto and will fold back onto the particle with which they were first attached. Just the right polymer concentration will provide the required number of adsorption

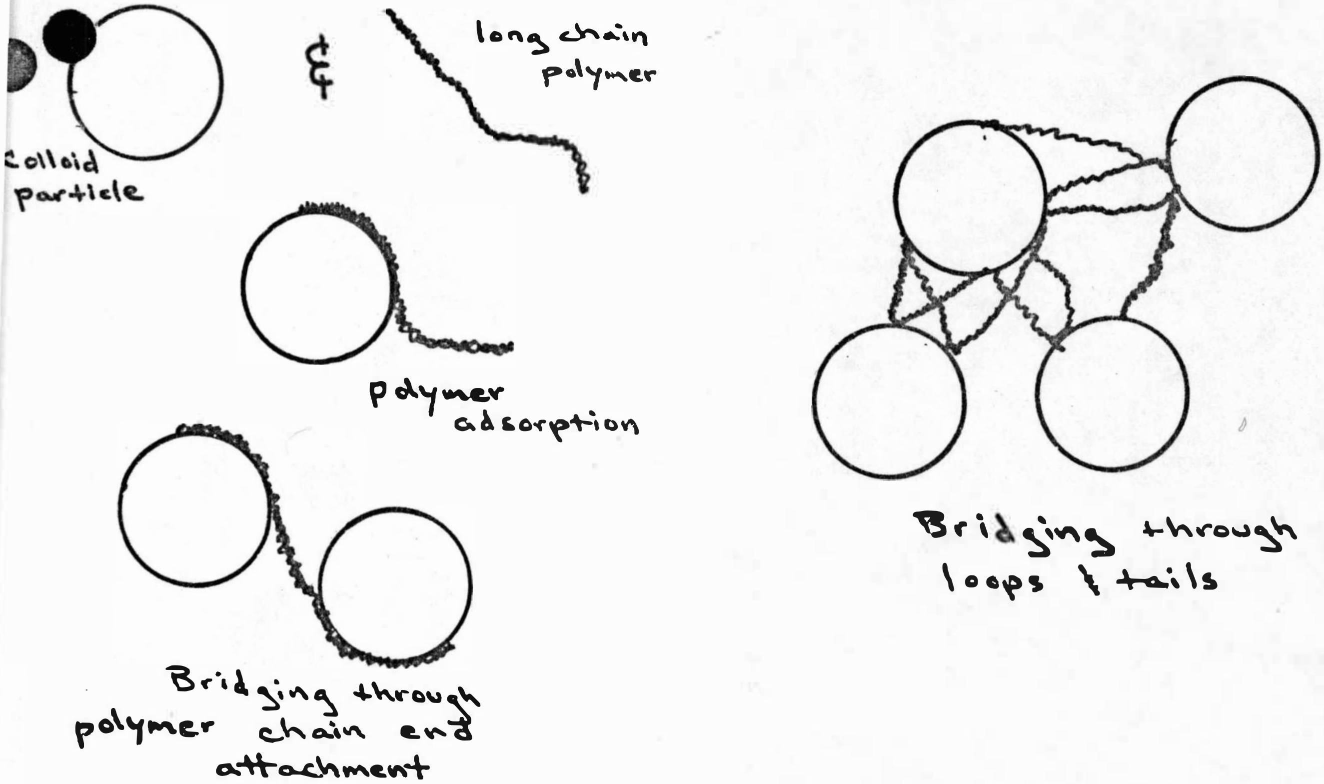


FIGURE III

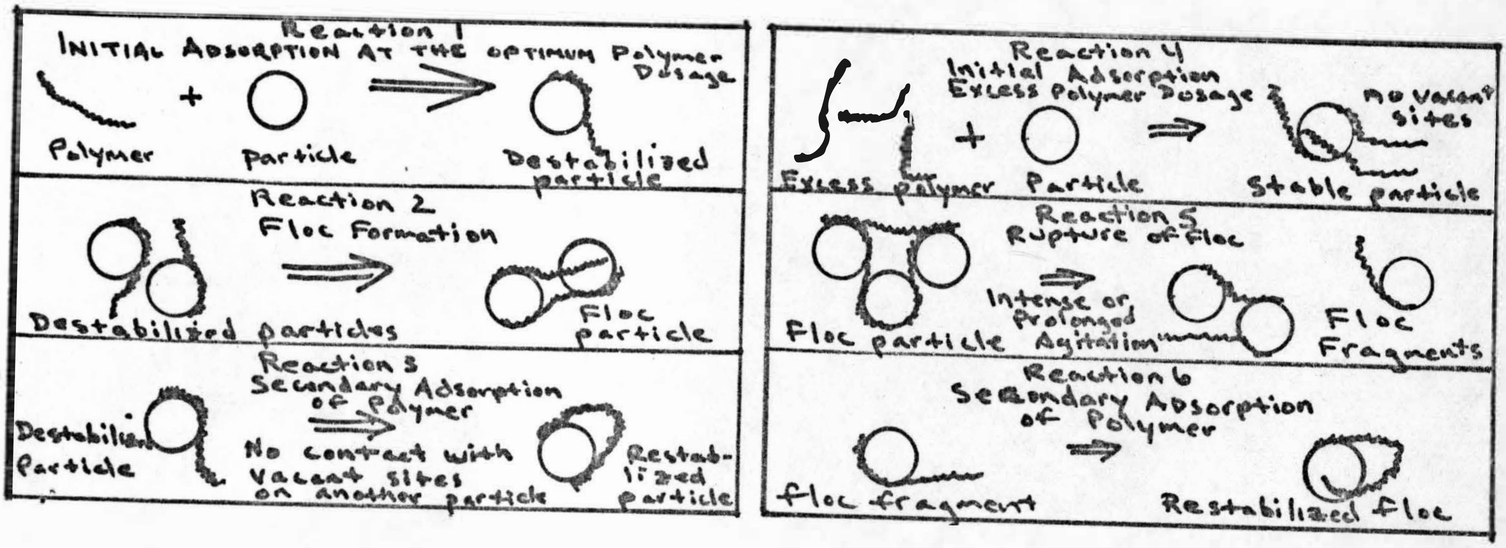


FIGURE IV

sites, without leaving any unused sites by the polymer. Figure IV is an illustration of the polymer concentration theory. Optimum dosage of polymer concentration is one area with which the experimental portion of this report will deal.

Particle Transport

Particle transport is highly important in coagulation operations. The rate of particle aggregation is dependent upon the rate at which collisions occur between colloidal particles (particle transport) and by the resulting attachment that occurs after the collious have taken place (particle destabilization).

It is generally accepted that there are three mechanisms which are responsible for interparticle contact (3): 1) contacts by thermal motion, often called Brownian motion; 2) contacts resulting from bulk fluid motion, i.e., mixing as a result of agitation; and 3) contacts resulting from differential settling of the particles where a rapidly settling particle overtakes and collides with a slower settling particle.

Brownian motion is a result of rapid and random bombardment of the colloidal particles by molecules of the fluid and is enhanced by the second mechanism mentioned, mixing. The mechanical energy of mixing not only adds to the energy of Brownian motion but also provides an even distribution of coagulant in the dispersion medium, producing a more uniform reaction.

The bridging mechanism of destabilization is greatly influenced by agitation as pointed out by LaMer and Healy (6). First, the polymer is adsorbed strongly and irreversibly on particle surfaces and therefore inadequate agitation causes intensive adsorption on particles around the point of addition leaving particles unflocculated in other parts of the system. Secondly, mixing enhances the chances for physical contact of polymers and particles to form bridges. However, vigorous agitation after the flocs formation causes the flocs to break up and the polymer bridge folds back to interact with the particle its other end is already attached to. After the flocs break up in this manner, the system cannot return to the previous state of flocculation. Both particle transport and contact time are important parameters in coagulation design and research and will be dealt with in the experimental portion of this report.

V. PARAMETERS IN TREATING FLEXOGRAPHIC WASHWATERS

Metals

As discussed previously, it is the heavy metals, i.e., lead, barium, and chromium, which make up the pigments in flexographic washwaters in which we are interested in removing by coagulation processes. These heavy metals are considered toxic and must be disposed of as a hazardous waste above minimum levels.

The concentration of metals in flexographic ink washwaters varies with ink formulation and with press cleaning methods. Although lead, chromium, and barium constitute the largest portion of heavy metals in flexographic inks, zinc, cadmium, copper, and nickel can also be detected in usually low concentration. The concentrations of these metals are generally low enough to be ignored when treating washwaters.

Color

Color removal, as classified earlier, is a secondary objective of treating flexographic washwaters.

There are two separate entities of color that must be discussed when considering its removal (5). The major portion of color in flexographic inks comes from apparent color. Apparent color is caused by suspended matter and in the case of flexographic inks, caused by the pigments which are comprised of the heavy metals. Therefore, heavy metals removal is directly proportional to color removal for this portion.

The other portion of color, and to a much lesser extent, comes from true color and is caused largely by dissolved matter. This dissolved matter appears as a result of "bleeding" of the ink pigments and is difficult if not impossible to remove by coagulation methods.

Total Solids Removal

Total solids removal is an important parameter in the treatment of flexographic inks in the boxboard industry or other printing operations. However, total solids in such an operation is the product of many extraneous wastes such as corrugated fiber dust, grease, dirt, etc. Since it would be impractical to include such things in a project such as this it will be excluded from the experimental portion of this paper and not be discussed further.

pH

pH is an important parameter in treating flexographic washwaters because it can affect the rate or degree of coagulation that can occur. pH controls the solubility of metals in inks and should be somewhat adjusted for optimum coagulation.

The optimum pH for most coagulation practices should be neutral or slightly below. The lower the pH of a solution, the lower the solubility constant of metals in solution. Therefore, by maintaining an optimum pH, it is ensured that coagulation will be optimized in relation to this parameter. Similar pH relationships are noticed for color removal also (13). The optimization of pH for effective coagulation will be discussed further in the experimental portion of this paper.

VI. STATE OF THE ART

The treatment of flexographic washwaters is receiving increasingly more attention as hazardous waste regulations become more stringent. Previous work on various treatment methods is somewhat broad and obscure. A lot of work has been done on using polymers in treating wastes but generally centers on treating biomass or various industrial wastes.

The latest work done on treating flexographic ink wastewaters was performed by O'Shaughnessy (5) and was presented at the 1980 Purdue Industrial Waste Conference. In his work he analyzed sedimentation (by coagulation), filtration, and centrifugation as treatment methods. Although he used three different coagulants prior to these processes, he did not compare the effects of the coagulants directly and did not utilize any organic polymers. His coagulants consisted of ferrous salts and were compared indirectly after the secondary processes were performed. The conclusions of this report were fairly broad and general and stated that the unit operations investigated for treating flexographic washwaters were fairly equivalent and satisfactory if used properly. However, O'Shaughnessy did cite that color removal was effected best when the flexographic wastes were oxidized with ozone after treatment.

VII. PRESENTATION OF PROBLEM

Throughout the preceding literature survey the area of flocculation and coagulation was reviewed and discussed. Also included was a discussion on flexographic inks and the environmental issues which face the flexographic and boxboard industry. The various physical and chemical aspects of flocculation and coagulation were presented to provide a better, more complete understanding of the entire area of these treatment parameters.

The primary goal of the second and experimental portion of this project was to define more closely the effect of various polymers on the treatment of flexographic ink washwaters containing heavy metal based pigments. It is hoped that the following experimental procedure and design will lead to a better understanding of coagulation and flocculation treatment parameters on flexographic washwaters.

VIII. EXPERIMENTAL

Laboratory jar tests were used in this experiment to determine coagulation and flocculation parameters on flexographic ink wash-waters. Jar tests are somewhat simple yet of great use when analyzing water or wastewater samples in the laboratory for research or in the control of plant operations. Jar tests simulate, as closely as possible, conditions under which coagulation and flocculation would take place in an industrial or municipal environment. Jar tests consist of a series of jars (or beakers) with agitators in them attached to the same drive shaft. These agitators are then run at the same time at the same speeds for reproducible mixing effects after the coagulants have been added. The agitators are stopped to allow for settling of floc formations and samples are taken subsequently.

These coagulation and flocculation tests are of great use in determining optimum chemical dosages for removal of turbidity, color, and auxiliary features such as pH adjustments. Other design parameters for large scale coagulation units can be derived from jar test data and include power requirements, settleability data of the flocs formed, clarity of the supernatant, and equipment sizing.

Experimental Design

Materials Used: Water-based flexographic ink - Hydro II GCMI #25 Green (Border Chemical Company)

Flocculants:
1) Alum, analytical grade $Al_2(SO_4)_3 \cdot 14H_2O$
2) Reten 521, furnished by Hercules Inc., anionic, high molecular weight retention aid

3) Betz 1260, furnished by Betz Laboratories Inc., cationic, medium molecular weight, low charge density flocculant

4) Ferric chloride, $FeCl_3 \cdot 6H_2O$

5) Alar F-201, furnished by Alar Engineering Corporation, cationic, inorganic flocculant

6) Nalco 7655, furnished by Nalco Laboratories, medium-high molecular weight, high charge density, cationic polymer.

Analytical Materials Used:

1) HACH Turbidimeter

2) Atomic Absorption Unit in Geology Department, Western Michigan University (tests were also run by Geology Department)

3) Corning - pH meter

Experimental Procedure

The procedure for the jar tests was taken from the standard methods of the American Society for Testing and Materials (ASTM). The experimental procedure follows ASTM's latest revisions and makes no major deviations from its method.

Part I - Preparation and Reaction of Polymers with Flexographic Ink Washwaters.

1) Measure equal volumes of samples into each of the jars to be used (1000 ml sample into 1500 ml beaker). Locate the beakers so that the paddles are off center, but clear the beaker wall by about ¼ inch. Record sample temperature at the start of the test.

2) Load the test chemicals (polymers) in the reagent racks. Use one rack for each series of chemical additions. All tubes should contain the same chemical but at various dosages to test for optimum concentrations.

3) Start the multiple stirrer operating at the "flash mix" speed of approximately 120 rpm. Add the chemicals, at predetermined

dosage levels and sequence. Flash mix for approximately one minute after the addition of chemicals. Record the flash mix time and speed (rpm).

4) Reduce speed as necessary, to the minimum required to keep floc particles uniformly suspended throughout the "slow mix" period. Slow mix for 20 minutes. Record the time for the first visible floc formation. Every five minutes during the slow mix period, record relative floc size and mixer speed (rpm).

5) After the slow mix period, withdraw the paddles and observe settling of floc particles. Record the time required for vertical particle movement to stop.

6) After 15 minutes of settling, record the appearance of floc on the beaker bottom. Record the sample temperature. By means of a pipet, withdraw an adequate sample volume of supernatant liquor from the jar at a point one half of the depth of the sample, to conduct color, turbidity, pH, and other various analyses.

Part II - Analyses of Supernatant.

The analysis of the supernatant was performed by using three main tests. These consisted of turbidity, pH, and heavy metals analysis (via atomic absorption). The procedures for these tests will not be dwelt upon since they were all run and calibrated according to their individual standard procedures.

1) Turbidity - HACH Model 2100A Laboratory Turbidimeter. Tests were run and calibrated according to the HACH wastewater analysis handbook (EPA approved).

2) pH - Corning pH meter. Tests were run and calibrated according to Standard Methods for Wastewater Analysis.

3) Heavy Metals - Atomic Absorption Unit, Geology Department, Western Michigan University.

Part III - Analysis of Flocs and Sedimentation.

The analysis of the floc structures and sedimentation effects induced by the flocculants was purely visual. These observations are included in the data tables.

IX. DATA

TABLE 1

Baseline Datum

Analysis of Raw 1:500 Dilution of
Simulated Flexographic Washwater

Flexographic Ink	-	Hydro II GCMI #25 Green (Borden Chemical Comp.)
Dilution	-	1 part Flexographic Ink 499 part Tap Water (process water)
Turbidity	-	3712 NTU
pH	-	7.10
Heavy Metals	-	Lead (Pb) 42.8 ppm Chromium (Cr) 11.2 ppm

TABLE 2

First Run
Flocculant - Alum
pH - 7.10
Temperature - 19.5°C

Flocculant Added (ppm)	Turbidity (NTU)	Final pH
10	off scale	7.10
20	off scale	7.10
30	off scale	7.10
40	off scale	7.10
50	210	7.05
60	245	6.95
70	230	6.90
80	180	6.80
90	125	6.80
100	89	6.80
110	52	6.70
120	67	6.70
130	15	6.60
140	16	6.60
150	17	6.60
160	13	6.60
170	17	6.60
180	21	6.50
190	22	6.45
200	14	6.40
210	17	6.40
220	17	6.30
230	19	6.25
240	15	6.25
280	22	6.50
320	18	6.45
400	25	6.45
600	40	6.43

Second Run

Temperature - 20°C

Flocculant Added (ppm)	Turbidity (NTU)
126	24
136	18
144	17
156	16
164	16
176	20
184	20
196	19
204	25
216	28
224	25
236	25
400	35
800	83

TABLE 3

First Run

Flocculant - Reten 521 with 160 ppm Alum
pH - 7.10
Temperature - 19.5°C

Flocculant Added (ppm)	Turbidity (NTU)	Final pH
1.0	3.1	6.95
2.0	2.9	6.95
3.0	3.3	6.95
4.0	4.4	6.95
5.0	3.4	6.95
7.5	3.5	6.95
10.0	3.4	6.95
12.5	3.1	7.05
15.0	3.8	7.05
17.5	4.3	7.00
20.0	4.4	6.95
22.5	4.9	6.95
25.0	4.4	6.95
40.0	4.6	6.95
60.0	5.6	6.95
90.0	5.8	6.95
120.0	8.8	6.90

Second Run

Temperature - 20°C

Flocculant Added (ppm)	Turbidity (NTU)
.5	18.0
1.5	2.5
2.5	3.0
3.5	4.0
4.5	4.0
6.0	3.8
9.0	3.5
11.0	4.1
14.0	4.1
16.0	4.0
19.0	5.5
21.0	6.0
24.0	6.5
26.0	6.5
29.0	7.1
31.0	7.0
34.0	8.5
36.0	8.5

TABLE 4

First Run

Flocculant - Ferric Chloride
pH - 4.5
Temperature - 17.5°C

Flocculant Added (ppm)	Turbidity (NTU)	Final pH
60	off scale	4.45
80	off scale	4.45
100	off scale	4.40
120	off scale	4.40
140	240	4.40
160	210	4.35
180	155	4.35
200	155	4.30
220	200	4.20
240	200	4.20
260	200	4.30
280	180	4.15
300	53	4.10
400	78	4.00
500	125	3.90
600	off scale*	3.85
800	off scale	3.85

Second Run

Temperature - 19°C

Flocculant Added (ppm)	Turbidity (NTU)
280	168
290	110
300	61
310	60
315	59
320	55
325	55
330	60
340	67
350	70
360	69
370	78
380	85
390	90
600	off scale

TABLE 5

First Run

Flocculant - ALAR F-201
pH - 7.10
Temperature - 19°C

Flocculant Added (ppm)	Turbidity (NTU)	Final pH
24	off scale	7.10
72	140	7.00
120	30	6.85
168	22	6.75
192	17	6.65
240	14	6.50
480	34	5.40
720	33	3.30
960	57	3.00
1200	86	2.80
1440	102	2.70

Second Run

Temperature - 21°C

Flocculant Added (ppm)	Turbidity (NTU)
120	40
144	35
168	25
192	23
216	18
240	18
264	25
300	24
360	25
420	30
480	38
1400	100

TABLE 6

First Run

Flocculant - NALCO 7655
pH - 7.10
Temperature - 22°C

Flocculant Added (ppm)	Turbidity (NTU)	Final pH
2	53	7.10
5	30	7.10
8	24	7.10
12	22	7.10
15	22	6.95
18	21	6.90
20	20	6.85
40	120	6.85
60	230	6.80
80	280	6.85
100	300	6.75
120	300	6.70

Second Run

Temperature - 21°C

Flocculant Added (ppm)	Turbidity (NTU)
5	45
7	30
9	20
11	18
13	20
17	20
18	25
20	35
22	40
26	45
30	75
35	100

TABLE 7

Heavy Metals Analysis (Atomic Absorption)
Flocculant - Alum

Flocculant Added (ppm)	Lead (ppm)	Chromium (ppm)
60	7.50	8.00
100	1.25	1.05
120	0.90	1.75
126	0.25	0.08
150	0.25	0.09
156	0.00*	0.10
160	0.00	0.00
164	0.10	0.10
180	0.10	0.15
210	0.35	0.10
216	0.32	0.10
280	0.40	0.10
400	0.50	0.25
600	0.75	0.00

*not detected under conditions of procedure

TABLE 8

Heavy Metals Analysis

Flocculant - Reten 521 with 160 ppm Alum

Flocculant Added (ppm)	Lead (ppm)	Chromium (ppm)
0.5	0.10	0.05
1.0	0.00	0.00
1.5	0.10	0.00
3.5	0.00	0.00
4.0	0.00	0.00
6.0	0.00	0.00
7.5	0.00	0.00
9.0	0.05	0.00
19.0	0.05	0.10
22.5	0.10	0.25
60.0	0.10	0.20
120.0	0.15	0.25

TABLE 9

Heavy Metals Analysis
Flocculant - Ferric Chloride

Flocculant Added (ppm)	Lead (ppm)	Chromium (ppm)
220	7.75	3.00
280	6.05	2.90
300	0.90	0.00
320	0.95	0.18
350	0.50	0.30
390	1.00	0.10
400	3.20	0.40

TABLE 10

Heavy Metals Analysis
Flocculant - ALAR F-201

Flocculant Added (ppm)	Lead (ppm)	Chromium (ppm)
120	0.50	1.50
168	0.60	0.60
192	0.00	0.00
240	0.22	0.85
264	0.95	1.10
420	1.30	1.30
720	1.00	4.70
1440	2.50	7.63

TABLE 11

Heavy Metals Analysis
Flocculant - NALCO 7655

Flocculant Added (ppm)	Lead (ppm)	Chromium (ppm)
2	2.00	1.60
5	1.60	1.20
8	0.30	0.12
11	0.45	0.97
15	0.21	0.10
18	0.23	0.75
20	0.30	1.10
60	6.90	2.95
120	7.10	3.55

TABLE 12

Sludge and Floc Characteristics
Visual Analysis

Flocculant - Alum

	Flocculant Added (ppm) - Optimum Range		
	120	220	320
Settling Characteristics	fast settling, 4.0 cm./min.		
Sludge Characteristics	coarse, final layer thickness, 3.5 cm.		
Floc Characteristics	coarse, bulky, 0.5 - 1.0 cm. width		
First Floc Formation	immediately - 10 seconds		

TABLE 13

Sludge and Floc Characteristics
Visual Analysis

Flocculant - Reten 521 with 160 ppm Alum

	Flocculant Added (ppm) - Optimum Range		
	1 ppm	6 ppm	11 ppm
Settling Characteristics	extremely fast settling, 9.0 cm./min.		
Sludge Characteristics	extremely coarse and lumpy, final layer thickness, 5.5 cm.		
Floc Characteristics	coarse, clumpy, 1.0 - 2.5 cm. width		
First Floc Formation	immediately - 5 seconds		

TABLE 14

Sludge and Floc Characteristics
Visual Analysis

Flocculant - Ferric Chloride

	Flocculant Added (ppm) - Optimum Range		
	260	380	500
Settling Characteristics	slow settling, 1.0 - 2.0 cm./min.		
Sludge Characteristics	fine, well-packed layer, final layer thickness, 2.5 cm.		
Floc Characteristics	fine floc formation, 0.1 - 0.5 cm. width		
First Floc Formation	30 seconds - 60 seconds		

TABLE 15

Sludge and Floc Characteristics
Visual Analysis

Flocculant - ALAR F-201

	Flocculant Added (ppm) - Optimum Range		
	120	420	720
Settling Characteristics	slow settling, 2.0 cm./min.		
Sludge Characteristics	relatively course and lumpy, final layer thickness, 4.0 cm.		
Floc Characteristics	coarse, bulky, 1.0 - 2.0 cm. width		
First Floc Formation	10 seconds - 30 seconds		

TABLE 16

Sludge and Floc Characteristics
Visual Analysis

Flocculant - NALCO 7655

	Flocculant Added (ppm) - Optimum Range 5 12 20
Settling Characteristics	fast settling, 5.0 cm./min.
Sludge Characteristics	relatively compact, final layer thickness, 2.5 cm.
Floc Characteristics	somewhat coarse, 0.5 - 1.0 cm. width
First Floc Formation	15 seconds - 30 seconds

FIG. VI

TURBIDITY AND HEAVY METALS REMOVAL VS. ALUM DOSAGE

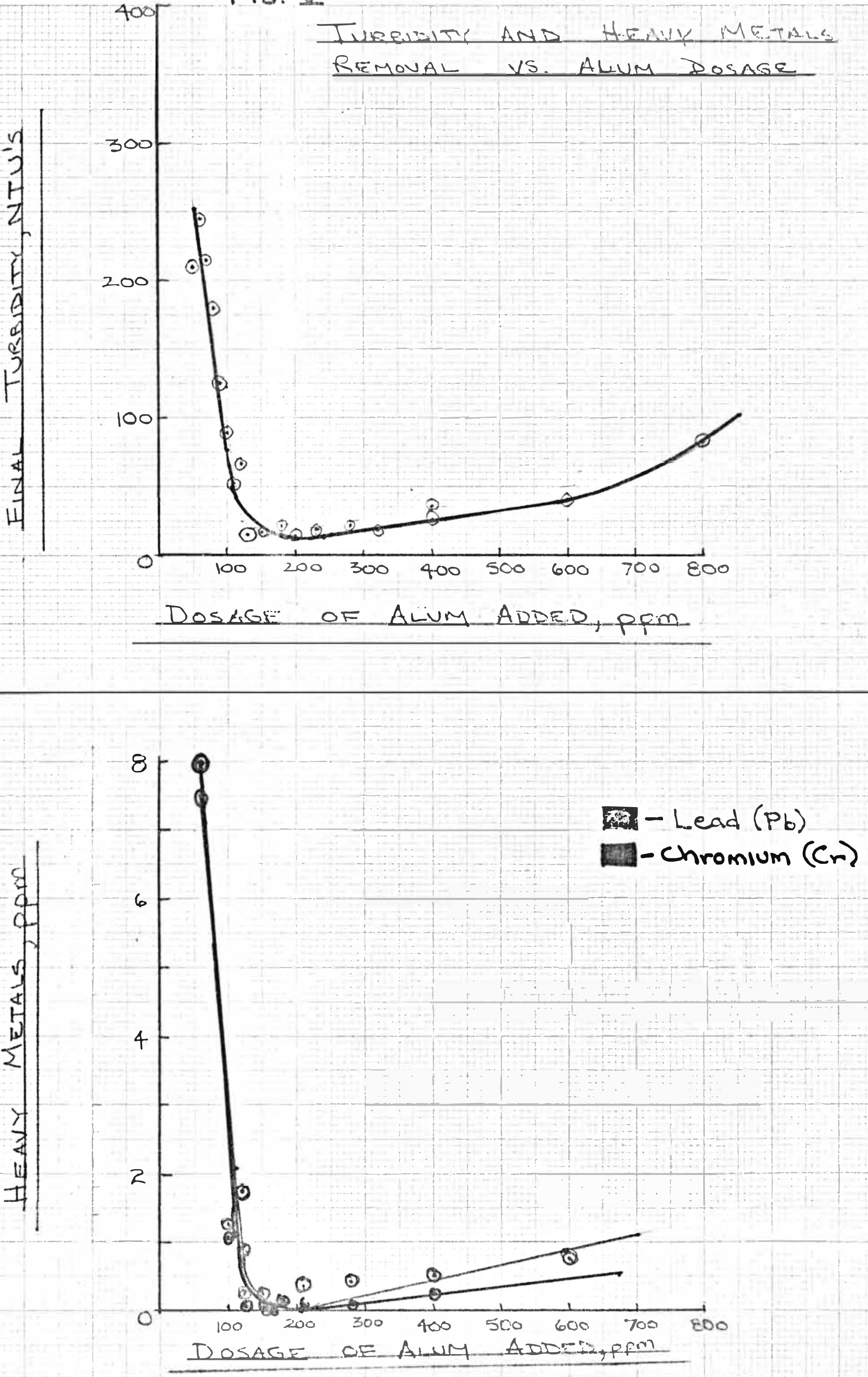


FIG. VI

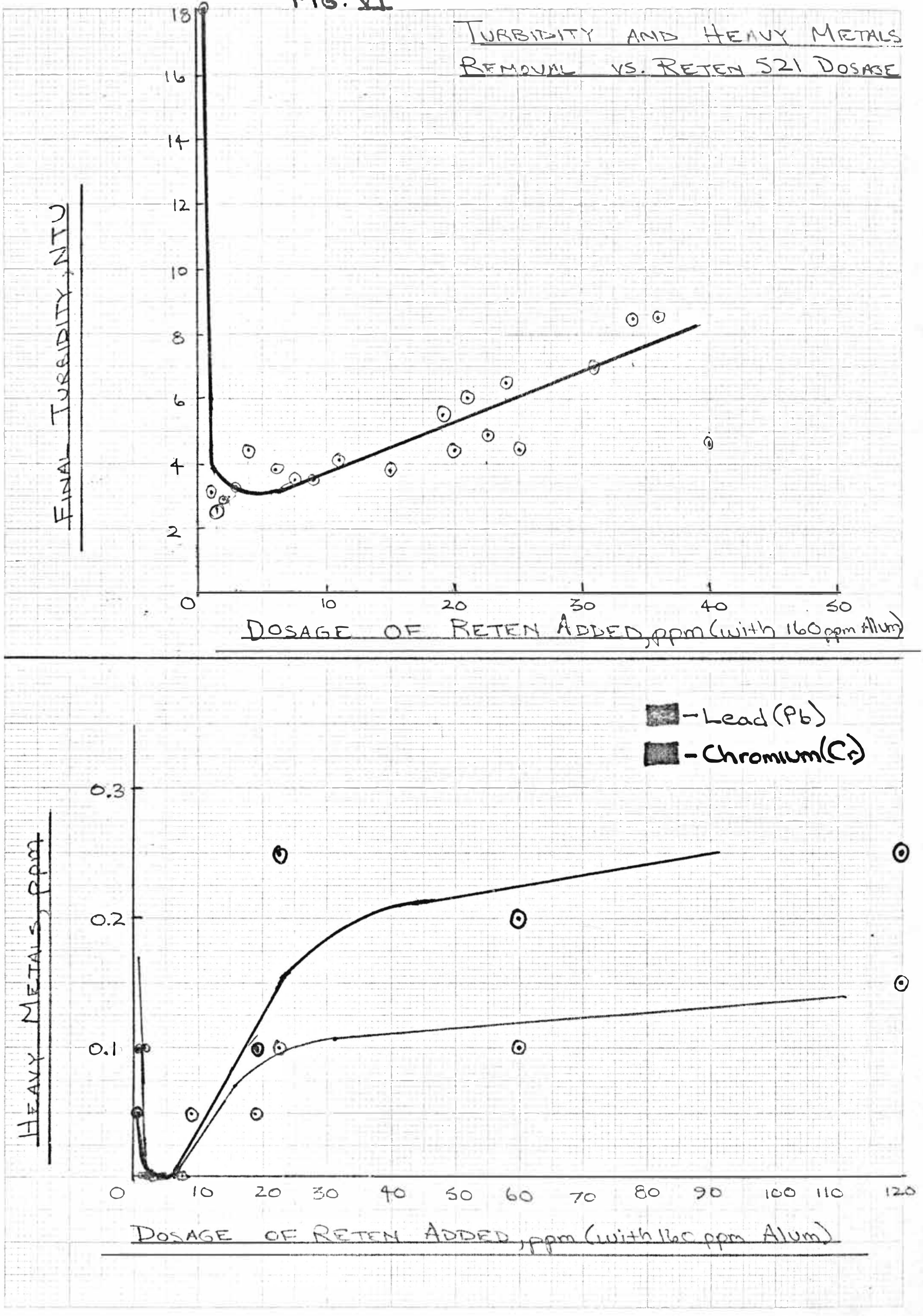
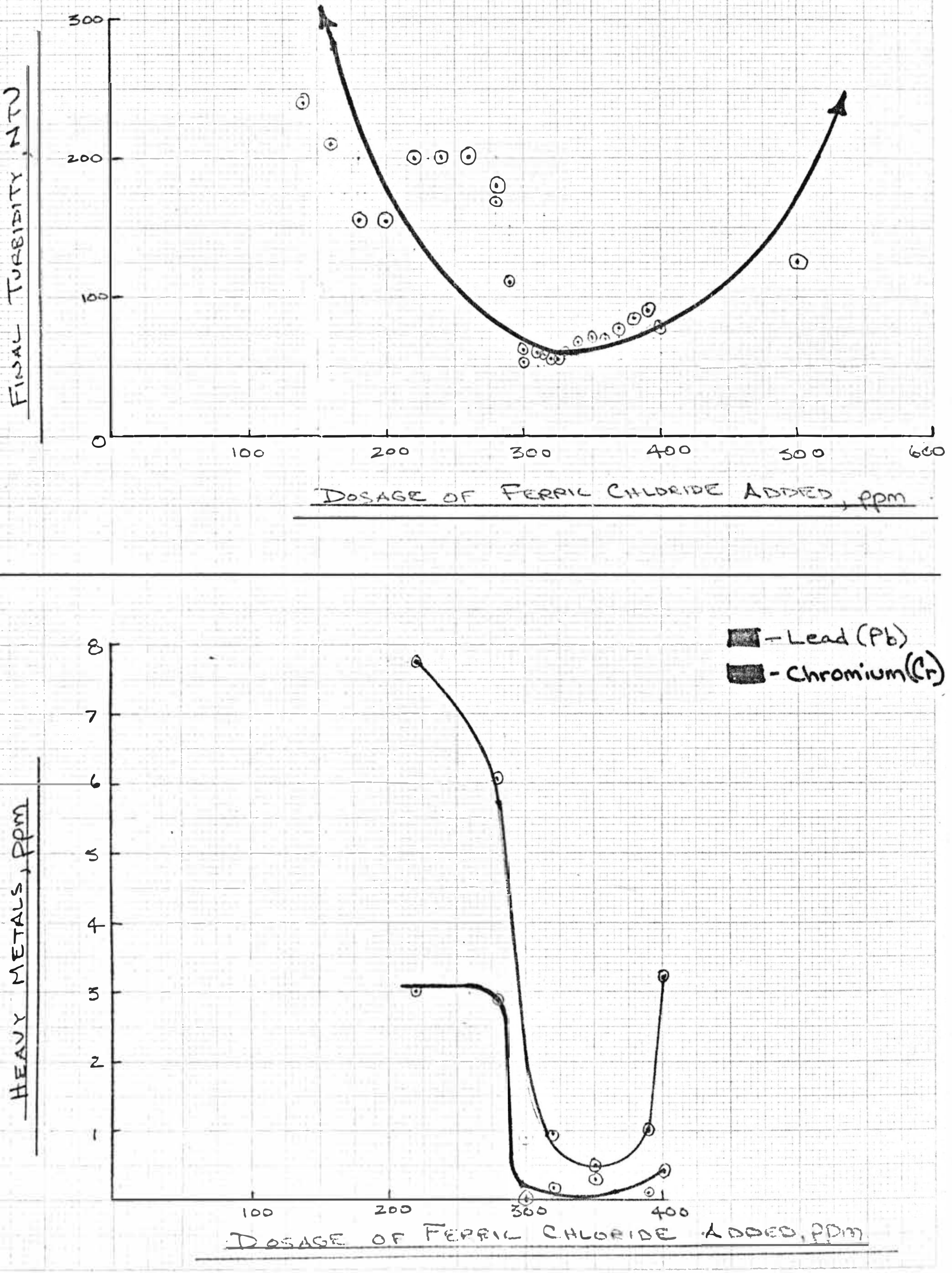

TURBIDITY AND HEAVY METALS REMOVAL VS. RETEN 521 DOSAGE

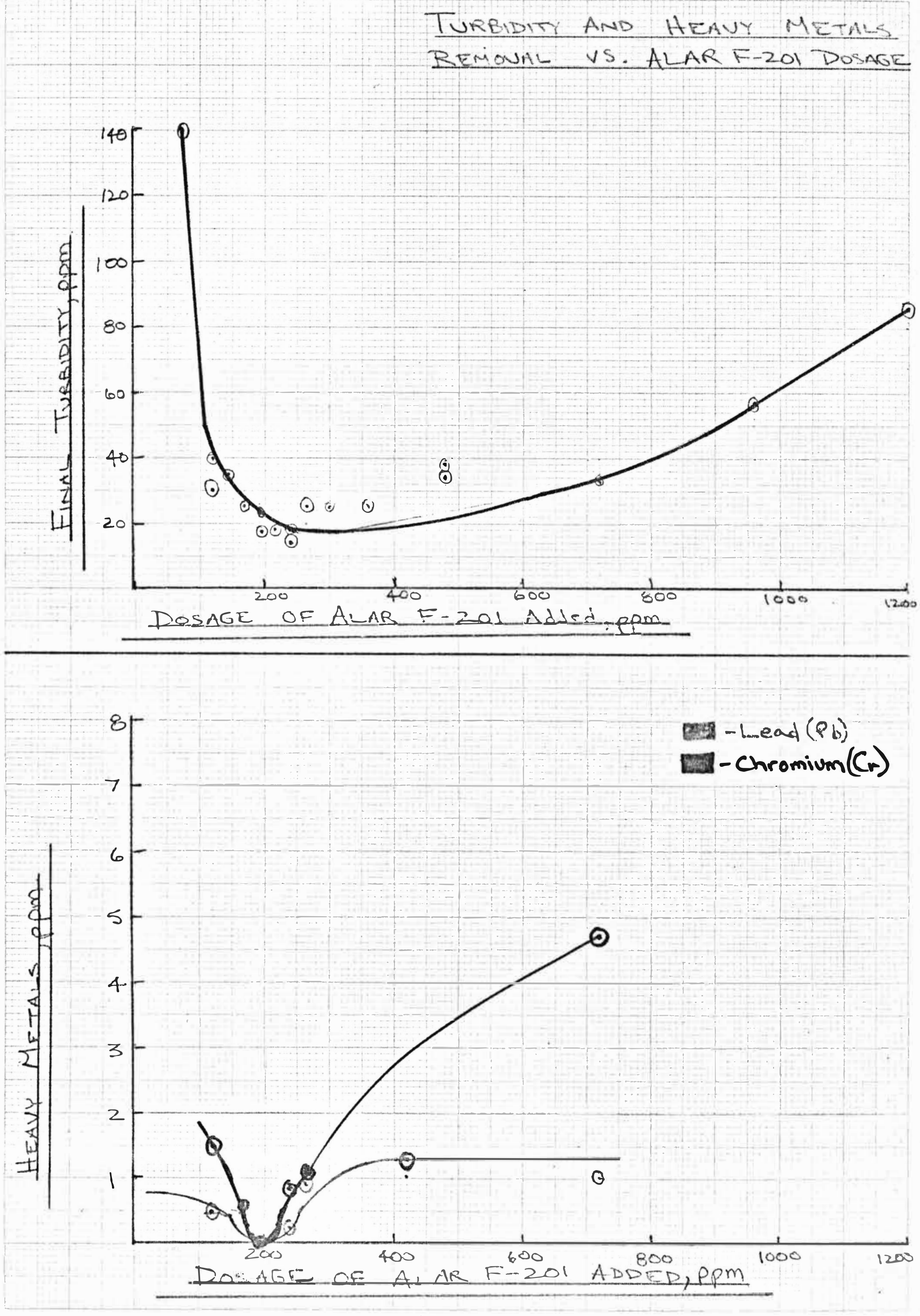
FIG. VII

TURBIDITY AND HEAVY REMOVAL VS. FeCl$_3$ DOSAGE



to the Inch

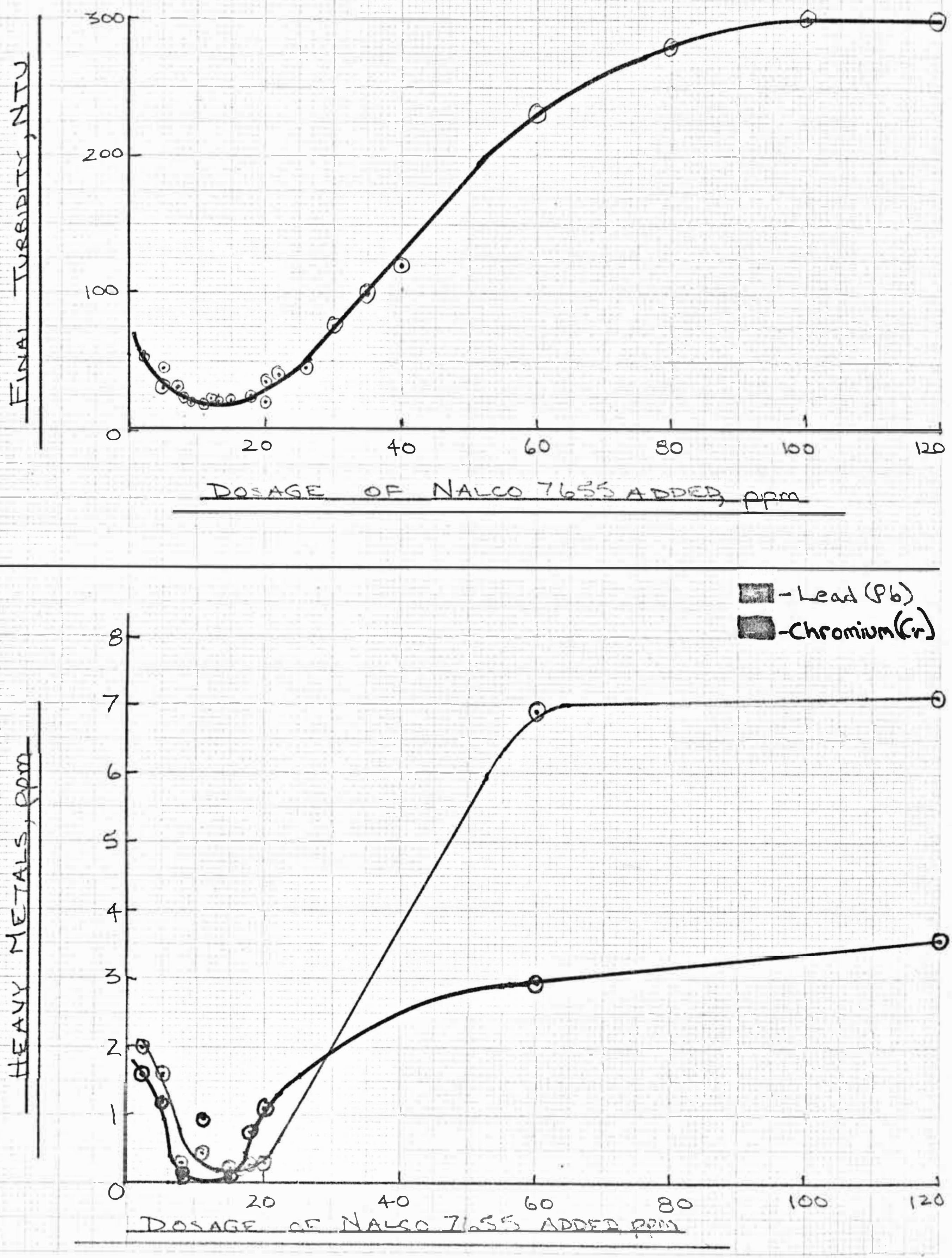
FIG. VIII



TURBIDITY AND HEAVY METALS REMOVAL VS. ALAR F-201 DOSAGE

FIG. IX

TURBIDITY AND HEAVY METALS REMOVAL vs. NALCO 7655 DOSAGE



X. DISCUSSION OF RESULTS

The experimental results of using various polymers as flocculants are displayed in Tables 2 to 16 and Figures V to IX. In the present investigation, the degree of treatment done on the flexographic press washings is indicated by the analysis of supernatant clarity, heavy metals removal, and settling characteristics.

Figure V and Tables 2 and 7 show the effects of various levels of addition of alum on supernatant clarity and heavy metals removal. The numbers assigned to alum addition (and all other polymers used in this experiment) represent the total percentage of flocculant present in the clarifier (1 liter).

The results show that optimum clarity, as indicated by turbidity response, occurs in the alum addition range of 150 - 200 ppm. Through this range, turbidity hits a low of 13 NTU while maintaining an average of 18 NTU. After the optimum range of alum addition is passed, turbidity increases but not quite as rapidly as it decreased to begin with.

Alum has somewhat the same effect on heavy metals as turbidity as shown by the bottom portion of Figure V. Lead and chromium seem to follow the same path of removal during the range of addition of alum. Both lead and chromium are effectively removed from the supernatant and do indeed decrease to 0 ppm at the same optimum range for turbidity removal.

The fact that turbidity and heavy metals respond in the same fashion and decrease in the same manner in an optimum range of concentration is of great consequence. If the same range for removal occurs for both, this greatly enhances the chance of flocculation being highly effective as an overall treatment for flexographic washwaters.

The pH drop effected by increasing addition of alum as shown in Table 2 seemed to have no detrimental effect. As discussed earlier in the literature survey, a low pH in a solution containing metals can decrease the solubility constant of the metals in the ink pigment and put them in solution. However, the pH dropped off only slightly in approaching the optimum range and apparently was not low enough to have any affect. If the metals were to go into solution, it is suspected that they would not have been affected by the bridging mechanism induced by the flocculant or meshed by the settling precipitate. This would have resulted in greater heavy metals content in the supernatant.

Table 12 contains settling and floc characteristic data for the optimum range of alum addition. Settling and floc characteristic data were taken by using a purely visual analysis and all dimensions were measured by an ordinary ruler. The settling rate of 4.0 cm./min. is a positive sign that gravity settling may be an effective way of letting the supernatant clear itself after treatment with a flocculant. This settling rate seems to be within typical ranges for industrial waste treatment. The sludge and floc characteristics also lend themselves to positive applications. The flocs were quite bulky with an average of 0.75 cm in width. This leads to the premise that sludge and supernatant post-treatment by means of filtering, centrifugal action, etc. could further optimize the treatment process and get even greater results in turbidity and metals removal.

Tables 3 and 8 and Figure VI demonstrate the results of using Reten 521 with 160 ppm alum. Reten 521 is a anionic flocculant used extensively in the paper industry. The idea behind using Reten 521 is to "floc the flocs" that are pre-formed by alum. Therefore, an optimum concentration of alum was chosen from the first run (160 ppm) and was added as a flocculant to the clarifiers. Reten 521 was then added under flash mix conditions in order to propogate complete contact with the alum flocs.

The top portion of Figure VI show that turbidity was remarkably reduced from the previous run using just alum. The best turbidity reading received while using alum as the flocculant was 13 NTU. On the other hand, Reten 521 added to a optimum concentration of alum resulted in a low turbidity figure of 2.5 NTU. It is also seen that this clarity was achieved at a very low addition of Reten.

In the lower portion of Figure VI, it is clear that while optimum clarity was being achieved, so was removal of lead and chromium. Again, as in the laboratory run with alum, lead and chromium dropped down to 0 ppm at an optimum level of flocculant addition. However, once outside a range of addition of 2 to 7 ppm, lead and chromium content rose sharply. This correlates the sharp dependency of heavy metals removal to concentration of Reten 521.

The sludge and floc characteristics of this experimental run were also excellent. Extremely fast settling occurred, 9.0 cm./min., showing a rate of double that of alum. Flocs were characterized as being rather large, 1.0 - 2.5 cm. in width, and forming quickly.

Tables 4 and 9 and Figure VII contain the results from the experimental run using ferric chloride as the flocculant. In order to optimize the flocculation process with ferric chloride, the pH of the flexographic press washings was dropped to 4.5 using concentrated hydrosulfuric acid. The pH was not dropped any further because of the fear that the solubility constant of the metals would be dropped extensively.

The top portion of Figure VII shows that ferric chloride was not nearly as effective in producing clarity in the supernatant as alum or Reten 521. The best turbidity produced was 53 NTU and this was at a relatively high addition of 300 ppm.

Lead removal, as indicated by the lower portion of Figure VII was not as good as was seen with alum, with and without Reten 521. Chromium removal was substantially achieved (0 ppm) but at a slightly different addition of flocculant.

The settling characteristics of these flocs were characterized by slow settling as shown in Table 14. The fine floc formations undoubtedly contributed to this as well as the decrease in clarity not seen in the other flocculants.

Tables 5 and 10 and Figure VIII give the results in using ALAR F-201 as a flocculant. ALAR F-201 is an inorganic chemical developed by ALAR engineering and is a multi-purpose flocculant.

The top portion of Figure VIII shows optimum clarity reached at a relatively fast rate with best results at around 240 ppm. The turbidity again increases after this but at decreasing rate.

Lead and chromium removal are achieved efficiently and reaches a minimum of 0 ppm. However, both of these metals are best removed at 19 ppm which is below the rate of addition at which optimum clarity results. Although the difference between the optimum flocculant additions are minimal, this could be a major factor in choosing a coagulant to meet treatment objectives.

Table 15 indicates that floc characteristics are good in that the flocs are coarse, 1.0 - 2.0 cm. in width, and form relatively fast, 30 to 60 seconds. However, the settling rate is reduced compared to the other flocculants, 2.0 cm./min..

Tables 6 and 11 and Figure IX show turbidity and heavy metals removal versus the addition of the flocculant, Nalco 7655. Nalco 7655 is a high molecular weight cationic flocculant frequently found in use in the paper industry.

Nalco 7655 minimizes turbidity at a relatively low range of addition but increases quite rapidly outside of a zone of 10 ppm. The best turbidity value obtained was 18 NTU and was fairly consistent within a range of 5 ppm.

Heavy metals reduction was achieved within the same range as clarity. However, lead did not achieve the same removal as chromium. Lead seemed to provide some difficulty in removal during all additions of the flocculant. Heavy metals reduction was also analogous to turbidity in that outside a short range of maximum removal, lead and chromium concertration in the supernatant rose sharply.

Table 16 lists the settling and floc characteristics for the Nalco 7655 Run. The flocs were characterized by being somewhat coarse, 2.5 cm. in width, but resulting in a relatively compact layer after sedimentation. The flocs settled quickly at an average rate of 5.0 cm./min. and formed quickly at 15 to 30 seconds.

Linear Dependency Between Heavy Metals Removal and Turbidity Removal as a Function of Flocculant Dosage

In order to more clearly demonstrate the relationship between turbidity removal and heavy metals removal as a dependent function on flocculant dosage, a simple linear regression analysis was performed and is presented here as part of the results presentation.

The procedure for this analysis was to plot heavy metals vs. turbidity for the flocculant. A least squares analysis was then performed to find the "best" line through these set of points by deriving a slope and y-intercept to fit the point-slope formula.

Figure X shows the linear fit for lead and chromium vs. turbidity as a function of alum dosage. This figure clearly demonstrates the linear dependency between heavy metals and turbidity. Table 17 contains the linear equations and standard deviations for the least squares fit for each flocculant. A linear analysis was not performed for ferric chloride because the data did not allow for enough points for a good fit.

Also listed in Table 17 is the standard deviation for all the slopes (σ_m) and y-intercepts (σ_b). The largest deviation encountered was with Reten 521, lead removal vs. turbidity. The standard deviation of the slope was ± 0.756 while the deviation for the y-intercept was ± 0.407. These figures are respectable and indicates that all the other deviations for the trials are minimal and of no consequence.

This linear dependency demonstrates that turbidity is proportional to heavy metals content in the flexographic press washwaters. This is understandable when it is precluded that the pigments which contain the heavy metals are the cause for the turbidity and their removal effects removal of the lead and chromium as well as the color.

FIG. X

Heavy metals vs. TURBIDITY as a function of Alum dosage.

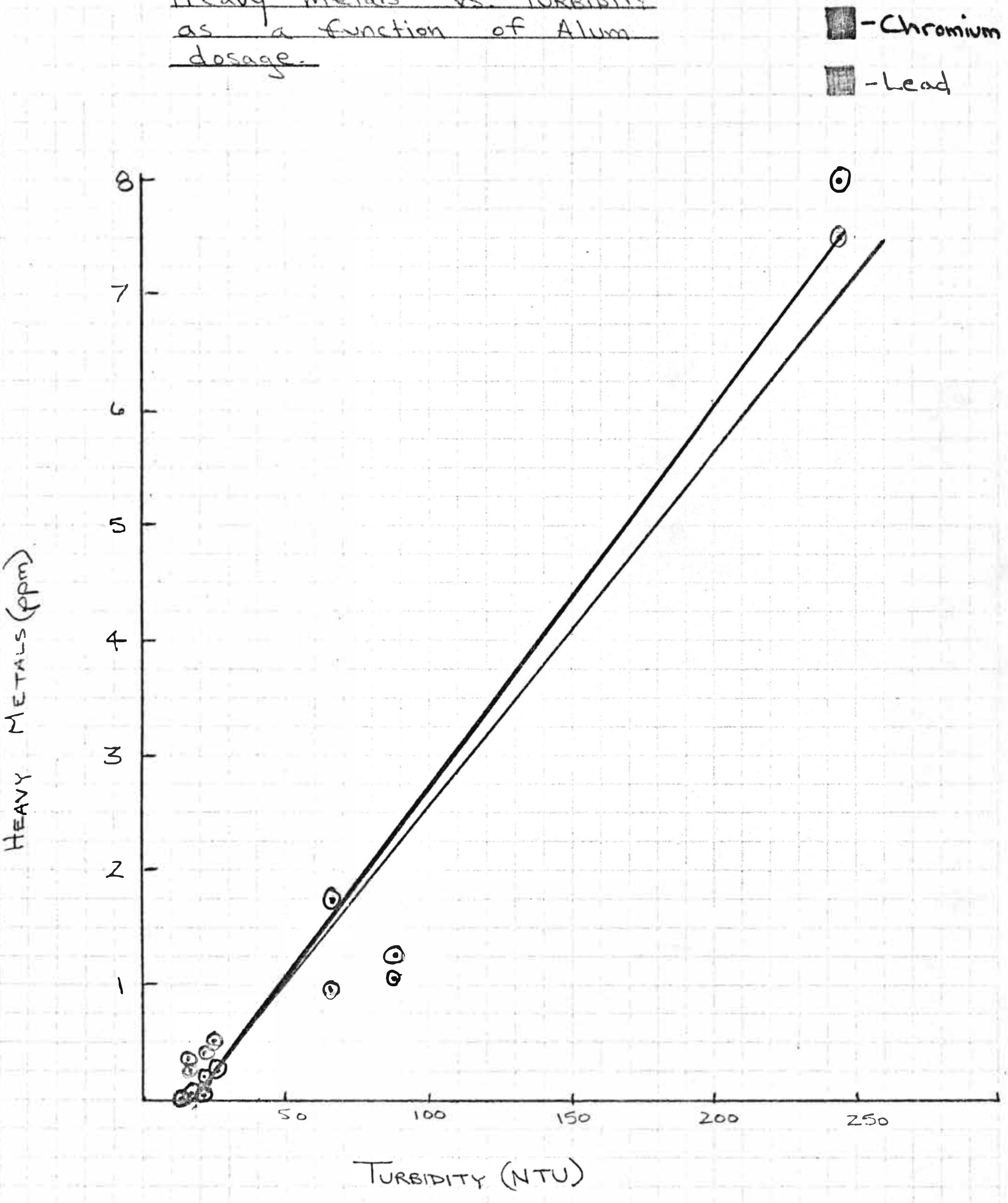


TABLE 17

Linear Dependence Between Heavy Metals and Turbidity as a Function of Flocculant Dosage

Alum

Lead Removal vs. Turbidity:

$y=0.031x-0.525$ $(y-mx+b)$

$\sigma_m=\pm 0.0024\ \frac{ppm}{NTU}$

$\sigma_b=\pm 0.223$ ppm

Chromium Removal vs. Turbidity:

$y=0.034x-0.662$

$\sigma_m=\pm 0.0025\ \frac{ppm}{NTU}$

$\sigma_b=\pm 0.228$ ppm

Reten 521 with 160 ppm Alum

Lead Removal vs. Turbidity:

$y=0.0287x-0.086$

$\sigma_m=\pm 0.756\ \frac{ppm}{NTU}$

$\sigma_b=\pm 0.407$ ppm

Chromium Removal vs. Turbidity:

$y=0.048x-0.126$

$\sigma_m=\pm 0.0203\ \frac{ppm}{NTU}$

$\sigma_b=\pm 0.110$ ppm

(continued on next page)

TABLE 17 (continued)

NALCO 7655

Lead Removal vs. Turbidity:

$y=0.026x-0.024$

$\sigma_m=\pm 0.0022 \ \frac{\mathrm{ppm}}{\mathrm{NTU}}$

$\sigma_b=\pm 0.291$ ppm

Chromium Removal vs. Turbidity

$y=0.0104x+0.517$

$\sigma_m=\pm 0.0015 \ \frac{\mathrm{ppm}}{\mathrm{NTU}}$

$\sigma_b=\pm 0.192$ ppm

ALAR F-201

Lead Removal vs. Turbidity:

$y=0.0253x+0.0215$

$\sigma_m=\pm 0.0046 \ \frac{\mathrm{ppm}}{\mathrm{NTU}}$

$\sigma_b=\pm 0.197$ ppm

Chromium Removal vs. Turbidity

$y=0.084x-0.648$

$\sigma_m=\pm 0.016 \ \frac{\mathrm{ppm}}{\mathrm{NTU}}$

$\sigma_b=\pm 0.683$ ppm

Results in Perspective

In an effort to put the results in perspective, Tables 18 and 19 have been prepared. Table 18 is presented in order that the treatment characteristics of each flocculant used in this project may be compared to federal safe drinking water standards (17). Two items are worthy of mention in Table 18. First, the heavy metal figures listed in this table are the minimum levels that may be obtained with optimum addition of the flocculant. Secondly, a turbidity figure for safe drinking water could not be located. Therefore, the turbidity figure under the heading of safe drinking water standards is actually the result of running a turbidity analysis on tap water in the laboratory.*

Table 19 is prepared in an effort to show the reduction from the stock solution in heavy metals and turbidity produced by each flocculant. Again, the heavy metals and turbidity figures for each flocculant are the minimums obtained in the optimum treatment range.

TABLE 18

	Safe Drinking Water Standards	Alum	Reten with Alum	Ferric Chloride	ALAR F-201	NALCO 7655
Pb (ppm)	0.05	0.0	0.0	0.5	0.0	0.21
Cr (ppm)	0.05	0.0	0.0	0.9	0.0	0.10
Turbidity (NTU)	3.80*	13.0	2.5	53.0	14.0	18.00

TABLE 19

	1:500 Stock Solution
Pb (ppm)	42.8
Cr (ppm)	11.2
Turbidity NTU	3712.0

	Alum	Reten	Ferric Chloride	ALAR F-201	NALCO 7655
Pb (ppm, % reduction)	0.0, 100%	0.0, 100%	0.5, 98.8%	0.0, 100%	0.21, 99.5%
Cr (ppm, % reduction)	0.0, 100%	0.0, 100%	0.9, 92.0%	0.0, 100%	0.10, 99.1%
Turbidity (NTU, % reduction)	13, 99.6%	2.5, 99.9%	53, 98.6%	14, 99.6%	18, 99.5%

XI. CONCLUSIONS

General conclusions regarding flocculation as a treatment method for flexographic washwaters are summarized as follows:

1) Treatment: Overall, flocculation produces excellent results in the removal of heavy metals and turbidity in flexographic washwaters. In many cases it was shown that no form of tertiary treatment need be performed to further optimize the treatment of the supernatant.

2) Linear Relationship: Heavy metal and turbidity removal have a strict linear relationship to one another as a function of flocculant dosage. This relationship demonstrates the dependency of the treatment efficiencies of both removal parameters on flocculant dosage.

3) Optimum Dosage: Each flocculant was demonstrated as having a narrow optimum range for turbidity and heavy metal removal. Outside of this range, turbidity and heavy metal content in the supernatant increased drastically as shown in Figures V through IX. This conclusion alludes to the importance of preliminary laboratory studies before flocculants are to be used in industrial applications and continued quality control monitoring during use.

4) Optimum Flocculant: The best flocculation for this particular project occurred under the use of an anionic polymer to "floc the flocs" pre-formed by a cationic polymer (in this case, alum followed by Reten 521). This resulted in excellent clarity and heavy metals removal as well as good floc formations and settling characteristics.

5) Settling and Sludge Characteristics: Gravity settling appears to be suitable for industrial practices in separating the floc structures from the supernatant. The sludge characteristics lend themselves to easy handling after the removal and separation process.

XII. RECOMMENDATIONS

The work and results presented in this paper should provide a sound starting place for several other studies. Some work in the area of tertiary treatment on the supernatant and sludges to further optimize the overall process should be performed and expanded.

The effects of pH on the flocculation of ink pigments as it affects the solubility of metals is another area where study could be instigated to give future insight into the overall treatment objective of flexographic washwaters.

The jar test mixing and retention dynamics as it affects the flocculation parameters of flexographic washwaters is yet another area from which to approach further study.

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