THE USE OF FLOCCULANTS TO CONTROL TURBIDITY IN PLACER MINING EFFLUENTS

A

, ·

THESIS

Presented to the Faculty of the University of Alaska in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

By

Yun-Hwei Shen

Fairbanks, Alaska

May 1987

ABSTRACT

In this study, two placer mine discharge waters of different characteristics were tested in order to determine the applicability of organic polymer flocculants to achieve reduced levels of turbidity. The water samples from both mines were characterized both as to their chemical and physical properties.

The jar test was employed to establish the optimum operation conditions of the flocculation process. The best results were obtained employing a cationic polymer Superfloc 340 produced by American Cyanamid Company. The optimum dosage for water samples from both mines were 15 ppm and 40 ppm respectively. Optimum agitation time was within the range of 3 to 9 minutes depending on the agitation rate and the pulp density of water sample.

The utilization of settling ponds, in conjunction with flocculation is believed to be a practical method to control the turbidity level of placer mine discharge water.

TABLE OF CONTENTS

Abstract
Table of Contents
List of Figures
List of Tables
Acknowledgments
CHAPTER 1. Introduction 1
1.1 Introduction to Placer Mining 1
1.2 Legislation and Regulations
1.3 Present Technology
A. Settling Pond
B. Filters and Centrifuges 5
C. Hydrocyclones
D. Flocculation 6
1.4 Purpose and Scope of Study
CHAPTER 2. Theory of Flocculation
2.1 Physico-chemical Factors
A. Van der Waals Forces
B. Electrical Forces
C. Flocculant Bridging Force
2.2 Evdrodynamic Factor
A. Agitation
B. Temperature
(Duln Dangity 13
ce the height seass seass seass the the

TABLE OF CONTENTS (continued)

	D.	Part	icle	Size	÷.	• •	٠	•	• •	•	•	•	•	•	•	•	•	13
	ε.	Meth	od of	E Flo	occul	Lant	Ad	ldi	tic	n	•	•	•	•	•	•	•	13
2.3	The	Natu	re o	E Flo	occul	lant	•	•	• •	•	•	•	•	•	•	•	•	14
	Ά.	Phys	ical	Stat	е.		•	•	• •	•	•	•	•	•	•	•	•	14
	в.	Mole	cula	c Wei	ght		•	•	•	•	•	•	•	•		•	•	14
	с.	Char	ge Cl	narac	ter	lsti	CS	•		-	•		•	•	•	•	•	15
CHAPTER 3	. sa	ample	Sele	ectio	on ai	nd A	nal	.ys	is		•	•	•	•	•	•	•	1 9
3.1	Sam	ple S	elec	tion			•	•		-	•	•	•	•	•	•	•	19
3.2	Sam	ple A	naly	sis		• •	•	•	•		•	*	•	•	•		•	21
	A.	Turb	idity	y and	i So	liđ	Cor	nte	nt	Me	asi	Jre	eme	ent	5	•		21
	в.	Part	icle	Size	e Di	stri	but	ic	n i	Ana	ly:	sis	3	•	•	•	•	22
	c.	Mine of S	ralo uspe	gical nded	L Coi Sol	mpos ids	iti •	lon	. Aı	hal	ys: •	18	•		•	•	•	30
	D.	Zeta	Pot	entia	al M	easi	irei	en	its	•	•	•	٠	•	•	•		33
	E.	pH V	alue	Meas	sure	ment	:8	•	•	• •	•		•	•	•	•	•	34
CHAPTER 4	F. T	loccu ests	lant	Sele	ecti	on a	nd	F] •	.0C	cul	at:	Loi	n •	•	•	•	•	36
4.1	Flo	ccula	nt S	elect	tion		•	•	•	• •	•	•	•		•		•	36
4.2	Plo	ccula	tion	Test	ts.		• •	٠	•		•	•	•	•	•	•	•	42
	A.	Floc	cula	nt D	osag	e ai	nd I	Pu]	p	Den	si	ty	•	•	•	•	•	42
	в.	Zeta	Pot	entia	al o	f Pa	art	ic]	le		•	•	•	•	•			46
	C.	Agit	atio	n Ti	m e a	nd 1	Rati	è	•	• •	•	•	•	•	•	•	•	46
	D.	Floc	cula	nt A	ddit	ion	Rat	te	•	• •	٠	•	٠	•	•	•	•	52
	E.	pH V	alue			•		•		• •	•	•	•	•	•	•	•	56

.

Page

TABLE OF CONTENTS (continued)

F. Temperature	}
G. Dual Flocculant Program 60)
CHAPTER 5. Conclusions and Recommendations 65	;
5.1 Conclusions	\$
5.2 Recommendations	7
A. Practical Application 67	7
B. Economic Evaluation 69)
C. Recommendation for Further Study 70)
REFERENCES	L
APPENDIX A	5
APPENDIX B	7
APPENDIX C	3

.

Page

LIST OF FIGURES

Fig.	1.	Sheet structure of (a) silica tetrahedrous (b) aluminums octahedrons	10
Fig.	2.	The generation of surface charge on clay minerals	10
Fig.	3.	Bonding mechanism for anionic polymers	17
Fig.	4.	Bonding mechanism for cationic polymers	18
Fig.	5.	The configurations and locations of sample collection sites in study areas	20
Fig.	6.	Particle size distribution curve of sample A.1	24
Fig.	7.	Particle size distribution curve of sample A.2	25
Fig.	8.	Particle size distribution curve of sample A.3	26
Fig.	9.	Particle size distribution curve of sample A.4	27
Fig.	10.	Particle size distribution curve of sample B.1	28
Fig.	11.	Particle size distribution curve of sample B.2	2 9
Fig.	12.	The X-ray diffraction patterns of samples A and B	31
Fig.	13.	The effect of different pulp densities on optimum flocculant dosage for sample A	44
Fig.	14.	The effect of different pulp densities on optimum flocculant dosage for sample B	45
Fig.	15.	The effect of different agitation times and rates on residual turbidity for high pulp density sample A.5	48

LIST OF FIGURES (continued)

-			
Fig.	16.	The effect of different agitation times and rates on residual turbidity for low pulp density sample A.6	49
Fig.	17.	The effect of different agitation times and rates on residual turbidity for low pulp density sample B.1	50
Fig.	18.	The effect of different agitation times and rates on residual turbidity for high pulp density sample B.2	51
Fig.	19.	The effect of flocculant addition rates on residual turbidity for sample A.5 and B.1	53
Fig.	20.	The effect of flocculant addition rate on floc settling rate	54
Fig.	21.	The effect of multi- and single stage addition of flocculant during the flocculation process	55
Fig.	22.	The effect of pH value on residual turbidity	57
Fig.	23.	The effect of temperature on residual turbidity	5 9
Pig.	24.	Initial water sample condition before flocculation	61
Fig.	25.	Flocculation during the first stage	61
Fig.	26.	Flocculation during the second stage	62
Fig.	27.	Flocculation during the final stage	62
Fig.	28.	The effect of anionic flocculant dosage on floc settling rate	63
Fig.	29.	The floc size difference between cationic flocculant added sample and both cationic and anionic flocculant added sample	64
Fig.	30.	The recommended flow sheet of flocculation process	68

LIST OF TABLES

-

.

Table 1.	Result of turbidity and solid content measurements for samples from both study areas	1
Table 2.	Flocculant list	,
Table 3.	Flocculant evaluation criteria)
Table 4.	The result of flocculant selection test 40)

ACKNOWLEDGMENT

I wish to express my deepest appreciation to my Advisory Committee, Dr. Donald J. Cook, Dr. David R. Maneval and Dr. Timothy Tilsworth, for their guidance and assistance throughout this study.

I particularly acknowledge my Committee chairman Dr. Cook, for his invaluable advice, encouragement, and supervision which have been most helpful in this study. Thanks is also extended to the U.S. Bureau of Mines. This research has been supported by the Department of the Interior's Mineral Institutes program administered by the Bureau of Mines under allotment grant number Gl164102. Without its support, this project could not have been accomplished.

I must express my sincere gratitude to my wife for her continual encouragement and assistance.

X

CHAPTER ONE

Introduction

1.1 Introduction to Placer Mining

Placer mining has played a major role in the exploration and development of Alaska and continues to be important to the Alaska economy. Placer gold usually occurs in the gravel layer that overlies bedrock. The gold-bearing gravels may also be overlain by deposits of barren alluvium and loess. This overlying material is commonly referred to as over-burden. The gravel layer usually ranges from 4 to 20 feet in thickness and is usually mantled by the over-burden which may be up to 100 feet. In this situation, the materials processed during placer mining are mostly gravel, sand and fine slit.

The methods used for placer mining can be classified into the following systems:

(1) Hydraulic mining - The gold-bearing gravel is washed into the sluice box by hydraulic giants and the subsequent tailings are stacked hydraulically. Over-burden removal was previously accomplished by hydraulic means.

(2) Mechanical mining - A sluice plate is utilized at the head of the sluice box to receive material conveyed by a bulldozer or a loader. Tailing may be stacked by either a bulldozer, a loader or a dragline. Over-burden usually has been removed by application of mechanical equipment.

Coarse tailings are usually moved as short a distance as possible from the sluicing area and deposited as tall piles. Fine tailings are carried downstream by water in the tailrace to a settling pond. The volume of water used for sluicing varies from a few hundred gallons per minute (gpm) to many thousand gpm. The method and effectiveness of wastewater treatment depends on the volume of water used. The most common treatment method is a settling pond or ponds in series. Placer mining today, however, is more tightly regulated than in the past, largely out of a concern over its impact on water quality. The Federal Water Quality Administration studied the effect of placer mining on water quality in Alaska and concluded (Alaska Water Laboratory, 1969):

- Placer mining operations degrade downstream water quality as evidenced by an increase in turbidity, a reduction in dissolved oxygen (D.O.), and a resulting significant reduction of fish and fish-food organisms.
- The major impact on water quality from placer mining comes from the hydraulic stripping and sluicing operation.
- 3. The termination of mining operations does not necessarily eliminate water quality degradation.
- Technique for the control of sediments from mining operations are available but are generally not being employed at the present time.

1.2 Legislation and Regulation

The Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) is one of the primary regulations causing concern in the mining industry in regards to environmental issues. Under this Act, the effluent limitation requirements are:

- Best practicable control technology currently available (BPCTCA) shall be achieved not later than July 1, 1977.
- 2. Best available technology economically achievable (BATEA) shall be applied not later than July 1, 1983.
- 3. New source effluent limitations and/or standards, to be applied to the construction of all new operations which are initiated after proposed standards are first published.

It is anticipated that with application of the above criteria, the national goal of zero source pollution will be met.

In May 1976, the Environmental Protection Agency (EPA) issued the first National Pollutant Discharge Elimination System (NPDES) permits. Under these permits the effluent limitations are:

- The volume of settling ponds should be large enough to contain the water supply of one day's operation and the maximum concentration of settleable solids from mining operations shall not exceed 0.2 ml/liter.
- 2. The turbidity at a point 500 feet downstream from the discharge shall not be higher than 25 Jackson Turbidity Units compared with the turbidity level in the receiving stream. Recent proposed EPA criteria are presented in Appendix A.

In October 1973, The Alaska Department of Environmental Conservation (ADEC) issued its water quality standards as Alaska Administrative Code (AAC) Title 18, chapter 70, to which amendments were made in January 1979. According to this code, the limitations for effluents from placer mining are:.

- 1. The turbidity shall not be 25 NTU greater than that in the receiving water.
- 2. The temperature shall not exceed 25°C.
- 3. The PH value shall be within the range 5.0-9.0.
- 4. The dissolve oxygen shall not cause detrimental effects on established water supply treatment levels.

Among these limitations, the concentration of settleable solids and turbidity are the most serious problems for placer mining in Alaska. The ADEC has recently certified federal water quality standards of 0.2 ml/l settleable solids and 5 NTU turbidity, as assuring reasonable compliance with state standards for water quality.

1.3 Present Technology of Turbidity Reduction

There are basically four approaches for the removal of settleable and suspended solids. These include settling pond, filters and centrifuges, hydrocyclones, and flocculation (Maneval, 1984).

A. Settling Pond

Settling ponds are the most common means for removing settleable solids from placer mining wastewater, that require a treatment scheme. Settling ponds provide a relatively large, quiescent area where particles settle according to the concepts of Stokes Law. To be effective, the pond must be large enough to remove a certain percentage of the suspended particles and provide sufficient storage capacity for sediment removed from suspension. Many of the factors adversely affecting settling pond performance are related to short circuiting in the pond. These factors are described by Weber (1972). The extensive use of settling ponds as a treatment method is due to their low cost relative to other possible approaches.

B. Filters and Centrifuges

Filters process a suspension through a path of cloth screening or other membranes in order to remove both settleable and suspended solids. A vacuum is applied below the surface so that the water and solids are drawn to it.

Centrifugal dryers are machines used to create high gravity forces for the purpose of dewatering fine solid particles. Properly operated centrifuges are generally used to dewater coarse materials but have also been used for extremely fine particles. There are three principal types of perforated basket machines: 1) one basket without the transporting device; 2) a basket with positive type discharge; 3) vibrating basket type. It shall be obvious that the operation of these devices is costly (Maneval, 1984).

C. Hydrocyclones

The hydrocyclone, probably because of its basic simplicity, has been used for various classification applications since before 1890. The hydrocyclone usually depends on external power for its operation most commonly in the form of a pump to obtain the desired pressure. Feed velocity head and pressure head are converted to both angular and linear acceleration, creating a cyclone effect where the angular acceleration increases as the feed liquid moves from the outside wall of the cyclone toward the axis of rotation. As the angular acceleration increases, the centrifugal forces also increase, causing the separation of particles by size and/or specific gravity.

D. Flocculation

Among these four approaches, flocculation is the most promising technology to reduce turbidity to meet federal and state regulations. The main factor is particle size; the operations of the other three approaches are controlled by the gravitational property of suspended particles. As the size and mass of particles becomes smaller, the ratio of the surface area to its mass is very high, thus the surface properties, such as electrical charges, become more important. On the other hand the gravitational property may become ineffective in solid/liquid separations. When the concentration of fine particles in placer mine effluents is high, flocculation is the best approach for solid/liquid separation and controlling the effluents turbidity.

1.4 Purpose and Scope of Study

This study is limited to the investigation of the application of certain flocculants to reduce turbidity at selected placer mining sites. Since the turbidity of placer mining effluents is caused mainly by suspended fine clay particles, the essence of this study is an investigation of the flocculation process applicable to the clay-water system of placer mining discharges, therefore the scope of this study includes:

- 1. Analysis of the suspended solids in the system.
- 2. Review of the theories of flocculation.
- 3. Determination of factors affecting flocculation process.
- 4. Optimization of the flocculation process to control the turbidity of placer mine effluents effectively and economically.

CHAPTER TWO

Theory of Flocculation

The term flocculation is often confused with coagulation, although the two refer to quite different processes. Coagulation is basically electrostatic in that it is brought about by a reduction of the repulsive potential of the electrical double layer. Flocculation is brought about by the action of high molecular weight materials such as starch or polyelectrolytes, where the material physically forms a bridge between two or more particles, uniting the solid particles into a random, threedimensional structure which is loose and porous (Moss, 1972).

Flocculation depends primarily upon collision, adhesion during collision and minimum redispersion. Collision itself occurs due to external forces introduced by methods such as stirring. Whether collision is successful in causing adhesion depends on both the physico-chemical interactions between the particles and the hydrodynamic condition in the system (Somasundaran, 1982).

2.1 Physico-chemical Factors

Physico-chemical interactions that are important in flocculation process are composed of the Van der Waals attractive forces, electrical double layer forces and bridging forces between adsorbed polymer and particle surfaces.

A. Van der Waals Forces:

The Van der Waals forces arise from London dispersion forces, Keesom interactions between permanent dipoles and Debye interactions between permanent and induced dipoles and the resultant energy of interaction, E_v , is related to particle radii a_1 and a_2 and distance of separation between the particles H_0 in the following manner (Hamaker, 1937):

$$E_v = - \frac{A a_1 a_2}{6 (a_1 + a_2) H_0}$$

Where A is the Hamaker constant.

However, this force is not of as much importance in the system under consideration here.

B. Electrical Forces:

Electrical forces arise from the charges on particles in solution. The nature and magnitude of the charge are dependent on the mechanisms responsible for the charge generation on their surface. In the system under this study, the surface charges of clay particles originate from crystal imperfections.

According to clay mineralogy, clay minerals belong to the family, "phyllosilicates". The principal building elements of the clay minerals are two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminum-hydroxyl octahedra (Fig. 1). In most clay minerals, such sheets of tetrahedra and of octahedra are superimposed in different fashions. In the tetrahedral sheet, tetravalent Si is sometimes



partly replaced by trivalent Al. In the octahedral sheet, there may be replacement of trivalent Al by divalent Mg. The replacement is often referred to as isomorphous substitution. In this case an atom of lower positive valence replaces one of higher valence resulting in a deficit of positive charge, or in other words, an excess of negative charge on the surface (Fig. 2). The magnitude of surface charge depends on the extent of this substitution.

With a charged surface, mineral particles in water acquire an electrical double layer. As the double layer on the particles begin to overlap, repulsion is observed. This force is given by the following expressions (Thomas, 1978):

 $V_{\rm R} = P = E_0^2 \ln [1 + \exp(-K E_0)]$

Where P is the permeability of the medium, E_0 is the surface potential, and K is the double layer thickness, H_0 is the distance between particles.

C. Flocculant Bridging Forces:

This is the most important force in the flocculation process. Adsorption of flocculant on minerals is a very complex process since it is influenced by a number of factors including flocculant properties such as molecular weight, type and concentration of functional groups, mineral properties including surface charge, porosity, surface purity and oxidation state, and solution properties such as pH, ionic strength and temperature. Forces responsible for flocculant adsorption arise mainly from electrostatic adsorption, hydrogen bonding and chemical bonding (Somasundaran, 1986).

Electrostatic: Adsorption is possible when the flocculant and the mineral surface are of opposite charge, resulting in nonspecific electrostatic interaction. In theory, any positively charged mineral should adsorb any anionic flocculant, and vice versa. With large amounts of adsorbed flocculant, recharging of the particles and stabilization should occur, and since the particle will then be of opposite charge to the initial charge, further adsorption of flocculant will cease.

Hydrogen Bonding: Hydrogen bonding is an important method of adsorption in the case of non-ionic flocculants. The individual bond strength is relatively low but the overall bonding force is high. A feature of the hydrogen bond is the short distance between the atoms linked by the hydrogen. The interacting atoms must therefore assume close proximity by other methods before hydrogen bonding can take place.

Chemical Bonding: Bonds can also form by the formation of insoluble salts, for example, when polyacrylic acid is adsorbed on clay, limestone, and other calcium-containing minerals as insoluble calcium polyacrylate is formed.

2.2 Hydrodynamic Factors

In the flocculation process, particle-particle adhesion, which permits floc formation, is chemically controlled for the most part. Subsequent growth of the flocs and the development of their structures are probably determined primarily by hydrodynamic factors (Hogg, 1986).

A. Agitation

Agitation during the flocculation process, is required for two reasons: to provide adequate mixing of the flocculant with the suspension, and to promote particle-flocculant and particleparticle collisions leading to destabilization and floc growth. Two of the most important factors with regard to agitation are agitation time and rate.

B. Temperature

Physically, temperature will affect the rate of diffusion of flocculant and the rate of collision of particles.

C. Pulp Density

The pulp solids content should affect the optimum dosage since it determines the number of interparticle collisions. The rate at which aggregates form is proportional to the square of the concentration of the particles (Moss, 1972).

D. Particle Size

On fine particles, the optimum flocculant/solid ratio has been found to be directly proportional to the surface area of solid, therefore, a decrease in particle size means an increase in flocculant demand.

E. Methods of Flocculant Addition

Multistage addition gives a gradual build up of floc formation which tends to encourage more flocculant bridging and generally imparts greater physical strength to the resulting flocs (Moss, 1972).

2.3 The Nature of Flocculant

In 1967, the first non-toxic and completely synthetic organic polymer was introduced and accepted by the U.S. Public Health Service for treatment of municipal water supplies. Since then, a wide range of polymers has been developed for use in wastewater treatment and mining and mineral processing industry. This section provides a discussion of the general properties of polymer flocculants.

A. Physical State:

There are three kinds of physical states of polymers produced today:

Dry powders or granules - which are dispersed and dissolved in water at a low concentration before use.

Emulsions - which are also pre-dispersed and dissolved prior to use, but which generally dissolve much more rapidly than the powdered products.

Liquids or solutions - which are readily diluted in-line as they are being applied (Dauplaise, 1982; Werneke, 1982).

B. Molecular Weight

Synthetic polymers are available in a wide range of molecular weights, varying from tens of thousands (relatively low) to many millions (very high). Molecular weight is a measure of the degree of polymerization of the polymer, or more simply,

the number of monomer (repeating) units which have been joined together to form the large, chain-like molecule. For example, a polyacrylamide,



(molecular weight of the repeating unit is 71) with an average molecular weight of 10,000,000 contains an average of 140,845 repeating acrylamide units making up a single molecule; in other words, n=140,845.

Molecular weight may also be a relative term within a family of similar polymers. Three samples of polyacrylamide having molecular weights of 4, 8 and 12 million would all be considered high molecular weight, but could be described as low, medium and high in relation to each other. Three samples of a highly cationic polyamine with molecular weights of 50, 100 and 200 thousand would all be classified as low molecular weight polymers, but would also be low, medium and high in relation to each other (Dauplaise, 1982; Werneke, 1982).

C. Charge Characteristics

Non-ionic - Non-ionic polymers are by definition uncharged and form attachments to suspended solids via a hydrogen-bonding mechanism.

Anionic - The majority of anionic polymers derive their negative charge from a carboxylic acid function and usually form

bonds via one of two mechanisms. As shown in Fig. 3, they can attach directly to the surface of a particle, for example, which contains a metallic ion in the lattice, such as aluminum, silicon, iron, calcium, etc. An alternate mechanism is attachment to negatively charged particles via a cationic bridge, such as alum or cationic polymer. These anionic polymers can vary widely in their degree of anionic charge, from less than one mole percent of anionicity to 100 mole percent. The choice of the optimum degree of charge is critical to obtaining maximum performance from the flocculant on a given substrate.

Cationic - These polymers are of two main types; that is, the low molecular weight, highly (100 mole %) cationic polymers and the high molecular weight, lower charged (2-30 mole % cationicity) materials. Choice of material will depend largely on characteristics of the substrate. All the cationic polymers bond directly to negatively charged particles. (Fig. 4).



Fig. 3. Bonding mechanism for anionic polymers. (from Werneke, 1982)



Fig. 4. Bonding mechanism for cationic polymers. (from Schwarz, 1982)

.

CHAPTER THREE

Sample Selection and Analysis

3.1 Sample Selection

For this study, water samples were collected from two placer mine sites in Alaska; one located in the Fairbanks area and the other located in the Circle area. Fig. 5 shows the configurations and locations of sample collection sites on both areas. The samples from the Fairbanks area were labeled A.1, A.2, A.3, A.4 and A.5 in accordance with the order of settling ponds from which water samples were taken. Sample A.6 was taken one mile downstream below the operation. Designations B.1 and B.2 represent the samples taken from the influent and the effluent of a settling pond at the Circle area mine site.

The placer mining system in both study areas was similar in that mechanical methods were used to transport materials to a sluice box, and the sluice tailing slurry discharged to one or more settling ponds. A common character of effluents from both sites is extremely high turbidity as a result of extremely high fine solid content. It is this material character that makes the settling ponds employed at both mines somewhat ineffective in reducing the solid content in pond-effluents. In this context, flocculation seems to be the most promising method to control the turbidity of effluents from both mines.





3.2 Sample Analysis

Water samples collected for this study from both mines were subjected to a series of basic analyses for the purpose of determining their physical and chemical characteristics prior to flocculation testing. Those analyses are described in detail below.

A. Turbidity and Solid Content Measurements

Turbidity in water is caused by colloidal particles and other fine dispersions. Turbidity analysis in water is based on the optical property of light scattered or absorbed by the suspended particles as it passes through the sample. Turbidity is dependent upon the size, shape and refractive index of suspended particles rather than density considerations.

Particle size is an important consideration in the measurement of turbidity. The smaller the particle size, the greater the specific surface area which results in greater light scattering and higher turbidity.

The turbidity measurements were conducted within 24 hours after the samples were taken from the field to eliminate irreversible changes in turbidity caused by longer storage. The Nephelometric Turbidity Unit (NTU) measurements in this study utilized a DRT-100 Nephelometric Turbidimeter.

The total solid content of a water sample is the combination of settleable solid content and suspended solid content in that sample. The total solid content was determined easily by drying and weighing. The settleable solid content can be determined by use of the Imhoff Cone Test. Then, the difference between the - total solid content and the settleable solid content is the suspended solid content.

The results of the Nephelometric Turbidity Unit tests and solid content tests of the water samples from the two study areas are presented in Table 1. This table indicates extremely high turbidity caused by high suspended solid content for all samples with a tendency of increasing turbidity with increasing solid content in the water. Theoretically, settling ponds are designed to remove the total solid content from the pond-effluent. From Table 1, the author found that when the suspended solid content in the water was high the settling pond was also effective in removing a considerable amount of suspended solids in the pondeffluents.

B. Particle Size Distribution Analysis

As mentioned in the preceding chapter, particle size is an important factor in the flocculation process. The grade scale most commonly used for particle size analysis is the Wentworth scale which is described in Appendix B The particle size distribution of water samples from both mines were determined by a Sedigraph 5000ET Particle Size Analyzer with results as shown on Figs. 6, 7, 8, 9, 10 and 11. It is evident that nearly 70% of the solid content in all water samples is smaller than I um which is the upper limit size of clay according to the Wentworth

Semple No.	A.1	A.2	A.3	A.4	A.5	A.6	B. 1	B.2
Total Bolké	35805	14383	10085	7748	6685	2286	2223	2340 (3608)
Bolilatio Bolid	250	0	0	0	0	0	0	0
Bubanda d Bolid	36555	14383	10085	7748	6685	2286	2223	3608
Iwbidky	16000	12500	11000	0006	8250	2750	2800	4000
Bolid Con	tent Unit ::	. 1/8m	ibidity Unit	: NTU . C	oncentrate	d for Expe	erimental	Purposes.

	samples	
	for	
¢	measurements	
	content	
	solid	
	and	
	Results of turbidity	from both study areas
	-	
	Table	











,




Fig. 11. Particle size distribution curve of sample 8.2.

29

scale. In this situation, the surface property of the solid particles becomes important due to the increasing surface area with decreasing particle size.

C. Mineralogical Composition Analysis of Suspended Solids

The suspended solid contained in the supernatant water from the Imhoff Cone analysis was extracted and analyzed by X-ray diffraction and DCP spectrometric methods.

X-ray Diffraction Analysis

Extracted solid samples from water samples were evenly spread on a petrographic glass slide with a drop of water and allowed to dry, giving a randomly oriented sample slide. The samples were then used to identify unknown minerals by a computerized RIGARU diffractometer.

The results of this analysis are shown in Fig. 12. The lack of intensive peaks within the scanned 20 range indicated that both samples are materials with low degree of crystallization. With the help of the Joint Committee on Powder Diffraction Standard Index Book after transferring 20 angles to d-spacing, the only recognizable mineral in both samples was kaolinite. Another important discovery was that samples A and sample B are identical materials. This can be verified by comparing the diffraction peak patterns occurring in the scanned 20 range of both samples. The conclusion of this analysis is that sample A and sample B are identical low crystallized clay with kaolinite as the major phase.





DCP Spectrometric Analysis

Although a DCP spectrometric analysis is unable to distinguish between the valence states of Fe and determine water content, it is a convenient method to analyze the major element constituents due to its capability of rapidly determining these elements simultaneously. The sample solution preparation, by using the lithium metaborate fusion dissolution method, is described in Appendix C. Upon the completion of the dissolution, the solution was analyzed for major elements using a Spectrometric Spectraspan IV Plasma Emission Spectrometer.

The results of this analysis were as follow:.

Samp]	le A.	Sample B.		
element	8	element	8	
SiO2	30.6	sio ₂	31.3	
A1203	20.9	A1203	26.7	
Fe	18.2	fe	19.7	
CaO	4.5	CaO	2.0	
MgO	3.3	MgO	1.4	
Na ₂ O	0.9	Na20	0.3	
R ₂ O	1.3	K 20	0.8	

The X-ray diffraction analysis indicated that sample A and sample B were the same clay mineral with kaolinite as the major phase. Kaolinite is made up of a regular sequence of structural units which consists of a tetrahedral Si layer united with an octahedral Al layer. By comparing the major element constituents of both samples, it was found that the divalent element Mg, Ca content was higher in sample A but the trivalent element Al content was higher in sample B. On the grounds that sample A and B are two-layer clay minerals built by the same unit, it is reasonable to assume that the extent of replacement for trivalent Al by divalent Mg and Ca within the octahedral Al layer is larger in sample A. It also means the amount of excess negative charges on the particle surface of sample A is higher than that on sample B. This can be verified by comparing the compensated ions K, Na content in both samples.

D. Zeta Potential Measurements

For many decades, the concepts of zeta potential has been acknowledged as the governing factor in colloidal chemical phenomena. According to Moss (1972) zeta potential can be define as follow: If the surface has a negative charge, positive ions will be attracted to it, forming a bound layer of positive ions. From this layer, a diffuse layer of counter ions extend outward. When a particle moves in the liquid, the shear takes place in a plane outside the layer of bound ions, i.e. only the bound ions move with the particle. The potential which exists between the shear plane and the diffuse layer is the zeta potential. The zeta potential of a mineral surface is also an index of surface charges on the mineral surface.

Zeta potential of the mineral particles is never determined directly, but is calculated from a measurement of the particle's electrophoretic mobility. Electrophoretic mobility is the movement of a suspended particle through the suspending liquid. When a liquid containing charged particles is placed within an electric field, the negative particles are attracted to the anode. Because the motion of charged particles in an electrical field is independent of their size or shape and dependent on zeta potential, the measurement of particle mobility affords a rapid and accurate method of determining the magnitude of zeta potential.

In order to get properly diluted water samples, the tested samples are the supernatant liquids from water samples after centrifuging for one hour at 30 rpm. A zeta potential meter made by Zeta Potential, Inc., was used to measure the zeta potential in this study. Twenty colloidal particles were read to obtain an average particle mobility for each test sample. The result of the tests showed that the zeta potential of sample A is -24 mv and the zeta potential of sample B is -16 mv. This verifies the previous assumption that the amount of excess negative charges on the particle surface of sample B.

E. pH Value Measurement

The pH value indicates the acidic or basic nature of water and is defined as the logarithm of the reciprocal of the hydrogen-ion concentration in moles per liter. In many cases, the particle surface in water has surface charges dependent on the solution pH and can exhibit both positive and negative surface charges. The pH corresponding to a surface charge of zero is defined as the zero point of charge (ZPC). Above the ZPC the surface charge will be negative and below the ZPC the charge will be positive. For example, the ZPC for kaolinite is 3.3 to 4.6, for montmorillonite is 2.5 (Parks, 1967).

An electronic pH meter was used to measure the pH of each water samples with the following results:

 Sample No.
 A.1
 A.2
 A.3
 A.4
 A.5
 A.6
 B.1
 B.2

 pH
 6.3
 6.4
 6.5
 6.6
 6.6
 6.5
 6.5

CHAPTER FOUR

Flocculant Selection and Flocculation Tests

4.1 Flocculant selection

Flocculants produced by Dow Chemical Company, American Cyanamid Company and Nalco Chemical Company were tested in this study. A complete listing of the chemicals tested, with information concerning charge property, molecular weight, and product form is present in Table 2.

It is impossible, at the present time, to specify the optimum type of flocculant for a given application based on knowledge of the material to be tested. The standard method is to choose the most likely flocculant which will be effective, then study the optimum operating conditions for that flocculant.

The most widely used test in the laboratory for the flocculation process is the "jar test". The equipment utilized in the jar tests consisted of a laboratory multiple stirrer accompanied by six 1,000 ml beakers. Each stirrer consisted of a 3 in. blade capable of variable speed operation between 0 to 180 rpm.

The jar test attempts to simulate the full-scale plant process and has remained as a control test in the laboratory since its first introduction in 1918. Nickel has indicated that proper mixing in the jar test will show a definite relation to the dosage that must be utilized in plant operations to obtain satisfactory operation. However the rotation rate of the paddle,

PRODUCT	TYPE		
FRODUCT		FORM	
Naico 7107	Cationic	Llquid	Low
Naico 7134	Cationic	Liquid	Low
Naico 8100	Cationic	Llauid	Low
Nalco 8103	Cationic	Liquid	Low
Naico 7120	Cationio	Liguid	High
Nalco 7122	Cationic	Liquid	High
Naico 7123	Catlonic	Liguid	High
Naico 7129	Cationic	Llquid	High
Dow M178	Cationic	Liquid	Low
Dow M266	Cationic	Liquid	High
Aa. Cyan. SF360	Cationic	Liquid	High
Aa. Cyan. SF365	Cationic	Liquid	High
Aa. Cyan. SF350	Cationic	Liquid	High
Aa. Cyan. SF340	Cationic	Llauld	High
Naico 7182	Anionic	Liquid	High
Nalco 7786	Anionic	Llauld	High
Nalco 7763	Anionio	Llauid	High
Dow M248	Antonía	Solid	High
Dow M249	Anionic	Solid	Hlgh
Dow M265	Anionia	Solid	High
Dow M810	Anionic	Llauid	High
Dow M530	Anionic	Liquid	High
Az. Cyan. SF204	Anlonic	Solid	Hìgh
As. Cyan. SF208	Anionia	Solid	High
Aa. Cyan. SF210	Anianic	Solid	High
Nalco 7181	Non-ionia	Llauid	High

Table 2. Flocculant list.

.

the design of the blade and the time of mixing are all variables in the jar test which must be more or less correlated to the plant design.

Flocculants were added by pipet from prepared stock solutions directly into the sample while agitating at 100 rpm. A reaction time of 5 minutes was normally allowed and the stirring abruptly stopped. Floc size, settleability and supernatant clarity were rated as described in Table 3. The water sample A.5 was subjected to a preliminary flocculant selection test in order to select the optimum flocculant and establish approximate solution concentration of flocculant for this study.

The results of the preliminary flocculant selection tests are detailed in Table 4. This table lists the results of the jar tests using the rating format outline in Table 3. The results of these tests show that all cationic flocculants, regardless of low or high molecular weight could reduce the turbidity of the tested sample to 10-100 (NTU) with dosages from 20 to 40 ppm. On the other hand, all anionic and non-ionic flocculants used in this test were ineffective in turbidity removal even with very high dosage. Recalling that the surface of particles in water samples was negatively charged, i.e. with a negative zeta potential, it is reasonable to argue that the non-specific electrostatic interaction between the cationic flocculant and negatively charged particles play an important role in the flocculation process of this study. Based on this argument, the bridging

FLOCCULANT EVALU	JATION CRITERIA
FLOC SIZE	
Reting	interpretation
None	None
Small	Less than 1 mm
Medium	1 - 2 mm
Large	Greater than 2 mm
FLOC SETTLEABILITY	
Poer	
Fair	Less than 10 cm/min
Good	More than 10 cm/min
Very Good	More than 20 cm/min
Excellent	More than 40 cm/min
SUPERNATANT CLARITY	
Poor	1000 NTU
Fair	100 to 200 NTU
Good	10 to 100 NTU

Table 3. Flocculant evaluation criteria.

、

Flocculant	Stock(\$)	Dose	Floc size	Settleability	Clarity
NALCO7 107	25	15	Small	Fair	Poor
	25	30	Small	Fair	Fair
	25	45	Small	Fair	Good
NALCO7134	21	15	Small	Fair	Poor
	21	30	Small	Fair	Fair
	25	45	Small	Fair	Good
NALCO8100	23	15	Small	🧭 Fair	Poor
	25	30	Small	Fair	Goad
	4	45	Small	rair	Good
NALCOSTOS	23	15	Small	Fair	Foor
	23	30	Small	rair	Fair
NAL COR 100	21	40		rair Cast	
NALLUT 120	17	10	negium	Good	POOR
	17	20	Medium	Good	2000
NAL COR 100	12	30			
NALUU/122	176	10	medium	5000	rair
	17	20	Medium	6000	5000
NAL 000100	17	30	Medium	DOOD	6000
NALLOT 123	17	10	Medium	6000	Poor
	(7) 1 #	20	Medium	6000	6000
NAL COT 1 DO	1.0	30	Medium	6000	
MALLU/ 129	176	10			Foor
	14	20		Good	rair Seda
	1,0 1,00	20			
		30			0000
DOMM 1/0	27	10	Small	rair Foir	roor
	23	20		rair Fair	rair
DOLINOS 6	23	47		rair Cood	0000
DOWINEOD	17	10	mealum	Good	rair
	F 26	20		Good	
55360	12	30		Good	
21,200	19	50	Small	rair Foim	Poor
	1	50		rair rair	Good
36245	1.8	10	Small	Fair	Boos
SE 202	14	20	Seal 1	ratr Faim	Good
	1	30	Small	Fair	Good
	1 🔎	20		(dil	0000
SF350	1\$	10	Small	Fair	Poor
	11	20	Small	Fair	Poor
	15	35	Small	Fair	Good
SF340	15	Ĩõ	Medium	Good	Fair
-	1\$	20	Medium	Good	Good
	15	30	Medium	Good	Good
NALCO7 182	0.5%	5	Large	Excellent	Poor
• •	0.5%	15	Large	Excellent	Poor

Table 4. The result of flocculant selection test.

.

_

•			Table	4. (Conti	e)	_
		0.5%	30	Large	Excellent	Poor
	NAL COTTES	0.5%	45	Large	Excellent	Poor
		0.53	16	Large	Excellent	Poor
		0.55	30	range	Excellent	Poor
		0.55	45	Large	Excellent	Poor
1	NALCO7763	0.5%	5	Large	Excellent	Poor
		0.5%	10	Large	Excellent	Poor
		0.55	30	Large	Excellent	Poor
		0.55	45	Large	Excellent	Poor
	DOWM248	0.55	5	Large	Excellent	Poor
			30	Large	Excellent	Poor
			30	Large	Excellent	Poor
	DCI-110240	0.55	*5	Large	Excellent	Poor
		0.55	10	Large	Excellent	Poor
		0.5	30	Large	Excellent	Poor
		0.55	45	Large	Excellent	Poor
1	DOWM265	0.5%	5	Large	Excellent	Poor
		0.5%	15	Large	Excellent	Poor
		0.55	30	Large	Excellent	Poor
,		0.5%	45	Large	Excellent	Poor
		0.53	15	Large	Excellent	Poor
		0.55	30	Large	Excellent	Poor
		0.55	45	Large	Fucellent	Poor
1	DOWH530	0.5%	5	Large	Excellent	Poor
	• -	0.5%	15	Large	Excellent	Poor
		0.55	30	Large	Excellent	Poor
		0.5%	45	Large	Excellent	Poor
:	SF204	0.5%	5	Large	Excellent	Poor
		0.5%	15	Large	Excellent	Poor
			30	Large	Excellent	Poor
	80032	0.54	40	Large	Excellent	Poor
•	01 200	0.51	15	Large	Excellent	Poor
		0.5%	30	Lante	Excellent	Poor
		0.5%	45	Large	Excellent	Poor
:	SF210	0.5%	5	Large	Excellent	Poor
		0.5%	15	Large	Excellent	Poor
		0.5%	30	Large	Excellent	Poor
I	NAL COT 181	0.5%	45	Large	Excellent	Poor
1		0.5%	20	Maddum	Gacel	Paar
		0.51	30	Madi	6.00	Paar
•		0.5%	<u>لا</u> ج	madium	Go col	Pane

Unit of dose ; PPM.

•

•

41

effect of anionic flocculants was jeopardized by the electrical repulsion between negatively charged particles and the anionic flocculants.

The high molecular weight cationic flocculant, superfloc 340, was found to be the best flocculant among those tested. This cationic flocculant resulted not only in the least residual turbidity with the least amount of dosage, but also produced faster settling flocs in the tested water samples. Thus, Superfloc 340 was selected as the optimum flocculant and subjected to the following tests.

4.2 Flocculation Tests

The important factors which affect the flocculation process are flocculant dosage, pulp density, zeta potential of particles, agitation time, agitation rate, flocculant addition rate, temperature, pH value and dual flocculant process. In water treatment, an optimum flocculation process represents the achievement of an equilibrium of great complexity in which the above factors are involved. In the following sections, all of these factors were studied in detail by jar testing. One important aspect in this study is that when one factor was tested other factors were constant.

A. Flocculant Dosage and Pulp Density

In order to determine the optimum flocculant dosages for different pulp density water samples, samples A.4, A.5 and A.6 with pulp densities at 7748(mg/1), 6685(mg/1) and 2286(mg/1)

respectively were chosen as samples representing high, medium and low pulp densities. Also, samples B.1 and B.2 with pulp densities of 2223(mg/1) and 3608(mg/1), were chosen as another set of samples of high and low pulp density. In this test, residual turbidity at various flocculant dosages was measured for each tested sample.

The results of these tests are presented in Figs. 13 and 14. In these two figures, each curve represents a specific pulp density sample. The dosage of flocculant that produces the lowest residual turbidity is called the optimum dosage of the tested sample. It is obvious that the optimum flocculant dosage increases with the increasing pulp density of the tested samples. This can be easily understood by the fact that the higher the pulp density the higher the number of solid particles in the water sample, and the larger the surface area available to consume flocculant.

Another important feature in this test was that the ability to resist overdose decreases with decreasing pulp density of the tested sample. This can be explained by the fact that decreasing pulp density results in decreasing particle surface area and the number of interparticle collisions during agitation. If excessive flocculant is added, the flocculant segments may saturate the limited particle surface area so easily that no sites on the particle surface are available for the formation of flocculant bridging under the limited number of interparticle collisions



Fig. 13. The effect of different pulp densities on optimum flocculant dosage for sample A.



Fig. 14. The effect of different pulp densities on optimum flocculant dosage for sample B.

during agitation. This substantially reduces the ability of resisting overdose in low pulp density water samples.

B. Zeta Potential of Particle

In the above tests, the solid contents of samples A.4 and A.5 are much higher than the solid contents of samples B.1 and B.2. According to the conclusion that the optimum flocculant dosage increases with the increasing pulp density, the optimum flocculant dosage for samples A.4 and A.5 shall be higher than that for samples B.1 and B.2, but when comparing Figs. 13 and 14 the result was opposite to this argument. This can be explained by the concept of zeta potential. Because the non-specific electrostatic interaction between cationic flocculant and negatively charged particle surface play an important role in the flocculation process, the particle with higher negative zeta potential; i.e. higher negative surface charge is more amenable to flocculation with a cationic flocculant. Based on this idea, the optimum flocculant dosage of sample A with zeta potential of -21 my will be less than that of sample B with zeta potential of -16 my regardless of the effect of pulp density.

C. Agitation Time and Rate

During the flocculation process, agitation of the suspension during flocculant addition is a primary factor in determining performance. Agitation is required to provide adequate mixing of the flocculant with the suspension and to promote the particleparticle collisions necessary for floc growth. At the same time, agitation leads to floc breakage. When a flocculant is added continuously at a fixed rate to an agitated suspension, flocs grow to some limiting size. However, continued agitation, in the absence of further flocculant addition lead to an irreversible floc breakdown.

The effects of varying agitation time and agitation rate in the jar testing procedure for the residual turbidities of samples A.5 and A.6 with pulp densities of 6685(mg/1) and 2286(mg/1)respectively and in samples B.1 and B.2 with pulp densities of 2223(mg/1) and 3608(mg/1) are shown in Figs. 15, 16, 17 and 18.

For the same pulp density water samples, the samples agitated at a high rate consistently exhibited shorter agitation time to complete the flocculation process. The reason is that the high agitation rate increases the particle-flocculant and particle-particle collision rate and accelerates the flocculation process. Also, in the higher pulp density samples A.5 and B.2, the floc degraded resulting in a higher residual turbidity when the agitation time increase to a certain extent. This situation did not occur on the two lower pulp density samples A.6 and B.1. The reason is due to interparticle collision. As a prerequisite to bridging, the rate of formation of multiple particle aggregates from the primary particles through the bridging effect of flocculant is dependent upon the number of particles initially in the sample. In a high pulp density sample, the opportunity of interparticle collision is



Fig. 15. The effect of different agitation time and rate on residual turbidity for high pulp density sample(B.2).

49



Fig. 16. The effect of different agitation times and rates on residual turbidity for low pulp density sample (A.6).

۰.



Fig. 17. The effect of different agitation times and rates on residual turbidity for low pulp density sample (B.1).



Fig. 18. The effect of different agitation times and rates on residual turbidity for high pulp density sample (A.5).

greater than that in a low pulp density sample. Thus, the time for the particles in high pulp density samples to form the aggregates is faster than the particles in the low pulp density samples. If extended agitation occurs, the particles will be restabilized due to the breaking of flocculant-particle surface bonds and the subsequent folding back of the extended flocculant segments on the surface of particles.

D. Flocculant Addition Rate

The purpose of this test was to determine the effect of flocculant addition rate on residual turbidity and floc settling rate. Floc settling rate is an important factor in the later solid-liquid separation process after flocculation and it was obtained by direct observation of the fall of the "mud line" in the flocculation vessel. The residual turbidity and the floc settling rate of tested samples were measured after being flocculated at different flocculant addition rates. The result shown in Fig. 19 indicates that there is an optimum flocculant addition rate for decreasing turbidity. Fig. 20 indicates that slow flocculant addition rate always helps floc settling. This effect can be depicted simply by Fig. 21. When the flocculant was added by multi-stage (slow addition rate), a progressive reduction of the enormous effective surface area of the particles is reduced by each flocculant dose increment. The overall effect is to prevent local over-adsorption and waste of flocculant and to form uniform large size flocs. This helps the overall effect



Fig. 19. The effect of flocculant addition rates on sample A.5 and B.1.



Fig. 20. The effect of flocculant addition rate on floc settling rate.



Fig. 21. The effect of multi- and single stage addition of flocoulant during the flocoulation process.

• •

of turbidity removal. On the other hand, with a too slow flocculant addition rate, the rate of floc disintegration caused by agitation is greater than the rate of floc formation as a result of flocculant addition. The overall effect for decreasing turbidity would then be jeopardized.

E. pH Value

The purpose of these tests was to decide the effect of pH value on the flocculation process. The pH was varied from 2 to 10 with the addition of either nitric acid or sodium hydroxide. These tests utilized the jar testing with other factors maintained as constants.

The variation in pH of these tested samples control the extent of surface ionization of the particles in the samples, as the potential-determining ions, H^+ and OH^- , are introduced into it. Potential-determining ions are responsible for the existence of the double layer and determine the electrical potential difference between the solid and liquid phase (Packhom, 1962).

The results shown in Fig. 22 indicate that a higher pH value results in a higher residual turbidity after flocculation. At high pH values, the particle surface is highly negative as it absorbs the hydroxyl ions resulting in higher negative zeta potential. When the negative charge on the particle surface is too high, more cationic flocculant is absorbed on a single particle by non-specific electrical attraction forces and local over-adsorption take place. This inhibits the bridging between



Fig. 22. The effect of pH value on residual turbidity.

- .

particles. The lower pH value represents more hydrogen ions in the samples, thus the negatively charged particles are neutralized by these hydrogen ions. This phenomenon results in decreasing the zeta potential as well as the repulsive force between particles. The Van der Waals' force will then dominate, increasing the floc-forming collision. At a certain concentration of hydrogen ions, a point of zero charge occurs and at this pH the non-specific electrical interaction between cationic flocculant and particle surface become so weak that the floc disintegrates easily and results in a higher residual turbidity.

F. Temperature

. .

As the flocculation tests were conducted at room temperature in the laboratory, adjustments were made to run the flocculation tests to simulate field temperatures for those selected samples which had been tested by the jar test.

Tested samples were flocculated at temperatures of 5° , 23° and 45° (C). The results, shown in Fig. 23 indicate that residual turbidity is a little higher when tested at low temperature condition. The reason is that as the temperature decreases, the viscosity of the water increases. As the viscosity of the water decreases, the particles in the water show a decrease in the probability of floc-forming interparticle collision. This effect can be overcome by a longer mixing period. However, if the particle concentration of the sample is



Fig. 23. The effect of temperature on residual turbidity.

high, this lower temperature effect on decreasing interparticle collision is too small to be of significance and the residual turbidity is not significantly changed.

G. Dual Flocculant Process

At this point, the important factors affecting the flocculation process have been studied in detail. A flocculation process operating under these optimum conditions is expected to obtain good results. Figs. 24 through 27 show the actual flocculation process as tested in the laboratory sequence. The overall results of this procedure were good but presented a problem in that the floc size is too small. A small floc size results in a low floc settling rate which causes difficulty in later solid-liquid separation processes. This problem can be solved by adding a small amount of a high molecular weight anionic flocculant Dow 248. High molecular weight anionic flocculants enhance particle aggregations by forming bridges between aggregations of particles to produce larger flocs which can settle more rapidly. Fig. 28 indicates the addition of few parts per million of high molecular weight anionic flocculant enhances the floc settling rate. The effect of improving floc size of high molecular weight anionic flocculant can be seen on Fig. 29.



Initial water sample condition before flocculation. Fig. 24.



Flocculation during the first stage. Fig. 25.



Fig. 26. Flocculation during the second stage.



Fig. 27. Flocculation at the final stage.



Fig. 28. The effect of anionic flocculant dosage on floc settling rate.

۰.


The floc size difference between cationic flocculant added sample and both cationic and anionic flocculant added sample. Fig. 29.

CHAPTER FIVE

Conclusions and Recommendations

5.1 Conclusions

The mechanism of flocculation using polymers is a very complex process and poorly understood at the present time. Based on the test results, the author believes that the non-specific electrostatic forces between cationic flocculants and negative charged particle surfaces plays a governing role in the flocculation process investigated under this study. The study resulted in the following conclusions.

1. If the non-specific electrostatic force is important, the selection of a proper flocculant will depend on the sign of surface charge of the particle surface. With negative surface charge particles, the cationic flocculant is expected to be effective. On the other hand, an anionic flocculant is expected to be effective when the particle surface is positively charged. Also, the amount of surface charge on the particle surface affects the magnitude of electrostatic force between flocculant and particle surface.

2. Generally speaking, the higher the pulp density, the more flocculant is consumed because of the larger surface area of the particles. The optimum flocculant dosage also depends on the amount of surface charge on the particle surface which affects the magnitude of electrostatic bridging force between flocculant and particle surface. 3. The ability of resisting overdose for a certain water sample decreases with decreasing pulp density of that sample. To avoid overdose, the optimum dosage must be decided precisely when low pulp density samples are encountered.

4. A high agitation rate will reduce the agitation time needed to complete the flocculation process but the probability of over-agitation is increased at high agitation rates.

5. The ability of resisting over-agitation for a certain water sample decreases with increasing pulp density of that sample. To avoid over-agitation, the proper agitation time and rate must be controlled carefully when high pulp density samples are encountered.

6. There is an optimum flocculant addition rate for decreasing turbidity; if a flocculant is added faster or slower than the optimum, the overall turbidity removing effect will be jeopardized. In this study, a slow flocculant addition rate always enhanced the floc settling rate.

7. A lower pH value enhances the flocculation results, as the existence of H^+ ion may neutralize the negative charged particles and cause the reduction of the repulsive force between particles, but when the point of zero charge is reached the lower pH value becomes detrimental to the flocculation result.

8. The lower the temperature, the higher the viscosity of the water resulting in a lower settling rate of the flocs. The temperature effects on residual turbidity after flocculation are neglected in the high pulp density samples as interparticle collisions of these are not affected.

9. Adding a small amount of high molecular weight anionic flocculant enhances floc size and strength dramatically. If highly intensive shear force is encountered in the later solidliquid separation process, for example, a hydrocyclone, the addition of a small amount of high molecular weight anionic flocculant to strengthen the flocs is highly recommended.

10. In so far as the special conditions of placer mining in Alaska are concerned, the author believes that a settling pond is one of the most practical methods for treating discharge water, if economically achievable for the individual mining operation. Also, a settling pond is the most practical method for the solidliquid separation after flocculation.

3.2 Recommendations

A. Practical Application

A recommended practical application of the flocculation process to control turbidity of effluents from a placer mine site is shown on Fig. 30. The wastewater discharge from a sluice box passes through a series of settling ponds where a considerable amount of suspended solids are removed. The number of settling ponds employed is dependent on the pulp density of the discharged water. When the pulp density of discharged water is high, more settling ponds are needed to reduce the amount of flocculant consumed in the flocculation process. The effluent of the first



Fig. 30. The recommended flowsheet of flocculation process.

two settling ponds is fed into two mixing tanks alternatively in order to maintain continuous operation. Diluted flocculant stock solution or solutions is added at this point and mixed thoroughly with settling ponds effluents for at least 3 minutes. The discharge from mixing tank is then delivered to the final "polishing" pond where solid-liquid separation take place and the effluents are discharged to the stream.

B. Economic Evaluation

The cost of the recommended application comes from four major categories which include settling ponds construction, disposal of sediments, mixing system and chemicals. The cost of settling ponds and disposal of sediments are cost inherent to placer operation with or without chemical-aided settling. The cost of a mixing system including mixing tanks, pumps and power supply and was estimated from \$40,000 to \$70,000 for a normal capacity operation by Stanley Association Engineering (1985). The optimum concentration and dosage for Superfloc 340 is 1% and 15 ppm for water sample from the Gilmore Creek area. This reagent consumption can be converted to 0.25 1b Superfloc 340 required for treatment of 1000 gallons of wastewater. Chemical costs can be calculated under the optimum conditions and following assumptions:

> Average water consumption: 3,000 gal/min Recycled water percentage: 80% Treated water percentage: 20%

69

Operating hours per day: 10 hours

Operating days per year: 150 days

The chemical cost based on this assumption is \$8,100 per year. Costs which should be taken into account to perfect a treatment design, such as of labor, utilities, etc., are neglected here.

C. Recommendations for Further Study

1. The development of quantitative models for the interactions between flocculant and particle surface.

2. The application of flocculation to treat placer mine effluents in Alaska merits further field testing to determine usable products, efficient dispersal systems, and relative cost.

3. A variety of flocculants should be jar tested at several placer mine sites in interior Alaska under site specific temperature and water chemistry conditions to identify the most efficient flocculants.

4. Treatment with flocculants should be tested in conjunction with other treatments, including filtration and cyclone solid-liquid separation.

REFERENCES

"Alaska Administrative Code", Title 18, Chapter 70, 1979.

- Alaska Water Laboratory, "Effect of Placer Mining on Water Quality in Alaska", 1969.
- Ash, S. G., "Polymer Adsorption at the Solid/Liquid Interface", Colloid Science, Vol. 1, The Chemical Society, London, 1973.
- Black, A. P., Birkner, F. B. and Morgan, J. J., "Destabilization of Dilute Clay Suspensions With Labeled Polymers", Journal AWWA, Vol. 57, 1965
- Chang, S., "Water Quality Studies of Placer Mining Operations on Livengood and Harrison Creeks", M.S. Thesis, University of Alaska, 1979.
- Cohen, J. M., Hannah, S. A., "Coagulation and Flocculation", Water Quality and Treatment, AWWA Prep., McGraw-Hill Book Co., New York, 1971.
- Dauplaise, D. L., Werneke, M. F., "American Cyanamid Company's Use of Flocculant for Dewatering and Consolidation of Fine Particles", Proceedings of Fine Particle Conference, University of Alabama, 1985.
- Fitch, B., "Sedimentation Process Fundamentals", AIME Transaction, Vol. 223, 1962.

Hamaker, H. C., "Physica", 4th edition, 1937.

- Healy, T. W., "Principles of Dispersion and Aggregation of Mineral Fine", Beneficiation of Mineral Fine, New York, 1978.
- Healy, T. W., La Mer, V. K., "The Energetics of Flocculation and Redispersion by Polymers", Journal of Colloid Science, Vol. 19., 1964.
- Hogg, R., Klimpel, R. C., "Agglomerate Structure in Flocculate Suspensions and It's Effect on Sedimentation and Dewatering", Preprint of SEM Annual Meeting, New Orleans, 1986.
- La Mer, V. K., Healy, T. W., "Adsorption-Flocculation Reactions of Macromolecules at the Solid-Liquid Interface", Review of Pure and Applied Chemistry, Vol. 13. 1963.

- Linke, W. F., Booth, R. B., "Physical-Chemical Aspect of Flocculation by Polymer", AIME Transactions, Vol. 217, 1960.
- Maneval, D.R., "Technical Approaches to Turbidity Reduction at Placer Mining Sites", Proc. of Sixth Conference on Alaskan Placer Mining, University of Alaska-Fairbanks, MIRL Report No. 69, 1984.
- Mason, B., Berry, L. G., "Mineralogy", New York, 1978.
- Michales, A. S., "Aggregation of Suspensions by Polyelectrolytes", Industrial and Engineering Chemistry, Vol. 46, 1954.
- Moss, N., "Theory of Flocculation", Mineral Eng. Handbook, Flocculation Section, File No: PL/Ol/O.
- Nemerow, N. L., "Liquid Waste of Industry--Theories Practices and Treatments", Addision-Wesley Publishing Co., California, 1971.
- O'Brien, J. H., Novak, J. T., "Effect of pH and Mixing on Polymer Conditioning of Chemical Sludge", Journal AWWA, Vol .69, 1977.
- Oliver, R. H., "Flocculation-Key to More Economical Solid-Liquid Separation", AIME Transactions, Vol .220, 1962.
- O'Melia, C. R., "Coagulation and Flocculation", Physico-chemical Processes for Water Quality Control, Weber, W. J., Willey-Interscience, New York, 1972.
- Ottewill, R. H., "Particulate Dispersion", Colloid Science, Vol. 1. The Chemical Society, London, 1973.
- Packhom, R. F., "The Coagulation Process", J. Appl. Chem., 1962.
- Packhom, R. F., "Some Studies of The Coagulation of Dispersed Clays With Hydrolyzing Salts", J. Colloid Science, 1965.
- Parks, G. A., "Aques Surface Chemistry of Oxides and Complex Oxide Minerals", Advance in Chemistry Series, No. 67, American Chemical Society, Washington, 1967.
- Pearse, M. J., "Allied Colloids' Use of Flocculants and Surfactants for Dewatering and Consolidation of Fine Particles in The Mineral Processing Industry", Proceeding of Fine Particles Conference, University of Alabama, 1982.
- Riddick, T. M., "Zeta Potential: New Tool for Water Treatment, Part I", Chemical Engineering, Vol. 68, No. 13, 1961.

- Riddick, T. M., "Zeta Potential: New Tool for Water Treatment, Part II", Chemical Engineering, Vol. 68, No. 14, 1961.
- Riddick, T. M. "Control of Colloid Stability Through Zeta Potential", Zeta-Meter, Inc., New York, 1968.
- Sennett, P., Olivier, J. R., "Colloidal Dispersions, Electrokinetic Effects and the Concept of Zeta Potential", Industrial and Engineering Chemistry, Vol. 57, 1965.
- Smelley, A. G., "Flocculation Dewatering of Florida Phosphatic Clay Wastes", Report of Investigations 8349, USBM, 1972.
- Smelley, A. G., "Large Scale Dewatering of Phosphatic Clay Waste From Northern Florida", Report of Investigation 1985, USBM, 1985.
- Somasundaran, P., "Flocculation Fundamentals", Proceeding of Fine Particles Conference, University of Alabama, 1986
- Stanley Associates Engineering, "Development and demonstration of treatment technology for the placer mining industry", Final Report prepared for Environmental Protection Services, Whitehorse, Yukon, 1985.
- U.S. Congress, "An Act to Amend the Federal Water Pollution Control Act", Public Law 92-500, Environmental Protection Agency, 1972.
- U.S. Environmental Protection Agency, National Pollution Discharge Elimination System Permit No. AR-002429-5.
- Van Olphen, H, "An Introduction to Clay Colloid Chemistry", 2nd Edition, Willey-Interscience, New York, 1977.
- Wayman, C. H., "Adsorption on Clay Mineral Surface", Principal and Applications of Water Chemistry, John Wiley and Sons Inc., New York, 1967.
- Weber, W.J., "Physico-chemical processes for water quality control", John Wiley & Sons, New York, 1972.
- Williams, R. E., "Waste Production and Disposal in Mining, Milling and Metallurgical Industries", Miller Freeme Publication Inc., San Francisco, 1975.
- Yang, G., "Water Quality Studies of Selected Placer Mining in the Circle Area, Alaska", M. S. Thesis, University of Alaska, 1979.

- Zatko, J. R., "Preliminary Studies on the Dewatering of Coal-Clay Waste Slurries Using a Flocculant", Report of Investigation 8636, USBM.
- Zemansky, G. M., Tilsworth, T., Cook, D. J., "Alaska Mining and Water Quality", IWR Report No. 74, University of Alaska, 1972.

۰.

(*

APPENDIX A

Summary Excerpts from EPA Proposed Effluent Limitations

PROPOSAL

Subcategory	BPT	BCT	BAT	NSPS=BAT
<20 yds ³ /day	No limitations	None	None	
>20 yds ³ /day to 500 yds ³ /day all mines	0.2 ml/L SS 2,000 mg/L TSS (Simple settling)	BCT-BPT	BAT-BCT	=BPT
all exc. large dredges > 4,000 yds/day	same as above i	Process water- no discharge (recycling) excess water- 0.2 ml/L SS 2,000 mg/L TSS (simple settlin	BAT=BCT	: :
dredges > 4,000 yds ³ /day	Process water no discharge (recycling) excess water- 0.2 ml/L SS 2,000 mg/L TSS (simple settling)	BCT-BPT	BAT=BCI	=BPT

POSSIBLE REVISIONS

Subcategory	BPT	BCT	BAT	<u>NSPS</u>
<1,500 yds/yr.	No limita- tions	None	None	None
>1,500 <70,000 ydg ³ /yr. (small open-cut)	0.2 ml/L SS (Simple setting)	BCT=BPT	Process water- no discharge (recycling) excess water- 0.2 ml/L SS Bimple settling	NSPS=BAT

70,000-230,000 yda ³ /yr. (medium, open-cut)	3 0.2 ml/L SS (Simple settling or	Process water- no discharge (recycling) excess water- 115 mg/L TSS (chemical treatment) no limitation (simple settling)	Process wat no discharce (recycling) excess wate 0.2 ml/L Sa (simple sett or 0.2 ml/I and 115 mg/ (chem. treat	ter- same ge options as at er- BAT S tling) L SS (L TSS Iment)
>230,000 ydg ³ /yr. (large, opencut)	0.2 ml/L SS (simple settling)	same options as for medium, open cut mines	Same	8800 0
D redges	no discharge (recycling) excess water- 0.2 mg/L SS (simple settling)	same options as medium and large open-cut mines	8211C	Same

. .

APPENDIX B

.

Wentworth Size Class

Wentworth Size Class Granule Very coarse sand	Ph1 -1.5 -1.25 -1.0 -0.75 -0.5	Microns	Millimeter 2.83 2.38 2.00 1.68 1.41	U.S. Mesh 7 8 10 12 14
Coarse sand	-0.25 0.0 0.25 0.5 0.75 1.0	500	1.00 0.84 0.71 0.59 0.50	18 20 25 30 35
Medium sand	1.25 1.5 1.75 2.0	420 350 300 250	0.42 0.35 0.30 0.25	40 45 50 60
Fine sand	2.25 2.5 2.75	210 177 149	0.210 0.177 0.149 0.125	70 80 100
Very fine sand	3.25 3.5 3.75	105 88 74 62-5	0.105 0.088 0.074 0.0625	140 170 200 230
Coarse silt	4.25 4.5 4.75 5.0	53 44 37 31	0.053 0.044 0.037 0.031	270 325
Fine silt	6.0 7.0 8.0	15.6 7.8 3.9	0.0156 0.0078 0.0039	
Clay	9.0 10.0 11.0 12.0 13,0 14.0	2.0 0.98 0.49 0.24 0.12 0.06	0.0020 0.00098 0.00049 0.00024 0.00012 0.00006	

APPENDIX C

Sample Solution Preparation Procedure

for DCP Spectrometric Analysis

Mix 0.20 g of -200 mesh sample with 1.00 g of lithium metaborate, transfer to a high-purity graphite fusion crucible and place in a muffle furnace at 1000 degree C for 10 minutes. With a pipet transfer 100.0 ml of the 4% ENO3 dissolving solution to a flat-bottomed 200 ml teflon or polypropylen beaker and add a teflon-covered stirring bar. Remove the crucible from the furnace, swirl to gather uncoalesced beads of molten material and pour the melt into the beaker. Cover to limit evaporation loss, and stir gently over a magnetic stirring unit without heating until solution is complete. Transfer the solution to a clean plastic bottle with a tightly fitting cap. Pipet 4.0 ml of 2000 ppm solution and add 69.0 ml of the 10 ppm Ge solution by means of a pipet. The concentration of the sample for the determination of Al, Ca, Fe, K, Mg, Na, Si is 125 ppm.