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FUNDAMENTAL MODELING FOR MAGNETICALLY SEEDED
SOLID-LIQUID SEPARATIONS

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Abstract

Progress on quantifying the interaction between magnetic particles, as well as magnetic and non-magnetic particles, in liquid suspensions and under the influence of a magnetic field is described in this report. Primary forces acting on individual particles, including gravity and magnetic attraction, are examined and quantified, as are van der Waals, electrostatic, magnetic dipole, and hydrodynamic interparticle forces. A mathematical statement of the overall relative velocity is developed from the net force acting on a particle. Two limiting cases are discussed: Brownian diffusion dominating and external force (gravity and magnetic) dominating. For the latter case, the equation of relative motion for two particles in cylindrical coordinates is derived. A computer model is then used to solve this equation repeatedly to find the particle trajectory borderline between collision and noncollision, thus determining the collision efficiency and collision frequency. The effect of a variety of parameters on collision efficiency and collision frequency is then explored. This work will be extended towards the development of a mechanistic model for magnetically seeded solid-liquid separations using a turbulent shear flocculation regime. Results to be obtained from the model will be compared with experimental results obtained at Oak Ridge National Laboratory using synthetic, surrogate, and sorbent particles.
Introduction

Magnetic separation has been suggested as a recovery and pollution control process for a manifold of environmental problems. Among these are the treatment of effluent from steel mills (1, page 590), desulfurization of coal (2), and separation and concentration of mining ores and wastes (3). Current industrial uses of magnetic separation include clay benefaction (4) and nuclear reactor coolant water filtration (5). Furthermore, magnetically seeded solid-liquid separations extend magnetic separation to include the removal of non-magnetic substances from a suspension. For example, magnetically seeded flocculation has been used for the removal of yeast from process streams (6), purification of drinking water sources (7), and treatment of domestic wastewater (8). Additionally, magnetically seeded solid-liquid separations may be of enormous value in the remediation of radioactive groundwater contamination (9).

The interaction between magnetic particles, as well as magnetic and non-magnetic particles, in liquid suspensions and under the influence of a magnetic field has not been extensively examined in the literature. Incorporating hydrodynamic, van der Waals, electrostatic, and orientation-averaged magnetic forces in a Brownian flocculation model, Tsouris and Scott (10) considered flocculation of paramagnetic particles in a study important to the development of the present modeling approach. Tsouris et al. (11) considered the heterogeneous flocculation of paramagnetic colloidal particles, using an interparticle force potential that includes hydrodynamic, van der Waals, electrostatic, and magnetic forces. Schewe et al. (12) developed expressions for particle-filter element attractions and hydrodynamic resistance for the laminar-flow case, leading to calculations of particle trajectories. Moyer et al. (13, 14) also formulated expressions for the capture of magnetic particles, in this case using a free surface condition, and ignoring electrostatic and van der Waals forces. Friedlaender et al. (15) studied single sphere high-gradient magnetic separation (HGMS), neglecting all but the collector-particle magnetic force and hydrodynamic forces. Cummings et al. (16) examined magnetic, drag, and gravitational forces in HGMS single-wire capture. The present study builds on and extends previous work in order to provide a fundamental modeling approach for magnetically seeded separations.

Other works important to the present study include that of Zhang and Davis (17), who looked at the coalescence of drops operating under Brownian or gravitational motion and determined collision rates and efficiencies from particle trajectories. The hydrodynamic resistance function expressions derived by Haber and coworkers (18, 19) and Zinchenko (20) were of great importance, as was their development by Zhang (21).

This work investigates the interaction between magnetic particles, as well as magnetic and non-magnetic particles, in liquid suspensions and under the influence of a magnetic field. Particle-particle interactions are examined under quiescent or laminar-flow conditions.
Gravitational and magnetic external forces are included in the analysis, as well as van der Waals, electrostatic, magnetic dipole, and hydrodynamic particle-particle forces. The inertial force is neglected (i.e., it is assumed that the particles immediately assume their terminal velocity under the given net force), as are thermocapillary effects. Additionally, it is assumed that the particles are spherical, and that the magnetic field and magnetic field gradient do not vary when the two particles approach each other, that is to say, the external magnetic force behaves like gravity. This assumption is reasonable for the low-magnetic-susceptibility particles considered in this study. A general analysis is provided which also includes the contribution of Brownian diffusion to the particles' relative motion. Then two limiting cases are discussed separately: Brownian diffusion dominating and external force (gravity and magnetic) dominating. More detailed discussion is provided for particles outside the size range where Brownian diffusion is important. Stated mathematically, results valid for Péclet numbers much greater than one are presented. From this theoretical foundation, a differential equation relating the relative position of the two particles is derived. This equation is then solved repeatedly by a computer code using an ordinary differential equation solver to reveal the limiting trajectory. Collision efficiencies and collision frequencies (normalized collision rates) can then be calculated from this limiting trajectory. The effect of the direction of the magnetic field on collision efficiency and collision frequency is demonstrated first, followed by the effects of various other factors that may become important during various stages of the magnetically seeded separation processes. In the analysis of the particle-particle interactions, all calculations were made by considering that the magnetic field and magnetic field gradient are aligned with gravity.

Model Development

Forces Acting on Particles in Suspension

As noted in the introduction, the forces considered in the analysis presented here include gravity, magnetic attraction, van der Waals, electrostatic, magnetic dipole, and hydrodynamic forces. The different forces are divided into interparticle forces—forces acting between two particles—and external forces that act on individual particles. Brownian relative diffusivity is treated separately. These various phenomena are examined below.

External Forces

The external forces, gravity and magnetic attraction, are of interest to the extent that they affect the two interacting particles in question differently. This becomes obvious if one considers two particles at some distance from each other, where interparticle forces are negligible. For the particles to collide, they must approach each other so that interparticle forces
can lead to attachment. If both particles are affected by external forces similarly, they will both move with the same velocity, and never get closer to each other. If the particles are not affected by external forces to the same degree, then their velocities will differ, and assuming the particles are fortuitously positioned, one particle will overtake the other, possibly leading to collision. This difference in velocities is called the relative velocity, expressed as the motion of one particle from the point of view of the other. With this goal in mind, gravity and magnetic attraction's contribution to particle-particle collision can be examined.

**Gravity**

The gravitational force, \( F_g \), acting on a particle in suspension is given by:

\[
F_g = \rho_p V_p g,
\]

where \( \rho_p \) is the density of the particle, \( V_p \) is the volume of the particle, and \( g \) is the gravitational acceleration. The buoyant force, \( F_b \), acting on a particle is given by:

\[
F_b = \rho V_p g,
\]

where \( \rho \) signifies the density of the fluid. Given the assumption that inertial forces are negligible, or that Reynolds numbers are much less than one, it is considered that the particle immediately accelerates to its terminal settling velocity (or its terminal velocity upward) through the fluid. Thus, a drag force, \( F_d \), develops that is equal and opposite to the net buoyant and gravitational forces:

\[
F_d = -C_D A_p \rho \frac{v^2}{2} \hat{g},
\]

where \( A_p \) is the cross-sectional area of the particle, \( C_D \) is the coefficient of drag, \( v \) is the magnitude of the velocity of the particle, \( v \), and \( \hat{g} \) is the unit vector of the gravitational acceleration. Assuming laminar flow, \( C_D = 24 / \mathfrak{R} \), where \( \mathfrak{R} \), the Reynolds number, is defined as \( \mathfrak{R} = 2 \rho v a / \eta \), \( a \) is the particle radius, and \( \eta \) is the dynamic viscosity. Substituting these expressions into the force balance equation and assuming spherical particles, allows the equation to be solved for velocity \( v \). The far-field relative gravitational velocity, \( v^{(0)}_{12g} \), for two particles will just be the difference of their respective individual velocities, \( v_1 \) and \( v_2 \). Mathematically
stated, \( v_{12g}^{(0)} = v_1 - v_2 \). Combining like terms in the expressions for \( v_1 \) and \( v_2 \) brings forth the expression for relative gravitational velocity:

\[
v_{12g}^{(0)} = \frac{2[(\rho_1 - \rho)a_1^2 - (\rho_2 - \rho)a_2^2]g}{9 \eta},
\]

where \( a_1 \) and \( a_2 \) are defined as particles' one and two respective radii, and \( \rho_1 \) and \( \rho_2 \) their respective densities. The larger particle is designated as one and the smaller particle is designated as two.

**Magnetic Attraction**

Assuming a small particle of radius \( a \), the magnetic force, \( F_m \), on a particle can be given in terms of the magnetic field (1, page 4):

\[
F_m = \frac{4}{3} \pi a^3 \frac{\chi}{\mu_0} B \nabla B,
\]

where \( \chi \) is the volume magnetic susceptibility, \( \mu_0 \) is the permeability of free space, and \( B \) is the magnitude of the magnetic induction vector \( \mathbf{B} \). In free space, the magnetic induction vector, \( \mathbf{B} \), and the magnetic-field strength vector, \( \mathbf{H} \), are not independent but related by the equation

\[
\mathbf{B} = \mu_0 \mathbf{H}.
\]

Developing the analysis as in the previous section and solving for the relative magnetic velocity, \( V_{12m}^{(0)} \), gives:

\[
V_{12m}^{(0)} = \frac{2B \nabla B}{9 \eta \mu_0} \left( \chi_1 a_1^2 - \chi_2 a_2^2 \right),
\]

where \( \chi_1 \) and \( \chi_2 \) are the two particles' respective magnetic susceptibilities.
Interparticle Forces

The forces acting between the two interacting particles are fundamentally different from the external forces in that they change in strength as the one particle approaches the other. In the case of the magnetic dipole force, the magnitude and sign of the force are also functions of the orientation of the two particles with respect to the magnetic field. This characteristic of the interparticle forces will be of importance when solving the differential equation of motion: the potential between the particles changes after each iteration of the solution. The coordinate system used in quantifying the interparticle forces is illustrated in Figure 1.

van der Waals Forces

Hamaker (22) calculated the van der Waals interparticle force potential, \( V_{vdW} \), for unequal sized spheres as a function of separation:

\[
V_{vdW} = -\frac{A}{6} \left[ \frac{8\lambda}{(s^2 - 4)(1 + \lambda)^2} + \frac{8\lambda}{s^2(1 + \lambda)^2 - 4(1 - \lambda)^2} \right] + \ln \left[ \frac{(s^2 - 4)(1 + \lambda)^2}{s^2(1 + \lambda)^2 - 4(1 - \lambda)^2} \right],
\]

where \( A \) is the Hamaker constant (actually a function of the particles' composition), \( s = 2r/(a_1 + a_2) \) (dimensionless particle separation), \( r \) is the center-to-center particle separation, and \( \lambda = a_2/a_1 \) (particle radius ratio).

Electrostatic Forces

Following Tsouris and Scott (10), the electrostatic potential, \( V_{el} \), is given by two formulas, one for large separations and one for small separations.

Linear Superposition Approximation

The linear superposition approximation (23) is indicated for thin double layers and large interparticle separations:

\[
V_{el} = 4\pi e^2 \left( \frac{kT}{e} \right)^2 Y_1 Y_2 \frac{a_1 a_2}{r} e^{-\kappa l}, \quad \text{for } \kappa l \geq 4,
\]

where

\[
Y_i = 4 \tanh \left( \frac{\Phi_i}{4} \right), \quad \text{for } \kappa r \geq 10, \ \Phi_i < 8, \text{ and } i = 1, 2,
\]

[10a]
Figure 1: Coordinate system used in quantifying the interparticle forces.
\[ \Phi_i = \frac{ze\Psi_{oi}}{kT}, \quad \text{for } i = 1,2 \tag{10b} \]

\[ \kappa \equiv 5.552 \times 10^{-6} \sqrt{l/ekT}, \tag{10c} \]

\[ l \equiv (s-2)\left(\frac{a_1 + a_2}{2}\right). \tag{10d} \]

$T$ is the absolute temperature, $\varepsilon$ is the permittivity of the medium, $e$ is the electron charge, $k$ is the Boltzmann constant, $z$ is the valence of the symmetric electrolyte in the solution, $\Psi_{oi}$ refers to the particles' surface potential, and $l$ is the ionic strength of the solution.

**Derjaguin Approximation**

For interparticle separations less than that at which the linear superposition approximation applies, the Derjaguin approximation is used (24):

\[ V_{el} = \frac{4\pi\varepsilon a_1 a_2 (\Psi_{o1}^2 + \Psi_{o2}^2)}{4(a_1 + a_2)} \left[ \frac{2\Psi_{o1} \Psi_{o2}}{\Psi_{o1}^2 + \Psi_{o2}^2} \ln\left(\frac{1 + e^{-\kappa l}}{1 - e^{-\kappa l}}\right) + \ln\left(1 - e^{-2\kappa l}\right) \right]. \tag{11} \]

In the employment of both Eqs. [9] and [11], it is assumed that the potential of one particle is undisturbed in the presence of other particles.

**Magnetic Dipole Attraction**

The interaction between two magnetically susceptible particles is expressed with the potential, $V_{mag}$, given by (25; 26, page 322):

\[ V_{mag} = \frac{4\pi B^2 a_1^3 a_2^3 \chi_1 \chi_2}{9\mu_0 \left(s\frac{a_1 + a_2}{2}\right)} \left\{ \hat{\mu}_1 \cdot \hat{\mu}_2 - 3(\hat{\mu}_1 \cdot \hat{e}_r)(\hat{\mu}_2 \cdot \hat{e}_r) \right\}, \tag{12} \]
where \( \hat{\mu}_1 \) and \( \hat{\mu}_2 \) are the respective unit magnetic dipole vectors of particles one and two, and \( \hat{e}_r \) is the unit vector of the position vector (which has magnitude \( r \)). Equation [12] is in principle valid for a uniform magnetic field, and as a consequence the two particles have the same unit magnetic dipole vector; therefore, the first dot product becomes 1, and the second and third dot products have the same value. Furthermore, since \( \hat{\mu}_1 \), \( \hat{\mu}_2 \), and \( \hat{e}_r \) are all unit vectors, the value of the second and third dot products is simply the cosine of the angle between \( \hat{e}_r \) and \( \hat{\mu}_1 \), \( \hat{\mu}_2 \).

Equation [12] can thus be rewritten as

\[
V_{mag} = \frac{4\pi B^2 a_1^3 \chi_1 a_2^3 \chi_2}{9\mu_0 \left( \frac{a_1 + a_2}{2} \right)^3} (1 - 3\cos^2 \psi),
\]

where \( \psi \) is the angle between the magnetic dipole moment (which has the same direction of that of the magnetic field or magnetic induction) and \( \hat{e}_r \) (see Figure 1). Note that this magnetic dipole interaction is thus not the commonly used orientation-averaged magnetic dipole interaction.

The interparticle magnetic potential yields forces along and normal to the line-of-centers:

\[
F_{r}^{mag} = \frac{2\pi B^2 a_1^3 \chi_1 a_2^3 \chi_2}{\mu_0 s} \left\{ \frac{1}{3} + \cos[2(\alpha - \theta)] \right\},
\]

\[
F_{\theta}^{mag} = -\frac{4\pi B^2 a_1^3 \chi_1 a_2^3 \chi_2}{3\mu_0 s^4} \sin[2(\alpha - \theta)],
\]

where \( \alpha \) is the angle between the direction of the vertical axis and that of the magnetic field. The angle \( \psi \) defined earlier is related to \( \alpha \) by \( \psi = |\alpha - \theta| \).

The magnitudes of the radial and tangential interparticle magnetic forces dimensionalized by the factor \( 32\pi B^2 a_1^3 \chi_1 a_2^3 \chi_2 / \mu_0 (a_1 + a_2)^4 \), for three different values of the dimensionless separation distance \( s \) and values of \( \psi \) from 0 to 180°, are shown in Figures 2a and 2b. It is important to note that the maximum of the tangential force is usually smaller than that of the
Figure 2: Dimensionless magnetic-dipole force as a function of the angle $\psi$ between the magnetic field and the line joining the centers of two particles: (a) radial force and (b) tangential force.
radial force and both increase as the separation distance decreases. Also the radial force is attractive when $\psi = 0$, but becomes repulsive when $\psi = 90^\circ$. This observation implies that the direction of the magnetic field will play a significant role in the collision efficiency as will be shown later in this report.

The interparticle magnetic force as a function of the separation distance between the two particles, for $\psi = 0$, and for three different size ratios is shown in Figure 3. In the same figure, the magnitude of the van der Waals and that of the repulsive or attractive electrostatic forces are also shown. The results in Figure 3 demonstrate that the interparticle magnetic force predominates over a longer range of separation distance than the attractive van der Waals force and the attractive or repulsive electrostatic force. A similar observation was made by Tsouris and Scott (10) for the orientation-averaged magnetic dipole force. The electrostatic force is repulsive when both particles have either negative or positive charges and attractive when one particle has a positive charge and the other has a negative charge. An additional conclusion that comes from Figure 3 is that the interparticle magnetic force reaches a plateau, at small separations, in contrast to the van der Waals and electrostatic forces which change rapidly in the same region.

**Hydrodynamic Forces**

Haber et al. (18) and Zinchenko (20) developed exact solutions for the hydrodynamic resistance to particle collision using the method of bispherical coordinates: Haber et al.'s solution applying to axisymmetric motion of two drops (i.e., drops moving along their line-of-centers), and Zinchenko's applying to the asymmetric motion of drops (i.e., drops moving normal to their line of centers) (17). Although these solutions were originally calculated for drop motion, they can be easily applied to particle motion by assigning the ratio of drop viscosity to fluid viscosity a value of $10^3$ or greater. The derivations cited are quite tedious, and a full explication of them is beyond the scope of this report; however, an outline of Haber et al.'s and Zinchenko's results is presented below.

**Hydrodynamic Resistance to Axisymmetric Motion**

Haber et al. showed that the axisymmetric drag force, $\mathbf{F}_1$, acting on a particle with radius $a_1$ moving with a velocity $\mathbf{v}_1$ near another particle with radius $a_2$ and velocity $\mathbf{v}_2$ is given by (18):

$$\mathbf{F}_1 = -6\pi \eta a_1 (A_{11}\mathbf{v}_1 + A_{12}\mathbf{v}_2),$$  \hspace{1cm} [15]$$

where $A_{11}$ and $A_{12}$ are given by:
Figure 3: Magnetic-dipole (mag), van der Waals (vdW), and repulsive or attractive electrostatic (lell) forces as a function of the dimensionless distance between particle surfaces, for $\psi = 0$ and different size ratios. Other parameters include: $A=4 \times 10^{-20}$ J, $T=293$ K, $a_1=5 \times 10^{-6}$ m, $z=1$, $l=0.05$ M, $\psi_{o1} = |\psi_{o2}| = 0.03$ V, $B=5$ T, and $\chi_1 = \chi_2 = 0.001$.

\[ A_{11} = \frac{\sqrt{2} \sinh(\alpha)}{3c} \sum_{n=1}^{\infty} \frac{\delta_0 + \sigma_1 \delta_1 + \sigma_2 \delta_2 + \sigma_1 \sigma_2 \delta_3}{\Delta} , \quad \text{[16a]} \]

and

\[ A_{12} = \frac{\sqrt{2} \sinh(\alpha)}{3c} \sum_{n=1}^{\infty} \frac{\bar{\delta}_0 + \sigma_1 \bar{\delta}_1 + \sigma_2 \bar{\delta}_2 + \sigma_1 \sigma_2 \bar{\delta}_3}{\Delta} . \quad \text{[16b]} \]
Here $c$, $\alpha$, $\Delta$, and the $\delta$'s and $\sigma$'s are coefficients derived from the geometry and fluid conditions of the situation (also, Haber et al.'s $\lambda$'s have been exchanged for $\sigma$'s to avoid confusion); see Haber et al. for a detailed explanation.

The important feature to note is that the resistive force depends on an infinite series; upon calculation, the computer model described in this work allows the infinite series to converge to the desired accuracy and then truncates the series.

**Hydrodynamic Resistance to Asymmetric Motion**

Zinchenko developed solutions similar to Haber et al. for the case of particle motion normal to the line of centers (20):

\[ F_1 = -6\pi \eta a_1 [A_{11}(v_1 - v_2) + A_{12}v_2], \]  \[ 17 \]

with $A_{11}$ and $A_{12}$ defined as in (19), and the other variables defined as in the previous section [see (20) for details of these calculations].

**Relative Mobility Functions**

Zhang derived the axisymmetric relative mobility functions $L$ and $G$ from the above resistance functions $A_{11}$, $A_{12}$ and the functions $A_{21}$, $A_{22}$, where the latter pair of functions are the analogous resistance functions for the second particle in the analysis (Zinchenko, 20). Zhang arrived at the following expressions for $L$ and $G$ (21):

\[ L(\xi) = \frac{\lambda^2 A_{12} - A_{22}}{(\lambda^2 - 1)(A_{11}A_{22} + A_{12}A_{21})}, \]  \[ 18a \]

\[ G(\xi) = \frac{A_{12} + \lambda A_{22}}{(\lambda + 1)(A_{11}A_{22} + A_{12}A_{21})}, \]  \[ 18b \]

where $\xi = s - 2$. Similar expressions for the asymmetric relative mobility functions $M(s)$ and $H(s)$ can be found [see (21, 17) for further details]. It is important to note that the limiting values of these hydrodynamic mobility functions (i.e. values at large ratios of drop viscosity to fluid viscosity) agree with those obtained from the hydrodynamic mobility functions developed for rigid spheres (27, 28) and used in other studies (29, 30).
Relative Diffusivity

The relative diffusivity due to Brownian motion for two particles is expressed as:

\[
D_{12}^{(0)} = \frac{kT(1 + \lambda^{-1})}{6\pi\eta a_1}.
\]  

[19]

Equation of Relative Particle Motion

The forces acting on a particle pair have been examined and quantified. In order to use them in a theoretical model, the relations between the various forces have to be delineated, and like forces grouped together. In the sections below, the external forces of gravity and magnetic attraction and the Brownian relative diffusivity are combined into two dimensionless interparticle force parameters, while the interparticle forces are combined into a dimensionless interparticle potential.

Far-Field Relative Velocity

The far-field relative velocity between two particles is the vector addition of the gravitational relative velocity \(V_{12g}^{(0)}\) given by Eq. [4], and the magnetic-induced relative velocity \(V_{12m}^{(0)}\) given by Eq. [7]:

\[
V_{12}^{(0)} = \frac{2[(\rho_1 - \rho)a_1^2 - (\rho_2 - \rho)a_2^2]g + [2(\chi_1 a_1^2 - \chi_2 a_2^2)/\mu_0]B\nabla B}{9\eta}.
\]  

[20a]

As seen in Eq. [20a], the magnetically induced relative velocity depends on the direction of the magnetic field gradient. The problem is greatly simplified if this vector is aligned in the positive or negative vertical direction: this arrangement results in a cylindrical symmetry of forces about the axis along which one particle overtakes the other, in addition to reducing the vector addition to a scalar addition. Accordingly, whenever the external force of magnetic attraction is applied in this study, the analysis is restricted to the case where the magnetic-field gradient vector is oriented downward so that the magnetic relative velocity adds to that of gravity. The magnitude of the relative velocity vector, \(V_{12}^{(0)}\), thus becomes:
where \( g \) is the magnitude of the gravitational acceleration, and \(|\nabla B|\) is the magnitude of the magnetic induction gradient.

**Trajectory Equation of Particle-Particle Motion**

Using a similar analysis to that of Davis (29), the relative diffusivity (Eq. [19]) and the far-field relative velocity (Eq. [20b]) are related through three dimensionless parameters, the magnetic force parameter, \( Q_{12}^{mag} \), the interparticle force parameter, \( Q_{12} \), and the Péclet number, \( Pe \):

\[
Q_{12}^{mag} = \frac{(a_1 + a_2)^4 V_{12}^{(0)}}{2 \pi B^2 \chi_1 \chi_2 a_1^3 a_2^3 D_{12}^{(0)}/\mu_0 kT},
\]

\[
Q_{12} \equiv \frac{1}{2}(a_1 + a_2) V_{12}^{(0)} / AD_{12}^{(0)}/kT,
\]

\[
Pe \equiv \frac{1}{2}(a_1 + a_2) V_{12}^{(0)} / D_{12}^{(0)}.
\]

In the case of creeping flow, i.e., when the Reynolds number, \( \mathcal{R} = 2\rho V_{12}^{(0)} a_1/\eta \), is small enough so that inertia is neglected, the relative velocity, \( V_{12} \), obtained based on a force balance (31) is given by:
\[
V_{12} = v^{(0)}_{12} \left[-L(s)\cos(\theta)\hat{e}_r + M(s)\sin(\theta)\hat{e}_\theta \right] - \frac{D^{(0)}_{12}}{kT} \left[G(s)F_{\theta}^{\text{mag}}\hat{e}_\theta - H(s)F_{\theta}^{\text{mag}}\hat{e}_\theta \right] - \frac{D^{(0)}_{12}}{kT} G(s)(F_{\text{vdW}} + F_e)\hat{e}_r - \frac{V^{(0)}_{12}}{Pe} \left[G(s)\frac{\partial}{\partial s}(\ln p_{12})\hat{e}_r + \frac{H(s)}{s} \frac{\partial}{\partial \theta}(\ln p_{12})\hat{e}_r \right],
\]

where \( \hat{e}_\theta \) is the unit vector in the tangential direction (see Figure 1). \( F_{\text{vdW}} \) and \( F_e \) are the van der Waals and electrostatic forces, respectively, and \( p_{12} \) represents the normalized probability that particle 1 is at a given position relative to particle 2. Therefore, Eq. [22] includes both deterministic and probabilistic terms, and its solution depends on the functional form of \( p_{12} \). A general solution of Eq. [22], useful for particles in the micron size range, may be obtained using perturbation methods (32). The four terms on the right-hand side of Eq. [22] represent the contributions of (a) external gravity and magnetic forces, (b) interparticle forces including van der Waals and electrostatic, (c) magnetic dipole forces, and (d) Brownian diffusion, respectively.

**Collision Efficiency and Collision Frequency due to Brownian Diffusion**

In the case of \( Pe << 1 \), which usually occurs for submicron particles, Brownian diffusion dominates over external forces. The contribution of external forces is thus negligible, and only interparticle forces and Brownian diffusion are considered. In the presence of the magnetic field, the collision efficiency and collision frequency denoted by \( E_{12} \) and \( F_{12} \), respectively, can be determined using the following expressions:

\[
E_{12} = \left[ \int_2^{\infty} \exp \left[ \frac{(V_{\text{vdW}} + V_e + V_{\text{mag}})/kT}{s^2G(s)} \right] ds \right]^{-1} \quad [23a]
\]

\[
F_{12} = \frac{4\pi D^{(0)}_{12}}{a_1 + a_2} \int_0^\infty \frac{\exp \left[ (V_{\text{vdW}} + V_e + V_{\text{mag}})/kT \right]}{r^2G(r)} dr \quad [23b]
\]
In Eq. (23), the magnetic potential, $V_{\text{mag}}$, is integrated over all orientations of the particles in the magnetic field. Such an integration has been carried out by Chan et al. (33), and their results have been incorporated in a Brownian diffusion model by Tsouris and Scott (10).

**Collision Efficiency and Collision Frequency due to External Forces**

In the case of $Pe \gg 1$, which usually occurs for larger particles, the external forces dominate over Brownian diffusion, and the Brownian diffusion term in Eq. [22] (last term) can be eliminated. Also, Eq. [22] can be dimensionalized if divided by $V_{12}^{(0)}$ to give the overall dimensionless relative velocity, $u_{12}$:

$$u_{12} = \left[-L(s)\cos(\theta)\hat{e}_r + M(s)\sin(\theta)\hat{e}_\theta \right] - \frac{D_{12}^{(0)}}{kTV_{12}} \left[ G(s)F_r^{\text{mag}}\hat{e}_r - H(s)F_\theta^{\text{mag}}\hat{e}_\theta \right]$$

Separating the resulting dimensionless relative velocity into radial and tangential components and dividing the radial component by the tangential component, the differential trajectory equation given by Eq. [25] is obtained:

$$\frac{ds}{d\theta} = s \left\{ -L(s)\cos(\theta) - \frac{G(s)}{Q_{12}^{\text{mag}}} \left[ 1 + \cos[2(\alpha - \theta)] \right] \right\} - \frac{G(s)}{Q_{12}} \frac{d}{ds} \left( \frac{V_{vdW} + V_{el}}{A} \right)$$

This equation is the heart of the computer model presented in this report. By finding the numerical solution to this equation, the trajectory of a particle can be traced from an arbitrary starting position and its eventual fate determined (collision or non-collision with the other particle). Furthermore, by repeated applications of this numerical solution, the limiting or critical trajectory separating the particle's two fates can be found. As inspection of Eq. [25] will reveal, the limiting trajectory shows cylindrical symmetry about the $z$-axis for $\alpha = 0$, $\pi/2$, $\pi$. Thus, in these cases, trajectories which result in collision will originate within a certain horizontal distance $y^*_c$ of the $z$-axis shown in Figure 1 (34). From this critical radius parameter, the collision frequency and collision efficiency can be found.
The collision rate, $J_{12}$, for a given particle will be the number of collisions it experiences per unit time. In the cases of cylindrical symmetry given in the previous section, the collision rate can be thought of as the flux of potential collision partners that move through the circle the limiting trajectory forms about the z-axis. This flux, in turn, is just the concentration of potential collision partners multiplied by the area of the limiting trajectory circle and the (relative) flux velocity (note that the flow through the limiting trajectory circle is parallel to the flux direction). The overall collision rate per unit volume for the two particle classes will be the collision rate for a particular particle multiplied by the concentration of that class of particles. If the concentration of the two particle classes is unknown, a normalized collision frequency, $F_{12}$, can be defined as $J_{12}$ divided by the particle concentrations. Stating the above mathematically (17):

$$F_{12} = \frac{J_{12}}{n_1 n_2} = V_{12}^{(0)} \pi y_c^2,$$

where $n_1$ and $n_2$ are the number concentrations of particles one and two. Note that the collision frequency without particle-particle interactions, $F_{12}^{(0)}$, is given by (17):

$$F_{12}^{(0)} = \frac{J_{12}^{(0)}}{n_1 n_2} = V_{12}^{(0)} \pi (a_1 + a_2)^2,$$

i.e., particles overtaking one another will not flow around each other; they collide only if they were originally on a direct collision course, much like sticky billiard balls. This collision frequency is normally taken as the reference situation, with the collision efficiency, $E_{12}$, defined as the ratio of the actual and reference collision frequencies (17):

$$E_{12} \equiv F_{12} / F_{12}^{(0)} = \frac{y_c^2}{(a_1 + a_2)^2}.$$

Stated in a different way, the collision efficiency is the collision rate with interparticle forces divided by the collision rate without interparticle forces. Note that the collision efficiency thus defined can assume values above unity. It has been proposed to rename this function the "collision enhancement function," (11) but the term "collision efficiency" is retained here, in order to maintain consistency with the literature.
With the above definitions and equations, the theoretical framework for a particle-particle collision trajectory analysis model is sufficient for useful numerical simulations. The specifics of these simulations, and the results they give, are outlined in the Results and Discussion Section.

**Magnetically Seeded Flocculation**

In this case, the particle collision frequency given by Eq. [23b] or Eq. [26] can be calculated as a function of all parameters of the system. This collision frequency can then be used in a bivariate population balance model to estimate the flocculation as a function of time (11):

\[
\frac{dn_{ij}}{dt} = \frac{1}{2} \sum_{l=1}^{i-1} \sum_{m=1}^{j} n_{lm} n_{(i-l)(j-m)} F_{im,(i-l)(j-m)} - \sum_{l=1}^{N_s-1} \sum_{m=1}^{N^T_c-1} n_{ij} n_{lm} F_{ij,lm}
\]  

[29]

where \(n_{ij}\) is the number of particles of size \(i\) and magnetic susceptibility \(j\) (class \(ij\)), \(F_{ij,lm}\) is the collision frequency of particles in class \(ij\) with particles in class \(lm\), and \(N_s\), \(N^T_c\) are the total numbers of size and magnetic susceptibility classes, respectively. Some of the capabilities of this model in describing heterogeneous flocculation between paramagnetic particles of varying magnetic susceptibility are discussed by Tsouris et al. (11).

Finally, the modeling approach described here permits studies of magnetically seeded flocculation in which magnetic particles are added to a suspension of non-magnetic particles. Initially, flocculation of non-magnetic with magnetic particles will occur due to both external forces and interparticle forces, but no contribution will be provided by magnetic dipoles. The resulting flocs have higher magnetic susceptibility than the original non-magnetic particles and may respond in a magnetic field. This mechanism suggests that magnetically seeded flocculation can mathematically be described as a heterogeneous flocculation process, which can sufficiently be handled by the bivariate population balance approach shown by Eq. [29]. In addition, Eq. [29] can be used to predict size distribution in flocculation systems under different regimes than those presented in this report. For example, in the experimental work being conducted at Oak Ridge National Laboratory (ORNL), flocculation was induced by shear flow. The effect of shear flow on the particle size and magnetic susceptibility in a flocculation system can be predicted using Eq. [29].
Magnetically Seeded Filtration

In this case, the particle collision efficiency given by Eq. [28] can be calculated as a function of all parameters of the system. This collision efficiency can then be related to the filter coefficient, $\lambda^*$, by the expression (32):

$$\lambda^* = \frac{3}{4} \frac{(1 - \varepsilon)}{a_c} E_{ij}$$

where $\varepsilon$ is the porosity of the bed, $a_c$ is the filter collector radius, and $E_{ij}$ expresses the collision efficiency between the particle (magnetic or non-magnetic) in the suspension and the filter collector. The filter coefficient is then used to define the filtration rate, $N$, as:

$$N = u_s \lambda^* c$$

where $u_s$ is the flow approach velocity, and $c$ is the particle concentration in the fluid.

The macroscopic equation needed to be solved in order to describe the filter performance is given below:

$$u_s \frac{\partial c}{\partial \zeta} + N = 0$$

where $\zeta$ is the axial coordinate in the filter. It has to be pointed out here that the filtration rate varies with time as flocculation progresses. This variation will be included in the model through the variation of the collision efficiency.

Results and Discussion

The results presented here correspond to collision efficiencies and frequencies when the trajectory calculation outlined in the Model Development section can be employed. These results can have significance in magnetically seeded solid-liquid separations. The calculations were computed on an IBM RS/360 model workstation, configured with 64 MB of memory, using double-precision calculations. An ordinary differential equation solver with variable step (EPISODE; 35) was employed to solve the trajectory equation given by Eq. [25]. To verify the model developed in this study, a series of results by neglecting the magnetic forces were first
obtained; these results were found identical to those of other studies in which gravity induced coagulation encounters were analyzed via trajectory calculations (29, 30).

The results of model computations are discussed in the sections below, organized by the forces present during each set of calculations. In all calculations, the electrostatic force has been neglected. In other words, all particles are assumed to have no double-layer charge, and thus no electrostatic attraction or repulsion. Extending the calculations to study the effect of electrostatic forces on collision efficiency and frequency is the objective of future work.

The Collision Efficiency and Collision Frequency of Two Particles Under Magnetic, van der Waals, and Hydrodynamic Forces for a Variable Direction of the Magnetic Field

The first step in this study is to check whether the direction of the magnetic field plays a significant role in the collision efficiency and collision frequency, and to find the direction that gives the maximum efficiency and frequency. In these calculations, the external magnetic force has been neglected, i.e., the magnetic gradient has been considered negligible, and the angle $\alpha$ between the vertical axis and the direction of the magnetic field has been taken values of $0$, $\pi/2$, and $\pi$ in order to keep the cylindrical symmetry of the system. The two particles are assumed to have the same density, and their density difference ($\Delta\rho$) to that of the fluid has been considered 2000 kg/m$^3$. The results are shown in Figures 4a and 4b. It is clear from the figure that maximum collision efficiency and collision frequency occur when the magnetic field has the same or opposite direction to that of the vertical axis, i.e., $\alpha = 0$, $\pi$. The direction that gives the smaller efficiency corresponds to the case at which the magnetic field is perpendicular to the vertical axis, i.e. $\alpha = \pi/2$. In this case, both collision efficiency and collision frequency decrease with the magnetic field, approaching zero near a magnetic induction of 1.5; this phenomenon may be explained by the repulsive interparticle magnetic force that appears between the two particles when they come close together in the region of $\psi = 90^\circ$ (see Figure 2a). All the calculations that follow correspond to the case where $\alpha = 0$. It is shown with this example calculation, that the trajectory equation can be used to find the optimum direction of the magnetic field with respect to collision efficiency and collision frequency.

The Collision Efficiency and Collision Frequency of Two Particles Under Magnetic, van der Waals, and Hydrodynamic Forces

The purpose of the model developed in this study is the simulation of magnetically seeded solid-liquid separation processes. Accordingly, input parameters were chosen to reflect different stages and conditions under which these processes occur. Another, more specific goal is the comparison of the effects of various input parameters. The first set of input parameters
Figure 4: Effect of the direction of the magnetic field on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4\times10^{-20}$ J, $\eta=10^{-3}$ kg/m s, $T=293$ K, $a_1=5\times10^{-6}$ m, $\lambda=0.1$, $\chi_1=\chi_2=0.001$, and $\Delta \rho=2000$ kg/m$^3$. 
chosen represents the case of the initial stages of magnetically seeded flocculation and filtration, when magnetically susceptible particles have just been introduced to the solution. At this point, most flocculation events will be between magnetic and non-magnetic particles and the filter collector may interact with non-magnetic particles.

Figure 5a shows the collision efficiency for such a case, where $a_1=5\times10^{-6}$ m, $a_2=5\times10^{-7}$ m, the magnetically susceptible particle has a susceptibility of $\chi=0.001$, and the particles have a variable density expressed with the difference in their density compared to that of the fluid ($\Delta \rho$). Since in these calculations it is assumed that $\nabla B$ has direction of that of gravity, the collision efficiency is plotted against the magnetic strength, $B|\nabla B|$ (T m$^{-2}$). It has to be recognized that whenever there is interaction between magnetic and non-magnetic particles, the quantities $B$ and $|\nabla B|$ are multiplied by one another wherever they appear in an equation in this study; thus, the two quantities can be grouped as a single variable. Note that this is not true for interaction between two magnetic particles. Figure 5b shows the collision frequency for the same set of input parameters.

From Figure 5a, it can be seen that the collision efficiency decreases with increasing magnetic strength and increasing density difference ($\Delta \rho$). This can be attributed to the fact that the far-field relative velocity varies with the magnetic strength and density difference. As both magnetic strength and $\Delta \rho$, and thus the far-field relative velocity, increase, the two particles have less time to interact with each other through the attractive interparticle forces. As the magnetic strength and $\Delta \rho$ increase further, the collision efficiency reaches an asymptotic value. The effect of the density difference is the same as that of the magnitude of the magnetic gradient since both parameters influence the relative velocity by the same way.

The collision frequency, contrary to the collision efficiency, increases with the magnetic strength, the density difference, and thus the far-field relative velocity. This result stems from the fact that the particle flux onto a particular flocculating particle is proportional to the relative velocity (see Eq. [26]), an effect which masks the change in collision efficiency.

In this group of calculations, three other specific quantities are varied in addition to the density difference, and the results are discussed below. Figure 6a shows the effect of varying magnetic susceptibility (and magnetic strength) on collision efficiency. Recall that in this group of simulations, one particle is magnetic while another is non-magnetic, a condition likened to the first stages of magnetically-seeded separations. With no magnetic dipole effects between particles, the change in magnetic susceptibility is expected to have an effect similar to the variation in the magnetic strength. Indeed this is born out: the collision efficiency can be decreased either by increasing the magnetic strength or by increasing the magnetic susceptibility of the magnetically susceptible particle. Furthermore, the collision efficiency for various magnetic susceptibilities converges to the same asymptotic value for high magnetic strengths.
Figure 5: Initial stage of magnetically seeding solid-liquid separation: effect of density difference on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4\times10^{-20}$ J, $\eta=10^{-3}$ kg/m s, $T=293$ K, $a_1=5\times10^{-6}$ m, $\lambda=0.1$, $X_1=0.001$, and $X_2=0$. 

**Figure 5:** Initial stage of magnetically seeding solid-liquid separation: effect of density difference on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4\times10^{-20}$ J, $\eta=10^{-3}$ kg/m s, $T=293$ K, $a_1=5\times10^{-6}$ m, $\lambda=0.1$, $X_1=0.001$, and $X_2=0$. 
Figure 6: Initial stage of magnetically seeding solid-liquid separation: effect of magnetic susceptibility on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4\times10^{-20}$ J, $\eta=10^{-3}$ kg m s, $T=293$ K, $a_1=5\times10^{-6}$ m, $\lambda=0.1$, $\chi_2=0$, and $\Delta \rho=0$. 

...
Figure 6b shows the effect of magnetic susceptibility on the collision frequency, which is consistent with the results of Figure 5b: collision frequency increases with both magnetic strength and magnetic susceptibility.

The data in Figures 7a and 7b show a different effect. Here the Hamaker group, $A/kT$, is modulated. Essentially, the attractive force between the two flocculating particles is varied at a specific far-field relative velocity. The effect is simultaneous to the collision efficiency and the collision frequency; both are increased as the attractive force is increased. The data do suggest that the collision efficiency is not influenced much from the value of the Hamaker constant as the magnetic strength increases above a specific value; presumably the effect of Van der Waals forces becomes negligible as the magnetic force increases.

Perhaps the most intriguing results come from Figures 8a and 8b, where the size ratio between particles is co-varied with the magnetic force, $B|∇B|$. Here, an increasing size ratio is rewarded with both greater collision efficiency and collision frequency. As the sizes of particles are treated in some cases as normalized quantities in the computer model calculations, it is likely that the effect seen is due to both the ratio of sizes, as well as the size of one particular particle. Possibly this result is due to a decrease in the hydrodynamic resistance; such a correlation is hinted at in Haber et al. (18).

**The Collision Efficiency and Collision Frequency of Two Particles Under Magnetic, Magnetic Dipole, van der Waals, and Hydrodynamic Forces**

The last set of data considered in this work are for the case corresponding to the latter part of a magnetically seeded solid-liquid separation process, after the majority of non-magnetic particles have collided with magnetic particles. Further particle collisions will thus be influenced by the magnetic dipole force, which acts between two particles with magnetic susceptibilities. As was discussed previously, Eq. [13] applies only for a uniform magnetic field. Apparently the field uniformity is violated when the magnetic field gradient is non-zero. For the ranges of the magnetic field gradient used in this work (which correspond to most practical applications) and the distance in which the magnetic dipole force becomes important, the change in the magnetic induction is insignificant. Therefore, the magnetic dipole force is still calculated by Eq. [13]. One particle has a magnetic susceptibility fixed at 0.001, while the other varies as shown in Figures 9a and 9b.

The effects here are as expected. Both collision efficiency and collision frequency increase with the magnitude of the magnetic induction. Also, both quantities increase with increasing the magnetic susceptibility of the second particle. As in the simulations shown before for the collisions between magnetically susceptible and non-magnetically susceptible particles,
Figure 7: Initial stage of magnetically seeding solid-liquid separation: effect of Hamaker constant on (a) collision efficiency and (b) collision frequency. Other parameters include: $\eta = 10^{-3}$ kg/m s, $T = 293$ K, $a_1 = 5 \times 10^{-6}$ m, $\lambda = 0.1$, $\chi_1 = 0.001$, $\chi_2 = 0$, and $\Delta \rho = 0$. 

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Figure 8: Initial stage of magnetically seeding solid-liquid separation: effect of size ratio on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4\times10^{-20}$ J, $\eta=10^{-3}$ kg/m s, $T=293$ K, $a_1=5\times10^{-6}$ m, $x_1=0.001$, $x_2=0$, and $\Delta\rho=0$. 

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Figure 9: Progress of magnetically seeding solid-liquid separation: effect of magnetic susceptibility on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4 \times 10^{-20}$ J, $\eta=10^{-3}$ kg/m s, $T=293$ K, $a_1=5 \times 10^{-6}$ m, $\lambda=0.1$, $\chi_1=0.001$, and $\Delta \rho=0$. 
collision efficiency decreases with the magnetic field gradient, and thus the magnetic strength. On the other hand, the collision frequency increases with increasing the magnetic field gradient.

**Summary**

This study has examined the theoretical framework underlying magnetically seeded solid-liquid separations, developing expressions for the external forces acting on particles and the interparticle forces between them. From these considerations, a model was derived and implemented as a computer code. Through manipulation of input variables, this code and the physical system it represents revealed relationships between particle-particle and particle-collector forces and operating parameters. The particle size ratio was found to affect collisions, with evidence that this effect acts through the hydrodynamic resistance. The direction of the magnetic field plays a significant role in the collision efficiency and collision frequency, and it was found that when the direction of the magnetic field is parallel to the vertical axis, the system is at its optimum state in terms of flocculation. This last point is especially important, due to the influence it would have on the optimization of actual separation and recovery processes. The implication for magnetic seeding is the need for more efficient separation systems. With further research, the collision efficiency and collision frequency obtained in this study could be used in a dynamic model of particle flocculation or particle filtration, allowing full exploitation of this powerful technique.

**Future Work**

This work is in progress and its major objective is to develop mechanistic models that can predict the performance of magnetically seeded solid-liquid separation processes. Experimental results that are being conducted at ORNL will be used to verify the developed models. In the experiments conducted at ORNL, flocculation is being induced by shear flow and without the presence of a magnetic field. Collision frequencies for shear flow, available in the literature (36), will be used in combination with the bivariate equation given by Eq. [29] to investigate how the size and magnetic susceptibility of suspended particles change with time. Then, the approaches described in this work will be used to predict the performance of the magnetic filter.

**Notation**

- $A$ Hamaker constant (J)
- $A_p$ cross-sectional area of the particle (m$^2$)
- $a$ particle radius (m)
- $a_c$ filter collector radius (m)
- $B$ magnetic induction (T=V s m$^{-2}$)
\( B \)  \( \) magnitude of magnetic induction (T=V s m\(^{-2}\))
\( C_D \)  \( \) coefficient of drag
\( c \)  \( \) particle concentration in the fluid (kg m\(^{-3}\))
\( D_{12}^{(0)} \)  \( \) Brownian relative diffusivity
\( E_{12} \)  \( \) collision efficiency
\( \hat{e}_r \)  \( \) unit vector in the radial direction
\( \hat{e}_\theta \)  \( \) unit vector in the tangential direction
\( e \)  \( \) electron charge=1.6x10\(^{-19}\) C
\( F_1 \)  \( \) axisymmetric drag force of particle 1 (N)
\( F_b \)  \( \) buoyant force (N)
\( F_d \)  \( \) drag force (N)
\( F_g \)  \( \) gravitational force (N)
\( F_m \)  \( \) magnetic force (N)
\( F_{12} \)  \( \) collision frequency (m\(^3\) s\(^{-1}\))
\( F_e \)  \( \) electrostatic force (N)
\( F_{vdW} \)  \( \) van der Waals force (N)
\( F_{mag}^r \)  \( \) radial magnetic interparticle force (N)
\( F_{mag}^\theta \)  \( \) tangential magnetic interparticle force (N)
\( G(s) \)  \( \) axisymmetric relative mobility function
\( g \)  \( \) gravitational acceleration (m/s\(^2\))
\( \hat{g} \)  \( \) unit vector of the gravitational acceleration
\( g \)  \( \) magnitude of the gravitational acceleration=9.8062 m/s\(^2\)
\( H \)  \( \) magnetic field strength (A m\(^{-1}\))
\( H(s) \)  \( \) asymmetric relative mobility function
\( I \)  \( \) ionic strength of the solution (M)
\( J_{12} \)  \( \) collision rate (m\(^{-3}\) s\(^{-1}\))
\( k \)  \( \) Boltzmann constant=1.38x10\(^{-23}\) J K\(^{-1}\)
\( L(s) \)  \( \) axisymmetric relative mobility function
\( M(s) \)  \( \) asymmetric relative mobility function
\( N \)  \( \) filtration rate (kg m\(^{-3}\) s\(^{-1}\))
\( n_1 \)  \( \) number concentration of particle one (m\(^{-3}\))
\( Pe \)  \( \) Péclet number
\( p_{12} \)  \( \) normalized probability that particle 1 is at a given position relative to particle 2
\( Q_{12} \)  \( \) interparticle force parameter
\( Q_{12}^{mag} \)  \( \) magnetic force parameter
Reynolds number

\( R \)

center-to-center particle separation (m)

\( r \)

\( s \equiv 2r/(a_1 + a_2) \) (dimensionless particle separation)

\( T \)

absolute temperature (K)

\( t \)

time (s)

\( u_{12} \)

overall dimensionless relative velocity

\( u_s \)

flow approach velocity (m s\(^{-1}\))

\( V_{12}^{(0)} \)

far-field relative velocity (m s\(^{-1}\))

\( V_{12g}^{(0)} \)

far-field relative gravitational velocity for two particles (m s\(^{-1}\))

\( V_{12m}^{(0)} \)

relative magnetic velocity (m s\(^{-1}\))

\( V_{el} \)

electrostatic potential (J)

\( V_{mag} \)

interaction potential between two magnetically susceptible particles (J)

\( V_p \)

volume of the particle (m\(^3\))

\( V_{vdW} \)

van der Waals interparticle force potential (J)

\( V_{12}^{(0)} \)

magnitude of the far-field relative velocity (m s\(^{-1}\))

\( v \)

particle velocity (m s\(^{-1}\))

\( v^* \)

magnitude of particle velocity (m s\(^{-1}\))

\( y_c^* \)

critical horizontal separation (m)

\( z \)

valence of the symmetric electrolyte in the solution

\( \alpha \)

angle between the direction of the vertical axis and that of the magnetic field

\( \Delta \rho \)

density difference of particles to that of the fluid (kg m\(^{-3}\))

\( \varepsilon \)

permittivity of the medium=6.95x10\(^{-10}\) C V\(^{-1}\) m\(^{-1}\) for water

\( \zeta \)

axial coordinate in the filter (m)

\( \eta \)

dynamic viscosity (kg m\(^{-1}\) s\(^{-1}\))

\( \theta \)

angle between the vertical axis and \( r \)

\( \lambda \equiv a_2/a_1 \) (particle radius ratio)

\( \lambda^* \)

filter coefficient (m\(^{-1}\))

\( \mu_0 \)

permeability of free space=4 \( \pi \times 10^{-7} \) V s A\(^{-1}\) m\(^{-1}\)

\( \hat{\mu} \)

respective unit magnetic dipole vectors of particles

\( \rho \)

density of the fluid (kg m\(^{-3}\))

\( \rho_p \)

density of the particle (kg m\(^{-3}\))

\( \chi \)

volume magnetic susceptibility
\[ \psi \] angle between the magnetic field and \( r \)
\[ \Psi_{oi} \] particles' surface potential (V)

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LIST OF SYMBOLS

\( A \) \hspace{1cm} \text{Hamaker constant (J)}
\( a \) \hspace{1cm} \text{Wire radius (m)}
\( b \) \hspace{1cm} \text{Particle radius (m)}
\( b^* \) \hspace{1cm} \text{Relative mobility (sg\textsuperscript{-1})}
\( C \) \hspace{1cm} \text{Number concentration of suspended particles}
\( C_{in} \) \hspace{1cm} \text{Influent concentration}
\( C_{out} \) \hspace{1cm} \text{Effluent concentration}
\( Cov \) \hspace{1cm} \text{Covariant}
\( C_s \) \hspace{1cm} \text{Saturation concentration (captured particle volume/bulk volume in the filter)}
\( D_{ij} \) \hspace{1cm} \text{Relative diffusivity (m\textsuperscript{2}s\textsuperscript{-1})}
\( D_w \) \hspace{1cm} \text{Diffusivity in the absence of interparticle forces (m\textsuperscript{2}s\textsuperscript{-1})}
\( E_{ij,lm} \) \hspace{1cm} \text{Collision efficiency}
\( F_d \) \hspace{1cm} \text{Hydrodynamic drag force (N)}
\( F_g \) \hspace{1cm} \text{Gravitational force (N)}
\( F_i \) \hspace{1cm} \text{Inertial force (N)}
\( F_{ij,lm} \) \hspace{1cm} \text{Flocculation frequency of particles in class \( ij \) with particles in class \( lm \)}
\( F_m \) \hspace{1cm} \text{Magnetic force (N)}
\( F_{r(net)} \) \hspace{1cm} \text{Radial net force (N)}
\( F_{\phi(net)} \) \hspace{1cm} \text{Tangential net force (N)}
\( f_a \) \hspace{1cm} \text{Integrated effect of the shear stress}
\( G \) \hspace{1cm} \text{Gravitational force parameter}
\( g \) \hspace{1cm} \text{Gravitational acceleration (m s\textsuperscript{-2})}
\( H \) \hspace{1cm} \text{Magnetic field strength (Am\textsuperscript{-1})}
\( H_0 \) \hspace{1cm} \text{Applied magnetic field strength (Am\textsuperscript{-1})}
\( H_s \) \hspace{1cm} \text{Saturation magnetic field strength (Am\textsuperscript{-1})}
\( K \) \hspace{1cm} \text{Dimensionless parameter (\( =M_s/2 H_0 \), for \( H_0 > H_s \); \( =1 \), for \( H_0 < H_s \).)}
\( k \) \hspace{1cm} \text{Boltzmann constant= 1.38\times10^{-23} \text{ VCK}^{-1}}
$L$  Filter length (m)

$M$  Magnetization (Am$^{-1}$)

$M_s$  Saturation magnetization (Am$^{-1}$)

$N$  Number of particles per unit time

$N_{ci}$  Total number of initial magnetic susceptibility classes

$N_s$  Total number of size classes

$n_{ij}$  Number of particles of size $i$ and magnetic susceptibility $j$ (class $ij$)

$R$  Normalized radius

$R_c$  Critical Radius

$R_i$  Reynolds number

$r$  Center-to-center particle separation (m)

$r_b$  Loading radius of build-up (m)

$r_i$  Radius of particle $i$ (m)

$r_{XY}$  Correlation coefficient

$T$  Temperature (K)

$t$  time (s)

$t_s$  saturation time (s)

$t_{total}$  time for the filter complete saturated (s)

$V$  Volume of a particle (m$^3$)

$V_0$  Superficial velocity (ms$^{-1}$)

$V_A$  Particle interaction potential (CV)

$V_L$  Loading volume (m$^3$)

$V_{el}$  Electrostatic potential (CV)

$V_m$  Magnetic velocity (m s$^{-1}$)

$V_{mag}$  Magnetic potential (CV)

$V_r$  Radial superficial velocity (ms$^{-1}$)

$V_s$  Saturation velocity (m s$^{-1}$)

$V_{vdw}$  van der Waals potential (CV)

$V_\theta$  Tangential superficial velocity ms$^{-1}$

$x_s$  Active length of the filter matrix (m)

$\beta$  Angle between the gravitational force and horizontal axis

$\beta_{ij}$  the particle collision frequency

$\varepsilon$  Filter porosity (%)
\( \varepsilon^* \) Dielectric constant= \( 89 \times 10^{-10} \, CV^{-1} m^{-1} \) for water

\( \phi \) Angle between the vertical axis and \( r \)

\( \gamma \) Angle between the hydrodynamic drag force and horizontal axis

\( \eta \) Dynamic viscosity (Kgm\(^{-1}\)s\(^{-1}\))

\( \eta_X \) Mean of random variable \( X \)

\( \eta_Y \) Mean of random variable \( Y \)

\( \lambda \) Filter coefficient (m\(^{-1}\))

\( \lambda_0 \) \( r_i-r_j \), shortest distance from the surface of particle \( i \) and \( j \) (m)

\( \kappa \) Inverse Debye-Huckel length (m)

\( \mu_0 \) Permeability of free space (Hm\(^{-1}\))

\( \nu \) Kinematic viscosity (m\(^2\)s\(^{-1}\))

\( \rho_f \) Density of fluid (Kgm\(^{-3}\))

\( \rho_p \) Density of a particle (Kgm\(^{-3}\))

\( \sigma \) Porosity of the loading volume (\%)

\( \sigma_X \) Standard deviation of random variable \( X \)

\( \sigma_Y \) Standard deviation of random variable \( Y \)

\( \tau_0 \) Shear stress at the wall (m\(^{-1}\)Kgs\(^{-2}\)).

\( \chi_p \) Magnetic susceptibility of a particle

\( \psi_{0i} \) Surface potential of particle \( i \) (V)
SUMMARY

High-Gradient Magnetic Filtration (HGMF) has been used in various industrial processes, such as separation of heavy metals from wastewater, and recovery of hematite and chromite fines and ultra-fines. HGMF, however, is currently limited to remove only ferromagnetic or paramagnetic particles from waste streams. Magnetically-seeded filtration is a process in which magnetic particles are attached to waste particles to form flocs that can be easily removed by a high-gradient magnetic filter. Magnetically-seeded separation largely enhances the ability of HGMF to remove weakly magnetic or non-magnetic particles, thus increasing the applicability of HGMF in solid/liquid separations. This process can be used in several aspects of wastewater treatment, such as: (1) removal of solids, particularly those in the colloidal size range that are difficult to remove by conventional means, (2) removal of contaminants by precipitation processes, and (3) removal of contaminants by sorption processes. Since magnetically-seeded filtration has been shown to be a promising treatment process in environmental engineering, it is necessary to establish a theoretical analysis in order to optimize the geometry and select the right operating conditions for the separation of particles from a given suspension.

In this study, the effects of various parameters affecting magnetically-seeded filtration are theoretically and experimentally investigated. The parameters studied are filter geometry including packing material and density; particle properties including size,
concentration, and magnetic susceptibility; and operating conditions including magnetic field strength and suspension flow rate. A modeling approach, that includes trajectory analysis, a particle build-up model, a breakthrough model, and a bivariate population balance model, has been developed to predict the removal efficiency and breakthrough curves of high-gradient magnetic filtration. A good agreement between modeling and experiments is obtained in the present study.

The model developed in this study demonstrates a new approach to predict the performance of magnetically-seeded filtration without using empirical coefficients or fitting parameters. Given the characteristics of target particles, the optimum operating conditions, such as magnetic-field strength, flow rate, and filter geometry, can be calculated by the model. Compared to other models in which experimental results are needed to calculate the filter coefficient, this model will simplify the design of filtration processes.
CHAPTER I

INTRODUCTION

I.1 Background

High-Gradient Magnetic Separation (HGMS) has been introduced as a recovery and pollution control process for many environmental and industrial problems. The basic principle of magnetic separation is to remove magnetizable particles from a fluid stream by using a ferromagnetic matrix in a magnetic field. The development of HGMS began only in the sixties and the applicability of magnetic separation was extended to weakly paramagnetic and even diamagnetic particles of micrometer size after the cyclic and continuous magnetic separators were developed (Svoboda, 1987). Currently, the applications of HGMS in industrial wastewater treatment include filtration of nuclear reactor coolant (Heitmann, 1979), removal of phosphate from water (Shaikh and Dixit, 1992), recovery of hematite and chromite fines and ultra-fines (Wang and Forssberg, 1994), separation of dissolved heavy metals from wastewater (Terashima et al., 1986), and removal of oil and suspended solids from municipal sewage. In biotechnology applications, HGMS has been used to remove algae (Bitton et al., 1975), yeast (Dauer and Dunlop, 1991), and bacteria (Bitton and Mitchell, 1974) from wastewater.
Several researchers have investigated the theoretical aspects of magnetic separation from both microscopic and macroscopic points of view. The microscopic theories are aimed at the mechanisms of particle capture and the conditions under which the capture may be achieved. The macroscopic studies focus on the description of the separation phenomena, the prediction of filter performance, and its dynamic behavior. However, most branches of magnetic separation are still highly empirical and a systematic integration of different models to describe the process of magnetic filtration as a whole has not been attempted so far. The primary objective of the present study is to present an approach to predict the removal performance of HGMS by combining single element and phenomenological models and without the use of experimental data.

1.2 Literature Review

The interactions between particles and filter collectors under various conditions are investigated in this study to better understand the microscopic phenomena of magnetic separation. To simplify the inherent complexities in these systems, the interaction between a single particle and a single matrix element is considered. One of the early and important models was developed by Watson (1973; 1975). He formulated trajectory equations in which inertial and gravitational force were neglected and a potential flow was assumed to describe the capture of a particle by a ferromagnetic wire in a uniform magnetic field. Watson (1973) also derived macroscopic equations to predict the filter performance for a clean clean.
Schewe et al. (1980) and Cumming et al. (1976) compared the trajectory models under potential and laminar flow conditions, and proved that at low Reynolds number, laminar flow theory provides better description of flow conditions near a wire. A similar investigation using laminar flow model, but under different arrangements between the directions of flow velocity and magnetic field with respect to the wire, was examined by Birss et al. (1978). They found that under the axial orientation of wires which were orderly packed in a filter, the laminar flow theory gives good predictions of filter efficiency while a potential flow model usually overestimates the filter efficiency. Lawson et al. (1977) extended the trajectory model by including inertial and gravitational forces to fit a broad range of Stokes number and gave a more accurate description of particle trajectories, especially near the wire.

Trajectory models of a single particle captured by a ferromagnetic spherical collector have also been studied by many authors (Friedlaender et al., 1981; Moyer et al., 1984; Scott and Brumfield, 1988). In these studies, a better fit to experimental results was found by applying laminar flow models. Ebner et al. (1997) developed a model for nanolevel high gradient magnetic adsorption in which antiferromagnetic magnetite spheres were used as collectors. From modeling results, they found that small antiferromagnetic collectors with large curvatures produce magnetic fields with higher gradients and higher separation efficiency than wire collectors. By incorporating the distribution of particle size into the filter performance equation, Dauer and Dunlop (1991) obtained a good prediction on yeast removal by spherical
collectors under high flow rate. The removal efficiency reported by Dauer and Dunlop was applicable only for clean collectors. A theoretical model that extends the single-particle, single-collector model was developed by Reger et al. (1985) to describe the separation efficiency of weakly magnetic particles passing through an infinite array of ferromagnetic wires in a high-gradient magnetic field. The particle build-up on the surface of the wires was also described by this model.

As noted above, most trajectory modeling studies that predict the critical radius of particles or separation performance are limited to clean collectors. A model describing the buildup configuration and fully loaded conditions of the wire was investigated by Luborsky and Drummond (1976). They formulated the hydrodynamic force by considering the boundary layer thickness of a wire and calculated the critical angle for each layer of particles. They also obtained the loading volume of particles retained by each wire. Similarly to the work by Luborsky and Drummond (1976), Nesset and Finch (1979; 1981) and Nesset et al. (1980) calculated the boundary layer thickness by employing the Blasius solution. A good prediction was found at high Reynolds number under upstream capture. A modified model was examined under a downstream-capture system by Hollingwourh and Finch (1982) who claimed that for a single-wire longitudinal configuration the loading equation is not applied. Cowen et al. (1976) investigated the rate equation of particle buildup and obtained good predictions under various operating conditions. This model, however, is limited to predicting uniform size paramagnetic particles. Furthermore, it depends on empirical parameters.
The above trajectory and build-up models available in the literature are generally applied to paramagnetic particles. In real systems, however, many particles are weakly magnetic or non-magnetic. For these cases, a magnetic-seeding technique can be applied, as described in this work, which was motivated by the work of Tsouris et al. (1995). These investigators developed a bivariate population-balance model to predict both particle size and magnetic susceptibility distributions during heterogeneous magnetic flocculation under Brownian motion. Besides external-field forces, they also considered the interparticle forces which include van der Waals, double-layer, and magnetic-dipole forces.

In magnetic filtration, of colloidal particles (<< 1 µm), the interparticle forces and particle diffusion become significant. The effect of diffusion of ultra-fine particles in a magnetic filter has been investigated by various authors (Gerber et al., 1983; Takayasu et al., 1983; Reijers et al., 1986; Glew and Parker, 1984). Gerber et al. (1983) have found that, in this situation, the capture process is better described by a continuity equation model in which the diffusion term is included. Similarly, Glew and Parker (1984) and Reijers et al. (1986) considered interparticle interactions in the capture process. It has been suggested by Svoboda and Ross (1989) that the efficiency of particle capture can be determined by the combination of the magnetic dipole force and surface forces between the collector and the particles and between the particles themselves, especially for sub-micron size particles. This point was also made by Collan et al. (1978) who examined the magnetic separation performance from a macroscopic viewpoint. They developed a mathematical model for the
separation process of a general absorption filter. In the model of Collan et al., however, experimental information is needed for the estimation of some of the model parameters.

1.3 Scope of this Study

In this work, the effects of solution parameters, system geometry, and operating conditions on the filtration performance of high-gradient magnetic separation are investigated. In addition, a model is developed to predict the filtration process and performance without using empirical coefficients. The experiments were conducted with well-characterized, uniform polystyrene microspheres. The polystyrene particles provide a model system for more controlled investigation of the effects of process variables and for verification of the model development. The experiments were of three types:

1) magnetic-seeding, shear-flow flocculation and magnetic filtration,
2) magnetic-seeding, Brownian flocculation and magnetic filtration,
3) breakthrough of magnetic filtration.

In the modeling work, four models were investigated:

1) single-particle/single-collector trajectory model,
2) particle build-up model,
3) breakthrough model,
4) bivariate model (heterogeneous flocculation).

A description of experimental and modeling activities in this work is shown in Figure 1. The bivariate model provides the size and magnetic susceptibility
distributions of particles in the suspension. The removal efficiency of clean wires and the saturation concentration of the filter are calculated for each class of specific size and magnetic susceptibility by using trajectory and build-up models, respectively. Then, the filtration breakthrough curve can be predicted by the breakthrough model. A detailed description of the model formulation and experimental techniques is discussed in Chapters II and III. The materials and methods used in the experiments are shown in Chapter II. Chapter III presents the theory of magnetic filtration. Results of experiments and modeling are discussed in Chapter IV and also the comparisons between modeling and experiments. Conclusions of this study are given in Chapter V.
The experiments carried out in this work are classified into three categories: (1) magnetic-seeding, shear flocculation, and magnetic filtration; (2) breakthrough of magnetic filtration; and (3) magnetic-seeding, Brownian flocculation, and magnetic filtration. In the first part, experiments were conducted under different solution conditions such as pH, particle size, zeta potential of particles, and ionic strength, and different operating conditions such as magnetic-field strength, flow rate, and agitation speed. The effects of these parameters on the performance of magnetic-seeding, shear flocculation, and magnetic filtration were studied. A detailed discussion of magnetic-seeding shear-flocculation experiments are presented elsewhere (Chin, 1997).

Experiments conducted in the second and third parts of this work, as described above, are used to study the effect of operating conditions on the breakthrough curve of magnetic filtration. The results of these experiments were compared to modeling results.

II.1 Particle Characterization Measurements

Particles were characterized in terms of their size, zeta potential, and magnetic susceptibility. The size distribution of particles was measured by the Coulter LS 130
instrument (Coulter Corporation, Hialeah, FL) which can measure particle sizes ranging from 0.429 µm to 1000 µm.

Zeta potential measurements were obtained by using a Lazer Zee Meter, model 501 (Pen Kem, Inc., Bedford Hills, NY) for all particles. For magnetic susceptibility measurements, a magnetic susceptibility balance, model MSB-AUTO (Johnson Matthey Fabricated Equipment, Wayne, PA) was used.

II.2 Magnetic-Seeding Shear-Flocculation and Magnetic Filtration

Polystyrene latex and seeding polystyrene latex (containing 40% magnetite by weight) were used to study the effects of magnetic-seeding on the separation of well-characterized synthetic particles. Both types of particles were supplied by Bangs Laboratory, Inc. (Carmel, IN). Some relevant properties of these particles are listed in Table I. Analytical grade sodium chloride was the background electrolyte used for the adjustment of ionic strength. The solution pH was adjusted using NaOH (0.1 M) and HCl (0.1 M) solutions. Deionized water (electrical resistance >10MΩ) was used in the preparation of solutions and particle suspensions. The particles, as obtained from Bangs Laboratory, were in solutions that contained a fraction of solids. To obtain a desired concentration of these particles, the solution was weighed to select the proper amount of solids and then diluted in a volumetric flask to adjust the volume. The particles were initially prepared in high concentration stock solutions, so that dilution could be made to various concentrations for characterization and experimentation.
A general schematic of the magnetic-seeding separation process is shown in Figure 2. Turbulent-shear flocculation was carried out in a standard stirred tank of 100 mm diameter, 142.2 mm height, and equipped with four baffles, each 10 mm wide. The initial volume of the suspension used in each experiment was 600 mL. The mixture was stirred by a 6-blade impeller, 50 mm in diameter, with adjustable agitation speed. The agitation was produced by a Stir-pak motor, model 50002-40 (Cole-Parmer Instrument Co. Niles, IL). The filtration process was started after 5 or 10 minutes, to allow for flocculation of polystyrene particles with seeding polystyrene (paramagnetic) particles. The interval between flocculation and filtration is defined as “dead time.” The mixture from the stirred tank was pumped through 1/16-in. ID, 1/8-in. OD tubing by a Master Flex pump (Cole-Parmer Instrument Co. Chicago, IL). The filter used in these experiments was a 10-mm ID and 105-mm length glass tube of total volume 9.6 mL (including the space between fittings). Nickel wire of diameter 62.5 µm was cut into 5-mm pieces and randomly packed in the filter. The packing fraction was varied between 1% and 14% and the filter length was 100 mm. The filter was held in an aluminum housing and situated at the center of a bipolar magnet (Applied Magnetics Laboratory Inc., Baltimore, MD). The minimum gap between the two poles was 2 in., but a ferromagnetic disc was used to decrease it further to 0.75 in. in order to hold the filter aluminum housing firmly. A 15-mL sample from the outflow was taken periodically for effluent concentration analysis. The concentration was analyzed by a light scattering setup using a correlator (Model 1096, Langley Ford Instruments, Amherst, MA).
II.3 Breakthrough Experiments of Magnetic Filtration

The breakthrough experiments were conducted using only paramagnetic particles in order to simplify the system. Two types of paramagnetic particles were used: (1) seeding polystyrene latex; and (2) black iron oxide (magnetite) seed particles. Black iron oxide seed particles were supplied by Polysciences, Inc. (Warrington, PA) in powder form. Some properties of these two type paramagnetic particles are also listed in Table I. In order to obtain a desired concentration, the particles were weighed and suspended using the method suggested by Lee et al. (1996). The filter material and method of preparation were the same as described in the Section II.2, and the wire packing fraction was 5% (about 0.04 mL). The zeta potential of these paramagnetic particles was high (> 50 mV) under high pH (> 10) and low ionic strength (< 0.001M) conditions. The suspension was prepared under these conditions in order to prevent the particles from flocculation. Thus, the flocculation process was not included in these experiments. The other conditions were the same as described in Section II.2. The solution was pumped through a 5-mm ID tubing into the filter and effluent samples were collected periodically for concentration analysis.

II.4 Magnetic-Seeding Brownian Flocculation and Magnetic Filtration

Polystyrene latex and seeding polystyrene latex particles were used to study the effects of magnetic-seeding processes on the breakthrough of magnetic filtration. To simplify the complicated situation of a wide range of particle size and magnetic susceptibility distributions resulting from turbulent-shear flocculation, Brownian flocculation was investigated. Equipment and operating procedures were similar to shear
flocculation experiments, except the flocculation processes. Both polystyrene latex and seeding polystyrene latex solutions were prepared under high pH (>11) condition. After mixing them together, the solution pH was adjusted to around 3 at which the surface charge of particles is about zero for Brownian flocculation. After a period of flocculation, the solution pH was adjusted back to high pH (>10) to stop the flocculation process and then the solution was pumped through a 5-mm ID tubing to the filter. The filter was prepared in the same way as described in the Section II.2. Samples collected from the influent solution were analyzed by a light scattering instrument (Coulter LS 130, Langley Ford Instruments, Amherst, MA) for particle size distribution. Also, samples were collected from the effluent solution for concentration analysis using light scattering intensity measurements.
CHAPTER III

THEORY OF MAGNETICALLY-SEEDING FILTRATION OF COLLOIDAL PARTICLES

Various models of magnetic separation have been formulated based on the interaction between a particle and a collector. These models are used to predict the filtration efficiency of the collector and investigate the effects of various parameters on the performance of magnetic filtration. A limitation of these models, however, is that to a large extent they depend on empirical coefficients or parameters and therefore constrain themselves to specific circumstances.

In this chapter, a systematic approach describing particle captured by a single-wire, particle loading on a single-wire, and breakthrough of particles from the magnetic filter is investigated. Finally, a mathematical model combined with the bivariate population-balance equation is introduced to predict the magnetically seeded separation process without the use of fitting parameters or empirical coefficients.
III.1 Theory of Single-Particle/Single-Wire Trajectory Model

III.1.1 Limiting Trajectory and Geometric Configurations

Trajectories of a particle approaching the surface of a single-wire in a magnetic field have been investigated as a fundamental study for understanding the interaction between a particle and a collector. The exact path that divides the approaching particle trajectories into those leading in particle capture by the collector and those passing by the collector is called the limiting trajectory. As shown in Fig. 3, the distance between the limiting trajectory and the axis is the critical radius \( R_c \).

In the present study, particle diffusion and surface forces are not significant unless particle size is ultra-fine (\(<1 \mu m\)) and, thus, they are not included in modeling considerations. The trajectory equation is then determined by the force balance equation which includes inertial, gravitational, magnetic, and hydrodynamic drag forces.

Three possible geometric configurations between the directions of particle flow and magnetic field with respect to the wire are illustrated in Fig. 4. In Fig. 4, the wire is placed along the z-axis and a uniform magnetic field \( (H_0) \) which is always assumed orthogonal to the wire if applied in the x direction. The first arrangement (longitudinal orientation, L) is when the flow velocity is parallel to the external magnetic field, the second one (transverse orientation, T) is when the flow velocity is perpendicular to the magnetic field, and the third one (axial orientation, A) is when the flow velocity is parallel to the wire axis. A general coordinate system of a particle-wire interaction is shown in Fig. 5 where \( a \) is the wire radius, \( b \) is the particle radius, and \( V_0 \) is the flow velocity (Svoboda, 1987, p. 239-240).
III.1.2 Magnetic Force

The magnetic force, \( \vec{F}_m \), applied on a small spherical paramagnetic particle placed in a magnetic field is given by (Svoboda, 1987, p. 4):

\[
\vec{F}_m = \frac{\mu_0 \chi_p V}{1 + \frac{\chi_p}{3}} \left( \vec{H} \nabla \right) \vec{H}
\]

[1]

where \( \mu_0 = 4\pi \times 10^{-7} \text{ H/m} \) is the permeability of free space, \( \chi_p \) is volume magnetic susceptibility of a particle, \( \vec{H} \) is the magnetic field, and \( V \) is the particle volume. If \( \chi_p \ll 1 \), eq. [1] can be simplified as follows

\[
\vec{F}_m = \frac{1}{2} \mu_0 \chi_p V \nabla (H^2)
\]

[2]

The magnetic field strength \( H \) that consists of the external magnetic field strength (\( H_0 \)) and the magnetization of the wire (\( M \)) is given by

\[
H = H_0 + H_0 K \frac{a^2}{r^2}
\]

[3]

where, for \( H_0 < H_s \), \( K = 1 \), for \( H_0 > H_s \), \( K = M_s/2H_0 \), \( a \) is the radius of the wire, and \( r \) is the distance from the center of the wire to the center of the particle. Generally, the magnetization increases as the external magnetic field strength increases until the external
field is larger than the wire saturation value $H_s$, in which case the magnetization ($M$) of the wire will be constant and equal to the saturation magnetization ($M_s$). The first term in eq. [3] is the external magnetic field strength $H_0$ and the second term is the magnetization of the wire whose saturation value is $H_s$. Combining eqs. [2] and [3], the components of magnetic force, $F_{mr}$ and $F_{m\theta}$, in polar coordinates, $r$, $\theta$, are obtained as

$$F_{mr} = \frac{4pm_0 \kappa_p Ma^2 b^3}{3r^3} \left( \frac{Ma^2}{2r^2} + H_0 \cos 2\theta \right)$$  \hspace{1cm} [4a]

$$F_{m\theta} = -\frac{4\pi \mu_0 \chi_p Ma^2 b^3}{3r^3} H_0 \sin 2\theta$$  \hspace{1cm} [4b]

### III.1.3 Hydrodynamic Drag Force

The hydrodynamic drag force ($\vec{F}_d$) acting on a moving particle can be expressed by Stokes equation. The components of this drag force, $F_{dr}$ and $F_{d\theta}$, can be written as (Svoboda, 1987, p. 247-248)

$$F_{dr} = 6\pi \eta \rho \left( V_r - \frac{dr}{dt} \right)$$  \hspace{1cm} [5a]

$$F_{d\theta} = 6\pi \eta \rho \left( V_\theta - r \frac{d\theta}{dt} \right)$$  \hspace{1cm} [5b]
where \( \eta \) is the fluid dynamic viscosity and \( dr/dt \) and \( r\theta/dt \) are the components of fluid velocity at position \( r \). \( V_r, V_\theta \) are the components of particle velocity given as follows, by assuming that the flow is laminar:

\[
V_r = V_0 \frac{\ln\left(\frac{r}{a}\right) - 0.5 \left[1 - \left(\frac{a}{r}\right)^2\right]}{2.002 - \ln \Re} \cos(\theta - \gamma) \tag{6a}
\]

\[
V_\theta = -V_0 \frac{\ln\left(\frac{r}{a}\right) + 0.5 \left[1 - \left(\frac{a}{r}\right)^2\right]}{2.002 - \ln \Re} \sin(\theta - \gamma) \tag{6b}
\]

where \( \Re \) is the Reynolds number given by

\[
\Re = \frac{2V_0 \rho_f a}{\eta} \tag{7}
\]

### III.1.4 Gravitational and Inertial Forces

The components of the gravitational force (\( \vec{F}_g \)) in polar coordinates, \( F_{gr} \) and \( F_{g\theta} \), can be written as (Svoboda, 1987, p. 248)

\[
F_{gr} = \frac{4\pi b^3}{3} \left(\rho_p - \rho_f\right) g \cos(\theta - \beta) \tag{8a}
\]

\[
F_{g\theta} = \frac{4\pi b^3}{3} \left(\rho_p - \rho_f\right) g \sin(\theta - \beta) \tag{8b}
\]
where \( g \) is the gravitational acceleration and \( \rho_p \) and \( \rho_f \) are the particle and fluid densities, respectively.

The components of the inertial force (\( \vec{F}_i \)) in polar coordinates, \( F_r \) and \( F_\theta \), can be written as (Svoboda, 1987, p. 248)

\[
F_r = \frac{4\pi b^3 \rho_p}{3} \left[ \frac{d^2 r}{dt^2} - r \left( \frac{d \theta}{dt} \right)^2 \right] \\
F_\theta = \frac{4\pi b^3 \rho_p}{3} \left[ r \frac{d^2 \theta}{dt^2} + 2 \frac{dr}{dt} \frac{d\theta}{dt} \right]
\]

III.1.5 Trajectory Equation

The particle motion in a magnetic separator can be described by the force balance equation as

\[
\vec{F}_i = \vec{F}_d + \vec{F}_m + \vec{F}_g
\]

For low Reynolds numbers and laminar flows, such as the ones occurring in the magnetic filter, the inertial force is much smaller than the other forces and can be neglected. Thus, the radial and azimuthal components of the force balance equation can be rewritten as

\[
\frac{dr}{dt} = G \cos(\theta - \beta) + \frac{V_r}{a} - \frac{V_m}{a} \left( \frac{M}{2H_0} \frac{1}{R^5} + \frac{\cos 2\theta}{R^3} \right)
\]
\[ R \frac{d\theta}{dt} = -G \sin(\theta - \beta) + \frac{V_\theta}{a} - \frac{V_m \sin 2\theta}{R^3} \]  \hspace{1cm} [11b]

where \( R = r/a \) and

\[ G = \frac{2b^2 (\rho_p - \rho_f)}{9 \eta a} g \]  \hspace{1cm} [12a]

\[ V_m = \frac{2b^2 \mu_0 \chi_p MH_0}{9 \eta a} \]  \hspace{1cm} [12b]

By combining eqs. [11a] and [11b] the time-independent trajectory equation can be obtained as

\[ \frac{dR}{d\theta} = R \left( \frac{G \cos(\theta - \beta)}{a} - \frac{V_m}{a} \frac{M}{2H Ho R^5} \frac{1 + \cos 2\theta}{R^3} \right) - \frac{G \sin(\theta - \beta)}{a} - \frac{V_m \sin 2\theta}{R^3} \]  \hspace{1cm} [13a]

It is found that, if a particle is small enough, the gravitational force is insignificant, and can be neglected. By substituting eqs. [6a] and [6b] into eq. [13a], eq. [13a] can be rewritten as

\[ \frac{dR}{dq} = R \left( \frac{\ln(R) - 0.5(1 - R^{-2})}{2.002 - \ln 9R} \cos(\theta - \gamma) - \frac{V_m}{V_o} \frac{M}{2H Ho R^5} \frac{1 + \cos 2\theta}{R^3} \right) - \frac{\ln(R) + 0.5(1 - R^{-2})}{2.002 - \ln 9R} \frac{\sin(\theta - \gamma)}{V_o} \frac{V_m \sin 2\theta}{R^3} \]  \hspace{1cm} [13b]

19
Equation [13b] becomes a function of $V_m/V_0$ and $M/2H_0$. From eq. [13b], it is seen that $M/2H_0$ varies as $R^{-5}$, which means that this term is only important when a particle is near the wire. Therefore, the capture efficiency is mainly determined by $V_m/V_0$, and not by $V_m$ or $V_0$ separately. Solving this trajectory equation by numerical methods, one can obtain the limiting trajectory and the critical radius which determine whether a particle will be captured by a wire collector or not.

III.1.6 Removal Efficiency for a Clean Filter

Consider a high gradient magnetic separator matrix of length $L$, packed randomly with wire and having packed fraction $(1-\varepsilon)$. Then, the length of the wire in a differential section $dx$ of the filter per unit cross section area of the wire is $(1-\varepsilon)dx/\pi a^2$. Due to the random nature of the matrix, approximately two-thirds of the wire are considered effective for particle capture (the other one-third is assumed to be distributed along the direction of the field). Thus, the available cross section area for capture is $4R_c a/3$ and the effective area is $4(1-\varepsilon)R_c dx/3\pi a$. The accumulation rate of particles onto the matrix over $dx$ is then given as

$$\frac{\partial N}{\partial x} = -\left[\frac{4(1-\varepsilon)R_c}{3\pi a}\right] N$$  \hspace{1cm} [14]

where $N$ is the number of particles per unit volume. By solving eq. [14], the removal efficiency for a clean filter can be obtained as
Removal efficiency = \( 1 - \frac{N_{\text{out}}}{N_{\text{in}}} = 1 - \exp \left( -\frac{4(1 - \varepsilon)LR\varepsilon}{3\pi a} \right) \) \[15\]

III.2 Theory of Particle Build-Up Model

The dynamic behavior of a small paramagnetic particle approaching a single ferromagnetic wire in a magnetic field has been analyzed by a particle trajectory method in Section III.1. The trajectory model, however, is limited for a clean wire. Once particles are deposited on the surface of matrix elements or onto particles already deposited, changes in the surface characteristics of the collector will affect subsequent capture of particles.

To investigate the dynamic behavior of particle buildup, it is necessary to examine forces acting on the particles first. The forces that are mainly responsible for the particle retained on the matrix are magnetic and hydrodynamic forces. Figure 6 shows the force components acting on a particle on a wire surface (Nesset and Finch, 1979). For a particle to remain attached on a wire, the net forces in both the radial and tangential directions should be negative. Equations [16a] and [16b] give the expressions of force components acting in radial and tangential directions,

\[ F_{r(\text{net})} = F_{mr} + F_{gr} \] \[16a\]

\[ F_{\phi(\text{net})} = F_{m\phi} + F_d \] \[16b\]
where $F_{r(\text{net})}$, $F_{mr}$, and $F_{gr}$ are net, magnetic, and gravitational forces in the radial direction, respectively. $F_{\phi(\text{net})}$, $F_{m\phi}$, $F_d$ are net, magnetic, and drag forces in the tangential direction, respectively. The magnetic and gravitational forces are given by eqs. [4a], [4b], and eqs. [8a], [8b], respectively. The fluid drag force that is acting on the surface of a spherical particle can be expressed by (Nesset and Finch, 1979)

$$F_d = f_a 4\pi b^2 \tau_0$$  \[17\]

where $f_a$ represents the integrated effect of shear stress $\tau_0$ acting over the upper half of the sphere only, and if $\tau_0$ is assumed constant then $f_a$ is equal to $\pi/8$. The value of shear stress ($\tau_0$) can be determined by the form of Blasius series

$$\tau_0 = \rho_f \sqrt{\frac{V_0^3}{8\pi}} \left(9.861\phi - 3.863\phi^3 - 0.061\phi^7 \ldots\right)$$  \[18\]

where $\nu$ is the kinematic viscosity and $\phi$ is given in radians.

As illustrated in Fig. 7 (Nesset and Finch, 1979), the region of particle attraction about the wire can be determined by solving eqs. [16a] and [16b] for the conditions $F_r = 0$ and $F_\phi = 0$. Assuming that the particles are small enough that the gravitational force can be ignored, the build-up radius can be found by a force balance in azimuthal direction:

$$r_b = \left(\frac{\mu_0 \chi_p MBa^2 H_0 \sin(2\theta)}{3f_a \rho f V_0^{1.5} \nu^{0.5} 0.125^{0.5} B(\phi)}\right)^{0.4}$$  \[19\]
where $B(\phi)$ represents the Blasius series. The volume of particle build-up per unit volume of a wire, $V_L$, can then be obtained

$$V_L = \frac{\sigma}{4} \left( \frac{r_b}{d} \right)^2 - 1$$

where $\sigma$ is the porosity of the loading volume. The filter saturation concentration ($C_s$), defined as the retained particle mass per unit bulk volume in the filter, is expressed as

$$C_s = V_L \times \text{effective wire volume} / \text{bulk volume in the filter}$$

### III.3 Breakthrough Model

In contrast to the trajectory and particle build-up models in which the behavior between a single particle and a single wire is studied, the breakthrough model is developed to investigate the distribution of particles in a filter.

Considering particles traveling through a filter as illustrated in Fig. 8, one can obtain the mass balance of particles entering and leaving a differential element $dx$ by a macroscopic conservation equation and a rate equation as follows (Svoboda, 1987, p. 278)

$$\frac{\partial N(x,t)}{\partial t} = V_0 \frac{\partial C(x,t)}{\partial x}$$
and

$$-\left( \frac{\partial C}{\partial x} \right)_t = \lambda C$$ \hspace{1cm} [23]$$

where \( N(x, t) \) is the number of captured particles between \( x \) and \( x+dx \) at time \( t \), \( C(x, t) \) is the number of suspended particles at point \( x \), \( V_0 \) is the superficial velocity of a suspension, \( L \) is the filter length, and \( \lambda \) is the filter coefficient with dimensions of reciprocal length, \( \lambda = 1/L \), where \( l \) is the characteristic filtration length of the matrix material.

The solution of the rate equation (eq. [23]) can be written as

$$\frac{C(x)}{C_{in}} = \exp(-\lambda x)$$ \hspace{1cm} [24a]$$

$$\frac{C_{out}}{C_{in}} = \exp(-\lambda L)$$ \hspace{1cm} [24b]$$

where \( C_{in} \) and \( C_{out} \) are the influent and effluent concentrations. From eq. [24b], it is obvious that \( \exp(-\lambda L) \ll 1 \) (or \( L \gg l \)) for an efficient filtration to be achieved.

During the filtration processes, particles are continuously captured onto the collector surface from the suspension. The rate of trapped particles can then be written as
\[
\frac{dN(x, t)}{dt} = V_0 \lambda C(x, t)
\]  

[25]

If we assume that the collectors were clean at time \( t = 0 \), then

\[
N(x, t) = N(0, t) \exp(-\lambda x)
\]  

[26]

where \( N(0, t) \) is defined as the concentration \( N(x, t) \) at point \( x = 0 \). If \( \lambda \) is assumed to be constant and greater than zero before \( N(0, t) \) reaches the saturation concentration \( C_s \) of the matrix material, the saturation time is obtained as

\[
t_s = \frac{C_s}{C_{in}} \frac{1}{\lambda V_0}
\]  

[27]

Once the front end of the filter has become saturated, both \( C(x, t_s) \) and \( N(x, t_s) \) decrease exponentially with position \( x \) from the inlet to the outlet end of the filter. Also, the active length of the matrix decreases as a function of time (Collan et al., 1978),

\[
x_s(t) = \left( \frac{C_{in}}{C_s} \right) V_0 t
\]  

[28]

where the term \( \frac{C_{in}}{C_s} V_0 \) is defined as the saturation velocity \( V_s \) and \( x_s \) is the saturated length of the matrix. The concentration profiles \( C(x, t) \) and \( N(x, t) \) can be written as

\[
C(x, t) = C_{in} \exp\left[(x_s - x)\lambda \right]
\]  

[29a]
and

\[ N(x,t) = C_s \exp [(x_s - x)\lambda] \]  \hspace{1cm} [29b]

Considering the total length \( L \) of a filter, one can express the breakthrough curve by the effluent concentration as a function of time,

\[ C_{out}(t) = C_{in} \exp(-\lambda L) \quad \text{for} \quad t < t_s \]  \hspace{1cm} [30a]

and

\[ C_{out}(t) = C_{in} \exp[(V_0 t - L - l)\lambda] \quad \text{for} \quad t_{total} > t > t_s \]  \hspace{1cm} [30b]

As assumed above, the filter coefficient \( \lambda \) is constant until \( t > t_s \), so the effluent concentration remains constant before the filter becomes saturated. After the front end of the matrix becomes saturated, the output concentration increases until the filter reaches full saturation at time \( t_{total} = t_s + \left( L/V_s \right) \).

III.4 Magnetically-Seeded Separation

The microscopic or macroscopic models mentioned in the previous sections were studied for uniform particles in terms of their magnetic susceptibility. However, in real systems of magnetic-seeding processes, where seeding magnetic particles are added to flocculate with non-magnetic particles and form aggregates of significant magnetic
susceptibility, particles and flocs have varying sizes and magnetic susceptibilities. The bivariate population-balance (PB) equation (Tsouris et al., 1995) is able to give the size and magnetic susceptibility distribution of particles in a suspension. In order to enhance the applicability of the magnetic filtration model, which has been described in Section III.3, to more complex conditions, it is necessary to combine it with the bivariate PB equation.

The basic concept of the magnetic-seeding process is to have weakly magnetic or non-magnetic particles flocculate with paramagnetic particles to form paramagnetic flocs and then remove those flocs from suspensions by using magnetic filtration. In the present work, a Brownian flocculation batch system is studied and it is assumed that the particles and flocs are spherical. The bivariate PB equation for such a system is given by (Tsouris et al., 1995)

\[
\frac{dn_{ij}}{dt} = \frac{1}{2} \sum_{i=1}^{N_s} \sum_{m=1}^{N_{s}} n_{lm} n_{(i-1)(j-m)} F_{im,(i-1)(j-m)} - \sum_{i=1}^{N_s} \sum_{m=1}^{N_{s}} n_{ij} n_{lm} F_{ij,lm} \tag{31}
\]

where \( n_{ij} \) is the number of particles of size \( i \) and magnetic susceptibility \( j \) (class \( ij \)), \( t \) is the time, \( F_{ij,lm} \) is the flocculation frequency of particles in class \( ij \) with particles in class \( lm \), and \( N_s, N'_s \) are the total numbers of size and initial magnetic susceptibility classes, respectively. In eq. [31], the left-hand side of the equation presents the accumulation for particles of size \( i \) and magnetic susceptibility \( j \), the first term on the right-hand side is a source term due to flocculation of smaller particles, and the second term on the right-hand side presents a loss term due to flocculation to larger particles.
The flocculation rate of particles in classes $ij$ and $lm$ is defined as

$$F_{ij,lm} = \beta_{ij} (r_i, r_j) E_{ij,lm} (r_i, \chi_j, r_j, \chi_m)$$  \hspace{1cm} [32]$$

where $\beta_{ij}$ is the particle collision frequency, $E_{ij,lm}$ is the collision efficiency, $r_i$, $r_j$ are the radii of the particles, and $\chi_j$, $\chi_m$ are the magnetic susceptibilities of the particles. As shown by eq. [32], only the collision efficiency $E_{ij,lm}$ depends on the particle interaction forces. In the Brownian flocculation mechanism, the particle collision frequency is given by (Chandrasekhar, 1943):

$$\beta_{ij} = \frac{2}{3} \frac{kT (r_i + r_j)^2}{\eta r_i}$$  \hspace{1cm} [33]$$

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ is the viscosity of the surrounding phase. Also, in the Brownian diffusion regime, the collision efficiency is written as

$$E_{ij,lm} = \left\{ \left( 1 + \frac{r_j}{r_i} \right) \sum_{(1+\eta/\eta)}^{\infty} \left( D_\infty / D_{ij} \right) \exp \left[ V \left( r_i, \chi_j, r_j, \chi_m \right) / kT \right] \frac{ds}{s^2} \right\}^{-1}$$  \hspace{1cm} [34]$$

where $D_\infty$ is the diffusivity in the absence of interparticle forces and is expressed as

$$D_\infty = \frac{kT}{6\pi \eta} \frac{r_j + r_i}{r_i r_j}$$  \hspace{1cm} [35]$$
The relative diffusivity coefficient $D_{il}$ in eq. [34] represents the hydrodynamic force acting on particles $i$ and $l$ as they approach each other and is given by

$$D_{il} = b^* kT$$ \[36\]

where $b^*$ is the relative mobility. The particle interaction potential $V_A$ represents the forces acting on the flocculation of particles and is the summation of van der Waals ($V_{vdw}$), electrostatic ($V_{el}$), and magnetic dipole ($V_{mag}$) potentials:

$$V_A = V_{vdw} + V_{el} + V_{mag}$$ \[37\]

These potentials are given in the form of simple mathematical formulas as follows (Hamaker, 1937)

$$\frac{V_{vdw}}{kT} = -\frac{A}{6kT} \left\{ \frac{2r_i r_j}{r^2 - (r_i + r_j)^2} + \frac{2r_i r_j}{r^2 - (r_i - r_j)^2} + \ln \left[ \frac{r^2 - (r_i + r_j)^2}{r^2 - (r_i - r_j)^2} \right] \right\}$$ \[38\]

where $A$ is the Hamaker constant and $r$ is the distance between the centers of the particles $i$ and $l$. The electrostatic potential is given by (Hogg et al., 1966)

$$V_{el} = \frac{\varepsilon^* r_i r_j (\psi_{0i}^2 + \psi_{0l}^2)}{4(r_i + r_j)} \left\{ \frac{2\psi_{0i} \psi_{el}}{\psi_{0i}^2 + \psi_{0l}^2} \ln \left[ \frac{1 + \exp(-\kappa \lambda_0)}{1 - \exp(-\kappa \lambda_0)} \right] + \ln \left[ 1 - \exp(-2\kappa \lambda_0) \right] \right\}$$ \[39\]
where $\varepsilon^*$ is the dielectric constant ($\varepsilon^* = 89 \times 10^{-10} \, \text{CV}^{-1} \, \text{m}^{-1}$ for water), $\psi_{oi}$, $\psi_{ol}$ are the surface potentials of the particles $i$ and $l$, respectively, $\kappa$ is the inverse Debye-Huckel length, and $\lambda_o$ is the shortest distance between the surface of the particles. The magnetic dipole potential can be written as (Chikazumi, 1964)

$$
V_{\text{mag}} = \left( \frac{1}{6} \pi d_i^3 \chi_i B \right) \left( \frac{1}{6} \pi d_l^3 \chi_l B \right) \frac{4 \pi \mu_0 r^3}{\left[ (\hat{\mu}_i \cdot \hat{r}) (\hat{\mu}_l \cdot \hat{r}) \right] \left( 3 (\hat{\mu}_i \cdot \hat{r}) - 3 (\hat{\mu}_l \cdot \hat{r}) \right]} \tag{40}
$$

where $d_i, d_l$ are the diameters of the particles, and $B$ is the magnetic field strength. A simple formula for the average magnetic potential has been derived by Chan et al. (1985) by investigating the potential in all directions:

$$
\frac{V_{\text{mag}}}{kT} = s(x) \left[ -\frac{x^2}{3} \left( \frac{1}{1 + \left( x^2 \right)^{150}} \right) \right] + \left[ 1 - s(x) \right] \left[ -2x + \ln(6x^2) - \frac{2}{3x} - \frac{7}{9x^2} \right] \tag{41}
$$

where

$$
s(x) = \exp \left[ -\ln(2) \left( \frac{x}{2.4} \right)^8 \right], \quad x = \frac{1}{kT} \frac{\pi d_i^3 x_j d_l^3 x_m B^2}{144 \mu_0 r^3} \tag{42}
$$

The collision efficiency $E_{ij, lm}$ can then be calculated by eq. [34] as a function of particle size, hydrodynamic forces, magnetic field, magnetic susceptibility, van der Waals, and electrostatic potentials. By combining eqs. [34] and [33], the Brownian flocculation frequency can be obtained and then the bivariate PB equation can be solved.
by using eqs. [31] and [32]. In this work, Brownian flocculation occurred in the absence of a magnetic field, thus $V_{mag}$ in eq. [37] was zero.
CHAPTER IV

RESULTS AND DISCUSSION

This chapter is divided into three sections:

1) experimental results and discussion,

2) modeling results and discussion, and

3) comparison between modeling and experiments.

In the first section, the experiments carried out in this work are classified into three categories: (1) magnetic-seeding, shear flocculation, and magnetic filtration; (2) breakthrough of magnetic filtration; and (3) magnetic-seeding, Brownian flocculation, and magnetic filtration. The effects of various parameters, such as particle properties including size, magnetic susceptibility, and seeding-particles concentration, and operating conditions including magnetic-field strength, suspension flow rate, and dead time, on the performance of magnetic filtration are investigated.

In the second section, modeling work that includes trajectory analysis, a particle build-up model, a breakthrough model, and a bivariate population-balance model is discussed. For each model, a sensitivity analysis was conducted and the effects of model parameters were examined.
In the third section, modeling results were compared with experimental data. Two sets of experiments were conducted: 1) magnetic filtration of paramagnetic particles; and 2) magnetic-seeding filtration including Brownian flocculation and magnetic filtration.

IV.1 Experimental Results and Discussion

Experimental work was carried out to investigate the effect of various factors on the removal efficiency of magnetic separation, and the breakthrough of magnetic filtration with or without magnetic-seeding. All the experimental condition and results are shown in Appendix I.

Reproducibility: Shear-flow flocculation and magnetic filtration experiments were conducted using polystyrene latex and seeding polystyrene-magnetite latex particles. The reproducibility of removal efficiency vs. time was examined for varying pH, seeding particle concentration, and ionic strength. The results are shown in Fig. 9. A good reproducibility was found under a wide range of conditions. The differences observed in Fig. 9 (d) are due to the difference in pH. Also, at some conditions, the removal efficiency was found to increase with time. This behavior reveals the effect of heterogeneous flocculation kinetics between non-magnetic and magnetic seeding particles. Since the flocculation tank is operated in batch mode, as time increases, more polystyrene particles are seeded with paramagnetic particles leading to an increasing in removal efficiency. Some of the results, where the removal efficiency does not increase with time (e.g., Fig. 9 (f)), indicate that the particles do not flocculate. In summary, from Fig. 9, the maximum relative error of data obtained at similar conditions is 23%.
**Magnetic field strength:** The effect of the magnetic-field intensity on the separation of polystyrene particles was studied by varying the magnetic field strength between 0.18 and 0.81 Tesla. Figure 10 (a) shows a minor effect of the magnetic field on the removal of polystyrene particles, indicating that the flocculation rate is high enough to form large flocs that are efficiently removed by the magnetic filter which works like a conventional filter. The fact that an increase in the magnetic field did not enhance the separation means that those particles that escaped the filter in the absence of the field did not flocculate with the seed particles. The effect of the magnetic field strength is observed to be stronger in Fig. 10 (b), where the particles to be separated are approximately 45 times bigger in volume than the seed particles, suggesting that almost all large particles have flocculated with magnetic seed particles. Figures 10 (a) and (b) indicate that as the ratio of the seed particle diameter to the process particle diameter is decreased, the chances for successful seeding are increased. A smaller concentration of magnetic seed particles was used in the experiments presented in Fig. 10 (c). The results show a consistent effect of the magnetic field on the separation efficiency. The low separation efficiency observed in the absence of the magnetic field indicates that the flocculation rate is low, although the pH is close to the point of zero charge (PZC) for these particles. This behavior should be examined further in order to understand the difference between the results of Figs. 10 (a) and (c) in the absence of the magnetic field.

Figure 10 (d) shows the results of magnetic separation of only seeding polystyrene particles. The results of Fig. 10 (d) show a minor effect of magnetic field strength on the removal efficiency of paramagnetic particles. Since suspension flow rate was high (14
mL/min) and the filter length was short (10 mm), it is possible that the difference of magnetic field strength (0.2 T to 0.4 T) could not affect the removal efficiency to an appreciable extent.

**Particle size:** The effect of polystyrene particle size on the removal efficiency was significant. Table I presents the physical properties of five different size polystyrene particles used in this study. Figure 11 shows that the larger the polystyrene particle size, the higher the removal efficiency. The reason for this behavior is that the collision frequency increases as the particle size increases due to higher cross sectional area of the particles. On the other hand, the number of larger particles per gram is smaller than the number of smaller particles, therefore, there is higher probability for the large particles to flocculate with seed particles and thus the removal efficiency increases as the size of particles to be separated increases.

**Flow rate:** Figure 12 (a) shows the effect of flow rate on the removal efficiency of magnetic filtration. No significant difference was found when the flow rate was increased from 5 mL/min to 10 mL/min, as the magnetic field strength was held constant at 0.8 Tesla. A lower removal efficiency was observed at 15 mL/min flow rate. Thus, it appears that there is a threshold flux value above which removal efficiency decreases.

Figure 12 (b) shows the results of the magnetic filtration experiments only using paramagnetic particles. The experiments were conducted by varying flow rate from 14 mL/min to 22.5 mL/min. From Fig. 12 (b), it is found that the removal efficiency increases as the flow rate decreases.
Dead time: In order to increase the removal efficiency of the process particles, it is necessary to allow polystyrene and seed particles to flocculate for some time after contact. This time is defined as dead time. From the size measurements of the flocs, it was found that most of the shear-flow flocculation occurred in the first five minutes. Therefore, as shown in Fig. 13, the separation efficiency was unchanged by changing the dead time from 5 minutes to 10 minutes. However, the removal efficiency was increasing as filtration progressed even though most flocculation happened in the first five minutes. A possible reason is that the particles and flocs that captured by the filter become part of the filter and help in the removal of other particles due to increasing fiber diameter with along decreasing filter porosity (increased filter packing).

Magnetic susceptibility: The effect of particle magnetic susceptibility on the separation performance was studied by using 100 ppm black iron oxide seed particle or seeding polystyrene latex. The volume magnetic susceptibilities of black iron oxide and seeding polystyrene particles are 0.02 and 0.0059, respectively. Since the magnetic susceptibility of black iron oxide is much larger than that of seeding polystyrene particles, it is readily understood that the magnetic force working on a black iron oxide particle is larger than that on a seeding polystyrene particle of the same size under the same magnetic field strength. From Fig. 14, it was found that even at a higher flow rate, the effluent concentration of black iron oxide seed particles was much lower than that of seeding polystyrene particles before breakthrough occurred. Due to the high removal efficiency and high flow rate of black iron oxide particles, the filter was easily saturated, and, as
expected, the breakthrough of black iron oxide happened much earlier than that of the seeding polystyrene latex particles.

Seed particle concentration: Figure 15 shows the experimental results of the removal of polystyrene particles by shear-flow flocculation and magnetic filtration. The effect of seed particle concentration is studied for various values of the pH. It is found that there is an optimum seed particle concentration at which the removal efficiency is maximum. Figure 15 shows that the removal efficiency using 50 ppm seed particles was higher than other concentrations at pH 3 and 6, but at higher pH, the best separation occurred when 100 ppm seed particles were used (see Fig. 15 (c)). The possible reason for such results is that the zeta potential of seed particles becomes more negative and the repulsive electrostatic potential (i.e., the barrier for particle flocculation) increases as the concentration of seed particles increases. On the other hand, higher concentration of the seed particles increases the collision efficiency between seed and process particles. Thus, there are two competing trends related to the seed particle concentration.

A set of experiments in which polystyrene particles were removed by Brownian flocculation and magnetic filtration was conducted by using different seed particle concentrations with different sizes. As shown in Fig. 16, 0.6 µm and 1.2 µm seed particles were used at 50 ppm and 10 ppm concentrations, respectively. Although larger size seed particles were used, a lower seed particle concentration decreases the collision efficiency between seed particles and process particles. Therefore, the removal efficiency of 10 ppm seed concentration was found to be lower than that of 50 ppm seed particle concentration.
IV.2 Modeling Results and Discussion

There are four parts of modeling results discussed in this section. First, the effects of various parameters on the particle trajectory and the removal efficiency of magnetic filtration is presented. Then, the particle build-up model is discussed for varying operating conditions. By combining the trajectory and particle build-up models, the simulations of magnetic filtration breakthrough curves for particles of uniform size and magnetic susceptibility are demonstrated in the third part. Finally, the bivariate population-balance model was studied to predict the particle size and magnetic susceptibility distributions resulted from Brownian flocculation in the magnetic-seeding filtration process.

The calculations of the trajectory model were computed on a SUN ULTRA 1-140 workstation, configured with 64 MB of memory, while the calculations of the bivariate population-balance model were computed on an IBM RS/6000 model 360 workstation, configured with 64 MB of memory. The code of trajectory model was modified from a magnetic flocculation model (Yiacoumi et al., 1996). An ordinary differential equation solver with variable step (EPISODE; Hindmarch and Byrne, 1976) was employed to solve the trajectory equations and population balance equation presented in the trajectory and bivariate models, respectively.

IV.2.1 Trajectory Model

In order to simulate experimental conditions, all the results obtained from the trajectory model assumed that the initial velocity is perpendicular to the external
magnetic field, i.e. parallel to y axis, and the magnetic field is in the same direction as gravity. Also, a laminar flow was assumed for all the modeling work.

**Limiting trajectory:** The exact path that divides the approaching particle trajectories stopping in capture on the collector surface from those passing by is called the limiting trajectory, and the distance between the limiting trajectory and the y axis is the critical radius \( R_c \). Figure 17 shows the results of typical trajectory calculations for laminar flow. The parameters of the calculations are given in the figure caption. From Fig. 17, it is observed that if the initial approach position is within the critical radius, the particle will be captured, otherwise the particle will be swept away. The results of the effect of particle size on the limiting trajectory are shown in Fig. 18. From Fig. 18, it is found that the critical radius increases as the particle size is increased. It is because the magnetic force increases with an increase in particle size. Figure 19 shows the effect of particle size on the particle trajectory and collision with the collector. In Fig. 19, the initial approach position is the limiting trajectory for particle size 0.5 µm, and as expected, particles with sizes larger than 0.5 µm starting from the same initial position will be captured, while particles with sizes smaller than 0.5 µm will move away.

**Particle size:** Figure 20 shows the effect of particle size on the removal efficiency. As expected, the removal efficiency increases with an increase in the particle size. Since the removal efficiency is a function of the critical radius, wire radius, filter length, and packing fraction, the removal efficiency will increase as the critical radius increases while the other parameters are held constant, and as discussed above, the critical radius will increase as the particle size becomes larger. In other words, the magnetic force increases
with particle size. Figure 20 also shows the effect of magnetic field strength. From Fig. 20, the removal efficiency increases with an increase in the magnetic field strength.

**Magnetic susceptibility:** The effect of particle magnetic susceptibility on the filter removal efficiency is studied at varying particle size. As shown in Fig. 21, for particles of the same size, the removal efficiency increases as the magnetic susceptibility increases, and for the same magnetic susceptibility, the removal efficiency increases as the particle size increases. As seen in eq. [12], since the magnetic velocity is proportional to the square of particle size, it is readily understood that the effect of particle size on the removal efficiency is stronger than that of magnetic susceptibility.

**Magnetic field strength:** Figure 22 shows the effect of magnetic field strength on the removal efficiency. As expected, the removal efficiency increases as the magnetic field is increased. Since the relation between removal efficiency and magnetic field strength is logarithmic, the removal efficiency increases slowly when the magnetic field reaches a certain magnitude, and finding the optimum magnetic field strength will help to design the magnetic-seeding filtration process efficiently and economically.

**Flow rate:** The effect of flow rate on the removal efficiency is shown in Fig. 23. From Fig. 23, it is found that the removal efficiency increases as the flow rate decreases. Because the hydrodynamic force increases when the flow rate is increased, the particle will be easily carried away from the collector in higher drag force conditions.

**Packing fraction and filter length:** Figure 24 shows the effect of packing fraction on the removal efficiency. It is clear that the removal efficiency will increase when a higher packing fraction is used. Also, as shown in Fig. 25, the removal efficiency increases as
the filter length increases if the filter packing fraction is kept constant. The filter length
determines, however, the retention time of the suspension, so it is economically essential
to find a reasonable filter length with minimum packing fraction in which the filtration
process still can reach the required removal efficiency.

IV.2.2 Particle Build-Up Model

The particle build-up model is used to predict the maximum loading volume of a
clean filter, and the loading volume is determined by the build-up radius (see eq. [22]).
Therefore, the main parameters of the build-up radius equation such as magnetic field,
particle size, magnetic susceptibility, and flow rate are investigated for their effects on the
filter loading volume. All the modeling work done assumes that the particles will load on
the surface of the wire between $\phi = 90^\circ$ and $135^\circ$; $\phi = 135^\circ$ will be used in eq. [20] for all
cases.

**Magnetic field strength:** Figure 26 shows the effect of magnetic field strength on the
filter loading volume at various particle size. From Fig. 26, it is obvious that the loading
volume increases as the magnetic field strength increases. The effect of particle size on
the loading volume also shows in Fig. 26. As shown in Fig. 26, the loading volume
increases with an increase in the particle size.

**Flow rate:** The effect of suspension flow rate on the filter loading volume is shown in
Fig. 27. It is found that the loading volume drops quickly when the flow rate changes
from 0.001 m/sec to 0.002 m/sec and the decreasing rate becomes flat as the flow rate
keeps increasing. A possible reason is that as the magnetic force that acts on the outside
layer particles becomes smaller, once the flow rate increases, the particles will be easily
swept away. For the layers near the wire, the magnetic force is stronger, therefore, the particles are not easily carried away even when the flow rate increases.

Particle size and magnetic susceptibility: Figure 28 shows the effect of particle size and magnetic susceptibility on the filter loading volume. As expected, the loading volume increases as particle size or magnetic susceptibility increases because the loading radius is proportional to particle size and magnetic susceptibility (see eq. [21]).

IV.2.3 Breakthrough Model

The breakthrough model is used to predict the breakthrough curve of magnetic filtration. Generally, the breakthrough of a filtration process is determined by its filter coefficient and saturation concentration. Because the behavior of particles inside a filter is still not well established, most researchers obtain these two parameters from experimental data. In the present study, by combining the trajectory model which calculates the filter coefficient and a particle build-up model which gives the saturation concentration of a filter, a breakthrough curve is predicted without using fitting parameters.

In this section, the breakthrough curve has been examined by studying the effects of various parameters on the breakthrough time \( t_b \) and initial removal efficiency. The effects of parameters such as magnetic field strength and flow rate on the removal efficiency have been discussed in the previous section (trajectory model). The breakthrough time is a function of saturation concentration, filter coefficient, flow velocity, and suspension. For a given suspension with constant concentration, particle size, and magnetic susceptibility, the saturation concentration and filter coefficient are
functions of magnetic field strength and flow rate. Table II presents the results of sensitivity analysis of the magnetic-field strength and flow rate. Set A is a base condition, while Set B is a perturbed condition where the magnetic-field strength is doubled, and Set C is also a perturbed condition where the flow rate is half. The results of the sensitivity analysis are shown in Fig. 29. From Fig. 29, it is found that the removal efficiency increases as the magnetic field strength increases or flow rate decreases, and the breakthrough time increases when the magnetic field strength increases or flow rate decreases. The other interesting result is that although the filter coefficients and saturation concentrations in Set B and Set C are similar (see Table II), the breakthrough time of Set C is much longer than that of Set B. This means that the influent flow rate plays an important role in magnetic filtration performance.

**IV.2.3 Bivariate Model**

The bivariate population-balance model is used to predict heterogeneous flocculation between process particles and magnetic seeding particles, and will give the size and magnetic susceptibility distribution of particles in suspensions. Since this bivariate model is still under development and limited to Brownian flocculation and narrow size range, only a hypothetical simulation case will be discussed in this section. Figure 30 (a) shows the discrete size-concentration distribution at time $t = 0$. Initially, the particle size is uniform, at 0.25 µm diameter, and 50% of the particles are non-magnetic while the other 50% have a 0.0059 magnetic susceptibility. The zeta potential is also held constant at -5 mV. After ten minutes of Brownian flocculation, a significant number of flocs with various magnetic susceptibilities are formed (see Fig. 30 (b)). In Fig. 31 (a),
a simulation is shown with the same particle properties as in Fig. 30 but with different seed concentration; only 10% of particles are seed particles. The results of Brownian flocculation for 10 minutes are shown in Fig. 31 (b), although the number of flocs is small, some large size particles are formed with lower magnetic susceptibilities.

IV.3 Comparison between Modeling and Experiments

Modeling results are compared with experimental data in this section. Figure 32 shows the flow chart of the modeling approach. The size distribution is obtained from experimental data, and then the particle volume for each size \((V_i)\) in the influent is calculated. Assuming that particles have the same magnetic susceptibility, one can estimate the removal efficiency \((RE_i)\) from the trajectory model and the loading volume \((L_{vi})\) from the particle build-up model for each size. The particle removal volume for each size will be equal to \((V_i \times RE_i)\). Once the retained particle volume \(\sum_{i=1}^{n} V_i R_i\) reaches the loading volume corresponding to size \(i=1\) after the first breakthrough time \((t_{b1})\), the particles of size \(i=1\) cannot be removed by the filter anymore and will be carried out with the effluent. For particles of size \(i=2\), the loading volume then becomes \((L_{v2}-L_{v1})\), and the retained particle volume decreases to \(\sum_{i=2}^{n} V_i R_i\). The time needed to reach the loading volume \((L_{v2}-L_{v1})\) is given by \((t_{b2}-t_{b1})\). Following this procedure, the breakthrough time for each particle size and the effluent concentration at each breakthrough time can be obtained.
To evaluate whether the modeling results agree well with experimental data, a correlation coefficient between modeling results and experimental data is calculated in this section. The correlation coefficient ($r_{XY}$) of two random variables, $X$ and $Y$, is given by (Papoulis, 1984)

$$r_{XY} = \frac{Cov}{\sigma_x \sigma_y}, \quad -1 \leq r_{XY} \leq 1 \quad [43]$$

where $Cov$ is the covariance of $X$ and $Y$, and $\sigma_x$, $\sigma_y$ are the standard deviations of $X$ and $Y$, respectively. The definitions of the covariance and the standard deviation are given as

$$Cov = \frac{1}{n} \sum_{i=1}^{n} (X_i - \eta_X)(Y_i - \eta_Y) \quad [44a]$$

$$\sigma_X = \sqrt{\frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2}{n^2}} \quad [44b]$$

where $\eta_X$ and $\eta_Y$ are the means of $X$ and $Y$, respectively. For a good correlation between the two sets of data, the correlation coefficient will be near 1.

Figure 33 shows the comparison between modeling results and experiments of magnetic filtration using 50 ppm paramagnetic particles at 0.2-Tesla magnetic field and 22.5-mL/min flow rate. In Fig. 33, the dots represent experimental data, and the line
represents modeling results using particle distribution from experimental size measurements. The correlation coefficient \( r_{XY} \) between modeling results and experimental data is 0.92, which means that the trend of modeling results agrees well with the experimental data, although the model overpredicts the effluent concentration.

Figure 34 shows the comparison between modeling results and experiments of magnetic filtration using 50 ppm paramagnetic particles under 0.4-Tesla magnetic field and 14-mL/min flow rate. As shown in Fig. 34, the modeling results underestimate the effluent concentration, and show an earlier breakthrough. The correlation coefficient between modeling results and experimental data is 0.73.

The comparison between modeling and experiments of Brownian flocculation and magnetic filtration with 50 ppm polystyrene and 50 ppm polystyrene seed particles is shown in Fig. 35. From Fig. 35, it is found that the model underpredicts the effluent concentration at the beginning, and the correlation coefficient between modeling results and experimental data have a negative value which means that the model failed in this case. This result, however, is mainly due to the scattering observed in the experimental data.

Fig. 36 shows the comparison of magnetic filtration of black iron oxide particles. From Fig. 36, it can be seen that the trend of modeling results agrees well with the experimental data and the correlation coefficient is 0.87, though a longer breakthrough is observed in the modeling results.

The comparison between modeling and experiments of shear-flow flocculation and magnetic filtration of Argonne National Laboratory (ANL) magnetic sorbent particles is
shown in Fig. 37. The experimental results are obtained from Tsouris et al. (1997). Experimental conditions are shown in the figure caption. From Fig. 37, a good correlation coefficient (0.94) between the modeling and experimental data is obtained; some overprediction and underprediction, however, are found from modeling results.

The modeling approach developed in this work has been used to predict magnetically-seeded filtration processes, and in general, it shows a good agreement with experimental data obtained under a wide range of conditions. For paramagnetic particles, such as polystyrene seed, black iron oxide, and ANL particles, a good agreement between modeling results and experimental data is obtained. The maximum relative error between modeling results and experimental data is 35% found in Fig. 33, which is comparable to the maximum experimental relative error (23%, see Section IV.1). The reason for the differences between modeling and experiments maybe due to the fact that the particle size distribution at the inlet of the filter is used in the simulations, while in reality the size distribution may significantly change inside the filter due to the enhanced shear rate caused by the filter packing.
CHAPTER V

CONCLUSIONS

High-Gradient Magnetic Separation (HGMS) has been considered as a recovery and pollution control process for many environmental and industrial problems. For weakly magnetic and non-magnetic particles, a magnetically-seeded filtration process is used to form paramagnetic flocs and thus increase the removal efficiency of magnetic filtration. A systematic approach has been adopted in this study to (1) experimentally evaluate the effects of solution parameters, system geometry, and operating conditions on the filtration performance, (2) develop models for studying the interaction between particles and filter matrix, and (3) model experimental results without using empirical fitting coefficients. The main conclusions of this study are summarized as follows:

- The experimental results show that magnetic seeding flocculation processes play a significant role on the performance of magnetic filtration. During flocculation, particle size as well as magnetic susceptibility increase, thereby enhancing filter removal efficiency. Solution parameters, such as solution pH, ionic strength, particle size, and seed concentration, appear to be important factors in designing magnetically-seeded flocculation processes.
From magnetic filtration experiments, it is found that the removal efficiency increases with an increase in the magnetic field strength, filter packing fraction, or filter length. As the flow rate decreases, the removal efficiency, as well as the filter breakthrough time increases. Finding optimum operating conditions and system geometry is necessary for achieving economic and environmental requirements.

Based on sensitivity analyses of the trajectory, particle build-up, and breakthrough models, the filter performance is seen to depend on particle size, magnetic susceptibility, magnetic field, flow rate, and system geometry. The suspension flow rate, however, appears to have a larger effect on the filtration breakthrough time than other parameters.

In the model development, only external forces such as, gravitational, hydrodynamic drag, and magnetic, were considered. Under the system conditions of the present study, the interparticle forces, e.g., electrostatic, van der Waals, and magnetic dipole forces, are insignificant compared to external forces; however, these interparticle forces will become more important in the case of ultra-fine.

In summary, this study presents a mathematical approach to predict magnetically-seeded filtration without using empirical fitting coefficients. From the comparison between modeling and experiments, it is found that a good agreement between modeling results and experimental data is obtained. The maximum relative error obtained from the comparison between modeling results and experimental data (35%) is of the same order as the maximum experimental relative error (23%).
The observed differences between modeling predictions and experimental results are possibly due to the accuracy of particle size and magnetic susceptibility distributions as well as model limitations.

- Future studies should include experimental and theoretical work on (1) filter geometry (e.g., filter matrix orderly packed), (2) orientation between magnetic field and flow velocity, and (3) filter regeneration
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Table I. Properties of Polystyrene and Seed Paramagnetic Particles

<table>
<thead>
<tr>
<th></th>
<th>Mean diameter</th>
<th>Density (g/mL)</th>
<th>Number of particles per gram</th>
<th>Surface area (µm$^2$/g)</th>
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<td>Black iron oxide</td>
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Table II. Sensitivity Analysis of Breakthrough Model

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<td>Results from trajectory model</td>
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<td>Results from build-up model</td>
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<td>Results from breakthrough model</td>
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Build-up area

\[ F_{r(net)} = 0 \]

\[ F_{\phi(net)} = 0 \]

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Wire radius = 62.5 µm, magnetic field strength = 0.8 T, magnetic susceptibility = 0.0047.
Figure 24. Effect of packing fraction on the separation efficiency:
Wire radius = 62.5 µm, magnetic field strength = 0.8 T, magnetic susceptibility = 0.0047, flow rate = 0.001 m/s.
Figure 25. Effect of filter length on the separation efficiency:
Wire radius = 62.5 µm, magnetic field strength = 0.8 T,
magnetic susceptibility = 0.0047, flow rate = 0.001 m/s,
packing fraction = 1%.
Figure 26. Effect of magnetic field strength on the loading volume: Wire radius = 62.5 µm, magnetic field strength = 0.8 T, magnetic susceptibility = 0.0047, flow rate = 0.001 m/s.
Figure 27. Effect of flow rate on the loading volume:
Wire radius = 62.5 µm, magnetic field strength = 0.8 T,
magnetic susceptibility = 0.0047.
Figure 28. Effect of particle size and magnetic susceptibility on the loading volume: Wire radius = 62.5 µm, magnetic field strength = 0.8 T, flow rate = 0.001 m/s.
Figure 29. Effect of magnetic field strength and flow rate on the filtration breakthrough curve.
Figure 30. Heterogeneous flocculation of particles of the same number fraction: (a) Initial condition; (b) number fraction after 10 min of flocculation. Zeta potential = -5 mV.
Figure 31. Effect of seeding concentration on particle flocculation:
(a) Initial condition; (b) number fraction after 10 min of flocculation.
Zeta potential = -5 mV.
Size measurement: particle volume \((V_i)\) for each class \(i (i=1,2,\ldots,n)\)

Trajectory model for Removal efficiency \((RE_i)\)

Particle volume in influent

\[
\sum_{i=1}^{n} V_i
\]

Build-up model for loading volume \((L_{vi})\)

Continue

Do \(j = 2, n+1\)

Particle volume remain in filter

\[
\sum_{i=j}^{n} V_i RE_i
\]

Calculate breakthrough \(t_s(j-1)\)

Maximum loading volume for each class \(L_{v(j-1)}\)

Particle volume in effluent

\[
\sum_{i=j}^{n} V_i (1 - RE_i) + \sum_{m=0}^{j-2} V_m
\]

Plot breakthrough curve
Effluent concentration vs. time

Figure 32. Flow chart of modeling approach.
Figure 33. Comparison of modeling and experiments of magnetic filtration using 50 ppm paramagnetic particles: Magnetic field = 0.2 T, flow rate = 22.5 mL/min, magnetic susceptibility = 0.0059.
Figure 34. Comparison of modeling and experiments of magnetic filtration using 50 ppm paramagnetic particles: Magnetic field = 0.4 T, flow rate = 14 mL/min, magnetic susceptibility = 0.0059.
Figure 35. Comparison of modeling and experiments of magnetically-seeded filtration (Brownian flocculation): 50 ppm paramagnetic particles and 50 ppm polystyrene particles, magnetic field = 0.8 T, flow rate = 14 mL/min.
Figure 36. Comparison of modeling and experiments of magnetic filtration of black iron oxide particles: 100 ppm black iron oxide, magnetic susceptibility = 0.02, magnetic field = 0.8 T, flow rate = 22.5 mL/min.
Figure 37. Comparison of modeling and experiments of magnetic filtration of ANL particles (turbulent shear flocculation): 100 ppm ANL particles, magnetic susceptibility = 0.0061, magnetic field = 0.8 T, flow rate = 400 mL/min.
APPENDIX I

EXPERIMENTAL CONDITIONS AND RESULTS
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* The flow stopped suddenly after running 17.6 min, and restarted at time 30 min.

1: PS is defined as Polystyrene particles.
2: Paramag. is defined as Paramagnetic particles
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### Magnetic filtration of paramagnetic particles

#### Experimental conditions

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### Magnetic filtration of black iron oxide

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### Magnetic seeding filtration (Brownian flocculation)

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### Experimental Results

**Magnetic seeding filtration (shear-flow flocculation)**

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### Magnetic filtration of paramagnetic particles
**Experimental results**

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### Magnetic filtration of black iron oxide
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Magnetic seeding filtration (Brownian flocculation)
Experimental results

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BIBLIOGRAPHY


FUNDAMENTAL MODELING FOR MAGNETICALLY SEEDED SOLID-LIQUID SEPARATIONS

Final Technical Report Submitted to

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P.O. Box 2002
Oak Ridge, Tennessee 37831-6501

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FUNDAMENTAL MODELING FOR MAGNETICALLY SEEDED SOLID-LIQUID SEPARATIONS

Abstract

Progress on quantifying the interaction between magnetic particles, as well as magnetic and non-magnetic particles, in liquid suspensions and under the influence of a magnetic field is described in this report. Primary forces acting on individual particles, including gravity and magnetic attraction, are examined and quantified, as are van der Waals, electrostatic, magnetic dipole, and hydrodynamic interparticle forces. A mathematical statement of the overall relative velocity is developed from the net force acting on a particle. Three limiting cases are discussed: Brownian diffusion dominating, external force (gravity and magnetic) dominating, and turbulent shear dominating. For the second case, the equation of relative motion for two particles in cylindrical coordinates is derived. For the third case, the breakage of aggregates due to turbulent shear is considered. A computer model is used to solve the equation of relative motion repeatedly to find the particle trajectory borderline between collision and noncollision, thus determining the collision efficiency and collision frequency. The effect of a variety of parameters on collision efficiency and collision frequency is then explored. This work aims at developing a mechanistic model for magnetically seeded solid-liquid separations using a turbulent shear flocculation regime. The concept of fractal dimension is introduced to simulate the open structure of aggregates in flocculation systems. A trajectory model of a particle captured by a single-wire is also developed to predict the performance of a high gradient magnetic filter. Results from the models developed in this study will be compared with experimental results obtained at Oak Ridge National Laboratory using synthetic, surrogate, and sorbent particles.
3.0 THEORETICAL STUDIES

3.1. Introduction

Magnetic separation has been suggested as a recovery and pollution control process for a manifold of environmental problems. Among these are the treatment of effluent from steel mills (Svoboda, 1987; page 590), desulfurization of coal (Petrakis et al., 1981), and separation and concentration of mining ores and wastes (Svoboda et al., 1987). Current industrial uses of magnetic separation include clay benefaction (Lawver and Hopstock, 1974) and nuclear reactor coolant water filtration (Heitmann, 1979). Furthermore, magnetically seeded solid-liquid separations extend magnetic separation to include the removal of non-magnetic substances from a suspension. For example, magnetically seeded flocculation has been used for the removal of yeast from process streams (Dauer and Dunlop, 1991), purification of drinking water sources (Kohm et al., 1975), and treatment of domestic wastewater (de Latour, 1973). Additionally, magnetically seeded solid-liquid separations may be of enormous value in the remediation of radioactive groundwater contamination (Szabo and Rosholt, 1989).

The interaction between magnetic particles, as well as magnetic and non-magnetic particles, in liquid suspensions and under the influence of a magnetic field has not been extensively examined in the literature. Incorporating hydrodynamic, van der Waals, electrostatic, and orientation-averaged magnetic forces in a Brownian flocculation model, Tsouris and Scott (1995) considered flocculation of paramagnetic particles in a study important to the development of the present modeling approach. Tsouris et al. (1995) considered the heterogeneous flocculation of paramagnetic colloidal particles, using an interparticle force potential that includes hydrodynamic, van der Waals, electrostatic, and magnetic forces. Schewe et al. (1980) developed expressions for particle-filter element attractions and hydrodynamic resistance for the laminar-flow case, leading to calculations of particle trajectories. Moyer et al. (1984, 1985) also formulated expressions for the capture of magnetic particles, in this case using a free surface condition, and ignoring electrostatic and van der Waals forces. Friedlaender et al. (1981) studied single sphere high-gradient magnetic separation (HGMS), neglecting all but the collector-particle magnetic force and hydrodynamic forces. Cummings et al. (1976) examined magnetic, drag, and gravitational forces in HGMS single-wire capture. The present study builds on and extends previous work in order to provide a fundamental modeling approach for magnetically seeded separations. Trajectory analysis has been used to obtain the collision efficiency in many different flow regimes as discussed in previous studies (Adler, 1981; Melik and Fogler, 1984).

Other works important to the present study include that of Zhang and Davis (1991), who looked at the coalescence of drops operating under Brownian or gravitational motion and determined collision rates and efficiencies from particle trajectories. The hydrodynamic resistance
function expressions derived by Haber and coworkers (Haber et al., 1973; Haber and Hetsroni, 1973) and Zinchenko (1980) were of great importance, as was their development by Zhang (1992).

This work investigates the interaction between magnetic particles, as well as magnetic and non-magnetic particles, in liquid suspensions and under the influence of a magnetic field. Particle-particle interactions are examined under quiescent or laminar-flow conditions. Gravitational and magnetic external forces are included in the analysis, as well as van der Waals, electrostatic, magnetic dipole, and hydrodynamic particle-particle forces. The inertial force is neglected (i.e., it is assumed that the particles immediately assume their terminal velocity under the given net force), as are thermocapillary effects. Additionally, it is assumed that the particles are spherical, and that the magnetic field and magnetic field gradient do not vary when the two particles approach each other, that is to say, the external magnetic force behaves like gravity. This assumption is reasonable for the low-magnetic-susceptibility particles considered in this study. A general analysis is provided which also includes the contribution of Brownian diffusion to the particles' relative motion. Then three limiting cases are discussed separately: Brownian diffusion dominating, external force (gravity and magnetic) dominating, and turbulent shear dominating. More detailed discussion is provided for particles outside the size range where Brownian diffusion is important. Stated mathematically, results valid for Péclet numbers much greater than one are presented. From this theoretical foundation, a differential equation relating the relative position of the two particles is derived. This equation is then solved repeatedly by a computer code using an ordinary differential equation solver to reveal the limiting trajectory. Collision efficiencies and collision frequencies (normalized collision rates) can then be calculated from this limiting trajectory. The effect of the direction of the magnetic field on collision efficiency and collision frequency is demonstrated first, followed by the effects of various other factors that may become important during various stages of the magnetically seeded separation processes. In the analysis of the particle-particle interactions, all calculations were made by considering that the magnetic field and magnetic field gradient are aligned with gravity.

For the prediction of the size evolution in flocculation systems, the particles are usually assumed to be spheres, which corresponds to a fractal dimension of three. If the particle structure differs from that of a sphere, a smaller fractal dimension should be used. Preliminary results on the employment of fractal dimension in population balance models are discussed in this study.

A trajectory analysis model is developed to predict the behavior of magnetic seeded flocculation. A sensitivity analysis of the various parameters appearing in the model is presented in this report.
3.2. Model Development

Forces Acting on Particles in Suspension

As noted in the introduction, the forces considered in the analysis presented here include gravity, magnetic attraction, van der Waals, electrostatic, magnetic dipole, and hydrodynamic forces. The different forces are divided into interparticle forces—forces acting between two particles—and external forces that act on individual particles. Brownian relative diffusivity is treated separately. These various phenomena are examined below.

External Forces

The external forces, gravity and magnetic attraction, are of interest to the extent that they affect the two interacting particles in question differently. This becomes obvious if one considers two particles at some distance from each other, where interparticle forces are negligible. For the particles to collide, they must approach each other so that interparticle forces can lead to attachment. If both particles are affected by external forces similarly, they will both move with the same velocity, and never get closer to each other. If the particles are not affected by external forces to the same degree, then their velocities will differ, and assuming the particles are fortuitously positioned, one particle will overtake the other, possibly leading to collision. This difference in velocities is called the relative velocity, expressed as the motion of one particle from the point of view of the other. With this goal in mind, gravity and magnetic attraction's contribution to particle-particle collision can be examined.

Gravity

The gravitational force, $F_g$, acting on a particle in suspension is given by:

$$F_g = \rho_p V_p g$$  \hspace{1cm} [1]$$

where $\rho_p$ is the density of the particle, $V_p$ is the volume of the particle, and $g$ is the gravitational acceleration. The buoyant force, $F_b$, acting on a particle is given by:

$$F_b = \rho V_p g$$  \hspace{1cm} [2]$$

where $\rho$ signifies the density of the fluid. Given the assumption that inertial forces are negligible,
or that Reynolds numbers are much less than one, it is considered that the particle immediately accelerates to its terminal settling velocity (or its terminal velocity upward) through the fluid. Thus, a drag force, \( F_d \), develops that is equal and opposite to the net buoyant and gravitational forces:

\[
F_d = -CD A_p \rho \frac{v^2}{2} \hat{g}
\]  

where \( A_p \) is the cross-sectional area of the particle, \( C_D \) is the coefficient of drag, \( v \) is the magnitude of the velocity of the particle, \( v \), and \( \hat{g} \) is the unit vector of the gravitational acceleration. Assuming laminar flow, \( C_D = 24 / \mathcal{R} \), where \( \mathcal{R} \), the Reynolds number, is defined as \( \mathcal{R} = 2 \rho va / \eta \), \( a \) is the particle radius, and \( \eta \) is the dynamic viscosity. Substituting these expressions into the force balance equation and assuming spherical particles, allows the equation to be solved for velocity \( v \). The far-field relative gravitational velocity, \( V_{12g}^{(0)} \), for two particles will just be the difference of their respective individual velocities, \( v_1 \) and \( v_2 \). Mathematically stated, \( V_{12g}^{(0)} = v_1 - v_2 \). Combining like terms in the expressions for \( v_1 \) and \( v_2 \) brings forth the expression for relative gravitational velocity:

\[
V_{12g}^{(0)} = \frac{2[(\rho_1 - \rho)a_1^2 - (\rho_2 - \rho)a_2^2]g}{9\eta}
\]

where \( a_1 \) and \( a_2 \) are defined as particles' one and two respective radii, and \( \rho_1 \) and \( \rho_2 \) their respective densities. The larger particle is designated as one and the smaller particle is designated as two.

**Magnetic Attraction**

Assuming a small particle of radius \( a \), the magnetic force, \( F_m \), on a particle can be given in terms of the magnetic field (Svoboda, 1987; page 4):

\[
F_m = \frac{4}{3} \pi a^3 \chi \frac{\mu_0}{\mu} B \nabla B
\]

where \( \chi \) is the volume magnetic susceptibility, \( \mu_0 \) is the permeability of free space, and \( B \) is the magnitude of the magnetic induction vector \( B \). In free space, the magnetic induction vector, \( B \),
and the magnetic-field strength vector, \( \mathbf{H} \), are not independent but related by the equation

\[
\mathbf{B} = \mu_0 \mathbf{H}
\]  

Developing the analysis as in the previous section and solving for the relative magnetic velocity, \( \mathbf{V}^{(0)}_{12m} \), gives:

\[
\mathbf{V}^{(0)}_{12m} = \frac{2BVR}{9\eta\mu_0} \left( \chi_1 a_1^2 - \chi_2 a_2^2 \right)
\]

where \( \chi_1 \) and \( \chi_2 \) are the two particles' respective magnetic susceptibilities.

**Interparticle Forces**

The forces acting between the two interacting particles are fundamentally different from the external forces in that they change in strength as the one particle approaches the other. In the case of the magnetic dipole force, the magnitude and sign of the force are also functions of the orientation of the two particles with respect to the magnetic field. This characteristic of the interparticle forces will be of importance when solving the differential equation of motion: the potential between the particles changes after each iteration of the solution. The coordinate system used in quantifying the interparticle forces is illustrated in Figure 3.1.

**van der Waals Forces**

Hamaker (1937) calculated the van der Waals interparticle force potential, \( V_{vdW} \), for unequal sized spheres as a function of separation:

\[
V_{vdW} = -\frac{A}{6} \left[ \frac{8\lambda}{(s^2 - 4)(1 + \lambda)^2} + \frac{8\lambda}{s^2(1 + \lambda)^2 - 4(1 - \lambda)^2} \right] + \ln \left[ \frac{(s^2 - 4)(1 + \lambda)^2}{s^2(1 + \lambda)^2 - 4(1 - \lambda)^2} \right]
\]

where \( A \) is the Hamaker constant (actually a function of the particles' composition),
\( s = 2r/(a_1 + a_2) \) (dimensionless particle separation), \( r \) is the center-to-center particle separation, and \( \lambda = a_2/a_1 \) (particle radius ratio).

**Electrostatic Forces**

Following Tsouris and Scott (1995), the electrostatic potential, \( V_{el} \), is given by two
formulas, one for large separations and one for small separations.

**Linear Superposition Approximation**

The linear superposition approximation (Bell et al., 1970) is indicated for thin double layers and large interparticle separations:

\[
V_{el} = 4\pi\varepsilon \left(\frac{kT}{e}\right)^2 Y_1 Y_2 \frac{a_1 a_2}{r} e^{-\kappa l}, \quad \text{for } \kappa l \geq 4 \tag{9}
\]

where

\[
Y_i = 4 \tanh \left(\frac{\phi_i}{4}\right), \quad \text{for } kr \geq 10, \phi_i < 8, \text{ and } i = 1, 2 \tag{10a}
\]

\[
\phi_i = \frac{ze\Psi_{oi}}{kT}, \quad \text{for } i = 1, 2 \tag{10b}
\]

\[
\kappa \equiv 5.552 \times 10^{-6} \sqrt{1/\varepsilon kT} \tag{10c}
\]

\[
l \equiv (s - 2) \left(\frac{a_1 + a_2}{2}\right) \tag{10d}
\]

\(T\) is the absolute temperature, \(\varepsilon\) is the permittivity of the medium, \(e\) is the electron charge, \(k\) is the Boltzmann constant, \(z\) is the valence of the symmetric electrolyte in the solution, \(\Psi_{oi}\) refers to the particles' surface potential, and \(I\) is the ionic strength of the solution.

**Derjaguin Approximation**

For interparticle separations less than that at which the linear superposition approximation applies, the Derjaguin approximation is used (Hogg et al., 1966):

\[
V = \frac{4\pi\varepsilon^2}{3} \left(\frac{kT}{e}\right)^2 Y_1 Y_2 \frac{a_1 a_2}{r} e^{-\kappa l}, \quad \text{for } \kappa l < 4
\]
In the employment of both Eqs. [9] and [11], it is assumed that the potential of one particle is undisturbed in the presence of other particles.

**Magnetic Dipole Attraction**

The interaction between two magnetically susceptible particles is expressed with the potential, $V_{mag}$, given by (Chikazumi, 1964; Wangsness, 1986; page 322):

$$V_{mag} = \frac{4\pi B^2 a_1^3 \chi_1^2 a_2^3 \chi_2^2}{9\mu_0 \left( \frac{s}{a_1 + a_2} \right)^3} \left[ (\hat{\mu}_1 \cdot \hat{\mu}_2) - 3(\hat{\mu}_1 \cdot \hat{e}_r)(\hat{\mu}_2 \cdot \hat{e}_r) \right]$$  \hspace{1cm} [12]

where $\hat{\mu}_1$ and $\hat{\mu}_2$ are the respective unit magnetic dipole vectors of particles one and two, and $\hat{e}_r$ is the unit vector of the position vector (which has magnitude $r$). Equation [12] is in principle valid for a uniform magnetic field, and as a consequence the two particles have the same unit magnetic dipole vector; therefore, the first dot product becomes 1, and the second and third dot products have the same value. Furthermore, since $\hat{\mu}_1$, $\hat{\mu}_2$, and $\hat{e}_r$ are all unit vectors, the value of the second and third dot products is simply the cosine of the angle between $\hat{e}_r$ and $\hat{\mu}_1$, $\hat{\mu}_2$.

Equation [12] can thus be rewritten as

$$V_{mag} = \frac{4\pi B^2 a_1^3 \chi_1 a_2^3 \chi_2}{9\mu_0 \left( \frac{s}{a_1 + a_2} \right)^3} (1 - 3\cos^2 \psi)$$  \hspace{1cm} [13]

where $\psi$ is the angle between the magnetic dipole moment (which has the same direction of that of the magnetic field or magnetic induction) and $\hat{e}_r$ (see Figure 3.1). Note that this magnetic dipole interaction is thus not the commonly used orientation-averaged magnetic dipole interaction.

The interparticle magnetic potential yields forces along and normal to the line-of-centers:
where \( \alpha \) is the angle between the direction of the vertical axis and that of the magnetic field. The angle \( \psi \) defined earlier is related to \( \alpha \) by \( \psi = |\alpha - \theta| \).

The magnitudes of the radial and tangential interparticle magnetic forces dimensionalized by the factor \( \frac{32\pi B^2 a_1^3 a_2^3 \chi_1 \chi_2}{\mu_0 (a_1 + a_2)^4} \), for three different values of the dimensionless separation distance \( s \) and values of \( \psi \) from 0 to 180°, are shown in Figures 3.2a and 3.2b. It is important to note that the maximum of the tangential force is usually smaller than that of the radial force and both increase as the separation distance decreases. Also the radial force is attractive when \( \psi = 0 \), but becomes repulsive when \( \psi = 90° \). This observation implies that the direction of the magnetic field will play a significant role in the collision efficiency, as will be shown later in this report.

The interparticle magnetic force as a function of the separation distance between the two particles, for \( \psi = 0 \), and for three different size ratios is shown in Figure 3.3a. In the same figure, the magnitude of the van der Waals and that of the repulsive or attractive electrostatic forces are also shown. The results in Figure 3.3a demonstrate that the interparticle magnetic force predominates over a longer range of separation distance than the attractive van der Waals force and the attractive or repulsive electrostatic force. The electrostatic force is repulsive when both particles have either negative or positive charges and attractive when one particle has a positive charge and the other has a negative charge. An additional conclusion that comes from Figure 3.3a is that the interparticle magnetic force reaches a plateau, at small separations, in contrast to the van der Waals and electrostatic forces which change rapidly in the same region. A similar behavior can be observed using potentials instead of forces, and a demonstrative case is shown in Figure 3.3b.

The total dimensionless potential, as well as the electrostatic, van der Waals, and magnetic potentials, is shown in the figure, with the magnetic potential being calculated by the orientation-averaged magnetic dipole potential (Tsouris and Scott 1995).
**Hydrodynamic Forces**

Haber et al. (1973) and Zinchenko (1980) developed exact solutions for the hydrodynamic resistance to particle collision using the method of bispherical coordinates: Haber et al.’s solution applying to axisymmetric motion of two drops (i.e., drops moving along their line-of-centers), and Zinchenko’s applying to the asymmetric motion of drops (i.e., drops moving normal to their line of centers) (Zhang and Davis, 1991). Although these solutions were originally calculated for drop motion, they can be easily applied to particle motion by assigning the ratio of drop viscosity to fluid viscosity a value of $10^3$ or greater. The derivations cited are quite tedious, and a full explication of them is beyond the scope of this report; however, an outline of Haber et al.’s and Zinchenko’s results is presented below.

**Hydrodynamic Resistance to Axisymmetric Motion**

Haber et al. showed that the axisymmetric drag force, $F_1$, acting on a particle with radius $a_1$ moving with a velocity $v_1$ near another particle with radius $a_2$ and velocity $v_2$ is given by (Haber et al., 1973):

$$F_1 = -6\pi \eta a_1 (\Lambda_{11} v_1 + \Lambda_{12} v_2)$$  \[15\]

where $\Lambda_{11}$ and $\Lambda_{12}$ are given by:

$$\Lambda_{11} = \frac{\sqrt{2} \sinh(\bar{\alpha})}{3c} \sum_{n=1}^{\infty} \frac{\delta_0 + \sigma_1 \delta_1 + \sigma_2 \delta_2 + \sigma_1 \sigma_2}{\Delta}$$ \[16a\]

and

$$\Lambda_{12} = \frac{\sqrt{2} \sinh(\bar{\alpha})}{3c} \sum_{n=1}^{\infty} \frac{\bar{\delta}_0 + \bar{\sigma}_1 \bar{\delta}_1 + \bar{\sigma}_2 \bar{\delta}_2 + \bar{\sigma}_1 \bar{\sigma}_2}{\Delta}$$ \[16b\]

Here $c$, $\bar{\alpha}$, $\Delta$, and the $\delta$’s and $\sigma$’s are coefficients derived from the geometry and fluid conditions of the situation (also, Haber et al.’s $\lambda$’s have been exchanged for $\sigma$’s to avoid confusion); see Haber et al. for a detailed explanation.

The important feature to note is that the resistive force depends on an infinite series; upon calculation, the computer model described in this work allows the infinite series to converge to the desired accuracy and then truncates the series.
**Hydrodynamic Resistance to Asymmetric Motion**

Zinchenko (1980) developed solutions similar to Haber et al. for the case of particle motion normal to the line of centers:

\[ F_1 = -6\pi \eta a_1 [A_{11}(v_1 - v_2) + A_{12}v_2] \] \[ 17 \]

with \( A_{11} \) and \( A_{12} \) defined as in Haber and Hetsroni (1978), and the other variables defined as in the previous section [see Zinchenko (1980) for details of these calculations].

**Relative Mobility Functions**

Zhang derived the axisymmetric relative mobility functions \( L \) and \( G \) from the above resistance functions \( A_{11}, A_{12} \) and the functions \( A_{21}, A_{22} \), where the latter pair of functions are the analogous resistance functions for the second particle in the analysis (Zinchenko, 1980). Zhang (1992) arrived at the following expressions for \( L \) and \( G \):

\[ L(\xi) = \frac{\lambda^2 A_{12} - A_{22}}{(\lambda^2 - 1)(A_{11}A_{22} + A_{12}A_{21})} \] \[ 18a \]

and

\[ G(\xi) = \frac{A_{12} + \lambda A_{22}}{(\lambda + 1)(A_{11}A_{22} + A_{12}A_{21})} \] \[ 18b \]

where \( \xi = s - 2 \). Similar expressions for the asymmetric relative mobility functions \( M(s) \) and \( H(s) \) can be found [see Zhang (1992) and Zhang and Davis (1991) for further details]. It is important to note that the limiting values of these hydrodynamic mobility functions (i.e. values at large ratios of drop viscosity to fluid viscosity) agree with those obtained from the hydrodynamic mobility functions developed for rigid spheres (Spielman, 1970; Jeffrey and Onishi, 1984) and used in other studies (Davis, 1984; Melik and Fogler, 1984).

**Relative Diffusivity**

The relative diffusivity due to Brownian motion for two particles is expressed as:

\[ D_1^{(0)} = \frac{kT(1 + \lambda^{-1})}{6\pi \eta a_1} \] \[ 19 \]
Equation of Relative Particle Motion

The forces acting on a particle pair have been examined and quantified. In order to use them in a theoretical model, the relations between the various forces have to be delineated, and like forces grouped together. In the sections below, the external forces of gravity and magnetic attraction and the Brownian relative diffusivity are combined into two dimensionless interparticle force parameters, while the interparticle forces are combined into a dimensionless interparticle potential.

Far-Field Relative Velocity

The far-field relative velocity between two particles is the vector addition of the gravitational relative velocity $V^{(0)}_{12g}$ given by Eq. [4], and the magnetic-induced relative velocity $V^{(0)}_{12m}$ given by Eq. [7]:

$$\begin{align*}
V^{(0)}_{12} &= \frac{2[(\rho_1 - \rho)a_1^2 - (\rho_2 - \rho)a_2^2]g + [2(\chi_1 a_1^2 - \chi_2 a_2^2)/\mu_0]B\nabla B}{9\eta} \quad [20a]
\end{align*}$$

As seen in Eq. [20a], the magnetically induced relative velocity depends on the direction of the magnetic field gradient. The problem is greatly simplified if this vector is aligned in the positive or negative vertical direction: this arrangement results in a cylindrical symmetry of forces about the axis along which one particle overtakes the other, in addition to reducing the vector addition to a scalar addition. Accordingly, whenever the external force of magnetic attraction is applied in this study, the analysis is restricted to the case where the magnetic-field gradient vector is oriented downward so that the magnetic relative velocity adds to that of gravity. The magnitude of the relative velocity vector, $V^{(0)}_{12}$, thus becomes:

$$\begin{align*}
V^{(0)}_{12} &= \frac{2[(\rho_1 - \rho)a_1^2 - (\rho_2 - \rho)a_2^2]g + [2(\chi_1 a_1^2 - \chi_2 a_2^2)/\mu_0]B|\nabla B|}{9\eta} \quad [20b]
\end{align*}$$

where $g$ is the magnitude of the gravitational acceleration, and $|\nabla B|$ is the magnitude of the magnetic induction gradient.

Trajectory Equation of Particle-Particle Motion

Using a similar analysis to that of Davis (1980), the relative diffusivity (Eq. [19]) and the far-field relative velocity (Eq. [20b]) are related through three dimensionless parameters, the
magnetic force parameter, $Q_{12}^{\text{mag}}$, the interparticle force parameter, $Q_{12}$, and the Péclet number, $Pe$:

$$Q_{12}^{\text{mag}} = \frac{\left(\frac{a_1 + a_2}{2}\right)^4 V_{12}^{(0)}}{2\pi B^2 \chi_1 \chi_2 \alpha_1^3 \alpha_2^3 D_{12}^{(0)}/\mu_0 kT}$$  \[21a\]

$$Q_{12} = \frac{\frac{1}{2}(a_1 + a_2)V_{12}^{(0)}}{AD_{12}^{(0)}/kT}$$  \[21b\]

$$Pe = \frac{\frac{1}{2}(a_1 + a_2)V_{12}^{(0)}}{D_{12}^{(0)}}$$  \[21c\]

In the case of creeping flow, i.e., when the Reynolds number, $R = 2\rho V_{12}^{(0)} a_1/\eta$, is small enough so that inertia is neglected, the relative velocity, $V_{12}$, obtained based on a force balance (Tien, 1989) is given by:

$$V_{12} = V_{12}^{(0)}[-L(s)\cos(\theta)\hat{e}_r + M(s)\sin(\theta)\hat{e}_\theta] - \frac{D_{12}^{(0)}}{kT} \left[ G(s)F_{r}^{\text{mag}}\hat{e}_r - H(s)F_{\theta}^{\text{mag}}\hat{e}_\theta \right]$$

$$- \frac{D_{12}^{(0)}}{kT} G(s)(F_{vdW} + F_e)\hat{e}_r$$

$$- \frac{V_{12}^{(0)}}{Pe} \left[ G(s) \frac{\partial}{\partial s} (\ln p_{12})\hat{e}_r + \frac{H(s)}{s} \frac{\partial}{\partial \theta} (\ln p_{12})\hat{e}_r \right]$$  \[22\]

where $\hat{e}_\theta$ is the unit vector in the tangential direction (see Figure 3.1). $F_{vdW}$ and $F_e$ are the van der Waals and electrostatic forces, respectively, and $p_{12}$ represents the normalized probability that particle 1 is at a given position relative to particle 2. Therefore, Eq. [22] includes both deterministic and probabilistic terms, and its solution depends on the functional form of $p_{12}$. A general solution of Eq. [22], useful for particles in the micron size range, may be obtained using
perturbation methods (Tien, 1989). The four terms on the right-hand side of Eq. [22] represent the contributions of (a) external gravity and magnetic forces, (b) interparticle forces including van der Waals and electrostatic, (c) magnetic dipole forces, and (d) Brownian diffusion, respectively.

Collision Efficiency and Collision Frequency due to Brownian Diffusion

In the case of $Pe \ll 1$, which usually occurs for submicron particles, Brownian diffusion dominates over external forces. The contribution of external forces is thus negligible, and only interparticle forces and Brownian diffusion are considered. In the presence of the magnetic field, the collision efficiency and collision frequency denoted by $E_{12}$ and $F_{12}$, respectively, can be determined using the following expressions:

$$E_{12} = \left[ 2 \int_{s_2}^{\infty} \exp \left( \frac{(V_{vdW} + V_{el} + V_{mag})}{kT} \right) \frac{ds}{G(s)} \right]^{-1}$$  \hspace{1cm} [23a]

$$F_{12} = \frac{4\pi D_{12}^{(0)}}{\int_{a_1 + a_2}^{\infty} \exp \left( \frac{(V_{vdW} + V_{el} + V_{mag})}{kT} \right) \frac{dr}{r^2 G(r)}}$$  \hspace{1cm} [23b]

In Eq. (23), the magnetic potential, $V_{mag}$, is integrated over all orientations of the particles in the magnetic field. Such an integration has been carried out by Chan et al. (1985), and their results have been incorporated in a Brownian diffusion model by Tsouris and Scott (1995).

Collision Efficiency and Collision Frequency due to External Forces

In the case of $Pe \gg 1$, which usually occurs for larger particles, the external forces dominate over Brownian diffusion, and the Brownian diffusion term in Eq. [22] (last term) can be eliminated. Also, Eq. [22] can be dimensionalized if divided by $V_{12}^{(0)}$ to give the overall dimensionless relative velocity, $u_{12}$.
Separating the resulting dimensionless relative velocity into radial and tangential components and dividing the radial component by the tangential component, the differential trajectory equation given by Eq. [25] is obtained:

\[
\mathbf{u}_{12} = \left[ -L(s)\cos(\theta)\hat{\mathbf{e}}_r + M(s)\sin(\theta)\hat{\mathbf{e}}_\theta \right] - \frac{D_{12}^{(0)}}{kTV_{12}^{(0)}} \left[ G(s)F_{\theta}^{mag}\hat{\mathbf{e}}_r - H(s)F_{r}^{mag}\hat{\mathbf{e}}_\theta \right] - \frac{D_{12}^{(0)}}{kTV_{12}^{(0)}} G(s)(V_{vdW} + V_e)\hat{\mathbf{e}}_r
\]

This equation is the heart of the computer model presented in this report. By finding the numerical solution to this equation, the trajectory of a particle can be traced from an arbitrary starting position and its eventual fate determined (collision or non-collision with the other particle). Furthermore, by repeated applications of this numerical solution, the limiting or critical trajectory separating the particle's two fates can be found. As inspection of Eq. [25] will reveal, the limiting trajectory shows cylindrical symmetry about the z-axis for \( \alpha = 0, \pi/2, \pi \). Thus, in these cases, trajectories which result in collision will originate within a certain horizontal distance \( y_c^* \) of the z-axis shown in Figure 3.1 (Tien and Payatakes, 1979). From this critical radius parameter, the collision frequency and collision efficiency can be found.

The collision rate, \( J_{12} \), for a given particle will be the number of collisions it experiences per unit time. In the cases of cylindrical symmetry given in the previous section, the collision rate can be thought of as the flux of potential collision partners that move through the circle the limiting trajectory forms about the z-axis. This flux, in turn, is just the concentration of potential collision partners multiplied by the area of the limiting trajectory circle and the (relative) flux velocity (note that the flow through the limiting trajectory circle is parallel to the flux direction). The overall collision rate per unit volume for the two particle classes will be the collision rate for a particular particle multiplied by the concentration of that class of particles. If the concentration of the two particle classes is unknown, a normalized collision frequency, \( F_{12} \), can be defined as \( J_{12} \) divided by the particle concentrations. Stating the above mathematically (Zhang and Davis, 1991):
where \( n_1 \) and \( n_2 \) are the number concentrations of particles one and two. Note that the collision frequency without particle-particle interactions, \( F_{12}^{(0)} \), is given by (Zhang and Davis, 1991):

\[
F_{12}^{(0)} = \frac{J_{12}^{(0)}}{n_1 n_2} = V_{12}^{(0)} \pi (a_1 + a_2)^2
\]  

i.e., particles overtaking one another will not flow around each other; they collide only if they were originally on a direct collision course, much like sticky billiard balls. This collision frequency is normally taken as the reference situation, with the collision efficiency, \( E_{12} \), defined as the ratio of the actual and reference collision frequencies (Zhang and Davis, 1991):

\[
E_{12} = \frac{F_{12}}{F_{12}^{(0)}} = \frac{\gamma_c^* \pi}{(a_1 + a_2)^2}
\]

Stated in a different way, the collision efficiency is the collision rate with interparticle forces divided by the collision rate without interparticle forces. Note that the collision efficiency thus defined can assume values above unity. It has been proposed to rename this function the "collision enhancement function" (Tsouris et al., 1995), but the term "collision efficiency" is retained here in order to maintain consistency with the literature.

With the above definitions and equations, the theoretical framework for a particle-particle collision trajectory analysis model is sufficient for useful numerical simulations. The specifics of these simulations, and the results they give, are outlined in the Results and Discussion Section.

**Turbulent Shear**

**Collision Efficiency and Collision Frequency**

The collision efficiency for Brownian flocculation can be calculated by Eq. [23a]. Equation [23a] does not include, however, the effect of external forces and that of the flow regime. A trajectory model for homogeneous flocculation under shear flow was investigated by van de Ven
and Mason (1977), and a semi-empirical formula was derived by neglecting the electrostatic force:

\[ E_{12} = f(\bar{\lambda})C_A^{0.18} \tag{29} \]

The function \( f \) depends on \( \bar{\lambda} \), which is the ratio of the London wavelength over \( 2\pi a \). \( C_A \) is the ratio of attractive force to hydrodynamic force:

\[ C_A = \frac{A}{36\pi \eta G a^3} \tag{30} \]

where \( G \) is velocity gradient of the system.

When two particles collide under turbulent shear flow, the collision radius for a pair of particles with different size will be the sum of the radius, \( R = a_1 + a_2 \). The mean flux of fluid into a sphere of radius \( R \) is \(-\int_{U<0} UdS\), where \( U \) is the relative velocity in the radial direction and \( S \) is the sphere surface area. From the continuity of fluid, the following equation can be obtained.

\[ \int_{U<0} UdS + \int_{U>0} UdS = 0 \tag{31} \]

Then the flux can be given as

\[ -\int_{U<0} UdS = \frac{1}{2} \int UdS = \frac{1}{2} \int |U|dS = 2\pi R^2 |U| \tag{32} \]

For \( R \) smaller than Kolmogorov microscale, \( |U| = R |\partial U_x / \partial x| \). The mean square of the velocity gradient is related to energy dissipation per unit mass per time, \( \varepsilon \), and kinematic viscosity, \( \nu \), as \((\partial U_x / \partial x)^2 = \varepsilon / 15\nu\). If the velocity gradient is assumed normally distributed, then \( (\partial U_x / \partial x) = (2\varepsilon / 15\eta)^{1/2} \), and the collision frequency becomes

\[ F_{12} = 2\pi R^3 (\partial U_x / \partial x) = 2.3(a_1 + a_2)^3 \left( \frac{\varepsilon}{\nu} \right)^{1/2} = 2.3(a_1 + a_2)^3 G \tag{33} \]
The velocity gradient, $G$, can be obtained by

$$G = (e/v)^{1/2} = (P/\mu V)^{1/2} \quad [34]$$

where $V$ is the system volume and $P$ is the power dissipation in the system (Adler, 1981). The power dissipation can be given as

$$P = nC_D \rho w(2\pi N_a)^3 \left(D_o^4 - D_i^4 \right) \quad [35]$$

where $n$ is the impeller number, $w$ is the width of impeller, $D_o$ and $D_i$ are the outer and inner radii of the impeller, and $N_a$ is the agitation speed in the system.

To meet the condition in Eq.[33], the particles should be smaller than Kolmogorov length scale, $\eta_k = \left(v^3/\epsilon\right)^{1/4}$. The Kolmogorov length scale can be calculated as:

$$\eta_k = \left(v^3/\epsilon\right)^{1/4} = (\nu G)^{1/2} \quad [36]$$

For $R < \eta_k$, the collision frequency can be obtained from Eq. [33] (Saffman and Turner, 1956).

**Breakage**

During flocculation, mixing of the suspension causes the particle to collide and thus, improves the separation. The aggregation of particles can be promoted by increasing the mixing intensity. If the agitation is too strong, however, the turbulent shear force will break the aggregates into smaller particles. Three distinct breakage distribution functions were investigated by Spicer and Pratsinis (1996): binary breakage, ternary breakage, and normally distributed. Lu and Spielman (1985) proposed the breakage rate due to splitting, $\partial n_{bs}(v,t)/\partial t$, for aggregates with volume $v$:

$$\frac{\partial n_{bs}(v,t)}{\partial t} = -g(v)n(v,t) \quad [37]$$

where $g(v)$ is the frequency of splitting of aggregates with volume $v$, and $n(v,t)$ is the particle number concentration in the interval $(v,v + dv)$. 

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Magnetically Seeded Flocculation

In this case, the particle collision frequency given by Eq. [23b], [26], or [33] can be calculated as a function of all parameters of the system. This collision frequency can then be used in a population balance model to estimate the flocculation as a function of time (Tsouris and Scott, 1995).

The simple population balance equation in discretized form is given by:

\[
\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} F_{j(i-j)n_jn_{(i-j)}} - \sum_{j=1}^{N} F_{ij}n_in_j
\]  

[38]

where \( n_i \) and \( n_j \) are the populations of particles per unit volume in the discrete sizes of \( i \) and \( j \), respectively. \( N \) is the total number of discrete sizes. The flocculation frequency \( F_{ij} \) of particles under the influence of interaction forces can be obtained based on the specific flocculation regime.

Equation [38] can be extended to a bivariate population balance model to estimate the flocculation as a function of time (Tsouris et al., 1995):

\[
\frac{dn_{ij}}{dt} = \frac{1}{2} \sum_{l=1}^{i-1} \sum_{m=1}^{j} n_{lm}n_{(i-l)(j-m)}F_{lm,(i-l)(j-m)} - \sum_{l=1}^{N_s} \sum_{m=1}^{N_c} n_{ij}n_{lm}F_{ij,lm}
\]  

[39]

where \( n_{ij} \) is the number of particles of size \( i \) and magnetic susceptibility \( j \) (class \( ij \)), \( F_{ij,lm} \) is the collision frequency of particles in class \( ij \) with particles in class \( lm \), and \( N_s, N_c \) are the total numbers of size and magnetic susceptibility classes, respectively. Some of the capabilities of this model in describing heterogeneous flocculation between paramagnetic particles of varying magnetic susceptibility are discussed by Tsouris et al. (1995).

When the system is under vigorous shear flow, the breakage rate should be taken into consideration and Eq. [38] can be written as

\[
\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} F_{j(i-j)n_jn_{(i-j)}} - \sum_{j=1}^{N} F_{ij}n_in_j + \sum_{k=i+1}^{N} v_k g_k n_k P_{i,k} - g_i n_i
\]  

[40]

where \( v_k \) is the number of particles in which a particle of size \( k \) breaks into. The function \( g_k \) is the breakage rate of particles of size \( k \), and \( P_{i,k} \) is the probability to form particles of size \( i \) from
breakage of particles of size $k$. The first term in the right-hand side of Eq. [40] is the source due to the flocculation of smaller particles. The second term is the loss due to flocculation to larger particle. The third term expresses the source because of the breakage of larger particles and the fourth term is the loss due to breakage to smaller particles.

The modeling approach described here permits studies of magnetically seeded flocculation in which magnetic particles are added to a suspension of non-magnetic particles. Initially, flocculation of non-magnetic with magnetic particles will occur due to both external and interparticle forces, but no contribution will be provided by magnetic dipoles. The resulting flocs have higher magnetic susceptibility than the original non-magnetic particles and may respond in a magnetic field. This mechanism suggests that magnetically seeded flocculation can mathematically be described as a heterogeneous flocculation process, which can sufficiently be handled by the bivariate population balance approach shown by Eq. [39]. In addition, Eq. [40] can be used to predict size distribution in flocculation systems under turbulent shear flow. The effect of shear flow on the particle size and magnetic susceptibility in a flocculation system can be predicted using Eq. [40].

**Fractal Dimension**

In all the population models shown in the previous section, the particles were assumed to be spherical. The models can be extended for non-spherical aggregates when a characteristic aggregate radius which is a function of fractal dimension is introduced. Aggregates are fractal objects, which means that they have a non-integer fractal dimension, $D_f$. The fractal dimension is between one and three, the lower value representing a linear aggregate:

\[
\frac{a}{a_0} = A_f \left( \frac{v_f}{v_{f0}} \right)^{\frac{1}{D_f}}
\]

where $v_f$ is the volume of the floc and $a_0$ and $v_{f0}$ are the initial particle radius and volume, respectively. By assuming $A_f = 1$ (Wu and Friedlander, 1993), the radius of the floc, $a$, can be obtained as

\[
a = a_0 \left( \frac{v_f}{v_{f0}} \right)^{\frac{1}{D_f}}
\]
This characteristic radius can be used for different fractal dimensions to replace the particle size into Eqs. [38], [39], and [40]. With this approach, the fractal dimension is incorporated in the population balance equations.

Magnetic-Seeding Filtration

Theory

**Forces in Magnetic Field**

When a paramagnetic particle is placed in a magnetic field, the energy density stored in the particle is given by \( \mathbf{J} \cdot \mathbf{H} \), where \( \mathbf{J} \) is the magnetic polarization of a particle and \( \mathbf{H} \) is the magnetic field strength. Therefore, the magnetic force, \( \mathbf{F}_m \), can be written as (Svoboda, 1987)

\[
\mathbf{F}_m = \nabla \left( \mathbf{J} \cdot \mathbf{H} \right) dV_p
\]

where \( \nabla \) is the gradient operator, and \( V_p \) is the volume of a particle.

The magnetic polarization of a particle is given by

\[
\mathbf{J} = \frac{\mu_0 \chi \mathbf{H}}{1 + \frac{X}{3}}
\]

where \( \mu_0 \) is the permeability of free space, and \( X \) is the volume magnetic susceptibility.

Combining Eqs. [43] and [44] the magnetic force acting on a small spherical paramagnetic particle located in an external magnetic field will be written as

\[
\mathbf{F}_m = \left( \frac{\mu_0 X}{1 + \frac{X}{3}} \right) \nabla \left( \mathbf{H}^2 \right)
\]

Assuming \( X \ll 1 \), then the magnetic force can be written as
Competing Forces

In a magnetic field there are other forces competing with magnetic forces: inertial, gravitational, and hydrodynamic drag forces. For most cases of wet high-gradient magnetic filtration, the gravitational and hydrodynamic drag forces play a more important role than inertial forces. The equations of these three forces for a spherical particle are given by

\[
F_m = \frac{1}{2} \mu_0 X \nabla (\mathbf{H}^2) \tag{46}
\]

where \( F_m \) is the inertial force, \( \rho_p \) is the particle density, and \( V_p \) is the volume of the particle with radius \( a \), and \( \frac{d^2r}{dt^2} \) is the acceleration of the particle.

\[
F_I = \rho_p V_p \left( \frac{d^2r}{dt^2} \right) \tag{47}
\]

where \( F_I \) is the inertial force, \( \rho_p \) is the particle density, and \( V_p \) is the volume of the particle with radius \( a \), and \( \frac{d^2r}{dt^2} \) is the acceleration of the particle.

\[
F_g = V_p (\rho_p - \rho_f) g \tag{48}
\]

where \( F_g \) is the gravitational force, \( \rho_f \) is the fluid density, and \( g \) is the acceleration by gravity.

\[
F_d = 6\pi \eta a \left[ v(r) - \frac{dr}{dt} \right] \tag{49}
\]

where \( F_d \) is the hydrodynamic drag force, \( \eta \) is the dynamic viscosity of the fluid, \( v(r) \) is the velocity of the particle at position \( r \), and \( \frac{dr}{dt} \) is the velocity of the fluid.

It can be seen from Eqs. [46], [48], and [49] that the relative importance of the forces will depend on particle size, \( a \), since each force has a different dependence on \( a \). The gravitational force which depends on the third power of particle radius will be significant for large particles. The dependence of the hydrodynamic force on the first power of the particle radius means that the hydrodynamic force will be important for small particles. Thus, it is clear that the magnetic force will be greater than the other forces in a limited interval of particle size.
Particle Trajectories in a Single-Wire High-Gradient Magnetic Separation

**Geometrical Configuration**

The general configuration of a particle motion in a single-wire magnetic separator is shown in Figure 3.4. In Figure 3.4, there is a single wire of radius \( b \) and a spherical particle of radius \( a \) placed in a magnetic field with external field strength \( H_0 \), with \( u_s \) the fluid velocity.

**Particle Trajectory Equation**

The force balance that describes the particle motion is given by

\[
F_I = F_m + F_d + F_g \tag{50}
\]

For the magnetic force, the magnetic field strength \( H \), in Eq. [46] now includes the external magnetic field \( (H_0) \) and the field generated by the magnetized wire which is given by

\[
H_r = H_0 \cos \theta + H_0 W \left( \frac{b^2}{r^2} \right) \cos \theta \tag{51a}
\]

\[
H_\theta = -H_0 \sin \theta + H_0 W \left( \frac{b^2}{r^2} \right) \sin \theta \tag{51b}
\]

where \( H_r \) and \( H_\theta \) are the components of magnetic field strength in cylindrical coordinates and \( W = (\mu_w - \mu_f) / (\mu_w + \mu_f) \). \( \mu_w \) and \( \mu_f \) are the magnetic permeabilities of the wire material and fluid, respectively. Since the magnetic permeability of a ferromagnetic wire is much larger than that of fluid, \( W \) is approximately equal to one.

The second terms in both Eqs. [51a] and [51b] are produced by the magnetization of the wire. In general, the magnetization, \( M \), is proportional to the external field \( H_0 \) until it saturates. The saturation magnetization value, \( M_s \), is constant and does not increase with \( H_0 \). Therefore if the external field \( H_0 \) is larger than the field needed to magnetically saturate the wire, Eqs. [51a] and [51b] will be rewritten as

\[
\]
where \( K = \frac{M_s}{H_0} \) when the wire is saturated.

Inserting Eqs. [52a] and [52b] into Eq. [46], one can derive the magnetic force equation in polar coordinates:

\[
F_{mr} = \left(\frac{4\pi a^3}{3}\right) \mu_0 X_m s \left( \frac{b^2}{r^3} \right) \bar{H}_0 \left( \frac{M_s b^2}{2 r^3} + H_0 \cos(2\theta) \right)
\]  \hspace{1cm} [53a]

\[
F_{m\theta} = -\left(\frac{4\pi a^3}{3}\right) \mu_0 X_m s \left( \frac{b^2}{r^3} \right) \bar{H}_0 \sin(2\theta)
\]  \hspace{1cm} [53b]

where \( X = X_P - X_f \) is the difference between volume magnetic susceptibilities of the particle and fluid.

For hydrodynamic drag force, if laminar flow is assumed, the equations of velocity components are given by

\[
\begin{align*}
\upsilon_r &= \frac{\ln \left( \frac{r}{b} \right) - 0.5 \left[ 1 - \left( \frac{b}{r} \right)^2 \right]}{2.002 - \ln \bar{R}} \cos(\theta - \gamma) \\
u_{\theta} &= -\frac{\ln \left( \frac{r}{b} \right) - 0.5 \left[ 1 - \left( \frac{b}{r} \right)^2 \right]}{2.002 - \ln \bar{R}} \sin(\theta - \gamma)
\end{align*}
\]  \hspace{1cm} [54a]

\[
\frac{\upsilon_r}{2.002 - \ln \bar{R}}
\]

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where the Reynolds number, \( \mathcal{R} \), given by

\[
\mathcal{R} = \frac{2u_s \rho f b}{\eta}
\]

[55]

should be small (\( \mathcal{R} \ll 1 \)) for the case of laminar flow.

The components of drag force then can be written as

\[
F_{dr} = 6\pi \eta a \left( v_r - \frac{dr}{dt} \right)
\]

[56a]

\[
F_{d\theta} = 6\pi \eta a \left( v_{\theta} - \frac{rd\theta}{dt} \right)
\]

[56b]

To simplify the force equation, the analysis is limited to low Reynolds number and small particles (\( a < 75 \text{ mm} \)) that will make the gravitational force much smaller than the hydrodynamic force, i.e. the following condition is satisfied:

\[
\frac{2\rho_0 a^2}{9\eta} < 1
\]

[57]

The inertial and gravitational forces can therefore be neglected and then the force balance equation (Eq. [50]) can be written as

\[
\frac{dR}{dt} = \frac{v_r}{b} - \frac{v_m}{b} \left( \frac{K}{R^5} + \frac{\cos(2\theta)}{R^3} \right)
\]

[58a]
\[
\frac{Rd\theta}{dt} = \frac{v_\theta}{b} - \frac{v_m}{b} \left( \frac{\sin(2\theta)}{R^3} \right)
\]

where \( R = r/b \) and

\[
v_m = \frac{2\mu_0 XM_s H_0 a^2}{9\eta b}
\]

is defined as the magnetic velocity.

Dividing Eq. [58a] by Eq. [58b], the differential trajectory equation is obtained

\[
\frac{dR}{d\theta} = \frac{\left[ \frac{v_r}{b} - \frac{v_m}{b} \left( \frac{K + \cos(2\theta)}{R^5 + \frac{R^3}{R^3}} \right) \right]}{\left[ \frac{v_\theta}{b} - \frac{v_m}{b} \left( \frac{\sin(2\theta)}{R^3} \right) \right]}
\]

By using a numerical method, the solution of Eq. [60] can be found to predict the particle trajectory around the collector. Then, the critical capture radius of the limiting trajectories can be obtained. From this critical capture radius, \( y_c^* \), the filter performance in a magnetic field can be found.

**Filter Performance**

A high gradient magnetic separator matrix of length \( L \) is considered, which is randomly packed with wire of fraction \( (1 - \varepsilon) \). Then the length of the wire in a differential section \( dx \) of the filter per unit cross section is \( [(1 - \varepsilon)dx/\pi b^2] \). Due to the random nature of the matrix, approximately two-thirds of the fiber are considered effective for particle capture. Thus, the available cross section is \( 4y_c^*b/3 \), and consequently, the effective area is \( 4(1 - \varepsilon)y_c^*dx/3b \). The accumulation rate of particles onto the matrix over \( dx \) is then given as (Dauer and Dunlop, 1991)

\[
\frac{\partial N}{\partial x} = \left[ \frac{4(1 - \varepsilon)y_c^*}{3\pi b} \right] N
\]
where $N$ is the number of particles per unit volume.

By solving Eq. [61], the removal efficiency is obtained by

$$\text{Removal Efficiency} = 1 - \frac{N_{\text{out}}}{N_{\text{in}}} = \exp \left[-\frac{4(1-\varepsilon)L_{y_c}^*}{3\pi b}\right]$$

where $N_{\text{out}}$ and $N_{\text{in}}$ are the number of particles per unit volume in the effluent and influent streams, respectively.

### 3.3. Results and Discussion

There are several groups of results discussed in this section. These results can have significance in magnetically seeded solid-liquid separations. The calculations were computed on an IBM RS/360 model workstation, configured with 64 MB of memory, using double-precision calculations. An ordinary differential equation solver with variable step (EPISODE; Hindmarch and Byrne, 1976) was employed to solve the trajectory equations given by Eqs. [25] and [60] and the population balance equation given by Eq. [38]. First collision efficiencies and frequencies due to external forces (mainly magnetic) are presented. Then, some preliminary results on collision frequency due to shear flow are discussed, followed by a demonstration of the use of the population balance equations to predict magnetically seeded flocculation. The incorporation of fractal dimension in the population balance equations is shown through a comparison of model predictions with experimental results. Finally, a sensitivity analysis on the model developed for magnetically seeded filtration is presented.

**Collision Efficiency and Collision Frequency due to External Forces**

The results presented here correspond to collision efficiencies and frequencies when the trajectory calculation given by Eq. [25] can be employed. To verify the model developed in this study, a series of results by neglecting the magnetic forces were first obtained; these results were found identical to those of other studies in which gravity induced coagulation encounters were analyzed via trajectory calculations (Davis, 1984; Melik and Fogler, 1984).

The results of model computations are discussed in the sections below, organized by the forces present during each set of calculations. In all calculations, the electrostatic force has been neglected. In other words, all particles are assumed to have no double-layer charge, and thus no electrostatic attraction or repulsion. Extending the calculations to study the effect of electrostatic forces on collision efficiency and frequency is the objective of future work.
The Collision Efficiency and Collision Frequency of Two Particles Under Magnetic, van der Waals, and Hydrodynamic Forces for a Variable Direction of the Magnetic Field

The first step in this study is to check whether the direction of the magnetic field plays a significant role in the collision efficiency and collision frequency, and to find the direction that gives the maximum efficiency and frequency. In these calculations, the external magnetic force has been neglected, i.e., the magnetic gradient has been considered negligible, and the angle $\alpha$ between the vertical axis and the direction of the magnetic field has been taken values of 0, $\pi/2$, and $\pi$ in order to keep the cylindrical symmetry of the system. The two particles are assumed to have the same density, and their density difference ($\Delta \rho$) to that of the fluid has been considered to be 2000 kg/m$^3$. The results are shown in Figures 3.5a and 3.5b. It is clear from the figure that maximum collision efficiency and collision frequency occur when the magnetic field has the same or opposite direction to that of the vertical axis, i.e., $\alpha = 0, \pi$. The direction that gives the smaller efficiency corresponds to the case at which the magnetic field is perpendicular to the vertical axis, i.e. $\alpha = \pi/2$. In this case, both collision efficiency and collision frequency decrease with the magnetic field, approaching zero near a magnetic induction of 1.5; this phenomenon may be explained by the repulsive interparticle magnetic force that appears between the two particles when they come close together in the region of $\psi = 90^\circ$ (see Figure 3.2a). All the calculations that follow correspond to the case where $\alpha = 0$. It is shown with this example calculation, that the trajectory equation can be used to find the optimum direction of the magnetic field with respect to collision efficiency and collision frequency.

The Collision Efficiency and Collision Frequency of Two Particles Under Magnetic, van der Waals, and Hydrodynamic Forces

The purpose of the model developed in this study is the simulation of magnetically seeded solid-liquid separation processes. Accordingly, input parameters were chosen to reflect different stages and conditions under which these processes occur. Another, more specific goal is the comparison of the effects of various input parameters. The first set of input parameters chosen represents the case of the initial stages of magnetically seeded flocculation and filtration, when magnetically susceptible particles have just been introduced to the solution. At this point, most flocculation events will be between magnetic and non-magnetic particles and the filter collector may interact with non-magnetic particles.

Figure 3.6a shows the collision efficiency for such a case, where $a_1 = 5\times 10^{-6}$ m, $a_2 = 5\times 10^{-7}$ m, the magnetically susceptible particle has a susceptibility of $\chi = 0.001$, and the particles have a variable density expressed with the difference in their density compared to that of the fluid ($\Delta \rho$). Since in these calculations it is assumed that $\nabla B$ has direction of that of gravity,
the collision efficiency is plotted against the magnetic strength, $B|\nabla B|$ (T²/m). It has to be recognized that whenever there is interaction between magnetic and non-magnetic particles, the quantities $B$ and $|\nabla B|$ are multiplied by one another wherever they appear in an equation in this study; thus, the two quantities can be grouped as a single variable. Note that this is not true for interaction between two magnetic particles. Figure 3.6b shows the collision frequency for the same set of input parameters.

From Figure 3.6a, it can be seen that the collision efficiency decreases with increasing magnetic strength and increasing density difference ($\Delta \rho$). This can be attributed to the fact that the far-field relative velocity varies with the magnetic strength and density difference. As both magnetic strength and $\Delta \rho$, and thus the far-field relative velocity, increase, the two particles have less time to interact with each other through the attractive interparticle forces. As the magnetic strength and $\Delta \rho$ increase further, the collision efficiency reaches an asymptotic value. The effect of the density difference is the same as that of the magnitude of the magnetic gradient since both parameters influence the relative velocity in the same way.

The collision frequency, contrary to the collision efficiency, increases with the magnetic strength, the density difference, and thus the far-field relative velocity. This result stems from the fact that the particle flux onto a particular flocculating particle is proportional to the relative velocity (see Eq. [26]), an effect which masks the change in collision efficiency.

In this group of calculations, three other specific quantities are varied in addition to the density difference, and the results are discussed below. Figure 3.7a shows the effect of varying magnetic susceptibility (and magnetic strength) on collision efficiency. Recall that in this group of simulations, one particle is magnetic while another is non-magnetic, a condition likened to the first stages of magnetically-seeded separations. With no magnetic dipole effects between particles, the change in magnetic susceptibility is expected to have an effect similar to the variation in the magnetic strength. Indeed this is born out: the collision efficiency can be decreased either by increasing the magnetic strength or by increasing the magnetic susceptibility of the magnetically susceptible particle. Furthermore, the collision efficiency for various magnetic susceptibilities converges to the same asymptotic value for high magnetic strengths.

Figure 3.7b shows the effect of magnetic susceptibility on the collision frequency, which is consistent with the results of Figure 3.6b: collision frequency increases with both magnetic strength and magnetic susceptibility.

The data in Figures 3.8a and 3.8b show a different effect. Here the Hamaker group, $A/kT$, is modulated. Essentially, the attractive force between the two flocculating particles is varied at a specific far-field relative velocity. The effect is simultaneous to the collision efficiency and the collision frequency; both are increased as the attractive force is increased. The data do suggest that the collision efficiency is not influenced much from the value of the Hamaker constant.
as the magnetic strength increases above a specific value; presumably the effect of Van der Waals forces becomes negligible as the magnetic force increases.

Perhaps the most intriguing results come from Figures 3.9a and 3.9b, where the size ratio between particles is covaried with the magnetic force, $|\mathbf{B}| \mathbf{V}$. Here, an increasing size ratio is rewarded with both greater collision efficiency and collision frequency. As the sizes of particles are treated in some cases as normalized quantities in the computer model calculations, it is likely that the effect seen is due to both the ratio of sizes, as well as the size of one particular particle. Possibly this result is due to a decrease in the hydrodynamic resistance; such a correlation is hinted at in Haber et al. (1973).

The Collision Efficiency and Collision Frequency of Two Particles Under Magnetic, Magnetic Dipole, van der Waals, and Hydrodynamic Forces

The last set of data considered in this work are for the case corresponding to the latter part of a magnetically seeded solid-liquid separation process, after the majority of non-magnetic particles have collided with magnetic particles. Further particle collisions will thus be influenced by the magnetic dipole force, which acts between two particles with magnetic susceptibilities. As was discussed previously, Eq. [13] applies only for a uniform magnetic field. Apparently the field uniformity is violated when the magnetic field gradient is non-zero. For the ranges of the magnetic field gradient used in this work (which correspond to most practical applications) and the distance in which the magnetic dipole force becomes important, the change in the magnetic induction is insignificant. Therefore, the magnetic dipole force is still calculated by Eq. [13]. One particle has a magnetic susceptibility fixed at 0.001, while the other varies as shown in Figures 3.10a and 3.10b. The effects here are as expected. Both collision efficiency and collision frequency increase with the magnitude of the magnetic induction. Also, both quantities increase with increasing the magnetic susceptibility of the second particle. As in the simulations shown before for the collisions between magnetically susceptible and non-magnetically susceptible particles, collision efficiency decreases with the magnetic field gradient, and thus the magnetic strength. On the other hand, the collision frequency increases with increasing the magnetic field gradient.

Collision Frequency due to Turbulent Shear

The effect of size on collision frequency due to turbulent shear is shown in Figure 3.11a. Under the same thermal conditions, the Brownian collision frequency depends on the size ratio, but not the size (Figure 3.11b). The turbulent-sheared collision frequency also increases with increasing size ratio and rises much faster for larger particles (Figure 3.11a). The agitation speed changes the power dissipation in the system (Eq. [34]). The collision frequency increases as the agitation speed increases. Comparing the collision frequency of Brownian flocculation (Figure
3.11a) (i.e., without agitation) with turbulent-shear flocculation (Figure 3.11c), the latter has much higher frequency. Therefore, agitation makes the flocs grow much faster in turbulent-shear systems.

**Magnetically Seeded Flocculation**

A sensitivity analysis is implemented for the population balance modeling by varying input parameters such as number of discrete sizes, initial particle size, zeta potential, ionic strength, and particle concentration. An example shown in this report (Figure 3.12a) demonstrates that the particle growth behavior is changing rapidly when the zeta potential approaches \( -60 \text{ mV} \).

**Fractal Dimension**

The discretized population-balance given by Eq. [38] is used to simulate the growth of particles. The original model assumes spherical particles. There are two major calculations in estimating the flocculation frequency: one is related to the collision frequency and the other to the collision efficiency. The collision efficiency function includes the interaction potential term. Two implementations for estimating this term are used: the first one is to replace all the radius values of the particles with the characteristic radius given by Eq. [42]. This approach (approach 1) will increase the floc growth when fractal dimension is less than three. The second method (approach 2) replaces the radius values with the characteristic radius only in the microscopic equation (Eq. [38]). This approach is similar to the original (sphere) assumption at the beginning of flocculation, but the particle growth is slower than that of the sphere model \( (D_f = 3) \) for longer flocculation times. The results as shown in Figure 3.12b indicate that approach 1, which replaces the original radius with the characteristic radius in both the potential term and the flocculation frequency function, better describe the experimental data (Tsouris and Scott, 1995) for particles that have initially a broad size distribution.

**Magnetic Seeding Filtration**

The model has been tested by varying the magnetic field strength. All the results obtained from the model assumed that the initial velocity \( (u_x) \) is perpendicular to the external magnetic field, i.e. parallel to \( y \) axis.

**Magnetic field strength**

The effect of magnetic field on filter performance is tested by varying the magnetic field from 0.5 to 1.2 T. The values of parameters used are \( X = 0.003, \ M_s = 477464.8 \text{ A/m}, \) and \( b = 6.35 \times 10^{-5} \text{ m} \). Figure 3.13 shows a minor effect of magnetic field strength on the removal of
particles and this result is consistent with the experimental data. The modeling results show that once non-magnetic particles flocculate with magnetic seeding particles and produce paramagnetic flocs, they can efficiently be removed by a magnetic filter under a low magnetic field.

3.4. Summary of Theoretical Studies

This study has examined the theoretical framework underlying magnetically seeded solid-liquid separations, developing expressions for the external forces acting on particles and the interparticle forces between them. From these considerations, a model was derived and implemented as a computer code. Through manipulation of input variables, this code and the physical system it represents revealed relationships between particle-particle and particle-collector forces and operating parameters. The particle size ratio was found to affect collisions, with evidence that this effect acts through the hydrodynamic resistance. The direction of the magnetic field plays a significant role in the collision efficiency and collision frequency, and it was found that when the direction of the magnetic field is parallel to the vertical axis, the system is at its optimum state in terms of flocculation. For the turbulent shear system, the agitation speed was found to be the main factor for the collision frequency. In addition, the fractal dimension correction provides a better prediction of the experimental data. A trajectory model was developed to predict the performance of magnetically seeded particle filtration. From the sensibility analysis of this model, it was found that the magnetic field strength affects the removal efficiency. The implication for magnetic seeding is the need for more efficient separation systems. With further research, the results obtained in this study could be used in a dynamic model of particle flocculation or particle filtration, allowing full exploitation of this powerful technique.

This work is in progress and its major objective is to develop mechanistic models that can predict the performance of magnetically seeded solid-liquid separation processes. Experimental results that have been conducted at ORNL will be used to verify the developed models. In the experiments conducted at ORNL, flocculation without the presence of a magnetic field was induced by shear flow and then the suspension passed through a magnetic filter. The collision frequencies developed in this study will be used in combination with the bivariate equation given by Eq. [39] to investigate how the size and magnetic susceptibility of suspended particles change with time. The collision efficiency for turbulent shear flocculation will be developed. Then, the approaches described in this work will be used to predict the performance of the magnetic filter. The fractal dimension will also be used for more realistic simulations of the physical system.

3.5. Notation

\( A \) Hamaker constant (J)

\( A_f \) constant for fractal dimension calculations
\( A_p \)  cross-sectional area of the particle (m^2)
\( a \)  particle radius (m)
\( B \)  magnetic induction (T=V s m^{-2})
\( B \)  magnitude of magnetic induction (T=V s m^{-2})
\( b \)  wire radius (m)
\( C_A \)  ratio of attractive force to hydrodynamic force
\( C_D \)  coefficient of drag
\( D_{12}^{(0)} \)  Brownian relative diffusivity
\( D_o \)  outer radius of impeller (m)
\( D_i \)  inner radius of impeller (m)
\( D_f \)  fractal dimension
\( D_\infty \)  diffusivity in the absence of interparticle forces (m^2 s^{-1})
\( E_{12} \)  collision efficiency
\( \hat{e}_r \)  unit vector in the radial direction
\( \hat{e}_\theta \)  unit vector in the tangential direction
\( e \)  electron charge=1.6x10^{-19} C
\( F_1 \)  axisymmetric drag force of particle 1 (N)
\( F_b \)  buoyant force (N)
\( F_d \)  drag force (N)
\( F_g \)  gravitational force (N)
\( F_m \)  magnetic force (N)
\( F_{12} \)  collision frequency (m^3 s^{-1})
\( F_e \)  electrostatic force (N)
\( F_{vdW} \)  van der Waals force (N)
\( F_r^{mag} \)  radial magnetic interparticle force (N)
\( F_\theta^{mag} \)  tangential magnetic interparticle force (N)
\( G \)  velocity gradient (s^{-1})
\( G(s) \)  axisymmetric relative mobility function
\( g \)  gravitational acceleration (m/s^2)
\( \hat{g} \)  unit vector of the gravitational acceleration
\( g \)  magnitude of the gravitational acceleration=9.8062 m/s^2
\( g(\nu) \)  frequency of splitting
\( H \)  magnetic field strength (A m^{-1})
\( H_0 \)  external magnetic field strength (A m^{-1})
\( H(s) \)  asymmetric relative mobility function
$I$ ionic strength of the solution (M)

$J_{12}$ collision rate (m$^{-3}$ s$^{-1}$)

$k$ Boltzmann constant = $1.38 \times 10^{-23}$ J K$^{-1}$

$L$ filter length (m)

$L(s)$ axisymmetric relative mobility function

$M$ magnetization (A m$^{-1}$)

$M_s$ saturation magnetization (A m$^{-1}$)

$M(s)$ asymmetric relative mobility function

$Na$ agitation speed (s$^{-1}$)

$n$ number of impeller

$n_1$ number concentration of particle one (m$^{-3}$)

$P$ power dissipation (W)

$P_{i,k}$ probability to form particles of size $i$ from breakage of particles of size $k$.

$Pe$ Péclet number

$p_{12}$ normalized probability that particle 1 is at a given position relative to particle 2

$Q_{12}$ interparticle force parameter

$Q_{12}^{mag}$ magnetic force parameter

$Re$ Reynolds number

$r$ center-to-center particle separation (m)

$s$ = $2r/(a_1 + a_2)$ (dimensionless particle separation)

$T$ absolute temperature (K)

$t$ time (s)

$u_{12}$ overall dimensionless relative velocity

$u_s$ flow approach velocity (m s$^{-1}$)

$V^{(0)}_{12}$ far-field relative velocity (m s$^{-1}$)

$V^{(0)}_{12 g}$ far-field relative gravitational velocity for two particles (m s$^{-1}$)

$V^{(0)}_{12 m}$ relative magnetic velocity (m s$^{-1}$)

$V_{el}$ electrostatic potential (J)

$V_{mag}$ interaction potential between two magnetically susceptible particles (J)

$V_p$ volume of the particle (m$^3$)

$V_{vdW}$ van der Waals interparticle force potential (J)

$v^{(0)}_{12}$ magnitude of the far-field relative velocity (m s$^{-1}$)

$v$ particle velocity (m s$^{-1}$)

$v_m$ magnetic velocity (m s$^{-1}$)
\( \nu \) magnitude of particle velocity (m s\(^{-1}\))
\( \nu_f \) the volume of the floc (\( \mu m^3 \))
\( w \) width of impeller (M)
\( Y^*_c \) critical horizontal separation (m)
\( z \) valence of the symmetric electrolyte in the solution

\( \alpha \) angle between the direction of the vertical axis and that of the magnetic field
\( \Delta \rho \) density difference of particles to that of the fluid (kg m\(^{-3}\))
\( \varepsilon \) permittivity of the medium=6.95x10\(^{-10}\) C V\(^{-1}\) m\(^{-1}\) for water
\( \xi \) axial coordinate in the filter (m)
\( \eta \) dynamic viscosity (kg m\(^{-1}\) s\(^{-1}\))
\( \theta \) angle between the vertical axis and \( r \)
\( \lambda = a_2/a_1 \) (particle radius ratio)
\( \lambda_0 \) London wavelength/2\( \pi a \)
\( \mu_w \) magnetic permeability of the wire (V s A\(^{-1}\) m\(^{-1}\))
\( \mu_f \) magnetic permeability of fluid (V s A\(^{-1}\) m\(^{-1}\))
\( \mu_0 \) permeability of free space=4 \( \pi \times 10^{-7} \) V s A\(^{-1}\) m\(^{-1}\)
\( \hat{\mu} \) respective unit magnetic dipole vectors of particles
\( \rho \) density of the fluid (kg m\(^{-3}\))
\( \rho_p \) density of the particle (kg m\(^{-3}\))
\( \chi \) volume magnetic susceptibility
\( \psi \) angle between the magnetic field and \( r \)
\( \Psi_{oi} \) particles' surface potential (V)

3.6. References


3.7. Figures for the Modeling Section

Figure 3.1: Coordinate system used in quantifying the interparticle forces.
Figure 3.2: Dimensionless magnetic-dipole force as a function of the angle $\psi$ between the magnetic field and the line joining the centers of two particles: (a) radial force and (b) tangential force.
Figure 3.3a: Magnetic-dipole (mag), van der Waals (vdW), and repulsive or attractive electrostatic (lell) forces as a function of the dimensionless distance between particle surfaces, for $\psi = 0$ and different size ratios. Other parameters include: $A=5\times10^{-20}$ J, $T=293$ K, $a_1=5\times10^{-6}$ m, $z=1$, $I=0.05$ M, $\Psi_{o1}=|\Psi_{o2}|=0.03$ V, $B=5$ T, and $\chi_1=\chi_2=0.001$.

Figure 3.3b: Electrostatic, van der Waals, magnetic, and total particle potentials (Va). Other parameters include: $B=6$ T, $\Psi_{o1}=|\Psi_{o2}|=0.04$ V, $\chi_1=\chi_2=0.002$. 

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Figure 3.4: Coordinate system used in magnetically seeded filtration.
Figure 3.5: Effect of the direction of the magnetic field on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4\times10^{-20}$ J, $\eta=10^{-3}$ kg/m s, $T=293$ K, $a_1=5\times10^{-6}$ m, $\lambda=0.1$, $\chi_1=\chi_2=0.001$, and $\Delta\rho=2000$ kg/m$^3$. 
Figure 3.6: Initial stage of magnetically seeding solid-liquid separation: effect of density difference on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4 \times 10^{-20}$ J, $\eta=10^{-3}$ kg/m s, $T=293$ K, $a_1=5 \times 10^{-6}$ m, $\lambda=0.1$, $\gamma_1=0.001$, and $X_2=0$. 

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Figure 3.7: Initial stage of magnetically seeding solid-liquid separation: effect of magnetic susceptibility on (a) collision efficiency and (b) collision frequency. Other parameters include: \( A=4\times10^{-20} \) J, \( \eta=10^{-3} \) kg/m s, \( T=293 \) K, \( a_1=5\times10^{-6} \) m, \( \bar{\lambda}=0.1 \), \( \chi_2=0 \), and \( \Delta \rho=0 \).
Figure 3.8: Initial stage of magnetically seeding solid-liquid separation: effect of Hamaker constant on (a) collision efficiency and (b) collision frequency. Other parameters include: $\eta = 10^{-3}$ kg/m s, $T=293$ K, $a_1 = 5 \times 10^{-6}$ m, $\lambda = 0.1$, $\chi_1 = 0.001$, $\chi_2 = 0$, and $\Delta \rho = 0$.
Figure 3.9: Initial stage of magnetically seeding solid-liquid separation: effect of size ratio on (a) collision efficiency and (b) collision frequency. Other parameters include: $A=4\times10^{-20}$ J, $\eta=10^{-3}$ kg/m s, $T=293$ K, $a_1=5\times10^{-6}$ m, $\chi_1=0.001$, $\chi_2=0$, and $\Delta \rho=0$. 
Figure 3.10: Progress of magnetically seeding solid-liquid separation: effect of magnetic susceptibility on (a) collision efficiency and (b) collision frequency. Other parameters include:

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FUNDAMENTAL MODELING FOR MAGNETICALLY SEEDED SOLID-LIQUID SEPARATIONS

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LIST OF SYMBOLS

\( A \) : Hamaker constant (JK\(^{-1}\))

\( A(s) \) : center-to-center hydrodynamic function

\( A_{\alpha\beta} \) : two-sphere mobility functions

\( a \) : principal rate of strain (s\(^{-1}\))

\( B_{\alpha\beta} \) : two-sphere mobility functions

\( B(s) \) : normal-to-center hydrodynamic function

\( C_A \) : attractive force parameter = \( \frac{A}{36\pi\mu Gr_i^3} \)

\( C_D \) : drag coefficient (with impeller width/length ratio \( \sim 1 \), \( C_D = 1.18 \))

\( D_\infty \) : diffusivity in the absence of interparticle forces (m\(^2\)s\(^{-1}\))

\( D_{12}^{(0)} \) : relative diffusion coefficient (m\(^2\)s\(^{-1}\))

\( D_o, D_i \) : outer and inner radii of impeller (m)

\( E_{\text{eff}, Gr} \) : collision efficiency of gravity-induced flocculation

\( e \) : electron charge = 1.6 \( \times 10^{-19} \) C

\( \hat{e}_r, \hat{e}_\theta \) : radial and tangential unit vectors

\( F_{el} \) : electrostatic forces (N)

\( F_{ij} \) : flocculation frequency (m\(^3\)s\(^{-1}\))
Fr : Froude number = \frac{U_c^2}{\frac{1}{2}(r_i + r_j)g}

F_{vdw} : van der Waals forces (N)

f(\vec{\lambda}) : retardation function of van der Waals forces

G : shear rate (s\(^{-1}\))

G(s), H(s) : mobility functions for interparticle forces

g : gravitational acceleration = 9.8062 (ms\(^{-2}\))

I : ionic strength of the solution (M)

J : actual flocculation rate (m\(^3\)s\(^{-1}\))

J_0 : Saffman and Turner's flocculation rate (m\(^3\)s\(^{-1}\))

K_B : breakup constant

K_F : flocculation constant

K_P : paddle performance coefficient

K_S : energy spectrum constant

k : Boltzmann constant = 1.38 \times 10^{-23} \text{ JK}^{-1}

k_b : ratio of blade velocity relative to liquid velocity (0.3 is assumed here)

L : characteristic length

L(s), M(s) : mobility functions for settling velocity

N : total number of discrete sizes

N_a : agitation speed (rps)

n : impeller number
$n_i, n_j$: populations of particles per unit volume in the discrete sizes $i$ and $j$

$n_i^0$: initial number concentration of particle size $i$

$n_i^t$: number concentration of particle size $i$ at time $t$

$P$: power dissipation (W)

$\text{Pe} = \frac{1}{2} \left( r_i + r_j \right) U_c \frac{D_{12}}{D_{12}}$

$\text{Re} = \frac{U_c L \rho}{\mu}$

$[R]$: grand resistance matrix

$r$: distance between particles (m)

$r_i, r_j$: particle radii (m)

$[S]$: shear vector

$S$: sphere surface area (m$^2$)

$s$: dimensionless distance between two spheres $= \frac{2r}{r_i + r_j}$

$sc$: initial dimensionless distance between particles

$T$: absolute temperature (K)

$t$: time (s)

$\bar{t}$: mean residence time (s)

$[U]$: velocity vector (ms$^{-1}$)

$U_c$: characteristic velocity (ms$^{-1}$)
\( U_o^* \): characteristic velocity at the cross section of the limiting trajectory (ms\(^{-1}\))

\( V \): volume of the suspension (m\(^3\))

\( V_A \): van der Walls potential (VC)

\( V_{el} \): electrostatic potential (VC)

\( V_T \): summation of interaction potentials (VC)

\( w \): width of impeller (m)

\( y_c^* \): radius of the limiting trajectory cross section

\( z \): valence of the symmetric electrolyte in the solution

\( \Delta \rho \): density difference between particles and the suspending medium (kg m\(^{-3}\))

\( \bar{\varepsilon} \): energy dissipation per mass per time (m\(^2\)s\(^{-2}\))

\( \varepsilon \): permittivity of the medium = \(89 \times 10^{-10}\) CV\(^{-1}\) m\(^{-1}\) for water

\( \eta \): Kolmogorov’s microscale (m)

\( \lambda \): particle size ratio, \(0 < r_i/r \leq 1\)

\( \lambda_L \): London wavelength

\( \mu \): fluid viscosity (kg m\(^{-1}\)s\(^{-1}\))

\( \nu \): kinematic viscosity (m\(^2\)s\(^{-1}\))

\( \rho \): fluid density (kg m\(^{-3}\))

[\( \Phi \)]: shear resistance matrix

\( \Phi_{12} \): summation of interaction potentials (VC)
\( \psi_0 \) : stream function

\( \Psi_{ot} \) : particles’ surface potential (V)

\( \nabla \) : gradient
SUMMARY

Flocculation is a process in which small particles form larger aggregates that can be easily removed by sedimentation or filtration in potable and wastewater treatment. In this study, colloidal polystyrene and paramagnetic particles consisting of mixtures of polystyrene and magnetite are used to experimentally investigate flocculation kinetics in a stirred tank under turbulent shear flow. The effects of such parameters affecting the flocculation rate as agitation speed, solution pH, ionic strength, particle size, and particle concentration are investigated. A trajectory model applicable for turbulent-shear systems is formulated to describe particle flocculation in stirred tanks. The collision efficiency of particles is obtained from the limiting trajectory of a particle moving towards another particle. The collision frequency is determined as a function of particle size and energy dissipation. The flocculation frequency is then determined by multiplying the collision frequency by the collision efficiency. The flocculation frequency is incorporated into a population balance model to predict the particle size evolution. Results suggest that flocculation can be improved by providing higher agitation speed even though a higher agitation speed leads to lower collision efficiency. While the particle size ratio increases, the collision frequency increases and the collision efficiency decreases. Results also suggest that the breakup rate of aggregates in a turbulent shear flow is significant and has to be included in the population balance modeling in order to correctly predict the evolution of particle size distribution.
CHAPTER I

INTRODUCTION

1.1 Particle Flocculation

In potable and wastewater treatment, several separation processes, such as filtration, flotation, and sedimentation, are usually used to remove suspended particles from liquid systems. Each of these processes becomes more efficient as the size of particles increases. Primary particles are usually too small to be effectively separated; thus, increasing the size of particles into larger aggregates is often necessary. This process is widely known as flocculation, coagulation, or aggregation (Gregory, 1989).

Due to the different dominant mechanism, flocculation may fall into three categories: (1) Brownian flocculation; (2) gravity flocculation; and (3) shear flocculation. Interparticle forces, such as hydrodynamic resistance, van der Waals, and electrostatic forces, can be important in Brownian flocculation. In shear systems, fluid velocity plays an important role on particle flocculation (Lawler, 1993). In real systems, turbulent shear flow is preferred over laminar flow. The break-up of flocs in a turbulent flow also plays a significant role in the floc size. Related studies of the flow regimes, particle interaction, turbulent flocculation, and aggregate breakage are described in Chapter II.
Experimental studies are also conducted to obtain data for comparison with model calculations. Experimental procedures and material preparation are described in Chapter III.

Trajectory analysis, derived from the force balance on particles and the fluid velocity, is commonly used to study collision between particles. Collision efficiency can be determined from the limiting trajectory. Collision frequency is a function of particle size and flow regime. Flocculation rate is then determined by multiplying the collision efficiency, frequency, and number of particles. A population balance model, which incorporates the flocculation rate, is employed to study particle size evolution as a function of time, i.e., the dynamics of particle flocculation. A number of assumptions are made to simplify the modeling system. Examination of the assumptions of the trajectory equation is detailed in Chapter IV as well as the determination of the flocculation rate.

In Chapter V, the effects of various parameters on turbulent flocculation are examined using experimental data and model calculations. In Chapter VI, the conclusions of this work are presented.

1.2 Scope of this Work

Particle flocculation in turbulent flow has been studied experimentally. Empirical models are available for turbulent flocculation design but they are usually impractical when various physicochemical changes occur in the system. In this study, the main effort is to develop a model to predict particle flocculation in stirred tanks without using
empirical correlations. The model is developed by using trajectory analysis and a population balance equation. Another objective is to examine the effects of various parameters, i.e., pH, ionic strength, agitation speed, seeding particle concentration, and initial particle size and size ratio, on turbulent flocculation using both experimental and modeling investigations.
CHAPTER II

BACKGROUND

Flocculation regimes and colloidal interaction forces are important aspects in both experimental and modeling studies of particle flocculation. The various flocculation regimes are categorized in the following section based on the dominant forces during flocculation. Then, colloidal interaction forces encountered in flocculation are described, followed by a review of flocculation in turbulent systems. The concept of breakage of flocs due to strong shear forces is discussed in the last section of this chapter.

2.1 Flocculation Regimes

2.1.1 Brownian Flocculation

Particles to be flocculated may be small enough to fall into the colloidal size range, which is usually assumed between 1 nm and 1 µm. Random displacement of particles due to the thermal energy of the system, which is known as Brownian diffusion, becomes the dominant force that drives particles to collide together. In Brownian flocculation, interparticle forces can be very important. Valioulis and List (1984) derived the following expression, in which interparticle forces and Brownian diffusion were incorporated, to determine the collision efficiency, $Eff_d$, between unequal-size spheres in Brownian systems:
\[ \text{Eff}_{ij} = \left(1 + \frac{r_j}{r_i}\right)^{1+\frac{r_j}{r_i}} \int_1^{\infty} \left(\frac{D_\infty}{D_{12}^{(0)}}\right) \exp\left(\frac{V_T}{kT}\right) \frac{ds}{s^2} \right)^{-1} \]  

[2.1]

where \(r_i, r_j\) are particle radii, \(D_\infty\) is the diffusivity in the absence of interparticle forces, 
\(D_{12}^{(0)}\) is the relative diffusion coefficient, \(V_T\) is the summation of interaction potentials including van der Waals and electrostatic forces, \(k\) is the Boltzmann constant, and \(T\) is the absolute temperature. The effects of particle size ratio and van der Waals forces were examined, and the results showed that the collision efficiency increases as the particle size ratio increases. Tsouris and Scott (1995) used a similar equation with Eq. [2.1] with the addition of the magnetic force to describe flocculation of paramagnetic particles under the influence of a strong magnetic field.

### 2.1.2 Gravity Flocculation

If particles are bigger than the colloidal size, gravity forces become important. Particles of different sizes and densities settle at different rates and the resulting relative motion drives the particles to collide to each other. This flocculation regime is known as differential settling. Melik and Fogler (1984) studied flocculation by incorporating gravitational and interparticle forces and derived an empirical expression for the collision efficiency, \(\text{Eff}_{Gr}\):

\[ \text{Eff}_{Gr} = f(\bar{\lambda})N_G^{0.2} \]  

[2.2]
where

\[
N_G = \frac{\pi g \Delta \rho r_j^4}{3A} (1 + \lambda)^2 (1 - \lambda^2)
\]  \hspace{1cm} [2.3]

In Eq. [2.2], \( \lambda = \lambda_{l}/2 \pi r \), where \( \lambda_{l} \) is the London wavelength; \( f(\lambda) \) is the retardation function of van der Waals forces, \( \lambda \) is the particle size ratio, \( r/r_s \), \( g \) is the gravitational acceleration, \( \Delta \rho \) is the density difference between particles and the suspending medium, and \( A \) is the Hamaker constant.

Zhang and Davis (1991) studied collision rates due to Brownian or gravitational motion of small droplets. A trajectory analysis was also used by Yiacoumi et al. (1996) to study the mechanism of gravity-induced magnetic seeding flocculation. It was found in both studies that the collision efficiency decreases as the difference of particle density and fluid density increases.

\textbf{2.1.3 Shear Flocculation}

The collision rate can be increased enormously by stirring the suspension so that collisions between particles become dominated by fluid motion. Van de Ven and Mason (1976) studied coagulation between pairs of equal-size spheres in a simple laminar shear field, including the effects of interaction forces. A semi-empirical formula for the collision efficiency was derived, in which electrostatic repulsive forces were neglected (Van de Ven and Mason, 1977):
\[ \text{Eff}_{ij} = f(A^0.18) \]

where \( C_A \) is an attractive force parameter:

\[ C_A = \frac{A}{36\pi \mu G r_i^3} \]

In Eq. [2.5], \( \mu \) is the fluid viscosity and \( G \) is the shear rate in the system. Adler (1981) extended the studies by Van de Ven and Mason to a system of unequal-size spheres. Both approaches indicated that the collision efficiency decreases as the shear rate increases. Zeichner and Schowalter (1977) introduced relative force parameters and determined the stability plane for shear flow.

### 2.2 Colloidal Interaction Forces

When two particles approach each other, interaction forces between them affect the flocculation process. Initially, these colloidal interaction forces influence the collision efficiency. After aggregates are formed, colloidal interactions may affect the strength of aggregates, which, though important in determining their breakup rates, has not yet been thoroughly investigated.

The colloidal interaction forces include van der Waals attractions, electrostatic forces, and hydrodynamic resistance forces. These interaction forces are described in the following sections.
2.2.1 Van der Waals Forces

Van der Waals forces are universal attractive forces between atoms and molecules. Van der Waals forces between two approaching particles arise from spontaneous electric and magnetic polarizations, which result from the fluctuation of charges in the electric clouds of the interacting particles. Without these forces, floculation between particles will be prevented by hydrodynamic repulsive forces. Hamaker (1937) gave the following equation to determine the van der Waals potential, $V_A$:

$$V_A = -\frac{A}{6} \left[ \frac{2r_i r_j}{s^2 + 2r_i s + 2r_j s} + \frac{2r_i r_j}{s^2 + 2r_i s + 2r_j s + 4r_i r_j} + \ln \left( \frac{s^2 + 2r_i s + 2r_j s}{s^2 + 2r_i s + 2r_j s + 4r_i r_j} \right) \right] \quad [2.6]$$

where $s$ is the dimensionless distance between two spheres, $2r_i/(r_i+r_j)$, with $r$ being the distance between the particle centers. Hamaker constant, $A$, is a function of the particle’s composition.

Equation [2.6] is only valid for separations less than the London wavelength $\lambda_L$ (typically, 100 nm) (Zeichner and Schowalter, 1977). Schenkel and Kitchner (1960) included retardation for rigid equal-size spheres and provided a best-fit approximation for $s-2 << 1$:

$$V_A = -\frac{Ar_i}{12s} \left( \frac{1}{1 + 1.77 p} \right), \quad \text{when } p < 1$$
\[ = - \frac{Ar_i}{12s} \left( \frac{2.45}{5p} - \frac{2.17}{15p^2} + \frac{0.59}{35p^3} \right), \quad \text{when } p > 1 \quad [2.7] \]

where \( p = \frac{2\pi r}{\lambda_L}. \)

### 2.2.2 Electrostatic Forces

Particles in liquid suspensions are usually charged due to adsorption, ionization, hydration, or isomorphic replacement on the surfaces. The primary charge on the surface has to be counter-balanced in the system. The cloud of ions of primary and opposite charges around the particles is called the diffuse layer (Figure 2.1). The overlap of the diffuse layers of charged particles governs the interaction between them, and therefore, the potential at the Stern layer plays a more important role in colloidal interaction than the potential at the particle surface. There are no direct methods to obtain the Stern layer potential; however, it is believed that the zeta potential, which causes the motion of particles in electric field, is an adequate substitute for describing the electrostatic interaction between particles. There are two major subjects related to electrostatic interactions between particles, the surface potential and the double layer thickness. Surface potentials can be affected by the ionic strength and adsorbing counterions in the system. The electrical double layer is formed by the surface charge on a particle and the associated counterion charge.

Derjaguin and Landau (1941) and Verwey and Overbeek (1948) developed the DLVO theory to describe the double-layer compression due to indifferent electrolytes in solutions. The theory shows that higher ionic strength can lead to higher counterion
concentration in the diffuse layer which subsequently decreases the thickness of the diffuse layer.

2.2.3 Hydrodynamic Resistance Forces

When two spheres move towards each other, each sphere exerts a force, couple, and stress on the fluid. The change of the flow around the spheres can be described by the hydrodynamic resistance functions. The development of hydrodynamic resistance functions is based on the relative motion of two spheres, which can be separated into motions along and normal to their line of centers. Spielman (1970) incorporated viscous interactions between two spheres based on the assumption of additivity of the single particle Brownian diffusivity in coagulation. Exact solutions for spherical droplets in a low-Reynolds-number flow were derived by Haber et al. (1973) for axisymmetric flow along the line of centers and by Zinchenko (1980) for asymmetric motion normal to the line of centers.

Jeffery and Onishi (1984) developed solutions of the resistance and mobility functions for two unequal rigid spheres in a low-Reynolds-number flow. The hydrodynamic interaction between the spheres was described by a set of linear relations between the forces exerted by the spheres on the fluid and the translational and rotational velocities of the spheres.

Hydrodynamic resistance functions, as obtained by Batchelor (1982), are provided in Eqs. [2.8a] - [2.8d]:

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$L(s) = \frac{\lambda^2 \gamma A_{22} - A_{11}}{\lambda^2 \gamma - 1} + \frac{2(1 - \lambda^3 \gamma)A_{12}}{(1 + \lambda)(\lambda^2 \gamma - 1)}$ \hfill [2.8a]

$M(s) = \frac{\lambda^2 \gamma B_{22} - B_{11}}{\lambda^2 \gamma - 1} + \frac{2(1 - \lambda^3 \gamma)B_{12}}{(1 + \lambda)(\lambda^2 \gamma - 1)}$ \hfill [2.8b]

$G(s) = \frac{\lambda A_{11} + A_{22}}{1 + \lambda} - \frac{4\lambda A_{12}}{(1 + \lambda)^2}$ \hfill [2.8c]

$H(s) = \frac{\lambda B_{11} + B_{22}}{1 + \lambda} - \frac{4\lambda B_{12}}{(1 + \lambda)^2}$. \hfill [2.8d]

$L(s)$ and $M(s)$ are hydrodynamic functions derived for particle relative velocity due to gravity forces. $G(s)$ and $H(s)$, derived for the relative diffusivity tensor, can also represent mobility functions for interparticle forces. $A_{a\beta}$ and $B_{a\beta}$ are two-sphere mobility functions. Batchelor (1982) gave far-field analytical solutions for $A_{a\beta}$ and $B_{a\beta}$ that are simplifications of Jeffery and Onishi’s results (1984):

\begin{equation*}
A_{11} = 1 - \frac{60\lambda^3}{(1 + \lambda)^4 s^4} + \frac{32\lambda^3(15 - 4\lambda^2)}{(1 + \lambda)^6 s^6} - \frac{192\lambda^3(5 - 2\lambda^2 + 3\lambda^4)}{(1 + \lambda)^8 s^8} + O(s^{-10}) \quad [2.9a]
\end{equation*}

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In Eqs \[2.9a\]-\[2.9d\], \(O()\) is a function representing the error of the far-field solutions of 
\(A_{\alpha\beta}\) and \(B_{\alpha\beta}\). From the reciprocal theorem (Batchelor, 1982), \(A_{\alpha\beta} = A_{\beta\alpha}\) and \(B_{\alpha\beta} = B_{\beta\alpha}\). Thus,

\[A_{11}(s, \lambda) = A_{22}(s, \lambda^{-1})\]
\[B_{11}(s, \lambda) = B_{22}(s, \lambda^{-1})\]  \[2.10\]

The hydrodynamic functions given by Eqs. \[2.8a\] and \[2.8b\] were developed only for quiescent flows. When the fluid is in a shear motion, however, hydrodynamic resistance forces due to shear should be taken into account. Brenner and O’Neill (1971) included the mobility functions (Eqs. \[2.9a\] - \[2.9d\]) in a grand resistance matrix and studied the shear resistance matrix in a linear shear field. For neutrally buoyant particles, the velocities of particles are given by:
\[ [U] = -[R]^{-1}[\Phi][S] \]  \[2.11\]

where \([U]\) is the velocity vector, \([R]\) is the grand resistance matrix, \([\Phi]\) is the shear resistance matrix, and \([S]\) is the shear vector. A solution of the problem requires knowledge of both the grand resistance matrix and the shear resistance matrix.

### 2.3 Flocculation in Turbulent Flow

Saffman and Turner (1956) proposed a theory of collisions between small droplets in a turbulent flow field. In this theory, the collision efficiency is assumed unity, thus the flocculation frequency, \(F_{ij}\), is the same as the collision frequency:

\[
n_i n_j F_{ij} = n_i n_j \beta_{ij} = 1.3 \left( r_i + r_j \right)^3 n_i n_j \left( \frac{\overline{\epsilon}}{\nu} \right)^{0.5}
\]  \[2.12\]

where \(\beta_{ij}\) is the collision frequency, \(n_i, n_j\) are number concentrations of particles \(i\) and \(j\), \(\overline{\epsilon}\) is the energy dissipation per mass per time, and \(\nu\) is the kinematic viscosity. The constant 1.3 has been corrected to 2.3 by Pearson et al. (1984).

Delichatsios and Probstein (1975) developed a model for the coagulation rate between destabilized particles in isotropic turbulent flows, for both smaller and larger particle size than Kolmogorov's microscale. The model was based on mean-free-path concepts.
Smoluchowski (1917) derived an equation for the collision rate of particles of uniform size \( i \) in a laminar shear field:

\[
\frac{dn_i}{dt} = -\frac{16}{3} E_f r_i^3 n_i^2 G
\]  \[2.13\]

Based on Smoluchowski’s studies, Koh et al. (1984) employed different values of shear rate in each compartment of a two-compartment stirred tank. The collision efficiencies for coarse and fine particles in stirred tanks were correlated to the shear rate (Koh et al. 1987):

\[
Eff = 4.8 \times 10^{-14} G^{3.3}, \quad \text{for fine particles} \quad [2.14a]
\]

\[
Eff = 290.0 G^{-1.3}, \quad \text{for coarse particles} \quad [2.14b]
\]

De Boer et al. (1989) compared their experimental data to theoretical results presented by other researchers. They concluded that coagulation rates in stirred tanks can be best predicted by a shear model that includes the effect of hydrodynamic interaction between particles. Higashitani et al. (1982) claimed that because the particles are smaller than Kolmogorov’s microscale, the collision efficiency for laminar flow can be applied in turbulent systems as well. Kusters et al. (1997) also used laminar flow to study the aggregation of small particles in agitated vessels and included the electrostatic repulsive
forces. Pneuli et al. (1991) developed a turbulent-Brownian model for coagulation of aerosols. By neglecting the interparticle forces and Brownian diffusion, they obtained the collision efficiency between aerosols as:

\[
Eff = 7.5 \left( \frac{r_j}{r_i} \right)^2
\]  

[2.15]

2.4 Breakage of Aggregates due to Strong Shear Forces

In stirred tanks, increasing mixing can promote collisions between particles. On the other hand, turbulent shear forces can break the aggregates into smaller aggregates and primary particles if the agitation is vigorous. Lu and Spielman (1985) and Pandya and Spielman (1982) studied the breakage rate in agitated systems. Parameters for the breakage rate were determined by experiments. Argaman and Kaufman (1970) derived an equation to investigate the change of the concentration of particles due to flocculation and breakup:

\[
\frac{n_i^0}{n_i^t} = \frac{1 + K_F K_S K_p G t}{1 + K_B G^2 t}
\]

[2.16]

where \( n_i^0 \) is the initial number concentration of particle size \( i \), \( n_i^t \) is the number concentration of particle size \( i \) at time \( t \), \( K_F \) is the flocculation constant, \( K_B \) is the breakup constant. 

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constant, $K_s$ is the energy spectrum constant, $K_p$ is the paddle performance coefficient, and $\bar{t}$ is the mean residence time.

Tambo and Hozumi (1978) studied the maximum floc size, $d_{\text{max}}$, in inertia and viscous subrange as a function of the agitation speed (Eq. [2.17a] and Eq. [2.17b]) and concluded that the maximum floc size decreases as the agitation speed in the system increases:

$$d_{\text{max}} \approx N_a^{-(1.5-1.2)}, \; d >> \eta$$  \hspace{1cm} [2.17a]

$$d_{\text{max}} \approx N_a^{-(1.1-1.0)}, \; d << \eta$$  \hspace{1cm} [2.17b]

where $N_a$ is the agitation speed (rps) and $\eta$ is the Kolmogorov’s microscale given by:

$$\eta = \left( \frac{\nu^3}{\bar{\varepsilon}} \right)^{\frac{1}{4}}$$  \hspace{1cm} [2.18]

In summary, a number of studies dealing with particle flocculation and breakup of aggregates have been reported in the literature. Most of these studies have been devoted to quantifying the hydrodynamic resistance exerted by the fluid on approaching particles. Other investigations included van der Waals (attractive) and double layer (repulsive) interparticle forces. A modeling approach that considers interparticle and hydrodynamic
resistance forces is developed in this work to describe particle collision and flocculation in stirred tanks.
CHAPTER III

EXPERIMENTAL STUDIES OF PARTICLE FLOCCULATION IN STIRRED TANKS

Synthetic particles were used to study the effect of solution pH and ionic strength, particle size distribution, particle concentration, and agitation speed on the flocculation rate in a stirred tank. This chapter presents the preparation and properties of synthetic particles, the flocculation experiments in the stirred tank, and the method used to measure the size distribution and zeta potential of particles.

3.1 Materials

The experiments in this study were conducted as the first step in a two-step high-gradient-magnetic-seeding filtration process (Ying, 1997), in which particles with magnetic properties were flocculated with nonmagnetic particles. Polystyrene latex and magnetic polystyrene latex (containing 40% magnetite by weight) were used to study the flocculation in stirred tanks. The polystyrene microspheres were non-porous and smooth at the surface. Therefore, adsorption did not take place at the surface of particles and the zeta potential of particles did not change with time. Both types of particles were supplied
by Bangs Laboratory, Inc. (Carmel, IN), and some of their properties are listed in Table 3.1.

To study the effect of solution pH on the flocculation rate, hydrochloric acid was used to adjust the solution pH to 3, 6, and 9. Analytical grade sodium chloride was used for the adjustment of the ionic strength. In most of the experiments, the ionic strength of the solution was 0.1 M NaCl. Because particles have very negative zeta potentials and do not flocculate at very high pH solutions, a 0.1 M sodium hydroxide solution (pH~13) was prepared and used as freezing solution to prevent flocculation after sampling. Deionized water (>10 MΩ) was used in the preparation of solutions and particle suspensions. The particles obtained from Bangs Laboratory were in solutions that contained a known fraction of solids. To obtain a desired concentration of these particles, the solution was weighed to select the proper amount of solids and then diluted in a volumetric flask to adjust the volume. The particles were initially prepared in stock solution that had high concentration and high pH. Then, the solution was diluted to various concentrations for characterization and experimentation. In all the experiments, the concentration of polystyrene particles was 100 ppm.

3.2 Methods

Turbulent-shear flocculation experiments were conducted using a standard stirred tank of 100-mm diameter, 14.2-mm height, and equipped with four baffles, 10 mm wide each. The initial volume of the suspension used in each experiment was 600 mL. The mixture was stirred by a 6-blade impeller of 50 mm in diameter, using a Stir-pak motor,
model 50002-40 (Cole-Parmer Instrument Co., Niles, IL) to provide adjustable agitation speed. Figure 3.1 shows the schematic of the system. Desired amounts of solutions of two different particles, sodium chloride solution to adjust the ionic strength, and hydrochloric acid were poured into the stirred tank simultaneously and the agitation started as immediately at time = 0. In most of the experiments, the agitation speed was kept at 300 rpm. Agitation speeds 200 and 400 rpm were used to study the effect of agitation speed on the flocculation rate. For flocculation kinetics analysis, 1-2 mL samples were taken every minute for the first five minutes, then every 5 minutes up to 30 minutes. Samples were taken from the same location in the tank and diluted with freezing solution to 15 mL.

### 3.3 Characterization of Particles

Particles were characterized using size and zeta potential measurements. The instrument used for size measurements was a Coulter light-scattering instrument, model LS130, Coulter Corporation (Langley Ford Instruments, Amherst, MA), which provided the particle size distribution of the sample. The sample was poured into the analyzing cell of the machine of 15 mL volume. To have the optical obscuration (8~12%), which gave the best analysis, different sample volumes were used. The obscuration value was higher for larger flocs or higher particle concentration in the frozen sample, so smaller samples were taken from the tank in those conditions. If the obscuration was still too high, freezing solution was used to dilute the sample further. The zeta potential of particles at various values of pH, concentration, and ionic strength was measured using a
Lazer Zee Meter, model 501, Pen Kem, Inc. (Bedfore Hills, NY). A sample was injected into the analyzing cell with caution to avoid bubble formation. Figures 3.2 and 3.3 show the variations of zeta potential of the synthetic particles used in these experiments as a function of pH, ionic strength, and particle concentration. As expected the zeta potential was higher at higher ionic strength and lower pH (Figure 3.2), which is because the double layer is compressed by the higher concentration of ions. Figure 3.3 presents the zeta potentials of magnetic seeding particles and shows a higher zeta potential at lower particle concentration and lower pH, a result which is similar to that of Figure 3.2.
CHAPTER IV

MODEL DEVELOPMENT OF FLOCCULATION IN STIRRED TANKS

A model is developed to predict the evolution of particle size under turbulent-shear flocculation. The collision efficiency between particles is determined by trajectory analysis. Some assumptions are made to simplify the modeling approach and are examined in the first section of this chapter. The interparticle forces considered in this model are also discussed. The relative motion between particles and the model development for predicting the flocculation rate in stirred tanks are given in the last section.

4.1 Model Assumptions

Kolmogorov’s microscale is used to determine the smallest eddy size of turbulence in a system. The size of primary particles and the turbulence microscale are compared. To simplify the model, inertial forces, Brownian motion, and gravity forces are neglected. Reynolds, Peclet, and Froude numbers are used to examine these assumptions based on a particle of 1 µm diameter since most of the particles used in the experiments are around this size.
4.1.1 Kolmogorov’s Microscale

It is assumed that velocity fluctuations in a stirred tank are not seen by particles that are smaller than the smallest eddies in the system. In this case, particles are within the viscous subrange of the flow.

The length scale of the smallest eddies is given by Kolmogorov’s microscale (Eq. [2.18]). The mean energy dissipation per mass per time can be obtained from the power dissipated into the system (Barnes and Wilson, 1983):

\[ G = \left( \frac{\varepsilon}{\nu} \right)^{1/2} = \left( \frac{P}{\mu V} \right)^{1/2} \]  \hspace{1cm} [4.1]

where

\[ \varepsilon = -\frac{P}{\rho V} \]  \hspace{1cm} [4.2a]

\[ P = nC_D \rho w (1 - k_b)^3 (2\pi N_a)^3 \left( D_o^4 - D_i^4 \right) / 8 \]  \hspace{1cm} [4.2b]

\( V \) is the volume of the suspension, \( P \) is the power dissipation, \( n \) is the impeller number, \( C_D \) is the drag coefficient (with impeller width/length ratio ~1, \( C_D=1.18 \)), \( \rho \) is the fluid density, \( w \) is the width of impeller, \( k_b \) is the ratio of blade velocity relative to liquid velocity (0.3 is assumed here, Barnes and Wilson, 1983), \( N_a \) is the agitation speed, and \( D_o \) and \( D_i \) are outer and inner radii of the impeller. The mean value of energy dissipation per mass per time is used because the power input represents an overall value for the system.
The following calculation gives Kolmogorov’s microscale in the experimental system:

\[ P = nC_D \rho w (1 - k)^3 (2\pi N_a)^3 (D_o^4 - D_i^4) / 8 \]

\[ = 6 \times 1.18 \times 1000 \times 0.009 \times (1 - 0.3)^3 \times (2 \times 3.14159 \times 5)^3 \times (0.025^4 - 0.015^4) / 8 = 0.0288 \text{ W} \]

\[ \varepsilon = \frac{P}{\rho V} = 0.0288 / 1000 \times 600 \times 10^{-6} = 0.048 \text{ m}^2 \text{s}^{-3} \]

\[ \eta = \left( \frac{\nu^3}{\varepsilon} \right)^{1/4} = \left( \frac{(1.007 \times 10^{-6})^3}{0.048} \right) = 6.756 \times 10^{-5} \text{ (m)} = 67.56 \mu\text{m} \]

It is found that the primary particles as well as the flocs are all much smaller than Kolmogorov’s microscale (Table 3.1 and Appendix A). Therefore, it is assumed that the particles do not interact with fluid eddies causing velocity fluctuations and that particle collision can be described based on a laminar shear flow.

### 4.1.2 Inertial Forces

Reynolds number, Re, the ratio of inertial to viscous forces, is used here to examine whether inertial forces are important in the system of our study:
where $U_c$ is a characteristic velocity and $L$ is a characteristic length.

The characteristic length is defined as the summation of the diameters of two particles. The characteristic velocity, $U_c$, is defined as:

$$ U_c = 2aL $$  \hfill [4.4]

where

$$ a = \sqrt{\frac{\varepsilon}{12\nu}} $$  \hfill [4.5]

Symbol $a$ represents the principal rate of strain (Pneuli et al., 1991). Therefore, the Reynolds number can be written as:

$$ \text{Re} = \frac{4a(r_i + r_j)^2}{\nu} $$  \hfill [4.6]

If the Reynolds number is much smaller than 1, the inertia can be neglected.

$$ a = \sqrt{\frac{\varepsilon}{12\nu}} = \sqrt{\frac{0.048}{(12 \times 1.007 \times 10^{-6})}} = 63.24 \text{ s}^{-1} $$
Thus, $Re << 1$ for the system studied here and hence the inertia can be neglected.

### 4.1.3 Brownian Diffusion

As mentioned in Chapter II, Brownian diffusion is important if particles are smaller than 1 µm. In turbulent shear systems, however, the shear rate is so strong that the contribution of Brownian motion to particle motion during flocculation is usually relatively small. The relative importance of Brownian motion to the inertia force is given by the Peclet number, $Pe$:

\[
Pe = \frac{\frac{1}{2} (r_i + r_f) U_c}{D_{12}^{(0)}}
\]

where

\[
D_{12}^{(0)} = \frac{kT \left(1 + \lambda^{-1}\right)}{6 \pi \mu r_i}
\]

It is considered that the contribution of Brownian diffusion to particle motion is comparatively small if it is less important than the contribution of inertial forces, which has already been found very small (Section 4.1.2). So Brownian diffusion can be neglected if the Peclet number is greater than 1:
\[ D_{12}^{(0)} = \frac{kT(1 + \lambda^{-1})}{6\pi\mu r_i} = \frac{1.381 \times 10^{-23} \times 298.15 \times (1 + 1)}{6 \times 3.14159 \times 1.005 \times 10^{-3} \times 0.5 \times 10^{-6}} = 8.73 \times 10^{-13} \text{ m}^2\text{s} \]

\[ \text{Pe} = \frac{\frac{1}{2}(r_i + r_j)U_c}{D_{12}^{(0)}} = \frac{0.5 \times \left(0.5 \times 10^{-6} + 0.5 \times 10^{-6}\right) \times 2.53 \times 10^{-4}}{8.73 \times 10^{-13}} = 144.9 >> 1 \]

Since the Peclet number is much greater than 1, particle motion due to Brownian diffusion is negligible.

### 4.1.4 Gravity Forces

Particle motion due to gravity forces is important if particles are much larger than 1 \( \mu\text{m} \). Furthermore, the polystyrene particles used in the experiments of this study have density very close to the density of the surrounding solution. Thus, it is expected that the contribution of gravity forces can be neglected. The relative importance of gravity and inertial forces is compared using the Froude number, \( \text{Fr} \), the ratio of inertial forces to gravity forces:

\[ \text{Fr} = \frac{U_c^2}{\frac{1}{2}(r_i + r_j)g} \]  

[4.9]
Similarly to the contribution of Brownian diffusion that has been examined in Section 4.1.3, gravity forces are compared here to inertial forces that have already been found very small:

\[
Fr = \frac{U_c^2}{\frac{1}{2}(r_i + r_j)g} = \frac{\left(2.53 \times 10^{-4}\right)^2}{0.5 \times \left(0.5 \times 10^{-6} + 0.5 \times 10^{-6}\right) \times 9.8} = 0.013
\]

Unlike the results found in Section 4.1.3, the Froude number is much smaller than 1, which means that gravity forces are more important than inertial forces. Thus, the relative contribution of gravity forces to particle motion cannot be directly determined. Therefore, the ratio of Froude number to the Reynolds number is introduced here, which gives the relative importance of viscous forces to gravity forces:

\[
\frac{Fr}{Re} = \frac{0.013}{2.53 \times 10^{-4}} = 51.38
\]

Therefore, the viscous forces are more important than the gravity forces and it can be assumed that the contribution of gravity forces on particle motion is relatively small and negligible.

**4.2 Forces Acting on Particles in Suspension**

Based on the assumptions discussed in Section 4.1, gravity and inertial forces are not considered in this study. The interparticle forces considered include van der Waals and
electrostatic forces. Hydrodynamic resistance functions are included to represent the changes of flow around particles moving towards each other.

### 4.2.1 Van der Waals Forces

As mentioned in the Section 2.2.1, particles do not flocculate if there are no van der Waals forces. Van der Waals forces can be determined from the potential given by Eq. [2.6].

### 4.2.2 Electrostatic Forces

Following Tsouris and Scott (1995), the electrostatic potential, $V_{el}$, is given by two formulas, one for large separations and another for small separations.

**Linear Superposition Approximation**

The linear superposition approximation (Bell et al., 1970) is applicable for thin double layers and large interparticle separations:

$$V_{el} = 4\pi e\left(\frac{kT}{e}\right)^2 Y_1 Y_2 \frac{r_i r_j}{r} e^{-\kappa d}, \quad \text{for } \kappa d \geq 4 \quad [4.10]$$

where

$$Y_i = 4 \tanh\left(\frac{\Phi_i}{4}\right), \quad \text{for } \kappa r \geq 10, \quad \Phi_i < 8, \text{ and } i = 1, 2 \quad [4.11a]$$

$$\Phi_i = \frac{ze \Psi_{oi}}{kT}, \quad \text{for } i = 1, 2 \quad [4.11b]$$
\[ \kappa = 5.552 \times 10^{-6} \sqrt{I/kT}, \quad [4.11c] \]

\[ l \equiv (s - 2) \left( \frac{r_i + r_j}{2} \right), \quad [4.11b] \]

\( \varepsilon \) is the permittivity of the medium, \( r \) is the distance between particles, \( e \) is the electron charge, \( z \) is the valence of the symmetric electrolyte in the solution, \( \psi_{oi} \) refers to the particle surface potential, and \( I \) is the ionic strength of the solution.

**Derjaguin Approximation**

The Derjaguin approximation is used for interparticle dimensionless separations smaller than those at which the linear superposition approximation applies (Hogg et al., 1966):

\[ V_{el} = \varepsilon r_i r_j \left( \frac{\psi_{oi}^2 + \psi_{oj}^2}{2(\psi_{oi} + \psi_{oj})} \right) \left[ \frac{2\psi_{oi}\psi_{oj}}{\psi_{oi}^2 + \psi_{oj}^2} \log \left\{ \frac{1 + \exp(-\kappa l)}{1 - \exp(-\kappa l)} \right\} + \log \left\{ 1 - \exp(-2\kappa l) \right\} \right] \quad [4.12] \]

**2.2.3 Hydrodynamic Resistance Functions**

Batchelor and Green (1972) gave a general expression for the velocity of two freely-moving spheres in a linear shear flow field:
where $A(s)$ is the center-to-center hydrodynamic function, $B(s)$ is the normal-to-center hydrodynamic function, $E$ is the uniform rate-of-strain tensor, $I$ is the unit matrix, and $r$ is the unit vector in the direction of line-of-centers.

For large separation distances, i.e., $r >> r_i + r_j$, the hydrodynamic functions, $A(s)$ and $B(s)$, can be estimated as (Batchelor, 1982):

$$A(s) = 3 - \frac{s}{r^2} + \frac{6}{r^4}$$

$$B(s) = \frac{r_i^5 + r_j^5}{r^5} + \frac{\frac{5}{3} r_i^2 r_j^2 (r_i + r_j)}{r^5}$$

Equations [4.14a] and [4.14b] were compared with exact values for $\lambda = 1$ (Lin et al., 1970) and the agreement was considered satisfactory for this work.

4.3 The Relative Motion between Particles

4.3.1 Flow Regime of the Turbulent System

Saffman and Turner (1956) described the local shearing motion that leads to collisions between particles moving along with the fluid streamlines using a flow of
uniform strain (Fig. 4.1). The origin is at the center of the bigger particle and the coordinate axes are in the direction of the principal rates of strain. The flow field is assumed a local axisymmetric. Pneuli et al. (1991) gave the stream function, \( \psi_o \), for the flow field shown in Figure 4.1 in spherical coordinates:

\[
\psi_o = ar^3 \sin^2 \theta \cos \theta
\]  

[4.15]

where \( a \) is the principal rate of strain, and \( \theta \) is the angle between the vertical axis and vector \( r \). The stream function is axisymmetric and \( \phi \) independent, and therefore, there is no velocity component in \( \phi \) direction. In Eq. [4.15], the sign is different from that of Pnueli et al. (1991) because of the different coordinate system used here. The velocity components can then be found from the derivatives of the stream function:

\[
v_r = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta} = -ar(2 \cos^2 \theta - \sin^2 \theta)
\]  

[4.16a]

\[
v_\theta = \frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r} = 3ar \sin \theta \cos \theta
\]  

[4.16b]

### 4.3.2 Trajectory Equation of Particle Motion

The relative velocity, \( V_{12} \), between two rigid spheres has been presented by Bachelor (1982):
\[ V_{12} = V_{12}^{(0)} \left[ -L(s) \cos \theta \hat{e}_r + M(s) \sin \theta \hat{e}_\theta \right] \\
+ \left[ (1 - A(s)) (ar \sin^2 \theta - 2ar \cos^2 \theta) \hat{e}_r + (1 - B(s)) 3ar \sin \theta \cos \theta \hat{e}_\theta \right] \\
- \frac{D_{12}^{(0)}}{kT} \left[ G(s) \hat{e}_r + H(s) \hat{e}_\theta \right] \nabla \Phi_{12} - D_{12}^{(0)} \left[ G(s) \hat{e}_r + H(s) \hat{e}_\theta \right] \nabla \left( \ln p_{12}(r) \right) \]

\[ (4.17) \]

where \( \hat{e}_r \) and \( \hat{e}_\theta \) are radial and tangential unit vectors, \( V_{12}^{(0)} \) is the far-field relative velocity resulting from external forces, for example, gravity or magnetic forces, and \( p_{12}(r) \) is the pair-distribution function representing the probability that particle 1 is at position \( r \) relative to particle 2 with \( p_{12}(r) \to 1 \) when \( r \to \infty \).

In Eq. [4.17], the first term is due to external forces and can be eliminated because it is assumed in this study that external forces such as gravity are negligible. The second term is the relative velocity due to the shear flow and is a function of distance between the particles. The third term gives the contribution of interparticle forces to the relative velocity; the gradient of the summation of interaction potentials, \( \nabla \Phi_{12} \), represents the interparticle forces. Since the interparticle forces act along the line of particles’ centers, \( \nabla \Phi_{12} \) is multiplied by the mobility function in the \( r \)-direction only. The last term is the relative velocity caused by Brownian diffusion which is neglected in this study since it is assumed that Brownian diffusion is not important. Equation [4.17] can thus be rewritten as:
\[ V_{12} = (1 - A(s))(\sin^2 \theta - 2 \cos^2 \theta)\hat{e}_r + (1 - B(s))3\sin \theta \cos \theta \hat{e}_\theta \]

\[
- \frac{D^{(0)}_{12}}{kT} (F_{vdw} + F_{el}) G(s) \hat{e}_r
\]

where \( F_{vdw} \) is the van der Waals force and \( F_{el} \) is the electrostatic force.

The differential trajectory equation can be obtained by separating the relative velocity into the radial and tangential components and dividing the tangential component by the radial component:

\[
\frac{ds}{d\theta} = s \frac{(1 - A(s))\sin^2 \theta - 2 \cos^2 \theta - G(s) \frac{D^{(0)}_{12}}{kT} \left( \frac{2}{r_i + r_j} \right)^2 \frac{d\Phi_{12}}{ds}}{(1 - B(s))3\sin \theta \cos \theta}
\]

Equation [4.19] is an ordinary differential equation, the numerical solution of which provides the trajectory of a particle moving towards another particle that is fixed at the origin. To evaluate the collision efficiency of the particles, it is required that we know the limiting trajectory, defined as that leading to minimum separation between the particles (at \( s = 2 \)). The critical radius for the limiting trajectory, \( y^*_c \), can thus be determined by finding the numerical solution of Eq. [4.19].

**4.3.3 Collision Frequency due to Turbulent Shear Flow**

When two particles collide under turbulent shear flow, the collision radius for a pair of particles with different size will be just the sum of the radii, \( R = r_i + r_j \). The mean flux
of fluid into a sphere of radius $R$ is $- \int_{U<0} UdS$, where $U$ is the relative velocity in radial direction and $S$ is the sphere surface area. From the continuity of fluid, we can obtain Eq. [4.20].

$$\int_{U<0} UdS + \int_{U>0} UdS = 0$$  \[4.20\]

Then the flux can be given as

$$- \int_{U<0} UdS = \frac{1}{2} \int |U|dS = \frac{1}{2} \int |U|dS = 2\pi R^2 |U|$$  \[4.21\]

For $R$ smaller than Kolmogorov microscale, $|U| = R \frac{|\partial U_x / \partial x|}{\nu}$ (Saffman and Turner, 1956). The mean square of the velocity gradient is related to the energy dissipation per unit mass per time and the kinematic viscosity as $(\partial U_x / \partial x)^2 = \epsilon / 15 \nu$ (Townsend, 1976). If we assume that the velocity gradient is normally distributed, we will obtain $(\partial U_x / \partial x) = (2\epsilon / 15 \nu)^{1/2}$, and the collision frequency becomes:

$$\beta_{ij} = 2\pi R^3 (\partial U_x / \partial x) = 2.3 \left( r_i + r_j \right)^3 \left( \frac{\epsilon}{\nu} \right)^{1/2} = 2.3 \left( r_i + r_j \right)^3 G$$  \[4.22\]

4.3.4 Collision Efficiency due to Turbulent Shear Flow

The collision efficiency is defined as the ratio of the actual flocculation rate to Saffman and Turner’s flocculation rate in a system:

\[ \text{Eff} = \frac{J}{J_0} = \frac{\pi y_c^* U_0^*}{2.3(r_i + r_j)^3 G} \]  \[
\text{where}
\]

\[ U_0^* = 2a \cdot sc \cdot \cos \theta^* \cdot \frac{r_i + r_j}{2} \]  \[
\text{and}
\]

\[ y_c^* = sc \cdot \sin \theta^* \cdot \frac{r_i + r_j}{2} \]

The actual flocculation rate, \( J \), is the flux of particles flowing through the cross-section of the limiting trajectory by considering the interparticle forces and the hydrodynamic mobility functions. Saffman and Turner’s flocculation rate, \( J_0 \), is the flux of particles flowing through the same cross-section without taking interparticle forces and resistance functions into account. \( U_0^* \) is the characteristic velocity at the cross section of the limiting trajectory, \( sc \) is the initial dimensionless distances between particles, \( y_c^* \) is the radius of the limiting trajectory cross section, and \( \theta^* \) is the angular component of the limiting trajectory (see Figure 4.2).
4.4 Population Balance Model

The population balance model can be used to study the size distribution of particles and flocs in a flocculating system as a function of time (Tsouris and Scott, 1995). A simple population balance equation in a discretized form is given by:

\[
\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} F_{ji} n_j n_{i-j} - \sum_{j=1}^{N} F_{ij} n_i n_j
\]  \[4.25\]

where \(n_i\) and \(n_j\) are the populations of particles per unit volume in the discrete sizes \(i\) and \(j\), respectively, \(t\) is the time, and \(N\) is the total number of discrete sizes. The flocculation frequency \(F_{ij}\) of particles \(i\) and \(j\) is given by multiplying the collision efficiency by the collision frequency. The first term on the right-hand side is the source due to flocculation of smaller particles and the second term is the loss due to flocculation to larger particles. In this modeling approach, it was assumed that primary particles as well as flocs were spherical. A bivariate population balance equation has been derived and solved by Tsouris et al. (1995) for heterogeneous flocculation of paramagnetic particles. In the work of Tsouris et al., the properties of the particles considered in the equation were their diameter and magnetic susceptibility.
CHAPTER V

RESULTS AND DISCUSSION

Model calculations were computed on an IBM RS/360 model workstation, configured with 64 MB of memory, and using double precision calculations. The trajectory equation (Eq. [4.19]) and the population balance equation (Eq. [4.25]) were solved by an ordinary differential equation solver with variable step (EPISODE) (Hindmarch and Byrne, 1976). Computer codes for the trajectory analysis and population balance models were available from related work (Yiacoumi et al., 1996; Tsouris et al., 1995). Necessary modifications were made in order to investigate the problem studied in this work. Experimental data obtained from the size measurements are presented in this chapter and compared with modeling results.

5.1 Reproducibility of Experiments

Figures 5.1(a) - 5.1(c) present the reproducibility of experiments with identical conditions, each one at different solution pH and magnetic seeding particle concentration. Figures 5.1(a) - 5.1(c) show that the cumulative number fraction of different particle sizes were similar under the same experimental conditions and, therefore, the reproducibility of the experiments is satisfactory. It is also found that the particle size distribution shifts to
the right in Figure 5.1(c) more than in the other two figures (Figures 5.1(a) and (b)), which is because the particle flocculation is enhanced at low pH solution.

5.2 Dynamics of Turbulent Shear Flocculation

The change of particle size with time in a stirred tank was investigated. The experimental observations are given in Figures 5.2(a) - 5.2(c). The data show that the cumulative distribution of particle size shifts to the right as time increases indicating that particles aggregate into larger flocs. It is also found that the flocculation reaches equilibrium after 5 min and the particles size at equilibrium is larger at a lower solution pH, which is because particles aggregate easier at low pH solution. Therefore, in Figure 5.2(a), particles grow much faster from 1 min to 2 min and from 2 min to 3 min than in Figures 5.2(b) and (c). The numerical results from the population balance model with similar experimental conditions of those of Figure 5.2(a) also show the growth of particles as a function of time (Figure 5.3). It is found that the particle size obtained from the model is much larger than that from experimental observations.

5.3 Effect of Agitation Speed

Results from stirred tank experiments carried out at different agitation speeds are depicted in Figure 5.4. Slight increase of floc size is observed as the agitation speed becomes more vigorous, which could result from the increasing collision between particles.
The effects of agitation speed on collision efficiency and frequency are numerically examined in Figures 5.5 - 5.7. It is found that the collision efficiency decreases as the agitation speed increases when two particles have similar size (Figure 5.5(a)), which agrees with the results of Van de Ven and Mason (1977). The reason for this behavior could be because the more energetic shear flow drives a particle away from the other before the van der Waals force can bring them together. It is also found that the effect of agitation speed on the collision efficiency becomes negligible as the particle size ratio decreases (Figure 5.5(b)). Contrary to the collision efficiency, the collision frequency increases as both the agitation speed and the size ratio increase (Figure 5.6). The total effect of agitation speed on the flocculation frequency can be readily determined by multiplying the collision efficiency by the collision frequency. Figure 5.7 gives the total effect of agitation speed on the flocculation frequency. The results suggest that the flocculation frequency is enhanced with increasing agitation speed. It is also observed from Figure 5.7 that the decline of flocculation frequency becomes slower when the particle size ratio approaches 1.

5.4 Effect of Hamaker Constant

Figure 5.8 shows the effects of Hamaker constant and particle size on collision efficiency. The attractive force between two particles increases as the Hamaker constant increases; therefore, the collision efficiency is improved. The data show that the collision efficiency increases faster with increasing Hamaker constant for smaller particles. Figure 5.8 also shows that the collision efficiency can be enhanced by decreasing particle size.
5.5 Effect of Particle Size and Size Ratio

Figure 5.9 gives the results of experiments in which the initial size of polystyrene particle was varied and the initial size of magnetic seeding particles was the same, 0.56 µm. The difference of cumulative size distribution of particles between 1 min and 5 min for 0.1 µm polystyrene particles is more than that for 0.56 µm polystyrene particles, which indicates that the flocculation rate is higher in the smaller-size polystyrene particle system.

The effects of initial particle size on collision efficiency and frequency are also investigated theoretically. Figure 5.10 shows that the collision efficiency decreases as the particle size ratio increases. The influences of particle size and size ratio on collision frequency are shown in Figure 5.11. It is given in Eq. [4.22] that the collision frequency is proportional to the third power of particle size. The calculation gives the expected results that the collision frequency will increase much faster with larger particle size or size ratio.

Figure 5.12 shows that the flocculation frequency decreases as the particle size ratio increases. The data also show that the flocculation frequency decreases as the initial particle size becomes smaller, while Figure 5.9 gives the opposite results. It is because that in the 0.1 µm polystyrene particle system, the particle size ratio is initially much smaller than that in the 0.56 µm polystyrene particle system. Therefore, the flocculation frequency is higher in the 0.1 µm polystyrene particle system, which is as shown in Figure 5.9. It is also probably because the flocculation rate is influenced by the particle...
concentration. The concentration of particles is on a weight basis and the number of smaller particles per gram of solution is more than that of larger ones.

5.6 Effect of Electrostatic Forces

Two parameters, ionic strength and pH, play important roles in electrostatic repulsive forces. In high ionic-strength systems, the double layer becomes thinner. Thus, particles can move closer before entering the energy barrier region and it is easier to flocculate together. As expected, the experimental results show that particles flocculate into bigger aggregates much faster in a high ionic strength system (Figure 5.13).

It is shown in Figures 3.2 and 3.3 that the zeta potential of particles varies with different solution pH. The zeta potential of particles is very negative at high pH, which leads to strong electrostatic repulsive forces between particles and less effective collisions. Figures 5.14(a) - 5.14(c) show the experimental results at various values of solution pH. It is found that the flocculation is better in the low pH solution. In Figure 5.14(a), the difference of particle size distributions at different solution pH values is more obvious than that in Figure 5.14(b). In Figure 5.14(c), the solution pH has no obvious effect on particle flocculation. Therefore, Figures 5.14(a) - 5.14(c) conclude that with lower magnetic-seeding particle concentration, the effect of pH on particle flocculation is stronger.
5.7 Effect of Magnetic Seeding Particle Concentration

Figures 5.15(a)-5.15(c) present the results of experiments in which the magnetic seeding particle concentration was changed. The results conclude that the flocculation of a polystyrene and polystyrene/magnetite system can be improved by increasing the magnetic-seeding particle concentration. This is probably true because there are more particles in the system, and the flocculation rate is increased.

5.8 Comparison between Experimental and Modeling Results

Modeling results were compared to the experimental data, and the comparisons are shown in Figures 5.16(a) - (c). The parameters used in the modeling correspond to the experimental conditions. It is shown that the numerical calculations overpredict the flocculation rate. One possibility is that the shear rate is very strong in stirred tanks and breakage of flocs occurs, which is not considered in this work. The other possible reason is that the shear rate is not uniform in the stirred tank. The shear rate will be much smaller outside the impeller zone, thus the flocculation rate is expected to be smaller in that region. It is also found that the disagreement between experimental observations and modeling results in higher agitation speed becomes more obvious than that in lower agitation speed, which indicates that the breakage rate of aggregates is important for predicting the evolution of particle size in stirred tanks. The disagreement between experimental data and modeling results also implies that the breakage rate parameters could be a function of the agitation speed.
CHAPTER VI

CONCLUSIONS

Particle flocculation in stirred tanks was studied experimentally and theoretically in this work. A trajectory model, which incorporates interparticle forces, such as hydrodynamic resistance, van der Waals, and electrostatic forces, as well as fluid flow velocity, was developed to investigate particle flocculation in isotropic turbulent shear flow without using empirical correlations. Brownian diffusion, gravity, and inertial forces were examined and neglected in the trajectory model. The population balance model, in which the breakage rate of aggregates was not included, was then used to predict particle size evolution and distribution as a function of time. The effects of various parameters, such as solution pH, ionic strength, particle size and size ratio, agitation speed, and particle concentration on particle flocculation were examined.

The model calculations show that the collision efficiency can be enhanced by decreasing agitation speed and particle size ratio, as well as by increasing the Hamaker constant. The effects of agitation speed on the collision efficiency and frequency are opposite. The effects of particle size ratio on the collision efficiency and frequency are similar to those of agitation speed. The experimental observations and model calculations both conclude that the particle flocculation in stirred tanks can be enhanced by increasing agitation speed. The experimental observations also suggest that the
flocculation can be improved by lowering solution pH and increasing ionic strength, which is due to the reduction of electrostatic repulsive forces.

In summary, the model calculations qualitatively agree with the experimental observations and conclusions from other workers (Van de Ven and Mason, 1977). Therefore, the performance of the model is still satisfying. The comparison between model calculations and experimental observations suggests that it is necessary to include the breakage rate of aggregates in the population balance model. The possibility of different values of energy dissipation in different compartments in a stirred tank is another reason for the disagreement between experimental and theoretical works.

In this work, the calculation of hydrodynamic resistance forces was based on far-field solutions, which leads to error when two particles are very close. Near-field solutions of hydrodynamic resistance functions need to be found to obtain more accurate results. The effect of electrostatic forces on particle flocculation has only been examined experimentally in this study. In future studies, the effect of electrostatic forces needs to be investigated theoretically. Moreover, there are three comparison of experimental and modeling results provided in this work. More comparisons under different conditions will be provided in subsequent studies.

In the future, to include the breakage rate of aggregates, it is important to understand the physical and chemical characteristics of flocs. Experimental work will be necessary to obtain the correlation between breakage parameters and agitation speed in stirred tanks.
TABLES AND FIGURES
<table>
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<tr>
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<th>Number of particles (per gram)</th>
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<tr>
<td>magnetite</td>
<td>(40% by wt.)</td>
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Figure 2.1 Schematic of the diffuse double layer indicating the zeta potential of a negatively charged particle.
Figure 3.1 Schematic of the stirred tank.
Figure 3.2. Effect of pH and ionic strength on the zeta potential of 100 ppm polystyrene particles.

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Figure 4.1 Streamlines of the turbulent flow around a particle (Saffman and Turner, 1956).
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Figure 5.1 Cumulative size distribution under the same flocculation conditions after 2 minutes; polystyrene particle concentration = 100 ppm, agitation speed = 300 rpm, and ionic strength = 0.1 M NaCl: (c) polystyrene/magnetite particle concentration = 100 ppm.

Figure 5.2 Cumulative size distribution in the first 5 minutes; polystyrene particle concentration = 100 ppm, agitation speed = 300 rpm, and ionic strength = 0.1 M NaCl: (a) polystyrene/magnetite particle concentration = 50 ppm, pH = 2.88.
Figure 5.2 Cumulative size distribution in the first 5 minutes; polystyrene particle concentration = 100 ppm, agitation speed = 300 rpm, and ionic strength = 0.1M NaCl: (b) polystyrene/magnetite particle concentration = 50 ppm, pH = 9.71; (c) polystyrene/magnetite particle concentration = 10 ppm, pH = 6.72.
Figure 5.3 Cumulative size distribution from the population balance model; \( T = 293 \) K, \( 2r_i = 0.56 \ \mu m \), agitation speed = 300 rpm, \( A = 5E-20 \) J, \( \psi = -20 \) mV, and ionic strength = 0.1 M.

Figure 5.4 Cumulative size distribution at different agitation speeds and at 1 minute after flocculation; polystyrene particle concentration = 100 ppm, polystyrene/magnetite particle concentration = 50 ppm, and ionic strength = 0.1 M NaCl.
Figure 5.5  Effect of agitation speed on the collision efficiency; $T = 293 \text{ K}$, $A = 5\text{E-20 J}$, $\psi = -20 \text{ mV}$, ionic strength = 0.1 M: (a) $2r_i = 2r_j = 0.56 \mu\text{m}$, (b) $2r_i = 2.0 \mu\text{m}$. 

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Figure 5.6 Effect of agitation speed on the collision frequency; $2r_i = 2.0 \mu m$.

Figure 5.7 Effect of agitation speed on the flocculation frequency; $T = 293$ K, $2r_i = 2.0 \mu m$, $A = 5E-20$ J, $\psi = -20$ mV, and ionic strength = 0.1 M.
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Figure 5.9 Effect of different initial size of polystyrene on the cumulative size distribution; polystyrene particle concentration = 100 ppm, polystyrene/magnetite particle concentration = 50 ppm, pH~3, agitation speed = 300 rpm, and ionic strength = 0.1M NaCl.
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Figure 5.11 Effects of particle size and size ratio on the collision frequency; agitation speed=300 rpm.
Figure 5.12 Effects of initial particle size and size ratio on the flocculation frequency; $T = 293 \text{ K}$, $\psi = -20 \text{ mV}$, $A = 5E-20 \text{ J}$, ionic strength = 0.1 M, and agitation speed=300 rpm.

Figure 5.13 Cumulative size distribution at different ionic strengths and at 2 minutes after flocculation; polystyrene particles = 100 ppm, polystyrene/magnetite particles = 50 ppm, agitation speed = 300 rpm, and ionic strength = 0.1 M NaCl.
Figure 5.14 Cumulative size distribution at different solution pH and at 2 minutes after flocculation; polystyrene particle concentration = 100 ppm, agitation speed = 300 rpm, and ionic strength = 0.1 M NaCl: (a) polystyrene/magnetite particle concentration = 10 ppm: (b) polystyrene/magnetite particle concentration = 50 ppm.
Figure 5.14 Cumulative size distribution at different solution pH and at 2 minutes after flocculation; polystyrene particle concentration = 100 ppm, agitation speed = 300 rpm, and ionic strength = 0.1 M NaCl: (c) polystyrene/magnetite particle concentration = 100 ppm.

Figure 5.15 Cumulative size distribution at different magnetic seeding particle concentrations and at 2 minutes after flocculation; polystyrene particle concentration = 100 ppm, agitation speed = 300 rpm, and ionic strength = 0.1 M NaCl: (a) High pH.
Figure 5.15 Cumulative size distribution at different magnetic seeding particle concentrations and at 2 minutes after flocculation; polystyrene particle concentration = 100 ppm, agitation speed = 300 rpm, and ionic strength = 0.1M NaCl: (b) Intermediate pH; (c) Low pH.
Figure 5.16 Comparison of experimental and modeling results; cumulative number distribution at 1 minute after flocculation; experimental conditions: polystyrene particle concentration = 100 ppm, polystyrene/magnetite particle concentration = 50 ppm, pH=3.3, ionic strength = 0.1 M NaCl, T = 293 K, 2r_i = 0.56 µm; Modeling parameters: A = 5E-20 J and ψ = -20 mV: (a) agitation speed = 200 rpm; (b) agitation speed = 300 rpm.
Figure 5.16 Comparison of experimental and modeling results; cumulative number distribution at 1 minute after flocculation; experimental conditions: polystyrene particle concentration = 100 ppm, polystyrene/magnetite particle concentration = 50 ppm, pH = 3.3, ionic strength = 0.1 M NaCl, $T = 293$ K, $2r = 0.56$ µm; Modeling parameters: $A = 5E-20$ J and $\psi = -20$ mV; (c) agitation speed = 400 rpm.
APPENDIX A

EXPERIMENTAL CONDITIONS AND PARTICLE SIZE DISTRIBUTION MEASUREMENTS
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100 ppm polystyrene vs. 50 ppm paramagnetic particles
pH=9.68  I=0.1M
### 100 ppm polystyrene vs. 50 ppm paramagnetic particles

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EFFECT OF FRACTAL DIMENSION ON PARTICLE FLOCCULATION

A SPECIAL RESEARCH PROJECT

Presented to

The Faculty of the School of
Civil and Environmental Engineering

by

Shih-Chien Lu

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Environmental Engineering

Georgia Institute of Technology

December 1997
EFFECT OF FRACTAL DIMENSION ON PARTICLE FLOCCULATION

Approved:

Sotira Z. Yiacoumi

Costas Tsouris

Edward S. K. Chian

Date: December 1997
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I. Abstract

Particle flocculation plays a major role in water treatment. In flocculation kinetics models, we usually assume that two spherical primary particles collide together and form another spherical particle. Real aggregates, however, are of irregular shapes and can be considered as fractal objects. The structure of fractal objects can be described by a number called fractal dimension. This fractal dimension plays an important role in flocculation kinetics models.

Two-dimensional computer simulations of flocculation are carried out in this work to directly observe the evolution of particle size and to determine the fractal dimension of flocs. The computer program developed in this study simulates random particle motion as well as cluster growth. The simulation results are visualized using a Java development kit. The fractal dimension of the simulated clusters is determined based on a log-mass/log-size relationship. Results show that the Witten-Sander model gives higher fractal dimensions than the cluster-cluster aggregation model. Furthermore, the initial particle concentration and particle diffusivity have a strong effect on the fractal dimension.
II. Introduction

2.1 Flocculation

In water systems, particles are often too small to be effectively separated by such treatment methods as filtration, flotation, and sedimentation. It is thus necessary to build up the size of particles into larger ones in order to increase the separation efficiency. A commonly used process to increase the particle size is known as coagulation, aggregation, or flocculation (Amirtharajah and O'Melia, 1990). Flocculation is a very important process in water treatment. Due to different mechanisms, flocculation may fall into three categories: (1) Brownian flocculation; (2) gravity flocculation; and (3) shear flocculation (Elimelech et al., 1995). Brownian flocculation, examined in this work, is caused by Brownian motion which is due to the thermal energy of the system, and is also called perikinetic flocculation.

Most colloids in water have charges on their surfaces that develop a ‘double layer’ structure around the particle. When two similar colloidal particles approach each other, their diffuse layers begin to overlap and interact with each other. This electrostatic interaction between the particles results in a repulsive force. On the other hand, attractive forces called van der Waals forces exist between all types of particles. The van der Waals force between two particles decreases with increasing separation distance between them (Gregory, 1989). The attraction and repulsion forces are assumed to be additive and are combined to give the total energy of interaction between particles as a function of separation distance. The addition of the electrostatic and van der Waals forces forms the basis of the DLVO theory of colloid stability, which was developed independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948).


2.2 Fractal Dimension

The fractal concept is widely used in disordered systems. Many researchers regard fractal concept as a language to describe natural systems (Mandelbrot, 1977). Several complex geometrical structures observed in various experiments are fractals. Aggregation of similar particles is also a good example of these phenomena.

Flocculation kinetics models are often based on spherical particles. When two spherical primary particles collide, we usually assume that they form a new spherical floc. Aggregates in real systems, however, are often non-spherical. When two primary particles collide, they form a dumbbell-shaped aggregate (Elimelech et al., 1995). A third particle can attach in several different ways. In real aggregation processes, aggregates containing thousands of primary particles can arise and it will never be possible to provide a detailed description of their structure. Some convenient method, like the fractal dimension, is needed. The fractal concept enables aggregate structure to be characterized in general terms, but still conveys useful information.

Many irregular structures are ‘self-similar’ in a statistical sense (Vicsek, 1989). Their morphology is invariant with an increase in magnification. For example, a self-similar aggregate will always have a unique fractal dimension, irrespectively how we magnify the fractal. This fractal dimension is an important tool for describing geometric irregularity. It is also a good tool relating the Euclidean dimension to fractal structure (Pfeifer and Obert, 1989).

There are various ways to define and determine the fractal dimension. For a large surface, there is the surface fractal dimension; for porous material, there is the pore fractal dimension; for aggregates, we usually use volume and mass fractal dimensions. All of
these fractal dimension definitions are power-law relationships between length scale and properties such as mass, density, surface area, etc. For example, the mass fractal dimension is defined by (Elimelech et al., 1995):

\[ M \sim R^{D_f} \]  

where \( M \) is the mass of a cluster, \( R \) is the radius (or linear size) of a cluster, and \( D_f \) is the mass fractal dimension.

### 2.3 Particle Simulation

Computer simulations can represent in several ways fractal phenomena. The significant advantage of computer simulations lies in the possibility of providing essentially exact results for problems that would otherwise be solved only by approximate methods. Furthermore, simulation procedures may offer details and insights of real processes and thus assist in interpreting experimental results. We can put as many 'behaviors' of primary particles as the computer processing speed and memory allow (Elimelech et al., 1995). In our research we are concerned with simple models leading to the formation of fractal structures. First, we use the Witten-Sander model (Witten and Sander, 1981) for particle-cluster aggregation. We also construct a cluster-cluster aggregation model (Meakin, 1984) for simulating particle random collision and flocculation. The computer program shows a 'real-time' cluster structure on the screen as well as the particle-size ratio distribution and fractal dimension. A modern computer language, Java, is used in the simulations. Java is an object-oriented programming language, and the executable bytecode can be run on various platforms and operating systems (Flanagan, 1996). Since it is a window-based programming language, its visualization capability is suitable for particle simulation.
III. Literature Review

3.1 Flocculation Kinetics

Most discussions on the flocculation rate start from the work of Smoluchowski (1917). In the beginning, there are identical primary particles in the system. After a period of aggregation, the system contains aggregates of various sizes and the total number of clusters decreases. We can use aggregation rate to describe how fast the aggregation process is. The rate of aggregation is determined by the rate at which interparticle collisions occur.

A fundamental assumption is that aggregation is a second-order rate process. The number of collisions occurring between $i$ and $j$ particles in a unit time and unit volume, $J_{ij}$ is given by (Friedlander, 1977)

$$J_{ij} = \beta_{ij} n_i n_j$$  \hspace{1cm} (2)

where $n_i$ is the number concentration of particles of size $i$ and $\beta_{ij}$ is the collision frequency function. The 'size' here implies the number of primary particles comprising the aggregate. We can also speak of 'i-fold' and 'j-fold' aggregates.

It is assumed that particle collisions are predominately due to Brownian diffusion and that for dilute suspensions, only binary particle collisions occur. The collision frequency function for Brownian diffusion is given by (Tsouris and Scott, 1995)

$$\beta_{ij} = \frac{2}{3} \frac{kT (r_i + r_j)^2}{\mu r_i r_j}$$  \hspace{1cm} (3)

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\mu$ is the viscosity of the fluid. Symbols $r_i$ and $r_j$ correspond to the radius of particle $i$ and $j$, respectively. Equation (3) has the very important feature that, for particles of approximately equal size,
the collision frequency function becomes independent of particle size. Physically, this is because the increase in particle size leads to a lower diffusion coefficient but a larger collision radius, and these two effects cancel each other out when particles are of nearly the same size. For particles of different size, the collision frequency function will always be greater than that for equal particles (Elimelech et al., 1995). The assumption of a constant value, however, is a reasonable approximation for particles that differ in size by a factor of about 2 or less.

The flocculation frequency $F_y$ of particles under the influence of interaction forces is defined as the product of the collision frequency function $\beta_y$ with a collision efficiency factor $E_{ij}$ (Tsouris and Scott, 1995),

$$F_y = \beta_y E_{ij} \quad (4)$$

The collision efficiency factor incorporates the effect of particle interaction forces. If there is strong repulsion between particles then practically no collision occurs and collision efficiency will approach zero. The collision efficiency could be larger than one if there is an additional attractive force such as a magnetic force. The collision efficiency can be obtained from the solution of the generalized Smoluchowsky equation for the diffusing particle under the action of interparticle forces (Tsouris and Scott 1995),

$$E_{ij} = \left[ (1 + r_j / r_i) \int_{r_j / r_i}^{\infty} \left( D_{\infty} / D_y \right) \exp(V_A / kT) \frac{ds}{s^2} \right]^{-1} \quad (5)$$

where the interaction potential $V_A$ is the summation of electrostatic, Van der Waals, and other potentials, and $s = r/r_i$ is a dimensionless separation distance between the particles. The hydrodynamic interaction is incorporated in the ratio $D_{\infty} / D_y$, where $D_{\infty}$ is the diffusion coefficient in the absence of any interparticle forces and $D_y$ is the relative
diffusion coefficient between particles $i$ and $j$.

Once the flocculation frequency of particles is obtained as the product of collision frequency and collision efficiency [Eqs. (3)-(5)], it is possible to write a macroscopic population-balance equation to describe the growth of the $i$-fold particle flocs. In the absence of floc breakup, the discretized form of the population-balance equation is given by (Tsouris and Scott, 1995)

$$\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} F_{j\left(i-j\right)} n_j n_{\left(i-j\right)} - \sum_{j=1}^{N} F_{ij} n_j n_i$$

where $t$ is the time. The first term on the right-hand side represents the rate of formation of $i$-fold aggregates by collision of any pair of aggregates, $j$ and $(i-j)$. Carrying out the summation would mean counting each collision twice and hence the factor $1/2$ is included. The second term accounts for the loss of $i$-fold aggregates by collision with any other aggregate or primary particle. It is important to note that Eq. (6) is applicable for irreversible aggregation since no allowance is made for break-up of aggregates.

For continuous particle size distributions, an integral version of the population balance equation can be written. In principle, it is possible to derive the evolution of the aggregate size distribution with time, but in practice it is difficult to assign values for the rate coefficients. The simplest assumption is that spherical particles coalesce on contact to form a larger sphere with the same total volume. This assumption is physically unrealistic except for liquid (emulsion) droplets, but it has often been used in earlier treatments of aggregation kinetics. The real, non-sphere aggregate is a fractal object. The relationship between the sphere assumption and the real aggregate can be described with the fractal dimension.
3.2 Fractal Dimension

Aggregates can be recognized as fractal objects (Meakin, 1984). The concept of fractal was introduced by Mandelbrot (1977, 1982). Box counting is one of the approaches for determining the fractal dimension. We pick up a box of size \( \varepsilon \) and superimpose the box on the fractal object. By counting how many boxes are intersected by the fractal object, we can get a power law relationship:

\[
N_{\text{box}}(\varepsilon) \propto \varepsilon^{-D_f} \quad \text{for} \quad \varepsilon \to 0 \tag{7}
\]

If \( D_f \) coincides with \( D_{\text{top}} \), the topological dimension of the system (\( D_{\text{top}} = 0 \) for dust, i.e., for a set of disconnected points; \( D_{\text{top}} = 1 \) for a curve; \( D_{\text{top}} = 2 \) for a surface; \( D_{\text{top}} = 3 \) for a solid), then the system is called Euclidean or non-fractal. If \( D_f \) differs from \( D_{\text{top}} \), the system is called fractal or scaling. For any system, one has \( D_{\text{top}} \leq D_f \leq d \), where \( d \) is the embedding dimension (dimension of the embedding Euclidean space; in real systems usually \( d = 3 \)). The following are some useful rules about fractal dimension (Vicsek, 1993):

(a) Many times it is the projection of a fractal which is of interest or can be experimentally studied [e.g., a picture (\( d-m = 2 \), where \( m \) is the difference between Euclidean dimension and projection dimension) of a fractal embedded into a 3D system (\( d = 3 \)]. In general, projecting a \( D_f < (d-m) \) dimensional fractal onto a \( d-m \) dimensional surface results in a structure with the same fractal dimension \( D_p = D_f \), where \( D_p \) is the fractal dimension of the projection. For \( D_f \geq d - m \) the projection fills the surface, i.e., \( D_p = d - m \).

(b) Cutting out a \( d-m \) dimensional slice (cross-section) of a \( D_f \) dimensional fractal
embedded into a $d$-dimensional space usually leads to a $D_f - (d - m)$ dimensional object.

(c) Considering two sets A and B having fractal dimensions $D_A$ and $D_B$, respectively, and multiplying them together results in a fractal with $D_f = D_A + D_B$. For example, a fractal that is made of parallel sticks (fractal dimension 1) and arranged in such a way that its cross-section has a fractal dimension of 1.465, then the dimension of this object is $D_f = 1 + 1.465 = 2.465$.

(d) The union of two fractal sets A and B with $D_A > D_B$ has the dimension $D_f = D_A$.

(e) The fractal dimension of the intersection of two fractals with $D_A$ and $D_B$ is given by $D_{A \cap B} = D_A + D_B - d$

For a large number of aggregates, the mass is plotted against aggregate size (for example, radius), and the plot may be linear but with a non-integer slope (For a regular system embedded in three-dimensional space the slope of such plots is 3.0.) For aggregates, the slope of the line, $D_f$, is called the mass fractal dimension. The lower the fractal dimension, the more open (or 'stringy') is the aggregate structure.

For Brownian aggregation, the growth of aggregates gives an increasing collision radius and a reduced diffusion coefficient and these effects tend to cancel out giving a collision rate constant that is not greatly dependent on aggregate size. For fractal aggregates, the hydrodynamic radius (which determines the drag and the diffusion coefficient) is likely to be somewhat less than the outer 'capture radius', corresponding to the physical extent of the aggregate (Elimelech et al., 1995). For high degrees of aggregation, the ratio of the hydrodynamic radius to the capture radius has been
calculated to be about 0.6 (Torres et al., 1991), meaning that Brownian collisions will occur rather more rapidly than predicted from the rate constant. For aggregates greater than a few micrometers in size, however, Brownian aggregation is negligible and collisions induced by gravity or shear become far more important.

For lower values of fractal dimension, the aggregate size increases more rapidly and can give a dramatic increase in aggregation rate (Jiang and Logan, 1991). The implications for the evolution of aggregate size distribution have been discussed by Wiesner (1992). An obvious consequence of the fractal nature of aggregates is that the effective floc volume will not be conserved as assumed in the derivation of collision rates. There will be a substantial increase in floc volume for typical values of $D_f$ and this is the reason for the increased collision frequency.

### 3.3 Particle Simulation

The research on aggregation phenomena increased dramatically since the introduction in 1981 of the diffusion-limited aggregation (DLA) model (Witten and Sander, 1981). The development of this model was stimulated by the earlier experimental work which demonstrated that fractal structures could be generated by the aggregation of small metal particles in a dense gas. In the Witten-Sander model, particles are added one at a time and move randomly to a growing aggregate of particles. When the randomly moving particle collides with the aggregate, it sticks with the aggregate. Single-particle addition is not a realistic model since in many aggregation processes, growth occurs as a result of cluster-cluster encounters. In this case, computer simulations and experimental studies with a range of model colloids (Lin et al., 1989) showed much more open structures with a fractal dimension of around 1.8.
Meakin (1984) suggested a cluster-cluster aggregation model. During the initial stage of the simulation, lattice sites are randomly selected and occupied. The lattice contains a large number of isolated occupied sites and a few small clusters (occupied sites connected by nearest neighbor occupancy). In this model, objects (particles or clusters) are selected at random (or with a probability that depends on their size to represent the effects of a size dependent diffusion coefficient) and are moved by one lattice unit in a randomly selected direction on the lattice. After a particle or cluster has been moved, its perimeter is examined to determine if another object has been contacted and a new cluster has been formed. Clusters are formed irreversibly in this model and the sites in the cluster continue to move on the lattice as a single unit.

It is important to realize that both simulations discussed in this section are based on the assumption that particles attach permanently to other particles at first contact; the process is controlled entirely by diffusion - hence ‘diffusion-limited aggregation’ (DLA). When there is interparticle repulsion so that the collision efficiency is reduced, aggregation is then said to be ‘reaction-limited’ and very different aggregate structures can be obtained under these conditions. It is found (Lin et al., 1989) that reaction-limited aggregates are more compact than those produced by DLA for the cluster-cluster case. When the collision efficiency is low, particles (or clusters) need to collide many times before sticking occurs, and thus more opportunities exist to explore other configurations and to achieve some degree of inter-penetration (Elimelech et al., 1995).
IV. Research Approach

4.1 Fractal Dimension in Population Balance Equation

A modeling program for the population balance equation was developed by Tsouris et al. (1995). This program was written in FORTRAN and can run on an IBM RS-6000 machine with AIX 3.2 operating system. It uses the EPISODE package for solving ordinary differential equations (Hindmarch and Byrne, 1976).

The population balance equation is given by Eq. (6). The flocculation frequency \( F_{ij} \) is a function of interparticle forces, zeta potential, ionic strength, temperature, and radius. If we assume that the radius of a reference particle is \( r_0 \), and its volume is \( V_0 \), then for each cluster of radius \( r \) and volume \( V \) in the flocculation system we can obtain (Vicsek, 1989):

\[
\frac{r}{r_0} = A_f \left( \frac{V}{V_0} \right)^{\frac{1}{D_f}}
\]

(8)

where \( A_f \) is 1. From Eq. (8), we can get the radius of a cluster as a function of fractal dimension. By substituting Eq. (8) in the collision frequency function \( \beta_{ij} \) of Eq. (4), we can introduce the fractal dimension into the population balance equation.

4.2 Particle Simulation

Computer simulations can provide essentially exact results for problems that would otherwise be solved only by approximate methods. Simulation procedures may be able to offer details and insights of ‘real’ (other than ‘model’) processes and so assist in interpreting experimental results. In some instances, where experimental measurements are practically difficult to perform, simulation methodologies may even be able to replace experimentation.
Java, a modern computer language, is selected for the implementation of particle simulations. Java is a fully-featured, general-purpose computer language, which has similar syntax as C and C++ (Flanagan, 1996). Java is an object-oriented language system in which data and methods that operate on the data are stored together in a ‘class.’ We can arrange those classes in hierarchy so that a subclass can inherit behavior from its superclass. With this feature, programmers can reuse their codes in a robust way. Java is also an architecture-neutral language. The compiled byte-code can be run on any system as long as the system implements the Java Virtual Machine standard. Once we compile the code, we can run it on Mac, PC with Windows 95 or NT, and also high-end UNIX workstations. With ‘just in time’ (JIT) compiler, the performance of the compiled byte code is nearly as good as native C or C++. Java has a good class library, which made it suitable for both calculation and visualization.

In simulation programs, we construct a class called ‘particle.’ This particle class is an object that contains the position of a particle (or cluster if aggregated) in the simulation space. It also contains attributes (i.e., single particle, cluster member, or cluster seed), the cluster size, and the number of primary particles in a cluster. This particle class also contains a ‘move’ method and a ‘paint’ method. The move method makes a particle move in the simulated space with randomly selected direction. The ‘paint’ method paints the simulation result on the screen when simulation is in progress. The simulation program also generates the average particle size and length-mass relationship needed for fractal dimension calculations.
4.2.1 Witten-Sander Model

In the Witten-Sander model, the cluster is fixed. Particles are added, one at a time, to a growing cluster or aggregate of particles. Figure 4-1 shows a simulation example in which 475 particles are added one by one.

Particles are released at a very large distance from the cluster and follow random walks on a square lattice. In each step, the particle moves one lattice. If the particle collides to the growing cluster, it will 'stick' to the cluster, stay at the collision site, and become part of the cluster. The cluster radius $R$ is estimated from the largest distance between the edge of cluster and the aggregate kernel. The simulation program will provide the cluster radius and the number of primary particles or mass $M$ of the cluster. From Eq. (1), we can get the fractal dimension by calculating the slope of the log-mass/log size diagram obtained from the simulation result.

4.2.2 Cluster-Cluster Aggregation Model

In the cluster-cluster aggregation simulation (Meakin, 1984), particles are first generated at random position. In this initialization step, two particles should not exist at the same position. If multi-occupation occurs, one of the particles is relocated randomly until they find an empty lattice. At this step the lattice contains a large number of isolated occupied sites and a few small clusters (occupied sites connected by nearest neighbor occupancy).

Small particles in suspension can be seen to undergo continuous random movements. The diffusion coefficient of a spherical particle is given by the Stokes-Einstein equation (Elimelech et al., 1995):
From the above equation, we obtain:

$$D_i = \frac{kT}{6\pi\eta_1\mu}$$  \hspace{1cm} (9)

At each simulation step, particles (and clusters) are selected at random with probability that depends on their size to represent the effects of a size-dependent diffusion coefficient, and then are moved by one lattice unit in a randomly selected direction on the lattice. After a particle or cluster has been moved, its perimeter is examined to determine if another object has been contacted (via nearest neighbor occupancy). If another object has been contacted, a new cluster will be formed. Clusters are formed irreversibly in this model and the sites in the cluster continue to move in the lattice as a single unit. Given a very long simulation time, particles will eventually become one cluster. Figures 4-2 (a) and (b) are examples of the cluster-cluster aggregation simulation. Initially, 475 particles on the lattice and move randomly. After 1977 steps, bigger aggregates are formed.

### 4.3 Box-Counting Method

There are various ways to determine the fractal dimension of an aggregate; box-counting is one of them and can be used for both computer simulated and real aggregates. The following is an example of how the fractal dimension is determined by the box-counting method.

If we have an aggregate such as the one in Figure 4-3, as we magnify the aggregate, we will ultimately get a basic structure on a 3x3 grid. The linear size of this basic structure is 3 grids, and in each basic structure there are 5 grids occupied. Thus, the fractal dimension of this aggregate will be:
\[
\frac{\log 5}{\log 3} \approx 1.47
\]

In simulation systems, we can use a similar log-log relationship. From Eq. (1), we obtain
\[
\log M = D_f \log R + c,
\]
where \( c \) is a constant. By counting the radius and mass of each particle, we will get the fractal dimension from the log-radius vs. log-mass diagram.
V. Results and Discussion

5.1 Population Balance Equation

5.1.1 Sensitivity Analysis

There are many input parameters for the population balance equation model, including simulation time, number of classes, primary particle size, initial number of particles, viscosity, temperature, Hamaker constant, zeta potential, ionic strength, particle density, and particle concentration. The effects of particle concentration and ionic strength are discussed below.

Figure 5-1 shows the particle size growth at different initial concentrations. Initially, we set the diameter ratio as 1, and as simulation proceeds the average particle size increases. At $t = 600$ s, the particle size is 1.8 times of the initial size for concentration 100 mg/L. For initial concentration 10 mg/L, the particle size grows less than 20% at $t = 600$ s. Based on the results of Figure 5-1, we conclude that particle growth is slower as particle concentration decreases.

Figure 5-2 shows the effect of ionic strength. The ionic strength effect acts like a step function. At very low ionic strength, flocculation is almost non-existent, while for a large enough ionic strength, flocculation is enhanced. For all ionic strengths larger than the threshold, the modeling result is the same.

5.1.2 Fractal Dimension Correction

From Eq. (8), we can get (for $A_1 = 1$):

$$r = r_0 \left( \frac{V}{V_0} \right)^{\frac{1}{D_f}}$$

(11)

Applying Eq. (11) in Eq. (3), we can introduce the fractal dimension in the population
balance equation. Figure 5-3 shows the comparison for fractal dimension 3.0 and 2.4. The experimental values were obtained from Tsouris and Scott (1995). A fractal dimension 3.0 (the solid line in Figure 5-3) means that we do not consider the fractal dimension effect in the population balance equation. The dashed line is for a fractal dimension of 2.4. With lower fractal dimension, particles grow faster than with higher fractal dimension and are closer to the experimental values. Based on the results of Figure 5-3, we conclude that the fractal dimension is an important parameter for determining the average particle size growth.

5.2 Particle Simulation Results with the Witten-Sander Model

In the Witten-Sander model, one particle is kept at the center of the simulation space and other particles are added one at a time. Each particle moves with random walk. For each walk step, the particle's boundaries are checked for any collisions. If there is no collision, the particle keeps moving until it collides with the cluster located at the center of the simulation space.

The simulation platform of the Witten-Sander model is a Pentium-based Windows 95 machine, with 64MB RAM. The estimated time needed to complete a 475-particle simulation is about 12 hours.

When each particle is added, we can get a new cluster radius as well as a new cluster mass. Figure 5-4 is an example calculation of the fractal dimension from the Witten-Sander model. The fractal dimension from the Witten-Sander model was found to be between 1.7 and 1.9. In this model, particle structure is dense and the fractal dimension is high.

In summary, the Witten-Sander simulation is based on a 2-D system. A simulation
embedded in a 2-D system will give a maximum fractal dimension of 2. In the Witten-Sander model, we obtained a fractal dimension of 1.7 to 1.9 which is relatively high. In the Witten-Sander model, only a single cluster is formed, and this cluster is fixed in the middle of the simulation space. Only a small particle is added at a time into the system, and, since small particles have more chance to move into the center of the cluster, the cluster forms a more 'dense' structure.

In our simulation program, we assumed that particles attach permanently to other particles at the first contact. The process is controlled entirely by diffusion, hence 'diffusion-limited aggregation' (DLA) (Elimelech et al., 1995). From the literature (Witten and Sander, 1981), for single cluster DLA two-dimensional models, the typical fractal dimension value was found to be around 1.7. Our simulation result is similar to the value discussed in the literature using a higher (more than 400) number of particles.

5.3 Particle Simulation Results with the Cluster-Cluster Aggregation Model

In the cluster-cluster aggregation model, all clusters are moving randomly with a probability related to their size. In this simulation, we assume that there are no interparticle forces except for the attractive force that makes two particles stick together. When a cluster collides with another cluster, they form a bigger cluster.

For each cluster, we can measure its radius and number of particles inside the radius. By plotting mass vs. radius on a log-log scale, we can obtain the fractal dimension from the slope. Figure 5-5 is an example calculation. In this cluster-cluster aggregation model, every cluster is allowed to move. When a cluster collides with another cluster, the void space in the new cluster will be bigger than the void space of a cluster colliding with a particle. For a cluster, it is not probable to collide at the center of another cluster. Thus,
the structure will be less dense than that from the Witten-Sander model. The fractal
dimension obtained from the cluster-cluster aggregation model is about 1.0 to 1.4, which
is smaller than the value obtained from Witten-Sander model.

Meakin (1984) indicated that if $D_f = d$ (Euclidean dimensionality with a value of 2.0
for 2-D simulation), as clusters grow larger and larger they will approach a constant
limiting density, $C(r)$, or porosity. If $D_f < d$, however, the density of the cluster will
become smaller and smaller as the cluster grows larger and larger. Our simulation results
agree to this trend. Figure 5-6 shows the result of density (number of primary particle per
simulation area) distribution obtained from the simulation. Since $C(r) \sim M / R^d$ where $d$
= 2 in our simulation, we can have $C(r) \sim r^{(D_f-d)}$. If we plot the density versus radius on
a log-log scale, the slope will be a constant equal to $(D_f-d)$. Figure 5-7 shows the log-log
result from the simulation. The result is slightly different from the theory due to the error
of regression calculation. In Figure 5-7, $(D_f-d) = -0.8585$. The theoretical fractal
dimension obtained from the density function should be $D_f = d - 0.8585 = 2.0 - 0.8585
= 1.1415$. It is shown later in Figure 5-9 (b) that $D_f = 1.2259$, using the method from Eq.
(1), which gives an error of about seven percent.

5.3.1 Fractal Dimension vs. Simulation Steps

We calculated the fractal dimension every two hundred simulation steps, and the
results are shown in Figure 5-8. At the initial steps, fractal dimension is increasing.
After a longer simulation time, a stable fractal dimension is obtained, which is
independent of the number of simulation steps. It seems that a stable fractal dimension
can be found when there are enough clusters in the system. In our case, ten clusters or
greater are sufficient for simulation results. If there are not many clusters in the system, the fractal dimension may not be accurate.

5.3.2 Influence of Initial Particle Concentration

We used varying initial particle number of the same particle size and found that the fractal dimension for different initial number of particles will be different. If the initial particle number (or occupied lattice per unit area) is higher, the fractal dimension will be higher. Figures 5-9 (a) and (b) show two regression results with different initial particle numbers. In Figure 5-9 (a), 200 particles are used in the simulation. After 800 steps, we obtained a fractal dimension of 1.04 with a regression coefficient of 0.8659. In Figure 5-9 (b), we used 475 particles in the system. After 800 steps the fractal dimension is about 1.2 with regression coefficient 0.9548. With higher initial particle concentration, small particles can easily collide into a cluster, thus the fractal dimension will be higher.

Meakin (1984) used two different particle concentrations $<\rho>$ (initial particle number per total lattice number) in their simulations. The fractal dimension approached a limiting value when $<\rho>\to 0$. For higher concentration $<\rho>$, they obtained a higher fractal dimension. According to Figures 5-9 (a) and (b), our simulation results agree with this conclusion.

5.3.3 Fractal Dimension without Diffusivity

In our cluster-cluster aggregation model, particles are selected and move randomly with a probability related to their size. This is a way to simulate diffusivity. A particle with larger size will move slower in this method. Additionally, we tried another method in which all clusters are selected and move with the same probability, no matter how big the cluster is. Figures 5-10 (a) and (b) are two simulation results with and without
diffusivity. By comparing these figures, we found that the fractal dimension of simulation without diffusivity is lower than that with diffusivity. The reason for this difference is similar to the difference between the Witten-Sander model and cluster-cluster aggregation model. Big clusters are much more stable in the method with diffusivity than the method without diffusivity because bigger clusters have less probability to be selected to move. As we discussed in Section 5.3.1, when a cluster collides with another cluster, the new fractal dimension of the new cluster is less than the fractal dimension of a particle colliding with a cluster. If big clusters are more stable, they have more chances to stay at their original location. Thus, it is not easy for big clusters to collide with each other. On the other hand, if big clusters are as active as small particles, they have more opportunities to collide, and the fractal dimension will be lower.
VI. Summary and Conclusions

In natural systems, aggregates are often irregular. These irregular aggregates are fractal objects, and the fractal dimension can be used to describe their structure. The population balance equation is used to model flocculation kinetics. We introduced fractal dimension into the population balance equation model and found that the fractal dimension is an important parameter. Systems with smaller fractal dimension will have a higher flocculation rate, and the resulting particle size will be bigger.

For a self-similar aggregate, we obtained a power-law relationship between length and mass. The results of our simulation were in agreement with this power-law relationship. We used two different approaches to implement particle random-walk simulation. The first approach was the Witten-Sander model which gave a fractal dimension between 1.7 and 1.9. In the Witten-Sander model, particles are added one at a time and only one cluster is formed at the center of the simulation space. The second approach was the cluster-cluster aggregation model, in which all clusters in the simulation system are selected with probability related to their size. The fractal dimension obtained from the cluster-cluster aggregation model is about 1.2 to 1.4. The fractal dimension from the cluster-cluster aggregation method is smaller than that from the Witten-Sander model. In the cluster-cluster aggregation method, aggregates are more open in structure and, therefore, have a lower fractal dimension.
VII. Notation

\[ A_f \] constant in fractal dimension calculation
\[ C(r) \] density function (kg m\(^2\))
\[ D_f \] fractal dimension
\[ D_t \] diffusivity in simulation
\[ D_{ij} \] relative diffusion coefficient between particle \(i\) and \(j\)
\[ D_{\infty} \] diffusion coefficient without interparticle forces
\[ d \] Euclidean dimensionality
\[ E_{ij} \] collision efficiency factor
\[ F_{ij} \] flocculation frequency
\[ J_{ij} \] collisions rate occurring between \(i\) and \(j\) particle (m\(^3\) s\(^{-1}\))
\[ k \] Boltzmann constant = 1.38x10\(^{-23}\) J K\(^{-1}\)
\[ M \] mass of a cluster (kg)
\[ m \] the difference between Euclidean dimension and projection dimension
\[ n_i \] number concentration of particle of size \(i\) (m\(^{-3}\))
\[ R \] radius of a cluster (m)
\[ r_i \] radius of particle \(i\) (m)
\[ T \] absolute temperature (K)
\[ t \] time (s)
\[ \beta_{ij} \] collision frequency function (m\(^3\) s\(^{-1}\))
\[ \varepsilon \] box size in box counting method (m)
\[ \mu \] viscosity of the fluid (kg m\(^{-1}\) s\(^{-1}\))
\[ < \rho > \] particle concentration in simulation (m\(^{-2}\))
VIII. Acknowledgment

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IX. References


Figure 4-1 Simulation result using the Witten-Sander model: particle number = 475.
Figure 4-2  Simulation results using the cluster-cluster aggregation model:
(a) particle number = 475, particle size = 3 pixels, number of steps = 10
(b) particle number = 475, particle size = 3 pixels, number of steps = 1977
Figure 4-3  Example for the box-counting method, the magnified view shows the basic structure of this fractal object.
Figure 5-1  Effect of particle concentration on particle growth using the population balance equation the size evolution: zeta potential = -20 mV, ionic strength = 0.1 M, particle diameter = 0.44µm.
Figure 5-2  Effect of ionic strength on particle growth using the population balance equation: zeta potential = -20 mV, particle diameter = 0.44 µm, particle concentration = 100 mg/L.
Figure 5-3  Effect of fractal dimension on particle growth using the population balance equation: particle concentration = 3.8 mg/L, zeta potential = 0 mV.
Figure 5-4  Estimation of the fractal dimension from the Witten-Sander model: particle number = 200, steps = 200.
Figure 5-5  Estimation of the fractal dimension from the cluster-cluster aggregation simulation model: particle number = 475, number of steps = 1999.
Figure 5-6  Particle density distribution in cluster-cluster aggregation simulation:
particle number = 475, number of steps = 800.
Figure 5-7  Particle density distribution on log-log scale: particle number = 475, number of steps = 800.
Figure 5-8  Effect of simulation steps on fractal dimension: particle number = 475, particle size = 3 pixels.
Figure 5-9  Effect of initial particle concentration on fractal dimension: (a) particle number = 200, number of steps = 800, particle size = 3 pixels. (b) particle number = 475, number of steps = 800; particle size = 3 pixels.
Figure 5-10 Effect of diffusivity on fractal dimension: (a) particle number = 475, number of steps = 800, particle size = 3 pixels; without diffusivity effect. (b) Particle number = 475, number of steps = 800, particle size = 3 pixels; with diffusivity.

\[ y = 1.2259x + 0.9308 \]
\[ R^2 = 0.9548 \]

\[ y = 1.3132x + 0.6683 \]
\[ R^2 = 0.9092 \]
XI. Appendix

Program List

ParticleSim.java
Here is the description of classes:

particle class: basic definition like x, y, color, etc. Note that x and y are in the unit of particle size

brownian class: particle properties such as movement, forces (in the future) etc

clusters class: this class provides an image (a 3D array) for all particle positions. It also handles cluster-cluster aggregation

This class is a basic extension of the Applet class. It would generally be used as the main class with a Java browser or the Applet Viewer. But an instance can be added to a subclass of Container. To use this applet with a browser or the Applet Viewer, create an HTML file with the following code:

```html
<HTML>
<HEAD>
<TITLE>ParticleSim</TITLE>
</HEAD>
<BODY>

<APPLET CODE="ParticleSim.class" WIDTH=283 HEIGHT=190></APPLET>

</BODY>
</HTML>
```

You can add controls to ParticleSim with Cafe Studio.

(Menus can be added only to subclasses of Frame.)
public class ParticleSim extends Applet {

    static public int virtualimage[] = new int[500];
    static public int count1;     // counter for each particle

    static int NUM_PARTS = 500;
    static int PART_SIZE = 3;
    static int DELAYTIME = 1999;
    static int NUM_ITERATION = 50;
    static final int beaker_width = 600;
    static final int beaker_height = 480;
    static int v_width, v_height;

    Graphics offscreen;
    Image offimage;
    Frame beaker;
    barframe bfr;
    public particle[] bpart;

    public void init() {     // initialization of visual components

        super.init();

        // {INIT_CONTROLS
        setLayout(null);
        resize(280, 195);
        panel1 = new Panel();
        panel1.setLayout(null);
        add(panel1);
        panel1.reshape(0, 15, 182, 173);
        numfield = new TextField("100", 5);
        numfield.setFont(new Font("Dialog", Font.BOLD, 10));
        panel1.add(numfield);
        numfield.reshape(98, 15, 77, 23);
        label2 = new Label("Particle ":");
        panel1.add(label2);
        label2.reshape(14, 15, 77, 15);
        label3 = new Label("Steps:");
        label3.reshape(14, 15, 77, 15);
        label3. reshape(14, 15, 77, 15);
    }
panell.add(label3);
label3.reshape(14, 53, 77, 22);
stepfield=new TextField("50", 5);
panell.add(stepfield);
stepfield.reshape(98, 53, 77, 22);
label4=new Label("Size:");
panell.add(label4);
label4.reshape(14, 90, 70, 15);
sizefield=new TextField("3", 2);
panell.add(sizefield);
sizefield.reshape(98, 90, 77, 23);
label5=new Label("Speed:");
panell.add(label5);
label5.reshape(14, 128, 70, 15);
speedchoice= new Choice();
panell.add(speedchoice);
speedchoice.reshape(98, 128, 77, 30);
speedchoice.addItem("Cheetah");
speedchoice.addItem("Turtle");
startbtn=new Button("Start");
add(startbtn);
startbtn.reshape(191, 23, 82, 30);
pausebtn=new Button("Pause");
add(pausebtn);
pausebtn.reshape(191, 62, 82, 28);
exitbtn=new Button("Exit");
add(exitbtn);
exitbtn.reshape(191, 98, 82, 31);
aboutbtn=new Button("About..");
add(aboutbtn);
aboutbtn.reshape(191, 137, 82, 30);

public void followup(int up2) {
    int bosspart=bpart[up2].seedno;
    if (bosspart >=0) {
        bpart[up2].px=bpart[bosspart].px+bpart[up2].seed_dx;
        bpart[up2].py=bpart[bosspart].py+bpart[up2].seed_dy;

    } //}}

}
public void cluster_sync(int boss2) {
    int col;
    for (col=0; col<NUM_PARTS; col++) {
        if (bpart[col].seedno==boss2) {
            followup(col);
        }
    }
}

public void p_attach(int part1, int cluster1) {
    // attach particle to cluster
    int maxl,maxr,maxt,maxb;
    bpart[part1].seedno=cluster1;
    bpart[part1].pcolor=Color.blue;
    bpart[cluster1].seedno=-2;
    bpart[cluster1].pcolor=Color.red;
    bpart[part1].seed_dx=(bpart[part1].px-bpart[cluster1].px);
    bpart[part1].seed_dy=(bpart[part1].py-bpart[cluster1].py);
}

public void c_attach(int loser, int winner) {
    // attach "loser" cluster to "winner" cluster
    cluster_sync(loser);
    // make sure all particle follows the loser, then transfer to winner
    bpart[loser].seedno=winner;
    // !! Be sure it only runs on cluster-cluster case
    bpart[loser].pcolor=Color.blue;
    bpart[loser].seedno=-2;
    bpart[loser].pcolor=Color.red;
    bpart[loser].seed_dx=(bpart[loser].px-bpart[winner].px);
    bpart[loser].seed_dy=(bpart[loser].py-bpart[winner].py);

    for (int sclu=0; sclu<NUM_PARTS; sclu++) {
        if (bpart[sclu].seedno==loser) {
            // update all particles that attached to loser, now attach to winner
            bpart[sclu].seedno=winner;
            bpart[sclu].seed_dx=(bpart[sclu].px-bpart[winner].px);
            bpart[sclu].seed_dy=(bpart[sclu].py-bpart[winner].py);
        }
    }
}
public void clear_image() {
    for (int tempx=0; tempx<v_width; tempx++) {
        for (int tempy=0; tempy<v_height; tempy++) {
            virtualimage[tempx][tempy]=-1;
        }
    }
}

public void refresh_vimage() {
    for (int tempx=0; tempx<v_width; tempx++) {
        for (int tempy=0; tempy<v_height; tempy++) {
            virtualimage[tempx][tempy]=-1;
        }
    }
    for (int tempx=0; tempx<NUM_PARTS; tempx++) {
        int sx=bpart[tempx].px;
        int sy=bpart[tempx].py;

        virtualimage[sx][sy]=tempx;
        /*
        try {
            virtualimage[sx][sy]=tempx;
        } catch (ArrayIndexOutOfBoundsException e) {
            System.out.println("an exception occurred: " + e.getMessage());
            e.printStackTrace();
            System.out.println(tempx+"=bpart[tempx].px","=bpart[tempx].py");
        }*/
    }
}

public boolean handleEvent(Event event) {
if (event.id == Event.ACTION_EVENT && event.target == aboutbtn) {
    clickedAboutbtn();
    return true;
}

else
    if (event.id == Event.ACTION_EVENT && event.target == startbtn) {
        clickedStartbtn();
        return true;
    }

    if (event.id == Event.ACTION_EVENT && event.target == exitbtn) {
        clickedExitbtn();
        return true;
    }

    else
        if (event.id == Event.ACTION_EVENT && event.target == speedchoice) {
            selectedSpeedchoice();
            return true;
        }

    return super.handleEvent(event);
}

public void selectedSpeedchoice() {
    // to do: put event handler code here.
}
public void clickedStartbtn() {
    Integer numberofpart=Integer.valueOf(numfield.getText());
    NUM_PARTS=numberofpart.intValue();
    Integer stepnumber=Integer.valueOf(stepfield.getText());
    NUM_ITERATION=stepnumber.intValue();
    Integer sizenumber=Integer.valueOf(sizefield.getText());
    PART_SIZE=sizenumber.intValue();
    // Put delay handling routine (delayfield) here
    v_width=(int)(beaker_width/PART_SIZE);
    v_height=(int)(beaker_height/PART_SIZE);

    offimage=createImage((beaker_width+2*PART_SIZE), (beaker_height+2*PART_SIZE));
    offscreen=offimage.getGraphics();

    virtualimage= new int[v_width+40][v_height+40];

    clear_image();

    if (beaker==null) {} else { beaker.dispose(); }
    if (bfr==null) {} else { bfr.dispose(); }

    beaker=new Frame("V_Beaker");
    beaker.setResizable(false);
    beaker.setCursor(Frame.CROSSHAIR_CURSOR);
    beaker.show();
    beaker.reshape(200, 300, (beaker_width+PART_SIZE), (beaker_height+PART_SIZE));

    barframe bfr = new barframe("Pop Balance", NUM_PARTS+2);
    bfr.max_y=1.0f;

    bpart= new particle[NUM_PARTS];
    for (count=0; count<NUM_PARTS; count++) {
        bpart[count]=new particle(v_width, v_height);
    }

    Graphics gl=beaker.getGraphics();
    offscreen.setColor(Color.black);
for (int iter=0; iter<=NUM_ITERATION; iter++) {

    offscreen.setColor(Color.white);
    offscreen.fillRect(0,0,beaker_width, beaker_height); // clear offscreen buffer
    offscreen.setColor(Color.black);

    // ****************************************************** major loop

    for (count1=0; count1<NUM_PARTS; count1++) {
        if (bpart[count1].seedno==-2) { cluster_sync(count1); }
        bpart[count1].move();
        if (bpart[count1].seedno==-2) { cluster_sync(count1); }
        refresh_vimage();
        int ans= bpart[count1].check_collide();
        if (ans>=0) {
            // System.out.println("Collide!");
            switch (bpart[count1].seed.no) {
                case (-1): // count1 is free
                    if (bpart[ans].seedno<0) { p_attach(count1, ans); } // attach count1 to ans
                    else { p_attach(count1, bpart[ans].seedno); } // attach count1 to (seed of ans)
                    break;

                case (-2): // oops, count1 is a cluster seed
                    switch ( bpart[ans].seedno ) {
                        case (-1): // cluster-particle
                            p_attach(ans, count1);
                            break;
                        case (-2): // seed-seed attachment
                            c_attach(count1, ans); // usually, those who hit others are loser
                            break;
                        default: // seed-cluster attachment
                            int seednum2=bpart[ans].seedno;
                            c_attach(count1, seednum2);
                            break;
                    }
            }
        }
    }
}
switch ( bpart[ans].seedno ) {
    case (-1):
        p_attach(ans, bpart[count1].seedno);
        break;
    case (-2):
        c_attach(bpart[count1].seedno, ans);
        break;
    default:
        c_attach(bpart[count1].seedno, bpart[ans].seedno);
        break;
}
break;
if (bpart[count1].seedno==-2) { cluster_sync(count1); } // this line is probably redundant
if (bpart[count1].seedno>=0) { followup(count1); }
}

// ******************************************************************************* end iteration

for (int sclu=0; sclu<NUM_PARTS; sclu++) { // eliminate multiple follow problem
    if (bpart[sclu].seedno==0) {
        boolean gotya=false;
        int ulcs=bpart[sclu].seedno;
        while (gotya==false) {
            if (bpart[ulcs].seedno!=-2) {
                p_attach(sclu, bpart[ulcs].seedno);
                ulcs=bpart[ulcs].seedno;
            } else { gotya=true; }
        }
    }
}
for (int sclu=0; sclu<NUM_PARTS; sclu++) { // update size and box boundary
    if (bpart[sclu].seedno==-2) {
        bpart[sclu].masscenter_x=bpart[sclu].px;   // initialize the mass center
        bpart[sclu].masscenter_y=bpart[sclu].py;
        bpart[sclu].pradius=(float)0.5;
        for (int col=0; col<NUM_PARTS; col++) {
            if (bpart[col].seedno==sclu) {
                bpart[sclu].seedsize++;
                bpart[sclu].masscenter_x+=bpart[col].px;
                bpart[sclu].masscenter_y+=bpart[col].py;
                if ( (bpart[col].seed_dx<0) && (Math.abs(bpart[col].seed_dx)>bpart[sclu].max_left) ) {
                    bpart[sclu].max_left=Math.abs(bpart[col].seed_dx);
                }
                if ( (bpart[col].seed_dx>0) && (bpart[sclu].max_right) ) { // don't forget the volume
                    bpart[sclu].max_right=(bpart[col].seed_dx+1);
                }
            }
            bpart[sclu].max_top=0;
            bpart[sclu].max_left=0;
            for (int col=0; col<NUM_PARTS; col++) {
                float temp=(float)Math.sqrt((double)(((float)bpart[col].px-
                bpart[sclu].masscenter_x)*((float)bpart[col].px-
                bpart[sclu].masscenter_x) +
                ((float)bpart[col].py-bpart[sclu].masscenter_y)*((float)bpart[col].py-
                bpart[sclu].masscenter_y) ));
                if (temp > bpart[sclu].pradius) { bpart[sclu].pradius=temp; }
            }
        }
    }
}
System.out.print(" ");
System.out.print(iter);
System.out.print(" ");

// put bar frame routine here
int acc;
for (int index=0; index<NUM_PARTS; index++) {
    acc=bpart[index].seedsize;
    Integer indexi= new Integer(index);
    Integer NUM_PARTSi=new Integer(NUM_PARTS);
    Integer acci=new Integer(acc);
    bfr.y[acc]=bfr.y[acc] + 1.0f/NUM_PARTSi.floatValue(); //
    //acci.floatValue()/NUM_PARTSi.floatValue());
}

bfr.draw();
bfr.clear();

// ----- draw particles

if (iter==NUM_ITERATION) {
    System.out.println("----- Radius vs Mass ----- ");
    for (count=0; count<NUM_PARTS; count++) {
        bpart[count].paint(offscreen);
        if (bpart[count].seedno==-2) { // calculate fractal dimension
            // System.out.println( Math.sqrt((double)((bpart[count].max_left+bpart[count].max_right)*(bpart[count].max_left+bpart[count].max_right)
            +(bpart[count].max_top+bpart[count].max_bottom)*(bpart[count].max_top+bpart[count].max_bottom)) )+" 
            //+bpart[count].seedsize);
            System.out.println( bpart[count].pradius+" *bpart[count].seedsize);
        }
    }
} else {
    int cluster_number=0;
    for (count=0; count<NUM_PARTS; count++) {
        if (bpart[count].seedno<0) { cluster_number++;}
        bpart[count].paint(offscreen);
    }

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System.out.println(" + (float)NUM_PARTS/(float)cluster_number);
}

/* // draw particles from v-image
for (count1=0; count1<v_width; count1++) {
    for (int count2=0; count2<v_height; count2++) {
        if (virtualimage[count1][count2]>=0) {
            offscreen.drawRect(count1*PART_SIZE, count2*PART_SIZE, PART_SIZE, PART_SIZE);
        }
    }
}
*/

gl.drawImage(offimage, 0, 0, this);

// put all "clear" routines here
for (int sclu=0; sclu<NUM_PARTS; sclu++) {
    hpart[sclu].seedsize=1;
}

gl.drawImage(offimage, 0, 0, this);
bfr.dispose();
beaker.dispose();

public void clickedAboutbtn() {
    // to do: put event handler code here.
}

public void clickedExitbtn() {
    if (bfr!=null) {bfr.dispose();}
if (beaker!=null) { beaker.dispose();}
MAGNETICALLY-SEEDED FILTRATION OF COLLOIDAL PARTICLES

A Thesis
Presented to
The Academic Faculty

by

Tung-yu Ying

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Environmental Engineering

Georgia Institute of Technology
December 1997
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Approved:

Sotira Yiacoumi

Costas Tsouris

Edwards S. K. Chian

Date Approved
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<th>Description</th>
</tr>
</thead>
<tbody>
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<td>$A$</td>
<td>Hamaker constant (J)</td>
</tr>
<tr>
<td>$a$</td>
<td>Wire radius (m)</td>
</tr>
<tr>
<td>$b$</td>
<td>Particle radius (m)</td>
</tr>
<tr>
<td>$b^*$</td>
<td>Relative mobility (s g$^{-1}$)</td>
</tr>
<tr>
<td>$C$</td>
<td>Number concentration of suspended particles</td>
</tr>
<tr>
<td>$C_{in}$</td>
<td>Influent concentration</td>
</tr>
<tr>
<td>$C_{out}$</td>
<td>Effluent concentration</td>
</tr>
<tr>
<td>$Cov$</td>
<td>Covariance</td>
</tr>
<tr>
<td>$C_s$</td>
<td>Saturation concentration (captured particle volume/bulk volume in the filter)</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>Relative diffusivity (m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>$D_\infty$</td>
<td>Diffusivity in the absence of interparticle forces (m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>$E_{ij,lm}$</td>
<td>Collision efficiency</td>
</tr>
<tr>
<td>$F_d$</td>
<td>Hydrodynamic drag force (N)</td>
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<td>$F_g$</td>
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<tr>
<td>$F_{t(net)}$</td>
<td>Tangential net force (N)</td>
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<tr>
<td>$f_a$</td>
<td>Integrated effect of the shear stress</td>
</tr>
<tr>
<td>$G$</td>
<td>Gravitational force parameter</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravitational acceleration (m s$^{-2}$)</td>
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<tr>
<td>$H$</td>
<td>Magnetic field strength (Am$^{-1}$)</td>
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<tr>
<td>$H_0$</td>
<td>Applied magnetic field strength (Am$^{-1}$)</td>
</tr>
<tr>
<td>$H_s$</td>
<td>Saturation magnetic field strength (Am$^{-1}$)</td>
</tr>
<tr>
<td>$K$</td>
<td>Dimensionless parameter ($=M_c/2H_0$, for $H_0&gt;H_s$: 1, for $H_0&lt;H_s$)</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant = 1.38x10$^{-23}$ VCK$^{-1}$</td>
</tr>
</tbody>
</table>
\( L \)  
Filter length (m)

\( M \)  
Magnetization (Am\(^{-1}\))

\( M_s \)  
Saturation magnetization (Am\(^{-1}\))

\( N \)  
Number of particles per unit time

\( N_{CI} \)  
Total number of initial magnetic susceptibility classes

\( N_s \)  
Total number of size classes

\( n_{ij} \)  
Number of particles of size \( i \) and magnetic susceptibility \( j \) (class \( ij \))

\( R \)  
Normalized radius

\( R_c \)  
Critical Radius

\( \mathcal{R} \)  
Reynolds number

\( r \)  
Center-to-center particle separation (m)

\( r_b \)  
Loading radius of build-up (m)

\( r_i \)  
Radius of particle \( i \) (m)

\( r_{xy} \)  
Correlation coefficient

\( T \)  
Temperature (K)

\( t \)  
time (s)

\( t_s \)  
saturation time (s)

\( t_{total} \)  
time for the filter complete saturated (s)

\( V \)  
Volume of a particle (m\(^3\))

\( V_0 \)  
Superficial velocity (m s\(^{-1}\))

\( V_A \)  
Particle interaction potential (CV)

\( V_L \)  
Loading volume (m\(^3\))

\( V_{el} \)  
Electrostatic potential (CV)

\( V_m \)  
Magnetic velocity (m s\(^{-1}\))

\( V_{mag} \)  
Magnetic potential (CV)

\( V_r \)  
Radial superficial velocity (m s\(^{-1}\))

\( V_s \)  
Saturation velocity (m s\(^{-1}\))

\( V_{vdw} \)  
van der Waals potential (CV)

\( V_o \)  
Tangential superficial velocity ms\(^{-1}\))

\( x_s \)  
Active length of the filter matrix (m)

\( \beta \)  
Angle between the gravitational force and horizontal axis

\( \beta_{ij} \)  
the particle collision frequency

\( \varepsilon \)  
Filter porosity (%)
Dielectric constant = $89 \times 10^{-10} \text{ CV}^{-1} \text{ m}^{-1}$ for water

$\phi$ Angle between the vertical axis and $r$

$\gamma$ Angle between the hydrodynamic drag force and horizontal axis

$\eta$ Dynamic viscosity (Kgm$^{-1}$s$^{-1}$)

$\eta_x$ Mean of random variable $X$

$\eta_y$ Mean of random variable $Y$

$\lambda$ Filter coefficient (m$^{-1}$)

$\lambda_0$ $r_{i}-r_{j}$, shortest distance from the surface of particle $i$ and $j$ (m)

$\kappa$ Inverse Debye-Huckel length (m)

$\mu_0$ Permeability of free space (Hm$^{-1}$)

$\nu$ Kinematic viscosity (m$^2$s$^{-1}$)

$\rho_f$ Density of fluid (Kgm$^{-3}$)

$\rho_p$ Density of a particle (Kgm$^{-3}$)

$\sigma$ Porosity of the loading volume (%)

$\sigma_x$ Standard deviation of random variable $X$

$\sigma_y$ Standard deviation of random variable $Y$

$\tau_0$ Shear stress at the wall (m$^{-1}$Kgs$^{-2}$)

$\chi_p$ Magnetic susceptibility of a particle

$\psi_{0i}$ Surface potential of particle $i$ (V)
SUMMARY

High-Gradient Magnetic Filtration (HGMF) has been used in various industrial processes, such as separation of heavy metals from wastewater, and recovery of hematite and chromite fines and ultra-fines. HGMF, however, is currently limited to remove only ferromagnetic or paramagnetic particles from waste streams. Magnetically-seeded filtration is a process in which magnetic particles are attached to waste particles to form flocs that can be easily removed by a high-gradient magnetic filter. Magnetically-seeded separation largely enhances the ability of HGMF to remove weakly magnetic or non-magnetic particles, thus increasing the applicability of HGMF in solid/liquid separations. This process can be used in several aspects of wastewater treatment, such as: (1) removal of solids, particularly those in the colloidal size range that are difficult to remove by conventional means, (2) removal of contaminants by precipitation processes, and (3) removal of contaminants by sorption processes. Since magnetically-seeded filtration has been shown to be a promising treatment process in environmental engineering, it is necessary to establish a theoretical analysis in order to optimize the geometry and select the right operating conditions for the separation of particles from a given suspension.

In this study, the effects of various parameters affecting magnetically-seeded filtration are theoretically and experimentally investigated. The parameters studied are filter geometry including packing material and density; particle properties including size,
concentration, and magnetic susceptibility; and operating conditions including magnetic field strength and suspension flow rate. A modeling approach, that includes trajectory analysis, a particle build-up model, a breakthrough model, and a bivariate population balance model, has been developed to predict the removal efficiency and breakthrough curves of high-gradient magnetic filtration. A good agreement between modeling and experiments is obtained in the present study.

The model developed in this study demonstrates a new approach to predict the performance of magnetically-seeded filtration without using empirical coefficients or fitting parameters. Given the characteristics of target particles, the optimum operating conditions, such as magnetic-field strength, flow rate, and filter geometry, can be calculated by the model. Compared to other models in which experimental results are needed to calculate the filter coefficient, this model will simplify the design of filtration processes.
CHAPTER I

INTRODUCTION

1.1 Background

High-Gradient Magnetic Separation (HGMS) has been introduced as a recovery and pollution control process for many environmental and industrial problems. The basic principle of magnetic separation is to remove magnetizable particles from a fluid stream by using a ferromagnetic matrix in a magnetic field. The development of HGMS began only in the sixties and the applicability of magnetic separation was extended to weakly paramagnetic and even diamagnetic particles of micrometer size after the cyclic and continuous magnetic separators were developed (Svoboda, 1987). Currently, the applications of HGMS in industrial wastewater treatment include filtration of nuclear reactor coolant (Heitmann, 1979), removal of phosphate from water (Shaikh and Dixit, 1992), recovery of hematite and chromite fines and ultra-fines (Wang and Forssberg, 1994), separation of dissolved heavy metals from wastewater (Terashima et al., 1986), and removal of oil and suspended solids from municipal sewage. In biotechnology applications, HGMS has been used to remove algae (Bitton et al., 1975), yeast (Dauer and Dunlop, 1991), and bacteria (Bitton and Mitchell, 1974) from wastewater.

Several researchers have investigated the theoretical aspects of magnetic separation from both microscopic and macroscopic points of view. The microscopic theories are
aimed at the mechanisms of particle capture and the conditions under which the capture may be achieved. The macroscopic studies focus on the description of the separation phenomena, the prediction of filter performance, and its dynamic behavior. However, most branches of magnetic separation are still highly empirical and a systematic integration of different models to describe the process of magnetic filtration as a whole has not been attempted so far. The primary objective of the present study is to present an approach to predict the removal performance of HGMS by combining single element and phenomenological models and without the use of experimental data.

I.2 Literature Review

The interactions between particles and filter collectors under various conditions are investigated in this study to better understand the microscopic phenomena of magnetic separation. To simplify the inherent complexities in these systems, the interaction between a single particle and a single matrix element is considered. One of the early and important models was developed by Watson (1973; 1975). He formulated trajectory equations in which inertial and gravitational force were neglected and a potential flow was assumed to describe the capture of a particle by a ferromagnetic wire in a uniform magnetic field. Watson (1973) also derived macroscopic equations to predict the filter performance for a clean wire.

Schewe et al. (1980) and Cumming et al. (1976) compared the trajectory models under potential and laminar flow conditions, and proved that at low Reynolds number,
laminar flow theory provides better description of flow conditions near a wire. A similar investigation using laminar flow model, but under different arrangements between the directions of flow velocity and magnetic field with respect to the wire, was examined by Birss et al. (1978). They found that under the axial orientation of wires which were orderly packed in a filter, the laminar flow theory gives good predictions of filter efficiency while a potential flow model usually overestimates the filter efficiency. Lawson et al. (1977) extended the trajectory model by including inertial and gravitational forces to fit a broad range of Stokes number and gave a more accurate description of particle trajectories, especially near the wire.

Trajectory models of a single particle captured by a ferromagnetic spherical collector have also been studied by many authors (Friedlaender et al., 1981; Moyer et al., 1984; Scott and Brumfield, 1988). In these studies, a better fit to experimental results was found by applying laminar flow models. Ebner et al. (1997) developed a model for nanolevel high gradient magnetic adsorption in which antiferromagnetic magnetite spheres were used as collectors. From modeling results, they found that small antiferromagnetic collectors with large curvatures produce magnetic fields with higher gradients and higher separation efficiency than wire collectors. By incorporating the distribution of particle size into the filter performance equation, Dauer and Dunlop (1991) obtained a good prediction on yeast removal by spherical collectors under high flow rate. The removal efficiency reported by Dauer and Dunlop was applicable only for clean collectors. A theoretical model that extends the single-particle, single-collector model
was developed by Reger et al. (1985) to describe the separation efficiency of weakly magnetic particles passing through an infinite array of ferromagnetic wires in a high-gradient magnetic field. The particle build-up on the surface of the wires was also described by this model.

As noted above, most trajectory modeling studies that predict the critical radius of particles or separation performance are limited to clean collectors. A model describing the buildup configuration and fully loaded conditions of the wire was investigated by Luborsky and Drummond (1976). They formulated the hydrodynamic force by considering the boundary layer thickness of a wire and calculated the critical angle for each layer of particles. They also obtained the loading volume of particles retained by each wire. Similarly to the work by Luborsky and Drummond (1976), Nesset and Finch (1979; 1981) and Nesset et al. (1980) calculated the boundary layer thickness by employing the Blasius solution. A good prediction was found at high Reynolds number under upstream capture. A modified model was examined under a downstream-capture system by Hollingwourh and Finch (1982) who claimed that for a single-wire longitudinal configuration the loading equation is not applied. Cowen et al. (1976) investigated the rate equation of particle buildup and obtained good predictions under various operating conditions. This model, however, is limited to predicting uniform size paramagnetic particles. Furthermore, it depends on empirical parameters.

The above trajectory and build-up models available in the literature are generally applied to paramagnetic particles. In real systems, however, many particles are weakly
magnetic or non-magnetic. For these cases, a magnetic-seeding technique can be applied, as described in this work, which was motivated by the work of Tsouris et al. (1995). These investigators developed a bivariate population-balance model to predict both particle size and magnetic susceptibility distributions during heterogeneous magnetic flocculation under Brownian motion. Besides external-field forces, they also considered the interparticle forces which include van der Waals, double-layer, and magnetic-dipole forces.

In magnetic filtration, of colloidal particles (<< 1 µm), the interparticle forces and particle diffusion become significant. The effect of diffusion of ultra-fine particles in a magnetic filter has been investigated by various authors (Gerber et al., 1983; Takayasu et al., 1983; Reijers et al., 1986; Glew and Parker, 1984). Gerber et al. (1983) have found that, in this situation, the capture process is better described by a continuity equation model in which the diffusion term is included. Similarly, Glew and Parker (1984) and Reijers et al. (1986) considered interparticle interactions in the capture process. It has been suggested by Svoboda and Ross (1989) that the efficiency of particle capture can be determined by the combination of the magnetic dipole force and surface forces between the collector and the particles and between the particles themselves, especially for sub-micron size particles. This point was also made by Collan et al. (1978) who examined the magnetic separation performance from a macroscopic viewpoint. They developed a mathematical model for the separation process of a general absorption filter. In the
model of Collan et al., however, experimental information is needed for the estimation of some of the model parameters.

1.3 Scope of this Study

In this work, the effects of solution parameters, system geometry, and operating conditions on the filtration performance of high-gradient magnetic separation are investigated. In addition, a model is developed to predict the filtration process and performance without using empirical coefficients. The experiments were conducted with well-characterized, uniform polystyrene microspheres. The polystyrene particles provide a model system for more controlled investigation of the effects of process variables and for verification of the model development. The experiments were of three types:

1) magnetic-seeding, shear-flow flocculation and magnetic filtration,
2) magnetic-seeding, Brownian flocculation and magnetic filtration,
3) breakthrough of magnetic filtration.

In the modeling work, four models were investigated:

1) single-particle/single-collector trajectory model,
2) particle build-up model,
3) breakthrough model,
4) bivariate model (heterogeneous flocculation).

A description of experimental and modeling activities in this work is shown in Figure 1. The bivariate model provides the size and magnetic susceptibility distributions
of particles in the suspension. The removal efficiency of clean wires and the saturation
centration of the filter are calculated for each class of specific size and magnetic
susceptibility by using trajectory and build-up models, respectively. Then, the filtration
breakthrough curve can be predicted by the breakthrough model. A detailed description
of the model formulation and experimental techniques is discussed in Chapters II and III.
The materials and methods used in the experiments are shown in Chapter II. Chapter III
presents the theory of magnetic filtration. Results of experiments and modeling are
discussed in Chapter IV and also the comparisons between modeling and experiments.
Conclusions of this study are given in Chapter V.
CHAPTER II

MATERIALS AND METHODS

The experiments carried out in this work are classified into three categories: (1) magnetic-seeding, shear flocculation, and magnetic filtration; (2) breakthrough of magnetic filtration; and (3) magnetic-seeding, Brownian flocculation, and magnetic filtration. In the first part, experiments were conducted under different solution conditions such as pH, particle size, zeta potential of particles, and ionic strength, and different operating conditions such as magnetic-field strength, flow rate, and agitation speed. The effects of these parameters on the performance of magnetic-seeding, shear flocculation, and magnetic filtration were studied. A detailed discussion of magnetic-seeding shear-flocculation experiments are presented elsewhere (Chin, 1997). Experiments conducted in the second and third parts of this work, as described above, are used to study the effect of operating conditions on the breakthrough curve of magnetic filtration. The results of these experiments were compared to modeling results.

II.1 Particle Characterization Measurements

Particles were characterized in terms of their size, zeta potential, and magnetic susceptibility. The size distribution of particles was measured by the Coulter LS 130
instrument (Coulter Corporation, Hialeah, FL) which can measure particle sizes ranging from 0.429 µm to 1000 µm.

Zeta potential measurements were obtained by using a Lazer Zee Meter, model 501 (Pen Kem, Inc., Bedford Hills, NY) for all particles. For magnetic susceptibility measurements, a magnetic susceptibility balance, model MSB-AUTO (Johnson Matthey Fabricated Equipment, Wayne, PA) was used.

II.2 Magnetic-Seeding Shear-Flocculation and Magnetic Filtration

Polystyrene latex and seeding polystyrene latex (containing 40% magnetite by weight) were used to study the effects of magnetic-seeding on the separation of well-characterized synthetic particles. Both types of particles were supplied by Bangs Laboratory, Inc. (Carmel, IN). Some relevant properties of these particles are listed in Table I. Analytical grade sodium chloride was the background electrolyte used for the adjustment of ionic strength. The solution pH was adjusted using NaOH (0.1 M) and HCl (0.1 M) solutions. Deionized water (electrical resistance >10MΩ) was used in the preparation of solutions and particle suspensions. The particles, as obtained from Bangs Laboratory, were in solutions that contained a fraction of solids. To obtain a desired concentration of these particles, the solution was weighed to select the proper amount of solids and then diluted in a volumetric flask to adjust the volume. The particles were initially prepared in high concentration stock solutions, so that dilution could be made to various concentrations for characterization and experimentation.
A general schematic of the magnetic-seeding separation process is shown in Figure 2. Turbulent-shear flocculation was carried out in a standard stirred tank of 100 mm diameter, 142.2 mm height, and equipped with four baffles, each 10 mm wide. The initial volume of the suspension used in each experiment was 600 mL. The mixture was stirred by a 6-blade impeller, 50 mm in diameter, with adjustable agitation speed. The agitation was produced by a Stir-pak motor, model 50002-40 (Cole-Parmer Instrument Co. Niles, IL). The filtration process was started after 5 or 10 minutes, to allow for flocculation of polystyrene particles with seeding polystyrene (paramagnetic) particles. The interval between flocculation and filtration is defined as “dead time.” The mixture from the stirred tank was pumped through 1/16-in. ID, 1/8-in. OD tubing by a Master Flex pump (Cole-Parmer Instrument Co. Chicago, IL). The filter used in these experiments was a 10-mm ID and 105-mm length glass tube of total volume 9.6 mL (including the space between fittings). Nickel wire of diameter 62.5 µm was cut into 5-mm pieces and randomly packed in the filter. The packing fraction was varied between 1% and 14% and the filter length was 100 mm. The filter was held in an aluminum housing and situated at the center of a bipolar magnet (Applied Magnetics Laboratory Inc., Baltimore, MD). The minimum gap between the two poles was 2 in., but a ferromagnetic disc was used to decrease it further to 0.75 in. in order to hold the filter aluminum housing firmly. A 15-mL sample from the outflow was taken periodically for effluent concentration analysis. The concentration was analyzed by a light scattering setup using a correlator (Model 1096, Langley Ford Instruments, Amherst, MA).
II.3 Breakthrough Experiments of Magnetic Filtration

The breakthrough experiments were conducted using only paramagnetic particles in order to simplify the system. Two types of paramagnetic particles were used: (1) seeding polystyrene latex; and (2) black iron oxide (magnetite) seed particles. Black iron oxide seed particles were supplied by Polysciences, Inc. (Warrington, PA) in powder form. Some properties of these two type paramagnetic particles are also listed in Table I. In order to obtain a desired concentration, the particles were weighed and suspended using the method suggested by Lee et al. (1996). The filter material and method of preparation were the same as described in the Section II.2, and the wire packing fraction was 5% (about 0.04 mL). The zeta potential of these paramagnetic particles was high (> 50 mV) under high pH (> 10) and low ionic strength (< 0.001M) conditions. The suspension was prepared under these conditions in order to prevent the particles from flocculation. Thus, the flocculation process was not included in these experiments. The other conditions were the same as described in Section II.2. The solution was pumped through a 5-mm ID tubing into the filter and effluent samples were collected periodically for concentration analysis.

II.4 Magnetic-Seeding Brownian Flocculation and Magnetic Filtration

Polystyrene latex and seeding polystyrene latex particles were used to study the effects of magnetic-seeding processes on the breakthrough of magnetic filtration. To simplify the complicated situation of a wide range of particle size and magnetic
susceptibility distributions resulting from turbulent-shear flocculation, Brownian flocculation was investigated. Equipment and operating procedures were similar to shear flocculation experiments, except the flocculation processes. Both polystyrene latex and seeding polystyrene latex solutions were prepared under high pH (>11) condition. After mixing them together, the solution pH was adjusted to around 3 at which the surface charge of particles is about zero for Brownian flocculation. After a period of flocculation, the solution pH was adjusted back to high pH (>10) to stop the flocculation process and then the solution was pumped through a 5-mm ID tubing to the filter. The filter was prepared in the same way as described in the Section II.2. Samples collected from the influent solution were analyzed by a light scattering instrument (Coulter LS 130, Langley Ford Instruments, Amherst, MA) for particle size distribution. Also, samples were collected from the effluent solution for concentration analysis using light scattering intensity measurements.
CHAPTER III

THEORY OF MAGNETICALLY-SEEDING FILTRATION OF COLLOIDAL PARTICLES

Various models of magnetic separation have been formulated based on the interaction between a particle and a collector. These models are used to predict the filtration efficiency of the collector and investigate the effects of various parameters on the performance of magnetic filtration. A limitation of these models, however, is that to a large extent they depend on empirical coefficients or parameters and therefore constrain themselves to specific circumstances.

In this chapter, a systematic approach describing particle captured by a single-wire, particle loading on a single-wire, and breakthrough of particles from the magnetic filter is investigated. Finally, a mathematical model combined with the bivariate population-balance equation is introduced to predict the magnetically seeded separation process without the use of fitting parameters or empirical coefficients.
III.1 Theory of Single-Particle/Single-Wire Trajectory Model

III.1.1 Limiting Trajectory and Geometric Configurations

Trajectories of a particle approaching the surface of a single-wire in a magnetic field have been investigated as a fundamental study for understanding the interaction between a particle and a collector. The exact path that divides the approaching particle trajectories into those leading in particle capture by the collector and those passing by the collector is called the limiting trajectory. As shown in Fig. 3, the distance between the limiting trajectory and the axis is the critical radius \((R_c)\).

In the present study, particle diffusion and surface forces are not significant unless particle size is ultra-fine \((<<1 \, \mu m)\) and, thus, they are not included in modeling considerations. The trajectory equation is then determined by the force balance equation which includes inertial, gravitational, magnetic, and hydrodynamic drag forces.

Three possible geometric configurations between the directions of particle flow and magnetic field with respect to the wire are illustrated in Fig. 4. In Fig. 4, the wire is placed along the z-axis and a uniform magnetic field \((H_0)\) which is always assumed orthogonal to the wire if applied in the x direction. The first arrangement (longitudinal orientation, L) is when the flow velocity is parallel to the external magnetic field, the second one (transverse orientation, T) is when the flow velocity is perpendicular to the magnetic field, and the third one (axial orientation, A) is when the flow velocity is parallel to the wire axis. A general coordinate system of a particle-wire interaction is
shown in Fig. 5 where \( a \) is the wire radius, \( b \) is the particle radius, and \( V_0 \) is the flow velocity (Svoboda, 1987, p. 239-240).

III.1.2 Magnetic Force

The magnetic force, \( \vec{F}_m \), applied on a small spherical paramagnetic particle placed in a magnetic field is given by (Svoboda, 1987, p. 4):

\[
\vec{F}_m = \frac{\mu_0 \chi_p V}{1 + \frac{\chi_p}{3}} (\vec{H} \nabla) \vec{H} \tag{1}
\]

where \( \mu_0 = 4\pi \times 10^{-7} \text{ Hm}^{-1} \) is the permeability of free space, \( \chi_p \) is volume magnetic susceptibility of a particle, \( \vec{H} \) is the magnetic field, and \( V \) is the particle volume. If \( \chi_p \ll 1 \), eq. [1] can be simplified as follows

\[
\vec{F}_m = \frac{1}{2} \mu_0 \chi_p V \nabla (H^2) \tag{2}
\]

The magnetic field strength \( H \) that consists of the external magnetic field strength \( (H_0) \) and the magnetization of the wire \( (M) \) is given by

\[
H = H_0 + H_0 K \frac{a^2}{r^2} \tag{3}
\]

where, for \( H_0 < H_s \), \( K = 1 \), for \( H_0 > H_s \), \( K = M_s/2H_0 \), \( a \) is the radius of the wire, and \( r \) is the distance from the center of the wire to the center of the particle. Generally, the
magnetization increases as the external magnetic field strength increases until the external field is larger than the wire saturation value $H_s$, in which case the magnetization ($M$) of the wire will be constant and equal to the saturation magnetization ($M_s$). The first term in eq. [3] is the external magnetic field strength $H_0$ and the second term is the magnetization of the wire whose saturation value is $H_s$. Combining eqs. [2] and [3], the components of magnetic force, $F_{mr}$ and $F_{m\theta}$, in polar coordinates, $r$, $\theta$, are obtained as

$$F_{mr} = -\frac{4\pi\mu_0\chi_pMa^2b^3}{3r^3}\left(\frac{Ma^2}{2r^2} + H_0\cos2\theta\right)$$  \[4a\]

$$F_{m\theta} = -\frac{4\pi\mu_0\chi_pMa^2b^3}{3r^3}H_0\sin2\theta$$  \[4b\]

III.1.3 Hydrodynamic Drag Force

The hydrodynamic drag force ($F_d$) acting on a moving particle can be expressed by Stoke's equation. The components of this drag force, $F_{dr}$ and $F_{d\theta}$, can be written as (Svoboda, 1987, p. 247-248)

$$F_{dr} = 6\pi\eta b\left(V_r - \frac{dr}{dt}\right)$$  \[5a\]

$$F_{d\theta} = 6\pi\eta b\left(V_\theta - r \frac{d\theta}{dt}\right)$$  \[5b\]
where $\eta$ is the fluid dynamic viscosity and $dr/dt$ and $rd\theta/dt$ are the components of fluid velocity at position $r$. $V_r$, $V_\theta$ are the components of particle velocity given as follows, by assuming that the flow is laminar:

\[
V_r = V_0 \frac{\ln \left( \frac{r}{a} \right) - 0.5 \left[ 1 - \left( \frac{a}{r} \right)^2 \right]}{2.002 - \ln \mathcal{R}} \cos(\theta - \gamma) \quad [6a]
\]

\[
V_\theta = -V_0 \frac{\ln \left( \frac{r}{a} \right) + 0.5 \left[ 1 - \left( \frac{a}{r} \right)^2 \right]}{2.002 - \ln \mathcal{R}} \sin(\theta - \gamma) \quad [6b]
\]

where $\mathcal{R}$ is the Reynolds number given by

\[
\mathcal{R} = \frac{2V_0 \rho_f a}{\eta} \quad [7]
\]

**III.1.4 Gravitational and Inertial Forces**

The components of the gravitational force ($\vec{F}_g$) in polar coordinates, $F_{gr}$ and $F_{g\theta}$, can be written as (Svoboda, 1987, p. 248)

\[
F_{gr} = \frac{4\pi b^3}{3} \left( \rho_p - \rho_f \right) g \cos(\theta - \beta) \quad [8a]
\]
where \( g \) is the gravitational acceleration and \( \rho_p \) and \( \rho_f \) are the particle and fluid densities, respectively.

The components of the inertial force \( (\vec{F}_t) \) in polar coordinates, \( F_r \) and \( F_\theta \), can be written as (Svoboda, 1987, p. 248)

\[
F_r = \frac{4\pi b^3 \rho_p}{3} \left[ \frac{d^2 r}{dt^2} - r \left( \frac{d\theta}{dt} \right)^2 \right] \tag{9a}
\]

\[
F_\theta = \frac{4\pi b^3 \rho_p}{3} \left[ r \frac{d^2 \theta}{dt^2} + 2 \frac{dr}{dt} \frac{d\theta}{dt} \right] \tag{9b}
\]

### III.1.5 Trajectory Equation

The particle motion in a magnetic separator can be described by the force balance equation as

\[
\vec{F}_i = \vec{F}_d + \vec{F}_m + \vec{F}_g \tag{10}
\]
For low Reynolds numbers and laminar flows, such as the ones occurring in the magnetic filter, the inertial force is much smaller than the other forces and can be neglected. Thus, the radial and azimuthal components of the force balance equation can be rewritten as

\[
\frac{dR}{dt} = G \cos(\theta - \beta) + \frac{V_r}{a} - \frac{V_m}{a} \left( \frac{M}{2H_0} \frac{1}{R^5} + \frac{\cos 2\theta}{R^3} \right) \tag{11a}
\]

\[
R \frac{d\theta}{dt} = -G \sin(\theta - \beta) + \frac{V_\theta}{a} - \frac{V_m}{a} \frac{\sin 2\theta}{R^3} \tag{11b}
\]

where \( R = r/a \) and

\[
G = \frac{2b^2 (\rho_p - \rho_r)}{9\eta a} g \tag{12a}
\]

\[
V_m = \frac{2b^2 \mu_0 \chi_p MH_0}{9\eta a} \tag{12b}
\]

By combining eqs. [11a] and [11b] the time-independent trajectory equation can be obtained as

\[
\frac{dR}{d\theta} = R \frac{G \cos(\theta - \beta) + \frac{V_r}{a} - \frac{V_m}{a} \left( \frac{M}{2H_0} \frac{1}{R^5} + \frac{\cos 2\theta}{R^3} \right)}{-G \sin(\theta - \beta) + \frac{V_\theta}{a} - \frac{V_m}{a} \frac{\sin 2\theta}{R^3}} \tag{13a}
\]
It is found that, if a particle is small enough, the gravitational force is insignificant, and


can be neglected. By substituting eqs. [6a] and [6b] into eq. [13a], eq. [13a] can be

rewritten as

\[
\frac{dR}{d\theta} = R \frac{\ln(R) - 0.5\left(1 - R^{-2}\right) \cos(\theta - \gamma) - \frac{V_m}{V_0} \left(\frac{M}{2H_0} \frac{I}{R^5} + \frac{\cos 2\theta}{R^3}\right)}{2.002 - \ln R} 
\]

Equation [13b] becomes a function of \(V_m/V_0\) and \(M/2H_0\). From eq. [13b], it is seen that

\(M/2H_0\) varies as \(R^{-5}\), which means that this term is only important when a particle is near

the wire. Therefore, the capture efficiency is mainly determined by \(V_m/V_0\), and not by \(V_m\)

or \(V_0\) separately. Solving this trajectory equation by numerical methods, one can obtain

the limiting trajectory and the critical radius which determine whether a particle will be

captured by a wire collector or not.

III.1.6 Removal Efficiency for a Clean Filter

Consider a high gradient magnetic separator matrix of length \(L\), packed randomly

with wire and having packed fraction \((1-\varepsilon)\). Then, the length of the wire in a differential

section \(dx\) of the filter per unit cross section area of the wire is \((1-\varepsilon)dx/\pi a^2\). Due to the

random nature of the matrix, approximately two-thirds of the wire are considered
effective for particle capture (the other one-third is assumed to be distributed along the
direction of the field). Thus, the available cross section area for capture is \(4R_c a/3\) and
the effective area is $4(1 - \varepsilon)R_c \, dx / 3\pi a$. The accumulation rate of particles onto the matrix over $dx$ is then given as

$$\frac{\partial N}{\partial x} = -\left[\frac{4(1 - \varepsilon)R_c}{3\pi a}\right]N$$  \[14\]

where $N$ is the number of particles per unit volume. By solving eq. [14], the removal efficiency for a clean filter can be obtained as

$$\text{Removal efficiency} = 1 - \frac{N_{\text{out}}}{N_{\text{in}}} = 1 - \exp \left[\frac{-4(1 - \varepsilon)LR_c}{3\pi a}\right]$$  \[15\]

III.2 Theory of Particle Build-Up Model

The dynamic behavior of a small paramagnetic particle approaching a single ferromagnetic wire in a magnetic field has been analyzed by a particle trajectory method in Section III.1. The trajectory model, however, is limited for a clean wire. Once particles are deposited on the surface of matrix elements or onto particles already deposited, changes in the surface characteristics of the collector will affect subsequent capture of particles.
To investigate the dynamic behavior of particle buildup, it is necessary to examine forces acting on the particles first. The forces that are mainly responsible for the particle retained on the matrix are magnetic and hydrodynamic forces. Figure 6 shows the force components acting on a particle on a wire surface (Nesset and Finch, 1979). For a particle to remain attached on a wire, the net forces in both the radial and tangential directions should be negative. Equations [16a] and [16b] give the expressions of force components acting in radial and tangential directions,

\[
F_{r(\text{net})} = F_{mr} + F_{gr} \tag{16a}
\]

\[
F_{\phi(\text{net})} = F_{m\phi} + F_d \tag{16b}
\]

where \(F_{r(\text{net})}\), \(F_{mr}\), and \(F_{gr}\) are net, magnetic, and gravitational forces in the radial direction, respectively. \(F_{\phi(\text{net})}\), \(F_{m\phi}\), \(F_d\) are net, magnetic, and drag forces in the tangential direction, respectively. The magnetic and gravitational forces are given by eqs. [4a], [4b], and eqs. [8a], [8b], respectively. The fluid drag force that is acting on the surface of a spherical particle can be expressed by (Nesset and Finch, 1979)

\[
F_d = f_a 4\pi b^2 \tau_0 \tag{17}
\]
where $f_a$ represents the integrated effect of shear stress $\tau \theta$ acting over the upper half of the sphere only, and if $\tau \theta$ is assumed constant then $f_a$ is equal to $\pi/8$. The value of shear stress ($\tau \theta$) can be determined by the form of Blasius series

$$\tau_\theta = \rho_f \sqrt{\frac{V_0^3 \nu}{8}} (9.861\phi - 3.863\phi^3 - 0.061\phi^7...)[18]$$

where $\nu$ is the kinematic viscosity and $\phi$ is given in radians.

As illustrated in Fig. 7 (Nesset and Finch, 1979), the region of particle attraction about the wire can be determined by solving eqs. $[16a]$ and $[16b]$ for the conditions $F_r = 0$ and $F_\phi = 0$. Assuming that the particles are small enough that the gravitational force can be ignored, the build-up radius can be found by a force balance in azimuthal direction:

$$r_b = \left( \frac{\mu_0 \chi_p Mba^2 H_0 \sin(2\theta)}{3f_a \rho_f V_0^{1.5} \nu^{0.5} 0.125^{0.5} B(\phi)} \right)^{0.4}[19]$$

where $B(\phi)$ represents the Blasius series. The volume of particle build-up per unit volume of a wire, $V_L$, can then be obtained

$$V_L = \frac{\sigma}{4} \left[ \left( \frac{r_b}{a} \right)^2 - 1 \right][20]$$
where $\sigma$ is the porosity of the loading volume. The filter saturation concentration ($C_s$), defined as the retained particle mass per unit bulk volume in the filter, is expressed as

$$C_s = V_L \times \text{effective wire volume} / \text{bulk volume in the filter} \quad [21]$$

### III.3 Breakthrough Model

In contrast to the trajectory and particle build-up models in which the behavior between a single particle and a single wire is studied, the breakthrough model is developed to investigate the distribution of particles in a filter.

Considering particles traveling through a filter as illustrated in Fig. 8, one can obtain the mass balance of particles entering and leaving a differential element $dx$ by a macroscopic conservation equation and a rate equation as follows (Svoboda, 1987, p. 278)

$$\frac{\partial N(x,t)}{\partial t} = V_0 \frac{\partial C(x,t)}{\partial x} \quad [22]$$

and

$$-\left( \frac{\partial C}{\partial x} \right) = \lambda C \quad [23]$$
where $N(x, t)$ is the number of captured particles between $x$ and $x+dx$ at time $t$, $C(x, t)$ is the number of suspended particles at point $x$, $V_0$ is the superficial velocity of a suspension, $L$ is the filter length, and $\lambda$ is the filter coefficient with dimensions of reciprocal length, $\lambda=1/l$, where $l$ is the characteristic filtration length of the matrix material.

The solution of the rate equation (eq. [23]) can be written as

$$\frac{C(x)}{C_{in}} = \exp(-\lambda x)$$  \hspace{1cm} [24a]$$

$$\frac{C_{out}}{C_{in}} = \exp(-\lambda L)$$  \hspace{1cm} [24b]$$

where $C_{in}$ and $C_{out}$ are the influent and effluent concentrations. From eq. [24b], it is obvious that $\exp(-\lambda L) \ll 1$ (or $L >> l$) for an efficient filtration to be achieved.

During the filtration processes, particles are continuously captured onto the collector surface from the suspension. The rate of trapped particles can then be written as

$$\frac{dN(x, t)}{dt} = V_0 \lambda C(x, t)$$  \hspace{1cm} [25]$$

If we assume that the collectors were clean at time $t = 0$, then
\[ N(x,t) = N(0,t) \exp(-\lambda x) \]  

where \( N(0,t) \) is defined as the concentration \( N(x,t) \) at point \( x = 0 \). If \( \lambda \) is assumed to be constant and greater than zero before \( N(0,t) \) reaches the saturation concentration \( (C_s) \) of the matrix material, the saturation time is obtained as

\[ t_s = \frac{C_s}{C_{in} \lambda V_0} \]  

Once the front end of the filter has become saturated, both \( C(x, t_s) \) and \( N(x, t_s) \) decrease exponentially with position \( x \) from the inlet to the outlet end of the filter. Also, the active length of the matrix decreases as a function of time (Collan et al., 1978),

\[ x_s(t) = \left( \frac{C_{in}}{C_s} \right) V_s t \]  

where the term \( \frac{C_{in}}{C_s} V_0 \) is defined as the saturation velocity \( (V_s) \) and \( x_s \) is the saturated length of the matrix. The concentration profiles \( C(x, t) \) and \( N(x, t) \) can be written as

\[ C(x,t) = C_{in} \exp\left[(x_s - x)\lambda\right] \]  

and

\[ N(x,t) = N(0,t) \exp(-\lambda x) \]
\[ N(x,t) = C_s \exp[(x_s - x)\lambda] \]  \hspace{1cm} [29b]

Considering the total length \( L \) of a filter, one can express the breakthrough curve by the effluent concentration as a function of time,

\[ C_{out}(t) = C_{in} \exp(-\lambda L) \quad \text{for} \quad t < t_s \]  \hspace{1cm} [30a]

and

\[ C_{out}(t) = C_{in} \exp\left[\left(V_0 t - L - t\right)\lambda\right] \quad \text{for} \quad t_{total} > t > t_s \]  \hspace{1cm} [30b]

As assumed above, the filter coefficient \( \lambda \) is constant until \( t > t_s \), so the effluent concentration remains constant before the filter becomes saturated. After the front end of the matrix becomes saturated, the output concentration increases until the filter reaches full saturation at time \( t_{total} = t_s + \left(L/V_s\right) \).

**III.4 Magnetically-Seeded Separation**

The microscopic or macroscopic models mentioned in the previous sections were studied for uniform particles in terms of their magnetic susceptibility. However, in real systems of magnetic-seeding processes, where seeding magnetic particles are added to flocculate with non-magnetic particles and form aggregates of significant magnetic susceptibility, particles and flocs have varying sizes and magnetic susceptibilities. The
bivariate population-balance (PB) equation (Tsouris et al., 1995) is able to give the size and magnetic susceptibility distribution of particles in a suspension. In order to enhance the applicability of the magnetic filtration model, which has been described in Section III.3, to more complex conditions, it is necessary to combine it with the bivariate PB equation.

The basic concept of the magnetic-seeding process is to have weakly magnetic or non-magnetic particles flocculate with paramagnetic particles to form paramagnetic floes and then remove those floes from suspensions by using magnetic filtration. In the present work, a Brownian flocculation batch system is studied and it is assumed that the particles and floes are spherical. The bivariate PB equation for such a system is given by (Tsouris et al., 1995)

\[
\frac{dn_{ij}}{dt} = \frac{1}{2} \sum_{i=1}^{I-1} \sum_{m=1}^{J-1} n_{lm} n_{i(l-1)(j-m)} F_{im,(i-1)(j-m)} - \sum_{l=1}^{I} \sum_{m=1}^{J} n_{ij} n_{lm} F_{ij,lm} \tag{31}
\]

where \(n_{ij}\) is the number of particles of size \(i\) and magnetic susceptibility \(j\) (class \(ij\)), \(t\) is the time, \(F_{ij,lm}\) is the flocculation frequency of particles in class \(ij\) with particles in class \(lm\), and \(N_s, N^f\) are the total numbers of size and initial magnetic susceptibility classes, respectively. In eq. [31], the left-hand side of the equation presents the accumulation for particles of size \(i\) and magnetic susceptibility \(j\), the first term on the right-hand side is a source term due to flocculation of smaller particles, and the second term on the right-hand side presents a loss term due to flocculation to larger particles.
The flocculation rate of particles in classes $ij$ and $lm$ is defined as

$$ F_{ij,lm} = \beta_{il} \left( r_i, r_l \right) E_{ij,lm} \left( r_i, \chi_j; r_l, \chi_m \right) \quad [32] $$

where $\beta_{il}$ is the particle collision frequency, $E_{ij,lm}$ is the collision efficiency, $r_i, r_l$ are the radii of the particles, and $\chi_j, \chi_m$ are the magnetic susceptibilities of the particles. As shown by eq. [32], only the collision efficiency $E_{ij,lm}$ depends on the particle interaction forces. In the Brownian flocculation mechanism, the particle collision frequency is given by (Chandrasekhar, 1943):

$$ \beta_{il} = \frac{2}{3} \frac{kT}{\eta} \frac{(r_i + r_l)^2}{r_i r_l} \quad [33] $$

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\eta$ is the viscosity of the surrounding phase. Also, in the Brownian diffusion regime, the collision efficiency is written as

$$ E_{ij,lm} = \left\{ \left( 1 + r_i / r_l \right) \frac{1}{1 + r_j / r_i} \left( D_{\infty} / D_{il} \right) \exp \left[ V_{il} (r_i, \chi_j; r_l, \chi_m) / kT \right] \frac{ds}{s^2} \right\}^{-1} \quad [34] $$

where $D_{\infty}$ is the diffusivity in the absence of interparticle forces and is expressed as

$$ D_{\infty} = \frac{kT}{6\pi\eta} \frac{r_i + r_l}{r_i r_l} \quad [35] $$
The relative diffusivity coefficient $D_{il}$ in eq. [34] represents the hydrodynamic force acting on particles $i$ and $l$ as they approach each other and is given by

$$D_{il} = b^* kT$$  \[36\]

where $b^*$ is the relative mobility. The particle interaction potential $V_A$ represents the forces acting on the flocculation of particles and is the summation of van der Waals ($V_{vdw}$), electrostatic ($V_{el}$), and magnetic dipole ($V_{mag}$) potentials:

$$V_A = V_{vdw} + V_{el} + V_{mag}$$  \[37\]

These potentials are given in the form of simple mathematical formulas as follows (Hamaker, 1937)

$$V_{vdw} = -\frac{A}{6kT} \left\{ \frac{2r_ir_i}{r^2 - (r_i + r_i)^2} + \frac{2r_ir_i}{r^2 - (r_i - r_i)^2} + \ln \frac{r^2 - (r_i + r_i)^2}{r^2 - (r_i - r_i)^2} \right\}$$  \[38\]

where $A$ is the Hamaker constant and $r$ is the distance between the centers of the particles $i$ and $l$. The electrostatic potential is given by (Hogg et al., 1966)

$$V_{el} = \frac{e^*r_ir_i(\psi_{oi}^2 + \psi_{oi}^2)}{4(r_i + r_i)} \left\{ \frac{2\psi_{oi}\psi_{el}}{\psi_{oi}^2 + \psi_{oi}^2} \ln \left[ \frac{1 + \exp(-\kappa\lambda_0)}{1 - \exp(-\kappa\lambda_0)} \right] + \ln \left[ 1 - \exp(-2\kappa\lambda_0) \right] \right\}$$  \[39\]
where $\varepsilon^*$ is the dielectric constant ($\varepsilon^* = 89 \times 10^{-10}$ CV$^{-1}$ m$^{-1}$ for water), $\psi_{oi}$, $\psi_{ol}$ are the surface potentials of the particles $i$ and $l$, respectively, $\kappa$ is the inverse Debye-Huckel length, and $\lambda_o$ is the shortest distance between the surface of the particles. The magnetic dipole potential can be written as (Chikazumi, 1964)

\[
V_{\text{mag}} = \frac{\left(\frac{1}{6} \pi d_i^3 \chi_i B\right) \left(\frac{1}{6} \pi d_l^3 \chi_l B\right)}{4 \pi \mu_0 r^3} \left[\left(\hat{\mu}_i \cdot \hat{r}_l\right) - 3\left(\hat{\mu}_i \cdot \hat{r}\right)\left(\hat{\mu}_l \cdot \hat{r}\right)\right]
\]

where $d_i, d_l$ are the diameters of the particles, and $B$ is the magnetic field strength. A simple formula for the average magnetic potential has been derived by Chan et al. (1985) by investigating the potential in all directions:

\[
\frac{V_{\text{mag}}}{kT} = s(x) \left[ -\frac{x^2}{3} + \frac{1}{1 + \left(\frac{7x^2}{150}\right)} \right] + \left[1 - s(x)\right] \left[ -2x + \ln(6x^2) - \frac{2}{3x} - \frac{7}{9x^2} \right]
\]

where

\[
s(x) = \exp\left[ -\ln(2) \left(\frac{x}{2.4}\right)^8 \right], \quad x = \frac{1}{kT} \frac{\pi d_i^3 x_i d_l^3 x_l B^2}{144 \mu_0 r^3}
\]

The collision efficiency $E_{ij,lm}$ can then be calculated by eq. [34] as a function of particle size, hydrodynamic forces, magnetic field, magnetic susceptibility, van der
Waals, and electrostatic potentials. By combining eqs. [34] and [33], the Brownian flocculation frequency can be obtained and then the bivariate PB equation can be solved by using eqs. [31] and [32]. In this work, Brownian flocculation occurred in the absence of a magnetic field, thus $V_{mag}$ in eq. [37] was zero.
CHAPTER IV

RESULTS AND DISCUSSION

This chapter is divided into three sections:

1) experimental results and discussion,

2) modeling results and discussion, and

3) comparison between modeling and experiments.

In the first section, the experiments carried out in this work are classified into three categories: (1) magnetic-seeding, shear flocculation, and magnetic filtration; (2) breakthrough of magnetic filtration; and (3) magnetic-seeding, Brownian flocculation, and magnetic filtration. The effects of various parameters, such as particle properties including size, magnetic susceptibility, and seeding-particles concentration, and operating conditions including magnetic-field strength, suspension flow rate, and dead time, on the performance of magnetic filtration are investigated.

In the second section, modeling work that includes trajectory analysis, a particle build-up model, a breakthrough model, and a bivariate population-balance model is discussed. For each model, a sensitivity analysis was conducted and the effects of model parameters were examined.
In the third section, modeling results were compared with experimental data. Two sets of experiments were conducted: 1) magnetic filtration of paramagnetic particles; and 2) magnetic-seeding filtration including Brownian flocculation and magnetic filtration.

IV.1 Experimental Results and Discussion

Experimental work was carried out to investigate the effect of various factors on the removal efficiency of magnetic separation, and the breakthrough of magnetic filtration with or without magnetic-seeding. All the experimental condition and results are shown in Appendix I.

Reproducibility: Shear-flow flocculation and magnetic filtration experiments were conducted using polystyrene latex and seeding polystyrene-magnetite latex particles. The reproducibility of removal efficiency vs. time was examined for varying pH, seeding particle concentration, and ionic strength. The results are shown in Fig. 9. A good reproducibility was found under a wide range of conditions. The differences observed in Fig. 9 (d) are due to the difference in pH. Also, at some conditions, the removal efficiency was found to increase with time. This behavior reveals the effect of heterogeneous flocculation kinetics between non-magnetic and magnetic seeding particles. Since the flocculation tank is operated in batch mode, as time increases, more polystyrene particles are seeded with paramagnetic particles leading to an increasing in removal efficiency. Some of the results, where the removal efficiency does not increase
with time (e.g., Fig. 9 (f)), indicate that the particles do not flocculate. In summary, from Fig. 9, the maximum relative error of data obtained at similar conditions is 23%.

**Magnetic field strength:** The effect of the magnetic-field intensity on the separation of polystyrene particles was studied by varying the magnetic field strength between 0.18 and 0.81 Tesla. Figure 10 (a) shows a minor effect of the magnetic field on the removal of polystyrene particles, indicating that the flocculation rate is high enough to form large flocs that are efficiently removed by the magnetic filter which works like a conventional filter. The fact that an increase in the magnetic field did not enhance the separation means that those particles that escaped the filter in the absence of the field did not flocculate with the seed particles. The effect of the magnetic field strength is observed to be stronger in Fig. 10 (b), where the particles to be separated are approximately 45 times bigger in volume than the seed particles, suggesting that almost all large particles have flocculated with magnetic seed particles. Figures 10 (a) and (b) indicate that as the ratio of the seed particle diameter to the process particle diameter is decreased, the chances for successful seeding are increased. A smaller concentration of magnetic seed particles was used in the experiments presented in Fig. 10 (c). The results show a consistent effect of the magnetic field on the separation efficiency. The low separation efficiency observed in the absence of the magnetic field indicates that the flocculation rate is low, although the pH is close to the point of zero charge (PZC) for these particles. This behavior should be examined further in order to understand the difference between the results of Figs. 10 (a) and (c) in the absence of the magnetic field.
Figure 10 (d) shows the results of magnetic separation of only seeding polystyrene particles. The results of Fig. 10 (d) show a minor effect of magnetic field strength on the removal efficiency of paramagnetic particles. Since suspension flow rate was high (14 mL/min) and the filter length was short (10 mm), it is possible that the difference of magnetic field strength (0.2 T to 0.4 T) could not affect the removal efficiency to an appreciable extent.

**Particle size:** The effect of polystyrene particle size on the removal efficiency was significant. Table I presents the physical properties of five different size polystyrene particles used in this study. Figure 11 shows that the larger the polystyrene particle size, the higher the removal efficiency. The reason for this behavior is that the collision frequency increases as the particle size increases due to higher cross sectional area of the particles. On the other hand, the number of larger particles per gram is smaller than the number of smaller particles, therefore, there is higher probability for the large particles to flocculate with seed particles and thus the removal efficiency increases as the size of particles to be separated increases.

**Flow rate:** Figure 12 (a) shows the effect of flow rate on the removal efficiency of magnetic filtration. No significant difference was found when the flow rate was increased from 5 mL/min to 10 mL/min, as the magnetic field strength was held constant at 0.8 Tesla. A lower removal efficiency was observed at 15 mL/min flow rate. Thus, it appears that there is a threshold flux value above which removal efficiency decreases.
Figure 12 (b) shows the results of the magnetic filtration experiments only using paramagnetic particles. The experiments were conducted by varying flow rate from 14 mL/min to 22.5 mL/min. From Fig. 12 (b), it is found that the removal efficiency increases as the flow rate decreases.

**Dead time:** In order to increase the removal efficiency of the process particles, it is necessary to allow polystyrene and seed particles to flocculate for some time after contact. This time is defined as dead time. From the size measurements of the flocs, it was found that most of the shear-flow flocculation occurred in the first five minutes. Therefore, as shown in Fig. 13, the separation efficiency was unchanged by changing the dead time from 5 minutes to 10 minutes. However, the removal efficiency was increasing as filtration progressed even though most flocculation happened in the first five minutes. A possible reason is that the particles and flocs that captured by the filter become part of the filter and help in the removal of other particles due to increasing fiber diameter with along decreasing filter porosity (increased filter packing).

**Magnetic susceptibility:** The effect of particle magnetic susceptibility on the separation performance was studied by using 100 ppm black iron oxide seed particle or seeding polystyrene latex. The volume magnetic susceptibilities of black iron oxide and seeding polystyrene particles are 0.02 and 0.0059, respectively. Since the magnetic susceptibility of black iron oxide is much larger than that of seeding polystyrene particles, it is readily understood that the magnetic force working on a black iron oxide particle is larger than that on a seeding polystyrene particle of the same size under the same magnetic field.
strength. From Fig. 14, it was found that even at a higher flow rate, the effluent concentration of black iron oxide seed particles was much lower than that of seeding polystyrene particles before breakthrough occurred. Due to the high removal efficiency and high flow rate of black iron oxide particles, the filter was easily saturated, and, as expected, the breakthrough of black iron oxide happened much earlier than that of the seeding polystyrene latex particles.

**Seed particle concentration:** Figure 15 shows the experimental results of the removal of polystyrene particles by shear-flow flocculation and magnetic filtration. The effect of seed particle concentration is studied for various values of the pH. It is found that there is an optimum seed particle concentration at which the removal efficiency is maximum. Figure 15 shows that the removal efficiency using 50 ppm seed particles was higher than other concentrations at pH 3 and 6, but at higher pH, the best separation occurred when 100 ppm seed particles were used (see Fig. 15 (c)). The possible reason for such results is that the zeta potential of seed particles becomes more negative and the repulsive electrostatic potential (i.e., the barrier for particle flocculation) increases as the concentration of seed particles increases. On the other hand, higher concentration of the seed particles increases the collision efficiency between seed and process particles. Thus, there are two competing trends related to the seed particle concentration.

A set of experiments in which polystyrene particles were removed by Brownian flocculation and magnetic filtration was conducted by using different seed particle concentrations with different sizes. As shown in Fig. 16, 0.6 µm and 1.2 µm seed
particles were used at 50 ppm and 10 ppm concentrations, respectively. Although larger size seed particles were used, a lower seed particle concentration decreases the collision efficiency between seed particles and process particles. Therefore, the removal efficiency of 10 ppm seed concentration was found to be lower than that of 50 ppm seed particle concentration.

IV.2 Modeling Results and Discussion

There are four parts of modeling results discussed in this section. First, the effects of various parameters on the particle trajectory and the removal efficiency of magnetic filtration is presented. Then, the particle build-up model is discussed for varying operating conditions. By combining the trajectory and particle build-up models, the simulations of magnetic filtration breakthrough curves for particles of uniform size and magnetic susceptibility are demonstrated in the third part. Finally, the bivariate population-balance model was studied to predict the particle size and magnetic susceptibility distributions resulted from Brownian flocculation in the magnetic-seeding filtration process.

The calculations of the trajectory model were computed on a SUN ULTRA 1-140 workstation, configured with 64 MB of memory, while the calculations of the bivariate population-balance model were computed on an IBM RS/6000 model 360 workstation, configured with 64 MB of memory. The code of trajectory model was modified from a magnetic flocculation model (Yiacoumi et al., 1996). An ordinary differential equation
solver with variable step (EPISODE; Hindmarch and Byrne, 1976) was employed to solve the trajectory equations and population balance equation presented in the trajectory and bivariate models, respectively.

IV.2.1 Trajectory Model

In order to simulate experimental conditions, all the results obtained from the trajectory model assumed that the initial velocity is perpendicular to the external magnetic field, i.e. parallel to y axis, and the magnetic field is in the same direction as gravity. Also, a laminar flow was assumed for all the modeling work.

Limiting trajectory: The exact path that divides the approaching particle trajectories stopping in capture on the collector surface from those passing by is called the limiting trajectory, and the distance between the limiting trajectory and the y axis is the critical radius \( R_c \). Figure 17 shows the results of typical trajectory calculations for laminar flow. The parameters of the calculations are given in the figure caption. From Fig. 17, it is observed that if the initial approach position is within the critical radius, the particle will be captured, otherwise the particle will be swept away. The results of the effect of particle size on the limiting trajectory are shown in Fig. 18. From Fig. 18, it is found that the critical radius increases as the particle size is increased. It is because the magnetic force increases with an increase in particle size. Figure 19 shows the effect of particle size on the particle trajectory and collision with the collector. In Fig. 19, the initial approach position is the limiting trajectory for particle size 0.5 \( \mu \text{m} \), and as expected,
particles with sizes larger than 0.5 µm starting from the same initial position will be captured, while particles with sizes smaller than 0.5 µm will move away.

**Particle size:** Figure 20 shows the effect of particle size on the removal efficiency. As expected, the removal efficiency increases with an increase in the particle size. Since the removal efficiency is a function of the critical radius, wire radius, filter length, and packing fraction, the removal efficiency will increase as the critical radius increases while the other parameters are held constant, and as discussed above, the critical radius will increase as the particle size becomes larger. In other words, the magnetic force increases with particle size. Figure 20 also shows the effect of magnetic field strength. From Fig. 20, the removal efficiency increases with an increase in the magnetic field strength.

**Magnetic susceptibility:** The effect of particle magnetic susceptibility on the filter removal efficiency is studied at varying particle size. As shown in Fig. 21, for particles of the same size, the removal efficiency increases as the magnetic susceptibility increases, and for the same magnetic susceptibility, the removal efficiency increases as the particle size increases. As seen in eq. [12], since the magnetic velocity is proportional to the square of particle size, it is readily understood that the effect of particle size on the removal efficiency is stronger than that of magnetic susceptibility.

**Magnetic field strength:** Figure 22 shows the effect of magnetic field strength on the removal efficiency. As expected, the removal efficiency increases as the magnetic field is increased. Since the relation between removal efficiency and magnetic field strength is logarithmic, the removal efficiency increases slowly when the magnetic field reaches a
certain magnitude, and finding the optimum magnetic field strength will help to design the magnetic-seeding filtration process efficiently and economically.

**Flow rate:** The effect of flow rate on the removal efficiency is shown in Fig. 23. From Fig. 23, it is found that the removal efficiency increases as the flow rate decreases. Because the hydrodynamic force increases when the flow rate is increased, the particle will be easily carried away from the collector in higher drag force conditions.

**Packing fraction and filter length:** Figure 24 shows the effect of packing fraction on the removal efficiency. It is clear that the removal efficiency will increase when a higher packing fraction is used. Also, as shown in Fig. 25, the removal efficiency increases as the filter length increases if the filter packing fraction is kept constant. The filter length determines, however, the retention time of the suspension, so it is economically essential to find a reasonable filter length with minimum packing fraction in which the filtration process still can reach the required removal efficiency.

**IV.2.2 Particle Build-Up Model**

The particle build-up model is used to predict the maximum loading volume of a clean filter, and the loading volume is determined by the build-up radius (see eq. [22]). Therefore, the main parameters of the build-up radius equation such as magnetic field, particle size, magnetic susceptibility, and flow rate are investigated for their effects on the filter loading volume. All the modeling work done assumes that the particles will load on the surface of the wire between $\phi = 90^\circ$ and $135^\circ$; $\phi = 135^\circ$ will be used in eq. [20] for all cases.
Magnetic field strength: Figure 26 shows the effect of magnetic field strength on the filter loading volume at various particle size. From Fig. 26, it is obvious that the loading volume increases as the magnetic field strength increases. The effect of particle size on the loading volume also shows in Fig. 26. As shown in Fig. 26, the loading volume increases with an increase in the particle size.

Flow rate: The effect of suspension flow rate on the filter loading volume is shown in Fig. 27. It is found that the loading volume drops quickly when the flow rate changes from 0.001 m/sec to 0.002 m/sec and the decreasing rate becomes flat as the flow rate keeps increasing. A possible reason is that as the magnetic force that acts on the outside layer particles becomes smaller, once the flow rate increases, the particles will be easily swept away. For the layers near the wire, the magnetic force is stronger, therefore, the particles are not easily carried away even when the flow rate increases.

Particle size and magnetic susceptibility: Figure 28 shows the effect of particle size and magnetic susceptibility on the filter loading volume. As expected, the loading volume increases as particle size or magnetic susceptibility increases because the loading radius is proportional to particle size and magnetic susceptibility (see eq. [21]).

IV.2.3 Breakthrough Model

The breakthrough model is used to predict the breakthrough curve of magnetic filtration. Generally, the breakthrough of a filtration process is determined by its filter coefficient and saturation concentration. Because the behavior of particles inside a filter is still not well established, most researchers obtain these two parameters from
experimental data. In the present study, by combining the trajectory model which calculates the filter coefficient and a particle build-up model which gives the saturation concentration of a filter, a breakthrough curve is predicted without using fitting parameters.

In this section, the breakthrough curve has been examined by studying the effects of various parameters on the breakthrough time \( t_b \) and initial removal efficiency. The effects of parameters such as magnetic field strength and flow rate on the removal efficiency have been discussed in the previous section (trajectory model). The breakthrough time is a function of saturation concentration, filter coefficient, flow velocity, and suspension. For a given suspension with constant concentration, particle size, and magnetic susceptibility, the saturation concentration and filter coefficient are functions of magnetic field strength and flow rate. Table II presents the results of sensitivity analysis of the magnetic-field strength and flow rate. Set A is a base condition, while Set B is a perturbed condition where the magnetic-field strength is doubled, and Set C is also a perturbed condition where the flow rate is half. The results of the sensitivity analysis are shown in Fig. 29. From Fig. 29, it is found that the removal efficiency increases as the magnetic field strength increases or flow rate decreases, and the breakthrough time increases when the magnetic field strength increases or flow rate decreases. The other interesting result is that although the filter coefficients and saturation concentrations in Set B and Set C are similar (see Table II), the breakthrough
time of Set C is much longer than that of Set B. This means that the influent flow rate plays an important role in magnetic filtration performance.

IV.2.3 Bivariate Model

The bivariate population-balance model is used to predict heterogeneous flocculation between process particles and magnetic seeding particles, and will give the size and magnetic susceptibility distribution of particles in suspensions. Since this bivariate model is still under development and limited to Brownian flocculation and narrow size range, only a hypothetical simulation case will be discussed in this section. Figure 30 (a) shows the discrete size-concentration distribution at time $t = 0$. Initially, the particle size is uniform, at 0.25 µm diameter, and 50% of the particles are non-magnetic while the other 50% have a 0.0059 magnetic susceptibility. The zeta potential is also held constant at -5 mV. After ten minutes of Brownian flocculation, a significant number of floes with various magnetic susceptibilities are formed (see Fig. 30 (b)). In Fig. 31 (a), a simulation is shown with the same particle properties as in Fig. 30 but with different seed concentration; only 10% of particles are seed particles. The results of Brownian flocculation for 10 minutes are shown in Fig. 31 (b), although the number of floes is small, some large size particles are formed with lower magnetic susceptibilities.

IV.3 Comparison between Modeling and Experiments

Modeling results are compared with experimental data in this section. Figure 32 shows the flow chart of the modeling approach. The size distribution is obtained from
experimental data, and then the particle volume for each size \((V_i)\) in the influent is calculated. Assuming that particles have the same magnetic susceptibility, one can estimate the removal efficiency \((RE_i)\) from the trajectory model and the loading volume \((L_{vi})\) from the particle build-up model for each size. The particle removal volume for each size will be equal to \((V_i \times RE_i)\). Once the retained particle volume \(\sum_{i=1}^{n} V_i R_i\) reaches the loading volume corresponding to size \(i=1\) after the first breakthrough time \((t_{S1})\), the particles of size \(i=1\) cannot be removed by the filter anymore and will be carried out with the effluent. For particles of size \(i=2\), the loading volume then becomes \((L_{v2}-L_{v1})\), and the retained particle volume decreases to \(\sum_{i=2}^{n} V_i R_i\). The time needed to reach the loading volume \((L_{v2}-L_{v1})\) is given by \((t_{S2}-t_{S1})\). Following this procedure, the breakthrough time for each particle size and the effluent concentration at each breakthrough time can be obtained.

To evaluate whether the modeling results agree well with experimental data, a correlation coefficient between modeling results and experimental data is calculated in this section. The correlation coefficient \((r_{XY})\) of two random variables, \(X\) and \(Y\), is given by (Papoulis, 1984)

\[
\begin{align*}
\rho_{XY} &= \frac{\text{Cov}(X,Y)}{\sigma_X \sigma_Y}, \\
& \leq r_{XY} \leq 1
\end{align*}
\]

[43]
where $Cov$ is the covariance of $X$ and $Y$, and $\sigma_X, \sigma_Y$ are the standard deviations of $X$ and $Y$, respectively. The definitions of the covariance and the standard deviation are given as

$$Cov = \frac{1}{n} \sum_{i=1}^{n} (X_i - \eta_X)(Y_i - \eta_Y) \quad [44a]$$

$$\sigma_X = \sqrt{\frac{n \sum_{i=1}^{n} X_i^2 - (\sum_{i=1}^{n} X_i)^2}{n^2}} \quad [44b]$$

where $\eta_X$ and $\eta_Y$ are the means of $X$ and $Y$, respectively. For a good correlation between the two sets of data, the correlation coefficient will be near 1.

Figure 33 shows the comparison between modeling results and experiments of magnetic filtration using 50 ppm paramagnetic particles at 0.2-Tesla magnetic field and 22.5-mL/min flow rate. In Fig. 33, the dots represent experimental data, and the line represents modeling results using particle distribution from experimental size measurements. The correlation coefficient ($r_{XY}$) between modeling results and experimental data is 0.92, which means that the trend of modeling results agrees well with the experimental data, although the model overpredicts the effluent concentration.

Figure 34 shows the comparison between modeling results and experiments of magnetic filtration using 50 ppm paramagnetic particles under 0.4-Tesla magnetic field and 14-mL/min flow rate. As shown in Fig. 34, the modeling results underestimate the
effluent concentration, and show an earlier breakthrough. The correlation coefficient between modeling results and experimental data is 0.73.

The comparison between modeling and experiments of Brownian flocculation and magnetic filtration with 50 ppm polystyrene and 50 ppm polystyrene seed particles is shown in Fig. 35. From Fig. 35, it is found that the model underpredicts the effluent concentration at the beginning, and the correlation coefficient between modeling results and experimental data have a negative value which means that the model failed in this case. This result, however, is mainly due to the scattering observed in the experimental data.

Fig. 36 shows the comparison of magnetic filtration of black iron oxide particles. From Fig. 36, it can be seen that the trend of modeling results agrees well with the experimental data and the correlation coefficient is 0.87, though a longer breakthrough is observed in the modeling results.

The comparison between modeling and experiments of shear-flow flocculation and magnetic filtration of Argonne National Laboratory (ANL) magnetic sorbent particles is shown in Fig. 37. The experimental results are obtained from Tsouris et al. (1997). Experimental conditions are shown in the figure caption. From Fig. 37, a good correlation coefficient (0.94) between the modeling and experimental data is obtained; some overprediction and underprediction, however, are found from modeling results.

The modeling approach developed in this work has been used to predict magnetically-seeded filtration processes, and in general, it shows a good agreement with
experimental data obtained under a wide range of conditions. For paramagnetic particles, such as polystyrene seed, black iron oxide, and ANL particles, a good agreement between modeling results and experimental data is obtained. The maximum relative error between modeling results and experimental data is 35% found in Fig. 33, which is comparable to the maximum experimental relative error (23%, see Section IV.1). The reason for the differences between modeling and experiments maybe due to the fact that the particle size distribution at the inlet of the filter is used in the simulations, while in reality the size distribution may significantly change inside the filter due to the enhanced shear rate caused by the filter packing.
CHAPTER V

CONCLUSIONS

High-Gradient Magnetic Separation (HGMS) has been considered as a recovery and pollution control process for many environmental and industrial problems. For weakly magnetic and non-magnetic particles, a magnetically-seeded filtration process is used to form paramagnetic flocs and thus increase the removal efficiency of magnetic filtration. A systematic approach has been adopted in this study to (1) experimentally evaluate the effects of solution parameters, system geometry, and operating conditions on the filtration performance, (2) develop models for studying the interaction between particles and filter matrix, and (3) model experimental results without using empirical fitting coefficients. The main conclusions of this study are summarized as follows:

- The experimental results show that magnetic seeding flocculation processes play a significant role on the performance of magnetic filtration. During flocculation, particle size as well as magnetic susceptibility increase, thereby enhancing filter removal efficiency. Solution parameters, such as solution pH, ionic strength, particle size, and seed concentration, appear to be important factors in designing magnetically-seeded flocculation processes.
From magnetic filtration experiments, it is found that the removal efficiency increases with an increase in the magnetic field strength, filter packing fraction, or filter length. As the flow rate decreases, the removal efficiency, as well as the filter breakthrough time increases. Finding optimum operating conditions and system geometry is necessary for achieving economic and environmental requirements.

Based on sensitivity analyses of the trajectory, particle build-up, and breakthrough models, the filter performance is seen to depend on particle size, magnetic susceptibility, magnetic field, flow rate, and system geometry. The suspension flow rate, however, appears to have a larger effect on the filtration breakthrough time than other parameters.

In the model development, only external forces such as, gravitational, hydrodynamic drag, and magnetic, were considered. Under the system conditions of the present study, the interparticle forces, e.g., electrostatic, van der Waals, and magnetic dipole forces, are insignificant compared to external forces; however, these interparticle forces will become more important in the case of ultra-fine.

In summary, this study presents a mathematical approach to predict magnetically-seeded filtration without using empirical fitting coefficients. From the comparison between modeling and experiments, it is found that a good agreement between modeling results and experimental data is obtained. The maximum relative error obtained from the comparison between modeling results and experimental data...
(35%) is of the same order as the maximum experimental relative error (23%).

The observed differences between modeling predictions and experimental results are possibly due to the accuracy of particle size and magnetic susceptibility distributions as well as model limitations.

- Future studies should include experimental and theoretical work on (1) filter geometry (e.g., filter matrix orderly packed), (2) orientation between magnetic field and flow velocity, and (3) filter regeneration
TABLES AND FIGURES
Table I. Properties of Polystyrene and Seed Paramagnetic Particles

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<tr>
<th></th>
<th>Mean diameter (µm)</th>
<th>Density (g/mL)</th>
<th>Number of particles per gram</th>
<th>Surface area (µm²/g)</th>
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Table II. Sensitivity Analysis of Breakthrough Model

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Figure 1. Schematic of research work.
Figure 2. Schematic of the magnetically-seeded separation process.
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(a) 50 ppm paramagnetic seed, I= 0.1 M, pH~ 3. Q= 5 mL/min, magnetic field= 0.8 T, agitation speed= 300 rpm; 100 ppm polystyrene particles.
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(b) 50 ppm paramagnetic seed, I= 0.1 M, pH~ 6. Q= 5 mL/min, magnetic field= 0.8 T, agitation speed= 300 rpm; 100 ppm polystyrene particles.
Fig 9. Reproducibility of removal efficiency vs. Time:
(c) 50 ppm paramagnetic seed, I= 0.1 M, pH~ 9. Q= 5 mL/min, magnetic field= 0.8 T, agitation speed= 300 rpm, 100 ppm polystyrene particles.
Fig 9. Reproducibility of removal efficiency vs. Time:
(d) 10 ppm paramagnetic seed, I= 0.1 M. Q= 5 mL/min, magnetic field= 0.8 T, agitation speed= 300 rpm, 100 ppm polystyrene particles.
Fig 9. Reproducibility of removal efficiency vs. Time:
(e) 100 ppm paramagnetic seed, I= 0.1 M. Q= 5 mL/min, magnetic field= 0.8 T, agitation speed= 300 rpm, 100 ppm polystyrene particles.
Fig 9. Reproducibility of removal efficiency vs. Time:
(f) 50 ppm paramagnetic seed, $I = 0.01$ M. $Q = 5$ mL/min, magnetic field = 0.8 T, agitation speed = 300 rpm, 100 ppm polystyrene particles.
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(a) Polystyrene size= 0.56 µm. 50 ppm paramagnetic seed, Q= 5 mL/min, agitation speed= 300 rpm, I= 0.1 M.
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(c) 10 ppm paramagnetic seed, 100 ppm polystyrene (0.56 µm). Q= 5 mL/min, agitation speed= 300 rpm, I= 0.1 M.
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(d) 50 ppm paramagnetic seed, Q = 14 mL/min.
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agitation speed= 300 rpm, I= 0.1 M.
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agitation speed= 300 rpm, I= 0.1 M.
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(b) 50 ppm paramagnetic particles, magnetic field = 0.2 T.
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(2) paramagnetic seed particles: 100 ppm, Q= 5 mL/min, magnetic field= 0.8 T.
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agitation speed= 300 rpm, I= 0.1 M.
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(b) pH~ 6. 100 ppm polystyrene, Q= 5 mL/min, magnetic field= 0.8 T, agitation speed= 300 rpm, I= 0.1 M.
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agitation speed= 300 rpm, I= 0.1 M.
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Wire radius = 62.5 μm, magnetic susceptibility = 0.0047, magnetic-field = 0.8T, flow velocity = 0.001 m/s.
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flow velocity = 0.001 m/s.
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Wire radius = 62.5 µm, magnetic field strength = 0.8 T, magnetic susceptibility = 0.0047.
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Wire radius = 62.5 µm, magnetic field strength = 0.8 T,
magnetic susceptibility = 0.0047, flow rate = 0.001 m/s.
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Wire radius = 62.5 µm, magnetic field strength = 0.8 T,
magnetic susceptibility = 0.0047, flow rate = 0.001 m/s,
packing fraction = 1%.
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Wire radius = 62.5 µm, magnetic field strength = 0.8 T,
magnetic susceptibility = 0.0047, flow rate = 0.001 m/s.
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Wire radius = 62.5 µm, magnetic field strength = 0.8 T,
magnetic susceptibility = 0.0047.
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(a) Initial condition; (b) number fraction after 10 min of flocculation. Zeta potential = -5 mV.
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(a) Initial condition; (b) number fraction after 10 min of flocculation. Zeta potential = -5 mV.
Size measurement: particle volume \( (V_i) \) for each class \( i \) \((i=1,2,\ldots,n)\)

Trajectory model for Removal efficiency \( (RE_i) \)

Particle volume in influent
\[ \sum_{i=1}^{n} V_i \]

Build-up model for loading volume \( (L_{Vi}) \)

---

Continue

Do \( j = 2, n+1 \)

Particle volume remain in filter
\[ \sum_{i=j-1}^{n} V_i \cdot RE_i \]

Particle volume in effluent
\[ \sum_{i=j-1}^{n} V_i \cdot (1 - RE_i) + \sum_{m=0}^{j-2} V_m \]

Maximum loading volume for each class \( L_{V(j-1)} \)

Calculate breakthrough \( t_s(j-1) \)

Plot breakthrough curve
Effluent concentration vs. time

---

Figure 32. Flow chart of modeling approach.
Figure 33. Comparison of modeling and experiments of magnetic filtration using 50 ppm paramagnetic particles: Magnetic field = 0.2 T, flow rate = 22.5 mL/min, magnetic susceptibility = 0.0059.
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Figure 37. Comparison of modeling and experiments of magnetic filtration of ANL particles (turbulent shear flocculation): 100 ppm ANL particles, magnetic susceptibility = 0.0061, magnetic field = 0.8 T, flow rate = 400 mL/min.
APPENDIX I

EXPERIMENTAL CONDITIONS AND RESULTS
## Magnetic seeding filtration (shear-flow)

### Experimental conditions

<table>
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<tr>
<th>Exp. #</th>
<th>pH</th>
<th>I</th>
<th>Q</th>
<th>Dead Time</th>
<th>PS&lt;sup&gt;1&lt;/sup&gt; conc.</th>
<th>Paramag.&lt;sup&gt;2&lt;/sup&gt; conc.</th>
<th>Mag. Field</th>
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*The flow stopped suddenly after running 17.6 min, and restarted at time 30 min.*

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<tr>
<th>Exp. #</th>
<th>pH</th>
<th>I</th>
<th>Q</th>
<th>Dead Time</th>
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<th>Paramag.&lt;sup&gt;2&lt;/sup&gt; conc.</th>
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1: PS is defined as Polystyrene particles.
2: Paramag. is defined as Paramagnetic particles
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### Magnetic filtration of paramagnetic particles

**Experimental conditions**

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### Magnetic filtration of black iron oxide

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### Magnetic seeding filtration (Brownian flocculation)

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### Experimental Results

**Sample time after dead time (min)**

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### Magnetic filtration of paramagnetic particles

#### Experimental results

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<th>Exp. 4</th>
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### Magnetic filtration of black iron oxide

#### Experimental results

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