1970

Intrinsic classified withdrawal in continuous well mixed crystallization

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BECKER, Jr., George William, 1943–
INTRINSIC CLASSIFIED WITHDRAWAL IN CONTINUOUS
WELL MIXED CRYSTALLIZATION.

Iowa State University, Ph.D., 1970
Engineering, chemical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED
INTRINSIC CLASSIFIED WITHDRAWAL IN
CONTINUOUS WELL MIXED CRYSTALLIZATION

by

George William Becker, Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

Signature was redacted for privacy.

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Ames, Iowa

1970
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ABSTRACT

The purpose of this work was to investigate the applicability of the uniform withdrawal assumption, used in the development of the continuous crystallizer design equations, to laboratory scale continuous mixing vessels. A discussion of the pertinent laws of physics and the existing theory of anisokinetic sampling of aerosols was presented to show why this assumption is theoretically unrealistic. Phenomenological equations relating the concentrations of the various sized particles within a typical suspension were developed by assuming that the withdrawal operation could be characterized as a discrete state time homogeneous Markov process for which the particle concentrations are independently distributed.

An experimental draft tube mixing vessel was used to test the Markov model and to determine the behavior of particle residence times at various operating conditions. Dilute suspensions consisting of water and spherical particles whose density was slightly higher than that of water were used in the experimental work. The experimental data were quite adequately described by the Markov model and the assumption of independence was confirmed from the experimental results. Particle residence times were found to be a function of particle size, agitator R.P.M., and the volumetric flowrate at a constant vessel and outlet geometry. Particles that were relatively small compared to the outlet tube diameter
consistently had residence times very close to the total volumetric residence time. Larger particles usually had residence times significantly different from the total volumetric residence time, depending on the operating conditions. Particle residence times tended to become uniform and approach the total volumetric residence time at very high values agitator speed. This experimentally observed behavior contradicted what one would expect from considering the existing theory of anisokinetic sampling.

Empirical size dependent particle residence time functions were determined from the experimental data and were used to discuss the effect of classified withdrawal on continuous crystallization. It was shown that the crystal size distribution for the classified withdrawal case were markedly different from those predicted by the continuous crystallization design equations. The empirical size dependent particle residence time functions were also used to demonstrate the fact that size dependent growth cannot be distinguished from size dependent withdrawal from continuous crystallization data alone.
INTRODUCTION

In recent years the principle of conservation of numbers has been used extensively in modeling the crystal size distribution obtained from continuous crystallizers. In order to facilitate this analysis a series of assumptions were made by Randolph and Larson (29) and others. It was assumed that the suspension within the crystallizer is completely mixed, that there is no agglomeration or breakage of crystals, and that the suspension of crystals and fluid is uniformly withdrawn from the crystallizer. Therefore the crystals were assumed to be noninteracting and hydrodynamically indistinguishable from the fluid. As a consequence of these restrictions such things as agglomeration and breakage and the effects of differential fluid-crystal velocities on crystallization kinetics, mixing, and particle withdrawal were neglected in order to obtain workable design equations.

In spite of the above limitations a large body of experimental work by Chambliss (13), Timm (36), Murray (24), and many others has shown that the above assumptions can be justifiably made. These investigators determined empirical growth rate and nucleation rate expressions for various crystallizing systems by using analytical techniques based on the continuous crystallization design equations originally forwarded by Randolph and Larson (29). In fact the continuous crystallizer design equations have become standard tools for
obtaining empirical growth and nucleation rates from data generated by laboratory scale continuous crystallizers. These equations have also been used for industrial applications by Bennett (4, 5).

In principle, industrial sized crystallizers can be designed or sized and optimum operating conditions can be established once the fundamental kinetic relationships of crystallization, growth and nucleation, are defined. Therefore, it is important to determine if the assumptions of complete mixing and uniform withdrawal can be realized in laboratory scale continuous mixing vessels since crystallization kinetic data are usually determined from this size of equipment. The assumptions concerning agglomeration and breakage are not as critical as the above two assumptions. Methods for compensating for these mechanisms within the continuous crystallizer design equations have been established by Hulburt and Katz (18) and Randolph (28). Complete mixing can be realized in practice since with proper baffling and high levels of agitation complete mixing can be approached for most systems in experimental mixing vessels. However, the operating conditions and the proper design features of an experimental continuous crystallizer for which uniform withdrawal can be achieved are not known. This particular fact casts suspicion upon the applicability of the uniform withdrawal assumption used in the development of the con-
If classified withdrawal is an intrinsic phenomenon of laboratory scale continuous crystallizers this feature must be accounted for in the continuous crystallizer design equations. For instance, size dependent growth rate cannot be distinguished from size dependent particle withdrawal from an analysis of continuous crystallizer data alone. In order to be sure that the growth rate is fundamentally size dependent the exact nature of the particle withdrawal has to be specified. Therefore the need to investigate the applicability of the uniform withdrawal assumption from both a theoretical and experimental point of view is necessary so that the scope and validity of the continuous crystallizer design equations can be broadened.

The purpose of this work was to investigate the applicability of the uniform withdrawal assumption in laboratory scale continuous mixing vessels. The withdrawal behavior of suspensions from well mixed continuous crystallizers is an independent phenomenon which does not depend on the fact that crystallization is taking place. Further, withdrawal behavior will depend upon the vessel geometry and the overall operating conditions such as the level of agitation and the total volumetric flowrates of the input and output streams. In light of these facts the applicability of the uniform withdrawal assumptions was experimentally investigated in
this work by determining particle residence times of different sized particles at various operating conditions in a draft tube mixing vessel. The intent of these experiments was to determine if classified withdrawal exists, to ascertain the general behavior of classified withdrawal at various operating conditions, and to develop a model which incorporates the effects of classified withdrawal. In addition to the experimental work concerning this problem an attempt was made to show why uniform withdrawal is an unrealistic assumption from a purely theoretical standpoint.
THEORY OF CONTINUOUS CRYSTALLIZATION

Crystallization Kinetics

When considering a crystallizing solution, it is usually asserted that there are particles of a specific size $L_0$ such that all particles which are larger than $L_0$ will grow and all particles which are smaller than $L_0$ will dissolve. Particles of size $L_0$ are called nuclei and all particles larger than $L_0$ are called crystals. Therefore, two distinct phenomenon occurring simultaneously in a crystallizing solution can be defined, namely the production of nuclei and the growth of crystals. In defining the size of a crystal it has been tacitly assumed that there is a characteristic dimension of a typical crystal that completely specifies the size of that crystal and hence all crystals must have the same basic geometry.

In light of the above description of a crystallizing solution, it can be seen that there are two separate kinetic rates involved in crystallization, a nucleation rate and a crystal growth rate. The nucleation rate is defined as the rate at which nuclei are produced per unit volume of the suspension. The crystal growth rate is defined as the rate at which a characteristic linear dimension of a crystal elongates.

A more concise definition of growth rate can be written by focusing attention upon a typical crystal within a crys-
tallizing suspension. Suppose at time $t$ a particular crystal is size $L$ and that at a later time, $t'$, that same crystal has grown to a large size $L'$, then the growth rate of a particle of size $L$ at time $t$ is defined as

$$ r = \frac{dL}{dt} = \lim_{t' \to t} \frac{L' - L}{t' - t} $$

(1)

Crystal growth may be viewed as resulting from the series of kinetic steps consisting of the diffusion of the dissolved solute up to a fluid-crystal interface, adsorption of the solute onto the surface of the growing crystal, molecular orientation of the solute into the lattice of the growing crystal and finally the desorption and dissolution of by-products. However in many crystallizing systems growth can be adequately described by a series diffusion-surface reaction mechanism as shown in the work of McCabe and Stevens (23), Rumford and Bain (31), and Smythe (33).

If diffusion is an important step in the growth mechanism, then growth rate in a mixed crystallizing suspension can be a function of crystal size. This fact has been verified for several crystallizing systems by empirical size dependent growth rate models experimentally obtained by Canning and Randolph (11) and analyzed for by Abegg et al. (1) and Bramson and Palmer (9). On the other hand Saeman (32), McCabe (22), and others maintain that growth rate in a mixed crystallizing suspension is usually not a measurable
function of crystal size for many crystallizing systems. In the majority of cases the following empirical growth rate expression has been used with great success

\[ r = K_0 s^n \]  

(2)

by Timm (36), Bramson et al. (8), Murray (24), and many others. The term \( s \) is called the supersaturation and is defined as

\[ s = C - C_e \]  

(3)

where \( C_e \) is the equilibrium or saturation concentration of crystalline material in solution and \( C \) is the concentration of the crystalline material in solution while the terms \( K_0 \) and \( n \) are empirical coefficients.

In the following discussion the nucleation rate will be denoted by the symbol

\[ \text{nucleation rate} = \frac{dN_e}{dt} \]  

(4)

It is generally accepted that there are two types of nucleation mechanisms, homogenous nucleation and secondary nucleation. In homogenous nucleation nuclei are created solely by the phase change induced by the level of supersaturation. The theoretical aspects of homogenous nucleation have been discussed extensively by Neilson (27). Secondary nucleation accounts for the production of nuclei due to the presence of
crystals in a mixed crystallizing suspension as well as to the level of supersaturation. Larson et al. (21), Cayey and Estrin (12), Chambliss (13), and Timm (36) have investigated the effects of solids on nucleation in a mixed crystallizing suspension. These investigators found that secondary nucleation is dependent on such things as the type of seed crystals present, the level of supersaturation, and the total mass of crystal present.

Murray (24), Bennett and Van Buren (5), Murray and Larson (25), Timm and Larson (37), and many others have empirically correlated nucleation rates for several systems undergoing mixed suspension crystallization by

$$\frac{dN^0}{dt} = K_N s^p$$

(5)

where $p$ and $K_N$ are empirical constants.

There are other fundamental mechanisms besides growth and nucleation which can affect the number and size distribution of crystals in a mixed suspension crystallization. Two important mechanisms are agglomeration and breakage of crystals. The theoretical aspects of agglomeration were considered by Neilson (27), and a crude model for agglomeration is discussed by Hulburt and Katz (18). Randolph (28) presented a discussion of breakage in mixed suspension crystallization. In the following discussion the mechanisms of agglomeration and breakage will be neglected since
in the majority of crystallizing systems investigated to date the kinetic rates of growth and nucleation are found to be sufficient for the description of mixed suspension crystallization.

Population Density Function

The basic function used in the description of a continuous mixed suspension mixed product removal crystallizer is the population density function, \( n \),

\[ n = n(L,t) \]

which has dimensions of numbers per unit size per unit volume of suspension. Suppose that at time \( t \) the total volume of a suspension of crystals and fluid is \( V \). If the population density function is known the total number of crystals in any arbitrary size range, \([L_1,L_2]\), that are in the total volume \( V \) at time \( t \) can be calculated as follows:

\[
V \int_{L_1}^{L_2} n \, dL
\]  

(6)

The above relationship serves as a definition for the population density function.

The population density function can be used to calculate a set of moments, \( \mu_p(t) \), with the following formula

\[
\mu_p(t) = \int_0^\infty n(L,t)L^p \, dL ; \quad p = 0, 1, \ldots
\]  

(7)

The set of moments \( \mu_p(t) \) are uniquely determined by the
population density function. The various moments of a population density function have special statistical significance. For instance, \( u_1 \) divided by \( u_0 \) is the numbers averaged crystal size, \( u_4 \) divided by \( u_3 \) is the mass averaged crystal size, and \( u_0 \) is the total number of crystals per unit volume of the suspension. With the proper geometric factors one can calculate the total area or the total volume of crystals per unit volume of suspension since \( u_2 \) and \( u_3 \) are proportional to the total area and total volume of crystals per unit volume of suspension, respectively. The suspension density or the total mass of crystals per unit volume of suspension, \( M \), can be calculated by

\[
M = \rho_p K_v u_3
\]

where \( \rho_p \) is the density of the crystals and \( K_v \) is the appropriate volumetric shape factor.

It should be noted that the above definitions of the population density function and the moments of the population density function are for the case when the suspension of crystals under consideration is completely mixed. If the suspension is not well mixed the population density function will in general depend upon position within the suspension. It would be a simple matter to extend the above definitions to include this case but since the concern in the following treatment is with completely mixed suspensions this case is omitted.
Continuous Crystallizer Design Equations

The continuous crystallizer design equations describe a continuous mixed suspension mixed product removal crystallization. This type of operation consists of a vessel within which a mixed crystallizing suspension occupies the working volume which may vary with time. A stream containing a crystal distribution described by the population density function \( n_1 \) is continually introduced into the working volume at a volumetric flowrate of \( F_1 \). Simultaneously a portion of the suspension with a population density of \( n_0 \) is continually withdrawn from the working volume \( V \) at a volumetric rate of \( F_0 \). The object of the following analysis is to obtain a representation of the population density function within the volume \( V \).

Randolph and Larson (29) used the population density function to develop a set of design equations for the continuous mixed suspension mixed product removal crystallizer. The following material is essentially a restatement of the original derivation of the continuous crystallizer design equations of Randolph and Larson. The basic assumptions made by these authors were:

1. The crystals and fluid that make up the product stream are withdrawn uniformly from the working volume \( V \) at a volumetric flowrate of \( F_0 \). The crystals and fluid that comprise the inlet or feed stream are introduced uniformly
into $V$ at a volumetric flowrate of $F_1$.

2. The suspension of crystals and fluid within the working volume $V$ is completely mixed.

3. Agglomeration and breakage of crystals are negligible.

As a result of the complete mixing assumption the population density function, $n$, does not depend upon the position within $V$ and $n_0$, the outlet population density function, is the same as $n$.

The expression for growth rate in terms of the variables used in the above description of continuous crystallization is:

$$ r = r(L,t) $$

(9)

The nucleation rate will be a function of time, $t$. It should be noted that growth rate is fundamentally a function of size, temperature, and supersaturation while the nucleation rate is fundamentally a function of temperature and supersaturation. However supersaturation and temperature can be obtained as functions of time from appropriate heat and mass balances and therefore one can generally replace these fundamental variables by time.

To derive an expression relating the behavior of the population density function within the working volume, the growth progress of a specific group of crystals is followed.
Suppose at time $t_0$ attention is focused upon all the crystals in the working volume $V$ which are in the crystal size interval $[L_1, L_2]$. At a later time $t$ these same crystals will have grown into a new size interval $[L_1(t), L_2(t)]$ such that

$$L_1(t) = L_1 + \int_{t_0}^{t} r(L_1(t'), t') \, dt' \quad (10)$$

$$L_2(t) = L_2 + \int_{t_0}^{t} r(L_2(t'), t') \, dt' \quad (11)$$

The total number of crystals observed at any time is not necessarily equal to the total number of crystals observed originally at time $t_0$. The total number of crystals observed will change with time since crystals are continually being introduced into and withdrawn from the moving size interval $[L_1(t), L_2(t)]$ via the inlet and outlet streams. It is clear that the total number of observed particles at any time $t$ is equal to the total number of crystals originally observed at time $t_0$ plus the net amount of crystals that entered into the moving size interval $[L_1(t), L_2(t)]$ during the period of time between $t_0$ and $t$ as a result of the input and output streams. Utilizing the definition of the population density function, Equation 6, the above assertion can be expressed mathematically as

$$V(t) \int_{L_1(t)}^{L_2(t)} n(L', t) \, dL' = V(t_0) \int_{L_1}^{L_2} n(L', t_0) \, dL'$$

$$+ \int_{t_0}^{t} \int_{L_1(t')}^{L_2(t')} (F_i n_i(L', t') - F_o n(L', t')) \, dL' \, dt' \quad (12)$$
The first term on the right-hand side of Equation 12 is the total number of crystals originally observed at time \( t_0 \), the second term is the net amount added to the moving size interval \([L_1(t), L_2(t)]\) during the time period \( t_0 \) to \( t \) because of the input and output streams. The term on the left-hand side of Equation 12 is the total number of observed crystals at time \( t \). Taking the derivative of Equation 12 with respect to time \( t \), the following identity is obtained.

\[
\int_{L_1(t)}^{L_2(t)} \left[ \frac{\partial}{\partial t} \left( V(t) n_L(L', t) \right) + \frac{\partial}{\partial L} \left( \frac{r(L', t) n(L', t)}{\delta L} \right) \right. \\
- \left. F_1 n_1(L', t) + F_0 n(L', t) \right] \, dL' = 0 \tag{13}
\]

Since the original interval \([L_1, L_2]\) was completely arbitrary it follows that the argument in Equation 13 must be zero. Hence one obtains a partial differential equation in terms of the population density function

\[
\frac{\partial (nV)}{\partial t} + \frac{\partial n}{\partial L} = F_1 n_1 - F_0 n \tag{14}
\]

Equation 14 serves as the basis for the continuous crystallizer design equations.

The nucleation rate is fundamentally related to the population density function evaluated at the size of a nucleus and the growth rate. To show this property consider the total number of crystals in the working volume born during the time
interval \([t_0, t]\). By assuming that nuclei are of size zero this quantity can be calculated by

\[
N(L(t), t) = \int_0^{L(t)} V(t)n(L', t)dL'
\]  

(15)

and

\[
L(t) = \int_{t_0}^{t} r(L(t'), t')dt'
\]

Taking the derivative of \(N(L(t), t)\) with respect to time \(t\) yields the expression

\[
\frac{dN(L(t), t)}{dt} = \int_0^{L(t)} \frac{\partial V(t)n(L', t)}{\partial t} dL' + r(L(t), t)n(L(t), t)V(t)
\]  

(16)

and using Equation 14, Equation 16 becomes

\[
\frac{dN(L(t), t)}{dt} = V(t)r(0, t)n(0, t) + \frac{dF_1}{dt}N(L(t), t) - F_0N(L(t), t)
\]  

(17)

where \(N_1(L(t), t)\) is calculated by substituting the input population density function \(n_i\), into Equation 15. By allowing \(t\) to approach \(t_o\) in Equations 15 and 17 the following expression for the nucleation rate at time \(t_o\) obtains

\[
\frac{dN^0}{dt}(t_o) = \frac{dN(0, t_o)}{V(t_o)dt} = r(0, t_o)n(0, t_o)
\]  

(18)

Therefore the nucleation rate in a crystallizing suspension is related to the population density function and growth rate at any time, \(t\), by
\[ \frac{dN^0(t)}{dt} = r(0,t)n(0,t) \quad (19) \]

A set of equations can be obtained for the moments of the population density functions in a continuous mixed suspension mixed product removal crystallizer with the aid of Equation 14. To derive these equations the following formula is utilized.

\[ \int_0^\infty L^p \left( \frac{\partial (nV)}{\partial t} + V \frac{\partial (nr)}{\partial L} - F_1n + F_0n \right) dL = 0 \quad (20) \]

where \( p \) takes on the integer values 0, 1, 2,... The moment equations found after evaluating Equation 20 are

\[ \frac{d(\mu_0V)}{dt} = n(0,t)r(0,t) + F_1\mu_1,0 - F_0\mu_0 \quad (21) \]

\[ \frac{d(\mu_pV)}{dt} = p \int_0^\infty (nrL^{p-1}) dL + F_1\mu_{1,p} - F_0\mu_p \quad (22) \]

where \( \mu_{1,p} \) is the \( p \)-moment of the inlet population density function, \( n_1 \). Note that the first term on the right-hand side of Equation 21 is equal to the nucleation rate as expressed in Equation 19. In deriving Equations 21 and 22 it was assumed that nuclei are of size zero and that the product of \( nL^p \) for all real \( p \) evaluated as \( L \) approaches infinity is identically zero. The second of these assumed properties is necessary in order that the moments describe a physically realizable situation.

To complete the description of a continuous mixed
suspension crystallization a mass balance is written. The mass balance associated with this problem is

\[
\frac{d}{dt} \left[ V(C(1-kv_u) + kv_pu_3) \right] = u_{1,3} F_1 k_v n_p \\
+ (C)_{IN} F_1 - [C(1-kv_u) + kv_pu_3] F_0
\]

(23)

where (C)_{IN} and C are the inlet and bulk suspension concentrations of crystallizable material respectively and kv_u is the volume fraction of the suspension occupied by the crystals. Note that F_1 and F_0 are the same volumetric flow rates utilized in Equations 14, 21, and 22 which results from the assumptions of complete mixing and uniform withdrawal. The following material will pertain to cases when the temperature is constant within the working volume and therefore, the need for an associated heat balance is bypassed. Equations 14, 21, 22, and 23 form the continuous crystallizer design equations.

One can convert these equations over to design equations for a batch crystallization by neglecting all terms involving F_1 and F_0, the inlet and outlet volumetric flowrates. The continuous crystallizer design equations tell very little of the dynamics of continuous crystallization however the general solution to Equation 14 can provide a great deal of insight into this process.

Consider the continuous mixed suspension mixed product removal crystallization for which the feed stream is unseeded.
and the working volume is constant. In general, growth rate will be a function of time and crystal size.

\[ r = h(t)g(L) \quad ; \quad g(0) = 1 \]  

(24)

The form of Equation 24 is consistent with the empirical size dependent growth rates discussed by Bramson and Palmer (9), Abegg et al. (1), and Canning and Randolph (11). In this case the numbers balance equation, Equation 14, takes the form

\[ \frac{dn}{dt} + \frac{1}{r} \frac{dn(r)}{dr} = - \frac{n}{\tau_p} \]

(25)

and has the boundary conditions

\[ n(0,t) = \frac{dN^0(t)}{dt}/r(0,t) \]

(26)

\[ n(L,0) = f(L) \]

(27)

The term \( \tau_p \) in Equation 25 is called the residence time and it is equal to the working volume, \( V \), divided by the outlet flowrate, \( F_o \). Equation 26 is the definition of the nucleation rate given in Equation 19 rearranged, and Equation 27 is the initial population density function which is generally a known function. Equation 25 is a variable coefficient linear partial differential equation which can be analytically solved if the growth rate and nucleation rate are given. Of course these functions are not usually known; however these functions
are uniquely defined by the moment equations and mass balance, Equations 21, 22, and 23, if this set of equations can be closed at some finite moment. For instance, if $g(L)$ in Equation 24 is a constant, that is growth rate is independent of crystal size, then the first four moment equations, $p$ equal to 0, 1, 2, 3, and the mass balance equation form a closed set of ordinary differential equations.

Suppose that the growth rate, $r$ and the nucleation rate, $\frac{dN_0}{dt}$, are known and $f(L)$ is given. In this case ordinary LaPlace transform techniques, as in Wylie (41) or Brown and Nilsson (10), can be used to obtain a general solution. In order to write the general solution concisely the following definitions are introduced.

$$\psi = \int_0^t h(t')dt'$$  \hspace{1cm} (28)

$$\xi = \int_0^L \frac{dL'}{g(L')}$$  \hspace{1cm} (29)

The variable $\psi$ is considered a transform of the fundamental variable $t$ and $\xi$ a transform of the fundamental variable $L$. It is assumed that the inverse functions of $\psi$ and $\xi$ are one to one and are given by

$$t = T(\psi)$$  \hspace{1cm} (30)

$$L = L(\xi)$$  \hspace{1cm} (31)

The new variables $(\psi, \xi)$ replacing $(t, L)$ have a unique
physical interpretation. A crystal that was born at time zero will have grown to size $L$ at time $t$ and the size and age of this crystal is found from the following relation.

$$ \hat{\#}(t) = \xi(L) \quad (32) $$

Therefore all crystals at time $t$ with sizes obeying the inequality

$$ 0 < L < L(\hat{\#}) = L(\xi) \quad (33) $$

would have been born during the interval of time $[0,t]$. On the other hand, all crystals at time $t$ with sizes obeying the inequality

$$ L > L(\hat{\#}) = L(\xi) \quad (34) $$

were initially present within the crystallizer. With the definitions of $\hat{\#}$ and $\xi$ in hand the general solution to Equation 25 can be written as

$$ n(L,t) = \begin{cases} 
\frac{-t}{\tau_F} \left( \frac{dN_0}{dt} \left( \frac{t'}{r(0,t')} \right) \right)_{t' = T(\hat{\#}(t) - \xi(L))} & L < L(\hat{\#}(t)) \\
\frac{-t}{\tau_F} \left( \frac{f(L')g(L')}{\xi(L) - \hat{\#}(t)} \right)_{L' = L(\xi(L) - \hat{\#}(t))} & L > L(\hat{\#}(t)) 
\end{cases} \quad (35) $$

Equation 35 reveals that the population density function for a continuous mixed suspension mixed product removal crystallizer is almost totally dependent upon the type of crystalli-
zation kinetics one is considering. Equation 35 also offers an interesting explanation of the way disturbances in the population density vary with time.

There are several ways in which disturbances in the population density function can be created. A few of these ways are seeding, step changes in feed concentration, or production rate changes. Suppose that a disturbance takes the form of a peak in the population density function and that this peak is sufficiently narrow so that \( g(L) \) in Equation 24 is essentially uniform over the width of the peak and the central point of the peak is well defined. By definition the central point of the peak, \( L(p) \), will depend on time as follows.

\[
\psi(t) - \xi(L(p)) = \psi(t_0) - \xi(L_0(p))
\]  

(36)

where \( L_0(p) \) is the size at which the peak was observed originally and \( t_0 \) is the time at which the peak was first observed. If the disturbance occurred because of a shower of nuclei then \( \xi(L_0(p)) \) is zero and \( t_0 \) is the time at which this event produced a maximum in the nuclei population density. The progress of a peak can be followed by recording the location of the central point, \( L(p) \), at various times. The peak will travel along the size axis at a velocity equal to the growth rate and therefore

\[
r = \frac{dL(p)}{dt} \text{ at } t \text{ and } L(p)
\]  

(37)
If the relative height of the peak declines by a factor different from
\[ e^{-t/\tau_F} \] (38)
or if the peak changes its basic or original shape by a factor depending on crystal size then growth rate is size dependent. This fact comes directly from the general solution, Equation 35, since according to this equation the peak or the disturbance will be modulated by the factor
\[ \frac{e^{-t/\tau_F}}{g(L)} \] (39)
The above analysis of the behavior of disturbances in the population density has been experimentally observed by Murray (24), Murray and Larson (25), Timm (36), and Timm and Larson (37). However the above analysis was not developed at the time of these investigations.

The above discussion suggests a new method for obtaining an experimental nucleation rate and an experimental growth rate from one well designed unsteady state experiment. Suppose that during an experimental run M distinguishable peaks were observed and labeled by the index p equal to 1, 2, ..., M. Adhering to the analysis described above, it is possible to generate data in the form
\[ r \text{ at } t > t^{(p)} \text{ and } L(p) ; \quad p = 1, 2, ..., M \] (40)
where \( t(p) \) is the time at which peak number \( p \) was first observed. In principle data such as that of Equation 40 can be used to accurately correlate \( r(L,t) \) as well as \( h(t) \) and \( g(L) \) of Equation 24. To evaluate the nucleation rate it is necessary to have recorded the nuclei population density as a function of time during the entire run. Utilizing Equation 19 one can find the nucleation rate as a function of growth rate, \( r(0,t) \), since

\[
\frac{dN^0}{dt} = n(0,t) \cdot r(0,t) \tag{19}
\]

The key to this type of experimental analysis is of course an experimental design which can produce well defined peaks.

The most important feature of the continuous crystallizer design equations is that these relationships provide the tools for extracting empirical growth rate and nucleation rate expressions from steady state continuous mixed suspension mixed product removal crystallizer data. As previously mentioned, Equations 2 and 5 have been used with a great deal of success in correlating growth rates and nucleation rates from mixed suspension crystallizers. Combining Equations 2 and 5 so as to eliminate supersaturation an expression for the nucleation rate in terms of the growth rate is obtained

\[
\frac{dN^0}{dt} = k_n r^i \tag{41}
\]
where $i$ and $k_n$ are equal to $p/n$ and $K_N/(K_G)^p/n$, respectively. The following expression for the nuclei population density

$$n(0) = k_n r^{i-1}$$  \hspace{1cm} (42)

can be found with the aid of Equations 19 and 41. With kinetics of the type in Equations 41 and 42 the steady state population density function in a continuous crystallizer, as predicted by Equation 14, is

$$n(L) = k_n r^{i-1} e^{-L/r_p}$$  \hspace{1cm} (43)

The expressions for the steady state moments of the population density function, Equation 43, are

$$\mu_p = k_n r^{i-1}(r_p)^{p+1} p!$$  \hspace{1cm} (44)

where $p$ takes on the integer values of 0, 1, 2, ... 3. From a typical steady state run a plot of $\ln(n(L))$ against $L$ can be constructed and the slope of this plot will be the negative reciprocal of $r_p$ while the intercept will be $k_n r^{i-1}$. Therefore from several such experimental runs one can construct a plot of $\ln(n(0))$ against $\ln(r)$ so as to obtain the exponent $i$, called the order of the nucleation rate, and $k_n$ an empirical coefficient particular to the system under consideration. The above type of analysis was first suggested by Randolph and Larson (29) and has been applied to many systems undergoing continuous mixed suspension mixed product
removal crystallization by Bennett (4), Chambliss (13), Murray (24), Murray and Larson (25), Timm (36), Timm and Larson (37), and many others.

Statistical Interpretation of Design Equations

The continuous crystallizer design equations, Equations 14, 21, 22, and 23, are inherently statistical equations. To see this feature consider all the crystals in the size range \([L',\infty]\) within the working volume \(V\) such that

\[
\frac{1}{2} = V(u_0(t) - \int_0^{L'} n(L,t)dL) \tag{45}
\]

Equation 45 requires that at time \(t\) there is a crystal or crystals in the size range \([L',\infty]\) whose total number is \(\frac{1}{2}\). Of course this makes sense only from the point of view that the population density function is a statistical entity.

In addition to the statistical nature of the population density function the entire process of continuous mixed suspension mixed product removal crystallization can be viewed as a statistical process. In fact, Katz and Shinnar (19) have derived the numbers balance equation, Equation 14, by assuming that continuous crystallization is a time stationary mixed discrete state and continuous state Markov process. These authors found that Equation 14 is written in terms of the true mean value of the population density function based upon the underlying probability distribution of the assumed crystallization Markov process. In addition,
Katz and Shinnar (19) claim that statistical fluctuations about the true mean value for the population density function are negligible if the total number of crystals present at all times is very large. This makes sense since from statistics it is commonly known that the greater the amount of available data on a variable, the more accurate are the estimates for the true mean and true variance about the mean of that variable.

To further emphasize the role of the total number of crystals in determining statistical fluctuations in continuous crystallization, the production of crystals has been viewed as a time stationary discrete state Markov process (Appendix A). In Appendix A the case when the working volume \( V \) and the nucleation rate \( \frac{dN^0}{dt} \) are constants and the input stream is unseeded was considered. It was found that the steady state value for the true mean of \( (u_0)_{\text{T}} \), the total number of crystals present within \( V \), is

\[
(u_0)_{\text{T}} = V\tau_F \frac{dN^0}{dt}
\]

This result also obtains from Equation 21 evaluated at steady state. The steady state variance about the true mean value \( (u_0)_{\text{T}} \) is

\[
(\sigma_{u_0}^2)_{\text{T}} = (u_0)_{\text{T}}
\]

*These equations are found in Appendix A.
The ratio of \((\sigma_o)_T\) to \((u_o)_T\) yields some information about the relative statistical fluctuations to be expected because of the assumed underlying statistical nature of continuous crystallization. The ratio of \((\sigma_o)_T\) to \((u_o)_T\) is

\[
\frac{(\sigma_o)_T}{(u_o)_T} = \sqrt{\frac{1}{(u_o)_T}}
\]  

(209)*

The steady state value of \((u_o)_T\) is reliable only if the total number of crystals in \(V\) is very large. The above relations are based upon the assumed inherent statistical nature of crystallization. If \((u_o)_T\) was obtained experimentally additional sources of error would tend to increase the value of \((\sigma_o)_T\). However it can be generally stated that

\[
\frac{(\sigma_o)_T}{(u_o)_T}_{\text{experimental}} > \sqrt{\frac{1}{(u_o)_T}}
\]  

(210)*

or that the experimentally observed fluctuations about the calculated steady state total 0 moment, \((u_o)_T\), is bounded below by Equation 209.

To obtain some idea of the order of \(((\sigma_o)_T/(u_o)_T\) data from a typical continuous mixed suspension mixed product removal crystallizer experiment will be used. Chambliss (13) found that the continuous cooling crystallization of ammonia sulfate at a temperature of 72° F, a residence time of 15

*These equations are found in Appendix A.
minutes, and an inlet concentration of 44.26 grams of ammonium sulfate to 100 grams of water produced a \((\mu_0)_T\) of 2.545 x \(10^7\) in a 10.5 liter vessel. For this particular experiment \((\sigma_0)_{TV}/(\mu_0)_T\) was 2 x \(10^{-4}\) which from an engineering point of view is very small indeed. However if this identical experiment were run in a 1.05 ml vessel, a very small continuous crystallizer, then \((\sigma_0)_{TV}/(\mu_0)_T\) would be .02. Therefore in most experimental continuous mixed suspension mixed product removal crystallizations the underlying statistical nature of the process is of little importance. The continuous crystallizer design equations are reliable tools for analysis of continuous crystallizations.

Review of Mixing and Withdrawal Assumptions

The assumption of complete mixing within the working volume \(V\) and the assumption of uniform withdrawal of product used in the derivation of Equation 14, require a very special interpretation of the mixing model characterizing the continuous crystallizer design equations. The assumption of complete mixing necessitates that the slurry of crystals and fluid within the working volume \(V\) be homogeneous at all times. The uniform withdrawal assumption requires that the exit stream consist of crystals and fluid with exactly the same concentrations as in the homogeneous slurry within the working volume \(V\). It follows that the continuous crystallizer design equations can be characterized by the single residence
time distribution

\[ R(t) = \frac{1}{\tau_F} e^{-t/\tau_F} \]  

for the most common case when V and P are constants. Equation 46 applies for all crystals regardless of size, dissolved species, solvent, and the properties of the population density function such as total numbers \( N_0 \), total length \( V_{\text{bulk}} \), and so on.

It is important to note that the above mixing model as reflected in the residence time distribution function is determined by both the complete mixing and uniform withdrawal assumptions. This distinction must be made since in the processing of a fluid in a continuous mixing vessel the assumption of complete mixing alone implies a residence time distribution of the form given by Equation 46. In principle it is possible to have complete mixing and nonuniform or classified withdrawal. In this case the dissolved species would have the residence time distribution of Equation 46. However crystals of different sizes will be selectively removed because of nonuniform withdrawal and in general the residence time distribution for the crystals will depend on size, \( L \), in addition to time (30).

It is well known that the idealized completely mixed suspension is seldom achieved in large industrial crystallizers. As a consequence the size distributions predicted by
the continuous crystallizer design equations are seldom achieved. A paper by Becker and Larson (3) discussed the effect of various mixing concepts and process geometries on expected size distributions. Models assuming completely mixed and plug flow sections were discussed as well as segregated flow models. However these authors only considered continuous crystallizations for which there was uniform withdrawal of product.

Complete mixing and uniform withdrawal are idealized concepts. The assumption that these conditions exist for a continuous mixed suspension mixed product removal crystallizer simplifies the task of mathematically describing this process. If it would be possible to speak in terms of the degree to which these idealized conditions can be experimentally approached, it would have to be said that the complete mixing condition is far more realizable than the uniform withdrawal condition. Hence accepting the notion that uniform withdrawal is a highly idealized condition the more realistic alternative, nonuniform withdrawal, must be considered in developing design equations for continuous crystallization.

The following material will be devoted to showing that the condition of uniform withdrawal is rather difficult to achieve. A theoretical discussion drawing upon the laws of physics will be offered to show why the assumption of uniform
withdrawal is unrealistic. To further confirm this fact the results of an experimental investigation of the withdrawal characteristics of suspensions of different sized particles from a continuous draft tube mixing vessel will be presented. Therefore the following discussion will deal with the problem of describing the withdrawal behavior of suspensions of particles from continuous mixing vessels. However, since the motivation originated because of suspensions concerning the applicability of the uniform withdrawal assumption used in the derivation by Randolph and Larson (29) there will be frequent reference to continuous crystallization throughout the remaining portions of this work.
MOTION OF PARTICLES IN A VISCOUS FLUID

Equations of Motion

To discuss the motion of an arbitrary particle in a fluid, the equations of motion will be presented for the case when the particle density, \( \rho_p \), and the fluid density, \( \rho_f \), are both uniform. The laws of conservation of linear and angular momentum will be written in terms of the velocity of an arbitrary point \( O \) on the particle, \( \bar{u}_O \), and the angular velocity of the particle, \( \bar{\omega} \). The angular velocity, \( \bar{\omega} \), is a free vector and therefore point \( O \) does not necessarily have to lie upon the instantaneous axis of revolution of the particle. The velocity of any point on the particle is thus specified with the knowledge of the velocity, \( \bar{u}_O \), and the angular velocity, \( \bar{\omega} \), since the velocity \( \bar{u}_p \), of point \( p \) on the particle is given by

\[
\bar{u}_p = \bar{u}_O + \bar{\omega} \times \bar{r}_{po}
\]  

(47)

where \( \bar{r}_{po} \) is the position vector of point \( p \) relative to point \( O \). The equations of motion for an arbitrary particle are

\[
\rho_p V_p \frac{d\bar{u}_O}{dt} = \bar{F}_G + \bar{F}_B + \bar{F}_V - \frac{\rho_p V_p}{I_o} \bar{\omega}^v(0) \times \bar{r}_{mo}
\]  

(48)

\[
I_o \frac{d\bar{\omega}}{dt} = \bar{\omega}^g(0) + \bar{\omega}^h(0) + \bar{\omega}^v(0)
\]  

(49)

where \( V_p \) is the volume the particle, \( I_o \) is the rotational
inertie about point 0, and \( \vec{r}_{\text{mo}} \) is the position vector of the center of mass of the particle relative to point 0. The terms \( \vec{F}_G \), \( \vec{F}_B \), and \( \vec{F}_V \) are the gravitational force, the buoyant force, and the hydrodynamic force respectively. These forces are given by

\[
\vec{F}_G = \rho_p V_p \vec{g} \quad (50)
\]

\[
\vec{F}_B = -\sigma_f V_p \vec{g} \quad (51)
\]

\[
\vec{F}_V = \int_{S_p} \vec{T} \cdot d\vec{s} \quad (52)
\]

where \( \vec{g} \) is the gravitational vector, \( \vec{T} \) is the fluid stress tensor, and \( d\vec{s} \) is a directed element of the particle's surface \( S_p \) normal to the particle and directed into the fluid. The terms \( \vec{\tau}_G(0) \), \( \vec{\tau}_B(0) \), and \( \vec{\tau}_V(0) \) are the gravitational torque, the buoyant torque, and the hydrodynamic torque about point 0 of the particle and are given by

\[
\vec{\tau}_G(0) = \vec{r}_{\text{mo}} \times \vec{F}_G \quad (53)
\]

\[
\vec{\tau}_B(0) = \vec{r}_{\text{mo}} \times \vec{F}_B \quad (54)
\]

\[
\vec{\tau}_V(0) = \int_{S_p} \vec{r}_{\text{so}} \times \vec{T} \cdot d\vec{s} \quad (55)
\]

where \( \vec{r}_{\text{so}} \) is the position vector of points on the surface of the particle, \( S_p \), relative to point 0. If point 0 was chosen to coincide with the center of mass then \( \vec{\tau}_G(0) \) and \( \vec{\tau}_B(0) \) of Equation 49 and the last term of Equation 48 would
vanish.

The sum of the buoyant force and the gravitational force plays a large part in the mixing of suspensions. Consider a stagnant suspension contained in an open vessel. If the particle density, $\rho_c$, is larger than the fluid density then the particles will all eventually settle to the bottom of the container. If the opposite were true the particles would eventually all float to the surface of the fluid. Finally, if the density of the fluid and particles were identical then nothing would happen. The resulting behavior in these cases is due solely to the field forces on the particles

$$\vec{F}_P = \vec{F}_G + \vec{F}_B = (\rho_p - \rho_f) g V_p$$

(56)

It is obvious that the sign of $\vec{F}_P$ and the magnitude of $\vec{F}_P$ will have a great deal to do with the state of mixing in an agitated suspension. For instance, Weisman and Efferding (39) have shown that when, $\rho_p > \rho_f$, there is a minimum power input required to suspend a bed of particles by agitation such that no particles remain on the bottom of the vessel. It was found that this minimum power requirement depends on the system geometry, the fluid viscosity, the particle volume fraction and diameter, and on $\rho_c - \rho_f$. Weisman and Efferding also noted that at the minimum power requirement the bed of particles did not expand fully enough to fill the entire fluid volume and a distinct interface existed far below the fluid-
air surface. As a result, a much higher power input was necessary to fully expand the suspension of particles to fill the entire bed. This behavior of agitated suspensions of particles results mainly from the effect of the net field force, Equation 56, on each particle.

In order to obtain some idea of how a particle moves through a viscous fluid attention will be focused on a single particle moving through a fluid of infinite volume which is at rest with respect to fixed coordinates. If one makes the assumption that the fluid motion is in creeping flow, that is the motion of the fluid resulting from the particle moving, the general results of Happel and Brenner (15) can be applied. Happel and Brenner show that \( \bar{F}_V \) and \( \bar{n}_V^{(0)} \) are given by

\[
\bar{F}_V = -\mu (\bar{K} \cdot \bar{u}_0 + \bar{\xi}_o \cdot \bar{w}) \quad (57)
\]

\[
\bar{n}_V^{(0)} = -\mu (\bar{\xi}_o \cdot \bar{u}_0 + \bar{\xi}_o \cdot \bar{\omega}) \quad (58)
\]

when \( \frac{D|\bar{v}|_u}{u} \) and \( \frac{D^2|\bar{\omega}|_u}{u} \) are small. The tensor \( \bar{K} \) is called the translational tensor. The translational tensor is symmetric and depends solely on the geometry of the particle under consideration. The tensor \( \bar{\xi}_o \) is called the rotational tensor and it is also symmetric but in addition to depending on the geometry of the specific particles it also depends on the choice of the point \( 0 \). \( \bar{\xi}_o \) is called the coupling tensor and it is not symmetric in general. \( \bar{\xi}_o \) depends on the choice of position \( 0 \) as well as the geometry of the particle. Happel
and Brenner show that if $0$ coincides with the unique point called the center of reaction, $\vec{c}_o$ becomes symmetric. It can be seen that the coupling tensor, $\vec{c}_o$, couples the force, $\vec{F}_V$, with the spinning motion of the particle, $\vec{w}$, and the torque, $\vec{\pi}_V^{(0)}$, with the translational motion of the particle, $\vec{U}_o$.

For the case when the particle is a sphere of diameter $D$, $\vec{F}_V$, and $\vec{\pi}_V^{(0)}$ are given by

$$\vec{F}_V = - 3\pi Du \vec{U}_o$$

$$\vec{\pi}_V^{(0)} = - \pi u D^3 \vec{w}$$

when position $0$ coincides with the center of mass. Thus for a sphere there is no coupling between translation and rotation. The force, $\vec{F}_V$, is opposite to the direction of motion of the particle and the torque, $\vec{\pi}_V^{(0)}$, is opposite to the direction of the spheres angular velocity. The motion of a sphere is called isotropic. However, for odd shaped particles the motion may be anisotropic since the direction of the force, $\vec{F}_V$, is not in general opposite to the direction of the motion and the direction of the impressed torque, $\vec{\pi}_V^{(0)}$, is not opposite to the direction of the angular velocity of the particle. It should be noted that if the fluid is moving at the constant velocity, $V$, then the velocity $\vec{U}_o$ is replaced by $(\vec{U}_o - \vec{V})$ in Equation 59. Utilizing information found in Bird et al. (7) it can be determined that Equation 59 will be obeyed if the sphere diameter is in the range
defined by

\[ 0 < \frac{1.8\mu^2}{\sigma_0^2 (\rho_p - \rho_f)}^{1/3} \]  

for the case of pure settling of a single sphere. When additional spheres are present there are no simple expressions like Equations 59 and 60 for the hydrodynamic force and torque upon a typical sphere. The equations of motions for a typical particle in a suspension do not exist. However there has been some progress in this regard for arrays of particles (15). The exact solution of two spheres falling along their line of centers reveals that if two equal sized spheres are translating parallel to their line of center then the following modified form of Stokes law applies.

\[ \bar{F}_V = -3\pi\mu D \bar{u}_o \lambda \]  

Happel and Brenner (15) present calculated and experimentally determined correction factors, for various interparticle distances and it can generally be said that \( \lambda \) is essentially one when the interparticle distance is larger than 10 D.

The equations of motion for a crystal suspended in a mixed crystallizing solution help one to understand the extreme complexity of the dynamics of mixed suspension crystallization. For instance, the volume of a typical crystal is continually changing because of growth. When a typical crystal encounters other crystals or when it bumps
into the solid surfaces of the containing vessel its volume
may change either by agglomeration or breakage. As the
volume of a typical crystal is continually changing in a
mixed crystallizing suspension the field force on the crystal
will also change. This fact occurs because the field force is
proportional to the crystal volume as expressed in Equation
56. In addition, the hydrodynamic force and hydrodynamic
torque will also change continuously since by Equations 52
and 55 one can see that these quantities are also dependent
upon crystal geometry as well as the local fluid stress.
Finally, the rate at which the crystal grows will change
since by virtue of the crystals relative motion the environ­
ment the particle sees will in general be continuously
changing.

Differential Velocities in Mixed Suspensions

In a completely mixed solution containing several
dissolved species all of the components have identical
velocities. In this case the physics of the process requires
that there be no differential velocities since by definition
there are no concentration gradients within a completely
mixed solution and hence there can be no diffusion. However,
in a completely mixed suspension of particles and fluid there
may be relative velocities between the particles and their
neighboring fluid. This property of mixed suspensions results
from the fact that the motion of the particles are coupled
with the fluid motion only through the hydrodynamic force and hydrodynamic torque as described by Equations 48 and 49. Since differential velocities can be present even in the ideal case of a completely mixed suspension one can see that if transport of heat or mass takes place relative to the suspended particles then the presence of differential velocities will have an effect upon the appropriate boundary layers surrounding the individual particles. In addition the fact that suspended particles might have velocities different from their neighboring fluid will affect the withdrawal behavior of suspensions from continuous mixing vessels. This latter feature will be discussed more carefully in a subsequent section but the immediate attention will be focused upon discussing the magnitude and the effects of fluid-particle differential velocities in mixed suspensions.

Consider the mean square relative velocity, $\zeta V^2$, which is defined by

$$\zeta V^2 = \lim_{T \to \infty} \frac{1}{T} \int_0^T (\bar{u}(t) - \bar{v}(t))^2 \, dt$$

where $t$ is time, $\bar{u}(t)$ is the velocity of the center of mass of a typical particle, and $\bar{v}(t)$ is the average velocity of the fluid in the region of the particle of interest. To be more precise one might define this region as the fluid volume of at least 50 times the particles volume and symmetrically located about the particle. To obtain some
idea of the order of magnitude of the quantity $\zeta \overline{V}^2$ the case of a single spherical particle of diameter $D$ with a uniform density will be considered. The fluid will be flowing at a constant time averaged velocity of $\overline{V}$ and will be in the state of isotropic homogenous turbulence. The above conditions have been selected so as to obtain an approximate idea of the order of magnitude and functional form of $\zeta \overline{V}^2$ in a turbulent fluid. It is usually the case that well mixed suspensions are in turbulence but not necessarily isotropic homogeneous turbulence. However, the following development should at least approximate the behavior of a particle suspended within a well mixed suspension.

If one restricts attention to a spherical particle whose diameter $D$ is sufficiently small such that the inequality of Equation 61 holds and $D$ is much smaller than the average eddy size, $L$, then one can reasonably use Stokes law to describe the hydrodynamic force on the spherical particle. Under these conditions the following equation of motion for the spherical particle is applicable

$$\frac{du}{dt} = \left( \rho_p - \rho_f \right) \overline{g} + \frac{18 \, \mu}{\rho_p D^2} \left( \overline{V} - \overline{U} \right)$$  \hspace{1cm} (64)$$

where $\mu$ is the fluid viscosity and $\overline{g}$ is the gravitational vector. To be consistent all time averaged quantities in the sense of $\zeta \overline{V}^2$ in Equation 63 will be denoted by a bar appearing below the quantity. Therefore, the two perturbation
variables $\tilde{u}'$ and $\tilde{v}'$ are defined respectively by

\[ \tilde{u}' = \tilde{u}(t) - \bar{\tilde{u}} \quad (65) \]

\[ \tilde{v}' = \tilde{v}(t) - \bar{\tilde{v}} \quad (66) \]

in the present problem. It then follows from the definition of Equations 65 and 66 along with the equation of motion, Equation 64, that $\zeta \tilde{V}^2$ is given by

\[ \frac{\zeta \tilde{V}^2}{\rho} = (\tilde{\tilde{u}} - \tilde{\tilde{v}})^2 + (\tilde{\tilde{u}} - \tilde{\tilde{v}})^2 \quad (67) \]

where $(\tilde{\tilde{u}} - \tilde{\tilde{v}})$ is

\[ \tilde{\tilde{u}} - \tilde{\tilde{v}} = \left( \frac{\rho_d - \rho_f}{18 \mu} \right) p^2 \xi \quad (68) \]

and $\tilde{v}'$ is related to $\tilde{u}'$ by

\[ \frac{d\tilde{u}'}{dt} = \frac{18 \mu}{\rho_p D^2} (\tilde{v}' - \tilde{\tilde{v}}) \quad (69) \]

Equation 69 is a linear differential equation. If one can characterize the type of noise that the perturbation velocity of the fluid represents then the James, Nichols and Phillips method, as outlined in Brown and Nilsson (10) can be applied to determine the last term appearing in Equation 67.

When a viscous fluid is in the state of isotropic homogenous turbulence G. I. Taylor has shown, as reported in Knudson and Katz (20), that the perturbation velocity of the fluid, Equation 66, represents Markov noise. That
is, the autocorrelation function for \( \bar{v} \), \( \varphi_v(\theta) \) defined as

\[
\varphi_v(\theta) = \lim_{T \to \infty} \frac{1}{T} \int_0^T \bar{v}(t) \cdot \bar{v}(t+\theta) \, dt
\]  

(70)

is given by

\[
\varphi_v(\theta) = \frac{\sigma_v^2}{V} e^{-\gamma \theta}
\]  

(71)

where \( \sigma_v^2 \) is the time average mean square value of the perturbation velocity \( \bar{v} \) and \( \gamma \) is equal to \( (|\bar{v}|/L) \), the time averaged fluid velocity divided by the average eddy size.

Combining the statistical information embodied in Equations 70 and 71 with Equation 69 it can be determined that \( (\bar{u}' - \bar{v})^2 \) is given by

\[
(\bar{u}' - \bar{v})^2 = \frac{\sigma_v^2 \gamma D^2}{18 \frac{u}{\rho_p} + \nu D^2}
\]  

(72)

Finally combining Equation 72 with Equation 68 the following expression for \( \zeta \bar{v}^2 \) is obtained

\[
\zeta \bar{v}^2 = \left( \frac{(\rho_p-\rho_f)g D^2}{18 u} \right)^2 + \frac{\sigma_v^2 \gamma D^2}{18 \frac{u}{\rho_p} + \gamma D^2}
\]  

(73)

The first term in Equation 73 is the square of the terminal settling velocity of a sphere of density \( \rho_p \) in a fluid of density \( \rho_f \) and of viscosity \( u \). The second term of Equation 73 accounts for the random fluctuations of the fluid velocity about the constant time averaged fluid
velocity, \( \vec{V} \). For very small spherical particles \( \zeta V^2 \) is essentially zero and the value of \( \zeta V^2 \) is an increasing function with increasing sphere diameter, \( D \). In addition to the size dependence of \( \zeta V^2 \) Equation 73 shows that the only circumstance which can possibly allow for \( \zeta V^2 \) being zero is when \( \nu \), the fluid viscosity, becomes very large. Note that even if there are no settling effects, that is, if the fluid density and particle density are identical, \( \zeta V^2 \) cannot be taken as zero.

It is interesting to note that according to Equation 73 for the case of the motion of a suspension of very small particles \( \zeta V^2 \) is zero. Therefore emulsions or flocculated suspensions containing very small particles should behave like a homogeneous fluid with a certain characteristic rheology. This fact is well documented. For instance, Thomas (34, 35) shows that flocculated suspensions of particles in the size range from 13 to 35 microns and with particle volume fractions in the range from .02 to .33 behave like non-Newtonian fluids. In fact, at high shear rates these suspensions were found to behave in the same fashion as a Bingham plastic.

In a mixed crystallizing suspension, the resulting effects of differential crystal-fluid velocity on the degree of mixing, the kinetics of crystallization, and withdrawal behavior can undoubtedly be very important. According to
Equation 73, very small crystals will, on the average, witness no turbulent renewal of their boundary layers due to differential crystal-fluid velocity effects, whereas this same effect will become more and more pronounced as the size of the crystal under consideration is increased. In fact, Friedlander (14) shows that there is a size interval about nuclei sized particles for which particles within this interval do not witness turbulent renewal of their boundary layers. If the particle under consideration was a growing crystal and diffusion was an important factor in the growth mechanism then the diffusional resistance would diminish as the size of the particle increased as a result of the dependence of $\zeta V^2$ on size. If one believes the series diffusion-surface reaction model for crystal growth then it becomes obvious that crystal growth rate may be a function of size. That is, it is conceivable that diffusion might be the controlling the mechanism for very small crystals while large crystals whose boundary layers are renewed frequently may have a surface reaction controlled growth rate. This type of behavior was found by Baliga (2) in his investigations of boiling batch crystallizations for several systems. Further evidence of the effect of $\zeta V^2$ upon boundary layers surrounding particles suspended in mixed fluids comes from the work of Hixson et al. (16, 17). Hixson and co-workers have experimentally shown that diffusion coefficients for the dissolu-
tion of crystals in agitated suspensions is proportional to the level of agitation. This behavior is precisely what one would expect upon examining Equation 71, since as the level of agitation increased $\sigma_v^2$ would also increase. The increase in $\sigma_v^2$ would increase $\zeta V^2$ proportionately and thereby decrease the boundary layers about any particular sized particle. Finally, one would expect an increase in the nucleation rate upon an increase in the level of agitation of a crystallizing suspension if secondary nucleation occurs from the shearing off of surface nuclei from growing crystals.
WITHDRAWAL BEHAVIOR FROM CONTINUOUS MIXERS

The withdrawal behavior of completely mixed suspensions from continuous constant volume mixing vessels is an extremely complicated process which in general depends on the hydrodynamic conditions in the neighborhood of the outlet surface and upon the distribution of particles which are to be withdrawn. In most cases the state of complete mixing for a suspension can be approached in the sense that the variance about the volume averaged concentration $\bar{C}(D)$ of particles of an arbitrary size, $D$, defined as

$$\frac{1}{V} \int_V (C(D) - \bar{C}(D))^2 \, dV$$

is negligibly small. This condition is of some importance in the following analysis since in the case of classified withdrawal there may be a very small region in the neighborhood of the outlet surface in which the concentration of particles, $C(D)$, is markedly different from the mean concentration, $\bar{C}(D)$, of these particles in the entire working volume, $V$. The hydrodynamic conditions affecting the withdrawal characteristics from completely mixed suspensions can in part be specified by the pipe velocity, $v_p$, the approach velocity, $v_a$, and the angle $\theta$ between the directions of these two velocities. In the following discussion the condition when $v_p$ equals $v_a$ will be called isokinetic while the con-
dition when \( v_p \) differs from \( v_a \) will be called anisokinetic.

To illustrate how classified withdrawal naturally arises in the discharge of completely mixed suspensions of different sized particles from continuous constant volume mixing vessels, a simple limiting hydrodynamic case will be considered. The situation when the approach velocity and the pipe velocity are isokinetic and the direction between these velocities is given by \( \Theta \) will be discussed. To render this problem mathematically tractable it will be assumed that Stokes law applies and that there are no interactions between the particles in suspension. These two assumptions reduce the equation of motion to a linear differential equation and allow one to solve the problem for an individual spherical particle and then superimpose the results. Figure 1 illustrates the outlet geometry that will be considered and also indicates the idealized flow pattern that will be utilized in the following mathematical developments. The exact flow pattern in the neighborhood of the outlet pipe is dependent upon many arbitrary physical conditions and is in general very difficult to obtain. The flow pattern in Figure 1 was chosen to approximate what might be expected for the isokinetic condition.

The flow pattern indicated in Figure 1 shows a sudden change of direction when the fluid enters the mouth of the outlet pipe. Assuming then that the particles are in steady
Figure 1. Flow pattern for isokinetic withdrawal
motion outside the pipe one can easily calculate that a
particle of diameter \( D \) enters the pipe with an effective
velocity of

\[
u(D) = \frac{(\rho_p - \rho_f) g D^2}{18 \mu} + v_p \cos \theta \tag{75}
\]

From Equation 75 it is an easy matter to obtain the residence
time associated with a spherical particle of size \( D_p \).

\[
\tau_p = \frac{V}{\pi R^2 \left( \frac{(\rho_p - \rho_f) g D_p^2}{18 \mu} + v_p \cos \theta \right)} \tag{76}
\]

The residence time for a spherical particle of diameter \( D_p \)
is equal to the average length of time that this size
particle spends within the mixing vessel. For uniform
withdrawal of fluid and particles the residence time for
the fluid and for all the particles regardless of their size
is the same,

\[
\tau_F = \frac{V}{\pi R^2 \rho_f} \tag{77}
\]

In this simplified example there is only one condition, namely
when \( \theta \) is zero and the fluid density \( \rho_f \) is equal to the
particle density \( \rho_p \), for which there is uniform withdrawal.
This fact is obvious since under these circumstances Equation
76 becomes Equation 77. From this example it can be seen
that uniform withdrawal is practically impossible to achieve
experimentally since the very strict outlet geometry and hydrodynamic conditions in the neighborhood of the outlet surface are very difficult to obtain in practice.

By far, the anisokinetic condition represents a much larger range of possible hydrodynamic situations at the outlet surface than does the narrow class defined by the isokinetic conditions. In the following discussion attention will be restricted to cases for which the approach velocity and the pipe velocity are in the same direction and the gravitational field is directed opposite to the fluid motion. These restrictions are introduced so that the following discussion is directly related to experimental investigations which are to be discussed in a subsequent section.

The hydrodynamic conditions of the anisokinetic case can be divided into two categories. The first category encompasses those situations for which the approach velocity is greater than the pipe velocity. Under these circumstances the fluid streamlines will diverge in the neighborhood of the outlet surface. Figure 2-A illustrates typical fluid streamlines for the case when the approach velocity exceeds the pipe velocity. The second category consists of those situations for which the pipe velocity is greater than the approach velocity. Typical fluid streamlines for this case are illustrated in Figure 3-A. In both Figures 2 and 3 the suspension is assumed to possess the volume averaged concentrations of
Figure 2. Flow patterns when approach velocity is greater than pipe velocity
LIMITING PARTICLE STREAMLINE (DIAMETER, D_p)

LIMITING FLUID STREAMLINE

OUTLET PIPE

OUTLET PIPE
Figure 3. Flow patterns when approach velocity is less than pipe velocity
STREAMLINE - (2) OUTLET PIPE

LIMITING PARTICLE STREAMLINE (DIAMETER $D_p$)

OUTLET PIPE
particles and fluid at plane 1. In between planes 1 and 2, of Figures 2 and 3, the fluid directs the suspended particles into the outlet pipe.

To understand how particle withdrawal is affected by the hydrodynamic conditions in the neighborhood of the outlet surface it is helpful to consider the effect of changes in the fluid velocity upon particle motion. To accomplish this task the equation of motion for an arbitrarily shaped particle will be considered. For discussion purposes it will be supposed that the fluid density and the particle density are identical so that the net field force on a typical particle is zero. Under these conditions the equation of motion for a typical particle is

\[
\frac{d\vec{u}}{dt} = \frac{1}{\rho_p V_p} \int_{S_p} \vec{T} \cdot d\vec{S} \quad (78)
\]

where \( V_p \) is the volume of the particle, \( S_p \) is the set of coordinates defining the particle surface, \( \vec{u} \) is the velocity of the center of mass of the particle, and \( \vec{T} \) is the fluid stress tensor at the surface of the particle. In light of Equation 78, the following limiting identity for very small particles can be written

\[
\frac{d\vec{u}}{dt} = \lim_{V_p \to 0} \frac{1}{\rho_p V_p} \int_{S_p} \vec{T} \cdot d\vec{S} = \frac{\nabla \cdot \vec{T}}{\rho_p} = \frac{d\vec{v}}{dt} \quad (79)
\]

\[
\lim_{V_p \to 0} \frac{\vec{u}}{V_p} = \vec{v} \quad . \quad (80)
\]
provided that during the limiting process the fluid stress tensor is continuously extended into the particle region. Equation 80 indicates that regardless of the intensity of the changes in the direction and magnitude of the fluid velocity very small particles will essentially follow the motion of the fluid. In other words, the path swept out by an extremely small particle will coincide with a fluid streamline.

The equation of motion for a spherical particle whose density is identical to the fluid density is given by

$$T \frac{d\vec{u}}{dt} + \vec{u} = \vec{v} ; \quad T = \frac{\rho_p d^2}{18 \mu}$$  (81)

assuming Stokes law applies. The velocity of the center of mass of a spherical particle is denoted by $\vec{u}$ and $\vec{v}$ is the average velocity of the fluid in the near vicinity of the particle. Equation 81 is a first order differential equation and it can be easily recognized that $T$ is the time constant for the particle velocity equation. It is well known that for differential equations of the above type $\vec{u}$ will be essentially identical to $\vec{v}$ when the value of $T$ is very small. On the other hand when $T$ is relatively large $\vec{u}$ will take a long time to respond to changes in $\vec{v}$ and will remain essentially unchanged for a reasonably long time interval when a sudden step change in $\vec{v}$ is introduced. It can be seen that $T$ in Equation 81 is proportional to the square of the sphere
diameter, $D^2$. Therefore very small particles will flow with the fluid. However, in the present example the following relation obtains

$$\ddot{u} = \text{constant} \ ; \ D \text{ large} \quad (82)$$

when the changes in the direction and magnitude of the fluid velocity are not extremely severe or of long duration. Strictly, one cannot utilize Stokes law for very large particles as Equation 61 indicates a finite spherical diameter range for which this expression is applicable.

Therefore two general properties of the effects of changes in the fluid motion upon the motion of particles emerge upon considering the particle equation of motion. Very small particles will flow exactly like the fluid. On the other hand, large particles will be essentially unaffected, that is the trajectories of large particles will be unaffected, when the changes in the fluid velocity are not extremely severe or of long duration. The above properties of particle motion due to fluid velocity changes are an important factor in causing classified withdrawal from completely mixed suspensions.

Figure 2-B will be used to discuss the resulting withdrawal behavior for the general case when the approach velocity is greater than the pipe velocity. At plane 1 in Figure 2-B there are three concentric radii indicated. $R_0$ is the radius of the exit pipe. From the previous discussion pertaining to
Equation 82 it can be seen that the disk defined by the pipe radius is the largest possible disk from which particles can possibly be withdrawn. $R(D_p)$ is the radius associated with the limiting streamline for a particle of size $D_p$ that just enters the exit pipe. Note that if one is considering two different sized particles $D_1$ and $D_2$ such that $D_1$ is greater than $D_2$ then the discussion pertaining to Equations 78 and 81 implies that

$$R(D_1) > R(D_2)$$

(83)

Therefore the larger the size of the particle the larger the size of the disk associated with the particle at plane 1 in Figure 2-B. It has been mentioned in regard to Figure 2 that the suspension is completely mixed and possesses the same concentrations as the volume averaged concentrations at plane 1. Therefore it follows that large particles will have smaller residence times than small particles since the particle residence time will be inversely proportional to the area of the disk at plane 1 or

$$\tau_p = \frac{V}{v_a \pi (R(D_p))^2}$$

(84)

where $v_a$ is the magnitude of the velocity at plane 1.

Finally, $R_p$ is the diameter associated with the limiting fluid streamline that just enters the pipe mouth. Therefore the residence time of particles whose sizes are approaching
zero is
\[ \tau_F = \frac{V}{v_a \pi R_F^2} \]  
(85)

where \( \tau_F \) is the fluid residence time.

In discussing the resulting withdrawal behavior for the case when the approach velocity is smaller than the pipe velocity Figure 3-B will be utilized. There are three concentric radii indicated at plane 1 in Figure 2-B. Unlike the previous case where \( R_0 \) defined the largest possible disk at plane 1 and \( R_p \) defined the smallest disk at plane 1, in the present case, this order is reversed. In fact, the entire description for the case when the approach velocity is smaller than the pipe velocity is exactly opposite to the previous case when the approach velocity was taken to be greater than the pipe velocity. For instance, in the present case the following inequality applies

\[ R(D_2) > R(D_1) \]  
(86)

when the particle diameter \( D_1 \) is greater than the particle diameter \( D_2 \). Hence in this case smaller particles will have smaller residence times than larger particles since the area of the disk associated with \( R(D_2) \) at plane 1 in Figure 2-B is larger than the disk associated with \( R(D_1) \). Although the present case is an exact opposite to the previous case, Equations 84 and 85 still apply.
Limiting steady state conservation relationships may be written for very small particles, very large particles, and for the fluid for the two cases illustrated in Figures 2 and 3. At steady state the net rate at which the fluid streams between planes 1 and 2 in both Figures 2 and 3 must be zero and hence

$$\rho_f \pi (R_0)^2 v_p = \rho_f \pi (R_p)^2 v_a$$  \hspace{1cm} (87)

from which it follows that

$$\frac{R_0}{R_p} = \sqrt{\frac{v_a}{v_p}}$$  \hspace{1cm} (88)

The net rate at which very small particles flux between planes 1 and 2 in both Figures 2 and 3 must also be zero at steady state and therefore

$$\lim_{D \to 0} \left[ C(D) \pi (R_0)^2 v_p - \frac{C(D)}{\pi} (R_p)^2 v_a \right] = 0$$  \hspace{1cm} (89)

and upon rearranging Equation 89 the following relationship obtains

$$\lim_{D \to 0} \left( \frac{C(D)}{C(D)} \right) = 1$$  \hspace{1cm} (90)

The properties expressed in Equations 89 and 90 follow directly from the fact that very small particles will flow with the fluid. The term $C(D)$ is the bulk averaged concentra-
tration across the exit pipe surface of particles of size \(D\) while \(\bar{C}(D)\) is the volume average concentration of particles of size \(D\) within the mixing vessel. The following relationships can also be written for large particles

\[
\lim_{D \to \text{large}} \left[ C(D) \pi (R_o)^2 v_p - \bar{C}(D) \pi (R_o)^2 v_a \right] = 0
\]

(91)

and

\[
\lim_{D \to \text{large}} \frac{C(D)}{\bar{C}(D)} = \frac{v_a}{v_p}
\]

(92)

since it has been established that very large particles are essentially unaltered in their trajectories when subjected to fluid velocity changes of short duration and of moderate intensity. The properties expressed in Equations 88, 90, and 92 follow directly from the preceding general discussion of withdrawal behavior for the cases of converging and diverging fluid streamlines near the outlet surface. However, the above relationships only provide information on extreme particle sizes but a relationship for intermediate particle sizes is needed.

Watson (38) has developed an approximate theory for anisokinetic sampling. In effect, Watson assumes that the radius associated with the limiting streamline for a particle of size \(D_p\) that just enters the exit pipe, \(R(D_p)\) in Figures 2 and 3, is given by
\[ R(D_p) = R_o + (R_p - R_o) f(p_p) \]  

(93)

where \( f(p_p) \) is an unknown function of a dimensionless particle inertia \( p_p \) for a particle of size \( D_p \)

\[ p_p = \frac{D_p^2 p_p v_a}{36 \mu R_o} \]  

(94)

Assuming that this simplifying step is correct the following conservation relationship for a particle of size \( D_p \) can be written

\[ \frac{C(D_p)}{C(D_p)} \sim (R(D_p))^2 v_a = C(D_p) \pi (R_o)^2 v_p \]  

(95)

and after utilizing Equation 93 to eliminate \( R(D_p) \) the following relation obtains

\[ \frac{C(D_p)}{C(D_p)} = \frac{v_a}{v_p} \left[ 1 + \left( \frac{v_p}{v_a} \right)^{1/2} - 1 \right] f(p_p) \]  

(96)

Equation 96 may be converted into a relationship for the expected residence time for a particle of size \( D_p \) by utilizing the conservation equation for a continuous mixing vessel with a clear feed

\[ \frac{dC(D_p)}{dt} = - \pi \frac{R_o^2 v_p C(D_p)}{V} = - \frac{C(D_p)}{\tau(D_p, v_a, v_p)} \]  

(97)

and the general conservation relationship for this case. Therefore the Watson model for anisokinetic sampling yields
a particle residence time of

\[ \tau(D_p, v_a, v_p) = \frac{V}{\pi R_0^2 v_a [1 + \left(\frac{v_p^{1/2}}{v_a} - 1\right) f(p_p)]^2} \] (98)

Figure 4 has been constructed with the aid of Equation 98 to illustrate how the particle residence time behaves as a function of size for various hydrodynamic conditions near the exit pipe surface. The plot for the case when the approach velocity, \( v_a \), is equal to the pipe velocity, \( v_p \), emphasizes the fact that particles will all have the same residence time, regardless of their sizes. However when \( v_a \) is not equal to \( v_p \) the particle residence time will depend on size. Figure 4 also illustrates the facts that particle residence time will increase as particle size increases when \( v_a \) is less than \( v_p \) while the particle residence time will decrease as particle size increases when \( v_a \) is larger than \( v_p \). The values of the parameters utilized in the construction of Figure 4 were chosen to coincide with values obtained in various experiments which will be discussed subsequently.

The function \( f(p_p) \) appearing in Equation 98 was approximated by

\[ f(p_p) \approx e^{-0.57 p_p} \] (99)

This particular form of \( f(p_p) \) was chosen to coincide with
Figure 4. Particle residence times
the data of Watson (38) for spores transported in air. The value of $V$, $\mu$, and $(R_0^2 \pi v_p)$ were 6035 ml, .00098 gm/cm/sec, and 7.8 ml/sec, respectively.
A mathematical model is needed to describe the discharge behavior of a well agitated suspension from a continuous mixing vessel. In the following discussion this problem will be analyzed from the point of view that the above operation is a discrete state time homogeneous Markov process. There are several advantages in taking this approach to the present problem. For instance, this method is based on a careful dissection of the total dynamic process being considered. Each elementary mechanism of the total process is identified and then defined in terms of probabilities. These various mechanisms are then incorporated within the special mathematical machinery of Markov processes in order to develop pertinent phenomenological relations. Phenomenological equations relating the conditional expectation for functions defined upon the dynamic state of the system can be developed. Equations in terms of the probability distribution over the state of the system at any time can also be developed allowing one to calculate true means and variances for functions of the system's state. In all, this method allows one to determine under what circumstances significant statistical fluctuations about the conditional mean and true mean of arbitrary functions of the system's state will occur.

The process that will be considered here consists of a well mixed, continuously operated, and constant volume mixing
vessel from which a suspension of various sized particles is discharged continuously. Particles and fluids are continuously withdrawn from the mixing vessel such that the sum of the particle volumetric flowrate and the fluid volumetric flowrate is a constant. To maintain constant volume within the mixing vessel clear fluid is continuously introduced at a constant volumetric flowrate. Since the experimental operation of this process has been carried out with suspensions of particles of certain fixed sizes the following material will only deal with discrete size distributions.

In order to apply the concepts of a Markov process to the present problem one must first define what is meant by the state of the system. The following discussion is focused on a suspension of particles with a discrete and fixed set of particle sizes. Therefore, suppose that at time \( t \) there are \( m_i \) particles in size category \( i \) and that there are \( N \) distinct size categories. Under these circumstances the state of the system under consideration may be expressed by the set

\[
(m_1, m_2, \ldots, m_N, t) \quad (100)
\]

and the following inequality is immediately obvious

\[
m_i > 0 \quad i = 1, 2, \ldots, N \quad (101)
\]

for all times greater than zero. Particles from each of the
N size categories will be swept out of the vessel as time passes and therefore the following typical change in state will occur

\[(m_1, m_2, \ldots, m_N, t) \rightarrow (p_1, p_2, p_3, \ldots, p_N, T)\]

\[T > t\]  \hspace{1cm} (102)

\[m_i > p_i > 0 \quad i = 1, 2, \ldots, N\]

The elementary mechanism which is responsible for the above typical change in the state of the system is the withdrawal of particles. In the short time interval \([t, t+\Delta t]\) there is a distinct probability that each particle may be discharged from the mixing vessel. This short time probability will depend on several factors such as the hydrodynamic conditions in the neighborhood of the exit surface, the difference between the particle density and the fluid density, and the size of the particle under consideration. If the suspension of particles is dilute time varying hydrodynamic conditions near the exit surface can be reasonably neglected. Therefore the discussion will be further restricted to only dilute suspensions to avoid the above complications. The probability that a particle of size category \(i\) will be discharged from the mixing vessel in the short time interval \([t, t+\Delta t]\) is defined as

\[\frac{\Delta t}{m_i} \quad i = 1, 2, \ldots, N\]  \hspace{1cm} (103)
where $\tau_1$ is called the average residence time for particles in size category $i$. From the above discussion it can be said that $\tau_1$ is a function of the hydrodynamic conditions in the neighborhood of the exit surface, the relative density, and the size of the particle under consideration. For instance, $\tau_1$ might be related to $v_a$, $v_p$, and $D_1$ as in Equation 98.

The key function of a Markov process is called the transition probability. The transition probability gives the value of the probability for a change in state. For the typical change in state expressed by Equation 102 the transition probability is assigned the notation

$$P(m_1, m_2, \ldots, m_N, p_1, p_2, \ldots, p_N, T-t) \quad (104)$$

Note that the transition probability is only dependent on the interval of time elapsed between the two states. This unique property results from the assumption that the mixing process under consideration is a time homogeneous Markov process. The defining relationship for a discrete state time homogeneous Markov process is given by

$$P(m_1, \ldots, m_N, n_1, \ldots, n_N, S + t) =$$

$$\sum_{p_1=-\infty}^{\infty} \cdots \sum_{p_N=-\infty}^{\infty} P(m_1, \ldots, m_N, p_1, \ldots, p_N, S)P(p_1, \ldots, p_N, n_1, \ldots, n_N, t) \quad (105)$$
which is called the Chapman-Kolmogrov Equation. For a more thorough discussion of the above definitions consult Bharucha-Reid (6).

In order to develop the desired phenomenological equations the short term transition probability must be defined. That is, in the short time interval $[t, t+\Delta t]$ a limiting expression for the transition probability is desired for the change in state.

$$(m_1, \ldots, m_N, t) \rightarrow (p_1, \ldots, p_N, t+\Delta t)$$

$$m_i > p_i > 0 \quad i = 1, 2, \ldots, N$$

$$t > 0, \quad \Delta t > 0$$

In a small time interval there are two mutually exclusive events which may occur, a specific particle may be discharged or it may be retained within the mixing vessel. Therefore utilizing Equation 103 for the probability that a particle of size category $i$ may be discharged the following limiting relationship for the transition probability can be obtained

$$P(m_1, \ldots, m_N, p_1, \ldots, p_N, \Delta t) = (1 - \sum_{i=1}^{N} \frac{m_i \Delta t}{\tau_i})$$

$$\times \sum_{i=1}^{N} \zeta p_i, m_i + \sum_{j=1}^{N} \frac{m_j \Delta t}{\tau_j} \times \prod_{i=1}^{j-1} \zeta p_i, m_i$$

$$\times \prod_{i=j+1}^{N} \zeta p_i, m_i \times \zeta p_j, m_j^{-1}$$
where $\delta_{i,j}$ is the Kronecker delta function. The first term on the right-hand side of Equation 107 is equal to the probability that no change will occur and the second term equals the sum of the probabilities that a particle will leave each size category. The initial value of the transition probability emerges from Equation 107 as $\Delta t$ approaches zero

$$P(m_1, ..., m_N, p_1, ..., p_N, 0) = \prod_{i=1}^{N} \delta_{m_i, m_i}$$  \hspace{1cm} (108)$$

which reveals that the smaller $\Delta t$ becomes the more likely it is that there is no change in state. The next step is to use Equation 107 in the Chapman-Kolmogrov relationship, Equation 105, which now takes the form

$$P(m_1, ..., m_N, n_1, ..., n_N, t+\Delta t) = \sum_{p_1=-\infty}^{\infty} \sum_{p_N=-\infty}^{\infty} P(m_1, ..., m_N, n_1, ..., n_N, t) \delta_{p_1, p_1} \delta_{p_N, p_N} \Delta t$$

$$... \delta_{m_i, m_i} \delta_{n_i, n_i}$$

$$\delta_{p_1, p_1} \delta_{p_N, p_N} \Delta t)P(p_1, ..., p_N, n_1, ..., n_N, t)$$

$$\sum_{p_1=-\infty}^{\infty} \sum_{p_N=-\infty}^{\infty} \delta_{p_1, p_1} \delta_{p_N, p_N} \Delta t)P(p_1, ..., p_N, n_1, ..., n_N, t)$$

$$\sum_{p_1=-\infty}^{\infty} \sum_{p_N=-\infty}^{\infty} \delta_{p_1, p_1} \delta_{p_N, p_N} \Delta t)P(p_1, ..., p_N, n_1, ..., n_N, t)$$

Performing the indicated operations in the above form of the Chapman-Kolmogrov equation and rearranging, the following differential equation which has been evaluated in the limit as $\Delta t$ approaches zero was obtained

$$\frac{dP}{dt}(m_1, ..., m_N, n_1, ..., n_N, t) = \sum_{j=1}^{N} \sum_{m_{j-1}}^{m_j} \frac{m_j}{\tau_j} [P(m_1, ..., m_{j-1}, n_1, ..., n_N, t) -$$

$$P(m_1, ..., m_{j-1}, m_j+1, ..., n_N, n_1, ..., n_N, t)] -$$
for which Equation 108 serves as the initial condition. Equation 110 is called the Kolmogrov backward equation.

Equation 110 is rather complex, however the present problem is somewhat simplified by assuming that the transition probability is independent with respect to the various size categories. Essentially this assumption amounts to saying that is independent of the distribution of particles present in the suspension. The process defined by the typical change in state

\[(m_1, \ldots, m_N, t) \rightarrow (p_1, \ldots, p_N, t+T)\]  \hspace{1cm} (111)

\[m_i \geq p_i \geq 0 \quad i = 1, 2, \ldots, N\]
\[t \geq 0, \quad T \geq 0\]

can now be viewed in terms of the independent changes

\[(m_i, t) \rightarrow (p_i, t+T) \quad ; \quad i = 1, 2, \ldots, N\]  \hspace{1cm} (112)

\[m_i \geq p_i \geq 0\]
\[t \geq 0 ; \quad T \geq 0\]

It follows that the transition probability can be written as

\[P(m_1, \ldots, m_N, n_1, \ldots, n_N, t) = \prod_{i=1}^{N} p_i(m_i, n_i, T)\]  \hspace{1cm} (113)
where $P_i(m_i, n_i, T)$ is the transition probability for the change in the number of particles in size category $i$ from $m_i$ to $n_i$ in the time interval $T$. In addition, it is a simple matter to prove that each of the associated transition probabilities obeys an associated backward Kolmogrov equation of the form

$$\frac{dP_i(m_i, n_i, t)}{dt} = \frac{m_i}{\tau_i} (P_i(m_i-1, n_i, t) - P_i(m_i, n_i, t))$$

for which the initial condition is

$$P_i(m_i, n_i, 0) = \zeta n_i, m_i$$

Therefore the multidimensional problem given by Equations 110 and 108 has been reduced to a set of one dimensional problems, Equations 114 and 115 by assuming independence.

Attention will be focused on the arbitrary size category $i$. A set of differential equations for the transition probability for size category $i$ are obtained from Equations 114 and 115.

$$\frac{dP_i(m_i-j, n_i, t)}{dt} = \frac{m_i-j}{\tau_i} [P_i(m_i-j-1, n_i, t) - P_i(m_i-j, n_i, t)]$$

$$P_i(m_i-j, n_i, 0) = \zeta n_i, m_i-j$$

$$j = 0, 1, \ldots, m_i - n_i - 1$$
and for the case when \( j \) equals \( m_1 - n_1 \)

\[
\frac{\partial P_1(n_1, n_1, t)}{\partial t} = -\frac{n_1}{\tau_1} P_1(n_1, n_1, t)
\]

(117)

\[P_1(n_1, n_1, 0) = \zeta n_1, n_1\]

In order to solve the above closed set of ordinary differential equations for the transition probability \( P_1(m_1, n_1, t) \) the LaPlace transform of Equations 116 and 117 is taken. Afterward the resulting set of \( S \)-domain equations are combined in such a way as to eliminate the transformed transition probabilities for which \( j = 1, \ldots, m_1 - n_1 \). The resulting \( S \)-domain formula for \( P_1(m_1, n_1, S) \) is thus found to be

\[
P_1(m_1, m_1, S) = \frac{m_1 - n_1}{\sum_{j=0}^{m_1} \frac{m_1! \zeta n_1, m_1-j}{(m_1-j)! \prod_{p=1}^{j} (S \tau_1 + m_1 - p)}}
\]

(118)

and then taking the partial fraction expansion of the denominators in the above summation the following expression obtained

\[
P_1(m_1, n_1, S) = \sum_{j=0}^{m_1-n_1} \binom{m_1}{j} \zeta n_1, m_1-j \sum_{i=0}^{j} \frac{(-1)^{j-i}}{(S + \frac{(m_1-j)}{\tau_1})}
\]

(119)

The preceding \( S \)-domain formula for the transition probability is next transformed back to the time domain to give
\[ P_1(m_1, n_1, t) = \]
\[ \sum_{j=0}^{m_1-n_1} \left( \frac{m_1}{j} \right)^n_1 \frac{m_1-j}{\sum_{j=0}^{m_1-j}} \sum_{j=0}^{m_1-j} (\frac{m_1-j}{t}) (-1)^{j-n_1} e^{-\frac{(m_1-j)t}{\tau_1}} \]  
\[ P_1(m_1, n_1, t) = \]
\[ \sum_{j=0}^{m_1-n_1} \left( \frac{m_1}{j} \right)^n_1 \frac{m_1-j}{\sum_{j=0}^{m_1-j}} \sum_{j=0}^{m_1-j} (\frac{m_1-j}{t}) (-1)^{j-n_1} e^{-\frac{(m_1-j)t}{\tau_1}} (1-e^{-\frac{t}{\tau_1}})^j \]

which can be written more concisely as

\[ \sum_{j=0}^{m_1-n_1} \left( \frac{m_1}{j} \right)^n_1 \frac{m_1-j}{\sum_{j=0}^{m_1-j}} \sum_{j=0}^{m_1-j} (\frac{m_1-j}{t}) (-1)^{j-n_1} e^{-\frac{(m_1-j)t}{\tau_1}} (1-e^{-\frac{t}{\tau_1}})^j \]

Equation 121 is the exact solution for the transition probability for the change in the number of particles in size category 1 from \( m_1 \) to \( n_1 \) in the time interval \( t \).

The conditional expectation for the remaining population for size category 1 is denoted by

\[ C_1(t) \]

where the initial value of this function is given by

\[ C_1(0) = m_1 \]

The value of \( C_1(t) \) is equal to the number of particles that are conditionally expected to remain within the mixing vessel at time \( t \) if there were \( m_1 \) particles present initially.

To calculate \( C_1(t) \) the following defining relationship for the conditional expectation for functions defined on the state of the system is used
\[ C_i(t) = \sum_{n_1=0}^{m_i} P(m_1, n_1, t) C_1(0) \]  

Inserting Equations 121 and 123 into the preceding formula the following was obtained

\[ C_i(t) = \sum_{n=1}^{m_i} n \binom{m_i}{n} e^{-\frac{nt}{\tau_i}} (1 - e^{\frac{t}{\tau_i}})^{m_i-n} \]  

In the following discussion approximately the same mathematical treatment will be used over again and therefore the procedure for reducing the above summation into something more recognizable will be outlined. Substitution of the variables \( a \) and \( b \),

\[ a = e^{-\frac{t}{\tau_i}} \]
\[ b = 1 - e^{-\frac{t}{\tau_i}} \]  

into the above summation produces the identity of

\[ \sum_{n=1}^{m_i} n \binom{m_i}{n} a^n b^{m_i-n} = a \frac{d}{da} (a + b)^{m_i} \]  

and after differentiating Equation 127

\[ \sum_{n=1}^{m_i} n \binom{m_i}{n} a^n b^{m_i-n} = a_{m_i} (a + b)^{m_i-1} \]  

It follows from the above example calculation that the conditional expectation \( C_i(t) \), which is equal to the number of particles in size category \( i \) that are expected to remain
within the mixing vessel at time $t$ if there were $m_i$ particles initially present is given by

$$C_i(t) = m_i e^{-\frac{t}{\tau_i}}$$  \hspace{1cm} (129)$$

The probability distribution over the state of the system for size category $i$ is defined as

$$P_i(m_i, t)$$  \hspace{1cm} (130)$$

If there are $N_i$ particles initially present then the initial value of the probability distribution, $P_i(m_i, t)$ is given by

$$P_i(m_i, 0) = \xi m_i, N_i$$  \hspace{1cm} (131)$$

To calculate the probability distribution the following defining relationship is utilized

$$P_i(m_i, t) = \sum_{m_i=0}^{N_i} P(i, m_i, t)P_i(i, 0)$$  \hspace{1cm} (132)$$

and after inserting Equations 121 and 131 into the above expression $P_i(m_i, t)$ obtains

$$P_i(m_i, t) = \binom{N_i}{m_i} \left( e^{-\frac{m_i t}{\tau_i}} (1 - e^{-\frac{t}{\tau_i}})^{N_i - m_i} \right)$$  \hspace{1cm} (133)$$

where $m_i$ ranges from 0 to $N_i$. Equation 133 gives the probability for the number of particles remaining in size category $i$ being $m_i$ at time $t$ if there were initially $N_i$ particles of size category $i$ present within the mixing vessel.
The mean value for the population of particles in size category $i$ remaining in the mixing vessel at time $t$ is calculated with the formula

$$\overline{C_i(t)} = \sum_{m_i=0}^{N_i} m_i \, P_i(m_i, t)$$

(134)

Using methods similar to those outlined previously in connection with the conditional expectation for the population size, $C_i(t)$, the above definition for the mean population, $\overline{C_i(t)}$, can be evaluated as

$$\overline{C_i(t)} = N_i \, e^{-\frac{t}{\tau_i}}$$

(135)

Notice that the conditional expectation and the mean value for the remaining number of particles in the arbitrary size category $i$, Equations 129 and 135 respectively, are identical.

Finally, the variance about the mean value for the number of particles remaining in the mixing vessel that are in size category $i$ can be calculated by the following formula

$$\sigma_i^2(t) = \sum_{m_i=0}^{N_i} m_i^2 \, P_i(m_i, t) - (\overline{C_i(t)})^2$$

(136)

which is found to be

$$\sigma_i^2(t) = N_i \, e^{-\frac{t}{\tau_i}}(1 - e^{-\frac{t}{\tau_i}})$$

(137)

Since the variance $\sigma_i(t)$ is about the mean, $C_i(t)$, the following ratio will indicate the relative magnitude of
statistical fluctuations one might expect

\[
\frac{\sigma_i(t)}{C_i(t)} = \sqrt{\frac{e^{t/\tau_{i-1}}}{N_1}}
\]  

(138)

Equation 138 indicates that the larger the initial population of particles in size category i, \(N_i\), the larger the time interval t, during which negligible statistical fluctuations occur, will be. For instance, suppose that the initial number of particles present in size category i was \(10^6\) in experiment one and \(10^4\) in experiment two. Then according to Equation 138 statistical fluctuations about the mean \(\overline{C_i(t)}\) of the order \(.01 \overline{C_i(t)}\) would occur at time \(4.6 \tau_i\) in experiment one and at time \(.69 \tau_i\) in experiment two.

In the preceding discussion the discharge behavior from a continuous, constant volume, and completely mixed mixing vessel containing a suspension of various sized particles was modeled as a Markov process. The mean value as well as the conditional expectation of the population in any size category was developed, Equations 129 and 135 respectively. It was found that these two properties are identical. An equation relating relative statistical fluctuations, Equation 138, was also developed and this expression emphasized the role of large populations in reducing statistical fluctuations. The conservation equations for this process are
\[
\frac{dC_p}{dt} = -\frac{C_p}{\tau_p} \quad p = 1, 2, \ldots, N \tag{139}
\]

since the index \( p \) indicates a specific size category. Equation 139 can also be written as

\[
\frac{dC(D_p, t)}{dt} = -\frac{C(D_p, t)}{\tau_p} \quad D_p = D_1, D_2, \ldots, D_N \tag{140}
\]

so as to be consistent with the notation used previously.
EXPERIMENTAL

Equipment

The mixing vessel shown in Figure 5 illustrates the dimensions and overall design features of the experimental apparatus. The draft tube was fitted with three symmetrically located baffles which secured it firmly in the mixing vessel. The draft tube and baffles afforded good mixing conditions at relatively low levels of agitation. This condition was achieved because the baffles and draft tube directed the suspension downward in the center of the draft tube and upwards in the annular space. In addition, the baffles cut down vortex formations at the surface of the suspensions being processed. The draft tube design was chosen to take advantage of the above conditions and because this type of mixing vessel has been used in many previous investigations of continuous crystallization. Another important reason that the draft tube mixing vessel design was used in the experimental investigation was because the suspension flowed upward in the annular section where the withdrawal tube was located.

The suspensions were mixed by a Master Servodyne constant speed agitator. Figure 6 illustrates the Master Servodyne agitator as it appeared in the experimental equipment. The 5/16" stainless steel mixing shaft was fitted with a 3 blade 2 inch marine type impellor. The shaft was centrally located within the mixing vessel and the tip of the mixing shaft was
Figure 5. Mixing vessel
Figure 6. Photograph of experimental mixer
situated near the center of the draft tube. The Master Servodyne constant speed agitator was equipped with a speed selecting dial and R.P.M. meter. Utilizing these equipment features the R.P.M. could be adjusted to within ±15 R.P.M. of the desired value. The range of R.P.M. values that was used in the experimental investigations was from 600 to 1600 R.P.M. and it was noticed that for values of R.P.M. above 800 bubbles were induced into the mixing suspension.

During each of the experimental runs the working volume was maintained at 6035 ± 30 ml by manually matching the inlet volumetric flowrate with the outlet volumetric flowrate. The outlet stream was taken from the mixing vessel by means of gravity. During a typical run the effective head on the outlet stream was essentially constant and the inlet stream was adjusted with the aid of a rotameter and a throttling valve in order to maintain constant volume within the mixing vessel. The inlet stream was fed by a constant head tank as indicated in Figure 7. The equipment was originally fitted with a "chicken feeder" volume control device. However during the course of the experimental investigation it was found that the above manual control scheme was adequate. The outlet volumetric flowrate during a run was maintained to within ±1 percent of the average value for the particular run. The outlet volumetric flowrate increased only slightly during most of the runs. Since the suspensions
Figure 7. Flow sheet for equipment
being withdrawn became more dilute as each run progressed, it was concluded that the effective viscosity of the suspension decreased as the suspension became more dilute. This feature of suspension viscosity is discussed by Happel and Brenner (15) who derive Einstein's formula for the viscosity of a dilute suspension of spherical particles

\[ \mu_s = \mu (1 + 2.5 K_v \mu_3) \]  \hspace{1cm} (141)

where \( \mu_s \) is the suspension viscosity, \( \mu \) is the fluid viscosity, and \( K_v \mu_3 \) is the fraction of volume occupied by the particles. It should be mentioned that during runs in which the agitator speed was high and the effective outlet head was short, significant outlet volumetric flowrate changes were observed. In these experiments, the bubbles produced by high agitation would get held up in the outlet tube. However, at long effective outlet heads this problem was not observed. Figures 6 and 7 illustrate the above features of the experimental apparatus.

The outlet tube was constructed from stainless steel tubing with an outside diameter of 1/4" and a wall thickness of 1/16". The tip or mouth of the outlet tube was sharpened in order to project a very small tube width into the suspension. The outlet tube was situated between the draft tube and the vessel wall, and the tip of the outlet tube was located halfway down the length of the draft tube. The plane
of the outlet tube mouth was perpendicular to the direction of flow of the suspension in the annular space. Therefore the approach velocity and the pipe velocity were in the same direction. It was noticed, that on the average, suspensions motion was upward in the annular space but at all agitator speed there was a considerable amount of turbulence superimposed on this average velocity.

The key property that determines nonuniform withdrawal of suspensions of particles is the hydrodynamic condition in the neighborhood of the exit pipe surface. The experimental apparatus was designed to produce the extreme cases when the approach velocity exceeds the pipe velocity and when the pipe velocity exceeds the approach velocity. These two conditions could be obtained by varying the outlet head and the propellor speed. However, it will be seen that the overall design of the experimental apparatus had limited the investigation to cases for which the approach velocity exceeded the pipe velocity.

The auxiliary equipment utilized in the sampling and in the timing of samples consisted of graduated beakers, an electric timer, and a Mettler type H5 balance. The graduated beakers were calibrated in 5 ml increments and had a capacity of 500 ml. The electric timer was a Time It made by Precision Scientific Company and it could be read to the nearest tenth of a second. The Mettler balance was calibrated to
the nearest .0005 of a gram.

Materials

The particles that were used were Dylene 8 KPD 1037 beads made by Sinclair-Koppers Company, Pittsburgh, Pennsylvania. The Dylene beads were spherical polystyrene particles of a density of 1.05 gm/cc. The beads were separated by screening and the average size and range of particles used in the experimental investigation are listed in Table 1. It should be noted that sieve or screen number will be used interchangeably with the size of particles associated with the screen number in the following discussion.

Table 1. Sphere diameters

<table>
<thead>
<tr>
<th>U.S. Standard sieve number</th>
<th>Average diameter cm</th>
<th>Range cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>.09025</td>
<td>± .00795</td>
</tr>
<tr>
<td>30</td>
<td>.0651</td>
<td>± .0056</td>
</tr>
<tr>
<td>45</td>
<td>.0427</td>
<td>± .0073</td>
</tr>
<tr>
<td>60</td>
<td>.02735</td>
<td>± .00235</td>
</tr>
<tr>
<td>70</td>
<td>.0230</td>
<td>± .0020</td>
</tr>
</tbody>
</table>

The polystyrene spheres were very difficult to separate by dry screening because electrostatic charges were produced as soon as the particles were shaken. The electrostatic
charges made the beads cling together and to all the nearby surfaces. The screening procedure was greatly aided by adding a very small amount of Cab-o-sil which is made by Cabot Corporation, Boston, Massachusetts. Cab-o-sil is a finely divided silica of a maximum diameter of .015 microns and therefore the Cab-o-sil particles were more than 15,000 times smaller than the particles used in the experiments. Apparently, the Cab-o-sil particles adhered to the surfaces of the polystyrene beads and greatly reduced the electrostatic attraction of the beads. The amount of Cab-o-sil utilized was extremely small and this material did not affect any properties of the distilled water when suspensions were made with the screened particles.

Procedure

A sample of particles of a known weight was placed into the mixer and the vessel was filled with distilled water. As the level of the suspension reached the top of the draft tube, the agitator was started and adjusted to desired speed. The inlet flowrate was then adjusted to approximate the value of the outlet volumetric flowrate that would occur once the outlet stream was started. Usually slight adjustments in the inlet flowrate were necessary during a typical run in order to maintain constant volume. When the height of suspension reached the full volume level, which was indicated by a mark on the side of the mixing vessel, the outlet stream was
started.

The first sample of the suspension being withdrawn from the mixing vessel, denoted as sample zero, was taken for a sufficiently long time so as to compensate for start up irregularities. During the initial sample withdrawal bubbles trapped in the exit line were removed by tapping the outlet tube. The initial sample usually consisted of approximately 200 ml of suspension. Sample number one was then taken and simultaneously the electric timer was started. Afterward, subsequent samples were taken during constant intervals of time. For instance, sample number one consisted of the suspension removed from the vessel between 0 and 100 seconds and sample number two consisted of suspensions removed from the vessel between 100 and 200 seconds and so on. The above sampling procedure was adopted in order to cut down errors in reading times. At most the error in sample times associated with the above procedure was on the order of ± .3 seconds. After the run was completed the particles remaining in the system were collected in a beaker.

The volumes of suspension in samples number one, two, and so on were recorded in order to calculate a total volumetric flowrate for the entire run. The experimental error incurred in reading the sample volumes was of the order of ± 2 ml. It should be noted that samples were collected in 500 ml graduated beakers which were calibrated
in 5 ml increments. After recording the sample volumes the distilled water was separated from the particles of each sample by filtration through number 41 Whatman filter paper. The samples were then dried in an oven at about 65° C. The time needed for drying the samples varied with the size particles used in the particular run. In general, small particles took much longer than large particles to dry.

After the samples were dry they were removed from the oven and allowed to cool to room temperature. The samples were then weighed. For the experiments in which two different sizes of particles were present each dried sample was shaken with a trace amount of Cab-o-sil. After this procedure each sample was screened in order to separate the particles into the two size categories and each portion of the sample was then weighed. Therefore, for a typical run the data that were generated consisted of sample suspension volumes, particle weights, and times while the only pertinent experimental condition that was noted was the value agitator speed.

The frequency at which the fluid within the mixing vessel cycles around the draft tube was also experimentally determined. The procedure adopted to approximate this property consisted of counting the number of cycles a single particle made around the draft tube during a certain time interval. This technique was used to find the cycling frequency at various values agitator speed. Only one particle was present
in the vessel during the counting procedure. Therefore the results from the above technique can only approximate the true cycling frequency associated with a mixing suspension at a particular agitator speed.
RESULTS

Treatment of Data

The suspension volume of each sample and the time interval it took to obtain each sample were used to calculate the outlet volumetric flowrate. $V_1$ is the suspension volume of sample number 1 which was withdrawn from the mixing vessel during the interval of time of $t_{i-1}$ to $t_i$. For convenience $V_0$ and $t_0$ are taken as zero and the index $i$ will run from 0 to $n$. Therefore the total number of samples that were taken during a typical run was $n$. The cumulative volume of the suspension withdrawn from the mixing vessel during the time interval of 0 to $t_j$ is defined as

$$CV_j = \sum_{i=0}^{j} V_i \quad (142)$$

and it was assumed that $CV_j$ was related to the time $t_j$ and the outlet volumetric flowrate, $F$, by the following familiar formula

$$CV_j = Ft_j \quad (142)$$

In each of the experimental runs the value of $F$ was determined by the following least squares fit to Equation 142

$$F = \frac{\sum_{j=0}^{n} t_j CV_j}{\sum_{j=0}^{n} t_j^2} \quad (143)$$
and the units of $F$ were consistently recorded in terms of ml per second.

The sample volumes were read from 500 ml graduated beakers that were calibrated in increments of 5 ml. The sample times were read from an electric Time It timer made by Precision Scientific Company which was calibrated to the tenth of second. A reasonable estimate of the experimental errors associated with reading the graduate cylinders and the timer are $\pm 2$ ml and $\pm 0.3$ seconds, respectively. In the experiments that were performed a typical sample volume was 400 ml and the smallest time interval read from the timer was 50 seconds. The sample volumetric flowrate, $F_s$, for the typical values listed above is

$$F_s = 8.0 \text{ ml/second}$$  \hspace{1cm} (144)

However because of the uncertainties in the volume and time measurements one would have to expect that the true sample volumetric flowrate in this case is somewhere in the range of

$$7.913 < F_o < 8.089$$  \hspace{1cm} (145)

which represents a $\pm 1.1$ percent error about $F_s$, the sample volumetric flowrate. However, the flowrate $F$ for an entire run was not calculated in the above manner but from Equation 143 which tends to average out random experimental errors.

During each run the volumetric flowrate tended to
increase very slightly. The total density of the suspension
decreased very little during all the experiments performed
since Dylene particles are just slightly denser than water
and because the volume fraction occupied by the particles
was less than .017 and decreased during each run. Even if
the suspension density decreased markedly during the course
of each run this property would tend to slow down the outlet
volumetric flowrate since the outlet stream was siphoned off
by gravity as previously stated. The reason for the slight
but gradual increase in the outlet volumetric flowrate was
that the apparent viscosity of the suspension decreased
during each run. Happel and Brenner (15) discuss the deriva-
tion of Einstein's formula for the viscosity of a dilute
suspension of spherical particle. From the Einstein formula,
Equation 141,

\[ \mu_s = \mu (1 + 2.5 K \nu u_3) \]

Equation 141,

one can see that the apparent suspension viscosity, \( \mu_s \), is
linearly related to the volume fraction occupied by the
particles. In the course of each experiment the volume
fraction of particles decreased with time and in light of
Equation 141 the apparent suspension viscosity decreased
with time during the course of each run. The volumetric
flowrate through tubes is inversely proportional to
viscosity and therefore the above feature accounts for the
slight volumetric flowrate increase observed during the experimental runs.

To calculate the residence time for a specific size particle used in a typical run the sample weights and sample times were used. \( w_p(i) \) is the weight of particles of size \( p \) that were extracted from the mixing vessel during the time interval of \( t_{i-1} \) to \( t_i \). The weight of sample number zero, \( w_p(0) \), is obtained from the initial sample that was utilized to compensate for start up irregularities. The weight of the particles of size \( p \) left inside the mixing vessel, \( w_p(j) \), at time \( t_j \) was calculated by

\[
W_p(j) = W_p^0 - \sum_{i=0}^{j} w_p(i) \tag{146}
\]

where \( W_p^0 \) is the weight of particles of size \( p \) in the original charge. Equation 140 was utilized to relate \( W_p(j) \) to \( t_i \) and \( \tau_p \) for each run and in the present case this equation takes the following form

\[
W_p(j) = W_p(0) e^{-\frac{t_j}{\tau_p}} \tag{147}
\]

since \( C(D_p, t) \) of Equation 140, the number of particles of size \( D_p \) inside the mixing vessel, is equal to \( W_p \frac{6}{\pi D_p^3} \). In each of the experimental runs performed the residence time for particles of size \( p \) was determined from the following least squares fit to Equation 147.
and the value of $\tau_p$ so obtained was consistently reported in terms of seconds.

In a few of the experimental runs it was necessary to correct the sample weight data. For each run, the total weight remaining in the vessel, $W_p(j)$, was plotted against the time, $t_j$, on semi-log graph paper before applying Equation 148 to calculate the particle residence time. From this procedure, the bad data points could be easily recognized. The bad samples were probably caused by a significant loss of particles during the filtering procedure or in the transferring of the dried particles from the filter paper to the weighing beaker. The following form of Equation 147

$$\frac{dW_p(t)}{dt} = - \frac{W_p(0)}{\tau_p} e^{-\frac{t}{\tau_p}}$$  \hspace{1cm} (149)$$

was used to construct a plot from the sample weights $w_p(i)$ and times $t_i$. The experimental data were used to approximate $\frac{dW_p(t)}{dt}$ and $t$ as follows

$$\left. \frac{dW_p}{dt} \right|_{t = (t_i + t_{i-1})/2} = - \frac{w_p(1)}{t_i - t_{i-1}}$$  \hspace{1cm} (150)$$

and the above approximations were then plotted on semi-log
graph paper. In each of the cases when this procedure was used, the data point corresponding to the bad sample was easily recognized. Afterward a straight line was drawn through the consistent data points and a corrected value of the bad samples weight was obtained from the plot. The corrected sample weight was then used in the calculation of the particle residence time using Equation 148.

A distinct problem was encountered in attempting to duplicate specific runs. Slight variations in the outlet volumetric flowrate, $F$, would occur from run to run in a series of duplicate runs. Table 2 displays the values of the calculated particle residence times and outlet volumetric flowrates obtained in duplicate runs in which the agitator speed was 1500 R.P.M., the outlet head was 8-1/2"., and the particles were from screen number 70. The apparent cause of the variations in the outlet volumetric flowrates was attributed to bubbles that were induced into the mixing suspension. It seemed that in certain runs more bubbles were formed than in others and these bubbles would be withdrawn along with the suspension during the course of the run. As a result, in runs that were marked with an excess amount of entrapped bubbles the value of $F$ would be lowered.

If one examines the gross behavior of the calculated residence times and the volumetric flowrates listed in Table 2 a regular pattern emerges. Specifically, if $F$
Table 2. Calculated and corrected particle residence times for $F = 4.55 \text{ ml/second}$

<table>
<thead>
<tr>
<th>Outlet volumetric flowrate, ml/Sec</th>
<th>Calculated $\tau_{70}$ sec</th>
<th>Corrected $\tau_{70}$ sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5574</td>
<td>1321</td>
<td>1323</td>
</tr>
<tr>
<td>4.5464</td>
<td>1316</td>
<td>1315</td>
</tr>
<tr>
<td>4.5175</td>
<td>1323</td>
<td>1314</td>
</tr>
<tr>
<td>4.5736</td>
<td>1312</td>
<td>1319</td>
</tr>
<tr>
<td>4.5528</td>
<td>1313</td>
<td>1314</td>
</tr>
<tr>
<td>4.5600</td>
<td>1308</td>
<td>1311</td>
</tr>
</tbody>
</table>

...increases slightly then $\tau_p$ decreases slightly and if $F$ decreases slightly then $\tau_p$ increases slightly. This is only logical since the faster the outlet volumetric flowrate is the shorter the particle residence time will be. This type of behavior was consistently observed in all the duplicate runs performed and not just in the data listed in Table 2.

For each of the runs in a series of duplicate experiments the particle residence time, $\tau_p$, was corrected to correspond to a common outlet volumetric flowrate, $F$. Since the outlet volumetric flowrates varied slightly between the various runs in a series of duplicate experiments the following approximate formula was adopted to correct the...
data

\[(\tau_p - \tau_P) = \left(\frac{\delta \tau_p}{\delta F}\right)(\bar{F} - F)\]  \hspace{1cm} (151)

The term \(\left(\frac{\delta \tau_p}{\delta F}\right)\) is evaluated at \(\bar{F}\), \(\tau_p\) is the corrected particle residence time associated with \(\bar{F}\), and \(\tau_P\) and \(F\) are the calculated values of particle residence time and outlet volumetric flowrate for a typical run of a duplicate series. The particle residence time function of Equation 98 was used to obtain the following expression

\[\left(\frac{\delta \tau_p}{\delta F}\right) = -\left(\frac{\tau_p}{F}\right)^{3/2} f(\tau_p)\frac{1}{\sqrt{V \bar{F}}}\]  \hspace{1cm} (152)

by assuming that \(v_a\), the approach velocity, is only a function of R.P.M. and hence constant among the various runs of a duplicate series. However from the discussion pertaining to Equation 98 it is clear that the function \(f(\tau_p)\) is a hypothetical fabrication used by Watson (38) to present a concise description of anisokinetic sampling. Since \(f(\tau_p)\) is unknown for the present system it was assumed that the following limiting form of Equation 152

\[\lim_{D_p \to 0} \left(\frac{\delta \tau_p}{\delta F}\right) = -\frac{V}{F^2}\]  \hspace{1cm} (153)

is sufficient to use in the correction formula, Equation 151. Hence in each run of a series of duplicate experiments
the following formula was used

\[ \tau_p' = \tau_p + \frac{V}{F^2} (F - \bar{F}) \]  

(154)

in order to correct the individual particle residence times to correspond to a common outlet volumetric flowrate, \(F\).

Table 2 also lists the corrected particle residence times that correspond to a value of \(F\) of 4.55 ml/sec. From Table 2 it can be seen that this procedure has reduced the spread of particle residence times that was caused by the slight variations in outlet volumetric flowrates between the various runs. The results of all the experimental work can be found in Appendix B.

Applicability of Model

In the derivation of the mathematical model for the withdrawal of completely mixed suspensions from continuous constant volume mixing vessels it was assumed that the above operation could be characterized as a discrete state time homogenous Markov process. In addition, it was assumed that the underlying statistical rate of escape, \(\frac{1}{\tau_p'}\), for particles of size \(p\) depended upon the specific size \(p\) and the prevailing hydrodynamic conditions at the exit surface but not upon the concentrations of other size particles within the mixing vessel. To help insure that these conditions obtained during the experimental runs the volume fraction occupied by the
particles initially was kept very low. In fact the volume fraction occupied by the particles in the initial charge was below .016 in each experiment that was conducted. By adopting this general rule it was thought that variations in the hydrodynamic conditions near the exit pipe surface due to concentration changes during a typical run would be minimized. Therefore, it could be said that \( \tau_p \) only depends upon the size \( D_p \), agitator speed, and \( F \), which are the measurable experimental variables, according to the mathematical model.

The chief result of the above assumptions was the following relationship for the total number of particles of size \( p \), \( \overline{C}_p(t) \), left within the mixing vessel at time \( t \).

\[
\overline{C}_p(t) = \overline{C}_p(0) e^{-\frac{t}{\tau_p}} \quad (140)
\]

and from the above discussion it is apparent that \( \tau_p \) was assumed to have the following functional dependence

\[
\tau_p = \tau(D_p, \text{R.P.M.}, F) \quad (155)
\]

In the following discussion it will be shown that Equations 140 and 155 adequately describe the withdrawal behavior of completely mixed dilute suspensions of Dylene particles and water from the continuous constant volume experimental draft tube mixing vessel. Two cases were considered, a suspension of particles of a single size and a suspension of particles of two sizes. These two cases were considered
to check the validity of the assumed mathematical model.

**Suspensions of particles of one size**

It can be confidently stated that the assumed Markov process model adequately describes the withdrawal behavior of dilute and completely mixed suspensions of single sized Dylene particles and water from the experimental draft tube mixer. To support this claim the results of two especially long runs are presented in Figures 8 and 9. In each of these figures the log of the fraction of particles of size \( p \) remaining in the mixing vessel at time \( t \), \( x_p(t) \), defined by

\[
x_p(t) = \frac{\mathcal{U}_p(t)}{\mathcal{C}_p(0)} = \frac{W_p(t)}{W_p(0)}
\]

is plotted against time. According to the model, the experimental data should fall on a straight line of slope \((-\log_{10}(e)/\tau_p)\). It can be seen that the experimental data from these runs is represented almost exactly by the model.

Figure 8 was constructed from the data from run 1 listed in Appendix B. In this run particles from screen 20 were used and the agitator speed was at 600 R.P.M. while the head on the outlet stream was 42". Figure 9 was constructed from the data for run 2 which can also be found in Appendix B. Run 2 had the same agitator speed and outlet head as run 1 but particles from screen 70 were used to make up the suspension. Upon consulting Table 1 it can be
Figure 8. Withdrawal response for particles from screen 20

Agitator speed = 600 R.P.M.

\[ F = 7.949 \text{ ml/second} \]
\[ \tau_{20} = 664 \text{ seconds} \]
LOG OF WEIGHT FRACTION LEFT, $x_{20}$
Figure 9. Withdrawal response for particles from screen 70

Agitator speed = 600 R.P.M.

$F = 7.808 \text{ ml/second}$

$t_{20} = 755 \text{ seconds}$
seen that the diameter of the particles from screen 20 are approximately four times larger than the diameter of particles from screen 70. The ratios of the outlet tube diameter to the diameter of particles from screens 20 and 70 are approximately 3.5 and 14, respectively. Therefore, in terms of the outlet geometry, particles from screen 20 were relatively large and particles from screen 70 were relatively small.

In the run which contained particles from screen 20, illustrated in Figure 8, the last few data points fall off the straight line drawn through the bulk of the data. The reason for this behavior can be traced directly to the fact that the outlet volumetric flowrate increased gradually during this run. This feature of the experimental investigation has been discussed in the Treatment of Data section. It was concluded that the reason the outlet flowrate increased during each experimental run was that the apparent suspension viscosity correspondingly decreased during each run. The average outlet volumetric flowrate for the first four samples in run 1 was 7.785 ml/sec and 8.025 ml/sec for the last four samples of this run. In fact, upon closely examining the data from run 1 three distinct flowrate segments can be recognized and the resulting data from these segments are listed in Appendix B as runs 1-1, 1-2, and 1-3. It should be mentioned that all the runs listed in Appendix B with the
exceptions of runs 1, 2, and 3 were conducted over much shorter total time intervals in order to avoid the above flowrate complications. Even though the outlet volumetric flowrate increased slightly during this particular run the resulting plot of run 1 in Figure 8 is still a rather good verification of the assumed model as expressed by Equation 140. The calculated values of $T_p$ and $F$ for run 1 were 664 seconds and 7.949 ml/second, respectively.

It can be seen from Figure 9 that run 2 containing particles from screen 70 obeyed Equation 140 very closely. In this particular run the difference between the average outlet volumetric flowrate of the first four samples and the last four samples was .125 ml/sec whereas this difference was .240 ml/sec for run 1. Therefore run 2 illustrated in Figure 9 did not exhibit significant changes in the outlet flowrate as did run 1 illustrated in Figure 8. The particle residence time and outlet volumetric flowrate for run 2 were 755 seconds and 7.808 ml/second, respectively. Note that the same operating conditions as in run 2 also pertained to run 1 which contained particles from screen 20. However for this case the particle residence time and outlet volumetric flowrate were 664 seconds and 7.949 ml/second, respectively. After utilizing Equation 154 to correct each of these calculated values of $T_p$ to correspond to an outlet volumetric flowrate of 7.8 ml/second the following values
were found

\[ \tau_{20} = 679 \text{ seconds} \]

\[ \tau_{70} = 756 \text{ seconds} \]

Therefore at 600 R.P.M. and an outlet volumetric flowrate of 7.8 ml/sec there was a 77 second difference between the particle residence times for particles from screen 20 and 70. This fact verifies Equation 155 for the general case when particles of one size make up the suspension being processed.

Several statistical tests were applied to the data from run 2, to see just how well Equation 140 was obeyed. The ratio of the variance about the regression line of \( \log_{10} (10 \times y_{70}(i)) \) on \( t_i \) to the average value of \( \log_{10} (10 \times y_{70}(i)) \) for run 2, denoted as \( \left( \frac{\sigma}{\bar{y}} \right)_{70} \), was calculated from the following formula

\[
\left( \frac{\sigma}{\bar{y}} \right)_{70}^2 = \frac{\sum_{i=0}^{n} (\log_{10} (y_{70}(i)) + \frac{t_i \log_{10} (e)}{\tau_{70}})^2}{\left( \sum_{i=0}^{n} \log_{10} (y_{70}(i)) \right)^2}
\]

(157)

and the correlation coefficient \( r_{70} \) for \( \log_{10} (10 \times y_{70}(i)) \) and \( t_i \) was calculated with the aid of the following equation
The value of \( r_{70}^2 \) was found to be .002439. This indicates that there was very little deviation of the data from the straight line indicated on Figure 9. Therefore the mathematical model expressed by Equation 140 was almost exactly obeyed by the data from run 2. The value of the correlation coefficient \( r_{70} \) was .999993. According to Wine (40), when \( r_{70} \) is exactly one, all the experimental points would fall on the straight line indicated in Figure 9. On the other hand, if \( r_{70} \) was close to zero one could say that \( \log_{10} (10x_{70}(t)) \) and \( t \) are independent and are not related as in the model equation, Equation 140. In the light of the above statistical tests one can be very confident that the Markov model accurately predicts the withdrawal behavior of suspensions containing particles of a single size. Although the correctness of Equation 142 in predicting \( F \) has no fundamental importance in testing the applicability of Equation 140 the value of \( \frac{\sigma}{\bar{V}} \)
was calculated to complete the above statistical discussion concerning run 2. The value of \((\sigma_{CV})^2\) was found to be 0.00322 which indicates again that the flowrate \(F\) did not vary significantly during this particular run. Finally, at high suspension densities the above conclusions may not be applicable since dilute suspensions were used in the experimental work.

Suspensions of particles of two sizes

A key step in the development of Equations 140 and 155 was the assumption of independence among the various sizes of particles making up a typical suspension. The functional form of the particle residence time, written in terms of the experimental variable, for particles of size \(D_p\), Equation 155,

\[
\tau_p = \tau(D_p, R.F.M., F)
\]  

followed directly from the assumption of independence. In addition, this assumption made it possible to write the probability distribution, \(P(m_1, ..., m_N, t)\) over the state of the suspension, \((m_1, ..., m_N)\), at time \(t\) as

\[
(\sigma_{CV})^2 = \frac{n \sum_{i=0}^{n} (CV_i - F t_i)^2}{n \sum_{i=0}^{n} (CV_i)^2}
\]  

\(159\)
\[ P(m_1, \ldots, m_N, t) = \prod_{i=1}^{N} P_i(m_i, t) \quad (160) \]

\[ P_i(m_i, t) \text{ the probability distribution for particles of size } i, \text{ was found to be} \]

\[ P_i(m_i, t) = \left( \frac{N_i}{m_i} \right) e^{-\frac{tm_i}{\tau_i}} (1 - e^{-\frac{t}{\tau_i}}) N_i - m_i \quad (133) \]

when the state of the suspension at time equal to zero was \((N_1, \ldots, N_N)\). The averaging equation for any arbitrary function of the system's state, \( f(m_1, \ldots, m_N) \),

\[ f(m_1, \ldots, m_N)(t) = \sum_{m_1=0}^{N_1} \cdots \sum_{m_N=0}^{N_N} f(m_1, \ldots, m_N) P(m_1, \ldots, m_N, t) \quad (161) \]

was then utilized to calculate the mean value and variance about the mean value of the number of particles of size 1 remaining within the vessel at time \( t \). These quantities were presented in Equations 135 and 137

\[ \mu_1(t) = N_1 e^{-\frac{t}{\tau_i}} \quad (135) \]

\[ \sigma^2_1(t) = N_1 e^{-\frac{t}{\tau_i}} (1 - e^{-\frac{t}{\tau_i}}) \quad (137) \]

Therefore if the mathematical model expressed by Equations 140 and 155 is to be used to describe the withdrawal behavior of completely mixed suspensions the key property of inde-
dependence must first be experimentally demonstrated. In the following discussion the task of showing that Equations 140 and 155 are applicable in describing the withdrawal behavior of suspensions consisting of particles of two different sizes was undertaken.

Tables 3, 4, and 5 have been prepared from a series of duplicate runs for which the suspensions contained various concentrations of two different sizes of particles. The values of particle residence times have been corrected with the aid of Equation 154 to correspond to a constant outlet volumetric flowrate for each general case considered. The average value of the particle residence times and the

Table 3. Screen 70 and screen 45 particle residence times
R.P.M. = 1500 and $F = 4.5$ ml/sec

<table>
<thead>
<tr>
<th>Run numbers</th>
<th>Initial weight %</th>
<th>Residence times, seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70</td>
<td>45</td>
</tr>
<tr>
<td>12,13,14,15,16,17</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>23,24</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>27,28,29,30,31</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>25,26</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>18,19,20,21,22</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 4. Screen 70 and screen 20 particle residence times, R.P.M. = 1500, F = 7.8 ml/sec

<table>
<thead>
<tr>
<th>Run numbers</th>
<th>Initial weight</th>
<th>Residence times, seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>2,9,10,11</td>
<td>100</td>
<td>752.6 ( \pm ) 4.4</td>
</tr>
<tr>
<td>3,7,8</td>
<td>50 50</td>
<td>750.2 ( \pm ) 3.5</td>
</tr>
<tr>
<td>1,4,5,6</td>
<td>0 100</td>
<td>682.4 ( \pm ) 7.5</td>
</tr>
</tbody>
</table>

The various runs listed in the tables can be found in Appendix B. In the runs used to construct Table 3 many bubbles were observed in the suspensions and these bubbles were frequently trapped in the outlet line. This behavior was caused by the high level agitation used in these runs and because the outlet volumetric flowrate in these runs was too small to keep bubbles from being trapped in the outlet tube. These facts might account for the large variances found in Table 3.

According to Equations 140 and 155 the residence time for particles of size 1 is the same when the suspension being processed contains only particles of size 1 and when the suspension contains other sizes of particles besides...
Table 5. Screen 60 and screen 45 particle residence times, R.P.M. = 1000, $P = 6.11$ ml/sec

<table>
<thead>
<tr>
<th>Run number</th>
<th>Initial weight</th>
<th>Residence time, seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 % 45</td>
<td>760 745</td>
</tr>
<tr>
<td>32</td>
<td>100 0</td>
<td>977</td>
</tr>
<tr>
<td>33</td>
<td>75 25</td>
<td>975 966</td>
</tr>
<tr>
<td>34</td>
<td>50 50</td>
<td>974 971</td>
</tr>
<tr>
<td>35</td>
<td>25 75</td>
<td>953 986</td>
</tr>
<tr>
<td>36</td>
<td>0 100</td>
<td>976</td>
</tr>
</tbody>
</table>

size 1, provided the value of $P$ and R.P.M. are the same in each case. Tables 3 and 5 provide little verification of the assumed model's behavior. However, Table 4 does indicate that the above assumption was applicable to the experimental results of runs 1 through 11. Another reason Tables 3 and 5 provide very little information into the problem considered above is that the values of residence time are relatively close to one another. In Table 4, on the other hand, the residence times are quite different for each particle sizes.

A much more convincing test of experimental data was obtained from Equations 160, 133, 135, and 137. These
122

equations were used to develop the following identity

\[
    r_{ij}(t) = \frac{m_i m_j(t) - \overline{m}_i(t)\overline{m}_j(t)}{\sigma_i(t)\sigma_j(t)} = \begin{cases} 
    1 & i = j \\
    0 & i \neq j
\end{cases}
\]  

(162)

which was used to test the experimental data. Note that \( r_{ij}(t) \) is the correlation coefficient between the population of size \( i \) and size \( j \) that would obtain from the data of an infinite number of duplicate runs if the mathematical model was correct. In accordance with Wine (40), \( r_{ij}(t) \) is zero when \( i \) is not equal to \( j \) since independence was assumed in the development of Equations 160, 133, 135, and 137. The defining equation for \( r_{ij}(t) \) can also be written as

\[
    r_{ij}^2(t) = \lim_{n \to \infty} \frac{\left[ \sum_{t=1}^{n} \left( x_i(t, t) - \frac{1}{n} \sum_{s=1}^{n} x_i(t, s) \right) x_j(t, t) \right]^2}{\sum_{t=1}^{n} \left( x_i(t, t) - \frac{1}{n} \sum_{s=1}^{n} x_i(t, s) \right)^2 \sum_{q=1}^{n} \left( x_j(t, q) - \frac{1}{n} \sum_{r=1}^{n} x_j(t, r) \right)^2}
\]  

(163)

where \( x_i(t, t) \) and \( x_j(t, t) \) are the values of the fractions of size \( i \) and \( j \) left within the mixing vessel at time \( t \) in experimental \( t \) or

\[
    x_i(t, t) = \frac{m_i(t, t)}{N_i}
\]  

(164)
Run 3 was used to estimate \( r_{ij}(t) \). The suspension processed during this run contained particles from screen 20 and screen 70. The initial charge contained 49.9991 grams of particles from screen 70 and 49.9956 grams of particles from screen 20. The calculated values of \( \tau_{70} \), \( \tau_{20} \) and \( F \) were found to be 746 seconds, 674 seconds, and 7.846 ml/second, respectively. The outlet flowrate increased very slightly during this run however, not as significantly as in run 1 illustrated in Figure 8. The results of run 3 are plotted in Figure 10, and from this plot it can be seen that the general behavior predicted in Equation 140 was obeyed. For example, Equation 140 predicts that the plots of \( \log_{10} \left( 10 \times x_{70}(t) \right) \) and \( \log_{10} \left( 10 \times x_{20}(t) \right) \) against time should be two straight lines of slopes \( (-\log_{10}(e)/\tau_{70}) \) and \( (-\log_{10}(e)/\tau_{20}) \), respectively. These features are apparent in Figure 10.

The data from run 3 were used to estimate \( r_{ij}(t) \) when \( t \) is equal to 50 seconds. The estimate of \( r_{ij}(50) \) was calculated using Equation 163 for which \( x_{70}(50,t) \) and \( x_{20}(50,t) \) were obtained by

\[
x_{70}(50,t) = \frac{w_{70}(t)}{w_{70}(t-1)}
\]

\[
x_{20}(50,t) = \frac{w_{20}(t)}{w_{20}(t-1)}
\]

(165)

(166)
Figure 10. Withdrawal response for particles from screens 20 and 70

Agitator speed = 600 R.P.M.

\[ F = 7.846 \text{ ml/second} \]

\[ \tau_{20} = 674 \text{ seconds} \]

\[ \tau_{70} = 746 \text{ seconds} \]
since the data of run 3 were obtained in 50 second intervals. Therefore run 3 which contained 14 evenly spaced samples was split up into a series of 14 runs, each of which contained only one sample. The above procedure can be justified by the fact that it was assumed that the Markov process was time homogeneous, that is the transition probability, Equation 104, depends only on the time interval between possible changes in state, and because Equation 163 does not directly depend on the initial values of \( N_i \) but only upon the fractions \( x_i \). The estimate for \( r_{ij}(50) \) obtained from run 3 was

\[
r_{ij} = \begin{cases} 
1 & i = j \\
0.0259 & i \neq j 
\end{cases} 
\]

(167)

where \( i \) and \( j \) are understood to take on the values of 20 and 70, the screen numbers associated with the particles used in run 3. One other property resulting from the assumption of independence which obtains from Equations 160, 133, 135, and 137 is

\[
R_{i,j}(t) = \frac{X_i(t)X_j(t)}{X_i(t)X_j(t)} = 1
\]

(168)

and the estimate for \( R_{20,70}(50) \) obtained from run 3 was found to be

\[
R_{20,70} = 1.0000000284
\]

(169)
The results expressed in Equations 167 and 169 made it possible to conclude that the model, Equations 140 and 155, was adequate to describe the withdrawal behavior from the experimental draft tube mixer.

Finally, Table 6 was constructed from the corrected data of runs 1, 2, and 3. These particular runs were exceptionally long. The outlet volumetric flowrate increased slightly during each of these runs due to a decreasing apparent suspension viscosity. However, Table 6 indicates that the assumptions embodied in Equation 155 are reflected in the data from runs 1, 2, and 3. For instance, there is essentially no difference in \( \tau_{20} \) and \( \tau_{70} \) in each of the concentration cases considered in Table 6. In fact \( \tau_{20} \) is exactly the same for both the 100 percent and 50 percent concentration cases.

Table 6. Comparison of residence times from runs 1, 2, and 3, \( F = 7.8 \text{ ml/second}, \text{ R.P.M.} = 600 \)

<table>
<thead>
<tr>
<th>Run number</th>
<th>Initial weight %</th>
<th>Residence time, seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
initial weight fraction cases whereas the difference between $\tau_{70}$ for the two initial weight cases considered is insignificant. The results of runs 1, 2, and 3 are plotted in Figures 8, 9, and 10. It must be stated that the above conclusions may not be applicable to high suspension density cases since dilute suspensions were only considered in the experimental work.

Mixer Cycling Frequency

The cycling frequencies of the experimental draft tube mixer was determined by counting the revolutions made by a single particle in a specific time interval for several values of agitator speed. The results of these measurements are presented in Table 7. Figure 11 was also constructed by plotting the experimental values of $\log_{10}(\bar{\mu})$ against

Table 7. Cycling frequency of experimental mixer

<table>
<thead>
<tr>
<th>R.P.M. revolutions/minute</th>
<th>Cycling frequency $\bar{\mu}$ revolutions/second</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>.1762</td>
</tr>
<tr>
<td>600</td>
<td>.2261</td>
</tr>
<tr>
<td>700</td>
<td>.2685</td>
</tr>
<tr>
<td>800</td>
<td>.3307</td>
</tr>
<tr>
<td>1100</td>
<td>.4421</td>
</tr>
</tbody>
</table>
Figure 11. Plot of log of cycling frequency versus log of agitator R.P.M.
LOG OF CYCLING FREQUENCY, rev/min.

LOG OF RPM
log_{10}(R.P.M.). A least square fit of the following model

\[ \bar{w} = a (R.P.M.)^b \]  

was determined from the experimental data and the following empirical equation was obtained

\[ \bar{m} = 1.233 \times 10^{-4} (R.P.M.)^{1.173} \]  

The above model, Equation 171, has some foundation since Narayanan et al. (26) maintained that

\[ \bar{w} \propto (R.P.M.) \]  

in a baffled mixing vessel agitated by an 8 flat bladed impeller. It should be noted that Equation 171 only pertains to the cycling frequency of pure water and not for suspensions. However, since the suspensions used during the experimental investigation were dilute, Equation 171 should approximate the suspension cycling frequency.

An estimate of the average cycling velocity can also be obtained from Equation 171 by the following formula

\[ V_C = \bar{r} \bar{w} \]  

where \( \bar{r} \) is the average length of the loop the fluid traces as it cycles around the draft tube. The value of \( \bar{r} \) for the experimental apparatus was somewhere in the range between 25 to 13 inches. Using the average value, the following
estimate of the average cycling velocity in cm/sec was found

\[ v_c = 5.95 \times 10^{-3} \text{ (R.P.M.)}^{1.173} \]  \hspace{1cm} (174)

The range of agitator speeds used in this experimental work was from 600 to 1600 R.P.M. The cycling velocities at the agitator speeds of 600 and 1600 R.P.M. calculated with the aid of Equation 174 are 10.8 and 34.1 cm per second, respectively. Therefore, in terms of the cycling velocity, the range of R.P.M. values considered in this work provided a large range of possible hydrodynamic conditions within the experimental mixing vessel.

It should be emphasized that Equation 174 is intended to approximate the average cycling velocity of the fluid around the draft tube at various R.P.M. values. The approach velocity of the fluid that eventually is withdrawn through the outlet tube cannot be estimated by Equation 174. The main reason for this fact is that during the above experiments it was noted that the velocity was much faster in the central core of the draft tube and relatively slower in the annular space where the outlet tube was located. Further, \( \bar{w} \) accounted for all the flow regions within the mixer and in this respect it was noted that there were several dead spaces and regions where vortexes formed near the baffles. Therefore \( \bar{w} \) was calculated by averaging in the effects of all the flow regions and not just the flow region near the outlet tube.
However assuming that $v_c$ of Equation 174 is approximately equal to the approach velocity, $v_a$, in the annular space between the vessel wall and the draft tube the isokinetic conditions can be calculated. For instance, the outlet volumetric flowrates at 600 R.P.M. and 1600 R.P.M. are .85 and 2.7 ml per second, respectively. Therefore under the above assumptions if the experimental draft tube mixing vessel is operated at the $P$ and R.P.M. values listed above all the particles, regardless of size, and the fluid will have the same residence time, namely $\tau_p$ of Equation 175.

Effect of R.P.M. on Particle Residence Times

Several experiments were conducted to determine the effect of the mixer speed on particle residence times. A particle residence time function was previously derived using the basic ideas forwarded by Watson (38) and the following relationship was obtained

$$\tau_p = \frac{\nu}{\pi R_o^2 v_a (1 + ((\frac{v_a}{v_p})^{1/2} - 1) f(p))}$$  \hspace{1cm}[98]$$

Equation 98 predicts that $\tau_p$, the particle residence time of particles of size $D_p$, will increase as $v_a$, the approach velocity, decreases. R.P.M. and $P$ may replace $v_a$ and $v_p$ as the basic arguments of $\tau_p$ as in Equation 155 so that $\tau_p$ is

$$\tau_p = \tau(D_p, \text{R.P.M.}, F)$$  \hspace{1cm}[155]$$
in terms of the measurable experimental variables. Therefore according to Equation 98, \( T_p \) should increase as the R.P.M. decreases. This general behavior was not observed in the majority of systems that were investigated and Watson's theory, as represented by Equation 98, was of little use in explaining these experimental results.

Runs 37, 38, 39, and 40 were conducted to investigate the effects of mixer speed on the particle residence times for suspensions containing particles of one size. The results from these runs are tabulated in Appendix B. During each of these runs, several values of R.P.M. were considered. Runs 37 and 38 contained particles from screens 70 and 60 respectively. The corrected values of the particle residence times corresponding to an outlet volumetric flowrate of 4.57 ml/sec for runs 37 and 38, are listed in Table 8.

Neglecting the corrected data corresponding to 1100 R.P.M. the results from runs 37 and 38 confirm the behavior predicted by Equation 98. For instance, the particle residence times from runs 37 and 38 increased as the value of R.P.M. was decreased. Particles from screens 70 and 60 are relatively small compared to the outlet pipe diameter and the values of \( \tau_{60} \) and \( \tau_{70} \) should be close to \( T_p \) where

\[
T_p = \frac{V}{\pi R_o^2 \nu_p} = \frac{V}{F} \tag{175}
\]

according to Equation 98. The value of \( T_p \) based on the
Table 8. Corrected particle residence times for runs 37 and 38, $F = 4.57$ ml/sec

<table>
<thead>
<tr>
<th>R.P.M. revolutions/minute</th>
<th>Particle residence times, $\tau_{70}$ seconds</th>
<th>Particle residence times, $\tau_{60}$ seconds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>1317</td>
<td>1304</td>
</tr>
<tr>
<td>1100</td>
<td>1298</td>
<td>1306</td>
</tr>
<tr>
<td>700</td>
<td>1320</td>
<td>1308</td>
</tr>
</tbody>
</table>

outlet volumetric flowrate of 4.57 ml/sec is 1321 seconds, which is very close to the values of $\tau_{60}$ and $\tau_{70}$ listed in Table 8. Therefore, the general behavior predicted by Equation 98 was reflected in the results from runs 37 and 38.

The results from runs 39 and 40 could not be explained with the aid of Equation 98. Particles from screens 20 and 70 were used in runs 39 and 40, respectively. In terms of the outlet tube diameter, particles from screen 20 are relatively large and those from screen 70 are relatively small. Figures 12 and 13 have been prepared from the data of runs 39 and 40 by plotting $\log_{10} \left(10 \frac{W(t)}{W(0)}\right)$ against time, $t$, for the various R.P.M. values considered. In both these figures the value of R.P.M. and particle residence time are listed for each curve. From Figures 12 and 13 it is apparent that the particle residence times increased as
Figure 12. Withdrawal response for particles from screen 70 at various agitator speeds

\[ F = 2.290 \text{ ml/second} \]
LOG OF WEIGHT FRACTION, $\log(x_0)$

- $1600$ RPM, $\tau_0 = 2662$ sec
- $1260$ RPM, $\tau_0 = 2624$ sec
- $900$ RPM, $\tau_0 = 2582$ sec
- $600$ RPM, $\tau_0 = 2533$ sec

TIME, seconds
Figure 13. Withdrawal response for particles from screen 20 at various agitator speeds

\[ F = 2.275 \text{ ml/second} \]
1.00
0.98
0.96
0.94
0.92
0.90
0.88

\( t_{20} = 2864 \text{ sec} \)
\( t_{20} = 2707 \text{ sec} \)
\( t_{20} = 2549 \text{ sec} \)
\( t_{20} = 2373 \text{ sec} \)

\( \log \text{ of weight fraction, } x_{20} \)

\( \text{TIME, seconds} \)

- 1600 RPM, \( t_{20} = 2864 \text{ sec} \)
- 1200 RPM, \( t_{20} = 2707 \text{ sec} \)
- 900 RPM, \( t_{20} = 2549 \text{ sec} \)
- 600 RPM, \( t_{20} = 2373 \text{ sec} \)
the value of R.P.M. increased. This fact directly contra-
dicts the behavior of particle residence times implied by
Equation 98. The change in particle residence time for the
various changes in R.P.M. considered in these runs was more
pronounced in run 39 than in run 40. The reason for this
feature can be found in the fact that the particles in run
40 were much smaller than those in run 39. This same
general result was found in runs 37 and 38 both of which
contained relatively small particles.

Several runs were conducted with particles from screens
20, 30, 45, and 70 at 600 and 1600 R.P.M. values to determine
the particle residence time, \( \tau_p \), as a function of particle
size. The outlet head was 42 inches for each of these runs.
The corrected particle residence times corresponding to an
outlet volumetric flowrate of 7.8 ml/sec are listed in
Table 9. The run numbers also appear in Table 9. The
original data for these runs can be found in Appendix B.
The data from Table 9 was plotted in Figure 14. Two plots
of Equation 98 are also presented in Figure 14. To plot
Equation 98 \( V, F, \) and \( R_0 \) were taken as 6035 ml, 7.8 ml/
second, and 1/16 of an inch so as to correspond to the
experimental conditions. The approximate form of \( f (\eta_p) \),
Equation 99, and a viscosity of water at 70° C, .00098
gm/cm/second, were also used in Equation 98. A value of
\( (v_a/v_p) \) equal to 1.137 was chosen so that the resulting
Figure 14. Particle residence time versus particle diameter at agitator speeds of 600 and 1600 R.P.M.
PARTICLE RESIDENCE TIME, SECONDS

\[ v' = 3.460 \sqrt{d} \]

\[ d_{50} = 1.127 \sqrt{d} \]

This diagram represents the relationship between particle residence time in seconds and particle diameter in centimeters. The data points and lines indicate different conditions, with symbols marking specific RPM values: "O" for RPM = 600 and "□" for RPM = 1600.
Table 9. Corrected particle residence times at 600 and 1600 R.P.M., $F = 7.8$ ml/sec

<table>
<thead>
<tr>
<th>Screen number</th>
<th>R.P.M. = 600</th>
<th>R.P.M. = 1600</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Runs</td>
<td>Residence times</td>
</tr>
<tr>
<td>20</td>
<td>1,4,5,6</td>
<td>684(^a)</td>
</tr>
<tr>
<td>30</td>
<td>41</td>
<td>704</td>
</tr>
<tr>
<td>45</td>
<td>42</td>
<td>741</td>
</tr>
<tr>
<td>70</td>
<td>2,9,10,11</td>
<td>752(^b)</td>
</tr>
</tbody>
</table>

\(^a,b\)These entries are the average values of the runs indicated.

A plot of Equation 98 would approximately correspond to the data for the 600 R.P.M. case. It was assumed that $v_a$ was proportional to the cycling frequency, $\bar{w}$, of the experimental mixing vessel given in Equation 171. Therefore the following formula

$$\left(\frac{v_a}{v_p}\right)_1 = \left(\frac{v_a}{v_p}\right)_2 \left(\frac{R.P.M.}{R.P.M.}\right)_1 1.173 \quad (176)$$

was used to obtain the value 3.48 as an estimate for $\frac{(v_a/v_p)}{v_p}$ at 1600 R.P.M.

According to Equation 98 the particle residence time, $\tau_p$, decreases with increasing particle size, $D_p$, if $\frac{(v_a/v_p)}{v_p}$ is greater than one. In addition, as the value of $\frac{(v_a/v_p)}{v_p}$
is increased relative to one the above particle residence time behavior becomes magnified. These properties of Equation 98 can be seen in Figures 4 and 14. It should be noted that the plots of Equation 98 appearing in Figure 4 were constructed from the same values of $F, V, R_p, \mu$, and $f\left(\frac{V}{D_p}\right)$ as were considered above. The particle residence time decreases with increasing particle size in the experimental plot corresponding to the 600 R.P.M. case. Therefore Equation 98 implies that $(\frac{V_a}{V_p})$ is greater than one for the experimental operating conditions of $F$ and the agitator speed equal to 7.8 ml/second and 600 R.P.M., respectively. Since it has been established that the cycling frequency of the experimental mixing vessel increases as the agitator speed increases, Equation 171, it would be natural to expect that the value of $(\frac{V_a}{V_p})$ at 1600 R.P.M. is larger then that at 600 R.P.M. In light of the general behavior predicted by Equations 98 and 171 the experimental data for the 600 and 1600 R.P.M. case should have obeyed the following inequality

$$\tau_F = 774 > \tau(D_p, 600, 7.8) > \tau(D_p, 1600, 7.8) \quad (177)$$

$$D_p > 0$$

This feature is quite apparent in the plots of Equation 98 in Figure 14. In fact $\tau(D_p, 1600, 7.8)$ decreases so much faster than $\tau(D_p, 600, 7.8)$ that only a small portion of
the \( \tau(D_p, 1600, 7.8) \) curve appears on Figure 14. However the corresponding inequality implied by the experimental data in Figure 14 is

\[
\tau_F = 774 > \tau(D_p, 1600, 7.8) > \tau(D_p, 600, 7.8) \tag{178}
\]

Equation 178 implies that the approach velocity, \( v_a \), at 1600 R.P.M. was less than \( v_a \) at 600 R.P.M. since the pipe velocity, \( v_p \), was held constant. However in light of Equation 171 for the cycling frequency this possibility seems highly unlikely. Therefore Equation 98 cannot be used to explain the behavior of the experimentally determined plot of \( \tau(D_p, \text{R.P.M.}, F) \).

Perhaps the reason that Watson's theory, as reflected in Equation 98, does not explain the above experimental results can be found in the fact that there was a considerable amount of turbulence superimposed upon the average approach velocity at all levels of R.P.M. investigated. During each experiment the approach velocity was directed straight at the surface of the outlet tube on the average. However during runs in which the R.P.M. was greater than 900 there was a great deal of turbulence observed. The turbulence must have distorted the velocity profiles to the extent that the type of profiles such as in Figures 2 and 3 were no longer present. It should be noted that the basis of Equation 98 was extracted from considering ideal symmetric
converging or diverging profiles as in Figures 2 and 3. However, the major effect of turbulence at high values of R.P.M. was to produce an effective approach velocity that was much less than the average approach velocity based on Equation 176. In fact from the experimental data for the 1600 R.P.M. plot it appears that effective approach velocity is much closer to the pipe velocity than for the 600 R.P.M. plot.

**Effect of Classified Withdrawal on Crystal Size Distributions**

The data listed in Table 9 and plotted in Figure 14 can be used to construct empirical particle residence time functions. The following equations were obtained from this data

\[
\tau(D_p, 600, 7.8) = 774 (1 - 1.26 \ D_p)
\]

\[
\tau(D_p, 1600, 7.8) = 774 (1 - .292 \ D_p)
\]

where the notation of Equation 155, \(\tau(D_p, \text{R.P.M.}, F)\) is used above. It should be noted that \(D_p\) is in terms of cm, R.P.M. is in terms of revolutions per minute, and \(F\) is in terms of ml per second. Equations 179 and 180 are only to be used for particles in the size range from 0 to .1 cm. The particle residence times used to construct the above empirical equations were obtained from experiments in which particles of one size made up the suspensions being processed. However the key
property of independence was demonstrated with experimental data in the Markov Model section and therefore the particle residence times listed in Table 9 may be superimposed into continuous functions as above. Equations 179 and 180 will be used in discussing the effects of nonuniform withdrawal on continuous crystallization but before proceeding to this topic a general mixing problem will be discussed.

Consider the situation when the experimental draft tube mixer is continuously operated at steady state with a working volume of 6035 ml, a value of R.P.M. of 600, and an inlet and an outlet volumetric flowrate of 7.8 ml per second. Suppose that the inlet stream contains a particle size distribution described by \( n_1(D) \) which is defined for sizes between 0 and .1 cm and is zero elsewhere. Since this process is carried out at steady state the bulk averaged outlet population density, \( n_0(D) \), is equal to \( n_1(D) \). However the population density for the suspension inside the experimental vessel is given by

\[
    n(D) = n_1(D) (1 - 1.26 D)
\]

(181)

since at steady state the following conservation law must be obeyed

\[
    \frac{F}{V} n_1(D) = \frac{F}{V} n_0(D) = \frac{n(D)}{\tau(D, \text{R.P.M.}, F)}
\]

(182)
Therefore the population density for the suspension inside the vessel, \( n(D) \), is less than \( n_1(D) \) or \( n_0(D) \) for sizes greater than 0 and this trend increases as \( D \) gets close to .1 cm. The moments of \( n(D) \) are less than the corresponding moments of \( n_1(D) \) or \( n_0(D) \) since from Equation 181 the following general inequality can be written

\[
\mu_{i,p} = \mu_{0,p} > \mu_p = \mu_{i,p} - 1.26 \mu_{i,p+1}
\]

where \( \mu_{i,p} \) and \( \mu_{0,p} \) are the \( p \)-moments of \( n_1(D) \) and \( n_0(D) \) respectively and \( \mu_p \) is the \( p \)-moment of \( n(D) \). The average properties obtained from \( n(D) \) and \( n_1(D) \) or \( n_0(D) \) defined by

\[
(L_p^j) = \frac{\mu_{p+j}}{\mu_p}
\]

\[
(L_p^j)_1 = \frac{\mu_{i,p+j}}{\mu_{i,p}}
\]

such as \((L_0^1)\), the numbers average size of the particles, or \((L_3^1)\) the mass averaged size of the particles, also exhibit the above general behavior. Specifically, the average properties defined from \( n(D) \) are consistently less than the corresponding properties defined by \( n_1(D) \) or \( n_0(D) \), or

\[
(L_p^j)_1 > (L_p^j)
\]

The effect of nonuniform withdrawal in the above case is to lower the values of the population density function \( n(D) \), the moments of \( n(D) \), and the average quantities of \( n(D) \),
as in Equation 184, as compared to these properties of the particle size distribution in the inlet and outlet streams. If large particles had larger residence times than smaller particles, that is if the sign was positive instead of negative in Equation 179, all the above general properties would be reversed.

To discuss the effects of nonuniform withdrawal on continuous crystallization taking place within a mixing vessel similar to the experimental draft tube mixer the case of a constant growth rate, $r$, and the general operating conditions of Equations 179 and 180 will be considered. The general form of Equation 14 which applies to this situation is

$$\frac{dn}{dL} = \frac{n}{r\tau} \quad (187)$$

where $\tau$ for the specific nonuniform withdrawal conditions associated with 600 and 1600 R.P.M. values are given by Equations 179 and 180. The uniform withdrawal model will be characterized by a residence time of 774 seconds so as to correspond to the general operating conditions of Equations 179 and 180. The population densities for the uniform withdrawal model and the 600 R.P.M. and 1600 R.P.M. nonuniform withdrawal models are respectively given by

$$\frac{n(L)}{n(0)} = e^{-\frac{L}{r\tau}} \quad (188)$$
\[
\frac{n(L)}{n(0)} = (1 - 1.26L) \frac{1}{975} \frac{1}{r} \tag{189}
\]
\[
\frac{n(L)}{n(0)} = (1 - .292L) \frac{1}{262} \frac{1}{r} \tag{190}
\]
for the particle sizes between 0 and .1 cm. Note that the conventional symbol for particle size L will be used instead of D in this particular discussion. Figure 15 was prepared from the above equations for a value of \( r \) of 6 microns per minute. This particular value of growth rate is of the same order as those found for alum and ammonium sulfate in both the salting out and cooling crystallizations of these systems, see Timm (36) and Chambliss (13). It should be noted that Timm (36) and Chambliss (13) used approximately the same type of experimental mixer as was used in this investigation.

Figure 15 reveals that the population density that would result from each of the nonuniform withdrawal models is different from population density for the uniform withdrawal model. The plots for the 600 and 1600 R.P.M. cases increasingly fall off from the straight line of \( \log_{10} \left( \frac{n(L)}{n(0)} \right) \) versus L for the uniform withdrawal model. This behavior is to be expected since from both Equations 179 and 180 it can be seen that large particles have smaller residence times than small particles. The fact that the 600 R.P.M. model exhibits more extreme behavior than the 1600
Figure 15. Comparison of expected size distributions from uniform and classified withdrawal models
Log of dimensionless population density, $n(L)/n(0)$, against crystal size $L$, cm for 600 RPM classified withdrawal model, uniform withdrawal model, and 1600 RPM classified withdrawal model.
R.P.M. model can be explained by noting that Equation 179 for the 600 R.P.M. predicts larger changes in residence times over the size range considered than does Equation 180 for the 1600 R.P.M. case.

The above discussion suggests that size dependent growth rate and size dependent particle residence times cannot be distinguished from experimental data in the form of the plot of \( \log_{10}(n(L)/n(0)) \) against \( L \). For instance, both Equations 179 and 180 can be generally written as

\[
\tau(L, \text{R.P.M.}, F) = \tau_F(1 + \alpha L)
\]  

(191)

for \( L \) on 0 to .1 cm and for this general condition Equation 14 at steady state can be written as

\[
r = \frac{n(L)}{\tau(L, \text{R.P.M.}, F)}
\]

(192)

for particles in the same interval as above. On the other hand, Equations 191 and 192 can be utilized to develop the following size dependent growth rate

\[
r(L) = \left(\frac{r^2 \alpha \tau_F}{r \alpha \tau_F - 1}\right) (1 + \alpha L) \left(\frac{1}{r \alpha \tau_F - 1}\right) - \left(\frac{r}{r \alpha \tau_F - 1}\right)(1 + \alpha L)
\]

(193)

for which Equation 14 is written as

\[
\frac{dn(L)r(L)}{dL} = - \frac{n}{\tau_F}
\]

(194)
Therefore the plots of corresponding to $a$ equal to (- 1.26) and (- .292), the 600 and 1600 R.P.M. nonuniform withdrawal models, may be interpreted as resulting from the corresponding size dependent growth rate model, Equation 193. Therefore size dependent growth cannot be distinguished from nonuniform withdrawal of particles.

Abegg et al. (1) have presented the following three parameter growth rate model

$$r(L) = r_0(1 + v'L)^b, \ b < 1 \quad (195)$$

The population densities obtained with Equation 195 from Equation 194 are continuous, have convergent moments, and possess a great deal of versatility in fitting experimental data. In light of the above discussion, Equation 195, can be used to obtain the following three parameter empirical particle residence time function

$$\tau(L) = \tau_P \frac{(1 + v'L)(1 + by') \tau_{Pr_0}}{((1 + v'L)^{1-b} + by' \tau_{Pr_0}^2} \quad (196)$$

where $r_0$, $v'$, and $b$ are the same as above and $\tau_P$ is equal to $F$, the total volumetric flowrate, divided into the vessel volume $V$. In addition, the above statements concerning the convergence, continuity, and versatility associated with Equation 195 also apply to Equation 196.
CONCLUSIONS

1. A well mixed laboratory scale draft tube mixing vessel with a gravity discharge can be used to obtain reproducible and reliable particle residence times from withdrawal response experiments involving suspensions of particles.

2. The increase in the outlet volumetric flowrate due to a decreasing apparent suspension viscosity caused by the dilution of the suspension during the course of a typical withdrawal response experiment is negligible.

3. Slight differences in particle residence times, $\tau_p$, and outlet volumetric flowrates, $F$, will occur between individual runs of a series of duplicate runs due to varying degrees of entrained bubbles in each experiment. The values of $\tau_p$ from the duplicate runs can be adjusted so as to correspond to a common outlet volumetric flowrate, $\overline{F}$, with the use of the following formula

$$\overline{\tau_p} = \tau_p + \frac{V}{(\overline{F})^2} (F - \overline{F})$$

4. The withdrawal of dilute suspensions consisting of water and spherical particles of one or more sizes can be modeled as a discrete state time homogeneous Markov process. The underlying statistical escape frequency, $1/\tau_p$, for particles of diameter $D_p$ is independent of the size distri-
bution of particles within the dilute suspensions being processed.

5. The particle residence time is a function of particle size, the level of agitation, and the outlet volumetric flowrate when the outlet and vessel geometry are constant. Empirical size dependent particle residence time functions for spherical particles of a density of 1.05 gm/cc and diameters in the range of 0 to .1 cm processed in the 6035 ml experimental vessel are

\[ \tau_p = 774 \left( 1 - 1.26 D_p \right) \]

\[ \tau_p = 774 \left( 1 - .292 D_p \right) \]

for agitator speeds of 600 and 1600 R.P.M., respectively, and an outlet volumetric flowrate of 7.8 ml/second.

6. Particles that are relatively small compared to the outlet tube diameter will have residence times close to \( \tau_F \), the residence time based on the outlet volumetric flowrate. Larger particles will usually have residence times significantly different than \( \tau_F \) depending on the general operating conditions.

7. Particle residence times tend to become uniform and approach the residence time based on the outlet volumetric flowrate, \( \tau_F \), as the agitation is increased in a draft tube mixing vessel. This fact cannot be explained with the aid of the accepted theory of anisokinetic sampling.
8. The amount of turbulence superimposed on the suspension velocity approaching the outlet tube entrance increases as agitation increases. The velocity profile near the outlet tube mouth is probably distorted to the extent that the effective approach velocity becomes sufficiently close to the outlet pipe velocity so as to make the withdrawal process essentially isokinetic.

9. The effects of nonuniform withdrawal cannot be dismissed in the modeling of continuous well mixed experimental draft tube crystallizers. The population density function obtained in previous work from the continuous mixed product mixed suspension crystallizer model is markedly different from the crystal population density functions based on the empirical size dependent residence time functions developed in this work.

10. To account for nonuniform withdrawal within the population balance equation for dilute crystallizing suspensions undergoing well mixed continuous crystallization in an experimental draft tube vessel the following formula can be used

\[ \frac{\partial (n(L,t))}{\partial t} + \frac{\partial (n(L,t)r(L,t))}{\partial L} = - \frac{n(L,t)}{\tau(L, R.P.M., F)} \]

for the common case when the working volume is constant and the input stream is unseeded. The experimental methods used
in this work can be utilized to determine the functional \( \tau(L, R.P.M., F) \).

11. The distinction between a size dependent growth rate and a size dependent particle residence time function cannot be made from an analysis of continuous crystallizer data alone. Withdrawal response experiments as conducted in this work must be carried out to determine the particle residence time function. Once the particle residence time function is known then one can distinguish between size dependent growth and size dependent withdrawal behavior from continuous crystallizer data.

12. The relative motion between particles and their neighboring solution in a turbulent suspension increases as the size of the particle under consideration increases. Particles of extremely small size witness no relative motion. The resistance to heat and mass transfer due to boundary layers surrounding particles in turbulent suspensions is diminished as the size of the particle considered increases. This fact can account for crystal growth rates which depend on size and agitation. Nucleation models depending on total crystal area and the level of agitation can be explained with the aid of the above differential velocity properties. If secondary nucleation occurs from the shearing off of surface nuclei from growing crystals or from the production of nuclei sized crystals by collisions these mechanism will become more
pronounced at high levels of agitation. Further, the larger crystals will witness more severe differential velocities than smaller crystals and therefore larger crystals will give up more surface nuclei than smaller crystals.

13. In the course of this work a general solution to the unsteady state population balance equation was developed and therefore there is no longer any need for the computer solution of this equation. However the moment equations and mass balance equations must be solved in order to use the general solution presented in this work.
RECOMMENDATIONS

1. The techniques developed in this work could be used to investigate the effects of various outlet and mixing vessel geometries on particle withdrawal. The effects of particle shape, the relative density of particles to that of the solute, and the viscosity of the solute on the withdrawal behavior of suspensions from continuous mixing vessels should also be investigated.

2. Crystallizing systems which have been analyzed with the aid of the continuous crystallizer design equations and shown to exhibit size dependent growth rates should be reanalyzed. Techniques employed in this work should be used to determine particle residence times for these systems so that the distinction between size dependent particle withdrawal and size dependent growth rate can be made.
NOMENCLATURE

C concentration, mass/volume
\( C_{eq} \) saturation concentration, mass/volume
\( C_i \) conditional expectation for numbers of size \( D_i \) particles in vessel
\( \overline{C_i} \) true mean for numbers of size \( D_i \) particles in vessel
\( \hat{C}_0 \) coupling tensor
\( C(D) \) point concentration of size \( D \) particles, numbers/volume
\( \overline{C(D)} \) volume average concentration for size \( D \) particles, number/volume
\( CV \) cumulative volume
\( \frac{dN^O}{dt} \) nucleation rate, numbers/volume/time
\( D_p \) diameter of particle
\( F \) volumetric flowrate, volume/time
\( \overline{F} \) corrected volumetric flowrate, volume/time
\( \hat{F}_B \) buoyant force on particle
\( \hat{F}_G \) gravitational force on particle
\( F_i \) input volumetric flowrate, volume/time
\( F_o \) outlet volumetric flowrate, volume/time
\( F_s \) sample volumetric flowrate, volume/time
\( \hat{F}_V \) hydrodynamic force on particle
\( \hat{g} \) gravitational vector
\( h(L)g(t) \) generalized growth function
\( I_0 \) rotational interia about point 0 in a particle
\( k_n \) proportionality constant
\(K\) empirical constant
\(\overline{\mathbf{K}}\) translational tensor
\(K_G\) proportionality constant
\(K_N\) proportionality constant
\(K_V\) proportionality constant
\(L\) particle size, length
\(L_0\) size of nuclei, length
\(\bar{L}\) average vessel cycle loop, length
\(L_j^p\) average value of \((L)^j\) based on the p-moment of the population density
\(L(P)\) central size of a peak in size distribution
\(L(\xi)\) inverse of \(\xi(L)\), length
\(m_i\) number of particles of size \(D_i\) in vessel
\(M\) suspension density, mass/volume
\(n\) population density, numbers/size/volume
\(n_i\) input population density, numbers/size/volume
\(n_o\) outlet population density, numbers/size/volume
\(N_i\) initial number of particles of size \(D_i\) in vessel
\(p_i\) number of particles of size \(D_i\) in vessel
\(P_i(m_1, t)\) probability distribution for particles of size \(D_i\) in vessel
\(P_i(m_1, p_j, t)\) transition probability for particles of size \(D_i\) in vessel
\(P_i(m_1, ..., m_N, p_1, ..., p_N, t)\) transition probability
\(r\) growth rate, size/time
\(r_0\) empirical nuclei growth rate, size/time
\(\mathbf{r}_{po}\) position vector of point \(p\) relative to point \(0\) in a particle
$R_p$ effective fluid radius

$R_o$ outlet pipe radius

R.P.M. revolutions per minute of agitator

$R(t)$ residence time distribution

$s$ saturation concentration minus concentration, mass/volume

$t$ time

$\hat{T}$ fluid stress tensor

$T(\hat{t})$ inverse of $\hat{t}(t)$, time

$\vec{u}$ velocity of particles center of mass, length/time

$\vec{u}$ time averaged velocity of particles center of mass, length/time

$\vec{u}'$ perturbation velocity of particles center of mass, length/time

$\vec{u}_p$ velocity of point $p$ inside a particle, length/time

$\vec{v}$ velocity of fluid, length/time

$\vec{v}$ time averaged fluid velocity, length/time

$\vec{v}'$ perturbation velocity of fluid, length/time

$v_a$ approach velocity, length/time

$v_c$ cycling velocity of mixer, length/time

$v_p$ pipe velocity, length/time

$V$ volume of vessel

$V_1$ volume of sample number 1

$V_p$ volume of particle

$w_p(i)$ weight of particles of diameter $D_p$ in sample number $1$, mass

$w_p(t)$ weight of particle of diameter $D_p$ in vessel at time $t$, mass
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_p^0$</td>
<td>original weight of particles of diameter $D_p$ in vessel, mass</td>
</tr>
<tr>
<td>$x_p(t)$</td>
<td>weight, $W_p(t)$, divided by weight, $W_p^0$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>empirical constant</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>turbulent Markov coefficient</td>
</tr>
<tr>
<td>$\nu'$</td>
<td>empirical constant</td>
</tr>
<tr>
<td>$\zeta \nu^2$</td>
<td>time averaged mean square of particle-fluid relative velocity</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>angle</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>proportionality constant for Stokes' law</td>
</tr>
<tr>
<td>$u$</td>
<td>fluid viscosity, mass/time/length</td>
</tr>
<tr>
<td>$\mu_{1p}$</td>
<td>p-moment of input population density</td>
</tr>
<tr>
<td>$\mu_{0p}$</td>
<td>p-moment of outlet population density</td>
</tr>
<tr>
<td>$(\mu_0)_T$</td>
<td>total number of particles in vessel</td>
</tr>
<tr>
<td>$\mu_s$</td>
<td>suspension viscosity, mass/time/length</td>
</tr>
<tr>
<td>$g$</td>
<td>transform of particle size, L</td>
</tr>
<tr>
<td>$\pi_B(0)$</td>
<td>buoyant torque about point 0 on a particle</td>
</tr>
<tr>
<td>$\pi_G(0)$</td>
<td>gravitational torque about point 0 on a particle</td>
</tr>
<tr>
<td>$\pi_H(0)$</td>
<td>hydrodynamic torque about point 0 on a particle</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>fluid density, mass/volume</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>particle density, mass/volume</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>variance about mean number of particles of size $D_1$ in vessel</td>
</tr>
<tr>
<td>$\sigma_v$</td>
<td>variance of fluid velocity</td>
</tr>
<tr>
<td>$(\sigma_0)_T$</td>
<td>variance about total number of particles in vessel</td>
</tr>
<tr>
<td>$\tau_F$</td>
<td>residence time based on volumetric flowrate, time</td>
</tr>
</tbody>
</table>
\( \tau(D_p, \text{R.P.M.}, F) \)\nfunctional form of particle residence time, time

\( \tau(D_p, v_a, v_p) \)\nfunctional form of particle residence time, time

\( \tau_p \)\nrésidence time of particles of size \( D_p \), time

\( \phi' \)\nautocorrelation function for fluid perturbation velocity

\( \psi \)\ntransform of time, \( t \)

\( \bar{w} \)\ncycling frequency of mixer, revolutions/time

\( \hat{w} \)\nangular velocity, reciprocal time

\( \Omega_o \)\nrotational tensor
LITERATURE CITED


ACKNOWLEDGMENTS

The author wishes to thank Dr. M. A. Larson for his kind understanding and wise counsel which contributed greatly to this work.

The author also wishes to thank his wife, Wilma, for her patience and selfless aid in accomplishing this work.

Financial support for this work was given by the National Aeronautical and Space Administration, Phillips Petroleum Company, and by the Chicago Bridge and Iron Company.
APPENDIX A
In the following discussion the o-moment equation, Equation 21, will be derived by assuming that the production of crystals in a continuous crystallization is a time stationary discrete state Markov process. The growth rate, nucleation rate and working volume will be considered constants and the inlet stream will be unseeded. The state of the crystallizing suspension at time \( t \) is \( i \), the total number of crystals is the working volume \( V \). The probability that the state will undergo a change like \((i, t)\) to \((i+1, t + \Delta t)\) in a short time \( \Delta t \) is

\[
\approx V \frac{dN^0}{dt} \Delta t \quad (197)
\]

and the probability of a change like \((i, t)\) to \((i-1, t + \Delta t)\) is

\[
\approx \frac{\Delta t i}{\tau_F} \quad (198)
\]

The underlying statistical nature of the o-moment equation is expressed by the above two short time probabilities which represent the two fundamental disjoint events of birth and withdrawal.

With the aid of Equations 197 and 198 the following short time transition probability can be written

\[
P_{i,j}(\Delta t) = (1 - (V \frac{dN^0}{dt} + \frac{i}{\tau_F})\Delta t) \zeta_{i,j} + V \frac{dN^0}{dt} \Delta t \zeta_{i+1,j} + \frac{i \Delta t}{\tau_F} \zeta_{i-1,j} \quad (199)
\]
The term $P_{ij}(\Delta t)$ is the transition probability for the change in state of $i$ to $j$ in the short time $\Delta t$ and $\delta_{i,j}$ is the Kronecker delta. The Chapman-Kolmogorov equation for this process is

$$P_{ij}(t+s) = \sum_{\ell=0}^{\infty} P_{i \ell}(t) P_{\ell j}(s)$$

(200)

and with the aid of Equation 199 and the above Chapman-Kolmogorov equation can be used to generate the following two equations for the transition probability

$$\frac{dP_{ij}}{dt} = V \frac{dN^0}{dt} (P_{i,j-1} - P_{i,j}) + \frac{1}{\tau_F} ((j+1)P_{i,j+1} - jP_{i,j})$$

(201)

$$\frac{dP_{ij}}{dt} = V \frac{dN^0}{dt} (P_{i+1,j} - P_{i,j}) + \frac{1}{\tau_F} ((i-1)P_{i-1,j} - iP_{i,j})$$

(202)

Equations 201 and 202 are called the Kolmogorov backward and forward equations, respectively. For clarification of the details involved in the above discussion please consult Bhurucha-Reid (6).

Equations for the probability distribution over the state of the system, $i$, as well as equations for the true mean and the variance about the true mean of any function, $f(i)$, defined on the state, $i$, can be obtained from Equations 201 and 202. The following defining relationships
\[ P_j(t) = \sum_{i=-\infty}^{\infty} P_i(0) P_{ij}(t) \quad (203) \]

\[ \frac{d\bar{f}(t)}{dt} = \sum_{j=-\infty}^{\infty} f(j) \frac{dP_{ij}(t)}{dt} \quad (204) \]

\[ \frac{d\sigma^2_i}{dt} = \sum_{j=-\infty}^{\infty} \frac{d}{dt} \left( (f(j) - \bar{f}(t))^2 P_j(t) \right) \quad (205) \]

were used to obtain the phenomenological equations for the case when \( f(i) \) is 1, the total number of crystals in the working volume \( V \). The results of these equations were

\[ \frac{d(\mu_0)_T}{dt} = \mathcal{V} \frac{dN^0}{dt} - \frac{(\mu_0)_T}{\tau_p} \quad (206) \]

\[ \frac{d(\sigma^2_0)_T}{dt} = -\frac{2}{\tau_p} (\sigma^2_0)_T + \mathcal{V} \frac{dN^0}{dt} + \frac{(\mu_0)_T}{\tau_p} \quad (207) \]

where \((\mu_0)_T\) has replaced \( \bar{f} \) and \((\sigma^2_0)_T\) has replaced \( \tau_1^2 \) in order to conform to the standard notation used in the continuous crystallizer design equations. Equation 206 is exactly the same as Equation 21 but because of the assumed statistical nature of the Markov model a relationship for the variance about \((\mu_0)_T\) is also obtained.

Consider the steady state situation when \((\mu_0)_T\) is equal to \((\tau_p \mathcal{V} \frac{dN^0}{dt})\) and \((\sigma^2_0)_T\) is zero. If these values are used as initial conditions for Equations 206 and 207 the value
of \((u_0)_T\) that obtains is \((\tau_F V \frac{dN^0}{dt})\), a constant. This is precisely what is to be expected. In contrast to this fact is the following value of \((\sigma^2_0)_T\) obtained from Equation 207 for these initial conditions

\[
(\sigma^2_0)_T = (u_0)_T \left(1 - e^{-\frac{2t}{\tau_F}}\right)
\]

As time approaches infinity the ratio of \((\sigma^2_0)_T\) to \((u_0)_T\) becomes

\[
\frac{(\sigma_0)_T}{(u_0)_T} = \sqrt{\frac{1}{(u_0)_T}}
\]

Therefore, because of the assumed statistical nature of continuous crystallization the relative statistical fluctuations, as expressed by Equation 209, will be proportional to the square root of the reciprocal of \((u_0)_T\) at steady state. This particular fact points up the necessity of having a large number of crystals present in experimental continuous crystallizations in order to obtain reliable data since

\[
\frac{(\sigma_0)_T}{(u_0)_T} \text{ experimental} > \sqrt{\frac{1}{(u_0)_T}}
\]

due to experimental errors in the measurement of \((u_0)_T\).
Table 10. Data from run 1,\(^a\) screen 20 particles, 600 R.P.M., 42 inch outlet head

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Time, seconds</th>
<th>Weight of particles in vessel, gm</th>
<th>Sample volume, ml</th>
</tr>
</thead>
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<td>85.5700</td>
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<td>8.8519</td>
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</tbody>
</table>

\(^a\)Samples 0 to 9 formed run 1-1, samples 9 to 15 formed run 1-2, and samples 15 to 27 formed run 1-3.
Table 11. Data from run 2,\(^a\) screen 70 particles, 600 R.P.M., 42 inch outlet head

<table>
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<th>Sample number</th>
<th>Time, seconds</th>
<th>Weight of particles in vessel, gm</th>
<th>Sample volume, ml</th>
</tr>
</thead>
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<td>390</td>
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<td>350</td>
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<td>32.5566</td>
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<td>750</td>
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<td>25</td>
<td>1650</td>
<td>9.1881</td>
<td>2360</td>
</tr>
</tbody>
</table>

\(^a\)Samples 0 to 8 served as run 2-1, samples 8 to 13 served as run 2-2, and samples 13 to 25 served as run 2-3.
Table 12. Data from run 3,\textsuperscript{a} screens 20 and 70 particles, 600 R.P.M., 42 inch outlet head

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Time, seconds</th>
<th>Weight of number 20 particles left, gm</th>
<th>Weight of number 70 particles left, gm</th>
<th>Sample volume, ml</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<td>1000</td>
<td>10.6983</td>
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<td>791</td>
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</table>

\textsuperscript{a}Samples 0 to 8 served as run 3-1, samples 8 to 17 formed run 3-2.
Table 13. Interaction effects for particles from screens 20 and 70, 600 R.P.M., 42 inch outlet head

<table>
<thead>
<tr>
<th>Run number</th>
<th>Volumetric flowrate, ml/second</th>
<th>Initial volume fraction 20</th>
<th>Initial volume fraction 70</th>
<th>Residence time, seconds $\tau_{20}$</th>
<th>Residence time, seconds $\tau_{70}$</th>
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<td>(\tau_{45})</td>
<td>Initial volume fraction (70)</td>
<td>(\tau_{70})</td>
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<td>0.0077</td>
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<td>0.0077</td>
<td>1309</td>
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<td>29</td>
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<td>0.0076</td>
<td>1313</td>
<td>0.0076</td>
<td>1294</td>
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<td>0.0077</td>
<td>1308</td>
<td>0.0077</td>
<td>1301</td>
</tr>
<tr>
<td>31</td>
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<td>0.0077</td>
<td>1313</td>
<td>0.0077</td>
<td>1313</td>
</tr>
<tr>
<td>25</td>
<td>4.509</td>
<td>0.0114</td>
<td>1321</td>
<td>0.0038</td>
<td>1299</td>
</tr>
<tr>
<td>26</td>
<td>4.511</td>
<td>0.0107</td>
<td>1338</td>
<td>0.0036</td>
<td>1303</td>
</tr>
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<td>18</td>
<td>4.510</td>
<td>0.0121</td>
<td></td>
<td></td>
<td>1302</td>
</tr>
<tr>
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<td>0.0140</td>
<td></td>
<td></td>
<td>1340</td>
</tr>
<tr>
<td>20</td>
<td>4.528</td>
<td>0.0134</td>
<td></td>
<td></td>
<td>1315</td>
</tr>
<tr>
<td>21</td>
<td>4.517</td>
<td>0.0101</td>
<td></td>
<td></td>
<td>1309</td>
</tr>
<tr>
<td>22</td>
<td>4.526</td>
<td>0.0120</td>
<td></td>
<td></td>
<td>1309</td>
</tr>
</tbody>
</table>
Table 15. Interaction effects for particles from screens 45 and 60, 1000 R.P.M., 17-1/2 inch outlet head

<table>
<thead>
<tr>
<th>Run number</th>
<th>Volumetric flowrate, ml/second</th>
<th>Initial volume fraction, 45</th>
<th>Initial volume fraction, 60</th>
<th>Residence time, seconds $\tau_{45}$</th>
<th>Residence time, seconds $\tau_{60}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>6.133</td>
<td>.0126</td>
<td></td>
<td>973</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>6.146</td>
<td>.0038</td>
<td>.0113</td>
<td>960</td>
<td>969</td>
</tr>
<tr>
<td>34</td>
<td>6.112</td>
<td>.0077</td>
<td>.0077</td>
<td>971</td>
<td>974</td>
</tr>
<tr>
<td>35</td>
<td>6.151</td>
<td>.0115</td>
<td>.0038</td>
<td>975</td>
<td>946</td>
</tr>
<tr>
<td>36</td>
<td>6.070</td>
<td>.0143</td>
<td></td>
<td>982</td>
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</tr>
</tbody>
</table>
Table 16. R.P.M. effects for particles from screens 60 and 70 in runs^a 37 and 38, respectively, 8-1/2 inch outlet head

<table>
<thead>
<tr>
<th>R.P.M., revolutions/minute</th>
<th>Residence time, seconds</th>
<th>Volumetric flowrate, ml/second</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_{60} )</td>
<td>( \tau_{70} )</td>
</tr>
<tr>
<td>1500</td>
<td>1326</td>
<td>1321</td>
</tr>
<tr>
<td>1100</td>
<td>1314</td>
<td>1302</td>
</tr>
<tr>
<td>700</td>
<td>1386</td>
<td>1309</td>
</tr>
</tbody>
</table>

^aInitial volume fractions for runs 37 and 38 were .0089 and .0119, respectively.

Table 17. R.P.M. effects for particles from screens 20 and 70 in runs^a 39 and 40, respectively, 3 inch outlet head

<table>
<thead>
<tr>
<th>R.P.M., revolutions/minute</th>
<th>Residence time, seconds</th>
<th>Volumetric flowrate, ml/second</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_{20} )</td>
<td>( \tau_{70} )</td>
</tr>
<tr>
<td>1600</td>
<td>2864</td>
<td>2662</td>
</tr>
<tr>
<td>1200</td>
<td>2707</td>
<td>2624</td>
</tr>
<tr>
<td>900</td>
<td>2549</td>
<td>2582</td>
</tr>
<tr>
<td>600</td>
<td>2327</td>
<td>2533</td>
</tr>
</tbody>
</table>

^aInitial volume fractions for runs 39 and 40 were .0122 and .0128, respectively.
Table 18. Original data for runs 39 and 40 which contained number 20 and 40 screen particles, respectively

| R.P.M. revolutions/minute | Time, seconds | Weight left in vessel, gm  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>0</td>
<td>77.5839</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>72.4163</td>
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<tr>
<td></td>
<td>400</td>
<td>67.4390</td>
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<tr>
<td>1200</td>
<td>0</td>
<td>66.1902</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>61.4066</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>57.1308</td>
</tr>
<tr>
<td>900</td>
<td>0</td>
<td>44.9101</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>41.5157</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>38.3997</td>
</tr>
<tr>
<td>600</td>
<td>0</td>
<td>55.4076</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>50.8815</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>46.6818</td>
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</tbody>
</table>
Table 19. Effect of size on residence time,\textsuperscript{a} 42 inch outlet head

<table>
<thead>
<tr>
<th>Run number</th>
<th>Screen number</th>
<th>R.P.M.</th>
<th>Initial volume fraction</th>
<th>Volumetric flowrate ml/second</th>
<th>Residence time, second</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>30</td>
<td>600</td>
<td>.0137</td>
<td>7.850</td>
<td>698</td>
</tr>
<tr>
<td>42</td>
<td>45</td>
<td>600</td>
<td>.0132</td>
<td>7.715</td>
<td>749</td>
</tr>
<tr>
<td>43</td>
<td>20</td>
<td>1600</td>
<td>.0131</td>
<td>7.905</td>
<td>748</td>
</tr>
<tr>
<td>44</td>
<td>30</td>
<td>1600</td>
<td>.0098</td>
<td>7.904</td>
<td>742</td>
</tr>
<tr>
<td>45</td>
<td>45</td>
<td>1600</td>
<td>.0098</td>
<td>7.727</td>
<td>768</td>
</tr>
<tr>
<td>46</td>
<td>70</td>
<td>1600</td>
<td>.0127</td>
<td>7.704</td>
<td>783</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Data for particles from screens 20 and 70 at 600 R.P.M. can be found in Table 13.