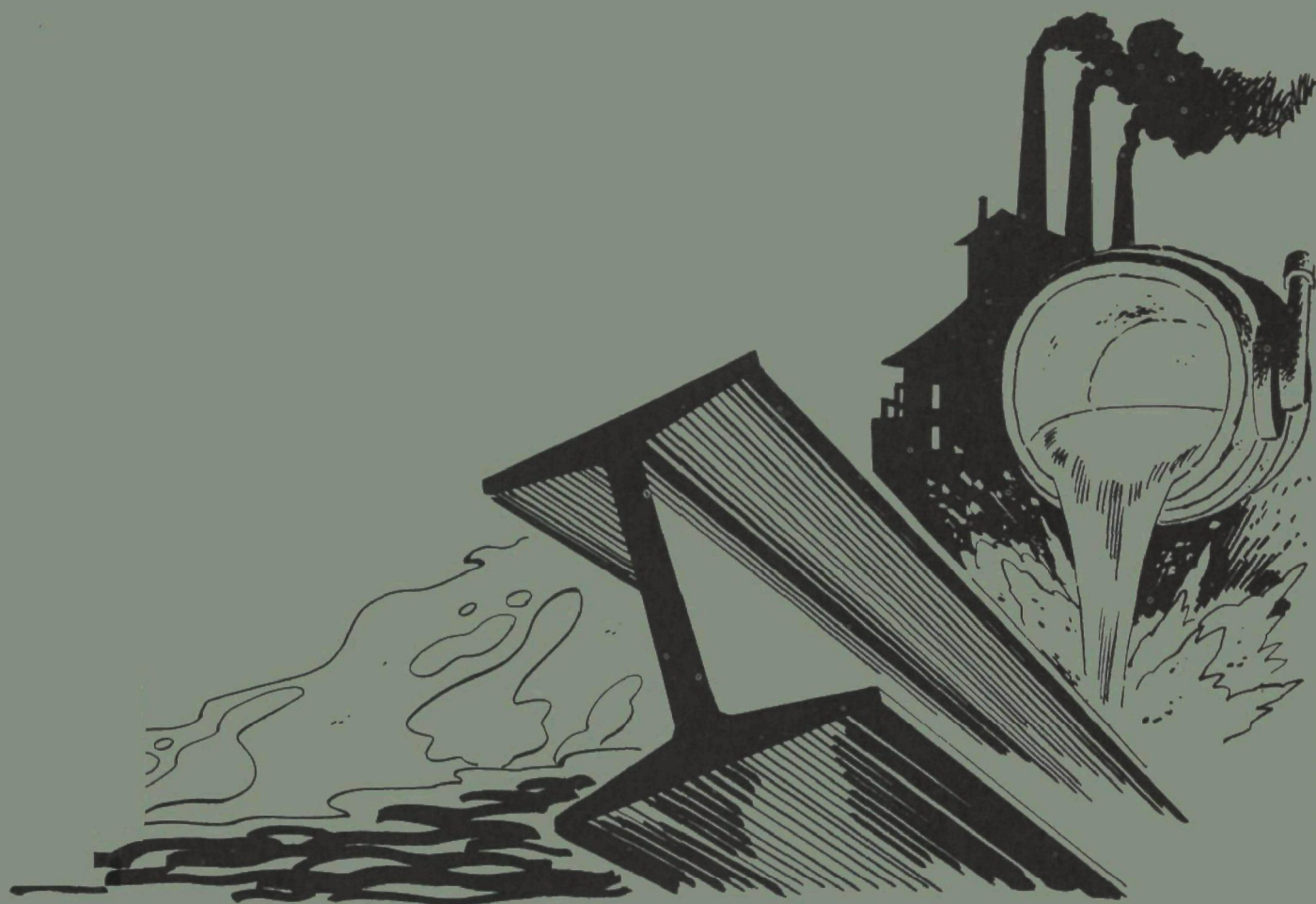




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# Treatment of Waste Water - Waste Oil Mixtures



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# **TREATMENT OF WASTE WATER - WASTE OIL MIXTURES**

**FEDERAL WATER POLLUTION CONTROL ADMINISTRATION  
DEPARTMENT OF THE INTERIOR**

**By**

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### FWPCA Review Notice

This report has been reviewed by the Federal Water Pollution Control Administration and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Federal Water Pollution Control Administration.

## ABSTRACT

Cold reduction of steel strip results in the production of large quantities of waste water containing variable amounts of oil. A five stand tandem cold mill located at Armco Steel Corporation's Ashland, Kentucky Works produces 200 to 500 gpm of waste water containing 400 to 4,000 ppm of oil. The COD of the waste varies from 400 to 20,000 npm.

A treatment process and facility was developed, constructed, and demonstrated, on full scale, for the treatment of cold mill wastes. The treatment process utilized chemical coagulation to break the emulsions. The chemicals employed included alum, lime, clay and organic polyelectrolyte. The process consisted of the following treatment steps; equalization, chemical addition and rapid mixing, flocculation, and dissolved air flotation. A number of treatment variables were studied in the laboratory and in the field in order to establish process kinetics and optimum treatment efficiency.

Zeta potential, streaming current, and particle size distribution were used in laboratory studies to describe the effect of the following variables on process kinetics; acid number, initial oil concentration, type of emulsifier, chemical dosage, order of chemical addition, reaction time, and final pH. Based on these studies, an hypothesis of the emulsion breaking mechanism was proposed.

Oil, COD, and turbidity were used in field studies to establish the effect of the following variables on treatment efficiency; chemical concentration, order of chemical addition, chemical mixing time, flocculation mixing time and speed, and air flotation time and recirculation rate. Based on these studies, design criteria and operating costs for this process were presented.

This report was submitted in fulfillment of Program No. 12010 EZV between the Federal Water Pollution Control Administration and the Armco Steel Corporation.

## KEY WORDS

Waste Water Treatment ✓  
Industrial Wastes ✓  
Steel Wastes

Emulsions ✓  
Coagulation ✓  
Flocculation ✓  
Oily Wastes

Flotation ✓  
Kinetics ✓  
Zeta Potential ✓

## CONTENTS

	<u>Page No.</u>
ABSTRACT	iii
SECTION I - CONCLUSIONS	1
SECTION II - RECOMMENDATIONS	5
SECTION III - INTRODUCTION	9
SECTION IV - BASIC RESEARCH	11
Present Theory and Practice	11
Experimental	19
Discussion	44
SECTION V - FIELD STUDIES	57
Batch Treatment of Concentrated Coolant	58
Continuous Treatment of Rinse Waters	65
Comparative Economics	79
SECTION VI - ACKNOWLEDGMENTS	85
SECTION VII - REFERENCES	87
SECTION VIII - GLOSSARY	89
SECTION IX - APPENDICES	93
APPENDIX A - Research & Development Work	93
APPENDIX B - Detailed Engineering Report and Drawings	103
APPENDIX C - Kinetic Relationships Employed	127
APPENDIX D - Kinetic Relationship for Sequential Reactors	129
APPENDIX E - Use of Single Channel Coulter Counter for Flocculation Kinetics	131
APPENDIX F - Samples and Reagents	135
APPENDIX G - Experimental Equipment	137

## LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
1.	VARIATION IN ZETA POTENTIAL AND pH OF SPENT MILL EMULSION WITH DILUTION	23
2.	VARIATION IN ZETA POTENTIAL WITH ALUM ADDITION	25
3.	VARIATION IN ZETA POTENTIAL WITH ADDED EMULSIFIER (TRITON X-100)	28
4.	VARIATION IN TURBIDITY OF "TYPICAL" ROLLING OIL EMULSION WITH TRITON X-100 EMULSIFIER	31
5.	FRACTION CHANGE IN TURBIDITY WITH DILUTION	36
6.	JAR TESTING OF ALUM, LIME, AND CLAY	39
7.	JAR TESTING OF "TYPICAL" NONIONIC EMULSION	40
8.	JAR TESTING OF "TYPICAL" ANIONIC EMULSION	41
9.	KINETICS OF FLOCCULATION: FRACTIONAL RESIDUAL TURBIDITY VS. FLOCCULATION TIME AT VARIOUS VELOCITY GRADIENTS	45
10.	FRACTIONAL RESIDUAL TURBIDITY AS A FUNCTION OF VELOCITY GRADIENT AT CONSTANT FLOCCULATION TIMES	53
11.	SIMPLIFIED FLOW DIAGRAM BATCH TREATMENT SYSTEM	61
12.	SIMPLIFIED FLOW DIAGRAM CONTINUOUS TREATMENT SYSTEM	66
B-1 thru B-10	DETAILED ENGINEERING DRAWINGS	APPENDIX B
E-1	FLOCCULATION OF A 200 ppm COMMERCIAL ROLLING OIL WITH ALUM VIA COULTER COUNTER TECHNIQUES	APPENDIX E
E-2	FLOCCULATION OF A 400 ppm COMMERCIAL ROLLING OIL EMULSION WITH ALUM VIA COULTER COUNTER TECHNIQUES	APPENDIX E
E-3	FLOCCULATION OF A 1,000 ppm COMMERCIAL ROLLING OIL EMULSION WITH ALUM VIA COULTER COUNTER TECHNIQUES	APPENDIX E

## LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
I.	TYPICAL ROLLING OIL COMPOSITION	13
II.	GENERAL STABILITY CHARACTERISTICS RELATIVE TO ZETA POTENTIAL	16
III.	STOCK OIL EMULSION COMPOSITIONS	20
IV.	VARIATION IN ZETA POTENTIAL OF 6,000 ppm SPENT MILL EMULSION WITH MILL MIX AND/OR CO <sub>2</sub> -FREE DEIONIZED WATER	22
V.	JAR TESTING COMMERCIAL ROLLING OIL EMULSIONS WITH ALUM, LIME, CLAY AND POLYMER	27
VI.	COMPARISON OF ROLLING OIL EMULSIONS AT DIFFERENT ACID NUMBERS	29
VII.	INITIAL COMPARATIVE JAR TEST RESULTS	32
VIII.	JAR TEST RESULTS FOR CONCENTRATION VARIATION	33
IX.	COMPARISON OF MEASURED AND CALCULATED TURBIDITIES	35
X.	pH OPTIMIZATION JAR TEST RESULTS	38
XI.	THE EFFECT OF ORDER OF ADDITION OF ALUM AND LIME DURING JAR TESTING	42
XII.	RESIDUAL TURBIDITY VS. VELOCITY GRADIENT AND ACID NUMBER	43
XIII.	SUMMARY OF INFLUENT ANALYTICAL DATA FOR CONCENTRATED COOLANT	59
XIV.	SUMMARY OF BATCH TREATMENT RESULTS	62
XV.	SUMMARY OF BATCH TREATMENT PERFORMANCE FOR VARIABLES EVALUATED	63
XVI.	INFLUENT ANALYTICAL DATA - RINSE WATER	70
XVII.	CHEMICAL ADDITION SCHEMES	72
XVIII.	DEMONSTRATION PROGRAM FIELD DATA	77



<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
XIX.	TREATMENT COST PER TON OF STEEL ROLLED (\$)	81
XX.	TREATMENT PLANT CAPITAL COSTS	82
AI and AII.	EFFECTS OF VARIOUS PARAMETERS ON MINIMUM CHEMICAL DOSAGES REQUIRED TO TREAT WASTES CONTAINING 1,000 ppm OIL.	APPENDIX A

## SECTION I

### CONCLUSIONS

An evaluation of the results of the studies conducted as part of this grant has resulted in a number of conclusions. Since the basic research studies and the field studies were to a great extent independent efforts, the conclusions drawn from the results of these two study areas will be presented separately.

With regard to the field studies, it should be noted that in general no two cold mills are operated identically. On this basis, the conclusions made with regard to the Ashland Works cold mill and the success of the related treatment plant cannot necessarily be extended to treatment of all cold mill wastes.

### BASIC RESEARCH STUDIES

1. The stability of concentrated wastes as measured by zeta potential is less than the same wastes diluted to oil concentrations equivalent to rinse water. This was indicated by a 24 percent reduction in zeta potential. This is due in part to the higher specific conductivity of the water phase in well used emulsion systems. (Pages 22-23, 49)
2. The particle size distribution of rolling oils is measurably shifted toward smaller mean particle sizes during the first few days of use, apparently as a result of the temperature, pressure, and shear to which the emulsion is subjected during use. (Page 22)
3. Colloid titration techniques were too insensitive for estimation of intrinsic emulsion stability. (Pages 20-21)
4. Relative streaming current techniques for measuring emulsion stability appear both feasible and amenable to process control. (Pages 21-22)
5. Maximum flocculation efficiency occurred:
  - a. Where anionic emulsifier was substituted for nonionic emulsifier at relatively low velocity gradients. However, the converse appears possible at velocity gradients higher than  $144 \text{ sec}^{-1}$ . (Pages 27, 49)
  - b. At a pH value of  $6.0 \pm 0.4$ . (Pages 39-41, 49)
  - c. When alum and lime flocculants are added simultaneously. (Page 42)

6. The effect of acid number on overall process efficiency was insignificant to at least acid number 16 for "typical" rolling oil formulations containing added emulsifier. (Pages 43, 48)
7. The following generalized mechanism for coagulation and flocculation is proposed. (Pages 5-52)
  - a. Coagulation occurs via reaction of positively charged hydroxo complexes of aluminum with oil droplets to form positive, negative, or neutral particles depending on emulsifier type and pH;
  - b. These particles subsequently react through coulombic and van der Waals forces with growing positively charged alum floc; and
  - c. The resulting floc grows with concomitant reduction of floc charge.
8. The increase of optimum alum dose is small over the oil concentration range 500 to 1,000 ppm. (Page 50)
9. Ideal flocculation kinetics were found to dominate commencing at mean velocity gradient values of between 28 to 60  $\text{sec}^{-1}$  for AN16 nonionically emulsified systems. Redispersion of floc does not occur at velocity gradients below the highest value tested (144  $\text{sec}^{-1}$ ). The composite flocculation rate constant ( $k_D$ ) was found to be about  $10^{-4} (\text{mg/l})^{-1}$ . Bench level testing proceeded under the influence of this rate constant for three minutes at which point the overall rate of flocculation decreased abruptly. (Pages 52-55)
10. Turbidity measurements in this work were found to be adequate for kinetics studies and the feasibility of using a single channel Model B Coulter Counter for more refined kinetics work was demonstrated. (Pages 127-128, 131-134)
11. The kinetics relationships presented indicate that the mean velocity gradient via shaft torque or shaft horsepower is preferred over tip speed measurements for jar testing. (Pages 127-128)

### FIELD STUDIES

#### Batch Treatment of Concentrated Coolant

1. The particular operating practice of the Ashland Works Cold Mill and the subsequent destination of the cold rolled product permitted operation of the mill on a recirculated coolant system which reduced waste water flows from the 1,500 gpm plant design flow to approximately 100,000 gallons per week. (Pages 57-58)

2. The type of rolling oil used and the type of emulsion breaker employed, determine the optimum treatment requirements. (Pages 60, 67, 82)
3. Treatment efficiency is reduced by either underdosing or overdosing with emulsion breaker. (Page 59)
4. The results of jar testing conducted during this study were more sensitive to changes in operating parameters and chemical concentrations than the results from the full-scale facility. (Page 65)
5. Under the conditions evaluated, heating the waste up to 150 F offered no advantage in treatment efficiency. (Pages 60-64)
6. Although some physical separation of oil (tramp) from concentrated coolant can be achieved, total oil removal is significantly greater with the use of a cationic polymer as an emulsion breaker. (Pages 62-63)
7. The treatment process and facility as operated is capable of greater than 90 percent removal of total oil and COD. (Pages 62-63)
8. The recovered oil is of fuel oil quality. (Page 64)

#### Continuous Treatment of Rinse Water

9. Effective treatment of combinations of oily rinse water and concentrated coolant can be obtained using alum, lime, clay, and organic polymer. Typical chemical dosages for the waste water received during this study were 175 ppm alum, 36 ppm lime, 15 ppm clay, and 0.5 ppm polymer. This represents a chemical cost of approximately \$0.05 per 1,000 gallons. (Pages 70-71)
10. Simultaneous addition of alum, lime, and clay to the same mix tank at the detention times studied did not significantly change treatment efficiency. (Pages 71-73)
11. A mixing period between the addition of other chemicals and polymer is necessary for efficient utilization of polymer. (Pages 71-73)
12. Equalization is an essential requirement for continuous effective treatment. (Pages 68-69)
13. Control of pH is a significant factor in maintaining effective treatment of oily rinse waters by coagulation with inorganic salts. (Page 69)
14. Air flotation of the oily floc produced by this process is required to achieve satisfactory separation with a separation detention time of 57 minutes or below. (Page 73)

15. For the system studied, flocculation equipment was unnecessary to achieve effective treatment of oily rinse waters. (Pages 73-74)
16. An air flotation detention time of 25 minutes including a recycle rate of 20 percent of the influent flow is adequate for floc separation. (Page 73)
17. The treatment process and facility as operated is capable of 90 percent removal of total oil, COD, and BOD. (Pages 75-79)
18. The recovered oil is adequate for use as road oil but due to its high water and solids content, it is unacceptable as a boiler fuel. (Pages 76-79)
19. Treatment plant operating costs range from \$0.04 to \$0.07 per ton of steel rolled depending upon the type of rolling oil and the waste volumes. (Page 81)
20. Based upon treatment considerations for concentrated coolant and rinse water, operation of the Cold Mill on a recirculated coolant system is preferred over the rinse water system. Batch treatment of concentrated coolant is favored on the basis of less discharged pollutants and more economical treatment. (Pages 79-83)

## SECTION II

### RECOMMENDATIONS

On the basis of the conclusions drawn, a number of recommendations are made below. Many of these recommendations are presented relative to the logical extension of this work. It is hoped that those recommendations based on experimental conclusions will assist the technologist in the field and that those pertinent to the extension of this work will provide a measure of guidance to those who wish to expand present knowledge in this area of pollution abatement.

#### BASIC RESEARCH STUDIES

1. Research should be expanded relative to the efficiency of emulsion breaking of "typical", virgin, used, and spent commercial rolling oils as a function of emulsifier content and type. The analytical procedure recently reported by Ludwig (7) may be of value in this regard.
2. Research should also be done relative to the lard oil to mineral oil ratio and its effect on flocculation efficiency.
3. A study of optimum alum-lime dose versus emulsion concentration should be conducted if quantitative relationships for emulsion flocculation are to be ultimately achieved.
4. Refined kinetics studies should also be performed, especially via the Coulter Counter in order to define effective rate equations for this process.
5. A study of velocity gradient should be extended to include the advantages of employing initially high velocity gradients followed by the lower values necessary to avoid redispersion in the latter stages of the process.
6. The velocity gradient effect should be investigated at the pilot plant level via the use of shaft torqueometers or other such means to estimate power dissipation versus process efficiency and engineering kinetics.
7. Pilot plant research of concentration and compositional effects on process efficiency should be performed.
8. Compositional effects on rolling characteristics should be studied in order to ultimately optimize emulsion breaking efficiency with rolling performance.
9. The use of relative streaming current devices as process control instruments should be investigated at both the pilot plant and full-scale plant level.

10. Some attempt should be made to monitor and control pH during waste emulsion flocculation at the full-scale plant level.

#### FIELD STUDIES

1. An extensive evaluation of the roll coolant and rinse water requirements of the production facility should be made prior to design of the associated treatment facility. Where possible, the economic trade-off between production flexibility and capital expense of the corresponding treatment facility should be fully evaluated in the interest of economic feasibility.
2. The use of a rinse water system on the tandem cold mill if not entirely necessary should be discouraged in the interest of reduced water pollution, and capital and operating expense.
3. Close communication between production and treatment facilities should be fostered and maintained.
4. Pilot plant studies should be encouraged prior to installation of the treatment facility, especially when functioning on a continuous process, to attempt to bridge the gap between batch-wise bench studies and continuous full-scale.
5. Jar testing should be used as a basis for chemical requirements, but continued reduction of chemicals at the full-scale facility should be attempted as long as effective treatment is maintained.
6. Changes in rolling oils should prompt immediate reevaluation of the chemical requirements.
7. Equalization capacity should be as large as is feasible. A detention time of at least one hour is recommended.
8. pH should be continuously monitored and used to control lime additions.
9. Centrifugal pumping of lime slurry is recommended over positive displacement pumping.
10. The design and use of flocculation equipment should be given further study to fully optimize the flocculation step of the process. Pilot plant studies should be undertaken to provide better direction on this process parameter.
11. The operation of the skimming mechanism should be performed at a frequency and duration so as not only to minimize the removal of unnecessary water in the scum but also to prevent the scum from dewatering to the point of being unmanageable in gravity flow lines.

12. Some type of shelter should be provided for the flotation unit to prevent destruction of the floated floc and reentrainment due to rainfall.



### SECTION III

#### INTRODUCTION

The process of cold rolling steel strip to light gauges requires lubrication and cooling of the rolls. Oil alone is inadequate as a coolant for a high-speed cold mill, so an oil-in-water (o/w) emulsion is used as a combination lubricant-coolant. Modern tandem cold mills have recirculating coolant systems capable of flooding each reduction stand with a large quantity of emulsion; this emulsion can be reused for weeks or months before it deteriorates to the point that it can no longer be used. In cases where strip cleanliness is of major concern, once-through rinse water is used in place of emulsion on the first and/or the last stands of the mill. This type of mill, then, produces two types of oily wastes: periodic dumps of spent emulsion from the coolant system; and, once-through rinse water from the first and/or last stands.

Commercial rolling oils are complex mixtures containing principally fats and mineral oil, with lesser amounts of free fatty acids, emulsifiers, bactericides, and sometimes rust inhibitors. Most rolling oil formulations are trade secrets, and historically the rolling oil user has not been successful in determining which parameters are most critical for rolling. Indeed, even seemingly similar rolling mills may require different oil formulations for optimum rolling efficiency. The chemical composition of a cold mill waste is, then, not only largely unknown; it also varies from mill to mill and as oil suppliers are changed on the same mill.

The more concentrated oily wastes, such as from batch dumps, can be disposed of relatively economically (contract hauling, chemical emulsion breaking, etc.); these are usually on the order of a few thousands of gallons per day or less. Much more difficult is the problem of efficient and economical treatment of rinse waters, which are on the order of a thousand gallons per minute or more. Past practice throughout the industry has been to send these wastes directly to the sewer, to discharge them to public waterways through lagoons in which oil can separate from unstable emulsions, or to apply some sort of chemical coagulation process which usually results in the formation of large quantities of an almost unmanageable sludge which is, in turn, a disposal problem. The coagulation of dilute o/w emulsions has been neither a science nor an art; little is known of the physico-chemical aspects of efficient treatment or of the mechanisms and kinetics involved.

An improved chemical coagulation process for treating cold mill rinse waters was developed by the Armco research laboratories. (Appendix A). Coagulation is initiated with relatively small amounts of alum and/or a cationic organic polyelectrolyte. Lime is used for pH control. Clay and an anionic or nonionic polymer are used to promote

growth of the oily floc. This floc is then separated from the water by dissolved air flotation; the water is sent to the sewer and the oil may then be destroyed by incineration or processed further to recover the oil.

A facility was designed and constructed by Armco (Appendix B) to apply this coagulation process to the wastes from a new five-stand tandem cold mill at the Ashland, Kentucky Works. A project was undertaken to optimize and demonstrate the full-scale facility and simultaneously to perform basic research concerning the conceptual mechanisms and apparent kinetics of the coagulation and flocculation of dilute o/w emulsions. The results of both the basic research and the operation of the facility are described in this report.

SECTION IV  
BASIC RESEARCH  
PRESENT THEORIES AND PRACTICES

The clarification of water containing spent rolling oil emulsion depends on two general factors: (a) the inherent stability of the system towards coagulation and the means of producing emulsion destabilization, and (b) the rate of flocculation of a destabilized system. The complete discussion of spent rolling oil emulsion waste treatment requires, therefore, an insight into both the various possible thermodynamic states of the system and the kinetics of change from one such state to another. Because of the present level of knowledge in this area of research the former was treated in a qualitative manner whereas the latter was studied from at least a semi-quantitative point of view.

Emulsion Stability

The "stability" of a system may be regarded as the relative tendency of the system to remain in the dispersed state. Most rolling oil emulsions are true colloids, exhibiting a measureable electrical potential at the "plane of shear"<sup>1</sup> between the oil droplet and the continuous phase. All other factors being equal, the larger the absolute magnitude of this "zeta" potential the more stable the system, the lower the magnitude the less stable. At very low zeta potentials the kinetic energy of particle motion (whether solely Brownian or under an induced velocity gradient) may exceed the repulsive energy between particles in which case coagulation and ultimately flocculation will occur.<sup>2</sup>

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<sup>1</sup>The electrical potential at the "plane of shear" is referred to as the zeta potential ( $Z_p$ ) and may be defined as the potential between the continuous or solvent phase and the boundary plane which separates the solvent adhering to a colloid in its motion and that which can move with respect to it. Zeta potential can be determined through the measurement of electrophoretic mobility. Relative surface charge has also been estimated through relative streaming current or colloid titration techniques(1).

<sup>2</sup>Coagulation is generally considered to mean electrical destabilization of particles or removal of forces of repulsion without proceeding to agglomeration or flocculation.

The zeta potential depends on the state of the oil droplet-continuous phase interface. The chemical composition of the rolling oil and of the continuous phase ultimately determines the state of the oil-water interface. Since these factors are the more easily determined, the relationship of zeta potential to chemical composition is frequently studied.

The composition of commercial rolling oils are invariably trade secrets. It is known however that they usually contain lard oil, mineral oil, emulsifiers and possibly such additives as bactericide, extreme pressure lubricants, etc. A typical rolling oil composition is given in Table I in terms of the major components(2).

The individual rolling oil components may be classed as active or inert towards emulsification. The mineral oil portion may be considered inactive, for example. Obviously, added emulsifiers are active components and may run as high as 4 percent in some commercial formulations. The primary active components in the lard oil portion are the free fatty acids. Most of the lard oil portion is composed of glyceryl esters of fatty acids. The unesterified free fatty acid content is variable among commercially available oils(3) from as low as about 3 to as much as 13 percent by weight of total formulation.

The added emulsifiers and the free fatty acids present at the oil droplet surface act as surfactants, rendering the oil droplet stable against coagulation and stabilizing the small colloid size of the droplet through surface tension effects. These effects will vary as the relative levels of added emulsifier and percentage of free fatty acid present, being generally more stable as these levels increase.<sup>3</sup>

Any changes in intrinsic stability of an emulsion may be regarded as arising from interactions and reactions at the continuous phase - oil droplet interface. These changes may arise from numerous factors among which are: pH, ionic strength, specific ion interaction and temperature.

The pH of the system exerts a significant influence on oil emulsion stability. Lowering the pH should lower the zeta potential by suppressing ionization of the free fatty acid. This is especially likely as the solvation radius of the proton is sufficiently small to cause it to adsorb beneath the plane of shear of the emulsified particle(4).

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<sup>3</sup>There are limits to this general rule however, as will be noted during the experimental and discussion portions of this work.

TABLE I  
TYPICAL ROLLING OIL COMPOSITION<sup>a</sup>

Non-Ionic

Lard Oil	48.10 to 52.30%
Mineral Oil -200 secs @ 100F	46.60 to 47.60%
Triton X-100 (Rohm & Haas)	2.00 to 3.00%
Bactericide	0.10%
Acid No. 15-19	

Anionic

Lard Oil	48.40 to 52.40%
Mineral Oil -200 secs @ 100F	46.50 to 47.50%
Atlas G-3300 (Sulfonate)	2.00 to 3.00%
Bactericide	0.10%
Acid No. 15-19	

<sup>a</sup> Compliments of Vendor "A"

The ionic strength of the continuous phase will also effect emulsion stability. However, there exists little or no evidence to indicate a direct relationship between electrical conductivity, per se, and colloid stability. This situation probably arises from two considerations. First, monovalent ions (other than hydrogen or lithium) exert a real but small effect on zeta potential because of their small charge/radius ratio. In general the effect of ionic strength arising from monovalent ions will be primarily that of zeta potential attenuation through reduction of the electrical capacitance in the aqueous phase. Bivalent ions and trivalent ions exhibit a more pronounced effect than monovalent ions on colloid stability and have led to such semi-quantitative comparisons as the Hofmeister Series and the Schulze-Hardy Rule(5). The hydrolysis products of multivalent ions may interact with an emulsion droplet in other ways than through reduction of field strength in the aqueous phase. These effects on emulsion stability may overshadow those of ionic strength.

The nature of a multivalent cationic species may vary depending upon the pH. At very low values it may exist as a simple hydrated ion. At higher values it may form positively charged hydroxo complexes and finally insoluble hydroxides. At sufficiently high pH values amphoteric substances such as aluminum may even form negatively charged hydroxo species in the form of anionic coordination complexes. The interaction of these different species with colloids can vary considerably. Thus, the pH range of flocculation is frequently critical.

It has been reported(6), for example, that the positive hydroxo complexes of aluminum (pH 4-5) most effectively destabilize colloids. Hydroxo complexes of multivalent ions should also be adsorbable through van der Waals forces as well as ionic forces, although this has been rarely discussed. Amphoteric metals in solution also exhibit a zero point of charge (ZPC) at which they demonstrate a low solubility and therefore promote rapid phase separation. The combination of these many effects has led to the rather wide usage of iron and aluminum salts as coagulant-flocculants.

Adsorption-charge reduction effects will vary with temperature as well as type. As would be expected the stability of an emulsion diminishes with increasing temperature due to numerous effects such as increased Brownian motion, increased reaction rates and decreased surface tension.

Spent rolling oil emulsions are less stable than fresh emulsions. Destabilizing factors include: (a) a build up in hardness in the aqueous phase due to solvent evaporation; (b) reduction of free fatty acid content through high pressure pyrolysis of unsaturated bond linkages(7) and reaction with iron fines(7,8); and (c) bacterial degradation. Partially off-setting these influences is the dispersive action of the mill. This latter effect will depend significantly on

such factors as roll pressure, volume of the emulsion system, and flow rate of the emulsion onto the mill stands. A significant portion of spent rolling oil emulsion will exhibit "break-out" of "tramp" oil on standing. The remaining emulsified oil may be rather poorly stable (Cf. Table II, and ref. 9).

The abovementioned factors will influence the stability of a system towards coagulation. These same factors plus some additional ones play the more pragmatic role of influencing the rate of flocculation of a destabilized rolling oil emulsion system.

### Flocculation Rates

Flocculation rates are influenced by both chemical and physical factors. Chemical factors include interaction among destabilized emulsion droplets, between such droplets and aggregates thereof with primary flocculants such as insoluble iron and aluminum hydroxo species, and so-called coagulant aids such as clay and polymer.

Insoluble positively charged iron and aluminum hydroxo species may react ionically with negatively charged emulsion droplets. However, van der Waals forces are also operative and independent of charge. The magnitude of these effects depends upon pH and concentration. Entrapment of oil by precipitating alum or iron floc may also occur. Kinetic effects related to insoluble metal floc interaction are largely unknown although previous work on the flocculation of kaolin suggested first-order kinetics for removal of the primary clay particles(10).

The role of clay as a flocculant aid can be attributed to its ability to adsorb charged particles. This results from the fact that clay platelets possess positively charged edges and negatively charged faces. Thus, clay particles can function as bridges between charged particles. The density of clay is such that when incorporated into the floc it may speed the sedimentation of the flocculated phase. Particulate matter such as clay also appears to improve floc strength and therefore retard "redispersion"(11).

Long chain polymers are also used as flocculant aids. These polymers may adsorb ionically and/or through van der Waals forces depending on the nature of the particular polymer being used. Under optimum conditions the polymer can adsorb on more than one colloid particle such that a bridging effect is achieved. Under such conditions a large interconnected network of microflocs can form leading to rapid phase separation(6).

The kinetics of rolling oil emulsion flocculation has remained largely unstudied. Slezak(9) has recently reported some significant work along these lines for spent rolling oil emulsions. However,

other detailed studies on the flocculation of oil-in-water (o/w) emulsions have been performed on atypical monodisperse systems at unrealistically slow rates of flocculation(12,13).

TABLE II  
GENERAL STABILITY CHARACTERISTICS  
RELATIVE TO ZETA POTENTIAL<sup>a</sup>

	Avg. Zeta Potential (mv.)
Maximum Agglomeration and Precipitation	0 to +3
Range of Strong Agglomeration and Precipitation	+5 to -5
Threshold of Agglomeration	-10 to -15
Threshold of Delicate Dispersion	-16 to -30
Moderate Stability	-31 to -40
Fairly Good Stability	-41 to -60
Very Good Stability	-61 to -80
Extremely Good Stability	-81 to -100

<sup>a</sup> From Riddick, T. M., "Control of Colloid Stability Through Zeta Potential" Vol I, p. 2, Livingston Publ. Co., Wynnewood, Pa. (1968)



Comparisons with real systems should include not only the proper pH and dosage control but also the appropriate energy input to the system necessary to produce practical rates of flocculation. The intrinsic rate constant for flocculation ( $k$ ) is related to the initial and instantaneous number of primary particles through the relationships (Appendices C, D):

$$\frac{N}{N_0} = \exp (-KDGN_0t) \quad (\text{batch process})$$

and

$$\frac{N}{N_0} = (1 + kDGN_0 \frac{t}{m})^m \quad (\text{series of continuous stirred-tank reactors})$$

where  $G$  is the velocity gradient ( $\text{sec}^{-1}$ ),  $D$  the particle size distribution coefficient,  $t$  the time of flocculation (secs),  $t/m$  the retention time per reactor and,  $m$  the number of reactors. The velocity gradient  $G$ , can be estimated from a number of physical parameters<sup>(14)</sup> including the experimentally measured torque on a stirrer being rotated in a reactor vessel<sup>(15)</sup> or through consideration of the shaft speed and paddle dimensions of an "infinitely thin" vertical paddle-on-shaft stirrer as originally derived by Camp<sup>(16)</sup>. These various approximations yield an estimate of  $G_m$  the mean velocity gradient, where

$$G_m = (\frac{W_m}{u})^{0.5} \text{ sec}^{-1}$$

and  $W_m$  is the mean power dissipated per unit volume per unit time in the system and  $u$  is the absolute viscosity.

Thus, approximation of  $W_m$  is necessary to estimate  $G_m$ . For the typical jar test,  $W_m$  may be estimated by the method of Camp<sup>(16)</sup> through the relationship:

$$W_m = \frac{239 C_d (1-K)^3 (n)^3 \text{Sum}(A(r_b)^3)}{V}$$

where  $C_d$  and  $K$  are constants,  $A$  the area of a paddle,  $r_b$  the distance of the center of the paddle to the center of the shaft,  $n$  the revolutions per second of the shaft, and  $V$  the volume of the system being flocculated.

Consequently, flocculation kinetics can be determined experimentally through measureable parameters. The value of  $N$  and  $N_0$  can be measured directly by means of a Coulter Counter<sup>4</sup>(11), estimated via number or weight concentrations or possibly through turbidity measurements under appropriate circumstances (as shown in this work). The value of  $D$  is very difficult to estimate under kinetic conditions although Harris<sup>(10)</sup>, et al have done so through use of a computer and size distribution data.

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<sup>4</sup>Trademark Coulter Electronics Div.

The flocculation rate increases with increasing work input to the system up to such work input levels where degradation of the floc becomes serious. Additionally, the rate constant,  $k$ , will not necessarily remain constant beyond some point at which the primary flocculant may change in character. Thus, optimization of the flocculation rates in real systems will require optimization of mean velocity gradient and reaction time as well as flocculant dosage and pH.

### Typical Commercial Processes

Historically a few general processes for emulsion breaking of o/w emulsions have developed. These approaches provide for the destabilization of the emulsion by acid, polyvalent ions or both. If polyvalent ions are employed, the pH is generally regulated by lime and controlled at a pH corresponding to the ZPC of the hydrous polyvalent metal floc. The pH for the zero point of charge of  $AlCl_3$  may be as high as 8-9 whereas for  $Al_2(SO_4)_3 \cdot 18H_2O$  it would be significantly less (pH 6-7) because the sulfate ion is more readily incorporated within the coordination sphere than are halide ions. Primary flocculation with such flocculants as alum and lime is frequently followed by clay addition in the same general pH range. Further treatment with polymer is also often employed.

### Scope of Unresolved Questions

A great deal of fundamental (and therefore practical) information is still lacking. The areas of deficiency include:

1. The effect of rolling oil composition on emulsion stability
2. The effect of history on emulsion stability
3. The mechanism of emulsion destabilization and flocculation under optimum dosage and pH conditions
4. The rate of flocculation

These questions have received the attention of this work, particularly at the 1,000 ppm emulsion concentration level. Dilute spent rolling oil wastes, normally expected to be in this range, constitute a more serious process problem than more concentrated wastes.

## EXPERIMENTAL

The experimentation performed in this work involved the following:

1. Emulsion stability was studied in terms of zeta potential and in a few cases via relative streaming current or colloid titration techniques. In a number of instances particle size distributions were also made.

Emulsion stability was examined in the following areas:

- a. As a function of composition of oil and/or aqueous phase for commercial and "typical" rolling oil emulsions;
  - b. As a function of mill time, ionic conductivity, pH and dilution for mill spent commercial rolling oil emulsions.
2. Turbidities of emulsions were examined as a function of concentration and composition for laboratory prepared commercial and "typical" rolling oil emulsions.
  3. Jar testing was extensively performed in the following areas:
    - a. On a comparative basis among several laboratory prepared commercial rolling oil emulsions;
    - b. On a laboratory prepared commercial rolling oil emulsion in terms of alum-lime addition and relative streaming current;
    - c. On "typical" rolling oil emulsions as a function of pH, chemical additions and order of addition thereof, as well as a function of oil composition, velocity gradient and time. (For stock solution compositions, see Table III.)
  4. Jar test kinetics studies were conducted on a "typical" rolling oil emulsion. An approximate composite rate constant was determined. An evaluation was also made of a direct particle counting technique for determining rate constants for flocculation of rolling oil emulsions at practical concentrations.

### Stability and Properties of Commercial Rolling Oils

The relative stability of unused and mill-spent waste commercial rolling oils was investigated from several points of view. These included particle size distribution analysis and zeta potential.

The particle size distribution of several samples were run. These included brand "C" emulsion after 2 hours and after 2 days use on the Ashland mill and a spent brand "A" emulsion. The "C" samples were run within 72 hours after the last sample was taken whereas the spent brand "B" emulsion was run about one month after sample taking.

The two hour "C" emulsion exhibited a slight maximum in weight percent at about 3-5 micrometers particle diameter as did the spent month old "A" waste emulsion. The two day "C" emulsion exhibited a shift to smaller particle sizes and a disappearance of the 3-5 micrometer maximum. As near as could be determined within the limitations of the instrument, dilution of the 2 day used emulsion did not measurably alter the particle size distribution. Unfortunately, comparison could only be made of this effect at relatively large particle diameters (greater than 12-15 micrometers) at which the total weight percent of oil is very small compared to that below about 12 micrometers particle diameter.

Stability estimates on laboratory prepared commercial rolling oil emulsions were made primarily via zeta potential measurements. Before receipt of the Zeta-Meter however, an evaluation of colloid titration techniques was conducted and use was made of the Relative Streaming Current Detector.

TABLE III  
STOCK OIL EMULSION COMPOSITIONS

<u>Stock Emulsion</u>	<u>Conc. (ppm)</u>	<u>A.N.<sup>a</sup> (±)</u>	<u>Mineral Oil Fraction<sup>b</sup></u>
1	8000	6	0.500
2	8096	8	0.494
3	8240	11	0.485
4	8480	16	0.472
5	8720	21	0.459
6	8960	26	0.446

<sup>a</sup> Acid number of oil

<sup>b</sup> Emulsions contain only mineral oil and lard oil

The colloid titration technique proposed by Kawamura and Tanaka(1) was examined. This technique involves treatment of a colloid sample with a positive polymer and back-titration with a negative polymer in the presence of an indicator dye sensitive to positive and negative colloids. The number of milliequivalents of positive polymer necessary to neutralize a milligram of negative colloid is referred to as the "colloid charge". To test this method a 10.0 weight percent "B" oil emulsion was prepared, and by successive binary dilutions, emulsions of 5.00, 2.50---0.00988 weight percent were also prepared. A 10.0 ml aliquot of 5.00 percent emulsion was found to be neutralized by about  $8.7 \times 10^{-3}$  meqs of "Cat-floc" when back-titrated with  $9.411 \times 10^{-4}$ N PVSF and o-toluidine blue indicator. The end point was somewhat sluggish. At concentrations lower than about 1.00 percent oil, the results were poor even under corrected blank conditions. Dilution of the indicator to a point where its blank value was acceptable resulted in indiscernable end points for emulsions less concentrated than about 0.2 weight percent.

The Relative Streaming Current Detector was also utilized for stability estimates. Brand "B" oil emulsions in deionized water gave relative streaming current (RSC) values of -128 for 1000 ppm, -104 for 500 ppm and -80 for 250 ppm oil concentrations. By comparison an "A" emulsion yielded a -34 to -40 value for a 500 ppm oil concentration. Treatment with 22 ppm alum resulted in a final RSC value of +7.5 in the latter case whereas all the "B" emulsions remained negative even at 1050 ppm in alum. Above about 20-25 ppm in alum the 1000, 500 and 250 ppm "B" emulsion exhibit RSC's of about -30 to -40 which diminished only very slowly upon further alum addition.

Various rolling oil emulsions were titrated with alum and lime with simultaneous measurement of the RSC. Most titrations were performed on 900 ml aliquots of 500 ppm "A" emulsions under gentle stirring conditions. The original "A" emulsion exhibited a pH of 5.9-6.1 and an RSC of -34 to -40. Upon alum and/or lime addition the RSC was always negative for pH values greater than 6.5-7.0, positive for pH values less than 6.5-7.0 and zero for pH values in the range 6.5-7.0. When alum and lime were added incrementally and alternately to the emulsion so as to avoid large variations in pH, pinpoint flocculation would occur in the range 6.5-7.0 at a definite minimum amount of added alum and lime. This minimum amount also corresponded closely to that necessary to produce a visible alum floc in distilled water at pH 6.5-7.0. In one experiment an excess of alum was added (0.1 g/0.45 g oil) and back-titrated with lime to produce a floc on the acid side. In this instance again, however, the RSC was zero at the flocculation point.

Zeta potential values were employed throughout the bulk of this study for comparative stability estimates. Because of the fact that commercial rolling oils were of unknown composition, such comparisons were made in reference to the effects of changes in the continuous water phase.

The effects of pH, dilution and specific conductivity were examined via zeta potential on the spent "B" rolling oil emulsion. The emulsified oil content of the sample was 6,000 ppm whereas the tramp oil content was 7,500 ppm. Samples more concentrated than about 300-500 ppm in emulsified oil were ultracentrifuged at 14,400 G's for 1.5 hours or more in order to obtain samples translucent enough for zeta potential measurement(18). Dilutions were made with CO<sub>2</sub>-free deionized water and as-received Ashland mill mix water in order to bring out the effects of pH and ionic conductivity. The results are plotted in Figure 1.

This spent "B" emulsion was also diluted to a given concentration (1200 ppm or a 4 to 1 dilution) with CO<sub>2</sub>-free deionized and mill mix water in different proportions with subsequent zeta potential and pH measurement. The results appear in Table IV. Pickup of CO<sub>2</sub> by the CO<sub>2</sub>-free deionized water during the course of these measurements affected the measured pH values slightly.

The "C" used emulsion was also investigated and found to have a zeta potential of -40.7 mv at "infinite dilution" (dilution to 30 ppm or less) in CO<sub>2</sub>-free deionized water after two hours mill time. The value after two days mill time was -45.8 mv. The specific conductivities in these measurements were 8 and 9 micromhos, respectively. The difference in the two values was due to the fact that in the two day mill sample virtually all the emulsion droplets exhibited the same electrophoretic mobility whereas the two hour sample was composed of particles 70-90 percent of which exhibited this same electrophoretic mobility while 10-30 percent of which moved more slowly under the 200 V. applied potential.

TABLE IV

VARIATION IN ZETA POTENTIAL OF 6,000 PPM SPENT MILL  
EMULSION DILUTED WITH MILL MIX AND/OR CO<sub>2</sub>-FREE DEIONIZED WATER

<u>Sample No.</u>	<u>Emulsion Conc. (ppm)</u>	<u>Mill Water/ Deionized Water</u>	<u>S.C.</u>	<u>pH</u>	<u>Zp (mv.)</u>
1	1200	Inf.	0.590K	6.40	-24.1
2	1200	1	0.470K	6.25	-25.0
3	1200	0.33	0.295K	5.90	-27.7
4	1200	0	0.205K	6.10	-29.2

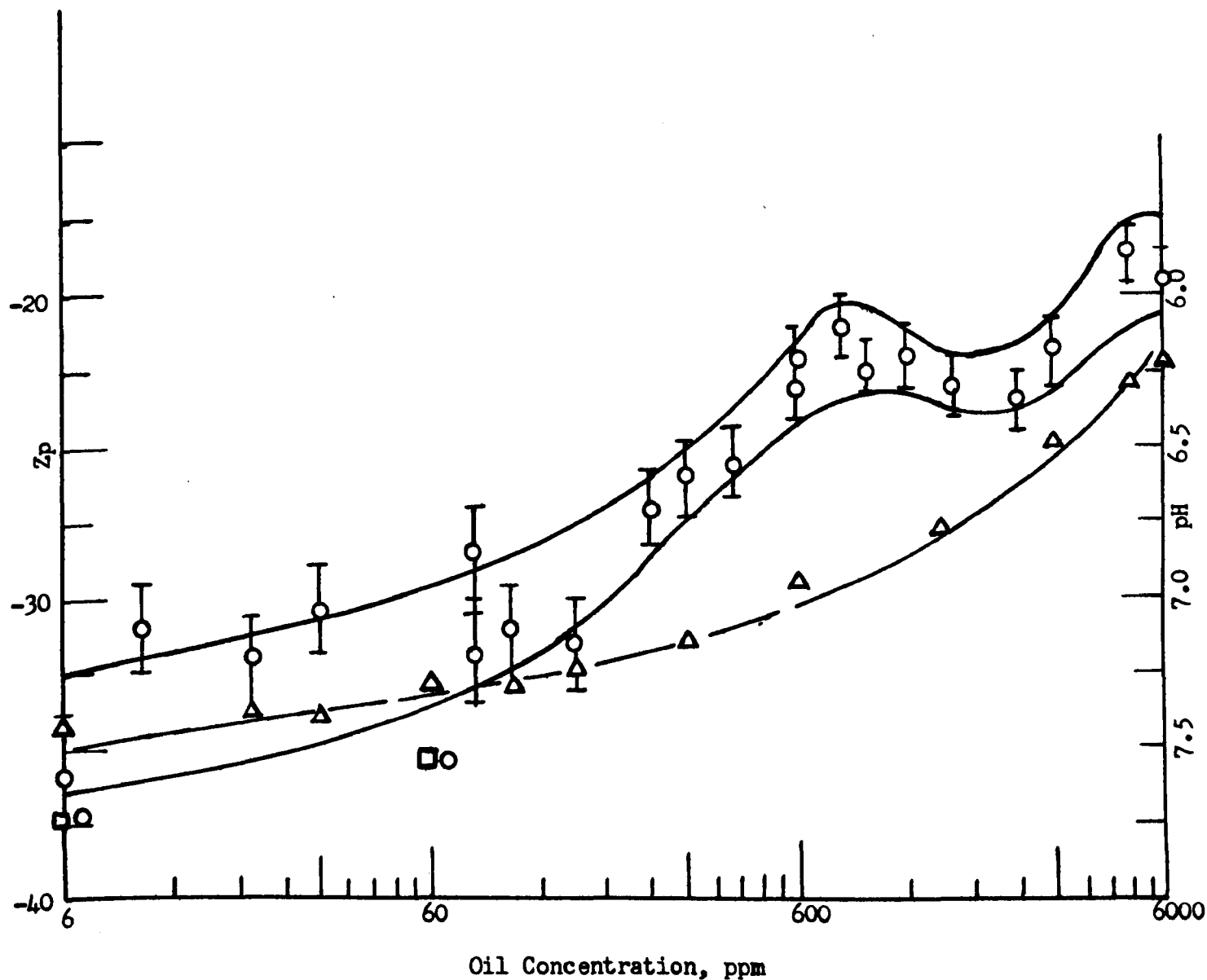
FIG. 1

# VARIATION IN ZETA POTENTIAL AND pH OF SPENT MILL EMULSION WITH DILUTION

○ Zp after dilution with mill mix water (mv.)

◻◻ Zp after dilution with CO<sub>2</sub> free deionized water (mv.)

△ pH at given dilution with mill mix water



A spent "A" rolling oil emulsion was also examined. After filtration over a 0.8 micrometer Millipore filter pad a 3,100 ppm emulsion was obtained. The zeta potential of the system was approximately -24 mv. Dilution with mill mix water in binary steps to 39 ppm failed to produce any significant change in zeta potential.

A sample of this same system diluted to 300-400 ppm with mill mix water was treated with dilute alum and lime. Upon the addition of alum alone the zeta potential of the emulsion increased from -24 mv. at pH 6.96 to +8.3 mv. at pH 4.90. Back treatment with lime to pH 10.3 yielded a zeta potential of -18.5 mv. Upon adding more alum and lime so as to form an alum floc and subsequently filtering over a 0.8 micrometer Millipore filter, a zeta potential of -21 mv. was observed on the few emulsion particles remaining in the system at pH 7.03. More alum was added to this treated and filtered system so as to reduce the pH to 4.57. The remaining particles were observed to be mostly immobile with a relative few having a zeta potential of -3.8 mv. with fewer still having a very small positive zeta potential.

The effect of polyvalent ion concentration on zeta potential was also investigated by treating another filtered and diluted "A" spent emulsion with various amounts of alum. The concentration of the filtered spent emulsion was 7,100 ppm and the sample tested was 645 ppm after dilution with deionized water. In a first series of tests the alum to oil ratio was varied by cumulative addition of alum to the original emulsion sample. A second series was also run in which the oil content was 260 ppm and each sample of emulsion plus alum was prepared separately and subjected to zeta potential measurement immediately after preparation. These results appear in Figure 2 wherein the ratio of the fractional change in zeta potential after alum addition is plotted versus the alum to oil ratio.

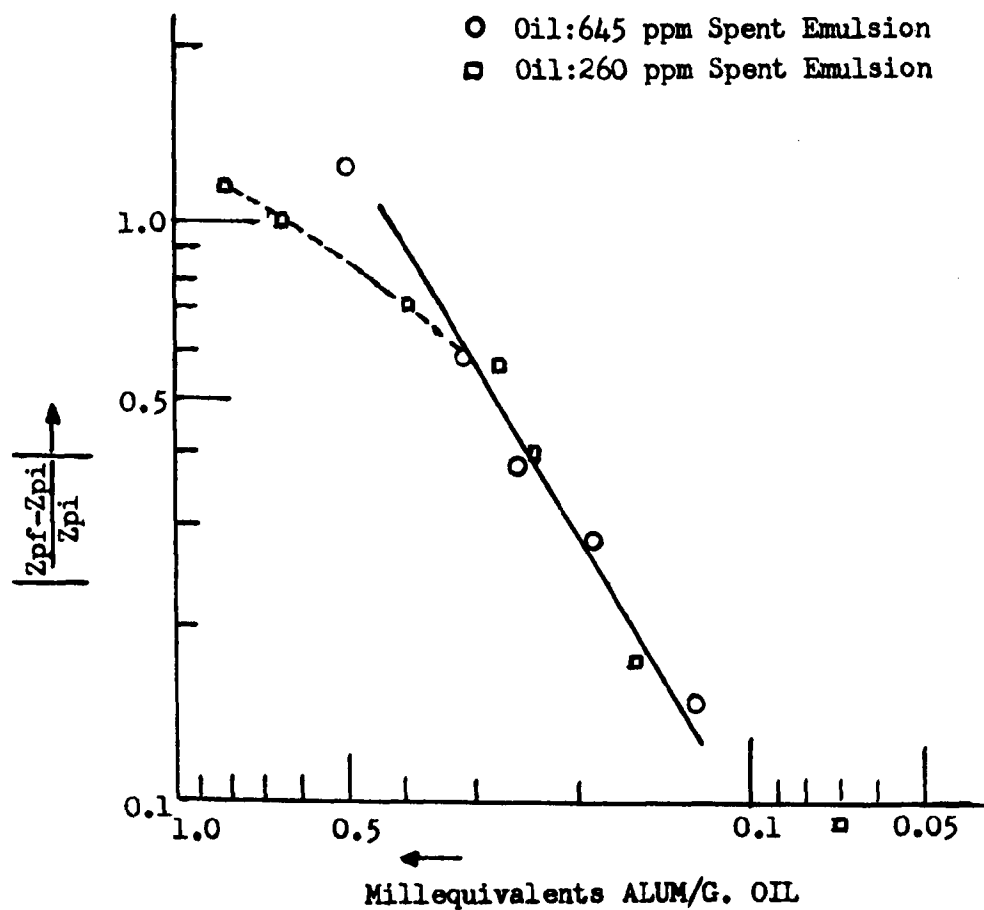
A "B" emulsion was also treated with alum. This emulsion did not exhibit a positive zeta potential in the presence of even large excesses of alum.

The turbidity of another laboratory prepared "B" rolling oil emulsion was determined. The as-prepared 942 ppm emulsion was then diluted with various amounts of deionized water and the resultant turbidities measured. The relationship between concentration and turbidity was found to be:

$$0.862 \frac{\ln C_d}{C_i} = \frac{\ln JTU_d}{JTU_o}$$



FIG. 2 VARIATION IN ZETA POTENTIAL  
WITH ALUM ADDITION



where:

$JTU_d$  = turbidity of diluted emulsion in JTU  
 $C_d$  = concentration of diluted emulsion in ppm  
 $JTU_o$  = turbidity as-prepared emulsion  
 $C_i$  = concentration of as-prepared emulsion

Jar testing was performed on laboratory prepared commercial rolling oils early in the grant period before the receipt of the Zeta-Meter or the turbidimeter. In these cases "relative clarity" was used as a criteria rather than turbidity. A pH of flocculation (6.5-7.0) was selected on the basis of current practice. The results of comparative jar testing results among the various commercial rolling oils is given in Table V for alum, lime, clay and polymer additions. In each instance alum was added first followed by lime addition. Stirring times of 5.0 minutes were employed throughout. The zeta potentials at "infinite dilution" given in Table V were determined considerably later from freshly prepared emulsions.

#### Emulsion Stability and Properties of "Typical" Rolling Oils

The effect of chemical composition on resultant zeta potential was studied for synthetic "typical" rolling oils having the mineral oil fractions given in Table III.

The effect of emulsifier content on synthetic "typical" rolling oils was studied on AN11 and AN16 "typical" oils. The oils in question contained only mineral oil and lard oil in the ratios 0.970 and 0.944 for the AN11 and AN16 cases, respectively. The emulsions were prepared from chloroform standard solutions at 850 ppm in deionized water with emulsification via the Waring Blendor for  $60 \pm 1$  secs. Each of these emulsions was then treated with various amounts of Rohm and Haas Triton X-100 (a nonionic polyethoxylated alkyl phenol emulsifier) and the zeta potential of each resultant system measured. In the AN16 case the oil concentration diminished (as a result of dilution by added emulsifier) from 850 ppm to 607 ppm. In the AN11 case the concentration was maintained at 699 ppm except at the 0.613 and 0.805 emulsifier to emulsion ratio levels by means of deionized water adducts. In each case the systems were stirred gently after each addition. These data are presented in Figure 3.

The zeta potential of "typical" oil emulsions of different oil acid numbers were correspondingly investigated. These included emulsions with and without added emulsifier (Triton X-100 at emulsifier to oil ratio 0.0242) at similar oil in water concentrations. These results appear in Table VI.

TABLE V

## JAR TESTING COMMERCIAL ROLLING OIL EMULSIONS WITH ALUM, LIME, CLAY AND POLYMER

Oil (a,b)	Zpo (mv.)	Alum, Lime Addition				Time to Visible Floc (min)	Clay, Polymer Addition <sup>c</sup>		
		Final Alum Conc. (ppm)	Final Lime Conc. (ppm)	Gm (sec.-l)	Rel. Clarity After 5 min. (Clear = 100)		Final Clay Conc. (ppm)	Final Polymer Conc. (ppm)	Rel. Clarity After 5 min.
"B"	-35.6	138	56	low (mag. stirring)	100	-	11	1	70(d)
"D"	-37.7	138	56	low ( " " )	70	-	11	1	70
"C"	-43.7	138	56	low ( " " )	60	-	11	1	60
"A"	-32.5	138	56	low ( " " )	50	-	11	1	60
"B"		134	56	59.6	90	1-3	9	1	100
"D"		134	56	59.6	75(b)	2-4	9	1	100
"C"		134	56	59.6	75-80(b)	3-5	9	1	90+
"A"		134	56	59.6	0	10	9	1	60
"B"		138	56	144	0	"Redispersed"	9	1	0
"D"		138	56	144	100	2-4	9	1	100
"C"		138	56	144	100	2-4	9	1	100
"A"		138	56	144	80	3-6	9	1	70

(a) Final oil concentration 854 ppm in all cases

(b) Clarity still improving at end of five minute jar test time

(c) Clay and polymer added after flocculation via alum and lime, clay, polymer treatment conducted at indicated velocity gradient for five minutes

(d) "B" air blown and redispersed

FIG. 3. VARIATION IN ZETA POTENTIAL WITH  
ADDED EMULSIFIER (TRITON X-100)

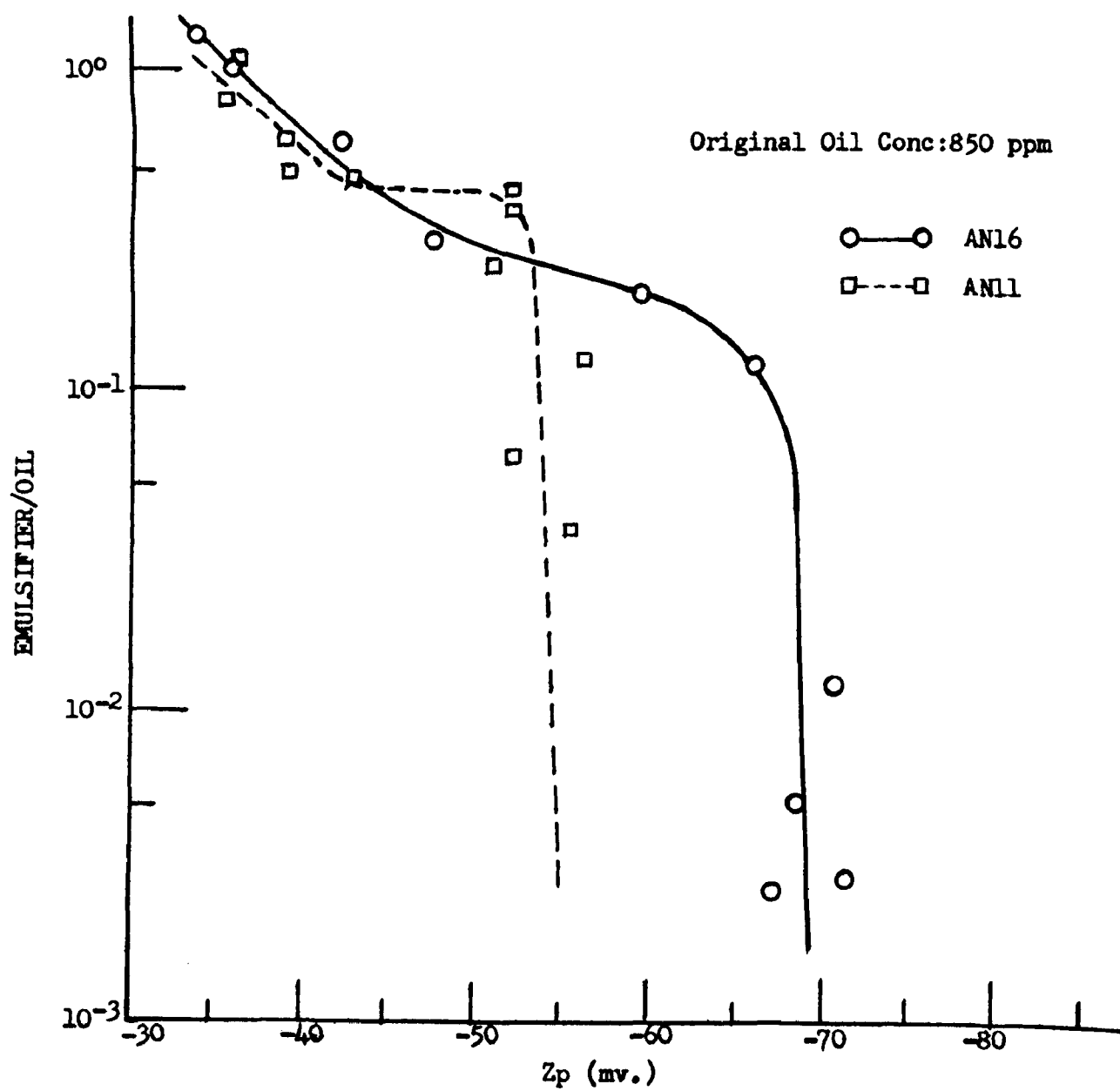


TABLE VI

COMPARISON OF ROLLING OIL EMULSION OF DIFFERENT ACID NUMBERS

<u>AN(±1)</u>	<u>Emulsifer Free</u>			<u>Containing Emulsifier<sup>a</sup></u>		
	<u>Conc. (ppm)</u>	<u>Zp (mv.)</u>	<u>Turbidity (JTU)</u>	<u>Conc. (ppm)</u>	<u>Zp (mv.)</u>	<u>Turbidity (JTU)</u>
6	800	-45.7	585	800	-37.6	270
8	712	-49.4	565	-	-	-
11	825	-55.8	285	800	-49.5	240
16	850	-83.9	285	800	-55.7	210
21	872	-58.6	325	800	-46.6	240
26	-	-	-	800	-43.4	250

<sup>a</sup> Triton X-100 emulsifier/oil = 0.0242 in all cases

The effect of emulsifier content on particle size distribution was also studied. Particle size distributions were made on AN16, 848 ppm "typical" rolling oil emulsions treated with various amounts of Triton X-100 and dispersed for  $120 \pm 1$  seconds via a Waring Blendor. These particle size distribution measurements revealed that the higher the emulsifier to oil ratio the smaller the mean particle diameter up to a ratio of 0.121. At a ratio of 0.677, however, the system exhibited a particle size distribution shifted toward larger diameters. It was also observed that creaming did not occur in the 0.121 ratio case even after two weeks shelf aging whereas in each of the other cases creaming was pronounced within less than 24 hours.

A comparison of particle size distributions resulting from different emulsifier types was also made. An acid number 16 oil emulsion was prepared with Atlas G-3300 (an anionic sulfonate emulsifier) for example, instead of Triton X-100 at a comparative emulsifier to oil ratio of 0.0241 and the particle size distribution determined. No difference in particle size distribution could be detected between this emulsion and an AN16 nonionically emulsified oil. Careful analysis revealed, however, that about 75 percent by weight of both emulsions was composed of particle sizes below the lower limit of instrumental detection.

Another "typical" emulsion, identical save the fact that it contained no emulsifier, yielded a particle size distribution measurably shifted to larger particle diameters.

The turbidity of "typical" rolling oil emulsions were investigated in reference to emulsifier content. In these experiments the concentration of an AN16 rolling oil was maintained constant at 848 ppm and the emulsifier content varied. This was achieved by dispersing a 50.0 ml aliquot of 8,480 ppm oil emulsion containing no added emulsion in 450 ml deionized water containing various amounts of Triton X-100 via a Waring Blendor for  $120 \pm 1$  seconds. The results appear in Figure 4. Dilution of the resultant 848 ppm emulsions to 424 and 212 ppm yielded the same relative turbidity distributions.

Because of the peculiarity in the turbidity distribution with emulsifier content, a comparison was made of the ultraviolet adsorption characteristics of the pure oil, the deionized water, the emulsifier in water and an emulsified oil. It was found that the emulsifier absorbed increasingly strongly as the wavelength was decreased below 400 millimicrometers whereas the oil exhibited essentially constant absorption characteristics in this same range.

The acid number and concentration effects on the turbidity of as-prepared emulsifier-free "typical" rolling oil emulsions are presented in Tables VII and VIII along with the values for turbidity after breaking the emulsions with the indicated dosages of alum and lime.

FIG. 4 VARIATION IN TURBIDITY OF "TYPICAL" ROLLING  
OIL EMULSION WITH TRITON X-100 EMULSIFIER

Oil: AN16, 848 ppm

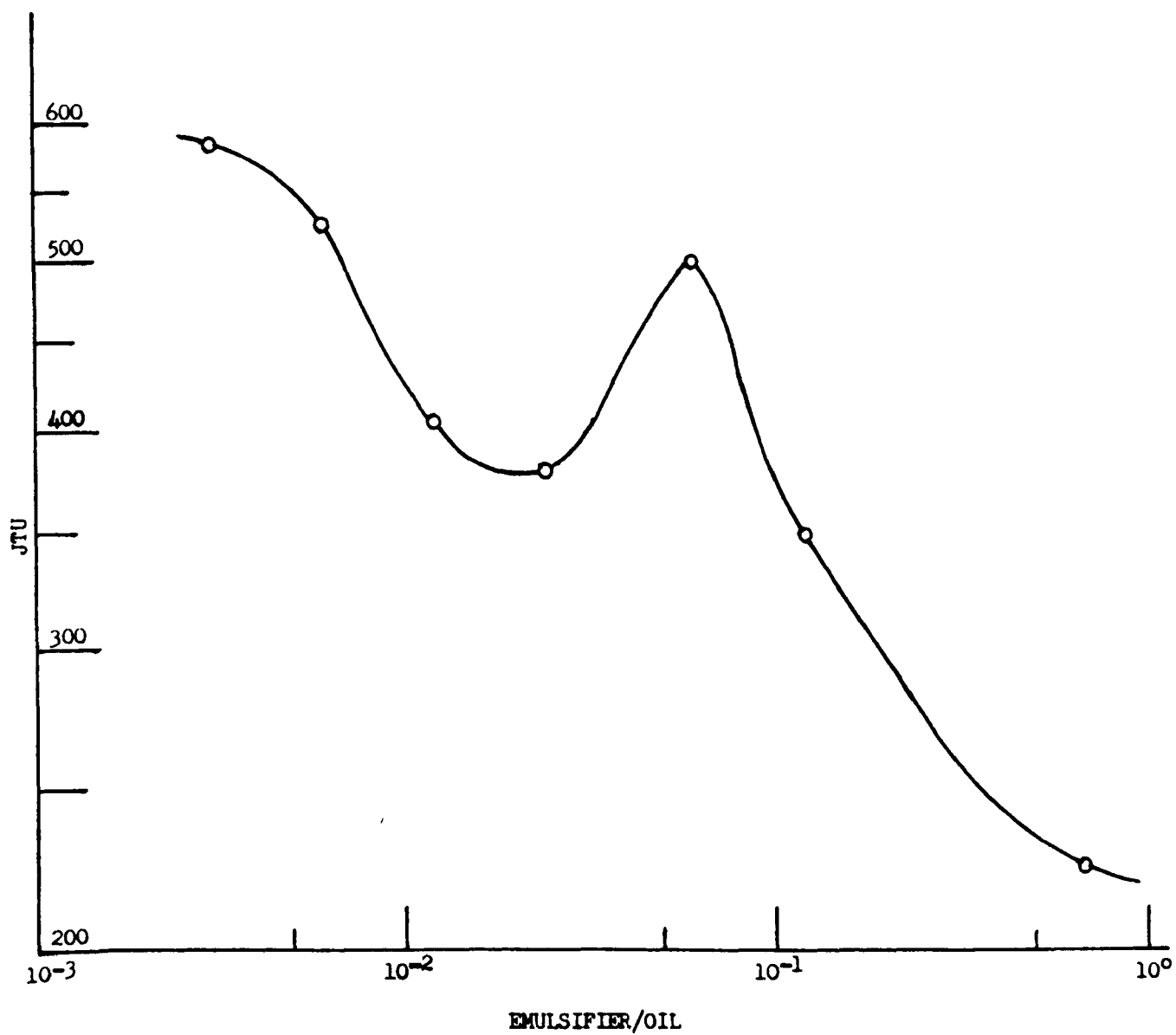


TABLE VII

INITIAL COMPARATIVE JAR TEST RESULTS  
( $G_m = 144 \text{ sec}^{-1}$ )

Sample No.	AN( $\pm 1$ )	Oil Conc. (ppm)	As-prepared Turbidity (JTU)	250 ppm alum + lime		250 ppm alum + lime		250 ppm alum + lime	
				pH <sub>f</sub> <sup>b</sup>	JTU <sub>f</sub> <sup>b,c</sup>	pH <sub>f</sub>	JTU <sub>f</sub>	pH <sub>f</sub>	JTU <sub>f</sub>
Blank	-	-	0.2	5.4	-	7.4	-	8.2	-
1	6	500	180	5.4	-	-	-	-	-
2	8	506	200	5.4	-	-	-	-	-
3	11	515	225	5.3	22 <sup>e</sup>	-	-	-	-
4	16	530	240	5.5	28	-	-	-	-
5	21	545	285	5.2	43	-	-	-	-
6	26	560	310	5.3	44	-	-	-	-
7	6	1000	310	5.3	4	7.6	13	8.1	14
8	8	1012	340	5.2	8	-	-	-	-
9	11	1030	390	5.4	9	-	-	-	-
10	16	1060	470	5.2	27	7.5	13	8.1	18
11	21	1090	510	5.2	42	-	-	-	-
12	26	1120	545	5.2	53	7.5	22	7.9	12
13	6	2000	525 <sup>a</sup>	d	21	-	-	8.3	13
14	16	2120	680 <sup>a</sup>	d	53	-	-	8.3	23

<sup>a</sup> At 2000 ppm and above the measured turbidity values are imprecise and may even decrease with increasing concentration as a nephelometric method was employed in these studies.

<sup>b</sup> pH<sub>f</sub>, JTU<sub>f</sub> are pH and turbidity values after flocculation.

<sup>c</sup> All turbidity values taken one hour after flocculation.

<sup>d</sup> pH meter became defective.

<sup>e</sup> Turbidity not attainable due to dispersion of large floc particles.



TABLE VIII

JAR TEST RESULTS FOR CONCENTRATION VARIATION

Dosage: Alum, 125 ppm; Lime, 25 ppm

<u>Conc., ppm</u>	<u>AN(±1)</u>	<u>pH orig.<sup>a</sup></u>	<u>As-prepared Turbidity (JTU<sub>i</sub>)</u>	<u>pH<sub>f</sub><sup>a</sup></u>	<u>JTU<sub>f</sub><sup>b</sup></u>	<u>Nature of Floc</u>
40	11	6.2	25	6.0	2	Settled
103	11	6.2	54	6.0	6	Settled
206	11	6.2	90	5.7	15	Settled
515	11	6.2	230	5.8	30	Suspended
1030	11	6.2	-	6.0	100	Suspended- Floated
2060	11	6.2	-	5.9	250	Floated

<sup>a</sup> The pH values reported are questionable as the pH meter was found to be functioning erroneously shortly after these tests. A probable final pH of 5.0 to 5.5 is assumed on the basis of the alum and lime dosages.

<sup>b</sup> Measured post-flocculation turbidity in JTU's.

An empirical relationship among acid number, concentration and turbidity of these as-prepared emulsifier-free emulsions was established as:

$$JTU_i^* = (C_i)^{0.747} (AN)^{0.311}$$

where:

$JTU_i^*$  = calculated turbidity value expressed in Jackson Turbidity Units

$C_i$  = as-prepared oil concentration of the emulsion in ppm

AN = acid number of the oil

These calculated and measured turbidity values are presented in Table IX. Also included in Table IX are turbidity values of some of these emulsions after being flocculated with 250 ppm added alum and enough lime to produce a final pH of about 5.2. Flocculation was performed for five minutes under a mean velocity gradient of  $144 \text{ sec.}^{-1}$ . An empirical relationship was established among acid number, concentration, as-prepared turbidity and post-flocculation turbidity (under these specific conditions) as:

$$JTU_f^* = 1.1 \times 10^{-3} JTU_i^* (AN)^{1.40}$$

or

$$JTU_f^* = 1.1 \times 10^{-3} (C_i)^{0.747} (AN)^{1.72}$$

where:

$JTU_f^*$  = calculated turbidity of the emulsion after flocculation

In Figure 5 is presented a plot of turbidity ratio versus concentration ratio for a "typical" rolling oil emulsion system. The various concentrations were produced by dilution of an as-prepared 1,060 ppm AN16 rolling oil emulsion having an emulsifier (Triton X-100) to oil ratio of 0.0242. The slope of the resulting curve was found to be such that:

$$0.850 \ln \frac{C_d}{C_i} = \ln \frac{JTU_d}{JTU_o}$$

A good deal of experimentation was conducted in reference to the jar testing of "typical" rolling oil emulsions of various compositions. These emulsions were prepared in deionized water by dilution of stock emulsions whose compositions are given in Table III for emulsifier free systems. Systems containing nonionic or anionic emulsifiers were prepared from stock emulsions having the same mineral oil fractions as given in Table III but additionally containing added emulsifier.

TABLE IX  
COMPARISON OF MEASURED AND CALCULATED TURBIDITIES<sup>a</sup>

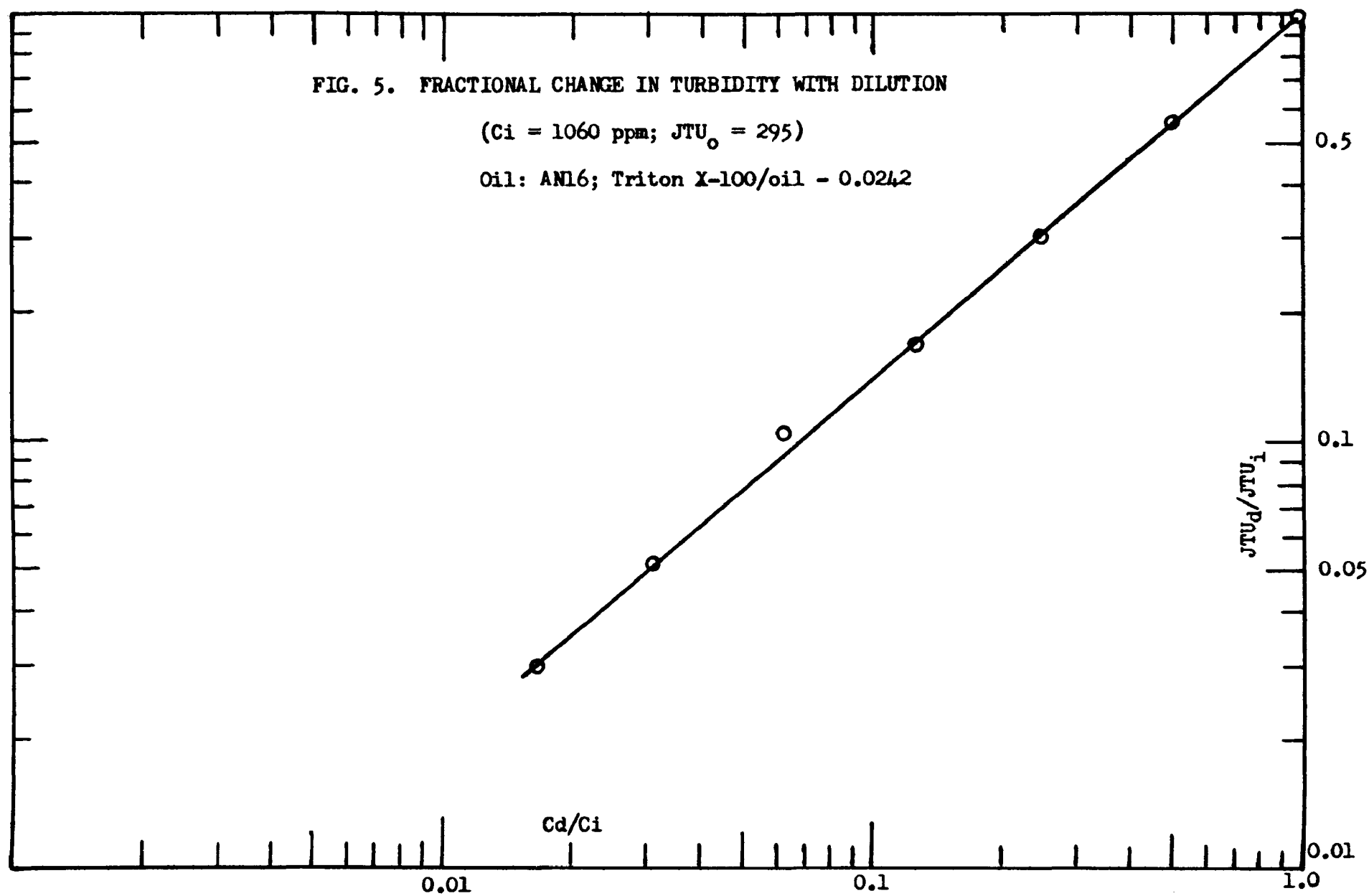
<u>Oil Conc.</u> <u>(ppm)</u>	<u>AN(±1)</u>	<u>JTU<sub>i</sub> (meas.)</u>	<u>JTU<sub>i</sub>* (calc.)</u>	<u>JTU<sub>f</sub> (meas.)</u>	<u>JTU<sub>f</sub>* (calc.)</u>
500	6	180	181	-	-
506	8	200	200	-	-
515	11	225	224	-	-
530	16	240	257	28	14
545	21	285	285	43	23
560	26	310	311	44	34
1000	6	310	304	4.2	4
1012	8	340	335	8.2	7
1030	11	390	375	9	12
1060	16	470	431	27	24
1090	21	510	479	42	38
1120	26	545	522	53	57
2000	6	525	510	21	8
2120	16	680	723	53	40
2240	26	-	876	145	95
40	11	25	33	-	-
103	11	54	67	-	-
206	11	90	113	-	-
515	11	230	224	-	-

<sup>a</sup> For as-prepared emulsions and emulsion flocculated at  $G_m = 144 \text{ sec}^{-1}$  for  $5.0 \pm 0.02$  minutes via dosage with 250 ppm alum, 49 ppm lime.

FIG. 5. FRACTIONAL CHANGE IN TURBIDITY WITH DILUTION

( $C_i = 1060$  ppm;  $JTU_o = 295$ )

Oil: AN16; Triton X-100/oil = 0.0242



The jar test results for emulsifier-free oils is given in Tables VII and VIII for various emulsion concentrations, alum-lime dosages and oil acid numbers.

An extensive jar testing program was also conducted on 1060 ppm, AN16 "typical" oil emulsions containing added emulsifiers. (The emulsifier to oil ratios were 0.0241 for anionic Atlas G-300 and 0.0242 for nonionic Triton X-100). In each case 125 ppm alum<sup>5</sup> was added first, immediately followed by various amounts of lime and 5.0 minutes stirring under a mean velocity gradient of 59.6 sec<sup>-1</sup>. Following this treatment the system was treated with 21-25 ppm montmorillonite clay and again subjected to 5.0 minutes stirring at a  $G_m$  of 59.6 sec<sup>-1</sup>.

In addition to the jar testing of the oil emulsions with alum, lime, and clay, testing was also performed on the individual components of the emulsion breaking process. That is, the alum-lime and alum-lime-clay reactions were examined in the absence of oil. The data for all these various tests are given in Table X in which the pH, specific conductivity, turbidity and zeta potential are reported in reference to alum-lime dose. A graphical summary of these data (except specific conductivity) appears in Figures 6-8.

The optimum dose for equivalent flocculation of an AN16 nonionically emulsified oil at 530 ppm was found to be 95 ppm in alum in comparison with the 119 ppm required for the same emulsion at 1060 ppm in oil. This experimentation was performed via successive approximation at the optimum flocculation pH of  $6.0 \pm 0.4$ . Successive approximation techniques also were used in establishing that only about 5 ppm of alum was necessary to neutralize the zeta potential of a 500 ppm system of this oil.

The effect of order of addition of alum and lime on post-flocculation turbidity of emulsifier containing emulsions was examined over the optimum pH range determined above. These results appear in Table XI. These runs were also conducted at a mean velocity gradient of 59.6 sec<sup>-1</sup> for the usual 5.0 minutes stirring time.

The effects of velocity gradient and acid number on post-flocculation turbidity were also studied. In these cases only nonionic emulsifier was employed at the usual 0.0242 emulsifier to oil ratio. These results appear in Table XII. Use of a Waring Blendor for producing high velocity gradients proved beneficial if employed for about 20-30 secs before transfer to the jar test rig.

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<sup>5</sup>The minimum alum-lime dose for acceptable post-flocculation turbidities under the experimental conditions employed.

TABLE X

pH OPTIMIZATION JAR TEST RESULTS

Final Conc. (ppm) Alum/Lime	Alum + Lime <sup>a</sup>				Alum + Lime + Clay <sup>b</sup>				Alum + Lime + Anionic Oil <sup>a</sup>			
	pH	S.C. <sup>d</sup>	Z <sub>p</sub> <sup>e</sup>	JTU	pH	S.C.	Z <sub>p</sub>	JTU	pH	S.C.	Z <sub>p</sub>	JTU
123/0	4.32	195	-	0.14	5.00	175	+13.0	0.8	4.37	260	-16.1	360
122/11.6	4.62	190	+16.6	1.1	5.26	160	+16.9	2.1	4.45	210	-23.7	325
120/23.0	4.80	190	+17.3	2.8	5.45	175	+16.5	2.7	4.81	205	+16.3	70
119/34.1	5.58	210	+23.1	7.1	6.55	200	+10.4	3.4	5.75	220	+10.5	32
118/44.9	6.55	255	+23.7	3.7	6.70	270	+ 8.36	4.5	7.05	265	-51.2	165
116/55.5	6.75	290	+20.9	4.1	-	-	-	-	-	-	-	-
115/65.8	7.35	355	+13.2	4.0	7.45	365	+ 6.11	5.4	8.30	315	-49.6	345
110/105	9.62	422	-29.4	1.1	9.18	360	- 8.47	27	9.62	460	-43.3	375
	Alum + Lime + Anionic Oil + Clay <sup>b</sup>				Alum + Lime + Nonionic Oil <sup>c</sup>				Alum + Lime + Nonionic Oil + Clay			
	pH	S.C.	Z <sub>p</sub>	JTU	pH	S.C.	Z <sub>p</sub>	JTU	pH	S.C.	Z <sub>p</sub>	JTU
123/0	4.40	235	-12.8	220	4.30	225	+ 7.78	390	4.25	200	+ 9.39	170
122/11.6	4.72	205	-11.2	145	4.55	202	+12.6	320	4.72	198	+ 8.18	200
120/23.0	5.05	195	+ 6.45	Ca.1-2	4.83	200	+18.3	375	5.02	198	+11.1	26
119/34.1	6.12	225	-14.4	Ca.6.5	5.80	240	+12.2	73	5.98	230	-16.4	Ca.10-20
118/44.9	7.38	270	-42.5	35	6.23	275	-34.9	170	6.65	270	-19.7	Ca.29
116/55.5	8.42	305	-33.3	220	7.15	360	-34.2	240	7.30	370	-22.5	72
115/65.8	-	-	-	-	-	-	-	-	-	-	-	-
110/105	9.95	405	-35.1	230	9.42	380	-31.3	340	9.72	345	-25.0	265

<sup>a</sup> Alum always added first followed by lime and system stirred 5.00 ± 0.02 min. @ G<sub>m</sub> = 59.6 sec<sup>-1</sup>

<sup>b</sup> Same as <sup>a</sup> except after first 5 min. clay added (21-25 ppm) and system stirred 5.00 ± 0.02 more

<sup>c</sup> Same procedure as in <sup>a</sup> but 2.58% Triton X-100 nonionic emulsified oil was employed in this case whereas 2.57% G-3300 anionic emulsifier employed in <sup>a</sup>.

<sup>d</sup> Specific conductivity in micromhos

<sup>e</sup> Zeta potential (millivolts)

<sup>f</sup> Post-flocculation turbidity in JTU's

FIG. 6. JAR TESTING OF ALUM, LIME, AND CLAY

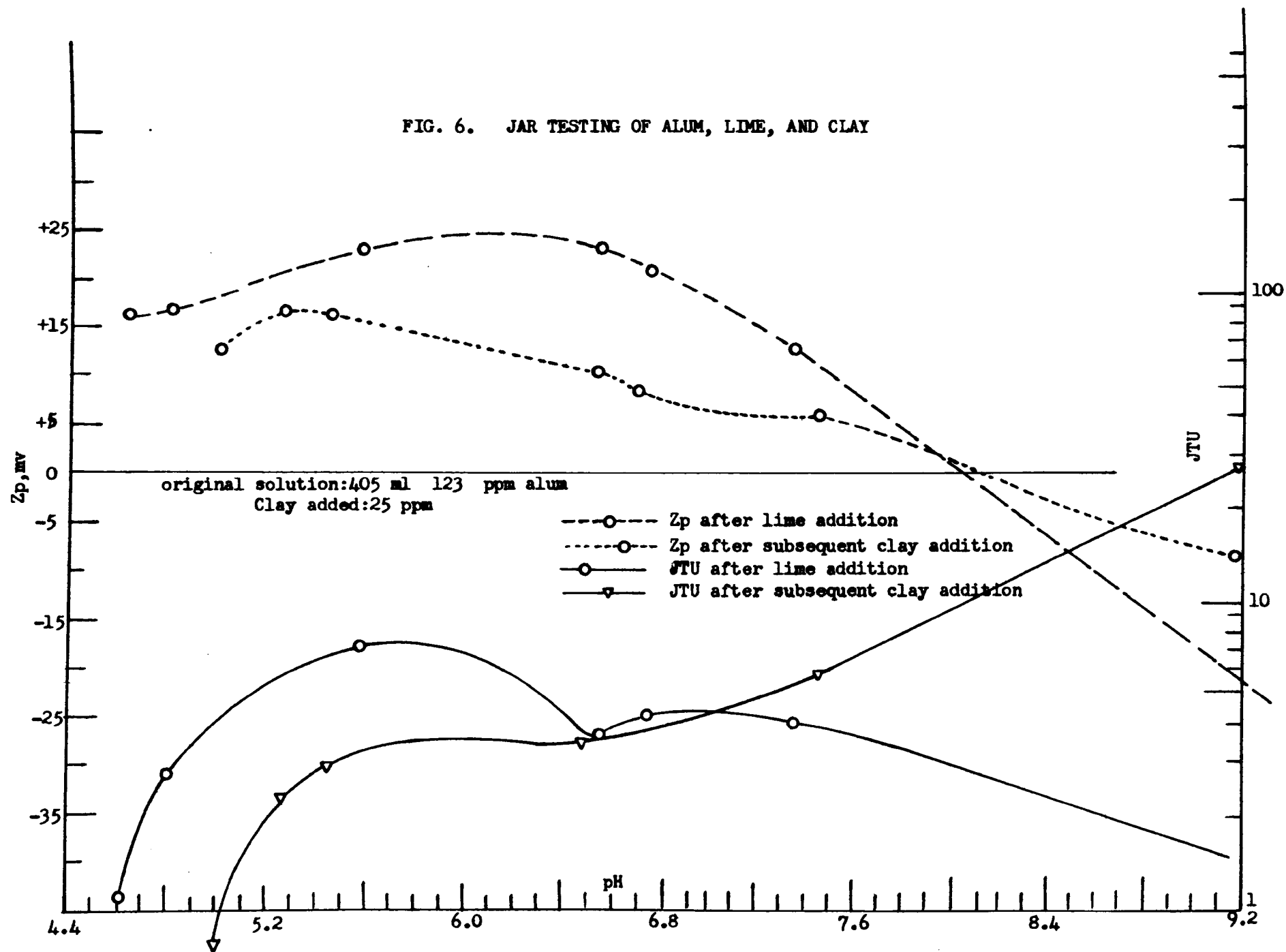


FIG. 7. JAR TESTING OF "TYPICAL" NONIONIC EMULSION

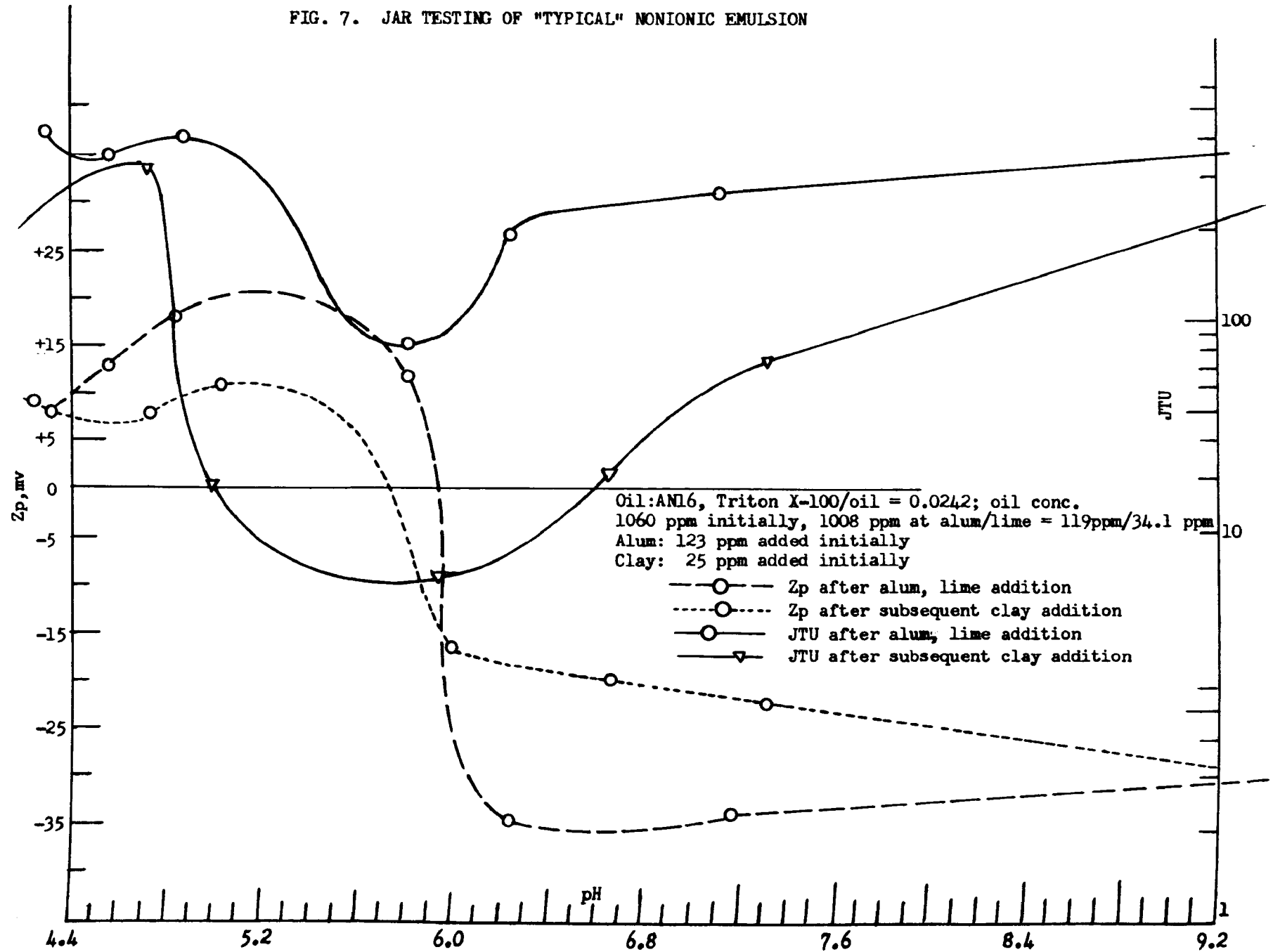




FIG. 8. JAR TESTING OF "TYPICAL" ANIONIC EMULSION

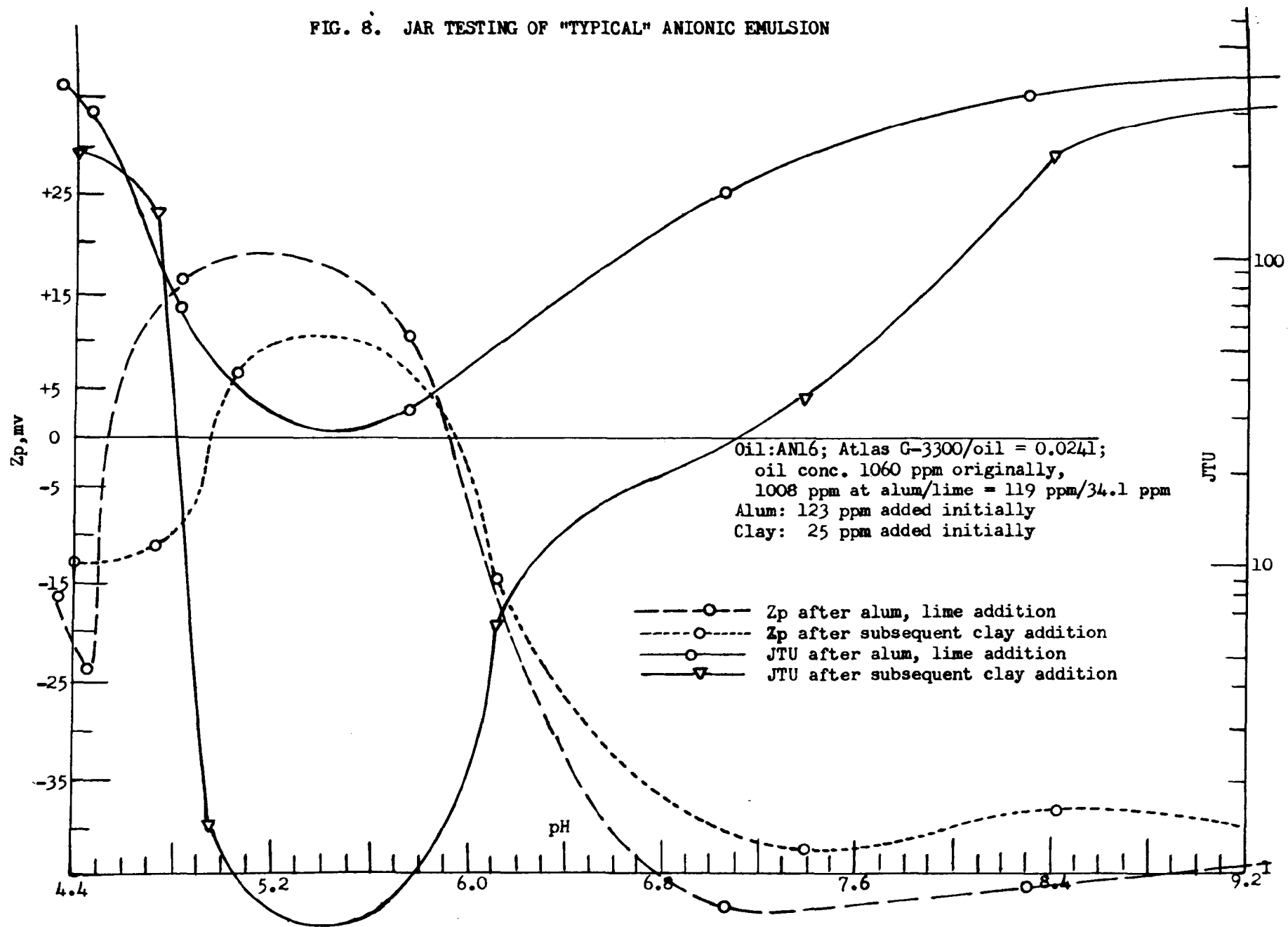


TABLE XI

THE EFFECT OF ORDER OF ADDITION OF ALUM AND LIME DURING JAR TESTING

("Typical" AN16 rolling oil 2.57-2.58% in emulsifier; emulsion is 1060 ppm initially; vel. grad.,  $G_m = 59.6 \text{ sec}^{-1}$ , reaction time,  $t = 300 \text{ secs}$ )

Run No.	Emul. <sup>a</sup>	Final Alum/Lime Dose (ppm/ppm)	Order of <sup>b</sup> Addition	Final pH	Final Turb.(JTU)
1	a	122/11.6	a-l	4.45	325
2	a	120/23.0	a-l	4.81	70
3	a	119/34.1	a-l	5.75	32
4	a	118/44.9	a-l	7.05	165
5	n	122/11.6	a-l	4.55	320
6	n	120/23.0	a-l	4.83	375
7	n	119/34.1	a-l	5.80	73
8	n	122/44.9	a-l	6.23	170
9	a	122/11.6	al	4.63	280
10	a	120/23.0	al	4.91	59
11	a	119/34.1	al	5.78	50
12	a	118/44.9	al	6.43	145
13	n	122/11.6	al	4.60	290
14	n	120/23.0	al	4.98	180
15	n	119/34.1	al	5.90	21
16	n	118/44.9	al	6.60	120
17	a	122/11.6	l-a	4.55	340
18	a	120/23.0	l-a	5.02	390
19	a	119/34.1	l-a	6.25	310
20	a	118/44.9	l-a	6.41	160
21	n	120/23.0	l-a	4.95	145
22	n	119/34.1	l-a	6.10	105
23	n	118/44.9	l-a	6.88	195

<sup>a</sup> Emulsifiers: a = anionic Atlas G-3300; n = nonionic Triton X-100

<sup>b</sup> Order of Addition: a-l = alum followed by lime; al = alum and lime added simultaneously; l-a = lime followed by alum

TABLE XII

RESIDUAL TURBIDITY VS. VELOCITY GRADIENT AND ACID NUMBER

(Final alum:lime = 119 ppm:34.1 ppm; reaction time 300 secs; oil composition; mineral oil:lard oil = 0.45 to 0.50; emulsifier: oil = 0.0242)

<u>AN(±1)</u>	<u>Final Oil Conc. (ppm)</u>	<u>Residual Turbidity</u>			
		<u><sup>a</sup>G<sub>m</sub> = 3</u>	<u><sup>a</sup>G<sub>m</sub> = 27.7</u>	<u>G<sub>m</sub> = 59.6</u>	<u><sup>a</sup>G<sub>m</sub> = 144</u>
6	952	95	67.5	34 <sup>a</sup> 40 <sup>b</sup>	21
11	980	75	62.5	47 <sup>a</sup> 46 <sup>b</sup>	32.5
16	1008	-	80	48 <sup>a</sup> 21 <sup>b</sup>	25.5
26	1066	220	220	195 <sup>a</sup> 202 <sup>b</sup>	155

<sup>a</sup> Alum added first followed by lime

<sup>b</sup> Alum and lime added simultaneously

## Flocculation Kinetics

Flocculation kinetics were conducted on a "typical" rolling oil emulsion (AN16, 1,060 ppm, Triton X-100 to oil ratio 0.0242). The oil:alum:lime ratio was 1,008 ppm:119 ppm:34.1 ppm. Alum and lime were added simultaneously at pH  $6.0 \pm 0.2$  in all cases. The mean velocity gradients for the three studies were 27.7, 59.6 and 144  $\text{sec}^{-1}$ . Samples were taken at various times and the turbidities measured (Cf. Figure 9). The data were analyzed by means of the relationship

$$1.18 \ln \frac{JTU_e}{JTU_i} = -kD N_o G t \quad (\text{Appendix C})$$

from which a value of  $k^* = kD = 1.3 \times 10^{-7} \text{ (mg/l)}^{-1}$  was obtained.

## Additional Studies

A number of additional studies or calculations were made which were of such a nature as to warrant presentation in the Appendices. These areas include:

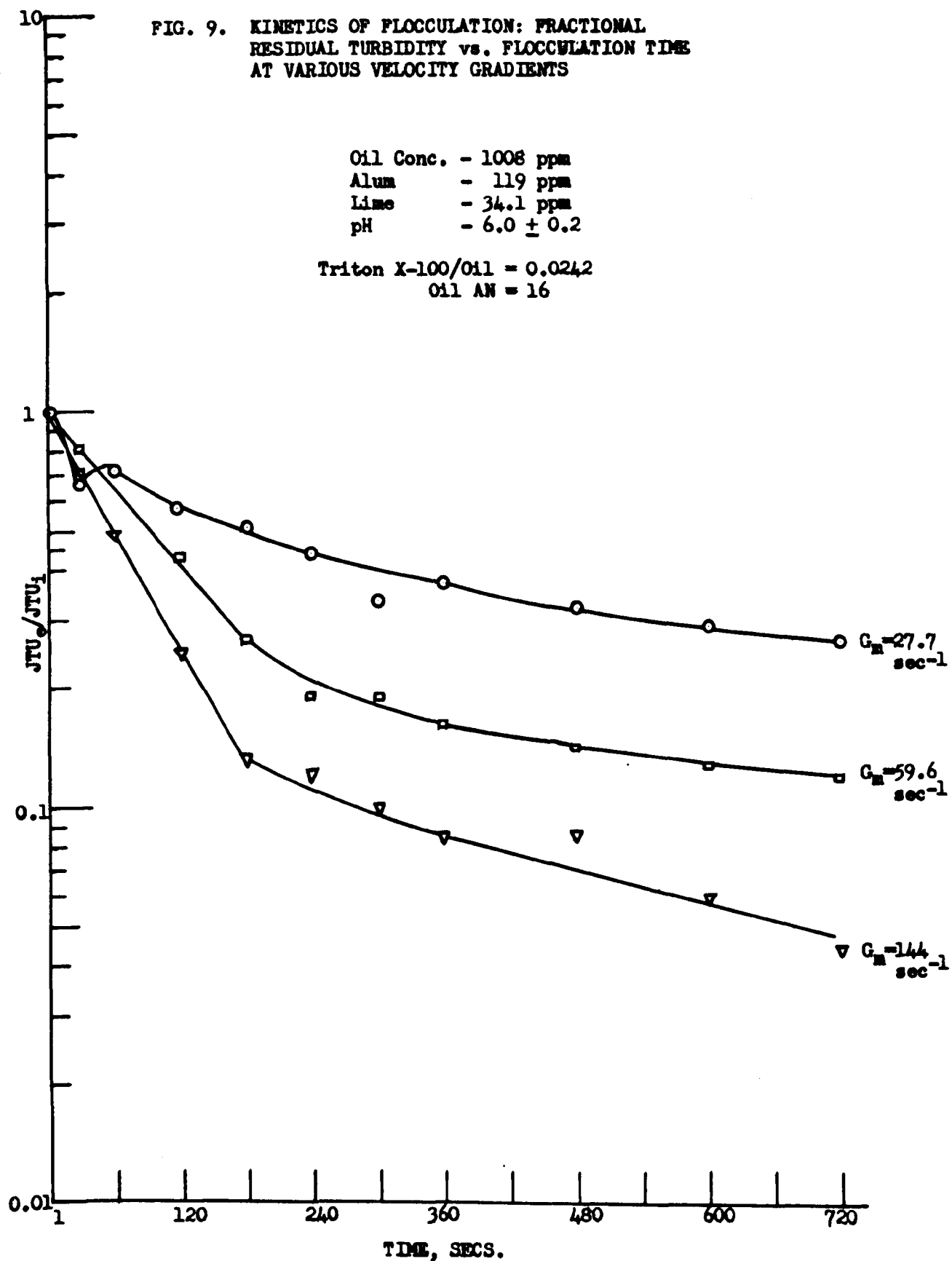
1. Derivation of the relationship between mean velocity gradient and paddle tip speed, and presentation of a working relationship for determination of the mean velocity gradient employed in this work (Appendix C);
2. Presentation of the kinetic relationship for sequential reactors (Appendix D);
3. Demonstration of the feasibility of using the single channel Model B Coulter Counter for flocculation kinetics studies (Appendix E).

## DISCUSSION

The scope of this work included investigation of the stability of rolling oil emulsions at low concentration (generally 1,000 ppm or less) and the rate of flocculation of such rolling oil emulsions.

Several kinds of rolling oils were used for this purpose. "Typical" rolling oil compositions were examined as well as laboratory prepared commercial rolling oil formulations and mill-used and mill-spent emulsions. These different systems were investigated in order to gain an insight into what produces a stable emulsion, what will destabilize an emulsion, and finally how rapidly and by what mechanisms emulsions are flocculated.

FIG. 9. KINETICS OF FLOCCULATION: FRACTIONAL  
RESIDUAL TURBIDITY vs. FLOCCULATION TIME  
AT VARIOUS VELOCITY GRADIENTS



## The Effects of Rolling Oil Composition and Concentration

The commercial rolling oils and the "typical" rolling oils studied are primarily composed of mineral oil, lard oil with associated free fatty acids, and added emulsifiers. Commercial oils may additionally contain bactericide, rust inhibitors, extreme pressure lubricants, etc., but the total content of these components is small and their effect on emulsion stability is probably not of major significance. As a result, the evaluation of chemical composition effects on emulsion stability in this work was concerned primarily with variations in acid number, emulsifier content, and emulsifier type. The oil fraction was 45-50 percent mineral oil and 50-55 percent lard oil in all cases.

In Table VI are compared "typical" rolling oil emulsions of different acid number, both emulsifier-free or having an emulsifier (Triton X-100) to oil ratio of 0.0242. It is significant that at AN16 a maximum in zeta potential and near minimum in turbidity were observed in the emulsifier-free system. In the emulsifier containing system, acid number had little effect on turbidity. The lower turbidity values for the emulsified oils is consistent with observations made relative to the ultraviolet absorption characteristics of the emulsifier (Cf. Figure 4). That the zeta potential is attenuated by added emulsifier can be explained by the fact that the Triton X-100 nonionic surfactant probably shifts the plane of shear further from the oil droplet surface. As a corollary, the emulsifier should also serve to diminish the ease of charge neutralization.

In Figure 3 it is shown that for the AN11 and AN16 cases studied there is a significant change in zeta potential over an emulsifier to oil ratio range of 0.1 to 0.4. Such an observation would be consistent with monolayer adsorption of the emulsifier on the oil droplets. Monolayer adsorption is also indicated by the fact that the particle size distribution is minimal at an emulsifier to oil ratio of 0.121 compared to either smaller or significantly higher ratios. The creaming of the emulsions was also a minimum at the 0.121 ratio. Thus, it would seem that typical emulsifier contents are well less than that necessary for monolayer adsorption but sufficient to exert an influence on emulsion droplet stability as indicated by both zeta potential and particle size distribution measurements.

The zeta potentials of emulsifier containing emulsions in Table VI are lower than those reported in Figure 3 for equivalent emulsifier to oil ratios. The only difference in the two cases appears to be in the method of preparation. The emulsifier was added with gentle stirring to the emulsions given in Figure 3 whereas in Table VI the emulsifier was added to the oil before emulsification.

There may also exist differences in emulsion stability as a function of emulsifier type. For example, it was mentioned in the experimental section that alum addition to an "A" emulsion could lead to positive

relative streaming current values whereas such an effect was not observed for a "B" emulsion. This might be explained by the fact that the "B" oil contains some anionic emulsifier whereas the several rolling oils familiar to us (about 3-4) contain only nonionic emulsifiers.

The concentration and nature of the particular aluminum species present in the continuous phase will determine the extent of charge reduction or reversal observed. These species may well have positive charges below pH 5.5-6.0. On the other hand, the free fatty acid molecules exposed at the surface of the oil droplet can ionize to but a single negatively charge state. Thus, charge reversal in nonionically emulsified oils may occur by incomplete polyvalent ion salt formation. Further, the aluminum-fatty acid soaps are quite stable and only small doses of alum should be required for this reaction to go to completion. This conclusion is supported by the fact that only about 5 ppm alum was found to be required to bring about the complete charge neutralization of a 400 ppm non-ionically emulsified oil whereas an excess of alum produced emulsion droplets of a positive zeta potential.

An anionically emulsified system may readily present another case, however. Firstly, one would not expect an anionic emulsifier to be replaced by the complex aluminum species (any more than would be a nonionic emulsifier) because the van der Waals forces holding such a molecule to the oil droplet surface would be fairly strong. Although the complex positive aluminum species can react with exposed free fatty acid, no such "neutralization" of the anionic emulsifier will occur because most of these materials are soluble salts of sulfonic acids of large pK values. Thus, for anionically emulsified systems the zeta potential may diminish to a certain minimum value but remain negative.

These assumptions concur with the fact that neither a brand "B" nor a "typical" anionically emulsified oil would yield positive zeta potentials even with excessive alum additions. It is worth noting, that in terms of particle size distribution no sensible distinction was evident between the typical anionically emulsified and non-ionically emulsified systems. Thus, while the emulsification properties of these two types of emulsifier are similar, their response towards alum is distinctly different<sup>6</sup>.

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<sup>6</sup>Further discussion on the effect of emulsifier type on jar testing is presented later.

The effect of acid number on jar test results appears to be significant. This is amply illustrated in Tables VII, VIII, and IX. The comparative jar tests (Tables VII, VIII) clearly show a relationship between the acid number of an emulsifier-free oil and the relative degree of post-flocculation turbidity. The reasonably good comparison between the measured post-flocculation turbidity and the calculated values is surprising.

Recalling that this relationship was:

$$JTU_f^* = 1.1 \times 10^{-3} (JTU_i)(AN)^{1.40}$$

it is evident that acid number plays a significant role in flocculation. The detrimental effect of increasing acid number of emulsifier-free emulsions on their degree of flocculation is postulated as being due primarily to the higher positive charge the emulsion particle can assume upon reaction with alum (alum was added before lime in these tests).

The effects of acid number on the post-flocculation turbidity of emulsifier containing systems was found to be significant only at high acid number values. In Table XII, for example, the post-flocculation turbidities of nonionically emulsified "typical" rolling oils is seen to vary only slightly for oils of AN's 6-16. At AN26, however, the post-flocculation turbidities of the identically treated systems was severalfold higher. Thus at least to AN16 the acid number effect appears overshadowed by the effect of the emulsifier. Whether the effect at AN26 is due to the acid number or is a consequence of an anomalously stable emulsion is not known.

The effects of concentration on post-flocculation turbidity was found to be somewhat linear for emulsifier-free systems. For example, the post-flocculation turbidities of emulsifier-free AN11 emulsions at various concentrations (Table VIII) were found to be such that

$$\ln JTU_f = 5/4 \ln C_i \text{ (approximately)}$$

Unfortunately time did not permit a similar study on emulsifier containing emulsions at optimum dosages and pH.

Additionally the effects of lard oil, mineral oil and emulsifier contents could not be studied. Such studies at the pilot plant level may assist in optimizing emulsion breaking efficiency with rolling performance. It is known, for example, that for a given rolling operation emulsions can be too "tight" as well as too "loose" for good performance.



## The Effects of pH and Clay

The extensive jar testing program on 1,060 ppm emulsifier containing "typical" rolling oil was undertaken because the pH effect was essentially unknown. The data given in Figures 7 and 8 would indicate that the optimum pH of flocculation is somewhat lower than in usual commercial practice. The reason for this anomalous behavior is unknown.

These jar test results (Figures 6-8 and Table X) provide an insight into the mechanism of flocculation of rolling oils by alum floc, however.

It is significant, for example, that the maximum in alum floc turbidity and the minimum in broken oil turbidity occur in the same pH range. This is consistent with a flocculation model requiring the coagulated (or destabilized) oil droplets to adsorb on or be occluded in the alum floc.

The maximum clarification of both the nonionically and anionically emulsified systems by alum and lime occurs over the pH range where the microscopically observable system is approaching zero charge although still positive<sup>7</sup>. The same analogy holds true for the alum and lime plus clay situation. The only significant distinction in the latter case is that the alum-lime-clay floc is less positive than the alum-lime floc. This would not be unexpected, however, as any clay adsorbed on the alum floc would tend to attenuate the zeta potential.

The anionically emulsified oil appears to be more efficiently broken than does the nonionically emulsified oil, however, in spite of their essentially identical histories, concentrations, particle size distributions, and as-prepared turbidities (300 vs. 295, resp.).

In the lower pH ranges (less than 4.5) where the zeta potential reflects the charge on the emulsion droplets, the zeta potentials are negative in the anionically emulsified system but positive in the nonionically emulsified system. These differences are believed to be related to both the nature of the various aluminum species present and their subsequent reaction on the emulsion droplets. The nature of the aluminum species varies as the pH (see below).

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<sup>7</sup>The zeta potential measurements for the oil + alum + lime and oil + alum + lime + clay "systems" probably reflects more the state of the hydrous aluminum oxide floc and associated oil and clay than any remaining free oil or clay at pH values above about 4.6 to 4.8. This is due to the fact that unflocced oil and clay is of near micron to submicron size whereas the alum floc is considerably larger and easier to detect.

In the absence of alum the pH appears to have less of an effect on emulsion stability than specific conductivity at moderate pH values. This is demonstrated by reference to Figure 1 and Table IV in which the zeta potential of a mill spent "B" emulsion was examined in terms of both pH (over the range 5.8 to 7.7) and specific conductivity.

Considering that only very small amounts of alum are necessary to neutralize the zeta potential of an "A" emulsion whereas dosages of 125 ppm were required for flocculation would indicate a dominate role for the alum floc during flocculation. This effect also serves to explain why an optimum alum dose of 100 ppm was required to floc a 530 ppm "typical" emulsions whereas the same emulsion at 1,060 ppm required only 125 ppm alum to achieve the same post-flocculation turbidity. These differences are also believed to be related to both the nature of the various aluminum species present and their subsequent reaction with the emulsion droplets containing the different emulsifiers.

#### Proposed Mechanism of Flocculation

The nature of the aluminum species in solution varies with pH. For simple aluminum salts (e.g.,  $\text{Al}(\text{NO}_3)_3$  or  $\text{AlCl}_3$ ) species such as  $\text{Al}(\text{H}_2\text{O})_6^{+3}$  will exist in strongly acid media whereas from about pH 4 to pH 7 species such as  $\text{Al}(\text{OH})_2^+$  will predominate(18). At higher pH values of 8 to 9, insoluble  $\text{Al}(\text{OH})_3$  will form. In between the extremes of pH 4 and pH 8-9, solid phase positively charged floc will exist to a limited degree. In commercial practice alum is used for waste treatment. Since the sulfate ion of alum is capable of coordination within the coordination sphere, the pH values at which soluble positively charged hydroxo species, positive floc, and neutral floc predominate will be shifted to lower pH values such as observed in this work.

The hydroxo complexes are apparently the most effective flocculants. Given sufficient time these species undergo hydrolysis to insoluble aluminates which settle out. For practical reaction times, however, the pH must be maintained such that insoluble floc (containing the broken emulsion) will form rapidly enough to permit of reasonable oil removal rates. The formation rates of these insoluble species are finite at normal operating pH values. Thus, the soluble species initially formed will increase in hydroxylation until intermediate positively charged pinpoint floc is generated. The total surface area at this small floc diameter is probably very large and highly sorptive. As precipitation continues, the floc becomes larger and the unit area charge diminishes so that in the end a visible "neutral" floc is finally achieved.

In the early to intermediate phases of alum-lime emulsion breaking (at optimum pH) there will be two species to consider; a positively charged insoluble alum floc and oil droplets that may be positive, negative, or neutral. If the emulsion particles are positive as we postulate for those nonionically emulsified, any long range coulombic forces will be repulsive. If the emulsion particles are negative, as we believe they will be for anionically emulsified systems, a net attraction will result.

The net result may be attraction or repulsion depending on the magnitude of the residual charge on the oil droplets.

Very short range van der Waals attractive forces will exist between the hydroxo complexes of aluminum on the emulsion and on the alum floc particles independent of coulombic charge effects<sup>8</sup>. Only at very close approaches will positive emulsion particles be attracted to the positive alum floc, therefore, whereas the attraction of positive floc for negative emulsion particles will prevail at all distances.

If these postulates are correct an anionically emulsified oil should break more effectively than a nonionically emulsified one under certain conditions. For example, brand "B" rolling oil contains both anionic and nonionic emulsifiers whereas "D" contains only nonionic emulsifiers. That "B" emulsion should break more easily than "D" was confirmed in the comparative jar testing studies (Table V).

The increased mean velocity gradient necessary to break the "D" emulsion might be explained as being the result of charge repulsion, viz., a higher velocity gradient was necessary to overcome the long range potential energy barrier to van der Waals adsorption of the positively charged oil droplets on the positive alum floc. Such a potential barrier might also explain the greater induction periods to visible floc.

"Redispersion" of the "B" emulsion at the higher mean velocity gradients has as yet no satisfactory explanation. It is possible that this may result from the anionic emulsifier adsorbing sufficiently strongly on the alum pinpoint floc that the floc cannot agglomerate due to anionic repulsion. This explanation seems tenuous without direct supporting evidence, however.

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<sup>8</sup>Coulombic forces diminish as the square of the distance of charge separation. Van der Waals forces will vary at about the fourth power of the separation distance of dipoles.

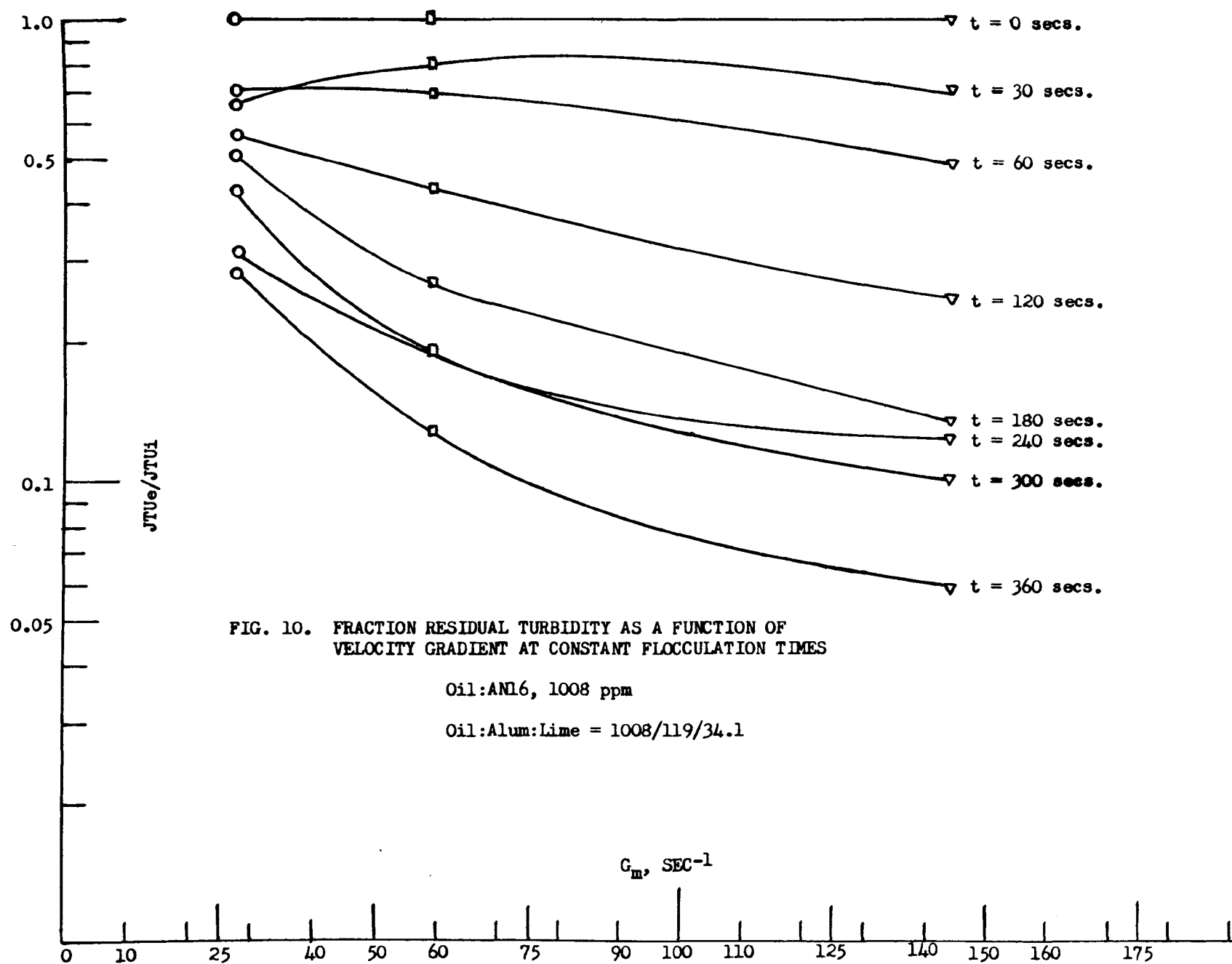
In considering the effect of pH on the aluminum species present and in turn the effect of these species on emulsion destabilization and flocculation, it is also necessary to consider the fact that the pH may not be constant during the process. At equilibrium a given pH (with experimental error) will result regardless of whether alum is added first, lime is added first, or both alum and lime are added simultaneously. However, if alum is added first, positive floc will form initially and proceed toward insoluble neutral floc. If alum and lime are added simultaneously the same process should occur but less time would be available for reaction of soluble positive aluminum species with the oil droplets. This is probably why the nonionically emulsified system was generally most efficiently broken when treated with alum and lime simultaneously whereas process efficiency in the anionically emulsified case showed little preference to whether alum was added initially or added simultaneously with lime (cf. Table XI). When lime is added initially followed by alum at the same dosages, however, process efficiency is quite poor for both emulsifier types. This is probably due to the fact that negative species such as  $\text{Al}(\text{OH})_4^-$  would be formed initially and proceed toward the insoluble alum floc state. Thus, the unneutralized negatively charged emulsion particles would be repelled by the negatively charged aluminum containing species in this latter case and whatever clarification is achieved might be due primarily to entrapment of the emulsion particles by the growing floc.

### Kinetics

Kinetic factors include the rate at which the coagulated emulsion particles are driven over the potential energy barrier to flocculation. For this reason the effect of velocity gradient was examined. In Table XII the final results after flocculation under various velocity gradients were given. More importantly, however, are the results of the kinetic runs given in Figures 9 and 10<sup>9</sup>.

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<sup>9</sup>For simplicity it was assumed in the kinetics portion of this work that  $\ln(JTU_e/JTU_i) = 1.18 \ln N/N_0$ . This assumption appears to be valid on the basis of the discussions presented in Appendices C and E.



In applying the flocculation kinetics relationships to these data it should be noted that the linearity in the plots of  $\ln(JTU_e/JTU_i)$  versus time in Figure 9 would tend to support the hypothesis of constant D during coagulation, at least from  $t = 60$  to  $t = 180$  sec for the  $G_m = 144 \text{ sec}^{-1}$  and  $59.6 \text{ sec}^{-1}$  cases. For the  $G_m = 27.7 \text{ sec}^{-1}$  case this does not appear valid. However, if one plots  $\ln(JTU_e/JTU_i)$  versus  $G_m$  at constant  $t$ , (Figure 10) it is found that one can expect true coagulation kinetics in the  $G_m = 27.7 \text{ sec}^{-1}$  case only at about  $t = 120$  secs.

The slope of the  $27.7 \text{ sec}^{-1}$  data at  $t = 120$  sec and the slopes of the  $59.6$  and  $144 \text{ sec}^{-1}$  cases over  $t = 60$  to  $t = 180$  secs, yield an average value of  $-1.09 \pm 0.05 \times 10^{-4}$  for  $-(kDN_0/1.18)$ . Thus the composite rate constant ( $K^*$ ) value is:

$$K^* = kD = 1.3 \times 10^{-7}(\text{mg/l})^{-1}$$

It is significant that the efficiency of coagulation with time diminished markedly at  $t = 180$  secs. Thus, it may be useful in pilot plant studies to investigate this efficiency-time factor as it influences engineering design/cost values. (It must be remembered, however, that the time required for a given degree of turbidity removal will be longer in a continuous flow consecutive reactor system per reactor than in a batch reactor of the same design and volume.)

Another unanticipated phenomenon observed is that in the  $G_m = 27.7 \text{ sec}^{-1}$  case the turbidity initially fell and then rose again. Although this could be due to experimental error, it is believed that this occurred as a result of (a) delayed growth of alum floc, and (b) a slow rate of interaction between emulsion and alum floc. The combination of these factors could readily lead to an intermediate state in which the total number of all particles present would increase somewhat leading to a short term increase in turbidity.

It is quite apparent that the equilibrium and time rate efficiency of flocculation are continuously increasing to the upper limit of mean velocity gradient tested ( $144 \text{ sec}^{-1}$ ). What the upper limit may be before "redispersion" occurs is not known. However, the quick tests via the Waring Blendor indicated that very high initial velocity gradients are beneficial if not maintained for long periods of time.

The "ideal" flocculation process would probably be such as to provide for a continuous velocity gradient. For example, in a continuous flow large volume system the velocity gradient near the inlet can be quite high, the values at all points in the bulk should be as large as possible without leading to excessive floc break-up, and the velocity gradient at the outlet should be sufficiently low so as to provide for the growth of the large and fragile floc particles.

The ideal system should also minimize the mixing of fully flocculated with partially flocculated material if possible. This contention is based on the fact that the optimum velocity gradient will, in general, diminish with increasing floc size.

SECTION V  
FIELD STUDIES

The five-stand tandem cold mill at the Ashland, Kentucky Works of the Armco Steel Corporation is capable of being operated with three individual cooling and lubricating systems. These coolant systems include once through water on the first stand; recirculated soluble oil emulsions on the middle stands; and once through water on the last stand. Therefore, three waste streams can be produced from this modern mill.

On the first stand, large volumes of water (1,500 gpm and up) are applied on a once through basis for roll cooling and to remove the coating oils which are applied at the exit end of the picklers. These coating oils are typically high viscosity mixtures of mineral oil and fat for rust and scratch protection during storage prior to cold rolling. The removal of these oils is desirable to minimize contamination of the coolant systems on the remaining stands. The resulting waste is a large volume of water contaminated with both free and emulsified oils.

On the middle stands of the cold mill, a recirculated coolant system is provided. This coolant is typically a tight oil-in-water (o/w) emulsion. Although this system does not result in a continuous waste, the coolant must be dumped due to contamination from a variety of sources. This batch dumping may involve as much as 40,000 gallons at a time of solution containing from 0.5 to 5.0 percent emulsified oil.

On the final stand of the mill, large volumes of water (1,500 gpm and up) are applied on a once through basis for roll cooling and removal of the last traces of emulsion carried from the recirculation system on the strip. The final rinsing step is often necessary to produce a high quality, clean steel strip the customer demands. The resulting waste is a large volume of water contaminated with a tight o/w emulsion.

A detailed evaluation of the water requirements on the cold mill by Armco research scientists and cold mill operating personnel was conducted. As a result, it was concluded that small concentrations of soluble oil and suspended solids in the water used to remove pickler coating oil at No. 1 stand would not harm the cold mill operation. It was, therefore, decided that the oily rinse water from No. 5 stand would be reused as rinse water on No. 1 stand prior to treatment. This approach reduced the size of the oily waste water treatment facility by one-third and the hydraulic loading by one-half. Design and construction of the facility were undertaken with this concept in mind.

From the standpoint of capital and operating cost, it was desirable to make further reductions in oily rinse water volumes. It was the



intention to include as part of the grant study an evaluation of two alternate schemes for reduction of waste volumes. These schemes included the use of recirculated emulsion on all five stands and the use of rinse water on No. 5 stand only. Prior to the start up of the treatment facility, the operating practice for the cold mill was changed to a completely recirculated coolant system on all five stands. Not only was this scheme found to be acceptable in terms of product quality but this method of operating was preferred by operating personnel. It should be noted that the ability to operate the cold mill entirely on a recirculated coolant system is a function of the final destination of the cold rolled product. This mill was able to do so because all cold rolled material was followed by subsequent pickling or annealing processes which removed any residual oils. It is probable that the sale of a cold rolled product directly from the cold mill would require a rinse water system to provide a cleaner strip. Thus, the operation of a cold mill and the actual and potential markets it serves are an important factor in determining the waste products. Therefore, not all cold mills would be provided a choice of coolant systems to be used.

The fact remains, however, that activities associated with this grant study were directly responsible for a sizable waste reduction. This change in operating practice substantially altered the nature of the wastes to be treated. Instead of the anticipated 1,500 gpm rinse water flow with periodic batch dumps of concentrated coolant, the waste consisted of concentrated coolant only. This waste was generated from a variety of miscellaneous sources such as spills, strip overflow, hydraulic leakage, and occasional batch dumps of contaminated coolant systems. Oil concentrations of this waste varied considerably; however, concentrations were sufficiently high to preclude the use of the coagulation process for treatment. Quantities were of small enough volume to permit the batch-wise treatment of these concentrated wastes with the use of a cationic polyelectrolyte emulsion breaker. A program was developed for full-scale evaluation of operating parameters for the treatment of concentrated coolant on a batch-wise basis. Subsequently, in order to evaluate the alum coagulation process for rinse waters on a continuous basis, arrangements were made with operating personnel to convert to a rinse water system similar to that for which the treatment facility was designed. A program for optimizing and demonstrating the alum coagulation of rinse waters on a continuous basis was developed and executed. Although the treatment plant is capable of treating either concentrated oily wastes on a batch-wise basis or oily rinse water on a continuous basis, it is important to note that preferred operation of the tandem cold mill will have a profound influence upon the quantity and character of the resultant waste and upon the costs involved.

#### BATCH TREATMENT OF CONCENTRATED COOLANT

Initial operation of the treatment facility was directed toward the

treatment of concentrated roll coolant generated by the tandem cold mill recirculated coolant system. The sources of this waste included spills, strip overflow, hydraulic leakage, periodic dumping of contaminated coolant systems, flushing and cleaning water, etc.

The characteristics of this incoming waste received over the period of testing are shown in Table XIII. It is apparent that large variations exist in the waste characteristics.

TABLE XIII

SUMMARY OF INFLUENT ANALYTICAL DATA FOR CONCENTRATED COOLANT

<u>Analysis</u>	<u>Number Samples</u>	<u>Average (ppm)</u>	<u>Range (ppm)</u>
Suspended Solids	21	1,025	156 - 3,010
COD	19	31,600	3,200 - 46,800
Total Oil	22	14,600	2,088 - 46,742
Emulsified Oil	23	3,494	53 - 10,078

Jar Testing Program

An extensive jar testing program was conducted to establish optimum chemical treatment and to evaluate various organic emulsion breaking chemicals. This program included the evaluation of 27 different emulsion breakers at various concentrations and temperatures. Most of the chemicals tested were not effective on the waste, which initially consisted primarily of Brand "A" rolling oil. A few were effective only at excessive concentrations. Two cationic polymers were found to be effective at 1,000 ppm or less. One of these products was in the developmental stage and not commercially available. The other (EB1) was therefore selected as the emulsion breaker to be used for treatment.

During jar testing it was found that the effective emulsion breakers were quite sensitive to overdosing and temperature. EB1 appears to have a limited range of concentrations within which it is capable of breaking the emulsion. At concentrations of 50 percent of the optimum or 125 to 150 percent of the optimum, this emulsion breaker was considered completely ineffective. These observations are consistent with the fundamental studies which indicated that charge reversal can occur in coagulation processes. In the case of cationic polyelectrolytes, it is conceivable that this may lead to emulsion restabilization. This conclusion was further supported by the fact that overdosing with emulsion breaker could be compensated for by subsequent dilution with more waste.

The optimum temperature for EB1 was found to be between 100 and 150 F.

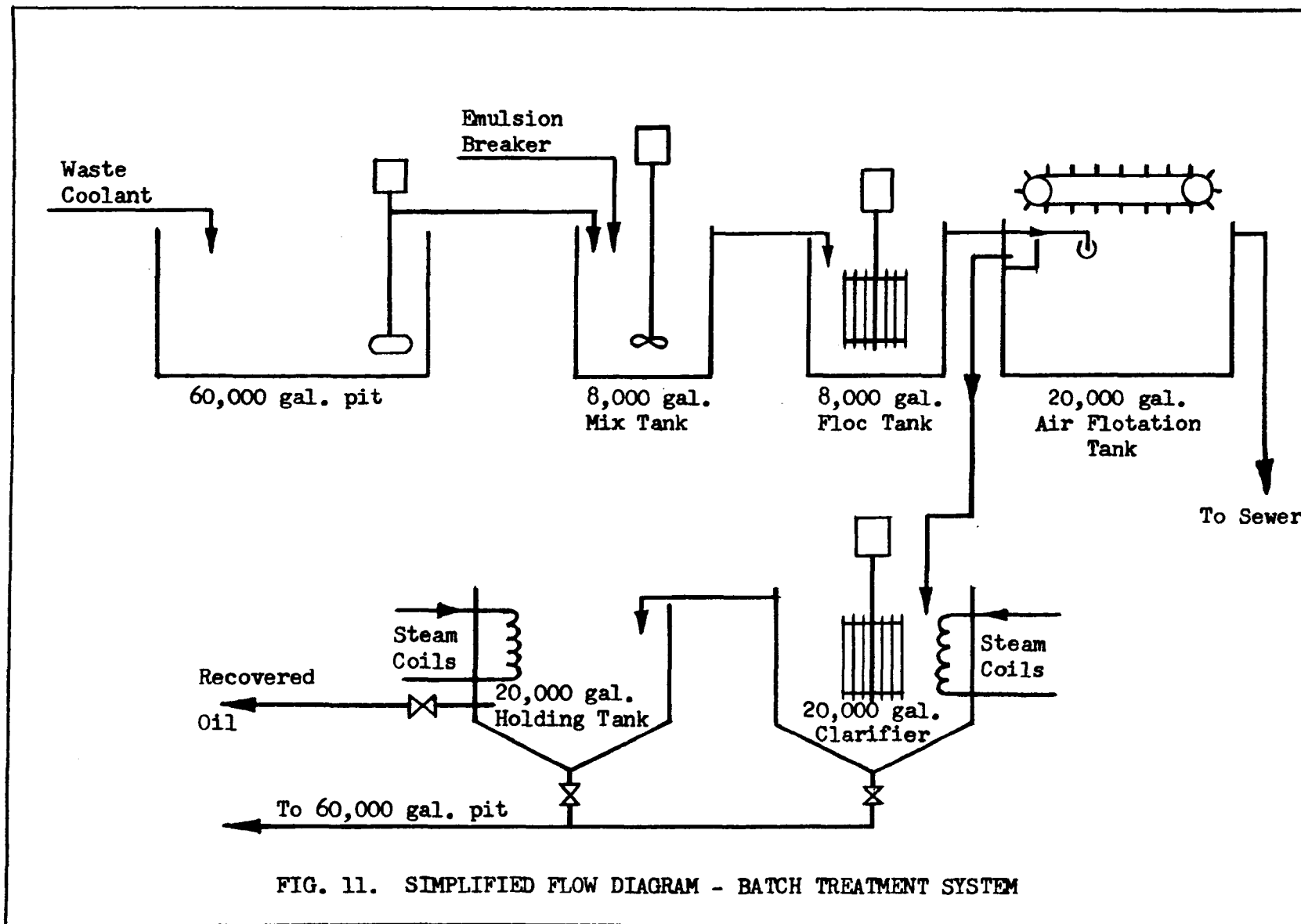
During the program for batch treatment evaluation, a change in rolling oils from "A" to "B" was made. Due to the specificity of emulsion breakers to oil types, several hundred additional jar tests were performed. Three emulsion breakers, including EBl, were found to be successful at similar concentrations for "B". To avoid introducing a new process variable into the evaluation program, treatment was continued with EBl.

#### Operations Testing Program

With the results of the preliminary jar testing, a program was established for full-scale evaluation of the treatment of concentrated coolant on a batch-wise basis. The following basic procedure for treating the coolant was established. Wastes were collected in the 60,000 gallon holding pit as they were received from the cold mill sources and heated with steam to a predetermined temperature (Figure 11). From the holding pit, the waste was pumped directly to the second of two rapid mix tanks where the emulsion breaker was added. The treated waste then flowed by gravity into one of two parallel flocculation tanks, into the corresponding air flotation tank, and into the receiving stream. Because of the small volumes, only one of the two parallel flocculation-flotation tank units was necessary at any time. The separated oil was skimmed from the flotation tank surface and pumped to the oil recovery area. This procedure allowed for treatment of an intermittent stream or treatment of a specified volume or "batch" of 60,000 gallons. The treated waste was permitted to settle until another quantity of waste was accumulated. Then another 60,000 gallons were treated, which purged the system of the previously treated waste, and again permitted to settle. The end result was a series of 60,000 gallon batch treatments.

A series of tests was established to evaluate three variables considered to be of importance. These variables included chemical concentration, temperature, and flow rate. Because of the sensitivity of chemical concentration to oil content as indicated by jar tests and because of the variability of the incoming waste, it was essential to vary chemical dosage with regard to the influences of the incoming waste. Thus, jar tests were performed for each batch to be treated, and the optimum chemical concentration as indicated by the jar test was used as a base value. To relate the plant-scale performance to jar test results, the three levels of chemical concentration evaluated were the optimum dose as indicated by jar test, one-half that optimum dose, and no chemical addition at all. The two temperature levels evaluated were 100 and 150 F. Flow rates evaluated were 200 gpm and 350 gpm. Total oil removal was used as the basis for evaluating performance under the various conditions.

A total of 21 tests for which valid analytical data were obtained were conducted. These represented ten combinations of operating conditions. The conditions and the results for these combinations are summarized in



Tables XIV and XV. As the values for total oil removal indicate, there is little difference in deviation of values for each variable over the ranges tested. It is believed that the reason for the lack of a significant difference in removals lies in the inherent batch technique employed. Because of the difference from the basic plant design flow, mixing times were in the range of 25-35 minutes as opposed to approximately five minutes used in jar testing. Furthermore, treated batches were permitted to settle for periods ranging from one to four days. These extended mixing and settling periods were sufficient to dampen any difference in process parameters.

A statistical analysis of the data permits the following observations to be made:

1. The addition of no chemical yields significantly lower oil removal than adding either one-half or the full optimum dose as determined by jar testing.

TABLE XIV  
SUMMARY OF BATCH TREATMENT TEST RESULTS

<u>Combination</u>	<u>Chemical<sup>a</sup> Dose</u>	<u>Temperature (F)</u>	<u>Flow Rate (gpm)</u>	<u>No. Runs</u>	<u>Average Total Oil % Removal</u>	<u>Standard Deviation</u>
A	0	150	200	1	66	-
B	0	150	350	1	49	-
C	$\frac{1}{2}$	150	350	2	80	15.5
D	1	150	350	4	92	9.6
E	$\frac{1}{2}$	100	350	3	95	4.4
F	1	100	350	2	86	13.5
G	$\frac{1}{2}$	100	200	4	95	4.5
H	1	100	200	1	89	-
I	$\frac{1}{2}$	150	200	2	90	10.6
J	1	150	200	1	84	-

<sup>a</sup> 0 = no chemical addition;  $\frac{1}{2}$  =  $\frac{1}{2}$  jar test optimum dose; 1 = jar test optimum dose

TABLE XV

SUMMARY OF BATCH TREATMENT PERFORMANCE FOR VARIABLES EVALUATED

<u>Variable</u>	<u>Number Runs <sup>b</sup></u>	<u>Average Total Oil % Removal</u>	<u>Standard Deviation</u>
Chemical Dose <sup>a</sup>			
0	2	58	12.0
$\frac{1}{2}$	11	91	9.0
1	8	88	8.3
Temperature			
100 F	10	93	9.1
150 F	9	87	9.8
Flow Rate			
200 gpm	8	92	6.5
350 gpm	11	89	9.7

<sup>a</sup> 0 = no chemical addition;  $\frac{1}{2}$  =  $\frac{1}{2}$  jar test optimum dose; 1 = jar test optimum dose

<sup>b</sup> Runs with zero chemical addition not included for averaging purposes for temperature and flow rate

2. There is no significant difference between applying one-half the optimum or the full optimum chemical dose.
3. There is no significant difference between waste temperatures of 100 F and 150 F for total oil removal.
4. There is no significant difference between running a batch at 200 gpm and at 350 gpm for total oil removal.

Based on these observations, it can be concluded that batch treatment can be performed under the most economical of the conditions studied without sacrificing performance as measured by total oil removal. This most economical set of conditions would be one-half the optimum jar test chemical dose, 100 F, and 350 gpm flow rate. The three runs actually performed under these conditions yielded the following average performance data:

1. 95% total oil removal
2. 92% COD removal
3. 95% emulsified oil removal
4. 74% suspended solids removal
5. 18% bottom water and solids in the scum
6. 1.8% solids in the scum

7. 1850 gallons of scum per 60,000 gallon run

No other set of conditions yielded appreciably better performance.

The chemical requirement, as determined by jar test for each run, was found to be highly dependent upon the oil being treated. For "B" the average optimum chemical dosage was 2.06 gallons/1,000 gallons of waste. For "A" only 0.60 gallons/1,000 gallons was required.

At \$3.74 per gallon for EBl, the cost to treat "A" would be \$2.24/1,000 gallons as compared to \$7.70/1,000 gallons for "B". Findings of this program indicate these cost figures may be halved by using one-half the jar test optimum without decreasing performance. It is conceivable that further reductions in chemical requirements are possible. The smaller chemical requirements indicate that the full-scale plant is somewhat more efficient than standard bench-scale jar testing techniques. (Appendix A)

If it is assumed that a 60,000 gallon batch of "B" waste is treated under the most economical situation, as mentioned above, and will yield 1,850 gallons of 82 percent oil, then a chemical cost of \$231 is required to recover 1,520 gallons of oil. The chemical cost is therefore 15.2¢/gallon of oil recovered for a product worth approximately 8.5¢/gallon as fuel oil. The same analysis for "A" will result in a chemical cost of 4.8¢/gallon of oil recovered. It should be emphasized that these figures are for chemical cost only and do not take into account the possibility of skimming tramp oils directly from the holding pit to the oil recovery area nor the non-chemical cost of processing the scum to an oil quality worthy of the 8.5¢/gallon credit. The designation of the recovered oil as fuel oil is not unrealistic in light of the fact that centrifugal analysis of Oil Holding Tank samples consistently showed bottom water and solids of less than one percent with virtually no solids. This improvement of oil quality over that of the collected scum was achieved by heating to 175 F and periodic mixing in the clarifier (cf Figure 11).

Over the course of the testing period, the cold mill averaged 116,000 gallons of waste per week for a 12-turn average week. However, volumes were substantially reduced toward the end of the period so that a volume of approximately 100,000 gallons may be anticipated for comparison of economics. This reduction was brought about as a direct result of this grant study. Quantities of waste were monitored and related to cold mill operating personnel. Alarmed at the quantity of coolant being lost in production, the operating personnel tightened their maintenance of the cold mill sources and effected the waste reduction.

On the basis of receiving 100,000 gallons per week, the chemical cost of treating the waste (assuming "B") would be \$385 per week or \$55/day on a proportionate basis. Credit received from the recovered oil would be \$215/week on the basis previously established or \$31/day. Therefore, the net chemical-cost vs. oil-credit result would be \$24/day. These

figures will be used for comparison with the cost of treating rinse water on an alum coagulation basis. It is obvious that a great reduction in the chemical cost of treating the waste, and therefore a net positive credit toward the operation, can be achieved if Brand "A" rolling oil is chosen over Brand "B".

In summarizing the results of the studies of batch treatment of concentrated coolant, it is apparent that the treatment plant is somewhat less sensitive to operating variables than would be indicated at bench scale. What were believed to be extremes in operating conditions actually revealed no significant difference in plant performance.

This discrepancy between bench and full-scale requirements is believed to be a result of the extended periods of mixing and settling provided by the batch treatment method as compared to the relatively short periods provided in jar testing procedures. It is inconceivable that operating conditions can be varied indefinitely without altering plant performance, as was indicated by reducing chemical addition to zero, but the results of this study do indicate that the plant as operated on a batch treatment basis is capable of performing satisfactorily over a wide range of operating conditions even for the relatively sensitive treatment technique employing an emulsion breaker.

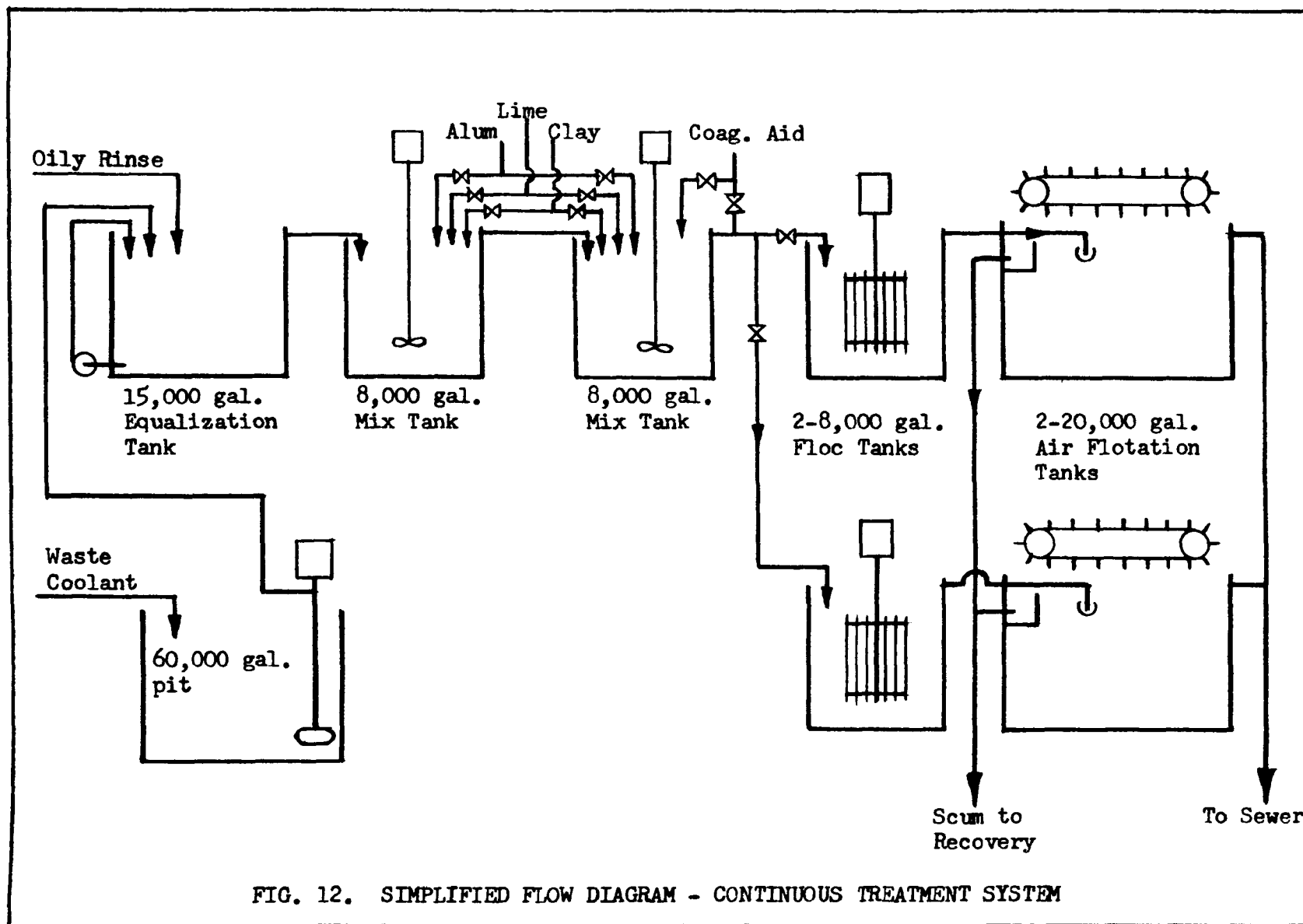
#### CONTINUOUS TREATMENT OF RINSE WATERS

In order to evaluate and optimize the alum coagulation process for the treatment of rinse water, the tandem cold mill was converted to a rinse water system on No. 1 stand. A recirculated coolant system was maintained on the other four stands. The rolling oil utilized during this period was Brand "C".

Prior to beginning an actual program for evaluating various parameters, a period of several weeks was utilized for preliminary bench studies and resolving various minor mechanical problems. A quantity of concentrated emulsion (from strip overflow, spills, floor drainage, etc.) continued to be received despite the conversion to rinse water on stand No. 1. The original intent was to separate the concentrated emulsions from the rinse water, if possible, and treat the emulsions on a batch basis during periods when the rinse water system was not operating. However, it soon became apparent that the quantities of concentrated emulsions were too great and associated storage capacity was too small to permit this total segregation. Hence, a small quantity of concentrated emulsion was metered into the rinse water stream and the resultant waste treated. Figure 12 shows a simplified flow diagram for this system.

Following the establishment of an initial set of operating conditions and the resultant production of a satisfactory effluent, a program was developed for determining the effects of operating parameters on the treatment plant's coagulation process. This program encompassed chemical dosage rates, chemical addition points, rapid mix detention





time, flocculator detention time, flocculator tip speed, air flotation detention time, and air flotation recycle rate. The order of evaluation was approximately as given, although dependent parameters such as air flotation and flocculation detention time necessarily were related due to the fact that the flocculation chamber and air flotation tank are physically one unit, separated only by a baffle under which the waste stream must pass. (Appendix B) The above parameters were varied over the maximum practical range. As the optimum condition for each parameter was established, the next parameter was evaluated. Operating cost, effluent water quality, and oily scum quality were the basis for evaluation.

The analytical work undertaken included: (a) pH, temperature, COD, total oil, soluble oil, and suspended solids for influent samples; (b) pH, temperature, COD, total oil, suspended solids, and turbidity for effluent samples; and (c) bottom water and solids for separated oil samples.

### Preliminary Bench Studies

Bench studies were performed to derive a first approximation of optimum chemical requirements for alum coagulation of the rinse water and to evaluate emulsion breaking chemicals capable of being used for treatment of Brand "C" rolling oil wastes.

A first approximation of optimum operating conditions was derived from an extensive series of jar tests. For a waste stream consisting of about one part of concentrated emulsion per 12 parts of rinse water (average total oil 895 ppm), the combination of 195 ppm alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ), 43 ppm lime, 32 ppm clay, and 1 ppm anionic coagulant aid was found to produce a satisfactory effluent. Jar tests on the waste also indicated that about 100 ppm alum may be added to the waste stream without requiring lime due to sufficient alkalinity in the water to maintain a pH of 6.0 or higher. At higher alum dosages, approximately one part lime for each additional two parts of alum is required. Although this information was used for a first approximation of the lime requirement, the actual pH in the rapid mix tank was used to govern the lime requirement on an operating basis.

Because of the specificity of emulsion breakers to type of rolling oil, an evaluation of various emulsion breakers was made for the Brand "C" oils for purposes of treating batches of concentrated emulsion or as a possible alum substitute in the coagulation process. EBl which was previously used for breaking concentrated emulsions of "A" and "B" was not well-suited for the "C" oil. A total of 54 polymers were evaluated as possible replacements for EBl. Of these, eight appeared to work at lower doses. Further evaluation resulted in the following findings:

1. One emulsion breaker was rejected because it produced a very sticky, gummy sludge.

2. Four other emulsion breakers were rejected because they were not effective at low oil concentrations.
3. The three remaining polymers were effective emulsion breakers at any oil concentration down to 0.5 percent and were still effective somewhat below 0.5 percent. One of these three was considerably more economical and was chosen for use for treating "C" on a batch basis if and when required to do so.

A series of jar tests was carried out to determine whether cationic polyelectrolytes could economically be substituted for part or all of the alum. This change would reduce the ash content of the recovered oil; it might also eliminate the need for lime in the process, which would eliminate the lime feeding problems (see below) as well as reduce the hardness and dissolved solids in the plant effluent. It was found that at least half the alum could be replaced with polymer, but at a cost of six to seven times the cost of the alum replaced. The substitution could not, then, be justified.

### Operational Problems

Definitive data on the effects of varying operating conditions were often difficult to obtain due to the influence of uncontrollable factors which in many cases were more influential than the process variations themselves.

The inability to maintain complete control over these extrinsic factors was a major concern during the optimization phase. A discussion of these factors appears to be in order in view of the fact that they represent a major concern in the design and operation of a similar treatment facility.

First, problems with operation of the cold mill itself were exhibited. Wastes from the recirculated coolant system and from the rinse water on stand No. 1 ideally are collected separately and pumped in separate lines to the treatment plant where the coolant is metered at a constant rate into the rinse water for treatment. Segregation of these wastes was a problem, however. Pumps at the mill periodically were down for maintenance. As a result, the combined collection of coolant and rinse water was necessary in order to avoid inundating the cold mill oil cellar. Thus, concentrated coolant sometimes was received through the rinse water line and vice versa. This action had pronounced effects on the oil concentration and treatability of the wastes.

The capacity of the holding pit for concentrated coolant is limited. Ordinarily, the rate of metering coolant into the rinse water was sufficient to maintain a satisfactory level in the holding pit. At times, however, the relative volumes of rinse water and coolant became unbalanced which resulted in rapid changes in holding pit levels. In order to prevent inundation of the treatment plant, a level control activated a pump, at a pre-established level, which conveyed the coolant to the process for treatment. This additional volume of coolant

during pit pump-downs increased the oil concentration of the waste to the point where system efficiency was substantially reduced. Periods of low rinse water flows were generally associated with converting to a completely recirculated coolant system on the cold mill as opposed to using rinse water on stand No. 1. This change was usually a result of required maintenance on the rinse water spray system or of cold mill operating schedules.

When operation was normal, the cold mill pumping system was still a source of concern. Pumping of wastes is controlled by sump level controls at the cold mill, so that when a specified level is reached the pumps are activated for a period of sufficient duration to empty the sumps. Observations revealed that this resulted in a cycle of perhaps five minutes of pumping at 1,300 gpm and ten minutes off altogether. Sufficient equalization was not provided to account for the problems encountered. It is believed that equalization capacity should be a prime consideration in future designs due to the unpredictable operation of the cold mill.

Another operational problem was pH control. Difficulties were encountered in attempting to pump lime slurries with positive displacement pumps. After many futile attempts, a centrifugal pumping system for lime was installed. This essentially eliminated the problem. During the period when lime pumping problems were encountered, the slightest malfunction was observed to have pronounced effects on the process. It was determined that when the pH was permitted to fall below 6.0 the alum floc precipitation did not occur. The reliable pumping of lime was found to be the single most important process factor. Future installations should be equipped with continuous pH monitoring of the effluents, and care should be taken in designing pumping facilities for lime slurries.

A good deal of emphasis was placed upon effluent turbidity as a measure of process performance due to its sensitivity and rapid response. This necessitates reliable instrumentation for turbidity. The turbidimeter employed in this installation required frequent cleaning to ensure reliable readings. It is believed that greater flow rates in the turbidimeter sample lines would alleviate the settling of solids and oil which creates plugging of these lines.

Physical destruction of the delicate floc structure was also observed. A primary cause of this problem was the hydraulic shock exerted on the system during a sudden start-up after an extended period when no waste was being received. Even the influence of a rain shower was observed to destroy the "air-floc" structure at the flotation tank surface so that effluent turbidity increased. The problem with sudden start-ups could be alleviated somewhat if adequate equalization or storage capacity was provided. The influence of rain suggests the need for some type of shelter for the flotation units.

When all the above factors could be controlled, the process operated in a highly desirable fashion. However, these difficulties recurred with such regularity and frequency as to represent significant problems. It is felt that these factors must be weighed with even more concern than the process parameters themselves when considering future treatment plant designs.

#### Chemical Dosage Rates

A first approximation of chemical dosage rates was derived from an extensive series of jar tests. For a waste stream consisting of one part of concentrated coolant per 12 parts of rinse water, the combination of 195 ppm alum, 43 ppm lime, 32 ppm clay, and 1 ppm coagulant aid was found to be a conservative chemical program to produce a satisfactory effluent. Characteristics of the incoming waste are given in Table XVI.

TABLE XVI

#### INFLUENT ANALYTICAL DATA - RINSE WATER <sup>a</sup>

<u>Analysis</u>	<u>No. Samples</u>	<u>Average</u>	<u>Range</u>
Suspended Solids (ppm)	22	80	16 - 280
COD (ppm)	40	5,556	1,040 - 37,600
Total Oil (ppm)	37	895	113 - 3,034
Emulsified Oil (ppm)	37	244	30 - 850
pH	57	7.07	6.2 - 8.1
Temperature (F)	57	91	79 - 100
BOD (ppm)	5	383	165 - 540

<sup>a</sup> Samples are for combined waste of rinse water and concentrated emulsion at a ratio of approximately 12:1.

The initial chemical program was applied to the full-scale facility and a satisfactory effluent was attained. Typical performance data is given below:

Effluent Turbidity	5-15 JTU
Effluent Total Oil	52 ppm
Effluent COD	765 ppm
Total Oil Removal	92%
COD Removal	87%

Chemicals were systematically reduced and the resulting treatment observed. It was found that chemical additions could be reduced to 175 ppm alum, 36 ppm lime, 16 ppm clay, and 0.5 ppm coagulant aid without diminishing effluent water quality. This reduction probably reflected the conservative nature of the recommended jar test program.

Attempts to further reduce chemical requirements met with varying success. Although an acceptable effluent was sometimes observed with lower chemical concentrations, the combination above is believed to be necessary in order to cope with influent oil concentrations and other variables. This combination of chemicals represents a chemical cost of \$.051/1,000 gallons of waste. The slight savings in chemical cost afforded by reduced chemical addition is not believed worth the reduction in treatment reliability. For example, the combination of 150, 24, 16, and 0.5 ppm was observed to give sporadic treatment at a cost of \$.046/1,000 gallons. At the waste volumes encountered, this represents only \$3.60/day savings in chemical costs.

Thus, for this particular application and mode of operation, the desirable chemical program is 175 ppm alum, 36 ppm lime, 16 ppm clay, and 0.5 ppm coagulant aid. It should be noted that any alteration in concentrated coolant to rinse water ratio would substantially alter this set of chemical requirements.

#### Chemical Addition Points and Rapid Mixing Time

Chemicals were capable of being added to the waste at a variety of locations. Alum, lime, and clay could be added to the first or second rapid mix tank. Coagulant aid was capable of being added to either the second mix tank or the entry line to the flocculation chamber. Previous to this evaluation, alum and lime were added to the first mix tank, clay to the second, and coagulant aid following the second prior to flocculation.

This scheme was based on jar testing which had indicated the necessity of 5 minutes mixing between alum and clay additions and 5 minutes mixing between clay and coagulant aid. Rapid mix tanks were sized based on this concept. However, flow rates were a maximum of approximately 500 gpm over an extended period as opposed to the 1500 gpm design flow. Thus, detention times in the mix tanks were a minimum of 15 minutes on a continuous basis. These extended mixing periods must be taken into account in interpreting results of changes in points of chemical addition.

Various schemes for applying the four chemicals to the waste were undertaken. These schemes appear in Table XVII.

TABLE XVII  
CHEMICAL ADDITION SCHEMES

<u>Scheme</u>	<u>Rapid Mix #1</u>	<u>Rapid Mix #2</u>	<u>Line to Floc Tank</u>
1	A,L	C	P
2	A,L,C	P	-
3	A,L,C	-	P
4	-	A,L,C	P
5	A	C,L	P
6	-	A,L,C,P	-
7	A,L	C,P	-

A = alum, L = lime, C = clay, P = polymer

Sharp contrasts in effluent quality for the different schemes were not found. General trends indicated, however, that schemes 6 and 7 were not capable of providing a consistently good effluent. These two schemes are distinguished by the fact that a period of mixing was not provided between the addition of clay and of coagulant aid. This observation is consistent with jar test findings and recommendations of polymer suppliers which indicate that coagulant aid functions most efficiently if added after other chemicals have been applied.

The lack of a significant difference for the separate addition of alum and lime indicates that this method offers no advantage. It was believed that pH adjustment for optimum flocculation after providing a period for emulsion breaking by the alum would prove beneficial. This idea was not substantiated, however.

The inability to note significant differences in treatment for other schemes leads to the conclusion that simultaneous addition of clay and alum does not appear to reduce treatment performance. It is possible that the total system serves to buffer effluent quality and renders it insensitive to subtle changes such as chemical addition points.

Although a period of mixing is required between the alum-clay addition and the coagulant aid addition, no significant difference between one mix tank or two mix tanks could be detected. However, this fact is necessarily qualified in light of the extended rapid mix detention times brought about by less than design flow rates. It is possible that a difference may be detected between 5 and 10 minutes, whereas none was noted between approximately 15 and 30 minutes.

In view of these findings, satisfactory treatment can be obtained with a more economical scheme than that of the design for the flow rates that were received. Such a scheme would consist of a single rapid mix tank with provisions for adding alum, lime, and clay to the mix tank and coagulant aid to the line leading from the mix tank to the flocculation chamber. This practice would eliminate the need for one mix

tank, one mixer, and miscellaneous chemical piping. Therefore, in terms of economics as well as treatability, this scheme must be considered most appropriate. However, it is also possible that two rapid mix tanks of less detention time would provide a more economical scheme.

#### Flocculation - Air Flotation Detention Time

Following chemical addition and rapid mixing, the waste flow splits into parallel flocculation - air flotation tanks. Detention time for flocculation and air flotation are interrelated. Prior to this evaluation of detention times, flow was diverted through both parallel units. Design detention times for flocculation and flotation were 10 and 20 minutes, respectively. However, the maximum flow rate attained on a continuous basis resulted in actual detention time of 32 and 57 minutes.

In an effort to evaluate the significance of detention time and at the same time approach design conditions, the entire flow was diverted through one of the parallel flocculation - flotation units. Under this condition, maximum flow rates attained on a continuous basis (500 gpm) resulted in actual detention times of 16 minutes for flocculation and 25, 28, or 33 minutes for flotation, depending upon the recycle rate.

The immediate effect of this halving of detention time was a gradual but significant rise in effluent turbidity. However, after several turnovers of the system, effluent quality returned to an acceptable level. This period of adjustment was believed to be another exemplification of the need for a fairly stable hydraulic loading. Nonetheless, an acceptable effluent was attained with the lesser detention times. Further reductions in detention time for the flocculation - flotation units may be possible.

Optimum detention time in terms of operation of a facility is academic since this is a function of incoming flow rate. Intuitively, the longer the detention the better will be the results. From a design standpoint, it can only be concluded that a combined flocculation - flotation detention time of 41 minutes has proven to be adequate and that lesser detention may be possible.

#### Flocculator Tip Speed

Flocculator tip speeds prior to the evaluation of this parameter were maintained at 0.6 feet per second (fps). When flow was still being diverted through both flocculation units, an experiment to test the effects of no mechanical flocculation was undertaken using one unit as a control. After several days of operation no significant difference in effluent quality could be detected between the unit employing a flocculator tip speed of 0.6 fps and that having the flocculator turned off altogether.



When detention time was halved by diverting the entire flow through one unit, four flocculator tip speeds were tested for performance. These were 0, 0.6, 1.8, and 3.6 fps. No difference in performance for any of these conditions was evident. Satisfactory treatment was achieved whether the flocculators were turned off completely or whether they were operated at maximum speed.

There are two possible explanations that might refute the conclusion that the flocculators are not needed. First, there is the matter of detention time. It is possible that the relatively long period provided for settling as a result of the decreased flows is sufficient to compensate for operation of the flocculators, whether beneficial or detrimental. Secondly, the hydraulics of the system may be such as to negate flocculator performance. The flocced waste must pass under a baffle and through a perforated distribution plate where dissolved air is introduced. This action may be violent enough to break up the delicate floc, regardless of how efficient the flocculator has been.

Nevertheless, because effective treatment is obtained with or without mechanical flocculation, the most economical condition is with the flocculators turned off. In designing a similar treatment facility, it appears that the flocculating equipment could be omitted and a corresponding savings realized. However, careful consideration of this facet should be given, particularly in relation to decreased detention times for the flocculation - flotation units.

#### Air Flotation Recycle Rate

The recycled portion of the effluent which is pressurized and saturated with dissolved air had been maintained throughout the program at 100 gpm. A specific percentage of recycle was unattainable due to the variation in waste flow rate. A recycle rate of 100 gpm results in a range from 100 percent to the flow for periods of no incoming waste to 40 percent of the flow at the maximum flow rates experienced over an extended period. Although the recycle system is capable of a range from 0 to 350 gpm, maintaining recycle flows below 100 gpm is impractical due to the relative insensitivity of the controls below this level.

During the period when flow was diverted through both flotation units and detention times were maximum, an experiment to test the need for the air was undertaken using one unit as a control. Within an hour after the recycle system was turned off in one unit, the effluent turbidity of that unit began to soar while the control unit maintained an excellent effluent quality. After several turnovers of the system, the air was turned back on for the test unit. Effluent quality improved immediately and returned to the original satisfactory quality. The treated waste during this test was observed to consist of an excellent floc, but one which remained suspended. The system as operated at this facility definitely requires air for efficient separation of the oily floc despite the extended detention times.

For operation through one unit of the system, an evaluation of the recycle rate was undertaken. The rates evaluated were 100, 200, and 300 gpm. These represent percentages of waste flow of 20, 40, and 60 percent at the maximum flow rates experienced over an extended period. The results of these tests indicated that no significant difference in effluent quality was observed for the three recycle rates. All were capable of producing a consistently good effluent.

The failure to detect differences in effluent quality for these large variations in recycle rate may be the result of compensating factors. One might expect the separation of oily floc to improve as the amount of dissolved air is increased. However, at the same time the detention time is decreased by the added recycle rate. For example, increasing the recycle from 100 to 300 gpm decreases detention time in the flotation unit by approximately 8 minutes. Furthermore, the influence of increased hydraulic agitation brought about by the higher recycle rates is not known. Other observations on the effects of hydraulic influences suggests that this may be a matter of significant importance.

The results of the evaluation of air flotation recycle rates indicates that some dissolved air is necessary for separation of oily floc but that the recycle rate required is independent of effluent quality, at least above 20 percent. The most economical condition, therefore, is the smallest quantity of recycle capable of being controlled or 100 gpm in the case of this installation.

#### Demonstration Program

Following the optimization of a number of treatment variables, an extended demonstration phase was undertaken to establish treatment efficiency and costs over a relatively long period. The conditions which were established and maintained throughout the demonstration period for most effective treatment are summarized as follows:

1. Chemicals

Alum - 175 ppm, added to second rapid mix tank

Lime - A sufficient quantity to maintain the pH between 6.5 and 7.5, added to the second rapid mix tank

Clay - 16 ppm, added to the second rapid mix tank

Coagulant Aid - 0.5 ppm, added between the second rapid mix tank and the flocculator

2. Flocculation - One flocculation tank on line with flocculator mechanism off

3. Air Flotation - One air flotation tank on line with the recycle rate at 100 gpm

4. Oil Recovery Area - Clarifier temperature 150 F with mixer operated eight consecutive hours out of each twenty-four, and holding tank temperature 180 F

Skimming of the oily floc from the surface of the air flotation tank was performed mechanically according to an intermittent on-off cycle. Operating experience indicated that a cycle of five minutes of operation out of each hour, the required time for one flight to travel the length of the flotation tank, minimized the amount of water skimmed to the oil recovery area, in addition to preventing dewatering of the scum to the point of being unmanageable.

Under these conditions, an extensive sampling and analysis program was established around the treatment facility. The results of this program are reported in Table XVIII.<sup>10</sup>

As shown in Table XVIII, the treatment facility is quite efficient in the removal of COD, BOD, and total oil with average removals in the range of 90 percent. Suspended solids removals, however, were found to be quite variable and in general quite low. The poor suspended solids removal is attributed to rapid variations in hydraulic loading which result in removal and carryover of solids previously deposited on the air flotation tank bottom and side walls. Substantial improvements in removal efficiencies for suspended solids in addition to COD, BOD, and total oil would be expected if additional equalization facilities were provided upstream of the treatment plant.

The oily scum produced in the air flotation tank was found to be quite variable in volume and composition ranging from 2,000 to 12,000 gpd and 10 to 90 percent oil by volume. These wide variations are primarily a result of variations in hydraulic loading and waste composition. Additional equalization would probably result in a more uniform scum quantity and quality.

In an attempt to determine whether the oil could be upgraded chemically, a bench scale test was performed employing the addition of an oil soluble polymer. Varying proportions of the polymer were added to oil samples and placed along with a blank into a drying oven at 175 F for 24 hours. Each sample was then observed to consist of a substance having no fluid characteristics whatsoever. No stratification was observed in these solid samples. It was apparent from this experiment that any concerted efforts to improve oil quality by simple dewatering (gravity separation) would result in an undesirable and unmanageable end product.

The oil recovered from the facility was found to be of insufficient

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<sup>10</sup> All analysis were performed in accordance with 12th Edition of Standard Methods for the Examination of Water & Waste Water.

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quality for use as fuel oil due to its high concentrations of water and solids. The average water and solids concentrations observed during this period were 8 percent and 2 percent by volume, respectively, as determined by centrifugal separation. The viscosity of the oil layer following centrifuging was observed to be extremely high, indicating that a large amount of solids remain with the oil. This observation coupled with the previously reported observation that complete dehydration of the scum results in the formation of a semi-solid material indicates that the simple application of heat and gravity separation is insufficient to produce an oil suitable for fuel oil use.

Although fuel oil quality appears to be unattainable, the recovered oil was in demand for use as road oil. The 107,000 gallons of recovered oil produced during this seven week period were given to nearby municipalities and counties for use on local roads.

During the demonstration phase of the program, the average rinse water flow when the mill was operating was 350 gpm. For a 12-turn operating week, this would total 2.02 million gallons. An additional 340,000 gallons<sup>11</sup> of concentrated coolant could be expected for a total quantity of waste of 2.36 million gallons to be treated. At a chemical cost of \$0.051/1000 gallons of waste, the weekly chemical cost would be \$121 or \$17/day.

The experience with disposal of recovered oil from rinse water treatment indicated that neither a credit nor an added cost can be applied. The quality of the oil that can be attained (10 percent bottom water and solids and 2 percent solids) is not adequate to permit its use as fuel oil. However, private concerns disposed of the oil at no cost as rapidly as it was recovered for use as road oil. Hence, no cost for incineration of the oil was incurred.

### COMPARATIVE ECONOMICS

In view of the fact that this tandem cold mill was operated successfully on either a completely recirculated coolant system or on a combination rinse water-coolant system, it is of interest to relate the treatment costs associated with the two operations. The cost data developed for each are necessarily based upon average operational information gathered during the field studies. However, it should be noted that the assumptions made in deriving these cost data are subject to drastic variations

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<sup>11</sup> This apparent increase in coolant volume is a result of contamination of the coolant with rinse water and does not mean that more coolant was necessarily lost when operating on the rinse water system. This 340,000 gallons of coolant is actually less concentrated than the 100,000 gallons received when operating on a completely recirculated system.

which may have significant effects on these figures. Of primary significance are the waste volumes received at the treatment plant and the type of rolling oil being utilized by the cold mill.

As mentioned previously, the net chemical cost vs. oil credit for the batch treatment of concentrated coolant consisting of "B" oil is \$24/day based upon the following assumptions:

Waste Volume	100,000 gallons/week
Chemical Cost	\$3.85/1,000 gallons
Oil Recovered	2,540 gallons/week
Oil Value	8.5¢/gallon
Total Chemical Cost	\$385/week
Total Oil Credit	\$216/week
Net Cost	\$169/week or \$24/day

For the use of Brand "A", a net credit of \$15/day can be realized when considering the chemical cost and value of the recovered oil based upon the following assumptions:

Waste Volume	100,000 gallons/week
Chemical Cost	\$1.12/1,000 gallons
Oil Recovered	2,540 gallons/week
Oil Value	8.5¢/gallon
Total Chemical Cost	\$112/week
Total Oil Credit	\$216/week
Net Credit	\$104/week or \$15/day

During the course of the 13 week batch treatment program, a total of 117,321 tons of steel was rolled by the tandem cold mill for an average of 9,000 tons/week. On this basis, the chemical treatment cost per ton of rolled steel is \$.019/ton for "B". Treatment of "A" would show a credit of \$.011/ton of steel.

The combined chemical cost and oil credit for the treatment of oily rinse waters consisting of "C" rolling oil is \$17/day based upon the following information gathered during the demonstration phase of the rinse water coagulation program:

Waste Volume	2,360,000 gallons/week
Chemical Cost	\$0.051/1,000 gallons
Oil Recovered	15,300 gallons/week
Oil Value	None
Total Chemical Cost	\$121/week
Total Oil Credit	None
Net Cost	\$121/week or \$17/day

Although at first glance it would appear that rinse water treatment of "C" is more economical than batch treatment of "B", it must be pointed

out that significant waste volume variations for rinse water are much more likely to occur than for batch treatment since the rinse water volume is strongly related to the preferred quantity utilized on the mill. An increase in chemical cost would not be directly proportional to increases in rinse water volume since the chemical requirement would probably be dependent more upon oil concentration than waste volume, and the oil lost on the mill would be essentially constant for a given production rate. However, the chemical dosage rate would have to be closely coordinated with rinse water volume in order to prevent unnecessary overdosing due to volume increases which contained lower oil concentrations. Furthermore, it must be pointed out that regardless of how economically the plant can be operated for treatment of rinse waters, the system cannot show improvement over the net credit resulting from batch treatment of Brand "A".

While the discussion of costs has been devoted to differences in chemical requirements and the value of the recovered oil, these differences must be viewed in the overall cost of operations. Other costs associated with the treatment plant were noted to remain essentially fixed whether the plant was handling concentrated coolant or rinse water. Forty man-hours per week were required for operation under both systems and averaged \$927 per month or about \$0.02/ton. Labor supervision, repairs, and utilities are each estimated to add an additional \$0.01/ton. Hence, a fixed operating cost of approximately \$0.05/ton is required irrespective of the nature of the waste or cold mill operating procedure. The costs for the various treatment methods are summarized in Table XIX.

TABLE XIX

TREATMENT COST PER TON OF STEEL ROLLED (\$)

	Batch Treatment Brand "B"	Batch Treatment Brand "A"	Rinse Water Treatment Brand "C"
Labor	.02	.02	.02
Supervision	.01	.01	.01
Repairs	.01	.01	.01
Utilities	.01	.01	.01
Chemicals	.045	.015	.01
Oil Credit	(.025)	(.025)	--
<b>TOTAL COST</b>	<b>.07</b>	<b>.04</b>	<b>.06</b>

Although approximately a twofold difference is represented in the range of treatment costs, the maximum difference is only \$0.03/ton. From this standpoint, therefore, it appears relatively unimportant as to the preferred operation of the cold mill.

Economics aside, the total quantity of pollutants to the stream over a given time period must be considered. Here the batch treatment prevails over rinse water. Even though the concentration of oil in the effluent is greater for the batch treatment, the relative volumes result in approximately three times as much oil to the stream over a given time period when using rinse water.

A breakdown of the capital costs for the installed waste oil treatment plant is given in Table XX. As has been indicated throughout this discussion and based upon the findings of this study, a number of changes are recommended if this plant were to be built again. Even though operation of the cold mill on a recirculated coolant system was found to be acceptable for current production requirements, the possibility of going to a rinse water system to provide a quality cold rolled product at some future date dictates that the corresponding treatment facility be provided with a similar flexibility. Furthermore, despite the fact that flow rates for a rinse water system were much less than the 1,500 gpm plant design rate, the plant would still be built for the 1,500 gpm flow as a result of management decision to incorporate this magnitude of flexibility into the cold mill operation.

Several components of the described treatment system were implicated as possibly being unnecessary. Among these were portions of the rapid mixing equipment and the flocculation equipment. Since it was not shown that these components would not be required at the maximum design flow, such equipment would still be incorporated into another similar facility contingent upon pilot plant findings. Aside from these uncertain changes, other alterations definitely would be made. Reductions in capital cost could be made by elimination of the incinerator and its foundations and by minimizing chemical piping costs. However, increased costs would result from the installation of larger equalization facilities, including pumps, additional needed instrumentation and controls, and more adequate piping insulation. The net result would be no significant change in capital cost within the bounds of estimated changes for these additions and deletions.

TABLE XX

TREATMENT PLANT CAPITAL COSTS

Yardwork	\$ 40,700
Structures	117,200
Permanent Equipment	495,700
Distribution Piping	49,100
Electrical	118,600
Indirect Costs	208,000
Contingency	<u>40,700</u>
TOTAL	\$1,070,000



All factors considered, if the choice between using a recirculated coolant system and a rinse water system on the first stand is available, treatment considerations definitely favor the recirculated coolant system. If the decision to use a recirculated system can be made prior to installation of the treatment facility, a significant savings in capital expense can be realized. This savings would result from the installation of a relatively inexpensive batch treatment system in place of the more complicated and costly continuous system described in this work.

## SECTION VI

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## SECTION VIII

### GLOSSARY

#### LIST OF TERMS

1. As-prepared emulsion - emulsions prepared in the laboratory.
2. Commercial rolling oil - rolling oil formulations, prepared by vendors and usable on commercial cold mills.
3. Coolant - Same as mill used emulsions.
4. Creaming - the partial separation of emulsion which in a very real sense is analogous to the separation of cream from un-homogenized whole milk.
5. Mill spent emulsion - recirculated emulsions used on the mill for such a period of time as to be unsuitable for rolling.
6. Mill used emulsion - recirculated emulsions used on the mill but still suitable for continued use.
7. Optimum - the value of a given parameter or set of parameters leading to maximum treatment efficiency as determined by observation.
8. Rinse water - water utilized for purposes of removing undesirable substances from the steel strip at stands No. 1 and/or No. 5. Generally, rinse water contains less than 1,000 ppm total oil.
9. Tramp oil - unemulsified oil which usually floats out of the emulsion at a fairly rapid rate on standing. Tramp oil may either be broken previously emulsified oil or extraneous oil which has leaked into the system. Tramp oil is usually dark in color.
10. "Typical" rolling oil - rolling oil formulations, with or without emulsifier which are prepared from mineral oil and lard oil in proportions typical of commercial rolling oils.
11. Virgin rolling oil - rolling oil emulsions (usually commercial) which have not been used on the mill.

## LIST OF ABBREVIATIONS

A	area of flat plate paddles (ft. <sup>2</sup> )
AN	acid number of oil, ASTM D117, Comm. D-2, p. 40, 9th Ed., Aug. 1969
Cd	drag coefficient (dimensionless), for flat plates Cd=1.2
C <sub>d</sub>	Concentration of 1,060 ppm emulsion after dilution
C <sub>i</sub>	as prepared concentration in ppm
D	particle size distribution function (dimensionless)
fps	feet per second
G <sub>m</sub>	mean velocity gradient (sec <sup>-1</sup> )
JTU	measured turbidity in Jackson Turbidity Units
JTU <sub>d</sub>	measured turbidity of diluted emulsion
JTU <sub>e</sub>	measured turbidity after partial flocculation (5 min.)
JTU <sub>f</sub>	measured turbidity after 5 min flocculation
JTU <sub>f</sub> *	empirically calculated post-flocculation turbidity
JTU <sub>i</sub>	measured as-prepared, initial untreated, or "influent" turbidity
JTU <sub>i</sub> *	empirically calculated value as-prepared turbidity
JTU <sub>o</sub>	turbidity of original emulsion, subsequently diluted
k	flocculation rate constant (N <sup>-1</sup> units)
K	ratio of rotating velocity of fluid to rotating velocity of flat plate paddles, equal to 0.32 according to Camp (16)
K <sub>2</sub>	a constant equal to W/u (s) <sup>3</sup> (sec/ft <sup>3</sup> )
K*	composite rate constant equal to kD (N <sup>-1</sup> units)
m	number of sequential reactors
n	revolutions per minute of stirrer shaft
N	number or mass of particles per unit volume at time, t

$N_o$	number or mass of particles per unit volume at $t=0$
ppm	parts per million of solute or dispersed phase by weight
$r_b$	distance from center of paddle to center of rotating shaft (ft)
s	stirring tip speed of paddle (ft/sec)
S.C.	specific conductivity (micromhos)
t	time (secs)
t/m	retention time per sequential reactor (secs)
u	absolute viscosity (lb-sec/ft <sup>2</sup> )
V	volume of reactor vessel (ft <sup>3</sup> )
W	power dissipated per unit volume per unit time (ft-lbs/sec-ft <sup>3</sup> )
Zp	zeta potential as determined directly on emulsion (mv)
Zpi	zeta potential of untreated reference emulsion state (mv)
Zpf	zeta potential of emulsion in absorption studies after treatment with alum (mv)
Zpo	zeta potential at "infinite dilution" (less than 30 ppm), in mv

## SECTION IX

### APPENDICES

#### APPENDIX A - RESEARCH AND DEVELOPMENT WORK

##### Description of Problem

A process is required to treat oily waste water from the new five-stand tandem cold mill at the Ashland Works. This process must be capable of treating 1,600 gallons per minute (gpm) of water containing up to 1,000 parts per million (ppm) of pickler coating oil from stand No. 1 and 1,600 gpm of water containing up to 1,000 ppm emulsified rolling oil from stand No. 5. The process must work at any concentration up to 1,000 ppm of any type or brand of oil and be capable of handling other miscellaneous oily wastes, including periodic dumps of spent rolling emulsion from the recirculating coolant systems containing up to 5 percent emulsified oil.

##### Review of Earlier Work

Several years ago, a great deal of experimental work was carried out on the treatment of aqueous wastes from the four-stand tandem cold mill at Middletown Works. Since coolant was being recirculated on all four stands of this mill, the only waste studied was the spent coolant; namely, water containing 1-5 percent emulsified oil.

The following scheme was developed:

- (a) Continuous skimming of floating "tramp" oils from the emulsion in the recirculating system.
- (b) Clarification of the oily skimmings at elevated temperature (e.g., 160 F) to reduce the moisture and solids contents to low levels.
- (c) Cracking discarded emulsion with an organic polyelectrolyte emulsion breaker, with the oily "sludge" thus produced being sent to the skimmings clarifier and the clear water being sent to the sewer. The above process was tested on a pilot scale at that time and has been recently applied in a full-scale plant.

##### Selection of a Treatment Process for the Ashland Cold Mill Wastes

An attempt to apply the previously-studied polyelectrolytes to wastes containing 1,000 ppm emulsified oil was unsuccessful; no breaking of the emulsion took place. Further investigation showed that these chemicals were not effective at oil concentrations below about 1 percent (10,000 ppm).

A new series of organic polyelectrolytes, claimed to be effective at low oil concentrations, were obtained and applied to this waste with



limited success. An acceptable water layer could be produced if the emulsion was treated and held at 100 F for 24 hours, then allowed to stand for another 2 or 3 days at room temperature. This approach is obviously not practical for treatment of a 1,600 gpm stream.

Another process which showed promise consisted of:

- (1) Production of a batch of oily sludge by cracking a concentrated emulsion (e.g., 5 percent) with an organic polyelectrolyte.
- (2) Treatment of the dilute waste emulsion by mixing with this sludge, then allowing the sludge to separate.

Although several series of experiments along these lines were successful, it became apparent that a considerable amount of research would be required to develop a reasonable understanding of the more fundamental factors involved in optimizing a process of this sort. This approach was abandoned in favor of coagulation.

It was found at bench scale that coagulation, using a ferric iron salt or alum as the primary coagulant, could be applied successfully to virtually any cold mill waste water containing a very broad range of concentrations of almost any type of oil. This process is readily adaptable to continuous operation and functions relatively quickly. It appeared that this process could be developed and applied to a full-scale plant within a reasonable period of time. Therefore, this line of investigation has been studied in considerable detail as reported in the following pages.

#### Description of Coagulation Process

The process of chemical coagulation of dilute oil-in-water emulsion is not completely understood. Several mechanisms appear to be involved; and as the conditions under which coagulation takes place are changed, the relative importance of each mechanism probably changes also.

The emulsion is first destabilized by the addition of a positively (and multiply-) charged ion called a primary coagulant. Ferric salts, alum, and cationic polyelectrolytes perform this function, which is essentially one of reduction of electrical charges on the oil droplets. Oil droplets are also absorbed on a precipitate of ferric or aluminum hydroxide; coagulation appears to work best in the pH range in which the hydroxide is least soluble. At this stage of the process a "pinpoint" floc is normally visible, though the water is still very turbid.

The process is then carried from coagulation to flocculation by the addition of one or more "coagulant aids" to consolidate the insoluble materials into large floc aggregates. This function is performed by certain clays and long-chain organic polymers. Best results are often obtained by treating first with a clay, then with a polymer. The clay appears to promote floc growth from pinpoint up to a clearly visible size by adsorption. Further floc growth may then be induced by adding

the polymer; the main action of the polymer appears to be mechanical entrapment, although the slight superiority of an anionic polymer over a nonionic suggests a function as co-coagulant working with the cationic materials.

### Experimental Procedures

Nearly all of these studies were carried out by the jar test technique, in which a series of identical test specimens are stirred with a gang mixer while different quantities of chemicals are added to the specimens. Since paddle sizes, container sizes, mixing times and mixing speeds are identical, the effects of the variations in chemical dosages can be determined visually.

In this case, a 500 ml specimen in an 800 ml beaker gave a specimen volume of about 3-3/4" in diameter by 3" deep. The mixer was equipped with four 1" wide (top to bottom) paddles, each sweeping a 2-1/2" diameter volume; speed was continuously variable up to 162 rpm (approximately 1-3/4 ft. per second maximum tip speed). The mixer was operated at maximum speed when "rapid-mixing" and at about 40 rpm when flocculating.

### Evaluation & Selection of Primary Coagulants

Four chemicals were evaluated as primary coagulants; namely, ferric sulfate, aluminum sulfate (alum), and two cationic polyelectrolytes. Eleven other cationic polymers were examined but did not perform satisfactorily.

One of the cationic polymers, EB-2, appeared to be more economical than the other polymers (based on performance). In some cases, EB-2 could be substituted for a major portion of the inorganic coagulant at a savings in total chemical costs; this would also appreciably reduce the ash of the reclaimed oil. In other cases, EB-2 could not be substituted for any portion of the inorganic coagulant.

Of the two inorganic coagulants, alum is preferable to iron salts. At concentrations normally used for coagulation, a good alum floc can be developed at a pH of 6, whereas an iron floc develops best at high pH values; therefore, less lime is required for pH control of alum coagulation. Also, an alum floc tends to float after coagulation of even trace amounts of oil, whereas an oily iron floc may float or sink; either floc could be recovered by dissolved air flotation, but an oily alum floc would normally float at all times, even if for some reason the air flotation equipment were out of operation.

All further work was carried out using alum and, where economical, EB-2 as the primary coagulants. Lime was also added along with the alum, where needed, to keep the pH above 6.

## Evaluation & Selection of Coagulant Aids

Two types of coagulant aids were studied, clay and organic polymers.

Bentonite clays from six different suppliers were examined; but by far the best performance was obtained by using one of the montmorillonite type.

Six different coagulant aids of the nonionic and anionic polyacrylamide type were applied to this process. When evaluated on an equal-cost basis, the anionic performed best with the nonionic performing nearly as well in most cases.

All further work was carried out using clay as necessary to promote the growth of the floc from the "pinpoint" size produced by the primary coagulants up to a size which could be successfully "blossomed" with a long chain polymer. Only minimum amounts of clay were used, however, since clay obviously adds to the ash of the reclaimed oil.

## Development of the Coagulation Program

The next step in this investigation was to determine the important parameters in the five-chemical program: cationic polyelectrolyte - alum - lime - clay - nonionic or anionic polyelectrolyte. Since these investigations involved over 300 separate experiments, the data presented in this report are limited to those selected to illustrate important points.

The results of these experiments indicate:

- (1) In some cases, EB-2 can be substituted for a portion of the alum. This seems to depend on brand of oil (type of emulsifier).
- (2) Where used, EB-2 addition should be followed by five-minute rapid paddle-type mixing prior to alum addition.
- (3) Addition of lime, if used, and alum should be followed by another five minutes of rapid paddle-type mixing. Propeller mixing, even for the first one minute, resulted in the eventual production of an inferior floc (smaller, more poorly agglomerated, and slower to rise).
- (4) Addition of clay should also be followed by five-minute rapid paddle-type mixing prior to addition of polymer coagulant aid.
- (5) If clay is added at the same time as the alum, the effectiveness of the clay is slightly reduced; the five-minute mixing times between cationic polyelectrolyte and alum additions and between clay and polymer coagulant aid are critical, however.
- (6) Addition of nonionic or anionic polymer should be followed by a short rapid mix and then five minutes slow mixing (flocculation).

- (7) Proper dosage of chemicals depends so much on type and concentration of emulsified oil (amount of emulsifier) that treatment of No. 1 and No. 5 stand wastes as two separate streams would be highly desirable. (Table AI)

Proper dosage also depends on history of emulsion (Table AI) and analysis of water (Table AII) as well as concentration of oil. Final adjustment of dosages will also depend on ultimate disposal of oil; the plant should be optimized for minimum operating costs if the oil is to be destroyed, but for minimum ash in oil if oil can be used for fuel. The plant should be capable of feeding the following dosages:

<u>Probable Maximum Dosage Required, ppm</u>		
	<u>Stand No. 1 Waste</u>	<u>Stand for No. 5 Waste</u>
Cationic Polyelectrolyte	10	10
Lime	-	150
Alum *	30	500
Clay	50	50
(Nonionic Polymer	1	2
( or		
(Anionic Polymer	1	1-1/3

\* Computed as  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$

#### Application of Dissolved Air Flotation

Several typical coagulation experiments, involving both pickler coating and rolling oils, were concluded with the application of dissolved air flotation to the final floc. In every case in which a satisfactory floc had been formed, the floc was floated successfully with a "too fast to measure" rise rate. It was found, however, that the final flocculation step (with nonionic or anionic polymer) had to be carried out in the same container in which flotation was to be applied; the floc was too fragile to withstand a transfer to another container.

#### Disposal of Oily Sludge

The sludge produced by this process can exhibit a very broad range of properties (moisture content, viscosity, ash, etc.).

At one extreme, a sample of stand No. 1 waste required very little chemical treatment to produce a sludge which dried relatively quickly to a product suitable for use as boiler fuel.

At the other extreme, a sample of stand No. 5 waste which required 350 ppm alum and 50 ppm clay to coagulate (at 1,000 ppm oil) produced a sludge which was 90 percent water, could be dried in five days at 160 F to 25 percent water, had an ash of 9 percent (based on dry oil), and at room temperature looked remarkably like ordinary axle grease.

It is not known at what point the recovered oil will actually fall between those extremes. It appears advisable at this time to plan to clarify at 160-180 F with mixing and to prepare to dispose of recovered oil by incineration.

Future studies will be directed to producing a type of recovered oil suitable for fuel usage.

#### Handling of Concentrated Waste Emulsion

Certain brands of rolling oil, such as those in use at Middletown Works which were referred to earlier in this report, are relatively easy to break from emulsion at the 1-5 percent oil level. Others, such as the brand "B" product currently used at Ashland, do not respond to this treatment.

It would appear necessary, then, to provide a tank to contain a "dump" from the recirculating system until it can be treated. If the emulsion can be broken at ambient temperature by addition of a polyelectrolyte, the emulsion could be cracked in this tank, the phases allowed to separate, the clear water sent to the sewer, and the oily sludge sent to the oil recovery area. Otherwise, the emulsion could be bled slowly into the stand No. 5 waste stream, where treatment by coagulation would take place. This flexibility of treatment schemes is necessary for maximum efficiency of operation.

#### Control Testing Procedures

Two simple and basic control tests for this process are the pH throughout the process (not less than 6.0) and the turbidity of the effluent to the sewer.

To date, however, no procedures have been developed to replace jar testing for determination of chemical dosage. It may prove difficult to train a plant operator to jar test a five-chemical program.

Good control testing is important, because underdosing of a single chemical will almost always hurt both water and oil quality; overdosing will in some cases hurt water quality, and in most cases will raise the ash content of the oil as well as increase operating costs.

Methods are needed which will minimize or eliminate operator judgment in determining dosages of at least two of the chemicals.

#### Summary and Conclusions

Coagulation appears to be the best approach to the treatment of waste of the type that will be produced by the Ashland Works tandem cold mill.

In order to be capable of handling the large variety of wastes which may be sent to this treatment plant, the plant should be designed for

a five-chemical program:

- (1) Cationic polyelectrolyte - as a primary coagulant, where economical to substitute for part of the alum.
- (2) Alum - as the main primary coagulant.
- (3) Lime - for pH control at large alum dosages.
- (4) Clay - as a coagulant aid to promote growth of the floc.
- (5) Nonionic or anionic polyelectrolyte - to further promote growth of floc.

The selection of chemicals to be used and dosages at which to apply them depend upon type of oil (amount of emulsifier), brand of oil (nature of emulsifier), concentration of oil, history of emulsion, water analysis, and ultimate disposal of reclaimed oil.

Since the stand No. 1 waste requires far less in the way of treatment chemicals than the stand No. 5 waste, it would be advisable to keep the streams separate and treat them separately.

Addition of cationic polyelectrolyte should be followed by five minutes of rapid paddle-type mixing. Addition of alum (and lime added simultaneously, if needed) should also be followed by five minutes rapid mixing. Addition of clay should also be followed by a five minute rapid mix. It is possible to add the clay with the alum and still achieve good coagulation, but it is important to mix a full five minutes after both cationic polyelectrolyte and clay. Addition of nonionic or anionic polymer should be followed by five minutes of slow mixing in the same vessel in which dissolved air flotation will take place.

Scum recovered from the air flotation units should be transferred to a heated (160-180 F) mixer-clarifier providing a few days retention time. Whether the product reclaimed oil will be suitable for use as boiler fuel or will have to be destroyed by incineration can only be determined after start up.

A separate tank should be provided to contain the periodic "dumps" from the recirculation system. This waste may then be handled one of two ways:

- (a) If the emulsion is of the type which can be broken with a polyelectrolyte emulsion breaker, the emulsion can be broken and oil separated in the tank, with clean water going to the sewer and oily sludge to the oil receiving area.

- (b) If the emulsion is of the type which does not respond to poly-electrolyte emulsion breakers, the emulsion can be disposed of by bleeding into the stand No. 5 waste stream and coagulating.

A few additional simple precise control testing procedures would be very helpful.

#### Recommendations for Further Work

1. It would be highly desirable to have some testing methods for plant control which are more objective and precise than visual inspection of the floc and water during jar tests. If coagulant dosage could be based on a colloid titration technique, for example, and lime dosage based on coagulant dosage, only clay and anionic polymer dosages would have to be chosen by operator judgment based on jar tests.
2. Whether oil can be reclaimed for use as boiler fuel cannot be determined until after plant start up. At that time, data should be collected on oil concentrations in the wastes, the amounts of "miscellaneous" oils coming into the system, brands of oil in use, frequency of coolant "dumps", etc. Then the chemical dosages in the plant should be optimized to give minimum ash in the oil (if it can be used as fuel) or minimum plant operating costs (if oil is to be destroyed by incineration).

EFFECTS OF VARIOUS PARAMETERS  
ON MINIMUM CHEMICAL DOSAGES REQUIRED TO TREAT  
WASTES CONTAINING 1,000 PPM OIL

Table AI - Various Sources and Types of Oil

<u>Specimen</u>	<u>Chemical Dosages, ppm</u>				
	<u>EB-2</u>	<u>Alum*</u>	<u>Lime</u>	<u>Clay</u>	<u>Nonionic Polymer</u>
Brand "A" Rolling Oil	7	20	-	10	1
Brand "A" Rolling Oil Middletown Cold Mill	7	20	-	10	1
Brand "B" Rolling Oil	10	60	-	20	2
Brand "B" Rolling Oil Ashland Cold Mill (Slow Speed)	-	70	10	20	2
Same, but mill running at faster speed	-	335	125	50	2
Pickler Coating Oil Ashland Cold Mill Stand #1 (Sample fortified with new oil to build conc. to 1,000 ppm)	-	10	-	20	0.5

\* Expressed as  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$



EFFECTS OF VARIOUS PARAMETERS  
ON MINIMUM CHEMICAL DOSAGES REQUIRED TO TREAT  
WASTES CONTAINING 1,000 PPM OIL

Table AII - Various Types of Water

Specimen: Used Brand "B" Rolling Oil,  
 Ashland Cold Mill operating at  
 slow speed; emulsion from recir-  
 culating system diluted to 1,000  
 ppm with water from various  
 sources.

<u>Water</u>	<u>Chemical Dosages, ppm</u>			
	<u>Lime</u>	<u>Alum</u>	<u>Clay</u>	<u>Nonionic Polymer</u>
Lime - Soda Softened	10	70	20	1
1 part tap * 1 part distilled	15	100	40	1
1 part tap 2 parts distilled	30	100	50	1
1 part tap 5 parts distilled	10	80	20	1

\* Middletown, Ohio, City Water

## APPENDIX B - DETAILED ENGINEERING REPORT & DRAWINGS

### INTRODUCTION

This Waste Water - Waste Oil Treatment Plant is primarily designed to prevent stream pollution due to contaminated water and coolant (rolling oil), resulting from the new five-stand Tandem Cold Mill.

As described below, this treatment plant is designed as a two-step treatment process. The first step consists of coagulation and flocculation of oil, followed by an air flotation process. This separation of oil and water takes care of the problem normally associated with cold mill operations.

### GENERAL DESCRIPTION

The Waste Water - Waste Oil Facilities are designed for a capacity of 1,600 gpm and will consist of underground pipe lines to carry the emulsified oil from the new five-stand Tandem Cold Mill to the oil treating facilities located southwest of the existing Maintenance and Diesel Repair Shops Building No. 729.

Spent rinse water from the five-stand Tandem Cold Mill will be pumped to an equalization tank, thence by gravity to the rapid mix unit (2 stage), then by gravity to the flocculation unit and by gravity to the air flotation unit. Cationic polyelectrolyte, clay, alum, and lime, will be fed into the influent of the rapid mix unit in proportion to the flow. Coagulant aid will be fed into the influent of the flocculation unit.

The periodic blow-down of spent coolant from stands No. 2, 3, and 4 of the Tandem Cold Mill will be pumped into a new 60,000-gallon holding pit. The holding pit will be provided with a 500 gpm recirculating pump, and suitable valving and pumping equipment to transfer the combined waste oils to the equalization tank at a rate of 20 gpm. When this occurs additional chemicals must be added to the influent of the rapid mix tank to compensate for the additional flow.

The effluent from the air flotation system will be sent to White Oak Creek. The bottom sludge, consisting of dirt and water, from both systems will be periodically drained by gravity to dumpster boxes for disposal at the dump.

The scum from the unit will be drained to a 800-gallon collecting tank and pumped to a waste oil treatment and disposal system.

The chemical storage, dilution and feeding facilities required to

support the above operations are, a cylindrical acid resistant liquid alum storage tank, a cylindrical cationic polyelectrolyte storage tank and two cylindrical dilution tanks for each of three chemicals; coagulant aid, lime and clay. Each dilution tank will hold a 24-hour supply and will be equipped with suitable mixing equipment to dissolve the chemicals in water and keep them in suspension. Suitable proportioning pumps and spares will be provided to feed the chemical solutions and slurries to the rapid mix units and flocculators.

Sufficient dry chemical storage space will be provided to handle a 20-day supply of coagulant aid, lime and clay.

An enclosure will be provided for all chemical storage, tanks and feeding equipment, the 60,000-gallon holding pit and oil treatment facilities.

Water for chemical mixing will be supplied from the recycle system of the air flotation tanks. The initial filling will be from the city water line.

The waste oil treatment and disposal system will consist of pumping the scum from the 800-gallon collecting tank to a heated clarifier. The separated oil will flow by gravity to a 20,000-gallon oil holding tank. From the holding tank the oil will flow by gravity to a 300 gph incinerator for disposal.

#### CONTROL

The influent lines to the equalization tank will have a flow meter to control the three-way solenoid operated valves on the suction side of all chemical feed pumps. These three-way solenoid operated valves admit either chemical or water to the pump suction as required. The capacity of all chemical feed pumps is adjusted manually. Scum pumps will be float controlled. The cationic polyelectrolyte, alum and oil storage tanks will have a liquid level gauge. All recycle pumps, storage pit effluent pumps and the alum unloading pumps will be manually controlled. All other functions are by gravity. Temperature of the heated clarifiers will be automatically maintained by temperature control valves.

Effluent to White Oak Creek will be monitored automatically and continuously with an effluent turbidimeter.

#### ENCLOSURE

The Waste Water - Waste Oil Treatment Enclosure will be 40 feet wide by 100 feet long by 20 feet high for a length of 80 feet, and 46 feet high for a length of 20 feet. The enclosure will contain the oil holding pit, alum storage tank, cationic polyelectrolyte storage tank,

storage area and mixing tanks for coagulant aid, lime and clay, plus the oil recovery equipment.

## MAJOR EQUIPMENT - MECHANICAL

### Equalization Tank

The equalization tank will be designed for 1,600 gpm at a retention time of 10 minutes and will be capable of 24-hour continuous operation. The tank will be 12 feet diameter by 19 feet vertical sidewall depth including 12 inches freeboard.

There will be a recirculating pump to equalize any variations in oil concentration. The effluent will flow by gravity to the rapid mix tanks.

### Rapid Mix Tanks

The pair of rapid mix tanks will each have a capacity of 7,850 gallons and will be 11 feet in diameter by 12 feet vertical sidewall, including 12 inches freeboard, with a 45 degree cone bottom. Influent and chemicals will enter the tank through a standpipe. Each tank will be equipped with a double turbine, 60 rpm mixer. The rapid mix tanks will be operated in series. Effluent from the No. 1 tank will flow to the No. 2 tank by gravity and from the No. 2 tank to the flocculation-air flotation tanks by gravity.

### Flocculation-Air Flotation Tanks

Each of the two flocculation tanks will be designed for 800 gpm at a retention time of 10 minutes, with paddle type mixers sufficient to promote the growth of floc. Each tank will be 11 feet long by 10 feet wide by 7 feet 2-inch vertical sidewall, including 6 inches freeboard, with a vee bottom. Each of the two air flotation tanks will be designed for 800 gpm at a retention time of 20 minutes for influent plus 25 percent recycle and will be capable of 24-hour continuous operation. Each tank will be 10 feet wide by 44 feet long by 7 feet 2-inch vertical sidewall depth including 6 inches freeboard. The bottom of the tanks will be a 45 degree vee with a screw conveyor for collection of sludge.

There will be a skimmer operating over the entire top of the tank for removal of the accumulated oil. The scum will be drained by gravity to the 800-gallon collecting tank. A recycle pump will be used to withdraw a portion of effluent and pump it to a pressure tank where air will be added. The recycle stream and raw flow will be blended at the inlet manifold.

### Holding Pit

The holding pit will have a capacity of 60,000 gallons. The pit will

be 18 feet wide by 38 feet long by 13 feet effective depth, reinforced concrete, with the bottom sloped to a clean-out area within the pit. The pit will have a 500 gpm recirculating pump. Effluent will be pumped alternately by one of two 20 gpm pumps to the equalization tank. Any solids which may accumulate on the bottom will be removed. All pumps will be of the submersible type with provisions made for easy removal for maintenance.

#### Scum Tank

The scum from the air flotation tanks will flow by gravity to the 800-gallon scum tank. Effluent from this tank will be pumped alternately by one of two 25 gpm pumps to the oil recovery system.

#### Heated Clarifier

The heated clarifier will have a capacity of 20,000 gallons and will be 12 feet in diameter by 22 feet vertical sidewall, with a 45 degree cone bottom and drain valve. The clarifier will be insulated.

There will be a 6 feet diameter by 7 feet deep, steam heated, plate coil, center well with a 4 feet by 4 feet, 5.2 to 20.6 rpm paddle type mixer in the center. Effluent will overflow a weir at the top of the clarifier to the holding tank. Access platforms will be provided to the top of the clarifier and holding tanks and also monorails and manually operated hoists for maintenance of the mixers and coils.

#### Holding Tank

The oil holding tank will have a capacity of 20,000 gallons and will be 12 feet in diameter by 22 feet vertical sidewall, with a 45 degree cone bottom and drain valve. The holding tank will be insulated and heated with a 6 feet diameter by 7 feet deep, steam heated, plate coil, center well. Oil will be pumped from the tank with a 0 to 300 gph pump to the incinerator for ultimate disposal. In the future, the holding tank can be converted to a second clarifier if it should prove desirable, and two additional 10,000 gallon holding tanks added.

#### Incinerator

The incinerator will have a capacity of 300 gallons per hour and designed to consume the scum from the 20,000-gallon holding tank. Anticipated operation of the incinerator will be intermittent. The incinerator will be complete with a target wall for personnel protection.

**PAGE NOT  
AVAILABLE  
DIGITALLY**

## APPENDIX C - KINETIC RELATIONSHIPS EMPLOYED

The basic relationship for flocculation kinetics is (18):

$$\frac{N}{N_0} = \exp (-kDN_0G_mt)$$

where:

$N$  = number or mass of particles per unit volume at time,  $t$

$N_0$  = number or mass of particles per unit volume at  $t = 0$

$k$  = rate constant in  $N^{-1}$  units

$D$  = particle size distribution function

$G_m$  = mean velocity gradient in  $\text{sec}^{-1}$

$t$  = time in secs

The  $\log_e$  form of this relationship is:

$$\ln (N/N_0) = -kDN_0G_mt$$

The nature of this equation is such that a working engineering relationship may be attainable if the values of  $N$  and  $N_0$  can be expressed in terms of some measureable parameter such as turbidity.

For example, in this work it was noted that for a diluted as-prepared typical rolling oil emulsion:

$$1.18 \ln \frac{JTU_d}{JTU_0} = \ln \frac{C_d}{C_1} = \ln \frac{N}{N_0}$$

where:

$JTU_0$  = turbidity of 1,060 ppm emulsion

$JTU_d$  = turbidity of diluted 1,060 ppm emulsion

$C_1$  = concentration of 1,060 ppm emulsion

$C_d$  = concentration of diluted 1,060 ppm emulsion

Therefore, if D remains constant during coagulation,

$$1.18 \ln (JTU_e/JTU_1) = -kDN_o Gt$$

where  $JTU_e$  and  $JTU_1$  are the "effluent" and "influent" turbidities, respectively.

The mean velocity gradient,  $G_m$ , is defined as:

$$G_m = (W_m/u)^{0.5}$$

where

$W_m$  = the mean power dissipated per unit volume per unit time in the system

$u$  = absolute viscosity

According<sub>2</sub> to Camp (16) if  $W$  is expressed in ft-lbs/sec -ft<sup>3</sup> and  $u$  in lb-sec/ft<sup>2</sup>:

$$W = \frac{239 Cd (1-K)^3 (n)^3 \text{Sum } (A(r_b)^3)}{V}$$

where:

$Cd$  = 1.2 and is based on the drag coefficient for flat plates

$A$  = Area of vertical paddles (ft<sup>2</sup>)

$r_b$  = distance from center of paddle to center of rotating shaft (ft)

$K$  = 0.32

$n$  = revolutions per minute of the stirring shaft

$V$  = volume of the reactor vessel in ft<sup>3</sup>

Obviously, the tip speed is related to  $n$  through the relationship

$$s(\text{ft/sec}) = n \times 4 (\pi) r_b \quad (r_b = 1/2 \text{ length of paddle})$$

If all the paddles are of identical size one obtains

$$G_m = (K_2 s^3)^{1/2}$$

where  $K_2$  includes the volume of the system, area and number of paddles, the absolute viscosity of the system and conversion constants.

Because of the tight restrictions required to compare systems on the basis of stirring tip speed, results should preferably be reported in terms of mean velocity gradient.



#### APPENDIX D - KINETIC RELATIONSHIP FOR SEQUENTIAL REACTORS

The flocculation kinetics relationship for a sequential continuous flow reactor system is (18):

$$\frac{N}{N_0} = (1 + kDG_m N_0 t/m)^{-m}$$

where:

$N$  = number of particles per unit volume at time  $t$

$N_0$  = number of particles per unit volume at  $t = 0$

$k$  = rate constant in  $N^{-1}$  units

$D$  = particle size distribution function

$G_m$  = mean velocity gradient in  $\text{sec}^{-1}$

$m$  = number of sequential reactors

$t$  = time in seconds

$t/m$  = retention time per reactor, secs

The flocculation kinetics relationship for the batch reactor type appears in Appendix C.

## APPENDIX E

### USE OF SINGLE CHANNEL COULTER COUNTER FOR FLOCCULATION KINETICS

It is generally assumed that during flocculation, coagulated particles or aggregates thereof can combine irreversibly to form larger aggregates and that particles and aggregates of virtually neutral charge have an equal probability of flocculating. On this basis one should be able to determine flocculation kinetics by following the decrease in the number of particles in the system with time after "coagulant" addition. For poly-dispersed systems kinetics data should be obtainable by monitoring the number of particles in a small and narrow size range wherein flocculation of particles having diameters less than the upper limit of the range necessarily result in new particles or aggregates having mean diameters greater than that upper threshold. For this purpose a Coulter Counter (Model B) was employed.

The flocculation studies were conducted on emulsions of a laboratory prepared commercial rolling oil treated with alum. These results appear in Figures E1-E3. The values for the final slopes necessarily include the relatively small but unknown mean velocity gradients.

Further such experiments were run with both alum and lime addition to produce alum floc. In these instances the rate of particle loss within the 6.52 to 9.41 micrometer range increased rapidly from the typical values given in Figures E1-E3 (about  $-10^{-4}$  sec $^{-1}$ ) to values of  $-0.6$  sec $^{-1}$  and greater.

Because of the unknown velocity gradient under these conditions, a more sophisticated reactor-unit was sought. Such a unit was obtained on loan from Dr. S. A. Hannah of the FWPCA, Taft Engineering Center, Cincinnati. This equipment was previously used to measure floc strength and has been described elsewhere by Dr. Hannah. (11)

Unfortunately the instrumental noise encountered in attempting to use this piece of equipment was too excessive for meaningful work. While this problem probably could have been overcome with a relatively small expenditure of time, too little time remained within the grant period to perform enough reaction studies to be of value. On the other hand it is clear from what has been presented above that the single channel Coulter Counter can be used for flocculation kinetics studies.

FIG. E-1. FLOCCULATION OF 200 PPM EMULSION WITH ALUM VIA COULTER COUNTER TECHNIQUES

(@0.45 meqs alum/g emulsion)

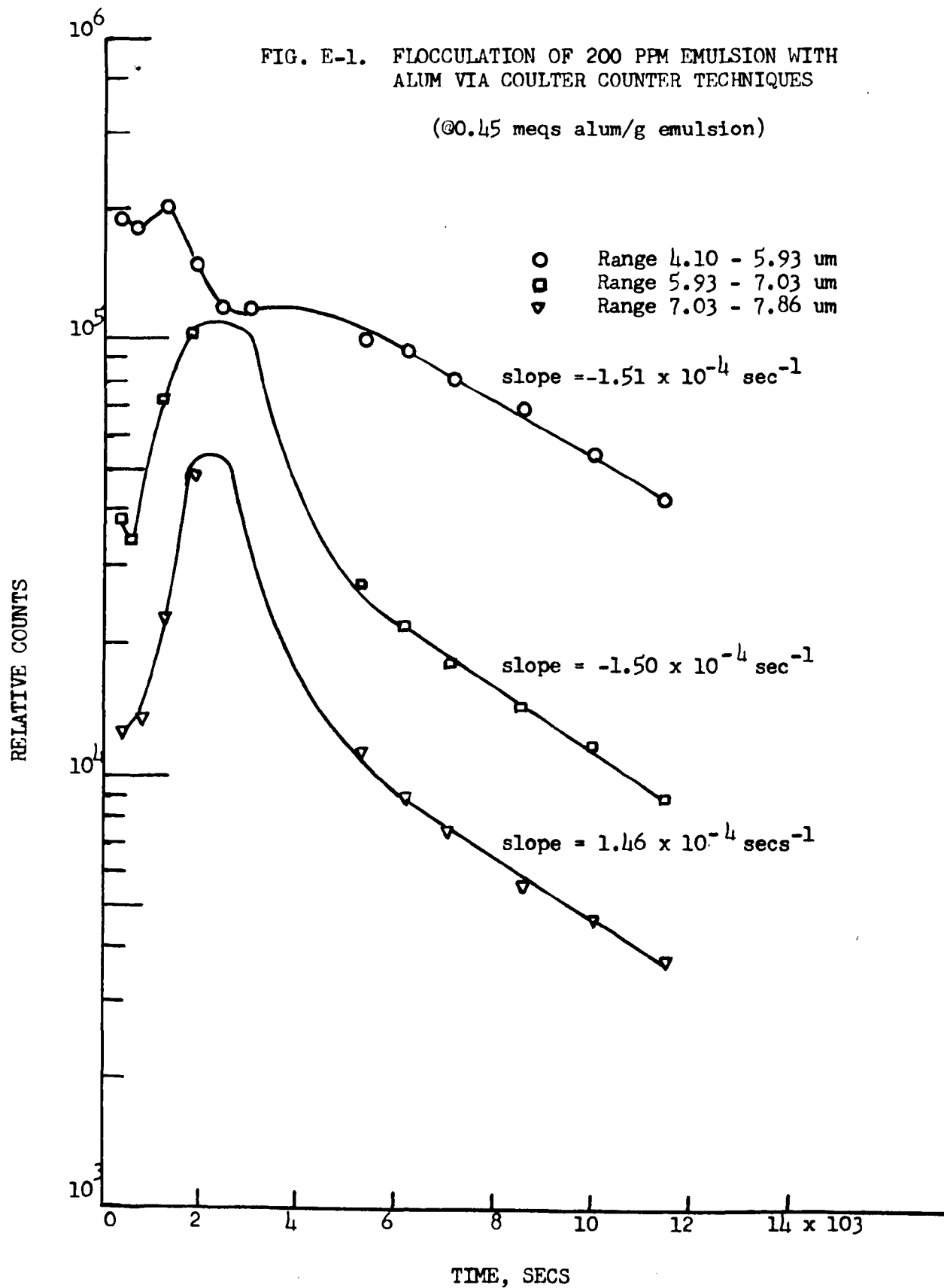


FIG. E-2 FLOCCULATION OF 400 PPM EMULSION WITH ALUM VIA  
COULTER COUNTER TECHNIQUES

(@ 0.225 meqs alum/g emulsion)

○ Range 5.14 - 7.41  $\mu\text{m}$

□ Range 7.41 - 8.81  $\mu\text{m}$

△ Range 8.81 - 9.83  $\mu\text{m}$

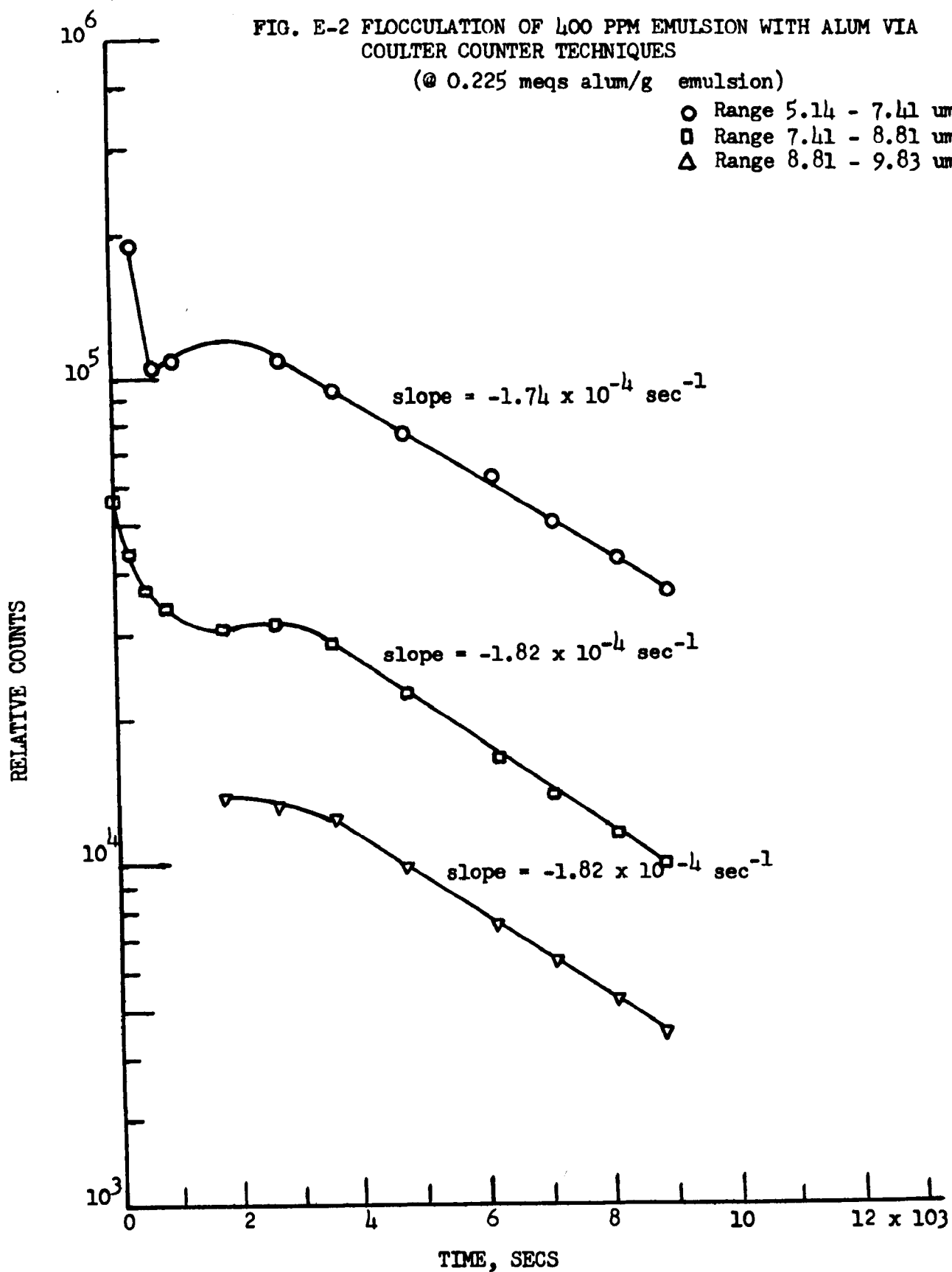
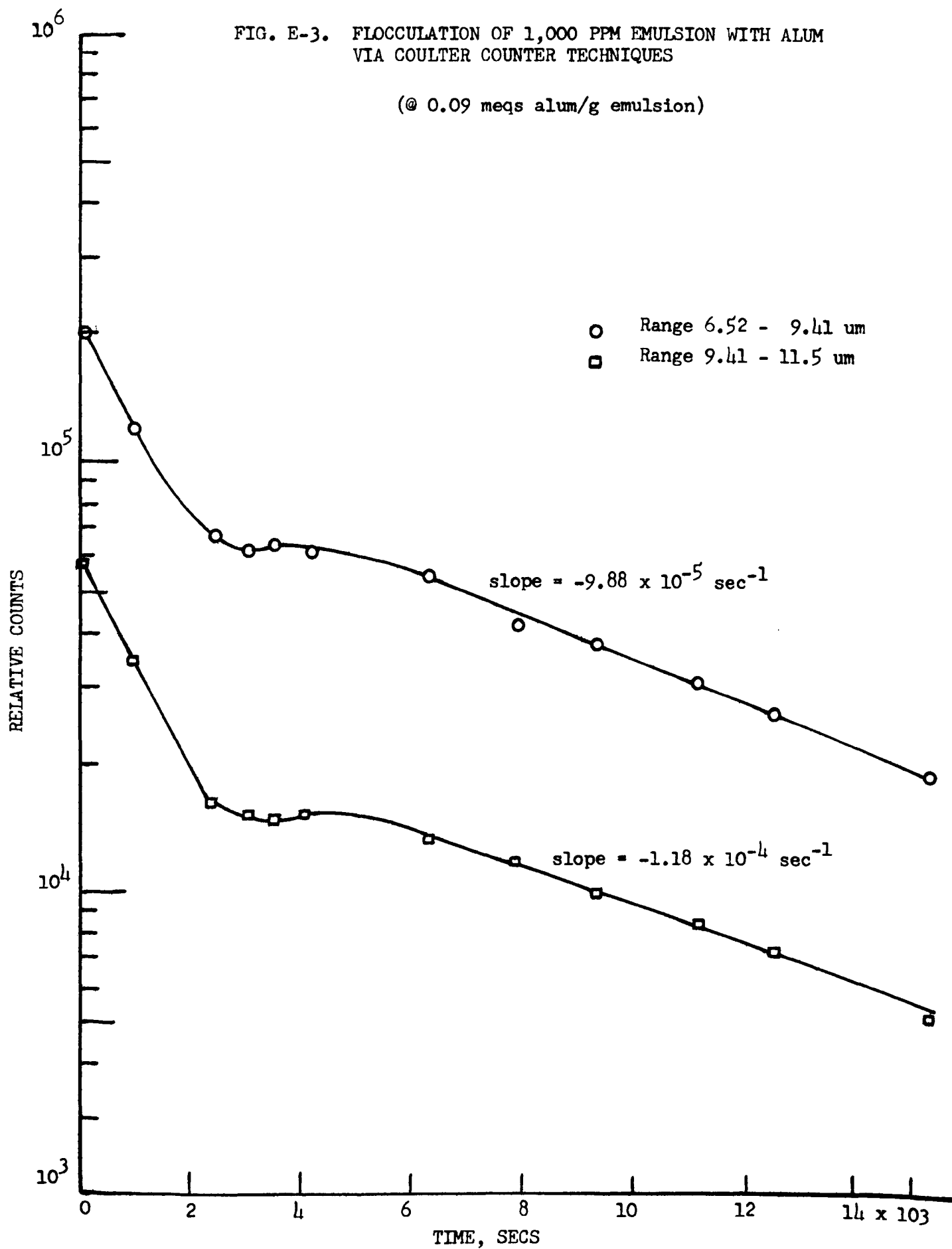


FIG. E-3. FLOCCULATION OF 1,000 PPM EMULSION WITH ALUM  
VIA COULTER COUNTER TECHNIQUES

(@ 0.09 meqs alum/g emulsion)



## APPENDIX F - SAMPLES AND REAGENTS

- Alum - 99.7 percent purity  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$  prepared at 10,000 ppm in distilled deionized water
- Lime - Reagent grade  $\text{Ca}(\text{OH})_2$  prepared at about 950 ppm level in distilled deionized water and filtered hot over 0.2  $\mu\text{m}$  Millipore Filter pads. Concentration was determined for given stock solutions by titration against standard 0.00551N hydrochloric acid with phenolphthalein as indicator.
- Clay - A montmorillonite prepared at 5,000 ppm and dispersed 1.0 min. via a single speed Waring Blendor.
- Mill Mix Water-Lime softened Ohio River water, deionized via filtration over 0.2  $\mu\text{m}$  Millipore Filter pads. This water had a specific conductivity (s.c.) of about 500 micromhos and a pH of approximately 7.4.
- Deionized Water - pH 5.2 to 6.2 (depending on  $\text{CO}_2$  content), and s.c. ca. 10 micromhos.
- $\text{CO}_2$ -Free Deionized Water - Boiled deionized water cooled in stoppered flask, pH 6.78, s.c. ca. 6 micromhos.
- Electrolyte for particle size determination - 1.0 weight percent reagent grade NaCl in deionized water deionized to 0.2  $\mu\text{m}$  and having a pH of ca. 6 and an s.c. ca. 20,000 micromhos.
- Stock "typical" rolling oil solution (emulsifier-free) -  $50 \pm 0.5$  percent in lard oil (of various acid numbers),  $50 \pm 0.5$  percent in mineral oil dissolved in chloroform to a total concentration of 200 g per liter of solution.
- "Typical" rolling oil emulsion (emulsifier-free) - 20 ml aliquot of stock "typical" rolling oil solution evaporated in 500 ml volumetric flask at 110 C for 2 hrs., dispersed in 200-300 ml deionized water via a Wrist Action Shaker for 1-16 hours (followed by dilution to 500 ml with deionized water and emulsification via a single speed Waring Blendor for  $2.0 \pm 0.05$  minutes. For emulsifier containing emulsions, the emulsifier solution was added to the chloroform evaporated oil phase before dispersion.

Stock emulsifier solutions - 2.57 to 2.58 g Triton X-100 nonionic and Atlas G-3300 anionic emulsifiers dissolved in 1.00 liters deionized water.

PVSK standard solution -  $9.411 \times 10^{-3}N$ , prepared by direct weighing of 2.0530 g PVSK dissolved in 1.00 liters deionized water.

"Cat-Floc" standard solution -  $9.708 \times 10^{-3}N$ , prepared by dissolving ca. 9.7 g Calgon "Cat-Floc" (dimethyldiallylammonium chloride) in deionized water and standardized by titration against PVSK with Toluidine Blue as indicator.

Toluidine Blue standard indicator solution -  $4.80 \times 10^{-3}$  weight percent prepared by dissolving 0.0480 g o-toluidine blue reagent in 50.0 ml deionized water.

Standard KCl solutions - 0.1006N and 0.002012N prepared by dissolving 2.7500 g reagent grade KCl in 500 ml deionized water and dilution of 10.0 ml thereof to 500 ml, respectively.

Commercial rolling oils - Obtained from various companies having vendors identification letters "A", "B", "C", "D".

Commercial rolling oil emulsions - Prepared by weighing 0.50 grams of as-received commercial rolling oil into 500 ml volumetric flasks, dispersion in 250 ml deionized water, subsequent dilution to 500 ml and emulsification via a single speed Waring Blendor for  $1.00 \pm 0.02$  minutes.

Spent rolling oil emulsion - Obtained from Ashland 5 stand tandem cold mill. Four samples were taken: a brand "B" at 6,000 ppm emulsified, 7,500 ppm tramp; a brand "B" unanalyzed (about 10,000 ppm total); and two brand "C" unanalyzed, one having been on the mill two hours, the other being the same emulsion after 2 days on the mill.

## APPENDIX G - EXPERIMENTAL EQUIPMENT

In addition to the usual laboratory equipment the following equipment was employed:

Ultracentrifuge - International Equipment Co., Boston, Mass., Model V, Size 2 with No. 103 multispeed attachment and No. 296 four-place angle head.

Jar Test Stand - Nalco Chemical Co., Chicago, Illinois, Four-place 1.0 x 2.5 in. vertical paddle on 0.25 in. diameter shaft; variable tip speed 0-1.8 fps.

pH Meter - Beckman, Inc., Fullerton, Calif., Model 76

Turbidimeter - Hach Chemical Co., Ames, Iowa, Model 2100, standardized with 75 JTU polystyrene standard.

UV Spectrophotometer - Beckman Inst. Co., Fullerton, Calif., Model DU.

Coulter Counter - Coulter Electronics Div., Hialeah, Fla., Model B, standardized with 3.49 micrometer ( $\mu$ m) latex spheres; k of 30  $\mu$ m aperture, 0.1052/M\*; for 140  $\mu$ m aperture k = 14.52/M\*

Relative Streaming Current Detector - Water Association, Inc., Framingham, Mass., 4 cycle per second, polyethylene block and piston.

Zeta-Meter - Zeta-Meter, Inc., New York, New York, Standard Model, K factor =  $90.7 \pm 0.2$  @ 25 C by standardization with 0.002014N KCl. The conversion factor from electrophoretic mobility to zeta potential was 13.1 based on an estimated temperature of measurement of 24 C (17).



<p><b>BIBLIOGRAPHIC:</b></p> <p>Armco Steel Corporation, Treatment of Waste Water - Waste Oil Mixtures, FWPCA Publication (12010EZV 02/70), May, 1970, 137 pages, 25 figures, 22 tables, 32 references, 7 appendices.</p> <p><b>ABSTRACT:</b></p> <p>Cold reduction of steel strip results in the production of large quantities of waste water containing variable amounts of oil. A five stand tandem cold mill located at Armco Steel Corporation's Ashland, Kentucky Works produces 200 to 500 gpm of waste water containing 400 to 4,000 ppm of oil. The COD of the waste varies from 400 to 20,000 ppm.</p> <p>A treatment process and facility was developed, constructed, and demonstrated, on full-scale, for the treatment of cold mill wastes. The treatment process utilized chemical coagulation to break the emulsions. The chemicals employed included alum, lime, clay and organic coagulant aid. The process consisted of the following treatment steps; equalization, chemical addition and rapid mixing, flocculation, and dissolved air flotation. A number of</p>	<p><b>ACCESSION NO.</b></p> <p><b>KEY WORDS:</b></p> <p>Waste Water Treatment Industrial Wastes Steel Wastes Emulsions Coagulation Flocculation Oily Wastes Flotation Emulsifiers Zeta Potential</p>
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treatment variables were studied in the laboratory and in the field in order to establish process kinetics and optimum treatment efficiency.

Zeta potential, streaming current, and particle size distribution were used in laboratory studies to describe the effect of the following variables on process kinetics; acid number, initial oil concentration, type of emulsifier, chemical dosage, order of addition of chemicals, reaction time, mixing, and final pH. Based on these studies, a hypothesis of the emulsion breaking mechanism was proposed.

Oil, COD, and turbidity were used in field studies to establish the effect of the following variables on treatment efficiency; chemical concentration, order of chemical addition, chemical mixing time, flocculation mixing time and speed, and air flotation time and recirculation rate. Based on these studies, optimum design criteria and operating costs for this process were presented.

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