MODELING OF FLOCCULATION SYSTEMS USING
PARTICLE SIZE DISTRIBUTION

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TABLE OF CONTENTS

Chapter | Page
---|---
I. INTRODUCTION | 1
II. LITERATURE REVIEW | 5
   - Introduction | 5
   - Terminology | 5
   - Destabilization Mechanisms | 6
   - Particle Counting | 9
   - Turbidity | 10
   - Particle Counting Method | 12
   - PSD Application in Full Scale Water Treatment Plants | 18
   - Representation of PSD Data | 21
III. MODEL DEVELOPMENT | 28
   - Consideration of Interparticle Forces | 31
   - Consideration of Floc Density | 36
   - Consideration of Floc Shape | 41
   - Consideration of Floc Break-up | 45
   - Consideration of Velocity Gradient | 48
   - Consideration of Flow Pattern | 50
   - Summary | 52
IV. MODEL SIMULATION | 54
   - Comparison of Collision Frequency Function | 54
   - Case 1. Constant 1 μm Particle Size | 55
   - Case 2. Constant 10 μm Particle Size | 60
   - Description of the Computer Model | 64
   - Comparison of Reported Experimental Results with Predictions of the Model | 69
   - Case 1. Davis Water Treatment Plant in Austin | 70
   - Case 2. Southern Nevada Water System | 80
   - Case 3. Lab Data | 84
   - Uncertainty Analysis | 93
V. DISCUSSION | 105
VI. SUMMARY AND CONCLUSIONS | 114
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>REFERENCES</td>
<td>117</td>
</tr>
<tr>
<td>APPENDIXES</td>
<td>123</td>
</tr>
<tr>
<td>APPENDIX A - COMPUTER PROGRAM FOR FLOCCULATION MODEL</td>
<td>124</td>
</tr>
<tr>
<td>APPENDIX B - COMPUTER PROGRAM OUTPUT</td>
<td>142</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Approximation for Collision Frequency</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Efficiencies in Brownian Diffusion</td>
<td></td>
</tr>
<tr>
<td>II.</td>
<td>Approximation for Collision Frequency</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Efficiencies of Fluid Motion</td>
<td></td>
</tr>
<tr>
<td>III.</td>
<td>Approximation for Collision Frequency</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Efficiencies of Differential Sedimentation</td>
<td></td>
</tr>
<tr>
<td>IV.</td>
<td>Effects of the Factors Incorporated into the Collision Frequency Functions on</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Collision Frequency</td>
<td></td>
</tr>
<tr>
<td>V.</td>
<td>Mean Value of Varied Parameters</td>
<td>95</td>
</tr>
<tr>
<td>VI.</td>
<td>Total Variance and Percentage of Total Variance</td>
<td>97</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>1. Schematic of Double Layer</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>2. Schematic of a Turbidimeter and a Nephelometer</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>3. Size Distribution for Kaolinite Flocs Measured Using a Microscope before HIAC Analysis (Top), by HIAC (Middle), and Using a Microscope after the Floc Had Passed Through the HIAC Sensor (Bottom)</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>4. Comparison of Floc Size Distribution as Measured by an Electronic Particle Counter and by a Photographic Technique</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>5. Methods for Plotting Particle Size Distribution: Relative vs. Absolute and Differential vs. Cumulative</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>6. Example of Particle Size Distribution</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>7. Methods for Plotting Particle Size Distribution: Particle Size Distribution, Number Distribution, Surface Distribution, Volume Distribution</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>8. Influence of Particle Size on Modified Collision Frequency ( (d_1=1\mu m) )</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>9. Ratio of Modified and Original Collision Frequencies for Brown</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>10. Ratio of Modified and Original Collision Frequencies for Fluid</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>11. Ratio of Modified and Original Collision Frequencies for Diff. Sed.</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>12. Ratio of Modified and Original Collision Frequencies for Total</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>13. Influence of Particle Size on Modified Collision Frequency ( (d_1=10\mu m) )</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>14.</td>
<td>Assignment of Aggregated Particle to Standard Sizes</td>
<td>67</td>
</tr>
<tr>
<td>15.</td>
<td>Comparison of Measured Results versus Lawler’s and Modified Model Predictions (820 mg/L)</td>
<td>72</td>
</tr>
<tr>
<td>16.</td>
<td>Comparison of Measured Results versus Lawler’s and Modified Model Predictions (417 mg/L)</td>
<td>74</td>
</tr>
<tr>
<td>17.</td>
<td>Comparison of Measured Results versus Lawler’s and Modified Model Predictions (915 mg/L)</td>
<td>76</td>
</tr>
<tr>
<td>18.</td>
<td>Residual (Difference between the Measured and Predicted) Plot (820 mg/L)</td>
<td>77</td>
</tr>
<tr>
<td>19.</td>
<td>Residual (Difference between the Measured and Predicted) Plot (417 mg/L)</td>
<td>78</td>
</tr>
<tr>
<td>20.</td>
<td>Residual (Difference between the Measured and Predicted) Plot (915 mg/L)</td>
<td>79</td>
</tr>
<tr>
<td>21.</td>
<td>Comparison of Measured Results versus Modified Model Predictions</td>
<td>82</td>
</tr>
<tr>
<td>22.</td>
<td>Comparison of Measured Results versus Modified Model Predictions (G=22sec⁻¹)</td>
<td>86</td>
</tr>
<tr>
<td>23.</td>
<td>Comparison of Measured Results versus Modified Model Predictions, Change in the Number Distribution</td>
<td>87</td>
</tr>
<tr>
<td>24.</td>
<td>Comparison of Measured Results versus Modified Model Predictions, Change in the Volume Distribution</td>
<td>88</td>
</tr>
<tr>
<td>25.</td>
<td>Comparison of Measured Results versus Modified Model Predictions (G=60sec⁻¹)</td>
<td>90</td>
</tr>
<tr>
<td>26.</td>
<td>Residual (Difference between the Measured and Predicted) Plot (G=22 sec⁻¹)</td>
<td>91</td>
</tr>
<tr>
<td>27.</td>
<td>Residual (Difference between the Measured and Predicted) Plot (G=60 sec⁻¹)</td>
<td>92</td>
</tr>
<tr>
<td>28.</td>
<td>Frequency Distribution of Modified Model Predictions</td>
<td>100</td>
</tr>
<tr>
<td>29.</td>
<td>Convergence Characteristics of Monte Carlo Simulation with Modified Model (Third Compartment)</td>
<td>101</td>
</tr>
</tbody>
</table>
Figure page

30. Probability Distribution of N/No at Third Compartment ......................... 103

31. Relationship between Floc Density and Size ...... 110
CHAPTER I

INTRODUCTION

One of the primary purposes of a water treatment plant is the removal of solids. The main processes used to achieve this end are rapid mixing, flocculation, sedimentation, and filtration. The proper operation of a treatment plant depends on the effectiveness of these processes in removing particles. Many contaminants in water such as bacteria, viruses, metals, and other pollutants are either particles themselves or are adsorbed on particles. Therefore, the removal of these pollutants depends on the removal of particles. Traditionally, turbidity has been the indicator of the effectiveness of particle removal during water treatment. This indicator does not provide enough useful information to characterize the removal of the pollutant they carry; because this information comes from the indirect measurement of particulate material based on the light scattered by particles. To some extent, the emphasis on measurement of turbidity alone biases the investigator toward improvement of the physical parameters of the system. In addition, large changes in the particle size distribution during flocculation or sedimentation do not produce corresponding changes in turbidity, but do influence relative size of the particles (Lawler and
Wilkes, 1984). Various researchers have mentioned that particle size distribution is reliable for evaluating a flocculation process (Treweek and Morgan, 1977; Tate and Trussell, 1978; Akers, 1987; Lawler and Wilkes, 1984; Kuo et al., 1988). An efficient and effective water treatment plant design method based on removal of particles is needed. This study will investigate and model the changes in the number and size distribution of particles as they occur in the flocculation basin of a water treatment plant.

Flocculation is one of the primary unit processes used in a water treatment plant. In flocculation, particles in water are subjected to a combined physical/chemical system. Flocculation changes the size distribution of particles from a large number of small particles to a small number of large particles for removal in later processes. Little work concerning the joint physical and chemical nature of this system as it relates to particle size distribution has been published. In addition, only a few studies comparing predicted changes in particle size distribution against actual treatment plant performance have been reported. Lawler and Wilkes (1984) tested a model considering the physical system, which was based on the fundamental work of Smoluchowski (1917), against results from an actual water treatment plant. Under different operational conditions, the model predicted changes in either the small or large particles, but not both. The authors concluded that the model was too simple to reflect reality from a microscopic
viewpoint and not accurate enough to use routinely in design. The overall objective of this study is to make an attempt to develop a model that shows more realistically what happens to particles during flocculation by incorporating the mechanisms which underlie the process. A more realistic model might alleviate problems of design (over-design or insufficient capability) and operation (poor or inefficient performance). Verification of the model by testing it against data obtained from actual water treatment facilities will be made. Uncertainty analysis, sensitivity analysis and Monte Carlo simulation, will be applied to the model to assess the relative contributions of input parameters to uncertainty in the model and to determine the safety factor to be used with the model prediction in design. It is hoped the model will provide a tool to improve understanding of the process as well as the efficiency of the overall water treatment process.

The following list sets out the specific objectives of this modeling study:

1. Incorporating of interparticle forces (chemical system) to transport mechanisms (physical system) between particles.

Interparticle forces: Hydrodynamic Forces
   Electrostatic Forces
   Van der Waals' Forces.

Transport mechanisms: Brownian Motion
   Fluid Shear
Differential Sedimentation.

2. Consideration of floc (particle aggregates) break-up

3. Consideration of the density and shape effects of floc which are varied by the flocculation process.

4. Consideration of velocity gradients in the actual flocculation basin.

5. Verification of the model by different particle count techniques such as an electronic particle counter and an optical technique.

6. Uncertainty analysis of the model.
CHAPTER II

LITERATURE REVIEW

Introduction

Flocculation is an important step for the removal of finely divided particulate matter which, due to its small size, is difficult to remove in an economical time frame by sedimentation and filtration. If the particles to be removed are too small for effective separation, their size can be increased by causing them to form aggregates. An understanding of flocculation theory and previous related work is important in order to accomplish the objectives of this research.

Terminology

There are different terms used to describe the process of particle destabilization, transport and aggregation in water treatment. Commonly, two steps describe the forming of aggregates. The first step is to effect destabilization of particles. The second step is to transport particles for inter-particle contact.

O’Melia (1978) has used the term coagulation to describe both the destabilization and transport steps, whereas Gregory (1989) has used flocculation as a term
covering all steps involved. The two terms are often used interchangeably. Others use coagulation to describe aggregation due to electrolytes and flocculation to describe aggregation due to polymers (Stumm & Morgan, 1981). Montgomery (1985) used coagulation to describe destabilization and flocculation to represent transport steps. In this work, the term flocculation will be used to cover the overall process of aggregation.

Destabilization Mechanisms

The destabilization of contaminants, which usually occurs by means of chemicals that are added in the rapid mix reactor, is followed by provisions for particle contacts. Particle contacts are achieved in the rapid mixing, flocculation, sedimentation, and filtration portions of conventional water treatment. Destabilization mechanisms include compression of the electrical double layer, charge neutralization, formation of sweep floc and inter-particle bridging. The following short discussion of the destabilization mechanisms is taken from Montgomery (1985) and Gregory (1989).

Double layer compression occurs when ions of opposite charge to the particles are concentrated in the solution layer that is immediately adjacent to the particle. As a result, the electric potential that is projected into the bulk solution is mitigated. A schematic of the double layer is shown in Figure 1. As depicted in Figure 1, increasing
Figure 1. Schematic of double layer. (a) Effect of increasing concentration of indifferent electrolyte. (b) Reversal of potential by specific adsorption (Montgomery, 1985).
the ionic strength compresses the double layer, causing a
decrease in its thickness. The potential is determined by
an experimental method, particle electrophoresis. Particle
electrophoresis can be used to calculate the zeta
potential. Reduction of the zeta potential (below \( \pm 20 \text{ mv} \))
permits close approach of particulates such that short
range attractive forces (London Van der Waals forces) can
act to produce collisions. In addition to double layer
compression, particulates can be destabilized by
electrostatic attraction, which occurs when surfaces are
oppositely charged. Quite often the reaction between a
coagulant and particulates is strong enough that the bulk
concentration of coagulant is extremely low. This can be
promoted by the adsorption of specific ions on the surface
of the particulates. This is shown in Figure 1. If charge
neutralization is responsible for destabilization, then a
stoichiometry exists between the coagulant and contaminant,
and restabilization of the complex can occur upon
overdosing. If excessive coagulant is added, the system is
restabilized.

Particulates can be removed by means of association
with coagulant solids that are intentionally formed during
water treatment processes. For example, aluminum in alum
hydrolyzes and forms an insoluble precipitate. The
hydrolysis products are strongly adsorbed by many particles
and, because of their positive charge, can cause charge
neutralization and reversal. This can explain some observed
flocculation behavior, but it is not the whole story. In many practical applications, the precipitation of aluminum hydroxide plays a very important role. When alum is added to water, the hydroxide forms fairly rapidly, initially as a colloidal precipitate, with subsequent growth to form quite large flocs. During this precipitation and growth, many of the particles originally present in the water become coated with hydrolyzed species or colloidal hydroxide particles and enmeshed in the growing flocs. The original particles are said to be swept out of suspension by the hydroxide precipitate. Such a mode of action is referred to as sweep flocculation.

Particle Counting

Particle counting is a relatively new analytical tool used in water treatment plants. To gain a better understanding of this technique, it is appropriate to compare it to the traditional method of turbidimetry. Traditional flocculation research has been based on indirect measures of flocculation efficiency, such as settled water turbidity and filtered water turbidity (Lawler, 1987). Direct measurement of the particle size distribution allows the investigator to study directly the destabilization and aggregation of the particles, rather than measuring the end result of flocculation’s effect on sedimentation and filtration. The direct measurement of changes in the particle size distribution (PSD) by
flocculation allows a better focus on the effect of changing variables related to the flocculation process. The motivation for monitoring changes in PSD is to optimize the growth of particles into a size range that can be efficiently removed by the sedimentation and filtration processes. The desired final particle size could be controlled by a knowledge of the effect of changing variables related to flocculation. In this section, turbidity and several particle counting methods are discussed. One of the hindrances concerning the use of particle counting for application in flocculation is the different particle size measurements yielded by different particle counting methods.

Turbidity

The turbidity of a sample may be measured either by its effect on the transmission of light, which is termed turbidimetry, or by its effects on the scattering of light, which is termed nephelometry (Sawyer & McCarty, 1978). A schematic diagram of both a turbidimeter and a nephelometer are shown in Figure 2. Both turbidity methods are based on a total particle effect. In Standard Methods (APHA, 1985), turbidity is defined as "an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample". Standard Methods (APHA, 1985) also mentions that correlation of turbidity with the weight concentration of
Figure 2. Schematic of a turbidimeter and a nephelometer
suspended matter is difficult because the size, shape, and refractive index of the particulates also affect the light scattering properties of the suspension. As mentioned earlier, turbidity measurements are determined by the total light scattered by particles. Hutchinson (1985) mentioned that this gives no information about the PSD present in the sample. Due to the complexities of light scattering by particles, there is not necessarily a correlation between the particle distribution and the total number of particles in two samples with the same turbidity. Turbidity indicates what happened but the additional information provided by particle counting is most useful in understanding the operation of flocculation.

Particle Counting Method

Several researchers (Lawler, 1984; Hutchinson, 1985; Kuo et al., 1988) recommended the use of PSD information in process design, process selection, and operation decisions. In order to obtain more accurate PSD, selection of an appropriate particle counting method is important. It is essential to realize the practical limitations which are inherent in any method of analysis which is available. Three particle counting methods will be discussed here.

Coulter Type Counter. The Coulter counter works on the principle that floc volume is correlated to the electrical resistance generated when the flocs pass through an
electric field (Li and Ganczarczyk, 1986). There are, however, a number of concerns when using the instrument with floc. The followings are major considerations:

- Floc breakage.
- Coincident counts causing larger particle measurement.
- Measuring only a fraction of the flocs.

**HIAC Particle Counter.** The HIAC is a light blockage particle counter. The particles to be counted are suspended in a fluid which has a different refractive index than the particles. The HIAC also has the limitation of floc breakage. Gibbs (1981) mentioned that "extensive floc breakage was indicated for all samples after they passed through the HIAC sensor". His work on flocs of kaolinite and natural suspended sediment noted floc breakage in the upper two thirds of the recommended size range for the HIAC sensing cell. This severely limits the use of the particle counter for measuring floc size distribution. The breakage observed by other researchers is shown in Figures 3 and 4. Figure 3 illustrates the breakup observed by Gibbs (1981) and Figure 4 shows the comparison between HIAC PSD and PSD generated using a photographic technique by Reed and Mery (1986). Employing a large size of sensing cell to reduce breakup might cause coincident counts of relatively small particles. Reviewing the literature concerning the Coulter and HIAC counters, the following aspects were noticed:
Figure 3. Size distribution for kaolinite flocs measured by using a microscope before HIAC analysis (top), by HIAC (middle), and by using a microscope after the floc had passed through the HIAC sensor (bottom) (Gibbs, 1972).
Figure 4. Comparison of floc size distribution as measured by an electronic particle counter and by a photographic technique; raw water (Δ and ▲) and after flocculation (□ and ■) (Reed and Mery, 1986).
No electrolyte is needed for the HIAC so there are no electrolyte effects.

Porosity is considered in the HIAC.

Floc breakage occurs in both counters.

Sample dilution is needed in both counters.

Coincident counts of small particles are possible in both counters.

A conclusion can be drawn from these aspects that HIAC is a more accurate particle counter than the Coulter counter.

**Optical Particle Counter.** A serious concern when using an electronic particle counter is floc breakup. It is important that the electronic particle counters which are commonly used to count and size flocculated material should be evaluated for floc breakup. For reducing breakup, the optical particle counting method is very useful. However, using an optical microscope also has limitations such as time requirements and bias caused by operator involvement. Recently, an automated image analysis system coupled with an optical instrument has been developed. The method works in the following manner: An optical video signal created by the blocking of the light path by the flocs is converted to a two-level electrical binary signal which is then processed in the preselected measurement module (Li and Ganczarczyk, 1986).

Two potentially limiting aspects of this method have to be discussed. The first potential limitation is the
optical system itself. In order to measure the wide range of flocs, the image analyzer must be connected to the correct type of optical system. The most important part is to select the magnification of the system microscope. A 16x objective was used for a study of activated sludge flocs (Li and Ganczarczyk, 1986). A 20x objective (system magnification of 474.6x) was used for alum treated floc by Hanson (1989). If a wide range of floc sizes exists in the sample, a single microscopic lens may not cover the whole size range.

The second potential limitation is image processing itself. There are several commercially available image processing systems. Li and Ganczarczyk (1986) used an OMNICON 3000 image processing system for studying activated sludge flocs. Hanson used a Lemont OASYS image processing for studying alum flocs. The resolution of the image is limited by the magnification of the digitized object and image processing. Another concern is the number of features which must be counted by the image processing to give a statistically sound sample. Hanson (1989) reported the following guidelines to accomplish his flocculation research goal:

- a goal of a minimum of 1000 features measured, if they can be measured in less than 20 frames,
- a goal of a minimum of 500 features measured, if they can be measured in 30 frames,
- an absolute minimum of 250 particles measured,
o a minimum of 100 particles in the particle class which represents the mode of the distribution,
o a minimum of 10 particles in any particle class important to the shape of the distribution curve.

Hanson's (1989) image system took 30 minutes to count 1000 particles, but the HIAC he also used would count 60,000 particles in the same time. According to Baba et al. (1988), PSD was calculated at a statistically reliable level in 5 to 20 minutes based on 2000-10,000 particles in 10 -15 images by using a high speed image processor.

PSD Application in Full Scale Water Treatment Plants

A few applications of PSD information for monitoring and controlling flocculation have been reported. Interestingly, two case studies in the open literature report the reduction of chemical cost (coagulant dosage) by about 30% by applying PSD information to their solids/liquid separation systems. The Southern Nevada Water System (SNWS) has used HIAC for obtaining PSD and applying the PSD to operate their direct filtration facilities (Hutchinson, 1985; Monscvitz and Rexing, 1983). Baba et al. (1988) reported a particle size monitoring system with image processing for a conventional water treatment system in Japan. This section will discuss how PSD has been used for water treatment applications.

The conventional water system operating in Japan was
equipped with underwater television cameras (Baba et al., 1988). The system used the geometric mean diameters (GMD) calculated from the PSD data to evaluate the degree of floc formation. If the monitored GMD was between 0.55-0.60 mm in the first basin, they considered this to confirm floc formation. They mentioned that conserving coagulant is possible when floc image monitoring offers an assurance of floc formation in the first basin. The value of GMD increased with increased coagulant doses. However, the average effective density of the floc decreased at increased coagulant dosages. The expected increase in the magnitude of the settling velocity resulting from an increase in floc size is not always observed because of the reduction in floc density, which tends to reduce the settling velocity. These results showed that turbidity in the sedimentation basin outlet increased when more coagulant than an optimum dosage was injected.

The Southern Nevada Water System uses on-line particle counting using HIAC as a means of controlling solid/liquid separation. This system is one of the world’s largest direct filtration facilities (slightly over 600 cfs, 1500 ML/d). The on-line particle counting monitors the effectiveness of the treatment process (chemical dosage control) and initiates the automatic backwashing of filters. The system is designed so that particle size number can be observed. The system measures the PSD by on-line particle counters in the raw water after
predisinfection, after flocculation, after filtration, and at the effluent of the treatment plant. By means of the above observations of the PSD through the plant, they try to produce an optimum size particle for optimum filtration with deep filter media penetration. Excess coagulation results in visible sweep flocs of such size that most of the particles remain on the surface of the media. As a general rule, surface straining becomes important when the ratio of particle size to filter media size is larger than 0.2 (Kuo, 1988). Therefore, assuming an average media size of 0.5 mm, flocs which are larger than 100 μm should not be applied to a filter. SNWS developed a mathematical evaluation of the filter’s performance, termed the filter performance index equation. The equation is expressed as follows (Monscvitz and Rexing, 1983):

\[
FPI = \frac{20 \times \frac{XRF}{XPC} \times 3.4HR}{75.7 \times \frac{2.44}{WW} \times \frac{1}{HL}}
\]

Where:

- \( FPI \) = Filter performance index
- \( XRF \) = Average rate of flow in ML/day throughout filter run
- \( XPC \) = Average effluent particle count throughout filter run
- \( HR \) = Total hours of filter run
- \( HL \) = Head loss in meters at backwash
WW = Total wash water in ML

According to Monscvitz and Rexing (1983) if a filter performance index falls below 0.5 standard deviations of the mean (mean value in the SNWS was 194.25), there is a fair chance that something is wrong with the filter (mudballs, defective loss of head meters, inadequate backwashing, and breakthrough).

A second index developed by Monscvitz and Rexing (1983) is the dosage optimization index.

\[ k = \frac{p}{\text{kg/ML}} \]

Where:

- \( k \) = the dosage optimization index
- \( p \) = percent particle removal between raw and finished water
- \( \text{kg/ML} \) = coagulant dosage/water treated

This index evaluates percent particle removal between raw and finished water in relation to solids removal chemicals (coagulants, filter aids). The index varied from 0.27 to 0.33 in the SNWS.

Representation of PSD Data

In this section, some graphical and mathematical presentations of PSD are discussed. The simplest type of graphical representation is to plot the particle number or particle volume vs particle size. Number of particles (\( \Delta N \), in \( \#/\text{cm}^3 \)) in increments of particle size (\( \Delta d \)) can be
plotted. The plotting of $\Delta N$ vs $\Delta d$ takes the form of a histogram. In a histogram, the width of rectangles represents the size interval (increment) and the height the number of particles in each size interval. But the histogram may show a distorted picture of the particle size distribution because the height of any interval is dependent on the width of that interval. The same sample (particle size distribution) measured with another instrument with different particle increments would yield a different histogram. To overcome this, other representations of particle size distribution have to be made. Part B and D in Figure 5 illustrate cumulative number distributions. A cumulative number distribution plot can be prepared to see how the flocculation process affects the total number of particles. But the cumulative number distribution plot might not clearly show what size range of particles are affected by flocculation. Several researchers (Lawler et al., 1980; Stumm & Morgan, 1981; Lawler, 1987) discussed manipulating the PSD data to characterize PSD in a given environment by using a PSD function. The slope of the cumulative number distribution curve (Part D of Figure 5), $\Delta N/\Delta d$, is known as a particle size distribution function, $n(d)$, i.e.,

$$\frac{\Delta N}{\Delta d} = n(d) \quad (\text{number/cm}^3\mu\text{m})$$

Each value of $\Delta N$ is divided by the increment of particle size ($\Delta d$) corresponding to the value log $d$. This division
Figure 5. Methods for plotting particle size distribution: relative vs. absolute and differential vs. cumulative (Lawler, 1987).
accomplishes normalization, so that the same sample (particle size distribution) measured by different instruments (with different increments of log diameter) would show the same distribution on this graph. The differential curves illustrate what size range contains most of the particles more clearly. The size distribution of particles in water can often be characterized by the power law shown below (Montgomery, 1985):

\[ n(d) = Ad^{-b} \]

Where \( A \) is a constant and \( b \) is the power law coefficient. A plot of \( \log(\Delta N/\Delta d) \) versus \( \log d \) yields a straight line with slope \( b \), if the size distribution of the particles follows the power law. Several examples of power law size characteristics for suspensions are shown in Figure 6. The slope of the power law function is a useful parameter to characterize the type of suspensions being treated. A decrease in the slope (smaller \( b \) value) with time or each successive basin indicates the reduction of particle number due to flocculation.

The absolute differential distribution of the above particle size distribution (\( \Delta N/\Delta d \)) can be improved by dividing each cumulative particle number value by the logarithmic interval of particle size associated with each size, i.e. \( \Delta N/\log d \). This division again accomplishes normalization, so that the same suspension measured by different instruments (with different values of \( \Delta \log d \)) would yield the same distribution on this graph. This
Figure 6. Example of particle size distribution: (△) effluent, sedimentation basin, pilot-activated sludge plant; (*) Lake Zurich, 40 m; (□) Deer Creek Reservoir, Utah, 20 m; (○) digested primary and secondary sludge (Montgomery, 1985).
division also means that the area under the graph between two values of log \( d \) equals the particle number concentration between those two sizes. The total particle number concentration equals the area under the graph between the smallest and the largest size. Assuming that the particles are spherical, volume distribution and surface distribution also can be expressed as the following equations:

For the surface distribution,

\[
\frac{\Delta S}{\Delta \log d} = \left( \frac{\Delta N}{\Delta \log d} \right) \frac{d^2}{\pi}
\]

For the volume distribution,

\[
\frac{\Delta V}{\Delta \log d} = \left( \frac{\Delta N}{\Delta \log d} \right) \frac{d^3}{6\pi}
\]

If this assumption is not true, the area is proportional to surface or volume concentration. Four type of PSD graphs are shown in Figure 7. These methods of presenting data are all used in the subsequent sections. Although these representations are mathematically related and contain the same information, each one can provide specific insight into certain phenomena more easily than others.
Figure 7. Methods for plotting particle size distribution: particle size distribution function, number distribution, surface area distribution, volume distribution (Lawler, 1987).
CHAPTER III

MODEL DEVELOPMENT

The mathematical analysis of changes in particle numbers (flocculation) was developed by Smoluchowski (1917). He calculated the number of collisions between particles in a given time due to Brownian motion and fluid shear. Lawler et al. (1980) used the discrete form of the Smoluchowski equation as the basis of their model. The discrete form of the equation is as follows:

\[
\frac{dn_k}{dt} = \frac{1}{2} \alpha \sum_{i,j=k} \beta(i,j)n_in_j - \alpha n_k \sum_{i=1}^r \beta(i,k)n_i
\]

(1)

Where:

\[i, j, k = \text{subscripts denoting particle size } i, j, \text{ and } k,\]
\[r = \text{the maximum allowable value of } i, j, \text{or } k \text{ in the model},\]
\[n = \text{particle number concentration (cm}^{-3} \text{)},\]
\[t = \text{time (s)},\]
\[\beta(i,j) = \text{the sum of collision frequency functions for particles size } i \text{ and } j, \text{ and}\]
\[\alpha = \text{collision efficiency factor, which is the fraction of predicted collisions that result in attachment.}\]
The notation \( i+j=k \) in the first summation on the right hand side of equation 1 indicates that the summation is taken over those collisions for which the particles of size \( i \) and size \( j \) are involved. This also represents the generation of particles of size \( k \) by the collision of any two particles of size \( i \) and \( j \). The factor \( \frac{1}{2} \) is introduced because each collision is counted twice (i.e. \( i+j=k \) and \( j+i=k \)) in the summation. The second term represents the loss of particles of size \( k \) due to their collision with any size \( i \) particles. Separate collision frequency functions, \( \beta(i,j) \), for interparticle contacts brought about by Brownian motion, fluid motion, and differential sedimentation have been developed and are expressed (Lawler and Wilkes, 1984), respectively, as:

for Brownian motion

\[
\beta_B(i,j) = \left( \frac{2kT}{3\mu} \right) \left( \frac{1}{d_1^2} + \frac{1}{d_j^2} \right) (d_i + d_j) \tag{2}
\]

for fluid motion

\[
\beta_f(i,j) = \frac{1}{6} (d_i + d_j)^3 G \tag{3}
\]

for differential sedimentation

\[
\beta_d(i,j) = \frac{1}{4} (d_i + d_j)^2 |w_i + w_j| \tag{4}
\]

Where:

\( d_i, d_j \) = diameters of particles of sizes \( i \) and \( j \),
\( k \) = Boltzmann’s constant,
The settling velocity of a particle is calculated as

\[ \omega_i = \left[ \frac{4g}{3C_{di}} \left( \frac{\rho_p - \rho_w}{\rho_w} \right) d_i \right]^{1/2} \]  \hspace{1cm} (5)

The drag coefficient \( C_{di} \) is estimated using the following relationship:

\[ C_{di} = \frac{24}{Re} \quad \text{if } Re < 1 \]  \hspace{1cm} (6a)

\[ C_{di} = \frac{24}{Re} + \frac{3}{Re} + 0.34 \quad \text{if } Re > 1 \]  \hspace{1cm} (6b)

Where:

\[ Re = \text{Reynolds number} \]
\[ = \omega_i d_i \frac{\rho_p}{\mu} \]  \hspace{1cm} (7)

\( \rho_p, \rho_w = \text{the densities of the particles and water,} \)
\( \omega_i, \omega_j = \text{the settling velocity of particle } i \text{ and } j. \)

When \( Re < 1 \), the settling velocity is the Stokes settling velocity, but when \( Re > 1 \), the settling velocity is found by the trial-and-error solution of the equations 6b and 7.

All of the collision frequency functions, \( \beta(i,j) \), were developed with assumptions that: (1) there exists no interparticle force, but particles coagulate when they collide (2) there is no break-up of aggregates (3) the density of particles and aggregates are constant (4) the particles are spherical in shape. Thus, the new model has to improve the collision frequency functions to account for
the interparticle forces in nature such as the repulsive hydrodynamic forces, the attractive van der Waals' forces (interparticle attraction), and electrostatic repulsion. Flocculation is accompanied by the break-up of aggregates in most actual systems so that a consideration of break-up should be incorporated. Particle (aggregates or flocs) density and porosity effects need to be considered in the modeling.

Consideration of Interparticle Forces

Collisions predicted by the model, equations 1 - 4, with the previously mentioned assumptions were overestimated due to the lack of consideration of the interparticle forces between the approaching particles. These effects have been studied mathematically using trajectory analysis, a technique in which the forces acting on two particles as they approach one another are calculated and the resulting motions are determined. Research in this area has been performed by several investigators. For equal size spherical particles in a shear flow, van de Ven and Mason (1976) calculated the trajectories considering the effects of hydrodynamic interaction, interparticle attraction, and electrostatic repulsion. Higashitani et al. (1982) and Adler (1981) calculated the collision efficiency for unequal size particles in a shear flow using a method similar to that of van de Ven and Mason (1976). Valioulis and List (1984)
reported the collision frequency efficiency considering van der Waals’ forces and hydrodynamic interaction of particles for shear flow by doing a regression on Adler’s data. Also, they reported interparticle forces effects for Brownian motion. Melik and Fogler (1984) investigated interparticle forces effects for differential sedimentation.

In this study, Valioulis and List’s (1984) modified collision frequency functions for Brownian diffusion and fluid shear will be employed. They incorporated the influence of interparticle forces by multiplying collision frequency functions by a collision frequency efficiency term, $\gamma(i,j)$. Collision frequency efficiency is a function of the sizes of the interacting particles and is unique for each transport mechanism. For differential sedimentation, Melik and Fogler’s (1984) results will be employed in this study by regression of their data. All of the following expressions only account for hydrodynamic and van der Waals forces so that electric double layer repulsion was not considered. Although electric double layer repulsion can be included in trajectory analysis, it is still not possible to account for all chemical interactions.

Approximations for the collision frequency efficiencies in Brownian diffusion accounting for hydrodynamic and van der Waals forces were reported by Valioulis and List (1984). These collision frequency efficiency factors depend on the Hamaker groups ($H/(KT)$) and the ratio of the particle diameters. In the calculation
of Hamaker group values, $H$ is the Hamaker constant, $K$ Boltzmann's constant and $t$ the absolute temperature. The collision frequency efficiency factors are estimated by the following equation:

$$\gamma_b = a + b\lambda + c\lambda^2 + d\lambda^3$$

(8)

Where:

$$\lambda = d_i/d_j, \quad d_i > d_j$$

In this equation, $a$, $b$, $c$, and $d$ are determined on the basis of the values of $H/(KT)$ and shown in Table I (Valioulis and List, 1984). Approximations for collision frequency efficiencies of fluid motion are estimated by the following equation where $a$, $b$, $c$, and $d$ are determined on the basis of the value of $H/(18\pi\mu d^3G_i)$ and shown in Table II (Valioulis and List, 1984):

$$\gamma_f(i,j) = \left[ \frac{a + b\lambda}{1 + c\lambda + d\lambda^2} \right] \left[ \frac{8}{(1 + 1/\lambda)^2} \right]$$

(9)

The value of Hamaker constant depends on the density and polarizability of the material (Stumm and Morgan, 1981). Values of the Hamaker constant for materials in water were reported by Visser (1977). In his paper, values of the Hamaker constant for polystyrene and kaolinite in water were $3.5 \times 10^{-20}$ and $2 \times 10^{-19}$ J, respectively.

Recently, Gregory (1989) mentioned that dense mineral particles have values toward the upper end of this range, whereas low density, especially biological, materials have quite low values. A value of $2 \times 10^{-19}$ J will be used in
<table>
<thead>
<tr>
<th>$H/(KT)$</th>
<th>$a$</th>
<th>$b \times 10^{-2}$</th>
<th>$c \times 10^{-4}$</th>
<th>$d \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$</td>
<td>0.21811</td>
<td>2.9593</td>
<td>-4.9962</td>
<td>2.6953</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.25878</td>
<td>3.0338</td>
<td>-5.3031</td>
<td>2.9043</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>0.31151</td>
<td>3.0339</td>
<td>-5.4760</td>
<td>3.0409</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>0.37254</td>
<td>2.9251</td>
<td>-5.4055</td>
<td>3.0318</td>
</tr>
<tr>
<td>1</td>
<td>0.44285</td>
<td>2.6954</td>
<td>-4.3310</td>
<td>2.4569</td>
</tr>
<tr>
<td>10</td>
<td>0.53814</td>
<td>2.2834</td>
<td>-4.3310</td>
<td>2.4569</td>
</tr>
<tr>
<td>$10^2$</td>
<td>0.70480</td>
<td>1.3481</td>
<td>-2.4753</td>
<td>1.3845</td>
</tr>
</tbody>
</table>
**TABLE II**

APPROXIMATIONS FOR COLLISION FREQUENCY EFFICIENCIES OF FLUID MOTION

<table>
<thead>
<tr>
<th>$H/(18\pi \mu a^3 G_1)$</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-2}$</td>
<td>-1.189</td>
<td>0.118</td>
<td>-3.431</td>
<td>0.331</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>0.766</td>
<td>0.007</td>
<td>-0.006</td>
<td>1.547</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>0.145</td>
<td>-0.0006</td>
<td>-1.137</td>
<td>0.775</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>0.017</td>
<td>-0.001</td>
<td>-1.442</td>
<td>0.557</td>
</tr>
</tbody>
</table>
the model because kaolinite in water is similar to dirt in water.

Corrections for collision frequency efficiencies of differential sedimentation were mentioned but not explicitly expressed by Melik and Fogler (1984). Therefore, regressions were conducted using their reported graphical results which showed the effect of particle ratio on the collision frequency factors for various values of the dimensionless parameter, $N_g$. The collision frequency efficiency factors are estimated using the following equation:

$$\gamma_d = a\lambda^2 + b\lambda + c$$  \hspace{1cm} (10)

Where:

$$N_g = \frac{\pi g \Delta \rho d^4}{3H} (\lambda+1)^2(\lambda-1)^2$$  \hspace{1cm} (11)

Where $g$ is the local acceleration of gravity and $\Delta \rho$ is the density difference between the particles and the suspending medium.

Consideration of Floc Density

The density and shape of the floc are some of the most important factors of concern in flocculation because they are related to the settling velocity distribution. The volume of the flocculated particles is larger than the sum of the volumes of primary particles due to inclusion of water, so that the assumption of constant density should be changed. Tambo and Watanabe (1979) illuminated some
TABLE III

APPROXIMATIONS FOR COLLISION FREQUENCY
EFFICIENCIES OF DIFFERENTIAL SEDIMENTATION

<table>
<thead>
<tr>
<th>$N_g$</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-1}$</td>
<td>-0.31818</td>
<td>0.26333</td>
<td>0.41267</td>
</tr>
<tr>
<td>$10^2$</td>
<td>-0.12386</td>
<td>0.11031</td>
<td>0.03282</td>
</tr>
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<td>$10^6$</td>
<td>-0.03106</td>
<td>0.02792</td>
<td>0.0027</td>
</tr>
</tbody>
</table>
characteristics of clay-aluminum flocs by experiments and model floc simulation. Recently, Li and Ganczarczyk (1989) investigated the relationship between floc density and size for inorganic and biological flocs. They concluded that the size-density relationship and the structure of the flocs depend on their physical and chemical characteristics. The relationship between floc density and size, the floc density function, was expressed as the following equation:

$$\rho_e = \rho_f - \rho_w = \frac{a}{d_f^k}$$

(12)

Where:

- $\rho_e$ = the floc effective density (g cm$^{-3}$)
- $\rho_f$ = the floc density (g cm$^{-3}$)
- $\rho_w$ = the water density (g cm$^{-3}$)
- $a, k$ = constant
- $d_f$ = the floc diameter (cm)

This equation indicates that the effective density of a floc decreases as the floc size increases. There is a transition point in the floc density and size relationship. At a point smaller than this transition point, density varied slightly and flocs were formed by a process similar to particle addition and were more compact than the larger ones. This fact suggests that flocs smaller than the transition point can be assumed to have a constant density. Larger than this point, the floc density function is applied. As shown in equation 12, the floc density function
is characterized by two constants, k and a. Tambo and Watanabe (1979) reported values of the a ($14 \times 10^{-4}$ from $2 \times 10^{-4}$) and k (0.9 from 1.5) from experiments, and $13 \times 10^{-4}$ and 0.9 from computer simulation, respectively. These constants of the floc density function for clay-aluminum floc are not greatly affected by pH, agitation intensity, raw water alkalinity and small dosages of coagulant aids but are significantly influenced by the ratio of aluminum ion concentration dosage to the suspended particle concentration (ALT ratio). The relationship between the ALT ratio and the constants, k and a at a neutral pH can be expressed as the following linear equations:

\[
a = -0.00126 \log(\text{ALT}) - 0.00106 \tag{13}
\]

\[
k = 0.4854 \log(\text{ALT}) + 1.885 \tag{14}
\]

Where ALT is the ratio of aluminum ion concentration dosed to suspended particle concentration. The above equation 14 shows that an increasing aluminum ion concentration dosage relative to suspended particle concentration considerably increases the absolute value of the exponential constant k. Thus, the floc density at a fixed size increases as ALT decreases.

The decreased floc density with increased floc size implies that the porosity of floc increases as the floc size increases. The porosity of the floc describes the open space in floc occupied by water. The space indicates that the flow streamlines could cross the floc. The following are expressions obtained by the regression of Adler's
(1981) tabulated numerical results for fluid motion. For
differential sedimentation, expressions reported by Adler
(1981) are used to account for the open space in porous
floc:
For fluid motion
\[ \psi_f = 1.6185 \exp(-0.4902\xi) \]  \hspace{1cm} (15)

Where:
\[ \xi = \frac{d_i}{\bar{P}^{1/2}} \]
\[ p = \frac{c^2}{18} \left[ 3 + \frac{4}{1-e^{-3\left(\frac{8}{1-e^{-3}}\right)^{1/2}}} \right] \]
\[ c = \frac{1}{20} d_i \]
\[ e = \frac{\rho_p - \rho_f}{\rho_p - \rho_w} \]

For differential sedimentation
\[ \psi_d(i,j) = 1 - \frac{b}{\xi} - \frac{a}{\zeta} \]  \hspace{1cm} (16)

Where:
\[ a = -\frac{1}{\zeta}\left(\xi^5 + 6\xi^3 - \frac{\tanh\xi}{\xi}\right)(3\xi^5 + 6\xi^3) \]
\[ b = \frac{3\xi^3}{\zeta}\left(1 - \frac{\tanh\xi}{\xi}\right) \]
\[ \zeta = 2\xi^2 + 3 - \frac{3\tanh\xi}{\xi} \]

The above equations are used when the value of \( \xi \) is smaller...
When the value of $\xi$ is larger than 50 (when porosity, $e$, is less than 0.5), the collision efficiency, $\psi$, approaches 0 and when the value of $\xi$ decreases to 0 (when porosity, $e$, is close to 1), the collision efficiency, $\psi$, approaches 1.

Consideration of Floc Shape

During flocculation, particle aggregates and flocs are generated. The generated aggregates have irregularly shaped forms. Because of the irregular shape, the collision frequency function needs to be modified to include the shape effects.

The total particle volume consists of the raw water particle, together with the dissolved organic carbon (DOC) and coagulant absorbed on the particle. Wiesner and Mazounie (1989) suggested that particle volume concentration and floc volume concentration could be related by using the following equation:

$$V_{\text{floc}} = a \phi_t^{3/D}$$

(17)

Where:

$V_{\text{floc}}$ = floc volume concentration  
$a$ = constant  
$\phi_t$ = floc volume  
$= \phi_p + \phi_{Al} + \phi_{doc}$  
$\phi_p$ = raw particle volume  
$\phi_{Al}$ = coagulant added
\( \phi_{doc} = \text{DOC adsorbed} \)

\( D = \text{the fractal dimension} \)

They reported a fractal dimension of 2.3 for ferric chloride floc and 1.4 to 1.7 for aluminum floc. Comparison of these values shows that the ferric chloride flocs have a much less open structure. The fractal dimension represents the shape of floc used in the simulation of floc growth. A solid, three-dimensional body has a mass which depends on the third power of some characteristic length (such as the diameter of a sphere), so that a log-log plot of mass against size would give a straight line with a slope of three. When such plots are made for aggregates, lower slopes with noninteger values are found. The slope of the line is known as the fractal dimension, \( D \) (Gregory, 1989). Li and Graczarczyk (1989) determined the fractal dimension of aggregates formed in water and wastewater treatment processes by computer simulation and compared the result with literature values. According to them, the settling velocity, density, and mass of aggregates can be expressed in terms of the fractal dimension.

\[
\begin{align*}
    v & \propto d^{0.1} \\
    \rho & \propto d^{0.3} \\
    M & \propto d^0
\end{align*}
\]

The fractal dimension contains information on both the density and the shape of the floc in given physical and chemical environments and can be useful in comparing flocs of different origins and interpreting simulations of floc.
growth.

The above discussion suggests that resulting floc size, when two particles or flocs collide, is larger than the sum of the colliding particles' diameters. Assume that particles of diameter, d_i and d_j are colliding. The volumes of these particles are \( \phi_i \) and \( \phi_j \), respectively. If we use particle size distribution of raw water, we need to consider the increased diameter caused by the adsorbed DOC and coagulant amount added during rapid mixing. However, data concerning the proportional constant (a) and the fractal dimension (D) have not been fully reported. More research or another approach is needed to obtain this type of information. Coagulated floc consists of four components, namely, suspended particles in the raw water (\( \phi_p \)), hydrolyzed aluminum (\( \phi_{Al} \)), DOC adsorbed (\( \phi_{doc} \)) and water entrapped during floc growth. The hydrolyzed aluminum and DOC are adsorbed on the surface of the suspended particles. Therefore, the main components which make up floc size are divided into two parts as the solid part and void part (water part). The following relationships can be obtained:

\[
V_f = V_s + V_w \quad \text{(18)}
\]

\[
\rho_f V_f = \rho_s V_s + \rho_w V_w \quad \text{(19)}
\]

Where:

- \( V_f \) = the volume of floc
- \( V_s \) = the volume of the solid part
- \( V_w \) = the volume of the water part
\[ \rho_f = \text{the density of floc} \]
\[ \rho_s = \text{the density of solid part} \]
\[ \rho_w = \text{the density of water} \]

The volume of floc can be expressed by the following equation:

\[ V_f = k_1 d_f^3 \quad (20) \]

Where \( k_1 \) is constant. The volume of solid part can be found from the floc size and density relation of equation 11.

\[ (\rho_s + \rho_w)V_f = \rho_s k_2 d_s^3 + \rho_w (k_1 d_f^3 - k_2 d_s^3) \quad (21) \]

\[ \rho_s = \frac{(\rho_s - \rho_w) d_s^3}{d_f^3} = a d_f^{-k} \quad (22) \]

\[ d_s = \left( \frac{k_2}{k_1} \frac{\rho_s - \rho_w}{a} d_s^3 \right)^{\frac{1}{3-k}} \quad (23) \]

Where \( k_2 \) is constant and \( d_s \) is the volume equivalent diameter of the solid part. The above equation can be expressed using the fractal dimension, \( D \), as follows:

\[ d_f = \varphi^{1/D} d_s^{3/D} \quad (24) \]

Where:

\[ \varphi = \frac{k_2}{k_1} \frac{\rho_s - \rho_w}{a} \]

When two flocs collide, the resulting floc size is larger than the sum of colliding floc diameters. However, the mass of flocs would be conserved. In this study, conservation of floc solids rather than volume will be incorporated using volume equivalent diameter of the solid
part of the floc. According to several researchers (Reed and Mery, 1986; Jiang and Logan, 1991), the collision frequency of irregular shape floc, fractal floc, is greater than that of spherical floc. The increased chance of collisions are accounted by using the floc diameter, $d_f$, in calculating the collision frequency function, $\beta(i,j)$. The collision frequency efficiency, $\gamma(i,j)$, is calculated by also using the volume equivalent diameter of the solid part. In this modeling study, the volume equivalent diameter is set equal to $(k_2/k_1)d_m$, where $d_m$ is the size of particle measured by the particle counter.

**Consideration of Floc Break-up**

In existing models, aggregate size continues to grow infinitely as there is no upper size to limit the growth of the aggregates. Aggregation is accompanied by the break-up of some of the aggregates in all practical systems so that a consideration of break-up should be employed. Two floc break-up mechanisms (erosion and fragmentation) are believed to be occurring simultaneously in shear flow (Pandya and Spielman, 1982, Lu and Spielman, 1985. Akers et al., 1987). Several models for floc break-up mechanisms have been reported, such as the maximum stable aggregate size model, displacement model, number concentration model, and statistical model (Brown and Gratz, 1987). Each model has advantages and disadvantages. In this study, the maximum stable aggregate size model will be used. Reasons behind
choosing this model are (1) its simple description and (2) the fairly large amount of information on this model in the literature. Above all, approximate possible maximum sizes of floc can be initially guessed during the particle size distribution process for initial input data and then easily changed after comparing simulated particle size distribution data and actual flocculated particle size distribution data. The model which depends on shear is as follows, (Françoïs, 1987):

$$d_{\text{max}} = r'G'$$

Where $d_{\text{max}}$ is the maximum stable floc size, $r'$ and $r$ are characteristic constants, and $G$ is velocity gradient. A literature survey of the experimentally and theoretically obtained values of the constant, $r$, were reported by Françoïs (1987). The values of $r$ varied from 0.3 to 1 but values of $r'$ were not reported. For an estimation of the maximum stable floc size, values as a function of velocity gradient recently reported by Glasgow and Kim (1989) can be used.

In the modeling conducted for this study, a procedure which has a maximum floc limit will be employed to prevent the permanent formation of oversized flocs. The procedure was introduced by Koh (1987). He called the procedure a zero collision efficiency approach. The approach is to make the collision efficiency function zero for all possible collisions resulting in an aggregate size greater than the limiting size. This approach is to view oversized flocs as
unstable, subjected to immediate break-up from the hydraulic stresses of the fluid motion. The zero collision efficiency factor, $\delta(i,j)$, is expressed as follows:

$$\delta(i,j) = \left(1 - \frac{d_i + d_j}{d_{\text{max}}} \right)^r \quad 3 < r < 8$$  \hspace{1cm} (25)$$

By obtaining the expressions of collision frequency efficiencies, $\gamma(i,j)$ for Brownian motion, $\gamma(i,j)$ and $\psi(i,j)$ for fluid motion and differential sedimentation, the modified collision frequency functions are represented as follows:

$$\beta_b'(i,j) = \beta_b(i,j) \gamma_b(i,j)$$ \hspace{1cm} (26)

$$\beta_f'(i,j) = \beta_f(i,j) \left[ \gamma_f(i,j) + \psi_f(i,j) \right]$$ \hspace{1cm} (27)

$$\beta_d'(i,j) = \beta_d(i,j) \left[ \gamma_d(i,j) + \psi_d(i,j) \right]$$ \hspace{1cm} (28)

The expression of $\gamma(i,j) + \psi(i,j)$ describes how the collision efficiency, $\gamma(i,j)$, decreases due to hydrodynamic effect, but $\psi(i,j)$ increases due to porosity effect. The value of $\gamma(i,j) + \psi(i,j)$ is not larger than 1 so that the modified collision frequency function, $\beta'(i,j)$, predicts less collision frequency than the original function, $\beta(i,j)$.

The zero collision efficiency factor, $\delta(i,j)$, is multiplied by the sum of collision frequency functions to account for the particle break-up process

$$\beta_{\text{sum}}'(i,j) = \delta(i,j) [\beta_b'(i,j) + \beta_f'(i,j) + \beta_d'(i,j)]$$ \hspace{1cm} (29)$$
Consideration of Velocity Gradient

The velocity gradient (or mean shear rate) $G$ could be calculated from the power input $P$ to a tank of volume $V$:

$$G = \sqrt{\frac{P}{\mu V}}$$  \hspace{1cm} (30)

Where $\mu$ is the fluid viscosity. The velocity gradient in flocculation could be calculated from the energy input or energy dissipation in the basin and the paddle configuration of the flocculator. The procedure for calculating the mean velocity gradient for mechanical stirring with paddle flocculators is described elsewhere (Reynolds, 1982). From the procedure set out in Reynolds, the following equation is obtained:

$$G = \left( \frac{C_d A \rho_w v_r^3}{2 \mu V} \right)^{1/2}$$  \hspace{1cm} (31)

Where:

- $A$ = paddle cross-sectional area in a plane perpendicular to its direction of motion
- $C_d$ = coefficient of drag
- $\rho_w$ = density of the water
- $\mu$ = absolute fluid viscosity
- $V$ = volume of reactor
- $v_r$ = relative velocity of the paddle with respect to the fluid

The relationship of velocity gradient to energy dissipation
rate, $\varepsilon$, has been given somewhat different terms. Dentel et al. (1985) summarized various relationships as part of a literature review. A notable difference between the relationship is the proportional constant, $\omega$, shown below:

$$G = \sqrt{\frac{P}{\mu V}} = \omega \sqrt{\frac{\varepsilon}{v}}$$  \hspace{1cm} (32)

Where $v$ is the kinematic viscosity. The value of $\omega$ ranges from 0.49 to 9.73. Koh (1984, 1987) proposed a compartmentalized model for batch flocculation in turbine stirred tanks under various flow conditions. He mentioned that the effective mean shear rate for flocculation was not the same as the mean value obtained from power input per unit mass; rather, it is equal to the volume average value obtained from the first moment of the shear rate distribution. He proposed the following expression:

$$G_1 = \sqrt{\frac{\varepsilon_1}{v}}$$  \hspace{1cm} (33)

Where:

$G =$ the velocity gradient in a compartment 1
$\varepsilon_1 =$ the local mean rate of energy dissipation
$v =$ the kinematic viscosity

According to Koh, the volume average shear rate of flocculation could be approximated by three velocity gradients as shown below:

$$sv = V_1G_1 + V_2G_2 + V_3G_3$$  \hspace{1cm} (34)

Where:

$s =$ dimensionless volume average shear rate
$V_1, V_2$, and $V_3$ = The volume of impeller zone, bulk zone, and dead zone respectively

A basin is approximated by three compartments, each perfectly mixed and of uniform shear rate (velocity gradient). After he studied various multi-compartment models, he concluded that a single-compartment stirred tank incorporating the effective shear rate, $G_{eff}$, was adequate for predicting flocculation rates when collision efficiencies were small. The effective shear rate, $G_{eff}$, is defined as follows:

$$G_{eff} = sG$$

(35)

The parameter $s$ is highly dependent on geometry. Koh tabulated the value of $s$ for various geometries of turbine stirred tanks. He also reported a comparison between the effective shear rates in stirred tanks and those in other systems normally used for flocculation. For paddle-blade mixed systems, the values of 0.32 and 0.45 for parameter $s$ were reported. However, paddle dimensions were not reported. For incorporating $s$ into the new model, the average value of 0.39 will be used.

Consideration of Flow Pattern

Hydraulic residence times of the actual flocculation basins affect the degree of flocculation considerably. Residence time characteristics of basins can be evaluated as plug flow, mixed flow, and dead space characteristics. Residence time can be expressed as follows (Hudson, 1981):
1 - F(t) = e^{-\frac{1}{((1-P)(1-m))} \left[ \frac{t}{T} - F(1-m) \right]}

(36)

Where:

F(t) = fraction of the fluid retained in the flocculator for a duration less than time t

T = computed residence time

= Q/V

Q = rate of flow

V = flocculator basin volume

P = fraction of active flow volume acting as plug flow

m = fraction of total basin volume that is dead space

t = time

In order to get information about flow patterns, dead space, and detention time, a tracer study is required. In case there is no available information about flow pattern, the flocculation basins are assumed to be ideal continuous stirred tank reactors (CSTR). The flow patterns for a series of equal size CSTR's in series can be described with the following expression:

1 - F(t) = \left[ 1 + \frac{t}{T} + \left( \frac{t}{T} \right)^2 \right] + \ldots + \left( \frac{t}{T} \right)^{n-1} \left\{ \exp \left( -\frac{t}{T} \right) \right\}

(37)

Time corresponding to the F(t) values can be determined for each flocculator basin. To obtain the particle size distribution of each flocculator, the particle size
distribution calculated at values of $F(t)$ equal to 0.2, 0.4, 0.6, 0.8, and 0.975 are averaged.

Summary

The flocculation model was modified by incorporating terms for interparticle force, floc density, floc shape, floc break-up, and effective velocity gradient into the collision frequency functions. The flow pattern of the flocculation basins is incorporated using $F(t)$. The effects of factors incorporated into the collision frequency functions on the collision frequency are summarized in Table IV. The interparticle force, floc break-up, and effective velocity gradient affect to decrease the collision frequency. Whereas, the floc density and floc shape causes an increase in the collision frequency. With the modified collision frequency functions, the flocculation model calculates particle size distribution at 0.2 increments of the $F(t)$ value and averages the calculated particle size distributions.
**TABLE IV**

EFFECTS OF THE FACTORS INCORPORATED INTO THE COLLISION FREQUENCY FUNCTIONS ON COLLISION FREQUENCY

<table>
<thead>
<tr>
<th>factor</th>
<th>expression</th>
<th>effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>interparticle forces</td>
<td>$\gamma(i,j)$</td>
<td>decrease</td>
</tr>
<tr>
<td>floc density</td>
<td>$\psi(i,j)$</td>
<td>increase</td>
</tr>
<tr>
<td>floc shape</td>
<td>$d_f$</td>
<td>increase</td>
</tr>
<tr>
<td>floc break-up</td>
<td>$\delta(i,j)$</td>
<td>decrease</td>
</tr>
<tr>
<td>effective velocity gradient</td>
<td>$s$</td>
<td>decrease</td>
</tr>
</tbody>
</table>
CHAPTER IV

MODEL SIMULATION

Comparison of Collision Frequency Functions

Comparisons between the original collision frequency function, $\beta(i,j)$, and the modified collision frequency function, $\beta'(i,j)$, have been conducted. For development of comparisons, one particle is held constant at 1 $\mu$m in case 1 and 10 $\mu$m in case 2 and the other particle size is varied. Reasons behind choosing the two particle constants are:

1) 1 $\mu$m size particle is in the size range that contains most of the clay minerals in raw water (Stumm and Morgan, 1981).
2) Brownian diffusion collision is the primary mechanism to flocculate particles with a size less 1 $\mu$m.
3) 10 $\mu$m size particle is in the intermediate range which can produce large settleable floc.
4) Fluid shear and differential sedimentation collision can be the predominant mechanisms of flocculation of the 10 $\mu$m size particle.

Simulations have been made with values of typical operating parameters:

\[ G = 22 \text{ sec}^{-1} \]
temperature = 20 °C
particle density = 2.65 g/cm³
Hamaker constant (H) = 2.0 x 10⁻¹⁹ J

Case 1. Constant 1 μm Particle Size

The values of modified collision frequency functions are shown in Figure 8. Figure 8 shows that fluid shear and differential sedimentation are the predominant mechanisms for flocculation. The ratio of the modified collision frequency function, β'(i,j), versus original collision frequency function, β(i,j), for Brownian, shear, and differential sedimentation as a function of particle size are calculated and plotted in Figures 9, 10, and 11. The modified Brownian collision frequency function varied from 0.63 to 7.6 times of the original Brownian collision frequency function. Until the particle size reaches log d = 0.9 (d = 7.94 μm), the modified Brownian collision frequency function predicts less collision frequency than the original Brownian collision frequency function due to the hydrodynamic effects. However, above log d = 0.9, the modified Brownian collision frequency function predicts more collision frequency due to the increased floc diameter and irregular shape or fractal dimension of the floc (see equation 24). For shear, the modified collision frequency function underpredicts the original collision frequency, reaching a minimum value at log d = 1.0 (d = 10 μm), until log d = 1.42 and then predicts collision frequency more
Figure 8 Influence of particle size on modified collision frequency 
($d_1=1 \mu m$)
Figure 9. Ratio of modified and original collision frequencies for Brownian
Figure 10. Ratio of modified and original collision frequencies for fluid
Figure 11. Ratio of modified and original collision frequencies for differ sed.
increased collision frequency is due to the increasing porosity and floc diameter as the particle size grows. The ratio of the modified shear collision frequency function versus the original shear collision frequency function varies from 0.03 to 170. The ratio of the modified differential sedimentation collision frequency versus the original differential sedimentation collision frequency varies from 0.38 to 56. Figure 12 shows the ratio of the modified total collision frequency function versus the sum of the three original collision frequency functions. The modified total collision frequency function represents the sum of three modified collision frequency functions multiplied by the zero collision efficiency term. As mentioned earlier, the zero collision efficiency term describes floc break-up. The value of maximum floc size was set to 200 μm in the zero collision efficiency term. Figure 12 shows that the ratio is 0.31 at log d = -0.03 and 1 at log d = 1.2. It reaches a maximum of 2.33 at log d = 1.71 and drops to 0 at log d = 2.3. The zero collision efficiency reduces the sum of the three modified collision frequency functions more as the particle size approaches the maximum floc size.

Case 2. Constant 10 μm Particle Size

Figure 13 shows the values of the modified collision frequency functions. As expected, differential sedimentation and fluid shear are the more predominant
Figure 12. Ratio of modified and original collision frequencies for total

\( \frac{B'_{b(i,j)}}{B_{b(i,j)}} \)

- \( d_i = 1 \) um
- \( d_i = 10 \) um

Log of Particle Diameter (microns)
Figure 13. Influence of particle size on modified collision frequency ($d_1 = 10\mu m$)
mechanisms for flocculation. The ratio varies from 0.63 to 4.3 for Brownian, 0.026 to 162 for shear and 0.15 to 54 for differential sedimentation, as shown in Figures 10, 11, and 12. The fluctuation observed at log d = 1 in Figure 11 is caused by $N_6$. When the particle ratio ($\lambda$) approaches 1, $N_6$ goes to zero. Therefore, the ratio of modified and original collision frequency approaches 1 because no hydrodynamic effect exists. When $\lambda$ is equal to 1, however, the collision due to differential sedimentation does not exist since the particles are settling at the same rate. The modified collision frequency function predicts less collision frequency for small particle sizes but more for large particle sizes. The total ratio shown in Figure 12 varied from 0.59 at log d = -0.03, 1 at log d = 1.61, 1.4 at log d = 1.83 and 0 at log d = 2.3.

Comparisons between the original collision frequency function and the modified collision frequency function show that the modified collision frequency function predicts less collision frequency in the region of small particle sizes and more collision frequency in the region of large particle sizes. Lawler and Wilkes (1984) mentioned that their model based on the original collision frequency function overestimated the flocculation process. According to Lawler and Wilkes, the proposed collision frequency function had to predict less collision frequency than the original frequency function prediction. According to Jiang and Logan (1991), however, the original collision function
must be modified to predict more frequent collisions in order to account for the fractal geometry of the floc. The modified collision frequency function takes into account hydrodynamic effects to reduce collision frequency. The modified collision frequency function also represents the increasing collision frequency by considering the increased floc diameters and the porosity effects.

Description of the Computer Model

A computer model has been developed to predict the change over time of the particle size distribution during actual flocculation, using the equation for flocculation, equation 1, and the modified collision frequency functions. The program was written in FORTRAN 77 language, and consists of one main program and 8 subroutines. The order of the subroutines is set out below:

1. Start
2. Initialize variables and read input data
   Subroutine INITVA
   Subroutine EFLOW
3. Calculate collision functions
   Subroutine BETACA
4. Preliminary calculation of logarithmic divisions of particle size
   Subroutine FRACCA
5. Manipulate data for initial data output
   Subroutine MASSSU
Subroutine MASSSU

6. Print initial data

Subroutine OUTPUT

7. Execute numerical method until \( T > T_{\text{max}} \)
solve differential equations by Runge-Kutta method

Subroutine STIFDI
evaluate the terms in differential equation

Subroutine DIFFUN

8. Manipulate data for output

Subroutine MASSSU

9. Print output

Subroutine OUTPUT

10. End

Subroutine INITVA initializes values needed throughout the program and is the point at which input is given to the program. Inputs include information on the liquid (temperature, viscosity, density), the suspension (density and particle size relationship, Hamaker constant, maximum particle size, and particle size distribution), flow pattern (velocity gradient, detention time, number of flocculators, and F curve) and other control parameters such as print control, numerical step size, and maximum time etc. Residence time distributions (F curve) of equal volume flocculators are calculated by Subroutine EFLOW. If available, an experimentally derived F curve also can be used in the program.

Subroutine BETACA evaluates the collision frequency
functions for the three modified collision mechanisms and sums them.

Logarithmic division of particle sizes are used to describe the PSD. All particles within one of the standard particle sizes that are equally spaced on the basis of the logarithm of their equivalent volume (density = 2.65 g/cm³) are assumed to have the same size. The logarithmic division describes adequately the behavior of smaller particles in the suspension. If all possible particle numbers are assigned in equal divisions of particle volume, a large fraction of the total particle number size reside in the small standard size ranges because of the large number of small particles. Equal divisions of particle size would result in an inadequate description of the behavior of smaller particles. To save computer memory space, it is also convenient to use logarithmic size divisions. However, with standard particle sizes that are equally spaced on the basis of the logarithm of the volume, the arithmetic sum of any two standard volumes does not produce another standard volume. By using subroutine FRACCA developed by Lawler et al. (1980), weighted fractions of the new particle are assigned to standard particle sizes. A method to account for this is illustrated in Figure 14. When particles of size i and j aggregate, one new particle of equivalent volume, \((V_i \text{ and } V_j)\), is formed; and this new particle has an equivalent volume between standard sizes \(k\) and \(k+1\). This is handled by assigning the fraction \(a/c\) of the new particle
Figure 14. Assignment of aggregated particles to standard sizes
to standard size $k$ and the fraction $b/c$ to size $k+1$. This manipulation accomplishes the use of only standard size. This also allows the equivalent particle volume to be conserved. Finally, the equivalent particle volumes are converted to particle volume (floc volume) via the relationship of particle size and density.

This system is valid for all combinations of particles except when the resultant particle volume is greater than the largest standard size. The particle volume which is greater than the largest standard size is controlled by the zero collision efficiency factor (equation 25). The zero collision efficiency factor is described in the model development section. The largest size could be chosen from the available data for maximum stable particle size.

Subroutine DIFFUN evaluates each of the two terms on the right hand side of equation 1 for each standard size. The combinations which yield a total volume between size $k$ and $k+1$ are dictated by the choice of the log increment between particle sizes. If the log of volume increments were not 0.09 (the log of diameter increments = 0.03), a different set of combinations would result in the formation of particles between size $k$ and $k+1$ so that subroutine FRACCA would need revision to reflect this change.

Subroutine STIFDI is used for obtaining approximate solutions to a system of ordinary differential equations with the initial particle size distribution. A 4th order Runge-Kutta method is used.
Subroutine MASSSU evaluates several parameters, such as total particle number, total particle volume, total particle mass, particle size distribution, particle volume distribution, number fraction remaining, volume average diameter, surface average diameter, and number average diameter for desired output prints. Subroutine OUTPUT is used to print desired output.

Comparison of Reported Experimental Results with Predictions of the Model

In order to use the model to compare predictions with reported experimental results, initial values for particle size distribution have to be supplied. The reported particle size distribution (PSD) was expressed in several ways. The new computer program is able to use particle size distribution function ($\Delta N/\Delta d$), and number of particles within logarithmic particle size interval ($\Delta \log V$, which, as mentioned earlier, is $0.09$ or $\Delta \log d = 0.03$). In order to use PSD information in different particle size intervals for the model input, data manipulation has to be done. The number of particles within the preestablished model particle size intervals is calculated by obtaining the linear regression equation for reported experimental particle number and particle size range.

Several sources (Metcalf & Eddy, 1979, Peavy et al. 1985, Valioulis & List, 1984) defined suspended solids as all particles with diameters larger than 1 $\mu$m. The portion
of total solids retained by a glass-fiber filter is defined as suspended solids (APHA, 1985). A portion of the particles smaller than 1 μm could be retained according to the latter definition. In this work, suspended solids are defined as all particles with diameters larger than 0.89 μm, because the particle size of 0.89 μm was the smallest particle size for which particle size distribution information was obtained for the model verification.

**Case 1. Davis Water Treatment Plant, Austin, Texas**

Lawler and Wilkes (1984) reported a flocculation model. Their model was tested against actual treatment plant performance in terms of particle size distribution. Required particle size distribution data from the flocculation process in the operating water treatment plant was measured by a Coulter counter. The following is a brief description of the treatment plant. A more detailed description is given in their paper (Lawler and Wilkes, 1984). The plant is located adjacent to Lake Austin which is the source of water for the plant. This plant has a 100 MGD capacity. It has nine flocculation and sedimentation units and three filters for each unit. Each of the nine flocculation basins is divided into three sub-basins in series, with the volume of each sub-basin increasing from the first to the third basin. The lake has an average hardness of 170 mg/L, as calcium carbonate, so one of the primary treatment objectives is to reduce this hardness to
approximately 70 mg/L. The softening process uses 95 mg/L lime, as calcium oxide (CaO), to reduce the hardness. Small doses of ferrous sulfate (2.5 mg as FeSO₄·7H₂O/L) are added as a coagulant.

Required input data for this modeling study was read from their Figures 10, 12, and 13 (Lawler and Wilkes, 1984). Their results were plotted as log of particle size distribution function ΔN/Δd (μm cm⁻³) vs log of particle diameter (μm). The possibility exists that errors could be made while reading their data from the reported figures in order to obtain the data (influent) required to test the model. Model comparison and verification was also made by reading their effluent data from their Figures 10, 12, and 13.

Figure 15 shows the predictions of the two models using the measured influent (820 mg/L) and effluent particle size distribution of the Davis Water Treatment Plant. Lawler’s model used α = 0.2, and the model developed as part of this research used α = 1. In Lawler’s model, low collision efficiency factors (α < 1) were necessary to compensate for an overprediction of particle growths by the model. Using the value of α = 1 removes the need to compensate for an overprediction of particle growths by the model and essentially means no correction factor in the modified model. Input for the maximum particle size used was 100 μm. The predictions of both models agree well with the measured results in the size region log d < 0.1 (d <
Figure 15. Comparison of measured results versus Lawler's and modified model predictions (820 mg/L)
1.6 μm). The modified model predicts a greater particle number in the region \( \log d > 0.1 \) than actual measured particle number, while the comparison between Lawler’s model predictions and the measured results show good agreement until \( \log d < 1.4 \). A notable discrepancy appears between Lawler’s model predictions and the measured results of particles larger than \( \log d = 1.6 \). At the largest size particle \( \log d = 1.85 \), a sudden peak point can be noticed using Lawler’s model. According to Lawler et al. (1980), his model used the largest size as a sink for the flocculation process so that volume was not lost from the upper end of the size spectrum. The modified model predictions show better agreement with the measured results in the region of large particle sizes.

Each model’s predictions for the smaller concentration case (417 mg/L) are shown in Figure 16. Both models’ predictions agree with the measured results in the range of the large particles instead of the small ones. Actual removal of small particles by flocculation was much greater than the two models predict. The modified model predicts slightly less flocculation than Lawler’s model in the region of \( \log d < 0.7 \). The prediction of Lawler’s model shows a similar trend as before with a sudden peak point and production of larger particles in the larger particle size region. The modified model predictions show similar distribution shape to the measured result in this region. The modified model predictions fit the measured results in
Figure 16. Comparison of measured results versus Lawler's and modified model predictions (417 mg/L)
this region again.

A last comparison was made using another, greater, concentration case (915 mg/L). The predicted particle size distributions of Lawler’s and the modified model are shown in Figure 17 along with the measured results. In the previous two cases Lawler’s model used \( \alpha = 0.2 \), but a value of \( \alpha = 0.1 \) provided much better agreement with the measured results in this case. This change indicates that Lawler’s model is sensitive to influent concentration. Using \( \alpha = 0.1 \), Lawler’s model overestimates the particle number until \( \log d = 0.95 \), then underestimates the particle number. However, the modified model consistently used \( \alpha = 1 \). Like the first case, the model predictions agreed with the measured result in the small particle size region, \( \log d < 0.1 \). The modified model predictions are in reasonable agreement with the measured results in the small particle size region as well as in the large particle size region.

For a closer comparison between Lawler’s model and the modified model predictions against the measured results, residual plots of the three previous cases (Figures 18, 19 and 20) were made. The y axis represents the difference between the measured and predicted values of the particle size distribution function. The x axis represents the value of particle size distribution. The symbol \( \triangle \) represents the difference between Lawler’s model prediction and the measured result, the symbol \( \circ \) shows the difference between the modified and the measured results. The residual plots
Figure 17. Comparison of measured results versus Lawler's and modified model predictions (915 mg/L)
Figure 18. Residual (difference between the measured and predicted) plot (820 mg/L)
Figure 19. Residual (difference between the measured and predicted) plot (417 mg/L)
Figure 20. Residual (difference between the measured and predicted) plot (915 mg/L)
are interpreted such that the more points cluster around \( y = 0 \) along the \( x \) axis, the more accurate the model predictions. The three residual plots show that Lawler’s model’s predictions are closer to the measured results in case of concentration of 820 mg/L because more residual points are located around 0 of the \( y \) axis. The two models’ prediction for 417 mg/L reveal comparable results. However, the modified model better predicted the measured results for 915 mg/L. Also residuals of the modified model predictions in all three concentration show no residual in the region \( \log d > 1.55 \). This means better prediction in this region.

Comparisons between the modified model predictions and the measured results show that the modified model underestimates the particle number within the intermediate particle size. The underestimation of particle number in this region requires investigation of the collision frequency function. The discussion of this fact will be undertaken in the discussion chapter.

**Case 2. Southern Nevada Water System**

This system (SNWS) supplies water to the cities of Las Vegas, North Las Vegas, Boulder City, Henderson, and to Nellis Air Force Base from the treatment plant at Lake Mead. The primary treatment process is directed at the separation of solids from the raw influent water. Chlorine or chlorine dioxide is added as a predisinfectant prior to
preparing particles for optimum coagulation. The primary coagulant used is aluminum sulfate (alum). After the alum is mixed with the plant influent, four stages of tapered energy flocculation occur prior to direct filtration. On-line particle counters measure the particle number and size in the raw water immediately after predisinfection, prior to flocculation, after flocculation (prior to filtration), after filtration, and in the plant effluent.

For model simulation, the particle number and size prior to flocculation were used as model input data while the particle number and size after flocculation were used as verification of model predictions. Flocculator influent and effluent particle counts, collected every 15 minutes for 5 consecutive days starting January 7, 1991 were obtained (Rexing, 1991). The average operating conditions of the flocculators during this 5 day period are as follows:

- number of flocculation basins: 4
- detention time: 3.9 minutes per basin
- coagulant dosage: 0.6 mg/L of ferric chloride
- temperature: 12.4 °C
- velocity gradient of each basin: 36, 29, 21, 14.5 G

Particle number was obtained in six discrete particle size ranges: 5-6, 6-10, 10-20, 20-40, 40-150 μm. In order to use these data for model simulation, the data were manipulated. The log of particle size distribution, \( \log(\Delta N/\Delta d) \), vs log of particle size was prepared and a
Figure 21. Comparison of measured results versus modified model predictions
linear regression was conducted (Figure 21) because the size distribution of particles in water is often characterized by the power law. No particles were reported in the range of 40-150 μm in the influent or effluent so this range was not used in the regression. The regression yielded the following power law equation with the correlation coefficient of 0.993:

$$\Delta N/\Delta d = 144543.977 d^{-3.49}$$

The input particle size distribution was prepared using the above equation. The predicted size distribution by the model is shown in Figure 21. The obtained effluent size distributions are also included for comparison. The measured total particle numbers in the influent and effluent were 471 and 404, respectively. The flocculation process in the SNWS resulted in 81.4% of the total particle number remaining. The model predicted 99.1% of the total particle number remaining. Comparison of the measured results and the model predictions show that the model predictions overestimate the total particle number remaining. The total particle number remaining of the measured results was calculated based on the particle size range from 5 μm to 40 μm whereas the total particle number remaining of the predicted was calculated based on the particle size range from 0.89 μm to 40 μm. Considering the narrow size range in the measured results, the model prediction greatly overestimated the total particle number remaining; in other words, the model prediction
underestimated the flocculation rate. The model here seems to underestimate the degree of flocculation at low concentration. However, close examination of the measured results show that the number of large particle sizes also decreases. This fact indicated the loss of particle number by sedimentation in the flocculation basin. This might be one explanation for the difference.

Case 3. Lab Data

The particle size distribution measured by an automatic image analysis system (AIA) was reported by Hanson and Cleasby (1990). The work was carried out in a bench-scale batch reactor. They conducted flocculation experiments using several different operating conditions. Three coagulants (alum, ferric sulfate and cationic polymer), two temperatures (5 and 20 °C) and several velocity gradients were used in their experiments. For the purpose of comparison between the results predicted by the modified model and the experimental particle size distribution measured by the AIA under different operating conditions, two of Hanson and Cleasby's (1990) data sets were used. The two data sets for the comparison of the model predictions were selected because these data sets were obtained by performing the experiment in triplicate and used for the baseline conditions for their study.

Experimental results were reported as the number of particles within discrete particle size ranges. The number
of particles was reported at the log diameter increment of 0.0765. The model developed here needed a number at the log diameter increments of 0.03. In order to obtain the required particle number at the increments of each log diameter of 0.03, a linear regression between each two particle numbers at log Δd in the cumulative number distribution plot was conducted. The total number of the particles measured was 0.3947E+7 and that obtained by the regression equation was 0.3949E+7.

The particle size distribution measured by the AIA after 0, 5, 15, 20, 25, 30 minutes of flocculation were reported. The experiments were conducted at an alum dosage of 5 mg/L, pH of 6.8, velocity gradient of 22 sec⁻¹, and temperature of 20 °C in a batch flocculator equipped with turbine impeller. Since the experiments were conducted in a batch reactor, the model did not consider the flow effects. The value of s, effective shear rate constant, used was 0.70. The value of 0.70 was used by Koh et al. (1987) for a turbine geometry batch reactor. The comparison between experimental results and the model predictions is shown in Figure 22. Figure 22 also shows Lawler’s model predictions using α=1 and 0.2. The modified model prediction fit the experimental results well except for the large particle sizes (log d > 1.2). The number and volume distribution (Figures 23 and 24) show the comparison more clearly. The number distribution shows that the model predictions underestimate the flocculation process in the intermediate
Figure 22. Comparison of measured results versus modified model predictions ($G = 22$ sec$^{-1}$)
Figure 23. Comparison of measured results versus modified model predictions, Change in the number distribution
Figure 24. Comparison of measured results versus modified model predictions, Change in the volume distribution.
particle size region. The volume distribution plot shows that the volume of the experimental results in the region of large particle sizes was much greater than the model predictions. The fact will be deliberated in the discussion chapter.

Figure 25 shows the comparison between the model prediction and the experimental results obtained under the same conditions as the previous case except \( G = 60 \text{ sec}^{-1} \). The number of particles in the model prediction is greater than the experimental result. The response of the model to increased \( G \) is less sensitive than that of the experiment. This might be caused by \( G \) itself. Several researchers (Cleasby, 1984; Glasgow & Kim, 1984; Clark, 1985; Amirtharajah & Trusler, 1986) have debated if \( G \) adequately reflects turbulence intensity.

The residual plots of two cases, \( G = 22 \) and \( 60 \text{ sec}^{-1} \) were prepared for a comparison between Lawler's and the modified model predictions (Figures 26 and 27). The discontinuities shown in the plots were caused by either no particle number measured or a greater residual value than the \( y \) axis value. Figure 26 shows that the predictions of modified model fit better than the predictions of Lawler's model using \( \alpha = 1 \) or 0.2 (\( \alpha = 1 \) means no correction factor). Either value for \( \alpha \) is inadequate in this case. It seems that selecting an appropriate value between 1 and 0.2 for \( \alpha \) would provide better agreement. The residual plot for \( G = 60 \text{ sec}^{-1} \) is shown in Figure 27. Here, the predictions of
Figure 25. Comparison of measured results versus modified model predictions (G = 60 sec⁻¹)
Figure 26. Residual (difference between the measure and predicted) plot (22 sec⁻¹)
Figure 27. Residual (difference between the measured and predicted) plot (60 sec⁻¹)
Lawler's model using $\alpha = 1$ are better fit. But the predictions of Lawler's model using $\alpha = 0.2$ more underestimates to a greater extent the flocculation process in this case than the predictions of the modified model.

Uncertainty Analysis

The uncertainties associated with the model input parameters are not quantifiable since every aspect of particle growth and breakup are not understood. Sensitivity analysis can be used to determine the magnitude of the change in the value of model output (prediction) resulting from a change in the value of model input parameters. The sensitivity to an input parameter, $p_k$, is examined by perturbing one input at a time. The sensitivity of model prediction to a input parameter is called the sensitivity coefficient, $S_i$, and is defined as the ratio of the observed change in the predicted number of particles of size $i$ ($\Delta n_i$) to $\Delta p_k$ (Wolff, 1990):

$$ S_i = (\Delta n_i / \Delta p_k) $$

(38)

$S_i$ is a partial derivative of the $i$ size particle number (ith dependent variable) with respect to the $p_k$. Normalized sensitivity coefficients can have the following form:

$$ SN_i = (p_k / n_i)(\Delta n_i / \Delta p_k) $$

(39)

The components of variance for each output variable $n$ are the percentage of output variance attributable to input $p_k$, computed in the following manner (Brown and Barnwell, 1987):
Var(n_i) = Var(p_k)(Δn_i/Δp_k)^2  \hspace{1cm} (40)

Where:

\begin{align*}
\text{Var}(n_i) &= \text{variance of output variable } n_i, \\
\text{Var}(p_k) &= \text{variance of a input variable } p_k,
\end{align*}

The term \text{Var}(p_k) can be transformed as follows:

\text{Var}(p_k) = (CV \times p_k)^2  \hspace{1cm} (41)

Where CV is the coefficient of variation for the input parameter. Total number uncertainty associated with input parameters can be expressed as follows:

\text{Var}_{\text{tot}}(n_{\text{tot}}) = \sum_{k=1}^{K} \sum_{i=1}^{N} \text{Var}(n_i)  \hspace{1cm} (42)

Table I lists model parameters selected to illustrate the sensitivity analysis. The coefficients of variation of varied parameters were determined based on the information reported by Cockerham and Himmelblau (1974). Obtaining the information on the characteristics of input parameters without effort is difficult, if not impossible. For this study, the same value of the coefficients of variation used by Cockerham and Himmelblau (1974), 0.0333, was applied to the parameters of concern in the model. Values in Table V are mean values of parameters used in this study. In this study, the mean values of parameters were selected to represent a typical case in the flocculation process and assumed that all parameters were mutually independent. Constants a and k in the equation of the effective particle density (equation 12) are 0.0013 and 0.9, respectively.
TABLE V
MEAN VALUES OF VARIED PARAMETERS

<table>
<thead>
<tr>
<th>Varied parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>velocity gradient : $G = 25 , \text{sec}^{-1}$</td>
</tr>
<tr>
<td>effective shear rate constant : $s = 0.39$</td>
</tr>
<tr>
<td>Hamaker constant : $H = 2 \times 10^{-19} , \text{J}$</td>
</tr>
<tr>
<td>maximum particle size : $D_{\text{max}} = 200 , \mu\text{m}$</td>
</tr>
<tr>
<td>effective particle density : $\rho_f = a/d^k$</td>
</tr>
<tr>
<td>particle size distribution : $n(d) = A , d^{-8}$</td>
</tr>
<tr>
<td>detention time of each flocculator : $D_t = 15 , \text{minute}$</td>
</tr>
</tbody>
</table>
Constant A from particle size distribution equation (power law) is found using the assumption of a total solid concentration of 100 mg/L. The constant A was calculated to be 2.0E+7. The power law coefficient B was set to 4 (Lawler et al. 1980). The influent particle size distribution in the size from 0.89 to 30 μm was prepared by the power law. For d < 3.5 μm, the particle density was fixed at 2.65 g/cm³, otherwise the particle density relationship (effective particle density) was used. Seven varied parameters were selected, but the sensitivity study was conducted on nine input parameters, because two of the parameters have two characteristic constants. Three equal sized flocculation basins (15 minute detention time each) in series were assumed. The magnitude of the input perturbation, Δp_k/p_k is specified to be 0.0333.

The values of variance for each varied input parameter were computed at the third flocculator. Table VI shows variances and percentage contributions to the total variance by the nine parameters. The percentage contribution to uncertainty can be expressed by the percentage contributions to total variance. The parameters of power law coefficient, B, and effective density constant, k, are shown to contribute most to uncertainty in the total particle number remaining in the flocculation model.

In another approach, a Monte Carlo simulation led to more precise statements about the effect of uncertainty.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Total Variance</th>
<th>% of Total Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>7.9E+8</td>
<td>0.52</td>
</tr>
<tr>
<td>s</td>
<td>7.9E+8</td>
<td>0.52</td>
</tr>
<tr>
<td>H</td>
<td>1.8E+6</td>
<td>0.00</td>
</tr>
<tr>
<td>D&lt;sub&gt;max&lt;/sub&gt;</td>
<td>1.1E+9</td>
<td>0.75</td>
</tr>
<tr>
<td>a</td>
<td>3.5E+9</td>
<td>2.33</td>
</tr>
<tr>
<td>k</td>
<td>4.9E+10</td>
<td>32.55</td>
</tr>
<tr>
<td>D&lt;sub&gt;t&lt;/sub&gt;</td>
<td>1.5E+9</td>
<td>0.98</td>
</tr>
<tr>
<td>A</td>
<td>9.6E+7</td>
<td>0.06</td>
</tr>
<tr>
<td>B</td>
<td>9.4E+10</td>
<td>62.28</td>
</tr>
<tr>
<td>Total</td>
<td>1.5E+11</td>
<td>100.00</td>
</tr>
</tbody>
</table>
The Monte Carlo simulation can be used to estimate various statistics of the model output, although the Monte Carlo simulation does not reduce the existing uncertainty. The general procedure for the Monte Carlo simulation is set out as follows:

1. Determine random parameters and the characteristics of these parameters for the input data. In this study, nine parameters were chosen as the random parameters because they were expected to have the most uncertainty in the model.
2. Determine a number of simulations to assure that enough events were simulated to determine representative outputs of the model.
3. Repeat the determined number of the model simulations using the random parameters in order to obtain a set of the model output. The set of the model output is used to estimate the response statistics.

The varied parameters in Table I were used as the random parameters. The same value of the coefficients of variation, 0.0333, and mean values in Table I were used in this study of the Monte Carlo simulation. The normal random numbers with the above properties were generated using available programs developed by Press et al. (1986). The uniform random number generator, FUNCTION RAN2(IDUM) installed in SUBROUTINE INITIVA, generates a uniform random value between 0.0 and 1.0. The normal random number generator, FUNCTION GASDEV(IDUM) using RAN2(IDUM) was also
installed in SUBROUTINE INITIVA, and produces a normally distributed value with an ensemble mean of 0.0 and an ensemble standard deviation of 1.0. Then, normal random numbers are obtained as follows:

\[ X(i) = X + sZ(i) \] 

(43)

Where:

- \( X(i) \) = value of a normal random variable at some point in the sequence of random number
- \( X \) = deterministic variable
- \( s \) = the desired standard deviation of \( X(i) \)
- \( Z(i) \) = normal random number generated by the random number generator

Using the needed random values generated for the model inputs, the program performs repetitive execution until a desired number of results are obtained.

The fraction of the number of particles remaining, \( (N/No) \), was selected to observe the model responses. The number of particles remaining allows for prediction of the flocculation performance. Model outputs were prepared at compartments 1, 2, and 3 and shown in Figure 28. A determination of the number of simulations that can assure representative output and avoid numerous unwarranted simulations was conducted by running simulations 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 times. The number of simulations was increased until the average, upper and lower 95% confidence intervals reached a constant value. Results of this procedure are presented in Figure 29. The
Figure 28 Frequency distribution of modified model predictions
Figure 29. Convergence characteristics of Monte Carlo Simulation with modified model (third compartment)
95% confidence interval was computed with an assumption of normal distribution for each set and then plotted as \((N/No)\) versus the number of simulations performed. The results show that about 200 simulations are enough to obtain sufficient precision in the model output. Simulations were conducted 240 and 300 times to ensure that the choice of 200 simulations was enough.

The probability distribution of the third compartment was determined by plotting of the 200 run simulation results and is shown in Figure 30. As seen in Figure 30, the simulation results (particle number remaining) are distributed linearly so that the results could be expressed as a normal distribution. This figure indicates the previous assumption of normal distribution is valid. The probability figure can be used in the explanation of how safety factors for the flocculation process might be calculated (Berryman and Himmelblau, 1971; Cockerham and Himmelblau, 1974). When a design is conducted, a safety factor should be added to or multiplied into a design which is based on the model prediction in order to allow for uncertainty in the model and the operating process. The mean value of \(NjNo\) at a third compartment is 0.31. The upper confidence interval for the model response is 0.43. The safety factor, \(f\), in this case could be the ratio of the upper 95% confidence value to the mean value i.e., \(f = 0.43/0.31 = 1.39\). Cockerham and Himmelblau (1974) used Argaman and Kaufman's flocculation model and performed a
Figure 30. Probability distribution of N/No at third compartment
Monte Carlo simulation. They found that the safety factor was approximately 1.4 for variations of the flow rates. If they considered all the input parameters as random, the value of the safety factor was higher than for variations of flow rates.
A Coulter counter was used at the Davis Water Treatment Plant, Austin, Texas, to measure the particle size distribution. Lawler's model prediction more closely fit the measured results for the intermediate concentration (820 mg/L). The predictions of the modified model and Lawler's model overestimate the measured results for the small particle concentration (417 mg/L). But better agreement between the modified model predictions and the measured results occurred at the larger concentration (912 mg/L). However, Lawler's model (1984) required a value for the collision efficiency factor ($\alpha = 0.1$ or 0.2) in order to fit the model prediction to the experimental results. The value of $\alpha$, which is less than 1, is required to compensate for an overprediction of the frequency of particle collisions by the model. The modified model sets the value of $\alpha$ to 1.0. Setting $\alpha$ equal to 1 removed the need to use a correction factor for overprediction by the model. The removing of $\alpha$, which was used for calibrating, would be an indication of model improvement. This value has to be determined by calibrating the model to a set of experimental results. It is very likely that the value varies with the nature of the model used and the nature of
the coagulant types. Because $\alpha$, the collision efficiency factor, could not be measurable independently, its value had to be found via application of the old model. The approach was to take $\alpha$ as a correction factor to fit the model predicted PSD and the experimental PSD. In order to obtain knowledge about the range of $\alpha$, the literature was reviewed. According to Gregory’s literature review (1989), $\alpha$ is typically in the range 0.1 to 0.5. Lawler et al. (1983) reported values between 0.16 and 0.20 for $\alpha$ in batch flocculation; their model was formulated with equations 1, 2 and 3. Their model considered the particle removal from the suspension by sedimentation. Lawler and Wilkes (1984) used values of 0.1 and 0.2 for $\alpha$ in a full scale operating flocculation basin. The later model did not consider particle removal by sedimentation. Tambo and Watanabe (1979) reported the value of 0.33 for the optimum coagulation condition of clay-aluminum flocs. Lu and Spielman (1984) also reported a similar range from 0.32 to 0.35 at optimum dosage of clay-polymer flocs. Under different conditions and in different models, different values of $\alpha$ have to be used to fit the measured results.

The 280 $\mu$m aperture was the largest diameter used to measured the particle size distribution of the Davis Water Treatment Plant by Lawler and Wilkes (1984). According to Treweek and Morgan (1977), a Coulter counter measured particle size was reliable from 10 to 40 percent of the aperture diameter. Thus a 280 $\mu$m aperture can reliably
measure a particle size from 28 to 112 μm. The modified model selected 100 μm as the maximum particle diameter and compared the predicted particle size distribution to the particle size distribution data measured by the Coulter counter. The 100 μm maximum particle diameter (close to 112 μm) is fairly small compared to the reported experimental maximum particle size at G = 22 sec⁻¹. According to the data collected by Glasgow and Kim (1989), approximately 200 μm maximum particles were found at the operating velocity gradient (22 sec⁻¹). The relatively small size of the maximum particle measured by the Coulter counter implies that the Coulter counter causes particle breakup.

The Southern Nevada Water System uses a HIAC to measure the particle size distribution. The reported particle numbers were in five discrete particle size ranges. The discrete particle size ranges were larger than the preset particle size ranges in the model, therefore data manipulation was required. A power law relationship found by linear regression was used to obtain the number of particles less than 5 μm in size. For more accurate comparison, a more detailed particle size distribution in the range of the predetermined particle size ranges is required. The model prediction with the particle size distribution based on the power law relationship was compared to the measured results. Even if there was the possibility of the loss of particle number caused by sedimentation, the model prediction seemed to underestimate
the flocculation performance of the small number concentration seen in this case as well as the second data set from the Davis Water Treatment Plant.

The modified model predictions fit well the measured results from the AIA used at ISU (Hanson, 1989). However, the volume distribution plots demonstrated that the model predictions deviated in the region of the large particle size. This was due to limits in the accuracy of the particle size measuring capability of the AIA. According to Hanson (1989), the AIA was not able to provide a crisp image if the floc was in excess of 50 µm. The out of focus image was possibly measured as a larger particle size than the actual particle size. Hanson mentioned that the unfocused image was due to the microscope's limited depth of focus, called the focal depth. This limitation occurs when performing quantitative measurements on irregular objects whose vertical dimension is larger than the depth of focus. A 20x objective (system magnification of 474.6x) installed in the AIA is not appropriate to measured the particle sizes larger than 50 µm.

The comparison between the model prediction and the measured results in the three cases showed that the model underestimated the flocculation rates mostly in the intermediate size region (3 to 15 µm). The modified collision frequency function, $\beta'(i,j)$, employed in the modified model is a function of particle size and density. As mentioned earlier, floc size increases as the density
decreases so that the collision frequency increases.

However, the experimental data (Tambo and Watanabe, 1979) used in this study were obtained from the density of large particles because the experimental data for the density of small particles were scarce. The values of 0.0013 and 0.9 for \( a \) and \( k \) were used to describe the relationship between floc density and size. These values gave 3.5 \( \mu \)m as transition floc diameter (floc density = 2.65 g/cm\(^3\)) so that the density of particles below 3.5 \( \mu \)m was set to 2.65 g/cm\(^3\). The selected values of 0.0013 and 0.9 for \( a \) and \( k \) can be obtained from equations 13 and 14 when the ALT ratio approaches zero. The 3.5 \( \mu \)m particle size was the primary particle used in the experiment conducted by Tambo and Watanabe (1979). When the ALT ratio is zero, the transition floc diameter is equal to the primary particle. In this research the primary particle size is 0.89 \( \mu \)m so that other values of \( a \) and \( k \) need to be used in the model. The effects of the ALT ratio on the model predictions were not determined because equations 13 and 14 did not represent the floc density decreasing as the ALT ratio increases. Figure 31 shows the floc density and size relationships. As the ALT ratio increases, the transition floc diameter increase. To incorporate the ALT ratio into the model, the relationship between the floc size and density especially in the small range is required. Assuming constant density below the transition diameter causes an underestimating of the collision frequency. But the small
Figure 31. Relationship between floc density and size
value of 0.9 reduces the collision frequency in the large floc size range. As the value of k increases, more collision frequency will be predicted. When setting the fractal dimension \( D = 3-k \), the collision frequency increases as the fractal dimension, \( D \), decreases (k increases). Selecting the appropriate values of k and a are very important factors for model prediction. Recently, several researchers (Jiang and Logan, 1991; Wiesner 1992) derived the floc diameter expressions containing the fractal dimension assuming a primary particle size. This was used in the collision frequency function to calculate collision frequency. Both expressions fix a transition floc diameter as the primary particle size so the transition floc diameter size is not changed. Both results showed more collision frequency than the original collision frequency. But none of these results was verified with experimental data.

The uncertainties of the nine input parameters were handled by completing a sensitivity analysis and a Monte Carlo Simulation. Sensitivity analysis indicated that the power law constant, B, and the effective density constant, k, had the greatest effects on flocculation. This implies that particle size distribution is the most important information to describe the flocculation process. A reliable particle counter has to be employed to get good prediction. In the previous paragraph, the requirement for more work on the effective density constant was discussed.
Interestingly, the effect shear rate constant, s, and velocity gradient, G, had a small effect on flocculation. The model response due to changes in maximum particle size is closely related the parameters G and s. The sensitivity of s, G, and $D_{\text{max}}$ on model response should be considered together. However, the comparison between the model predictions and the ISU experimental data showed that the modified model response was little affected by velocity gradient. The comparison also illustrated that G had more effect on flocculation performance than the model prediction. Potentially, a more appropriate parameter for G in the model may be required. The significance of correlation among the input parameters on errors in the model response has to examined also. Song and Brown (1990) reported that correlation among the input parameters was important in output uncertainty from the Streeter-Phelps water-quality model. However, we do not know how the input parameters are correlated so we were unable to develop meaningful bounds for the random input parameters. Reliable quantitative information on the variances and correlation coefficients among the input parameters have to be used. The safety factor for the modified model obtained by Monte Carlo simulation was smaller than the safety factor estimated by Cockerham and Himmelblau (1974). The smaller safety factor to accommodate the reality of uncertainty is a recognition of the advancement of the flocculation model. Approximately 2 minutes, including compile time, was needed
for one model simulation using a 486 IBM compatible microcomputer with 4 Mb RAM.

The predictions of the flocculation model using particle size distribution proposed herein indicate what happens during the flocculation process and point out possibilities that warrant further development. The present water industry concern over two protozoal organisms, cysts of *Giardia lamblia* in the 8-12 μm size range and *Cryptosporidium* in the 3-5 μm size range, impacts on finished water quality (Amirtharajah, 1988). The existence of these organisms can be quantified in particle size distribution. These size could be controlled in the flocculation process in order to optimize water treatment process and improve water quality. However, the model applications for operation of an existing flocculation plant and design of new or modified flocculation plant is limited. A better understanding and improved expressions for some physical and chemical phenomena which occur during the flocculation process are necessary.
CHAPTER VI

SUMMARY AND CONCLUSIONS

In this research, the flocculation model was modified and its predictions tested using data from two operating water treatment plants and a lab scale data set. Each data set was measured using different measuring equipment. In order to assess the contribution of various input parameters to uncertainty in the model prediction and obtain a safety factor, sensitivity analysis and a Monte Carlo simulation were conducted. The following conclusions are drawn from the research. With a realization of the problems encountered, a number of recommendations are also made.

Conclusions

1. Improvements in a flocculation model were made by incorporating terms for interparticle forces, floc break-up phenomena, floc density, shape effects, and effective velocity gradient.

2. The modified model prediction without the collision efficiency factor (α) matched the measured results at the high concentration but underestimated the flocculation rate at low concentration. The modified
model predictions do not show the sudden peak point at the largest particle size which was noticed in Lawler’s model prediction.

3. In SNWS, the modified model underestimated flocculation rate for low particle concentration and the loss of particle number in measured results was observed.

4. The modified model predicted well the ISU particle size distribution, measured by an automatic image analyzer, results obtained while operating at $G = 22$ sec$^{-1}$. However, the modified model prediction overestimated the particle size distribution conducted at $G = 60$ sec$^{-1}$.

5. The sensitivity analysis indicated that the power law constant, $B$, which describes the particle size distribution, and the effective density constant, $k$, which relates the particle density and size, were the major contributors to uncertainty in the flocculation model.

6. The Monte Carlo simulation was applied to the modified model. The model output could be represented by a normal distribution. A safety factor was calculated from the model output mean and confidence interval.

**Recommendations**

1. More work on the relationship between the floc density and size is needed especially in small particle
2. Sensitivity analysis and Monte Carlo simulation have been shown to be useful tools in assessing the uncertainty in the model prediction. Reliable information on the variances and correlation coefficients among model parameters is important for these techniques to be used with confidence. Methods for determining input parameter correlation coefficients require further study.

3. With more sensitive and reliable particle counters, the improvement of flocculation model could be made.

4. Individual processes of water treatment, rapid mixing, flocculation, sedimentation and filtration, are combined in series to perform solid-liquid separation. More study to improve the present sedimentation and filtration model and linkage of each model is required to determine and predict the effect of one treatment process on those that follow.
REFERENCES


APPENDIXES
APPENDIX A

COMPUTER PROGRAM FOR FLOCCULATION MODEL

IMPLICIT REAL*8(A-H, O-Z)

ALPHA : STICKINESS FACTOR, FRACTION OF SUCCESSFUL COLL.
AVNUDI : NUMBER AVERAGE DIAMETER
AVSUDI : SURFACE AREA AVERAGE DIAMETER
AVVODI : VOLUME AVERAGE DIAMETER
BETA : SUM OF COLLISION EFFICIENCY, CM**3/SEC
BETABR : BROWNIAN COLLISION EFFICIENCY
BETASE : SEDIMENTATION COLLISION EFFICIENCY
BETASH : SHEAR COLLISION EFFICIENCY
BOLTZ : BOLTZMANS CONSTANT, GM-CM**2/(SEC**2*DEG.KELVIN)
CALCTI : THE CALCULATED TIME FROM FLOW EFFECT IN EACH COMPARTMENT
CONBET : CALCULATED CONSTANT FOR BETASE
CON3 : CALCULATED CONSTANT, (6/PI)**(1/3)
CON4 : CALCULATED CONSTANT, 2.3*PI/6
DCON : CONSTANT(A) IN PARTICLE SIZE-DENSITY RELATIONSHIP
DELTAD : PARTICLE DIAMETER INTERVAL
DKP : CONSTANT(K) IN PARTICLE SIZE-DENSITY RELATIONSHIP
DT : DETENTION TIME OF FLOCCULATION BASIN, MINUTES
DY : NUMERICAL VALUE OF DIFFERENTIAL EQUATION
EDEN : EFFECTIVE DENSITY
ERROR : ALLOWABLE % DIFFERENCE IN SETTLING VEL. TEST
FASTL : THE VALUE OF THE FASTEST CHANGING DERIVATIVE
FDEN : FLOC DENSITY
FRAC : FRACTION OF NEW PARTICLE ASSIGNED TO V(RESULT)
FRAREN : NUMBER FRACTION REMAINING, N/NO
GRAVCO : GRAVITATIONAL CONSTANT, 980 CM/SEC**2
H : STEP SIZE (TIME) WHEN INTEGRATING
HMIN : MINIMUM STEP SIZE
HMEX : MAXIMUM STEP SIZE
HMCON : HAMAKER CONSTANT, JOULES
NJ : NUMBER OF PARTICLE SIZE IN EXPERIMENTAL DATA
NPEAK : PARTICLE SIZE OF PEAK IN THE NUMBER DISTRIBUTION
NT1 : NUMBER OF OUTPUT CALL
OUTTIM : TIMES THAT OUTPUTS ARE DESIRED, MINUTES
PEAKNO : THE PEAK IN NUMBER DISTRIBUTION
PEAKVD : THE PEAK IN VOLUME DISTRIBUTION
PI : 3.1415926535
PLAW1 : POWER LAW CONSTANT
PLAW2 : PLAW2*PSIZE(I)**(-PLAW2)
PND : NUMBER DISTRIBUTION
PSIZE : PARTICLE DIAMETER, MICRONS
PSD : SURFACE DISTRIBUTION
PSZLOG : LOG OF PARTICLE DIAMETER
PVD : VOLUME DISTRIBUTION
RHO : DENSITY OF PARTICLES, GRAMS/CM**3
RHOWAT : DENSITY OF WATER, GRAMS/CM**3
T : TIME, SEC
TEMP : TEMPERATURE, KELVIN
TMAX : MAXIMUM TIME, SECONDS
TOTDIA : TOTAL DIAMETER OF PARTICLES
TOTMAS : TOTAL MASS OF PARTICLES
TOTNUM : TOTAL NUMBER OF PARTICLES
TOTSUM : TOTAL SURFACE OF PARTICLES
TOTVUM : TOTAL VOLUME OF PARTICLES
TOTYIN : TOTAL NUMBER OF INPUT PARTICLES
TT : TIME FOR HYDROLOGICAL CALCULATION
C V : VOLUME OF PARTICLES
C VCON : VOLUME AVERAGE SHEAR RATE
C VELGRA : VELOCITY GRADIENT
C VISCOS : VISCOSITY, GM/CM-SEC
C VPEAK : PARTICLE SIZE OF PEAK IN VOLUME DISTRIBUTION
C VSTLOG : LOG OF VOLUME STEPS
C Y : NUMBER OF PARTICLES PER ML
C

INTEGER PEAKND, PEAKVD
LOGICAL FAIL
EXTERNAL DIFFUN

DIMENSION BETA(100,100), TOTN(4,400), CALCTI(10,10), DELTAD(100),
* PSIZE(100), PND(100), PVD(100), FRAC(100,100), PSZLOG(100),
* PSD(100), OUTTIM(50), FDEN(100), VF(100), V(100), DY(100),
* Y(100), PNAVG(10,10,100), Y(100)

COMMON/B/ BETA
COMMON/F/ FRAC
COMMON FAIL
FAIL =.FALSE.

OPEN(UNIT=6,FILE="FLOC.OUT",STATUS='NEW')
LFLAG = 1
NINI = 0

DO 11 III=1, 300
CALL INITVA(N, NC, NT, MFLAG, KFLAG, H, HMIN, HMAX, ALPHA, RHO,
* RHOWAT, BOLTZ, PI, TEMP, VISCOS, T, MAX, GRAVCO, VSTLOG, DELTAD,
* PSIZE, PSZLOG, PVD, V, DY, TOTIN, NCALL, NTI, OUTTIM, CON3,
* CON4, VELGRA, CALCTI, HMCON, DCON, DPK,
* VCON, DMAX, IFLOC, NINI, IMON, NOUT)
CALL BETACA(N, GRAVCO, VISCOS, RHO, RHOWAT, BOLTZ, TEMP, PI,
* VELGRA, ALPHA, PSIZE, V, HMCON, DCON, DPK,
* VCON, DMAX, FDEN)
CALL FRACCA(N, V, VSTLOG)
CALL MASSSU(N, Y, V, DELTAD, PSIZE, PSD, PVD, PND, TOTNUM, TOTVOL,
* TOTSUR, TOTDIA, TOTMAS, TOTIN, AVVODI, AVVUDI, AVNUDI,
* PEAKVD, PEAKND, FRAREN, CONS, CON4, RHO, FDEN, VF, IFLOC)
IF (IMON.EQ.0) THEN
WRITE(6,68)
FORMAT(//, 2X, 'INITIAL PARTICLE SIZE DISTRIBUTION DATA')
CALL OUTPUT(N, NCALL, KFLAG, MFLAG, NTI, TOTNUM, TOTMAS, FRAREN,
* AVVODI, AVVUDI, AVNUDI, PSD, PVD, PND, PEAKVD, PEAKND,
* PSZLOG, PSIZE, DY, T, Y, VF, IFLOC, TOTVOL, FDEN)
ENDIF
DO 100 J=1, 500
IF (T .LE. MAX .OR. .NOT. FAIL) THEN
CALL STIFDI(N, H, HMIN, HMAX, KFLAG, Y, DY, T, LFLAG
* , NCALL, DIFFUN)
IF (MFLAG.EQ.1) THEN
DO 20 IM=1, NC
DO 25 JM=1, NT
IF (T.GE.CALCTI(IM, JM)) THEN
CALCTI(IM, JM) = TMAX + HMAX + 40000.
DO 30 I=1, N
PNAVG(IM, JM, I) = Y(I)
30 CONTINUE
25 CONTINUE
20 CONTINUE
ENDIF
IF (KFLAG.EQ.1) THEN
IF (T.GE.OUTTIM(NTI)) THEN
OUTTIM(NTI) = TMAX + HMAX + 1
IF (NTI.LE.NOUT) THEN
CALL MASSSU(N, Y, V, DELTAD, PSIZE, PSD, PVD, PND, TOTNUM, TOTVOL,
* TOTSUR, TOTDIA, TOTMAS, TOTIN, AVVODI, AVVUDI, AVNUDI,
* PEAKVD, PEAKND, FRAREN, CONS, CON4, RHO, FDEN, VF, IFLOC)
IF (IMON.EQ.0) THEN
CALL OUTPUT(N, NCALL, KFLAG, MFLAG, NTI, TOTNUM, TOTMAS, FRAREN,
* AVVODI, AVVUDI, AVNUDI, PSD, PVD, PND, PEAKVD, PEAKND,
* PSZLOG, PSIZE, DY, T, Y, VF, IFLOC, TOTVOL, FDEN)
ENDIF
ENDIF
END IF  
ELSE  
GOTO 110  
END IF  
100 CONTINUE  
110 CONTINUE  
C AFTER THE MODEL HAS RUN FOR ALL OF THE DESIGNATED BY  
C TMAX, THE DISTRIBUTIONS FOR EACH COMPARTMENT CAN  
C CALCULATED AND PRINTED WHEN THE NON-IDEAL CASE IS USED  
IF (MFLAG.EQ.1) THEN  
DO 50 IM=1, NC  
DO 51 1=1,N  
YY(I) = 0.0  
51 CONTINUE  
IF (IMON.EQ.O) THEN  
WRITE(6,60) IM  
60 FORMAT(//'THE MODEL PREDICTION AT COMPAREMENT NUMBER',110)  
END IF  
DO 65 JM=1, NT  
DO 65 1=1,N  
YY(I) = YY(I) + PNAVG(IM,JM,I)  
65 CONTINUE  
DO 66 I=1,N  
Y(I) = YY(I)/5.0  
66 CONTINUE  
*  
50 CONTINUE  
END IF  
IF (IMON.EQ.1) THEN  
WRITE(6,16) III,TOTN(1,111),TOTN(2,111),TOTN(3,111)  
16 FORMAT(5X,I4,2X,3F15.5)  
END IF  
IF (IMON.EQ.O) STOP  
11 CONTINUE  
STOP  
END  
SUBROUTINE INITVA(N,NC,NT,MFLAG,KFLAG,H,HMIN,HMAX,ALPHA,RHO,  * RHOWAT,BOLTZ,PI,TEMP,VISCOS,T,TMAX,GRAVCO,VSTLOG,DELTAD,  * PSIZE,PSZLOG,PSD,PSZ,PSY,PSYLOG,OUTTIM,CON3,CON4,VELGRA,CALCTI,HMKCQN,DCON,DKP,  * VCON,MAX,IFLOC,NINI,IMON,NOUT)  
IMPLICIT REAL*8(A-H, O-Z)  
DIMENSION CALCTI(10,10), DELTAD(100),PSIZE(100), V(100),  * PSZLOG,PSD,PSY,PSYLOG,OUTTIM(20),Y(100),DY(100),  * CY(100),DY(100),YI(100),XMKCD(300),XVCON(300),  * XVELGR(300),XDMAX(300),XDKP(300),XDCON(300),XDT(300),  * XPLAW(300),XPLAW2(300)  
OPEN(UNIT=5,FILE='ISU4530.IN',STATUS='UNKNOWN')  
INPUT DATA  
C IF MFLAG=1; THE OUTPUT WILL PRINTED BASED ON  
C THE NON-IDEAL FLOW CASE  
C IF MFLAG=0; THE IDEAL(PLUG FLOW) CASE  
MFLAG = 1  
C IF KFLAG=1; THE OUTPUT WILL PRINTED DESIGNATED TIME (MIN.) BY USER  
KFLAG = 0  
C IMON = 1; DO MONTE CARLO SIMULATION  
IMON = 0  
C IFLOC = 0 ; CONSTANT DENSITY WILL BE USED  
C IFLOC = 1 ; VARIABLE DENSITY WILL BE USED FOR  
C CALCULATION FLOC VOLUME  
IFLOC = 1  
C IFLOW = 1 ; CALCULATE F CURVE FOR EQUAL VOLUME OF  

C FLOCCULATOR SERIES
C !FLOW = 2 ; USE EXPERIMENTAL F CURVE DATA
C !FLOW = 1
C NUMERICAL PARAMETERS
H = 10.0
HMIN = 1.0
HMAX = 100
PVLOG(1) = -0.462
T = 0.0
TOTYIN = 0.0
TMAX = 8000.0
VSTLOG = 0.09
C
RHO = 2.65
RHOWAT = 1.0
TEMP = 293.0
GRAVCO = 980.
PI = 3.1415926535
BOLTZ = 1.38E-16
HMKCON = 2.0E-19
C
ALPHA = 1.
VELGRA = 25.0
VCON = 0.39
DMAX = 200.0
DT = 15.
DCON = 0.0013
DKP = 0.9
C
ALT = 1./20.
C
INPUT MFLAG
C
N=NUMBER OF DIFFERENT PARTICLE VOLUMES
NC=NUMBER OF COMPARTMENTS OR BASINS
NT=NUMBER OF AVERAGING TIMES
IF (MFLAG.EQ.1) THEN
N= 64
NC=3
NT=5
C
INPUT MATRIX OF TIMES USED TO AVERAGE THE Y VALUES
FOR USE IN THE FINAL OUTPUT FOR NON-IDEAL FLOW
CASE. TIMES ARE DETERMINED FROM EITHER MEASURED OR
THEORETICAL FLOW CURVES
C
IFLOW =1 : EQUAL VOLUME OF FLOCCULATOR SERIES
IFLOW =2 : DIFFERENT VOLUME OF FLOCCULATOR SERIES
IFLOW =3 : EXPERIMENTAL DATA FOR FLOW
C
IF (IFLOW.EQ.1) THEN
CALL EFLOW(NC,DT, CALCTI)
C ELSEIF (IFLOW.EQ.2) THEN
CALL DFLOW(NC, CALCTI)
ELSEIF (IFLOW.EQ.2) THEN
CALCTI(1,1) = 5.
CALCTI(1,2) = 7.2
CALCTI(1,3) = 11.2
CALCTI(1,4) = 19.2
CALCTI(1,5) = 47.4
CALCTI(2,1) = 14.4
CALCTI(2,2) = 20.
CALCTI(2,3) = 30.4
CALCTI(2,4) = 44.
CALCTI(2,5) = 90.4
CALCTI(3,1) = 28.
CALCTI(3,2) = 41.6
CALCTI(3,3) = 58.6
CALCTI(3,4) = 80.0
CALCTI(3,5) = 130.0
ENDIF
DO 322 I=1,NC
DO 323 J=1,NT
CALCTI(I,J) = CALCTI(I,J)*60.
DE
C NDCALL : NUMBER OF OUTPUT AT EACH SPECIFIED TIME (MIN)
NOUT = 6
OUTTIM(1) = 300.
OUTTIM(2) = 600.
OUTTIM(3) = 900.
OUTTIM(4) = 1200
OUTTIM(5) = 1500.
OUTTIM(6) = 1800.
C
GRAVC0=980.
PI=3.1415926535
NDCALL=0
NT! = 0
TOTYIN = 0.0
DO 30 I=1,N
DY(I)=0.
Y(I)=O.
30 CONTINUE
ERROR=O.
CON1=1.
CONBET=PI/4.**(6./PI)**(.5./0.6.)*4.*GRAVC0/3.*((RHO-RHOWAT)/
* RHOWAT))**(1./2.)*1.0E-04)**(0.5./2.)
CON3=(6./PI)**(1./3)
CON4=2.3*PI/6.
DO 200 I=2, N
PVLOG(I)=PVLOG(I-1)+VSTLOG
200 CONTINUE
DO 210 I=1, N
V(I)=10.**PVLOG(I)
PSIZE(I)=(6./PI*10**(PVLOG(I)))**(1./3.)
PSZLOG(I)=ALOG10(PSIZE(I))
DELTAD(I)=(6./PI*10**(PVLOG(I)+0.5*VSTLOG))**(1./3.)
* -(6./PI*10.**(PVLOG(I)-0.5*VSTLOG))**(1./3.)
210 CONTINUE
C INMODE ; INPUT MODE FOR PARTICLE SIZE DISTRIBUTION
C INMODE = 1 ; READ Y(I) NUMBER OF PARTICLE PER ML
C INMODE = 2 ; READ PARTICLE SIZE DISTRIBUTION
C INMODE = 3 ; READ PSD FUNCTION AND CALCULATE Y(I)
C INMODE = 4 ; READ Y(I), NUMBER OF PARTICLE PER ML WITH WITH
C PARTICLE DIAMETER D(I) UM
C
INMODE = 3
IF (INMODE.EQ.1) THEN
TY = 0.0
DO 230 I=1, N
IF (PSIZE(I).LE.10.0) THEN
Y(I) = 58.208*PSIZE(I) - 200.187 - TY
ELSEIF (PSIZE(I).GT.10.0.AND.PSIZE(I).LE.20.0) THEN
Y(I) = 9.1505*PSIZE(I) + 290.388 - TY
ELSEIF (PSIZE(I).GT.20.0.AND.PSIZE(I).LE.40.0) THEN
Y(I) = 0.363562*PSIZE(I) + 466.126 - TY
ELSE
Y(I) = 0.0
ENDIF
TY = TY + Y(I)
IF (Y(I).LE.0.5) GO TO 230
PSD(I)=ALOG10(Y(I)/DELTAD(I))
TOTYIN=TOTYIN+Y(I)
230 CONTINUE
ELSEIF (INMODE.EQ.2) THEN
DO 250 I=1, N
READ(5,270) PSD(I)
C 270 FORMAT(F10.5)
IF (PSD(I).EQ.0.0) THEN
Y(I)=O.
ELSEIF (PSD(I).EQ.999.0) THEN
Y(I)=O.
GOTO 250
ELSE
Y(l)=DELTAD(I)*10**PSD(I)
TOTYIN=TOTYIN+Y(I)
ENDIF
250 CONTINUE
ELSEIF (INMODE.EQ.3) THEN
C INPUT FOR POWER LAW CONSTANT
PLAW1 = 2.0E7
PLAW2 = 4.0
DO 252 I=1,N
C YOU NEED TO PUT PSD FUNCTION IN HERE
IF (PSIZE(I).LE.30) THEN
PSD(I) = PLAW1*PSIZE(I)**(PLAW2)
Y(I) = DELTAD(I)*PSD(I)
ELSE
Y(I) = 0.0
ENDIF
IF (Y(I).LE.0.5) Y(I)=0.0
TOTYIN=TOTYIN+Y(I)
252 CONTINUE
ELSEIF (INMODE.EQ.4) THEN
TOTYIN = 0.0
NJ = 15
DO 253 I=1,NJ
READ(5,254) DI(I),YI(I)
254 FORMAT(F7.2,E10.3)
257 FORMAT(2X,F7.2,2X,E10.3,2X,E12.5)
IF (DI(I).EQ.999.00) THEN
NI=I
GO TO 255
ENDIF
TOT = TOT + YI(I)
CY(I) = TOT
WRITE(6,257) DI(I),YI(I),CY(I)
253 CONTINUE
255 CONTINUE
TY = 0.0
J=2
DO 260 I=1,N
C WJ IS THE NUMBER OF PARTICLE SIZE
NJ = 17
262 CONTINUE
IF (PSIZE(I).LE.DI(J)) THEN
JJ=J-1
SLOPE = (CY(J)-CY(JJ))/(DI(J)-DI(JJ))
TRCPT = CY(J)-SLOPE*DI(J)
YY = SLOPE*PSIZE(I)+TRCPT
Y(I) = YY-TOTYIN
TOTYIN = TOTYIN+Y(I)
ELSEIF (PSIZE(I).GE.DI(NJ)) THEN
Y(I) = 0.0
ELSE
J = J+1
GO TO 262
ENDIF
260 CONTINUE
END IF
NINI = NINI + 1
IF (IMON.EQ.1) THEN
C MONTE CARLO SIMULATION
C CALL GAUSSIAN RANDOM NUMBER GENERATOR
C NEED TO SET IDUM IT ANY NEGATIVEL VALUE
C CVAR; COEFFICIENT OF VARIATION
IF (NINI.GE.2) GOTO 347
IDUM = -1
DO 342 I=1,300
CVAR = 0.0333
XHMKCO(I) = HMKCON + CVAR*HMKCON*GASDEV(IDUM)
XVCON(I) = VCON + CVAR*VCON*GASDEV(IDUM)
XVELGR(I) = VELGRA + CVAR*VELGRA*GASDEV(IDUM)
XDMAX(I) = DMAX + CVAR*DMAX*GASDEV(IDUM)
XDCON(I) = DCON + CVAR*DCON*GASDEV(IDUM)
XDKP(I) = DKP + CVAR*DKP*GASDEV(IDUM)
342 CONTINUE
XDT(I) = DT + CVAR*DT*GASDEV(IDUM)
XPLAY1(I) = PLAW1 + CVAR*PLAW1*GASDEV(IDUM)
XPLAY2(I) = PLAW2 + CVAR*PLAW2*GASDEV(IDUM)

CONTINUE

CONTINUE

VCON = XVCON(NINI)
DMAX = XDMAX(NINI)
DCON =XDCON(NINI)
DKP = XDKP(NINI)
DT = XDT(NINI)
PLAW1= XPLAY1(NINI)
PLAW2= XPLAY2(NINI)

WRITE(6,349) VCON,DMAX,DCON,DKP,DT,PLAW1,PLAW2

FORMAT(2X,7E10.4)

IF (IMON.EQ.0) THEN

WRITE(6,330)

FORMAT(/,2X,'**********MODEL INPUT**********')

WRITE(6,340)

FORMAT(/2X,5HALPHA,7X,7HMAKER,BX,4HTEMP,7X,9HVISCOSITY,7X,7HDENSITY)

WRITE(6,350)

FORMAT(2X,15X,3H(J),7X,8H(KELBIN),2X,11H(GM/CM-SEC),5X,10H(GM/CM**3))

WRITE(6,360) ALPHA,HMKCON,TEMP,VISCOS,RHO

WRITE(6,362)

FORMAT(/,2X,4HDMAX,10X,4HVCON,9X,2HDIT,10X,4HDCON,12X,3HDKP)

WRITE(6,364) DMAX,VCON,DT,DCON,DKP

WRITE(6,370)

FORMAT(/,2X,1HH,13X,4HHMIN,aX,4HHMAX,aX,4HTMAX)

WRITE(6,380) H, HMIN, HMAX,TMAX

END

END

SUBROUTINE EFLOW(NC, DT, CALCTI)
DIMENSION CALCTI(10,10), F(10)

THIS SUBROUTINE CALCULATE F(l) CURVES FOR EQUAL VOLUME OF COMPLETELY-MIXED REACTORS

DO 10 J=1,150

TT = J

IF (F(1).LE.0.2) THEN

CALCTI(1,1) = TT

ELSEIF (F(1).LE.0.4) THEN

CALCTI(1,2) = TT

ELSEIF (F(1).LE.0.6) THEN

CALCTI(1,3) = TT

ELSEIF (F(1).LE.0.8) THEN

CALCTI(1,4) = TT

ELSEIF (F(1).LE.0.975) THEN

CALCTI(1,5) = TT

ENDIF

DO 10 CONTINUE

FSUM = 0.

ISUM = 1

TSM = 1.

DO 15 J = 1, 150

TT = J

II = NC - 1

FSUM = 0.

ISUM = 1

DO 20 I=1,11

ISUM = ISUM*I

SSUM = (TT/DT)**I/ISUM

FSUM = FSUM + SSUM

IJ = I+1


\[
F(IJ) = 1 - (FSUM+1.)*\exp(-TT/DT)
\]

IF \((F(IJ) \leq 0.2)\) THEN
\[
\text{CALCTI(IJ,1)} = TT
\]
ELSEIF \((F(IJ) \leq 0.4)\) THEN
\[
\text{CALCTI(IJ,2)} = TT
\]
ELSEIF \((F(IJ) \leq 0.6)\) THEN
\[
\text{CALCTI(IJ,3)} = TT
\]
ELSEIF \((F(IJ) \leq 0.8)\) THEN
\[
\text{CALCTI(IJ,4)} = TT
\]
ELSEIF \((F(IJ) \leq 0.975)\) THEN
\[
\text{CALCTI(IJ,5)} = TT
\]
ENDIF

20 CONTINUE
15 CONTINUE
RETURN
END

SUBROUTINE BETACA(N,GRAVCO,VISCOS,RHO,RHOWAT,BOLTZ,TEMP,PI,
* VELGRA,ALPHA,PSIZE,Y,VMKCON,DCON,
* DKP,VCON,DMAX,FDEN)
IMPLICIT REAL*8(A-H,
0-Z)
DIMENSION BETA(100,100),BETASH(100,100),BETABR(100,100),
* BETASE(100,100),PSIZE(100),PSCM(100),DRAGCO(100),
* STOKSV(100),REYNN0(100),V(100),
* GBETA(100,100),GBBR(100,100),GBSH(100,100),GBSE(100,100),
* EDEN(100),FDEN(100),FSIZE(100),FSCM(100),FV(100),
* A1(7),B1(7),C1(7),D1(7),A2(4),B2(4),C2(4),D2(4),
* A3(3),B3(3),C3(3)
COMMON/B/
DATA A1/0.21811,0.25878,0.31151,0.37254,0.44285,0.53814,0.7048/
DATA B1/2.9593E-2,3.0338E-2,3.0339E-2,2.9251E-2,2.6954E-2,
* 2.2834E-2,1.3481E·2/
DATA C1/·4.9962E·4,-5.3031E-4,-5.4760E-4,-5.4055E-4,-5.0576E-4,
* -4.331E-4,-2.4753E-4/
DATA D1/2.6953E-6,2.9043E·6,3.0409E·6,3.0318E·6,2.855E-6,
* 2.4569E-6,1.3845E-6/
DATA A2/-1.189,0.766,0.145,0.017/
DATA B2/0.118,0.007,-0.0006,-0.001/
DATA C2/-3.431,-0.006,-1.137,-1.442/
DATA D2/0.331,1.547,0.775,0.557/
DATA A3/-0.301061,-0.12386,-0.31818/
DATA B3/0.027924,0.11031,0.26333/
DATA C3/0.0027,0.0328167,0.412667/
C
IN THIS PROCEDURE, THE DRAG COEFFICIENT IS CALCULATED AND
USE IN THE CALCULATION OF THE DIFFERENCE IN SETTLING VELOCITIES
FOR BETA-SED. THIS METHOD IS USED TO ACCOUNT FOR DIVERGENCE
FROM STOKES SETTLING BY LATGE PARTICLES
C
WRITE(6,1330) VCON,DCON,DKP
C 1330 FORMAT(2X,'VCON=' ,F10.4,2F15.5)
AK=(RHO-RHOWAT)/DCON
DO 155 I=1,N
PSM(I)=(AK*PSIZE(I)**3)**(1./2-KP))
FV(I)=1./6.*PI*FSIZE(I)**3
EDEN(I)=DCON/(FSIZE(I)**DKP)
FDEN(I)=EDEN(I)+RHOWAT
IF (FDEN(I).GT.RHO) THEN
FDEN(I)=RHO
PSCM(I)=PSIZE(I)
FSIZE(I)=FSIZE(I)
FV(I)=V(I)
ENDIF
WRITE(6,144) I,PSCM(I),EDEN(I),FDEN(I)
C 144 FORMAT(2X,15,2X,3F10.5)
155 CONTINUE
DO 300 I=1,N
STOKSV(I)=GRAVCO*(18*VISCOS)*(FDEN(I)-RHOWAT)**PSCM(I)**2
REYNN0(I)=STOKSV(I)*RHOWAT*PSM(I)/VISCOS
C
C
C
**Fortran Program Code**

```fortran
300 CONTINUE
CON=2.*BOLTZ*TEMP/(3.*VISCOS)
CON2=3./(4.*PI)
DO 10 I=1, N
DO 20 J=1, N
BETABR(I,J)=0.
BETASH(I,J)=0.
BETASE(I,J)=0.
20 CONTINUE
10 CONTINUE
C
DO 320 I=1, N
    IF (REYNNO(I).LE.1.) THEN
        DRAGC0(I)=24./REYNNO(I)
        SVEL(I)=STOKSV(I)
    ELSE
        VEL1=SVEL(I-1)
        VEL2=STOKSV(I)
    END IF
320 CONTINUE
C CONTINUE
    IF (ERROR.GE.0.01) THEN
        TRIVEL=(VEL2+VEL1)/2.
        RE=TRIVEL*RHOWAT*PSCM(I)/VISCOS
        CD=24./RE+3./RE**(1./2.)+0.34
        VELNEW=(4.*GRAVC0/(3.*CD)*((FDEN(I)-RHOWAT)/RHOWAT)**
        *PSCM(I))**(1./2.)
        ERROR=ABS((VELNEW-TRIVEL)/TRIVEL)
        IF (VELNEW.GT.TRIVEL) THEN
            VEL1=TRIVEL
        ELSE
            VEL2=TRIVEL
        END IF
        GO TO 330
    ELSE
        SVEL(I)=VELNEW
        REYNNO(I)=SVEL(I)*PSCM(I)*RHOWAT/VISCOS
        DRAGC0(I)=24./REYNN0(I)+3./REYNN0(I)**(1./2.)+0.34
        END IF
    ERROR=1.0
330 CONTINUE
C
DO 350 I=1,N
DO 360 J=1,N
    IF (PSIZE(I).GE.PSIZE(J)) THEN
        DRATIO = PSIZE(I)/PSIZE(J)
        BPSIZE = PSIZE(I)
        SPSIZE = PSIZE(J)
    ELSE
        DRATIO = PSIZE(J)/PSIZE(I)
        BPSIZE = PSIZE(J)
        SPSIZE = PSIZE(I)
    END IF
C BROWIAN MODIFICATION
AKT = HMKCON*1.0E7/(BOLTZ*TEMP)
    IF (AKT.LT.0.0001) THEN
        GAMABR=A1(1)+B1(1)*DRATIO+C1(1)*DRATIO**2+D1(1)*DRATIO**3
    ELSEIF (AKT.LT.0.001.AND.AKT.GE.0.0001) THEN
        BR1=A1(1)+B1(1)*DRATIO+C1(1)*DRATIO**2+D1(1)*DRATIO**3
        BR2=A1(2)+B1(2)*DRATIO+C1(2)*DRATIO**2+D1(2)*DRATIO**3
        GAMABR=BR1+(BR2-BR1)/0.0009*(AKT-0.0001)
    ELSEIF (AKT.LT.0.01.AND.AKT.GE.0.001) THEN
        BR1=A1(2)+B1(2)*DRATIO+C1(2)*DRATIO**2+D1(2)*DRATIO**3
        BR2=A1(3)+B1(3)*DRATIO+C1(3)*DRATIO**2+D1(3)*DRATIO**3
        GAMABR=BR1+(BR2-BR1)/0.009*(AKT-0.001)
    ELSEIF (AKT.LT.0.1.AND.AKT.GE.0.01) THEN
        BR1=A1(3)+B1(3)*DRATIO+C1(3)*DRATIO**2+D1(3)*DRATIO**3
        BR2=A1(4)+B1(4)*DRATIO+C1(4)*DRATIO**2+D1(4)*DRATIO**3
        GAMABR=BR1+(BR2-BR1)/0.09*(AKT-0.01)
    ELSEIF (AKT.LT.1.AND.AKT.GE.0.1) THEN
        BR1=A1(4)+B1(4)*DRATIO+C1(4)*DRATIO**2+D1(4)*DRATIO**3
        BR2=A1(5)+B1(5)*DRATIO+C1(5)*DRATIO**2+D1(5)*DRATIO**3
        GAMABR=BR1+(BR2-BR1)/0.9*(AKT-0.1)
    ELSEIF (AKT.LT.10.AND.AKT.GE.1.0) THEN
```
\[ \begin{align*} 
BR_1 &= A_1(5) + B_1(5) \cdot DRATIO + C_1(5) \cdot DRATIO^2 + D_1(5) \cdot DRATIO^3 \\
BR_2 &= A_1(6) + B_1(6) \cdot DRATIO + C_1(6) \cdot DRATIO^2 + D_1(6) \cdot DRATIO^3 \\
GAMABR &= BR_1 + \frac{(BR_2 - BR_1)}{9} \cdot (AKT - 9) \\
\text{ELSEIF} & \quad (AKT \lt 100 \text{ AND } AKT \geq 10) \\
& \quad \text{THEN} \\
& \quad BR_1 = A_1(6) + B_1(6) \cdot DRATIO + C_1(6) \cdot DRATIO^2 + D_1(6) \cdot DRATIO^3 \\
& \quad BR_2 = A_1(7) + B_1(7) \cdot DRATIO + C_1(7) \cdot DRATIO^2 + D_1(7) \cdot DRATIO^3 \\
& \quad GAMABR = BR_1 + \frac{(BR_2 - BR_1)}{90} \cdot (CAKT - 9) \\
\text{ELSE} & \quad \text{ENDIF} \\
\text{IF} & \quad (GAMABR \lt 0.2) \\
& \quad \text{GAMABR} = 0.2 \\
\text{IF} & \quad (GAMABR \geq 1.0) \\
& \quad \text{GAMABR} = \text{GAMABR} \\
\text{ENDIF} \\
& \quad \text{IF} (I \geq J) \\
& \quad \text{II} = I \\
\text{ELSE} & \quad \text{II} = J \\
\text{ENDIF} \\
\end{align*} \]
STOP
ENDIF
IF (PORO.LE.0.5) THEN
  ESH = 0.0
ELSE
  P = (FSIZE(I)/10)**2/18.*((3.+4./PORO)-3.*((8./PORO)-3))**0.5
  ZETA = FSIZE(I)/(2.*P**0.5)
  ESH = 1.6185*EXP(-0.4902*ZETA)
ENDIF
IF (ESH.LE.0.0) THEN
  ESH = 0.0
ELSEIF (ESH.GE.1.0) THEN
  ESH = 0.9999
ENDIF
SHEFF = GAMASH +ESH
BETASH(I,J)=(((CON2*FV(I))**(1./3.))+((CON2*FV(J))**(1./3.)))**3*4.*EVELGRA/3.*1.E-12
GSH(I,J) = SHEFF*BETASH(I,J)
IF (GSH(I,J).LE.0.0) THEN
  WRITE(6,12)
FORMAT(//,5X,'ESH IS LESS THAN ZERO')
STOP
ENDIF
C
C DIFFERENTIAL SEDIMENTATION
IF (I.EQ.J) THEN
  BETASE(I,J)=0.0
ELSE
  GN = ABS(SVEL(I)-SVEL(J))*3.0*VISCOS*PI*PSIZE(I)*PSIZE(J)**(1.+1/DRATI0)/(2.*HMKCON*DRATI0*1.0E15)
  IF (GN.GE.1.0E6) THEN
    GAMASE=A3(1)/DRATI0**2+B3(1)/DRATIO+C3(1)
  ELSEIF (GN.GE.100.0.AND. GN.LT.1.0E6) THEN
    SE1=A3(1)/DRATI0**2+B3(1)/DRATIO+C3(1)
    SE2=A3(2)/DRATI0**2+B3(2)/DRATIO+C3(2)
    GAMASE=SE1+(SE2·SE1)/999900.0*(1.E6-GN)
  ELSEIF (GN.GE.0.1.AND.GN.LT.100.0) THEN
    SE1=A3(2)/DRATI0**2+B3(2)/DRATIO+C3(2)
    SE2=A3(3)/DRATI0**2+B3(3)/DRATIO+C3(3)
    GAMASE=SE1+(SE2·SE1)/99.9*(100.0-GN)
  ELSE
    GAMASE=A3(3)/DRATI0**2+B3(3)/DRATIO+C3(3)
  ENDIF
  IF (GAMASE.LE.1.E-18) THEN
    WRITE(6,15)
    GAMASE=1.0E-5
  ELSEIF (GAMASE.GE.1.) THEN
    GAMASE=1.0
  ENDIF
ENDIF
IF (GAMASE.LE.1.E-18) THEN
  WRITE(6,15)
FORMAT(//,'GAMASE IS LESS THAN E-18')
STOP
ELSEIF (GAMASE.GE.1.) THEN
  WRITE(6,16)
FORMAT(//,'GAMASE IS LARGER THAN 1.')
STOP
ENDIF
C
C IF (PORO.LE.0.5) THEN
  EDS=0.0
ELSE
  ETA = 2.*ZETA**2+3.*TANH(ZETA)/ZETA
  AA = -1./ETA*(ZETA**5+6.*ZETA**3-TANH(ZETA)/ZETA)
  * (3.*ZETA**5+6.*ZETA**3))
  BB = 1./ETA**3.*ZETA**3*(1.-TANH(ZETA)/ZETA)
  EDS = 1.-BB/ETA**AA/ZETA**3
ENDIF
IF (EDS.GE.1.) THEN
  EDS = 0.9999
ELSEIF (EDS.LT.0.) THEN
    EDS = 1.0E-5
ENDIF

BETASE(I,J) = PI/4. *(FSCM(I)+FSCM(J))**2
* ABS(SVEL(I)*SVEL(J))

SDEFF = GAMASE + EDS
GBSE(I,J) = SDEFF*BETASE(I,J)

END IF

BETASE(l,J)=PI/4. *(FSCM(I)+FSCM(J))**2
*ABS(SVEL(I)*SVEL(J))

SDEFF = GAMASE + EDS
GBSE(I,J) = SDEFF*BETASE(I,J)

END IF

FLOC
BREAK-UP
FACTOR (ZERO COLLISION EFFICIENCY)
PSUM = PSIZE(I)+PSIZE(J)
IF (PSUM.LT.DMAX) THEN
    ZBETA = (1.-PSUM/DMAX)**3
ELSE
    ZBETA = 0.0
ENDIF

C CALCULATION OF BETA AND MODIFIED GBETA
BETA(I,J) = ALPHA*(BETABR(I,J)+BETASH(I,J)+BETASE(I,J))
GBETA(I,J) = ALPHA*ZBETA*(GBBR(I,J)+GBSH(I,J)+GBSE(I,J))
BETA(I,J) = GBETA(I,J)

MOON = 0
IF (MOON.EQ.1) THEN
    WRITE(6,1122) J,PSIZE(J),FSIZE(J),P,ZETA,ESH
1122 FORMAT(2X,15,2X,5F10.3)
ENDIF

360 CONTINUE
350 CONTINUE
RETURN
END

SUBROUTINE FRACCA(N,V,VSTLOG)
C IMPLICIT REAL*8(A-H,O-Z)
C
INTEGER RESULT
DIMENSION FRAC(100,100), V(100)
COMMON/F/FRAC
C
FRAC(K,1) IS THE FRACTION OF THE NEW PARTICLE FORMED FROM
PARTICLE I AND PARTICLE J THAT IS ASSIGNED TO V(RESULT)
RESULT IS THE NUMBER OF THE SMALLER OF THE TWO STANDARD
VOLUMES THAT THE SUM OF V(I) FALLS BETWEEN.
FRAC(K,1) IS TO BE USED WHEN RESULT < N
K=J-1+1, SO FOR EXAMPLE WHEN COMBINING A '6' PARTICLE
WITH A '9' PARTICLE, USE K=9-6+1=4
C
DO 10 I=1,N
    DO 20 J=1,N
        FRAC(I,J)=0.
20 CONTINUE
10 CONTINUE

K=J-1+1
DO 400 J=1,N
    K=J-1+1
    IF (K.GT.20) THEN
        RESULT=K
        ENDIF
    ELSE
        RESULT=I+ INT(ALOG10(1.0+10.**((J-1)*VSTLOG))/VSTLOG)
        ENDIF
        VOLIJ=V(I)+V(J)
        FRAC(K,1)=(V(RESULT+1)*VOLIJ)/(V(RESULT+1)-V(RESULT))
400 CONTINUE
C
FRAC(K,2) IS TO BE USED WHEN COMBINING A 'K' PARTICLE
WITH 'N' PARTICLE
ITS CALCULATION FOLLOWS
C
I=N
DO 410 J=1,N
    K=J
    VOLIJ=V(I)+V(J)
410 CONTINUE
**FRAC(K,2)=VOLIJ/V(N)**

**410** CONTINUE

**C**

**C** FRAC(K,3) IS TO BE USED WHEN COMBINING TWO PARTICLES BOTH OF

**C** LESS THAN SIZE 'N' THAT YIELD ONE LARGER THAN SIZE 'N'.

**C** KEY TO USING FRAC(K,3)

**C**

**I**

**J**

**K**

**C**

**N-3** **N-3** **1**

**N-2** **N-5** **2**

**N-2** **N-4** **3**

**N-2** **N-3** **4**

**N-2** **N-2** **5**

**N-1** **N-8** **6**

**N-1** **N-7** **7**

**N-1** **N-6** **8**

**N-1** **N-5** **9**

**N-1** **N-4** **10**

**N-1** **N-3** **11**

**N-1** **N-2** **12**

**N-1** **N-1** **13**

**C**

**C** THE CALCULATION OF FRAC(K,3) FOLLOWS

**C**

**I=N-3**

**K=0**

**J=N-3**

**K=K+1**

**VOLIJ=V(I)+V(J)**

**FRAC(K,3)=VOLIJ/V(N)**

**I=N-2**

**II=N-5**

**DO 420 J=II,I**

**K=K+1**

**VOLIJ=V(I)+V(J)**

**FRAC(K,3)=VOLIJ/V(N)**

**420** CONTINUE

**I=N-1**

**II=N-8**

**DO 430 J=II,I**

**K=K+1**

**VOLIJ=V(I)+V(J)**

**FRAC(K,3)=VOLIJ/V(N)**

**430** CONTINUE

**C**

**f=1**

**if (f.eq.0) then**

**WRITE(6,440)**

**440** FORMAT(/,5X,11HFRAC VALUES)

**DO 450 J=1,N**

**WRITE(6,470) J,(FRAC(J,I),I=1,3)**

**470** FORMAT(2X,I4,2X,3F12.4)

**450** CONTINUE

**endif**

**RETURN**

**END**

**C**

**C** SUBROUTINE STIFDI(N,H,HMIN,HMAX,KFLAG,Y,DY,T,**

**LFLAG,NDCALL,DIFFUN)**

**C**

**C** IMPLICIT REAL*8(A-H, O-Z)

**C** LOGICAL **FAIL**

**DIMENSION Y(100),DY(100),PNEXT(100),BETA(100,100),FRAC(100,100)**

**COMMON/B/ BETA**

**COMMON/F/ FRAC**

**COMMON**

**FAIL**

**CALL DIFFUN(N,Y,DY,NDCALL,TOTNUM)**

**FASTLO=0.**

**IQUICK=1**

**LFLAG =1**
DO 35 J=1,N
  I=J
  IF (.NOT.FAIL) GO TO 35
  IF (NDCALL.GT.4000) THEN
    WRITE(6,300)
  FORMAT(//,'TOO MANY DIFFUN CALL')
  STOP
ENDIF
  IF (DY(I).LT.FASTLO) THEN
    FASTLO=DY(I)
    IQUICK=I
  ENDIF
  IF (.NOT.FAIL) STOP
  PN=PN(I)+H*DY(I)
  IF (PNPEN(I).LT.FASTLO) THEN
    WRITE(6,20)
    FORMAT(//'PREDICTED NEG. PARTICLE CONC. AT T=',F10.5,2X,'FOR PARTICLE SIZE',I3)
    IF (H.EQ.HMIN) THEN
      WRITE(6,30)
      FORMAT(/'NO GO AT HMIN')
      KFLAG=-4
      LFLAG=0
    ENDIF
    IF (H.GT.HMAX) THEN
      H=HMAX
    ENDIF
  H=0.99999*ABS(Y(I)/DY(I))
  IF (H.LT.HMIN) THEN
    H=HMIN
  ENDIF
ENDIF
  I=I-1
END IF
35 CONTINUE
38 CONTINUE
T=T+H
DO 41 I=1,N
  41 YO(I)=Y(I)
  DO 42 I=1,N
    XK1(I)=H*DY(I)
    XX1(I)=YO(I)+XK1(I)/2.0
  CALL DIFFUN(N,XX1,DY,NDCALL,TOTNUM)
  DO 44 I=1,N
    XK2(I)=H*DY(I)
    XX2(I)=YO(I)+XK2(I)/2.0
  CALL DIFFUN(N,XX2,DY,NDCALL,TOTNUM)
  DO 46 I=1,N
    XK3(I)=H*DY(I)
    XX3(I)=YO(I)+XK3(I)
  CALL DIFFUN(N,XX3,DY,NDCALL,TOTNUM)
  DO 48 I=1,N
    XK4(I)=H*DY(I)
  DO 50 I=1,N
    Y(I)=YO(I)+(XK1(I)+2.0*XK2(I)+2.0*XK3(I)+XK4(I))/6.0
  IF (ABS(FASTLO).GT.1.0D-30) THEN
    H=ABS(0.75*Y(IQUICK)/FASTLO)
  ENDIF
  IF (H.LT.HMIN) THEN
    H=HMIN
  ENDIF
  IF (H.GT.HMAX) THEN
    H=HMAX
  ENDIF
RETURN
END
SUBROUTINE DIFFUN(N,Y,DY,NDCALL,TOTNUM)
   IMPLICIT REAL*8(A-H,0-Z)
   DIMENSION BETA(100,100),FRAC(100,100),Y(100),DY(100)
   COMMON/B/ BETA
COMMON/F, FRAC
C
THE CALCULATION OF THE DIFFERENTIAL EQUATIONS follows
C
K is the number of the differential equation, i.e., it is the
C
particle size number begin formed or lost.
C

NDCALL=NDCALL+1
DO 10 J=1,N
   TN=1.0E-10*TOTNUM
   IF (Y(J).LE.TN) THEN
      Y(J)=0.
   ENDIF
10 CONTINUE
GAINP1=0.
DO 20 K=1, N
   GAIN=GAINP1
   GAINP1=0.
   IF (K.EQ.N) GO TO 200

C COMBINATIONS WITH 'K' PARTICLES
IJ=K-8
   IF (IJ.GT.0) THEN
      DO 30 J=1, IJ
         GAIN=GAIN+BETA(J,K)*FRAC(K-J+1,1)*Y(K)*Y(J)
         GAINP1=GAINP1+BETA(J,K)*(1.-FRAC(K-J+1,1))*Y(K)*Y(J)
      30 CONTINUE
   END IF
C COMBINATIONS WITH 'K-1' PARTICLES
II=K-8
IJ=K-5
C   IF (II.GT.0) THEN
   DO 40 J=II, IJ
      IF (J.LT.1) GO TO 40
      GAIN=GAIN+BETA(J,K-1)*FRAC(K-J,1)*Y(K-1)*Y(J)
      GAINP1=GAINP1+BETA(J,K-1)*(1.-FRAC(K-J,1))*Y(K-1)*Y(J)
   40 CONTINUE
C COMBINATIONS WITH 'K-2' PARTICLES
II=K-5
IJ=K-3
   DO 50 J=II, IJ
      IF (J.GT.0) THEN
         GAIN=GAIN+BETA(J,K-2)*FRAC(K-J-1,1)*Y(K-2)*Y(J)
         GAINP1=GAINP1+BETA(J,K-2)*(1.-FRAC(K-J-1,1))*Y(K-2)*Y(J)
      END IF
   50 CONTINUE
J=K-3
   IF(J.GT.0) THEN
      GAIN=GAIN+0.5*BETA(J,K-3)*FRAC(K-J-2,1)*Y(K-3)*Y(J)
      GAINP1=GAINP1+0.5*BETA(J,K-3)*(1.-FRAC(K-J-2,1))*Y(K-3)*Y(J)
   ENDIF
   GO TO 210
C
THE CALCULATION FOR THE CREATION OF SIZE N PARTICLES follows
C COMBINATIONS WITH 'N' PARTICLES
200 CONTINUE
   DO 60 J=1, N-1
      GAIN=GAIN+BETA(J,K)*FRAC(J,2)*Y(K)*Y(J)
   60 CONTINUE
J=N
   GAIN=GAIN+0.5*BETA(J,K)*FRAC(J,2)*Y(K)*Y(J)
C COMBINATIONS WITH 'N-1' PARTICLES
II=K-8
IJ=K-2
   DO 65 J=II, IJ
      GAIN=GAIN+BETA(J,K-1)*FRAC(J-(N-14),3)*Y(K-1)*Y(J)
   65 CONTINUE
J=N-1
   GAIN=GAIN+0.5*BETA(J,K-1)*FRAC(J-(N-14),3)*Y(K-1)*Y(J)
C COMBINATIONS WITH 'N-2' PARTICLES
II=K-5
J=K-3
DO 70 J=II, I
    GAIN=GAIN+BETA(J,K-2)*FRAC(J-(N-7),3)*Y(K-2)*Y(J)
70 CONTINUE

C COMBINATIONS WITH 'N-3' PARTICLES
J=K-3
GAIN=GAIN+0.5*BETA(J,K-3)*FRAC(J-(N-4),3)*Y(K-3)*Y(J)

END OF CALCULATION OF GAIN

C LOSS CALCULATION FOLLOWS

210 CONTINUE
ALOSS=0
DO 80 I=1, N
ALOSS=ALOSS+BETA(I,K)*Y(I)*Y(K)
80 CONTINUE

END OF LOSS CALCULATION

DY(K)=GAIN-ALOSS
20 CONTINUE

RETURN

END

SUBROUTINE MASSSU(N,Y,V,DELTAD,PSIZE,PSD,PVD,PN, TOTSUR,TOTVOL,TOTDIA,TOTMAS,TOTYIN,AVVODI,AVSUDI,AVNUDI, PEAKVD,PEAKND,FRAREN,CON3,CON4,RHO, FDEN,VF,IFLOC)
IMPLICIT REAL*8(A-H,0-Z)
REAL NPEAK,VPEAK
INTEGER PEAKND,PEAKVD
DIMENSION PSD(100),PND(100),PVD(100),PSIZE(100),V(100), * Y(100),DELTAD(100),FDEN(100),VF(100),YMASS(100)
DO 10 I=1,N
PSD(I)=0.
10 CONTINUE
TOTDIA=0.
TOTMAS=0.
TOTNUM=0.
TOTSUR=0.
TOTVOL=0.
VPEAK=0.
NPEAK=0.
DO 20 I=1,N
PND(I)=0.
PVD(I)=0.
20 CONTINUE
DO 30 I=1,N
IF (Y(I).GT.O.) THEN
    PSD(I)=ALOG10(Y(I)/DELTAD(I))
    TOTNUM=TOTNUM+Y(I)
    YMASS(I)=RHO*V(1)*1.0E-12
    VF(I)=YMASS(I)/FDEN(I)*1.0E12
    IF (IFLOC.EQ.0) THEN
        TOTVOL=TOTVOL+Y(I)*V(I)
        TOTSUR=TOTSUR+Y(I)*V(I)**(2./3.)
        TOTDIA=TOTDIA+Y(I)*V(I)**(1./3.)
        TOTMAS=TOTMAS+Y(I)*V(I)*RHO*1.0E-6
    ELSE
        TOTVOL=TOTVOL+Y(I)*V(I)*RHO*V(1)/FDEN(I)
        TOTSUR=TOTSUR+Y(I)*V(I)**(2./3.)
        TOTDIA=TOTDIA+Y(I)*V(I)**(1./3.)
        TOTMAS=TOTMAS+Y(I)*V(I)*RHO*1.0E-6
    ENDIF
    PVD(I)=CON4*PSIZE(I)**4*Y(I)/DELTAD(I)
    PND(I)=2.3*PSIZE(I)*Y(I)/DELTAD(I)
    IF((PVD(I).GT.VPEAK) THEN
        VPEAK =PVD(I)
    ENDIF
END
PEAKVD=I
ENDIF
IF (PND(I).GT.NPEAK) THEN
  NPEAK=PND(I)
PEAKND=I
ENDIF
END IF
30 CONTINUE
FRAREN=TOTNUM/TOTYIN
AVVODI=CON3*(TOTVOL/TOTNUM)**(1./3.)
AVSUDI=CON3*(TOTSUR/TOTNUM)**(1./3.)
AVNUDI=CON3*(TOTDIA/TOTNUM)
RETURN
END
SUBROUTINE OUTPUTCN,NDCALL,KFLAG,MFLAG,NTI,TOTNUM,TOTMAS,FRAREN,*
  AVVODI,AVSUDI,AVNUDI,PSD,PVD,PND,PEAKVD,*
  PEAKND,PSZLOG,PSIZE,DY,T,Y,VF,IFLOC,*
  TOTVOL,FDEN)
C IMPLICIT REAL*BCA-H,0-Z)
C INTEGER PEAKND, PEAKVD
DIMENSION PSDC100),PVDC100),PNDC100),PSZLOG(100),PSIZEC100),*
  DYC100),YC100),VFC100),FDENC100),FLSIZEC100)
NTI=NTI+1.
TMINUT=T/60.
WRITE(6,10) TMINUT, KFLAG, MFLAG, NDCALL
10 FORMAT(/,2X, 'TIME (MINUTES)=', F5.1, 2X, 'KFLAG=', 12, 2X, 'MFLAG=', 12, 2X, 'NUMBER OF CALLS TO DIFFUN=', 14)
WRITE(6,20) TOTNUM
20 FORMAT(2X, 'TOTAL NUM CONC (#/cc) =', E11.4)
WRITE(6,22) TOTVOL
22 FORMAT(2X, 'TOTAL VOLUME (CM**3/cc) =', E11.4)
WRITE(6,23) TOTMAS
23 FORMAT(2X, 'TOTAL MASS (MG/L) =', E11.4)
WRITE(6,24) FRAREN
24 FORMAT(2X, 'NUM. FRAC. REMAIN =', F7.4)
WRITE(6,30) AVVODI
30 FORMAT(2X, 'VOLUME AVE. PSIZE =', F7.4)
WRITE(6,32) AVSUDI
32 FORMAT(2X, 'SURFACE AVE. PSIZE =', F7.4)
WRITE(6,34) AVNUDI
34 FORMAT(2X, 'NUMBER AVE. PSIZE =', F7.4)
WRITE(6,40)
40 FORMAT(/,20X, 'PARTICLE SIZE DISTRIBUTION ')
IF (IFLOC.EQ.0) THEN
WRITE(6,45)
45 FORMAT(/,6X,'I',3X,'PSIZE(I)',4X,'Y(I)',6X,'PSD(I)',* 5X,'PVD(I)',BX,'PND(I)')
DO 500 I=1,N
WRITE(6,50) I,ALOG10CPSIZECI)),Y(I),PSD(I),PVD(I), PND(I)
500 CONTINUE
ELSE
WRITE(6,55)
55 FORMAT(6X,'I',3X,'FSIZE(I)',1X,'FDEN(I)',7X,'Y(I)',6X,'PSD(I)',* 5X,'PVD(I)',BX,'PND(I)')
DO 502 I=1,N
IF (VF(I).GT.0) THEN
  FLSIZE(I) = ALOG10C(VF(I)*6.0/3.141592)**(1./3.)
WRITE(6,57) I,FLSIZE(I),FDEN(I),Y(I),PSD(I),PVD(I),PND(I)
502 CONTINUE
END IF
502 CONTINUE
ENDIF
WRITE(6,60) PEAKVD,PSZLOG(PEAKVD)
60 FORMAT(/,2X, 'VOLUME PEAK IS IN SIZE', * 13, 2X, 'WITH LOG DIAMETER=', F5.2)
WRITE(6,80) PEAKND, PSZLOG(PEAKND)
80 FORMAT(/,2X, 'NUMBER PEAK IS IN SIZE',
* I3, 2X, 'WITH LOG DIAMETER=', F5.2
RETURN
END

C

FUNCTION RAN2(IDUM)
PARAMETER (M=714025, IA=1366, IC=150889, RM=1./M)
DIMENSION IR(97)
DATA IFF /0/
IF (IDUM.LT.0.OR.IFF.EQ.0) THEN
  IFF=1
  IDUM=MOD(IC-IDUM,M)
  DO 11 J=1,97
    IDUM=MOD(IA*IDUM+IC,M)
    IR(J)=IDUM
  11 CONTINUE
  IDUM=MOD(IA*IDUM+IC,M)
  IY=IDUM
  J=1+(97*IY)/M
  IF (J.GT.97.OR.J.LT.1)PAUSE
  IY=IR(J)
  RAN2=IY*RM
  IDUM=MOD(IA*IDUM+IC,M)
  IR(J)=IDUM
RETURN
END

C

FUNCTION GASDEV(IDUM)
DATA ISET/0/
IF (ISET.EQ.0) THEN
  V1=2.*RAN2(IDUM)-1.
  V2=2.*RAN2(IDUM)-1.
  R=V1**2+V2**2
  IF (R.GE.1.) GO TO 1
  FAC=SQRT(-2.*LOG(R)/R)
  GSET=V1*FAC
  GASDEV=V2*FAC
  ISET=1
ELSE
  GASDEV=GSET
  ISET=0
ENDIF
RETURN
END
### APPENDIX B

#### COMPUTER PROGRAM OUTPUT

************MODEL INPUT**********

<table>
<thead>
<tr>
<th>ALPHA</th>
<th>HAMAKER</th>
<th>TEMP</th>
<th>VISCOSITY</th>
<th>DENSITY</th>
</tr>
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<tbody>
<tr>
<td>1.000</td>
<td>2.0E-18</td>
<td>293.0</td>
<td>.0100</td>
<td>2.65</td>
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<table>
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<tr>
<th>DMAX</th>
<th>VCON</th>
<th>DT</th>
<th>DCON</th>
<th>DKP</th>
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<tr>
<td>200.0</td>
<td>.4</td>
<td>15.0</td>
<td>.00130</td>
<td>.90</td>
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<table>
<thead>
<tr>
<th>H</th>
<th>HMIN</th>
<th>HMAX</th>
<th>TMAX</th>
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<tbody>
<tr>
<td>10.0</td>
<td>1.0</td>
<td>100.0</td>
<td>8000.0</td>
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</tbody>
</table>

**INITIAL PARTICLE SIZE DISTRIBUTION DATA**

- Time (Minutes) = 0.0
- KFLAG = 0
- MFLAG = 1
- Number of calls to DIFFUN = 0
- Total Num Conc (#/cc) = 0.1120E+08
- Total Volume (um^3/cc) = 0.5585E+08
- Total Mass (mg/l) = 0.9970E+02
- Num. Frac. Remain = 1.0000
- Volume Ave. PSize = 2.1197
- Surface Ave. PSize = 1.4006
- Number Ave. PSize = 1.2689

**PARTICLE SIZE DISTRIBUTION**

<table>
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<tr>
<th>I</th>
<th>FSIZE(1)</th>
<th>FDEN(1)</th>
<th>Y(1)</th>
<th>PSD(1)</th>
<th>PVD(1)</th>
<th>PND(1)</th>
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<tr>
<td>1</td>
<td>-.06</td>
<td>2.6500</td>
<td>2096293.00</td>
<td>7.54</td>
<td>2608554.00</td>
<td>69784100.00</td>
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<tr>
<td>2</td>
<td>-.03</td>
<td>2.6500</td>
<td>1703931.00</td>
<td>7.42</td>
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| TOTAL MASS (MG/L)| 0.9970E+02 |
| NUM. FRAC. REMAIN| 0.6993 |
| VOLUME AVE. PSIZE| 2.5073 |
| SURFACE AVE. PSIZE| 1.4471 |
| NUMBER AVE. PSIZE| 1.2993 |

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NUMBER PEAK IS IN SIZE 1 WITH LOG DIAMETER = -0.06

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TOTAL NUM CONC (#/cc) = 5492E+07
TOTAL VOLUME (UM**3/cc) = .7221E+08
TOTAL MASS (MG/L) = .9969E+02
NUM. FRAC. REMAIN = .4904
VOLUME AVE. PSIZE = 2.9283
SURFACE AVE. PSIZE = 1.4903
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VITA

Byung-Hyun Moon

Candidate for the Degree of

Doctor of Philosophy

Thesis: MODELING OF FLOCCULATION SYSTEMS USING PARTICLE SIZE DISTRIBUTION

Major Field: Civil Engineering

Biographical:

Personal Date: Born in Sooncheon, Korea, May 17, 1960, the son of Kwang-Hee Moon and Hok Lee.

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