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Studies of solid-solid interaction forces and the pneumatic handling of powders

Lee, Rhonda Joy, Ph.D.
The Ohio State University, 1993
STUDIES OF SOLID-SOLID INTERACTION FORCES AND
THE PNEUMATIC HANDLING OF POWDERS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Rhonda Joy Lee, B.S., M.S.

* * * *

The Ohio State University

1993

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To my Mother
ACKNOWLEDGMENTS

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My greatest thanks goes to my family and friends, who have given me undying support and love in good times and bad.
VITA

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NOTATION

A = Hamaker constant
C_{UV} = oscillator strength of ultraviolet adsorption peak
D = particle diameter
D_a = aerodynamic particle diameter
D = electric displacement vector
E = electric field
E_a = electric breakdown strength of air = 3 \times 10^6 \text{ V/m}
F_{el} = electrostatic force
F_{im} = electrostatic image force
F_{vdw} = van der Waals force
\hbar = 6.625 \times 10^{-34}/2\pi (\text{J} \cdot \text{s})
H = separation distance between solids
P_{vdw} = van der Waals pressure
q = electric charge
R = particle radius
S = surface area
S = surface vector
U^p = particle velocity
U^f = fluid velocity
T = absolute temperature

Greek Letters

\delta = thickness of insulating layer
\varepsilon_0 = permittivity of air = 8.8 \times 10^{-12} \text{ F/m}
\varepsilon(\omega) = \text{complex dielectric permeability } [\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)]
\varepsilon_r = \text{static dielectric constant}
\xi_n = \text{frequency at energy level } n
\eta(\omega) = \text{refractive index at frequency } \omega
\kappa = \text{Boltzman's constant} = 1.38062 \times 10^{-23} (\text{J}/\text{K})
\Phi = \text{volume fraction}
\omega = \text{frequency}
\mu^f = \text{viscosity of fluid}
\omega_{UV} = \text{frequency of ultraviolet adsorption peak}
\rho_p = \text{density of particle}
\rho_f = \text{density of fluid}
CHAPTER I
THE EFFECT OF SOLID INTERACTION FORCES ON THE
DISPERSION AND TRANSPORT OF CALCIUM-BASED
SORBENT POWDERS USED IN FLUE-GAS DESULFURIZATION

A. INTRODUCTION

The solid-solid interaction forces, i.e., van der Waals and electrostatic forces, become significant relative to gravity and hydrodynamic forces for fine powder particles in a gas stream. These fine powders are commonly described as Geldart's Group C (cohesive) powders (Geldart, 1972). Group C powders include all powders having a mean particle diameter less than about 30 \mu m, very wet or sticky materials and powders which agglomerate due to excessive electrostatic charging. Though Geldart's classification of Group C powders is based on their poor fluidization behaviour, these powders are naturally cohesive in all gas-solid processes. Therefore, this classification can be generalized to all cohesive particles in a moving gas stream.

The solid-solid interaction forces acting between individual powder particles are referred to as interparticle forces. These interparticle forces are cohesive if the interacting powder particles are of the same composition.
The solid-solid interaction between two materials of different compositions is adhesion. One example of adhesion is the attachment of a powder particle to a nearby surface of different composition. For a powder of one composition, both cohesion and adhesion may contribute to inefficient powder handling, i.e. powder losses and agglomeration. Cohesion occurs between individual particles/agglomerates whereas adhesive forces act between the particles/agglomerates and the feeder and transport tube, usually of different material compositions than the powder.

Group C dry powder feeding and transport processes are plagued by problems related to the dominating solid-solid interaction forces. Many fine powder dry feeders attempt to disperse or fluidize the powder first (Hamor and Smith, 1971; Davies, 1985; Gullet, 1987; Raghunathan, et. al., 1992). During gas-solid fluidization, a Group C powder will fluidize inhomogeneously, lifting as a plug or forming cracks and channels. Strong interparticle forces relative to gravity and hydrodynamic forces decrease the ability to disperse or de-agglomerate the fine powder particles from a static, bulk state. During pneumatic powder transport, an agglomerate that enters the transport system will be less likely to be broken up by the hydrodynamic and impact forces if held together by strong interparticle forces. Also, two dispersed particles that contact each other during transport are more likely to cohere and form an agglomerate if strong
interparticle forces exist. Finally, the particles may adhere to the walls of the transport tube where the ease of removal is related to the force of adhesion.

The consequences of inefficient powder handling are unfavorable in most fine powder processes. The inability to disperse the powder combined with removal of particles to the transport tube wall results in reduction of the available powder surface area. Maximizing powder surface area is important in gas-solid reaction processes where maximum powder utilization reduces production costs. The inability to break up agglomerates and the process of re-agglomeration during transport can result in solid settling (saltation) depending on the gas stream velocity. Powder saltation and adherence to transport walls can lead to restriction and eventual clogging of the transport line. In order to predict and/or prevent inefficient fine powder dispersion and transport, a clear understanding of the solid-solid interaction forces responsible is necessary.

Krupp (1967) describes the interaction between solids in three classes. Class I includes van der Waals and electrostatic forces which he describes as the long-range attractive interactions. Class II interactions are described as short-range attractive and include hydrogen bonding and chemical bonding (i.e. metallic, covalent and ionic primary bonding). Krupp describes Class III as interfacial reactions such as sintering effects, diffusive
mixing and mutual dissolution and alloying. The primary bonds formed in Class II interactions are not considered to be of significance at the surfaces of separated solids. Class III interactions are not likely to occur at room temperature and below. Therefore, for dispersion and transport of powders at room temperature, Class I interactions are the forces responsible for powder agglomeration and adhesion.

Not included in Krupp's classification is the force associated with capillary condensation. Capillary condensation between particles appears at air relative humidities greater than 65% and the resulting capillary forces dominate over electrostatic and van der Waals forces (Zimon, 1982; Balachandran, 1987). When the relative humidity is less than 65%, capillary forces play no part in powder agglomeration. For this reason, at low humidity conditions, capillary forces are not considered a factor in powder agglomeration.

Therefore, for a dry powder material in a gaseous environment at low humidity, the solid-solid interaction forces responsible for inefficient powder handling are van der Waals and electrostatic forces. The van der Waals force between two solid materials is due to the electromagnetic interactions of the atoms or molecules making up each solid. The magnitude of the van der Waals force is a function of the interacting atoms or molecules, the distance of
separation between solids and the solid-solid contact geometry. An electrostatic force of attraction exists between two oppositely charged solid surfaces. Frictional charging or triboelectrification is responsible for charge generation at powder particle surfaces during dispersion and transport processes. For non-metallic, resistive powder materials, the charges generated are not easily released to ground or absorbed into the particle material matrix, such as with semiconductor or metallic powder materials. The charges remain "locked" in the particle surfaces, increasing the possibilities for electrostatic interactions.

What controls the exchange of charge between contacting solids is not well understood. For contact between two unlike materials, such as between the powder particles and transport tube wall, charging can be explained in terms of the different material work functions or Fermi energies (Bailey, 1984). Experiments have shown that an exchange of charge also occurs during frictional contact between like powder particles (Kunkel, 1950). Some investigators have noted that charging of powders does not show much dependence on dispersion or transport parameters, e.g. apparatus material, airflow velocity, powder quantity, but is more dependent on powder chemical composition and surface properties (Kunkel, 1950; Boschung and Glor, 1980).
At particle/particle or particle/wall contact, van der Waals forces are believed to dominate over electrostatic forces (Krupp, 1967; Bailey, 1984; Balachandran, 1987; Visser, 1989). Contact is the equilibrium distance at which the maximum attractive force occurs, arbitrarily set at 4 Angstroms in most studies. However, this equilibrium distance may actually be a variable, dependent on the contacting materials (Visser, 1981). Electrostatic forces of attraction, on the other hand, are thought to play a role in bringing the particles to the contact point (Krupp, 1967; Balachandran, 1987), relevant to powder transport processes.

The feasibility of obtaining accurate quantitative estimations of the solid-solid interaction forces acting during a powder dispersion and transport process is questionable. Electrostatic charging by triboelectrification is highly variable even when dealing with the same process and, therefore, difficult if not impossible to predict. The theory of van der Waals forces for solids has made much progress since Hamaker (1937) but still requires the assumption of an ideal contact geometry before numerical calculation. However, estimations of the relative magnitudes of these forces can provide a means to evaluate powders for ease of handling. The evaluation involves making comparisons between powders based on the factors affecting cohesion and adhesion.
Specifically, this approach is used to evaluate the ease of dispersion and transport of Group C calcium-based sorbent powders used for flue-gas desulfurization in coal-fired power plants. The four calcium-based sorbent materials commonly used for flue-gas desulfurization are calcite, dolomite, dolomitic hydrate and hydrated lime. The calcium in these powders reacts with the sulfur in the flue gas to form solid calcium sulfate. The acceptance of this technology depends on the cost and performance of the calcium-based sorbents used. Increased reactivity is thought to be mainly due to a smaller average particle size and, therefore, greater surface area per volume. The majority of the reaction occurs in the pores of the individual powder particles. Greater powder dispersion results in a smaller average particle size and allows for better access to the particle pores. Access to the particle pores, in turn, decreases the resistance to diffusion of $\text{SO}_2$ through the pore structure and increases the useful surface area for reaction (Gullet, 1987). By evaluating the available sorbents for dispersability and efficiency of transport, greater performance and lower costs can be realized.

In this study, samples of the four sorbent types are characterized and then tested for dispersability and efficiency of transport. The chemical analyses of the four powders used in this study are shown in Table 1. As seen in
Table 1: Material Properties of Sorbents

<table>
<thead>
<tr>
<th>CHEMICAL COMPOSITION</th>
<th>CALCITE</th>
<th>DOLOMITE</th>
<th>HYDRATED LIME</th>
<th>DOLOMITIC HYDRATE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>96.4</td>
<td>54.6-55.7</td>
<td>0.35-0.75</td>
<td>-</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>3.1</td>
<td>44.6-45.8</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>-</td>
<td>97.0-98.0</td>
<td>63.10</td>
<td>-</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>0.33</td>
<td>0.06-0.1</td>
<td>0.15-0.25</td>
<td>0.30</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.2-0.3</td>
<td>0.35-0.48</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.06-0.1</td>
<td>0.15-0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.06-0.08</td>
<td>0.05-0.055</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>1.0</td>
<td>0.01-0.014</td>
<td>0.08-0.098</td>
<td>0.10</td>
</tr>
<tr>
<td>MgO</td>
<td>-</td>
<td>0.40-0.45</td>
<td>33.50</td>
<td></td>
</tr>
<tr>
<td>ρ (g/cm³)</td>
<td>2.71</td>
<td>2.83</td>
<td>2.23</td>
<td>2.60</td>
</tr>
<tr>
<td>εₗ</td>
<td>8.20</td>
<td>7.34</td>
<td>13.82</td>
<td>18.64</td>
</tr>
<tr>
<td>A (X10⁻²⁰) J</td>
<td>9.86</td>
<td>7.34</td>
<td>6.39</td>
<td>7.65</td>
</tr>
</tbody>
</table>
the table, the dolomite and hydrated lime weight compositions are given as a range of values. The dolomite is a compound made up of approximately a 55% CaCO$_3$ - 45% MgCO$_3$ mixture. The hydrated lime used in this study is 97 to 98% Ca(OH)$_2$ with the majority of the remainder consisting of small percents of impurities. The calcite is close to pure calcium carbonate (96.4%) but does contain 3.1% of magnesium carbonate or magnesite. Other impurities are negligible. The dolomitic hydrate is a compound consisting of a 63.1% - 33.5% mixture of Ca(OH)$_2$ and MgO with some small amounts of impurities.

The data obtained from the sorbent characterization, i.e. particle morphologies, particle size distributions, Hamaker coefficients and static dielectric constants, are used in analyzing the dispersion and transport results. This study attempts to show that with only the relative values of a few parameters related to solid-solid interaction forces, along with a knowledge of the powder particle size distribution and morphology, enough data are available to evaluate powders for dispersability and efficiency of transport.

B. THEORY OF SOLID-SOLID INTERACTION FORCES

This section includes a brief background into the development of the theory of van der Waals forces and describes the method used in this study to determine the Hamaker coefficient. Electrostatic forces are estimated
assuming maximum particle charging occurs, not an unreasonable assumption in pneumatic powder transport processes. Capillary forces are not treated since this study deals only with dry dispersion and transport conditions.

**Van der Waals Forces**

Van der Waals in 1873 noted the non-ideality of gases and attributed it to the existence of molecular or atomic interactions. These interactions were correctly thought to be due to interacting dipoles but incorrectly treated statically. London (1936) treated the interacting two atom system as dynamic and attributed van der Waals forces to the dispersion effect. The dispersion effect is the interaction between the instantaneous dipoles formed in the atoms by their rotating electrons. The very rapidly changing dipole of one atom produces an electric field that acts upon the polarizability of a neighboring atom. If the atoms exist in a vacuum, the induced dipole of the neighboring atom moves in phase with the original dipole, producing an attractive atomic interaction. The energy of interaction between atoms i and j separated by a distance H is given as:

\[ E = -\frac{\lambda_{i,j}}{H^6} \]  \hspace{1cm} (1)

where \( \lambda_{i,j} \) is London's constant, a function of the interacting atoms. This energy of interaction is attractive
provided the medium is not too optically dense such as in a vacuum or gas. Equation (1), however, is only valid at a distance less than the wavelength corresponding to the transition between the ground and excited states of the atoms, i.e. the absorption wavelength. At separations greater than this, retardation effects become important and the attractive interaction energy is inversely proportional to $H'$. Retardation effects are caused by the fact that the electromagnetic field has to travel farther at greater separations. By the time the field influences the neighboring atom, the original atomic dipole has changed its orientation. This effect causes the interaction to be slightly out of phase. The interaction energy is still attractive but has been reduced.

Van der Waals forces not only exist between individual atoms and molecules but also between solids. Hamaker (1937) used the additivity concept proposed by London (1936) to determine the equations for the van der Waals forces between solids. The additivity concept allows the force to be calculated based on the interaction between individual atoms making up the solids. The non-retarded energy of interaction between two particles, 1 and 2, of volumes $V_1$ and $V_2$ containing $q_1$ and $q_2$ atoms per cm$^3$ is:

$$E = -\int_{V_1} dv_1 \int_{V_2} dv_2 \frac{q_1 q_2 \lambda_{12}}{H^6}$$

(2)
The van der Waals force will be given by

\[ F_{VDW} = \frac{\partial E}{\partial \mathcal{H}} \]  

(3)

Equation (2) combined with Eqn. (3) has been solved for the van der Waals force equations between bodies of regular geometric form (Hamaker, 1937). For two spheres of radii \( R_1 \) and \( R_2 \)

\[ F_{VDW} = \frac{AR}{12H^2} \]  

(4)

where \( R \) equals the reduced radius or

\[ R = \frac{2R_1R_2}{R_1 + R_2} \]  

(5)

and \( A \) is called Hamaker's coefficient (or constant) and equals (for Hamaker's development):

\[ A = \pi^2 q_1q_2\lambda_{1,2} \]  

(6)

or a sphere of radius \( R \) and a plane surface

\[ F_{VDW} = \frac{AR}{6H^2} \]  

(7)

For two plane surfaces, the solution of Eqns. (1) and (2) is expressed as a pressure, \( P \), or van der Waals force per unit area of contact:

\[ P_{VDW} = \frac{A}{6\pi H^3} \]  

(8)

Equations (4), (7) and (8) describe non-retarded van der Waals forces for ideal contact geometries. The approach of
Hamaker assumes complete additivity of forces between individual atoms and is called the microscopic approach to van der Waals forces.

Lifshitz (1956) developed the macroscopic theory (also called the modern or continuum theory) of van der Waals forces between solids. He argued that the concept of additivity was unsatisfactory when applied to closely packed atoms in a condensed body. He attributed the non-additivity to the thermodynamic fluctuations always present in the interior of a material medium. The presence of spontaneous electromagnetic fluctuations in any region will, by Maxwell’s equations, change the fluctuation field in any surrounding region. This phenomenon is called screening.

Lifshitz (1956) derived the free energy per unit area for two half spaces with plane-parallel boundaries from Maxwell’s equations. For materials 1 and 2 separated by a vacuum or gas, the non-retarded approximation is given as (Hough and White, 1980; Prieve and Russel, 1987):

\[
E = \frac{\kappa T}{2\pi} \sum_{n=0}^{\infty} \int_0^\infty k \, dk \, \ln(1 - \Delta_1 \Delta_2 e^{-2\pi k})
\]  

(9)

where:

\[
\Delta_j = \frac{\varepsilon_j(i\xi_n) - 1.0}{\varepsilon_j(i\xi_n) + 1.0}
\]

(10)

\[
\xi_n = n\left(\frac{2\pi k T}{\hbar}\right) \quad n=0,1,2,\ldots.
\]

(11)
and $T = \text{absolute temperature, } K = \text{Boltzman's constant and } h = \text{Planck's constant divided by } 2\pi$. The prime on the summation in Eqn. (9) indicates that the $n = 0$ term is given half weight. The quantity $\varepsilon_j(i\xi_n)$ is related to the complex dielectric permeability, $\varepsilon(\omega)$. The complex dielectric permeability, $[\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)]$, is a macroscopic property that indicates the microscopic polarizability of the constituent atoms of a material. Since van der Waals forces are due to the polarization of interacting atoms between solids, the presence of the dielectric permeability in the macroscopic theory is understandable.

By a change of variable ($x = 2KH$), Eqn. (9) takes on the form (Hough and White, 1980):

$$E = -\frac{A}{12\pi H^2}$$

where:

$$A = \frac{3K^2}{2} \sum_{n=0}^{\infty} \left( \sum_{s=1}^{\infty} \frac{(\Delta_1 \Delta_2)^s}{s^3} \right)$$

Taking the derivative of Eqn. (12) with respect to the separation distance, $H$, gives the same force per area of contact equation as derived by Hamaker (Eqn. (8)) using the additivity concept. However, the Hamaker coefficient, $A$, now depends on the macroscopic material properties of the interacting solids through the functions $\varepsilon_j(i\xi)$. This approach is more realistic than Hamaker's which assumes $A$
depends on $\lambda_{i,j}$, a microscopic property of two interacting atoms.

If two identical solid materials are interacting in a vacuum or gas, Eqn. (13) reduces to:

$$A = \frac{3kT}{2} \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{(\Delta_{s}^{2})}{s^3}$$  \hspace{1cm} (14)

where:

$$\Delta = \frac{\varepsilon(i\xi_{n}) - 1.0}{\varepsilon(i\xi_{n}) + 1.0}$$  \hspace{1cm} (15)

Before Eqns. (11), (14) and (15) can be solved for the Hamaker coefficient, an expression for $\varepsilon(i\xi)$, related to the dielectric response, must be determined. The dielectric response of a material is represented by the complete dielectric spectra, i.e. $\varepsilon(\omega)$ versus $\omega$. The real portion of the complex dielectric permeability, $\varepsilon'(\omega)$, measures the transmission of electromagnetic radiation of frequency $\omega$ through a body. The imaginary portion, $\varepsilon''(\omega)$, measures the absorption of electromagnetic radiation of frequency $\omega$ through a body. This absorption determines the dissipation of energy in an electromagnetic wave propagated in the medium. It is the macroscopic property of absorption that determines the strength of the van der Waals interaction between solid bodies. The use of the real function $\varepsilon(i\xi)$ is for mathematical reasons since $\varepsilon(i\xi)$ is better behaved than the complex function $\varepsilon''(\omega)$ and is related through a Kramers-
Kronig relation (Landau and Lifshitz, 1960):

\[ \varepsilon(i\xi) = 1.0 + \frac{2}{\pi} \int_0^\infty \frac{x\varepsilon''(x)}{x^2 + \xi^2} \, dx \]  \hspace{1cm} (16)

Use of this equation requires the knowledge of \( \varepsilon''(\omega) \) at all frequencies (the absorption spectra). Parsegian and Ninham (1969) represented Eqn. (16) in another way:

\[ \varepsilon(i\xi) = 1.0 + \sum_{i=1}^{N} \frac{C_i}{1.0 + \left( \frac{\omega}{\omega_i} \right)^2} \]  \hspace{1cm} (17)

where \( C_i \) and \( \omega_i \) are related to the frequencies and oscillator strengths of the absorption peaks. From another Kramers-Kronig relation, a similar expression for \( \varepsilon'(\omega) \) can be derived:

\[ \varepsilon'(\omega) = 1.0 + \sum_{i=1}^{N} \frac{C_i}{1.0 - \left( \frac{\omega}{\omega_i} \right)^2} \]  \hspace{1cm} (18)

Hough and White (1980) stressed the overwhelming importance of the ultraviolet absorption for non-conductors when using Eqn. (17) to determine \( \varepsilon(i\xi) \). If the absorption spectra can be represented by one ultraviolet absorption peak of zero bandwidth, true for most non-conductors, Eqn. (17) can be expressed as:

\[ \varepsilon(i\xi) = 1.0 + \frac{C_{uv}}{1.0 + \left( \frac{\xi}{\omega_{uv}} \right)^2} \]  \hspace{1cm} (19)

where \( C_{uv} \) and \( \omega_{uv} \) are the oscillator strength and frequency,
respectively, of the ultraviolet absorption peak. To solve Eqn. (19) at a given \( \xi_n \), values for \( C_{uv} \) and \( \omega_{uv} \) must be determined for the material. This is where the similarity of Eqns. (17) and (18) is useful. If these equations are plotted against frequency, \( \varepsilon(i\xi) \) and \( \varepsilon'(\omega) \) are found to be constant and coincident between absorption peaks. Most non-conductors do not absorb in the visible region so that \( \varepsilon''(\omega) = 0 \) and the following relationship holds:

\[
\varepsilon(\omega) = \varepsilon'(\omega) = \varepsilon(i\xi) = \eta^2(\omega) \tag{20}
\]

where \( \eta(\omega) \) is the refractive index of the material at frequency \( \omega \). Substituting \( \xi = i\omega \) in Eqn. (19), combined with Eqn. (20), gives for the visible region:

\[
\eta^2(\omega) = 1.0 + \frac{C_{uv}}{1.0 - (\frac{\omega}{\omega_{uv}})^2} \tag{21}
\]

Using Eqn. (21), values for \( C_{uv} \) and \( \omega_{uv} \) can be determined from a plot of \([\eta^2(\omega) - 1]\) versus \([\eta^2(\omega) - 1]\omega^2\) called the "Cauchy plot". This plot should be linear with a slope equal to \( 1/\omega_{uv}^2 \) and intercept \( C_{uv} \).

The necessary data for determination of the parameters \( C_{uv} \) and \( \omega_{uv} \) are at least three values of the refractive index at frequencies in the visible range. This information is tabulated in the literature, e.g. The Particle Atlas, for many common substances, or can be measured. Once \( C_{uv} \) and \( \omega_{uv} \) have been determined from the refractive index data, \( \varepsilon(i\xi_n) \) can be determined from Eqns. (11) and (19) for \( n \geq 1.0 \).
When \( n = 0 \), \( \varepsilon(i\xi_n) \) is defined as equal to the \( \eta^2(0) \), obtained from the intercept of the Cauchy plot. If the ultraviolet absorption peak represent the total interaction, \( \eta^2(0) \) would be equivalent to the static dielectric constant, \( \varepsilon_o \). This difference, \( [\varepsilon_o - \eta^2(0)] \), indicates the importance of the absorption in the infrared frequency range. If this difference is much greater than one, by neglecting the infrared absorption, some of the interaction is lost and lower Hamaker coefficients will result. This effect is discussed in detail by Parsegian and Weiss (1981).

If the value of the Hamaker coefficient is desired for a solid made up of a mixture of components, \( \varepsilon(i\xi) \) can be determined using the Clausius-Mosetti representation (Hough and White, 1980):

\[
\frac{\varepsilon(i\xi) - 1}{\varepsilon(i\xi) + 2} = \phi \left( \frac{\varepsilon_1(i\xi) - 1}{\varepsilon_1(i\xi) + 2} \right) + (1 - \phi) \left( \frac{\varepsilon_2(i\xi) - 1}{\varepsilon_2(i\xi) + 2} \right)
\]

Equation (22) can be extended for more than 2 components.

To summarize, non-retarded Hamaker's coefficient can be determined for two identical solids separated by a gas using Eqns. (11), (14), (15) and (19) combined with the values for \( C_{uv} \) and \( \omega_{uv} \) obtained from refractive index versus frequency data in the visible range (at least three points) and the value of \( \eta^2(0) \). If a solid is made up of a mixture of
components, Eqn. (22) combined with the refractive index data for the pure components can be applied.

For the van der Waals interaction between two different solid materials, the Hamaker coefficient describing the interaction can be approximated by the geometric mean of the individual coefficients (Visser, 1989):

$$A_{12} = \sqrt{A_{11} A_{22}} \tag{23}$$

The theory described above is used to calculate non-retarded Hamaker coefficients for the four Group C calcium-based sorbent powders investigated in this study. The range of validity of this theory has been experimentally verified at a minimum separation of 10 Å (Israelachvili and Tabor, 1972) up to 100 Å (Langbein, 1971). In this study, the theory is applied at contact, assumed to be 4 Å, though experimental verification at this separation has not yet been reported.

Surface deformation is known to increase van der Waals forces by increasing area of contact (Krupp, 1967; Dahneke, 1972). The calcium-based sorbents investigated are of high hardness (2-4 Mhos), and surface deformation is assumed negligible.

The effect of surface absorption on van der Waals forces can have two effects. First, the thickness of the adsorbed layer may increase the distance of separation, H, between the powder particles, thereby decreasing the van der Waals force (Krupp, 1967). Second, if the thickness of the
adsorbed layer is greater than the separation distance, the dielectric properties of the adsorbed layer will dominate over the base material in the van der Waals interaction (Langbein, 1969). In this study, the powders are carefully dried to remove any adsorbed moisture prior to dispersion and transport. Dispersion and transport are performed with dry nitrogen or dry air, so adsorption of moisture is assumed negligible and not considered in the analysis of van der Waals forces.

**Electrostatic Forces**

In contrast to van der Waals forces, where the optical properties of the interacting bodies permits calculation, at least for ideal geometries, it is not possible to arrive at a general model based on a few material constants to calculate electrostatic forces. Electrostatic charging is extremely variable showing high sensitivity to impurities and the state of the surface. The electronic energy spectrum on or near the surface can be notably affected by as low as 1% surface coverage of adsorbate ions, e.g. moisture or oxidizing agents (Krupp, 1967; Bailey, 1984). Any small change in the surface condition has been found to cause large variations in observed effects (Kunkel, 1950).

In order to theoretically gauge the role of electrostatic forces in the dispersion and transport of different fine powders, a standard approach is required. A means of doing this becomes apparent when the maximum
theoretical charging (or force) is considered. When surfaces are charged by friction in air, such as during dry powder dispersion and transport, the surface charge density is frequently able to reach the Gaussian limit. The Gaussian limit is the point where the electric field adjacent to the surface reaches the level at which air ionizes, thereafter neutralizing the charge. Gauss’s law states that if a closed surface, $S$, of any shape, is constructed in a region where an electric field is present, then the surface integral of the normal component of the displacement, $D$, over the surface is equal to the net free charge, $q$, enclosed in the surface (Cross, 1987):

$$\int D \cdot ds = \Sigma q$$  \hspace{1cm} (24)

If the medium is air, $D = \varepsilon_0 E_p$, where $\varepsilon_0$ is the permittivity of air and $E_p$ is the electric field normal to the surface. For this case, Eqn. (23) may be written:

$$\int E_p \cdot ds = (\Sigma q) / \varepsilon_0$$  \hspace{1cm} (25)

If the particle is a dielectric of relative permittivity $\varepsilon_r$ ($\varepsilon_r$ defined as the static dielectric constant of the material), the polarization of the atoms in the particle modifies the field at the surface. The surface field
becomes equal to $pE_p$ where $p$ equals:

$$p = \frac{3\varepsilon_r}{(\varepsilon_r + 2)}$$  \hspace{1cm} (26)$$

In air, electric breakdown occurs at an electric field strength $E_b$ equal to $3 \times 10^6$ V/m. The permittivity of air is $8.8 \times 10^{-12}$ F/m. Substituting these values into Eqn. (25) allows calculation of the maximum charge in Coulombs a particle surface can sustain before the ionization of air:

$$q_{\text{max}} = (2.64 \times 10^{-5}) \cdot S \cdot p$$  \hspace{1cm} (27)$$

The maximum electrostatic force possible acting on the charged particle can be calculated from the relation $F_{el} = qE_p$. Substituting $q = q_{\text{max}}$ and $E_p = E_b$, $F_{el,\text{max}}$ equals

$$F_{el,\text{max}} = (7.92 \times 10^1) \cdot S \cdot p$$  \hspace{1cm} (28)$$

A limitation of Eqn. (27) is that the derivation assumes the charge is uniformly distributed over the surface of the particle. For a non-uniform surface, regions of higher than average curvature will support higher than average surface charge densities. The result will be greater than average electrostatic forces felt in regions of high curvature, such as at the corners of angular particles or at surface asperities.

From this analysis, it is concluded that the maximum theoretical electrostatic force acting on a particle is shown to be a function of the surface area of the particle, the particle material's static dielectric constant and the
particle morphology. In a way similar to the Hamaker coefficient, the static dielectric constant appears to be a material property that relates to the relative magnitude of the electrostatic forces between materials.

C. EXPERIMENTAL

Powder Characterization

**Particle Morphology.** Since the geometry of the contact point affects both the magnitude of the van der Waals forces and the distribution of electrostatic charge, the particle morphology is an important powder characteristic to be considered in the analysis. Scanning electron microscopy (SEM) yields high resolution images of a specimen surface making it an ideal technique for investigating particle surface morphologies of powders. This technique is used to evaluate and compare particle morphologies of the four sorbents.

**Size Distribution.** The magnitudes of the solid-solid interaction forces are found to depend upon the size or surface area of the particles interacting. Therefore, when comparing the relative magnitudes of forces between different powders, the difference in average size and the distribution of sizes around the average is important. One problem with comparing experimentally determined particle size distributions between powders is that the resulting distributions are a function of powder density and morphology. Both effects must be considered when comparing
size distributions between different powders.

The particle size distributions for each powder are measured with a Sedigraph 5100 V3.02, an instrument that measures sedimentation rates. The Sedigraph analysis is the preferred method for fine powders (Halldin, 1984) to give as accurate as experimentally possible the primary particle size distribution. The Sedigraph results consist of plots of the cumulative volume percent versus aerodynamic diameter for each sorbent powder. In this study, the Sedigraph distribution will be used as a benchmark for comparing the dispersibility of the sorbent powders.

**Static Dielectric and Hamaker Constants.** The static dielectric constants of the sorbent materials are used to give one indication of the relative magnitudes of the electrostatic forces between powders. The values for calcite and dolomite are taken from the Handbook of Chemistry and Physics. The values for hydrated lime and dolomitic hydrate are not available in the literature and have to be measured. These values are obtained by taking capacitance measurements on pressed powder pellets.

Values of the Hamaker constant are determined from optical data, i.e., refractive index as a function of frequency in the visible range, for each sorbent. The refractive indices of materials are commonly measured at three wavelengths; C (red, 656 m\(\mu\)), D (yellow, 589 m\(\mu\)) and F (blue, 486 m\(\mu\)). These are the values normally tabulated and
provide the minimum requirement (3 measurements) for the Hamaker constant determination.

Calcite, dolomite and hydrated lime are birefringent materials, having uniaxial crystals with two major optic axes, and, therefore, two reported values of indicies of refraction per frequency. Average values are calculated as two thirds the ordinary values plus one third the extraordinary values.

The refractive indices as a function of these three frequencies for calcite and dolomite were measured rather than using tabulated values. These measurements were performed to assure greater accuracy since tabulated values were found to vary significantly depending on the source (e.g., Particle Atlas, McCrone and Delly, eds., Volume IV (1973) versus Winchell and Winchell (1951)). The hydrated lime used in this study was found to be in the crystalline form of epezite and the values for this material were also measured. The refractive indices of the dolomitic hydrate tested in this study could not be measured because the average particle size was too small. In this case, Eqn. (8) was used for the two components; hydrated lime (Ca(OH)$_2$) and periclase (MgO).

**Powder Dispersion and Transport**

The experiments used to test the dispersion and transport properties of the four sorbent materials are described. The transport experiments are performed with two
different transport systems designated as Transport I and Transport II. Both transport experiments are operated under the condition of dilute solid-gas pneumatic transport.

**Dispersion.** The dispersion experiments are performed using the AeroSizer particle measuring system (Amherst Process Instruments, Hadley, MA) with a dry powder disperser. With this instrument, a sample of powder is placed in a small cup. The dry disperser uses a pulsed jet to carry the powder particles out of the sample cup and into the carrier gas flow stream. The particles are then impacted upon a disperser pin to break up agglomerates. Finally, the gas-solid dispersion is carried into the sensing unit for particle sizing. The particle sensing unit is two laser beams between which each particle's time of flight is measured and converted into a particle diameter.

With the AeroSizer system, the powders are dispersed dry, and, therefore, the degree of dispersion can be correlated with the magnitude of the interparticle forces relative to the energy input for dispersion. The disperser conditions, i.e. disperser flow pressure and disperser pulse pressure, are preset and computer controlled. The disperser flow pressure, which controls the carrier gas flow stream to the disperser pin, is kept constant throughout the measurement. The pulse jet pressure, which lifts the particles from the sample cup into the carrier gas stream, is automatically incremented with a feedback system to
maintain the particle count rate in a pre-set range. The majority of the powder dispersion is assumed to occur with the impingement on the disperser pin. Therefore, as long as the disperser flow pressure is the same for all experiments, the energy input for dispersion is assumed to be essentially equal for all experiments.

The dispersion experiments are conducted in the following manner. Each of the four sorbents are tested by placing a small mass of powder in the sample cup and, under the same carrier gas flow pressures, dispersed into the measurement region. These experiments assume that, for the same energy input, the degree of sorbent dispersion should be related to the interparticle forces acting between particles. Each dispersion experiment is fast (≈ 1 minute or less) so that many tests can be run quickly to determine repeatability without worry about surface contamination with moisture. The results are plotted as cumulative volume percent versus aerodynamic diameter and directly compared with the Sedigraph results. This comparison is possible since both systems analyze the aerodynamic diameter based on the same basic principle, i.e. Newton’s law applied to particle motion in a fluid.

Transport I. The experimental apparatus used in the Transport I experiments is shown in Fig. 1. The powder is dispersed out of the feeder system into a secondary gas stream flowing down the transport tube. The tube material
Figure 1: Schematic of Transport I experimental apparatus.
used for all the transport experiments is polyethylene. Polyethylene tubing is chosen as the transport tube due to the ease of removal for cleaning between runs and monitoring powder deposition inside the tube. The gas used in the transport experiments is high-purity nitrogen from a cylinder to assure moisture into the system is minimal.

As the powder exits the transport tube, it is diluted with dry air in the column. This is required so that the powders can be sampled isokinetically to obtain an accurate particle size distribution. The particle size analyzer used is an Anderson Mark III cascade impactor. The cascade impactor is a multi-jet, multi-stage inertial impactor. There are nine jet plates that fractionate the particles into nine aerodynamic size ranges. For more information on cascade impactor principles, see Lodge and Chan (1986).

The feeder system consists of a plexiglas column with a cylindrical top and a conical bottom. Inserted into the bottom region is a 1.2 cm ID tube fitted with a porous disc. A capillary tube located at the center allows jet flow into the feeder. Gas is fed into the annular region surrounding the capillary tube and flows up through the porous plate. The flow of gas through the porous plate loosens or locally fluidizes the powder in the immediate vicinity. The annular flow is pulsed to provide for better particle loosening. The off-take tube, a 0.63 cm OD stainless steel tube, is attached to a vibrator to help with particle loosening.
More details into this feeder system is presented in Raghunathan, et. al. (1992).

The four sorbent powders are tested in the Transport I apparatus using a 0.32 cm diameter X 122 cm long polyethylene transport tube. The total amount of solids transported for each run can be maintained within a range of approximately ± 10% as long as the powder is stirred between runs. However, with this feeder, the solids feed rate cannot be made continuous and feeding is described as pulse-feeding. Based on the low mass of powder fed per pulse (= 1.5 mg/pulse, 30 pulses/min) and the high transport velocities, the mode of transport is assumed to be dilute solid-gas pneumatic transport.

The procedure used to test for the transport characteristics of each powder is as follows. First, the particle size distribution out of the feeder is directly measured by attaching the cascade impactor to the feed outlet tube with a short piece of tubing. This distribution is designated the pre-transport size distribution. The post-transport size distribution is measured as the powder exits the transport tube in the cascade impactor using isokinetic sampling.

**Transport II.** For comparison purposes, the powders are tested in a different transport system. Like in the Transport I experiments, the pre-transport size distributions, measured directly out of the feeder, are
compared with the size distributions measured after powder transport. If both systems give similar findings, there will be greater confidence that the results are material dependent and not system dependent.

A schematic of the Transport II system is shown in Fig. 2. The polyethylene transport tube dimensions are 0.95 cm in diameter X 100 cm in length. The volumetric flow of dry air is kept constant at 18 liters/min. The particle sizing instrument in this system is the AeroSizer described in the dispersion experiments. The feeder used in this system is a Sibata Micro Feeder MF-2. This feeder supplies a continuous solids feed rate by aspirating solids from grooves in a stainless steel turntable. The ejected particles are then centrifuged in a glass tube to break up agglomerates. The amount of powder in each groove along with the rotation rate of the turntable determines the solids feed rate. The solids feed rate is kept constant at approximately 50 mg/min for each sorbent material, resulting in dilute solid-gas pneumatic transport.

D. RESULTS

Powder Characterization

**Scanning Electron Microscopy (SEM).** SEM micrographs of the four sorbent materials are shown in Fig. 3. These micrographs give general indications of the sorbent particle morphologies. The calcite and dolomite (the carbonates) have more angular morphologies than the hydrates. The fine
Figure 2: Schematic of Transport II experimental apparatus.
Figure 3: SEM Micrographs of Four Sorbent Powders.
particles of the carbonates (D \leq 1 \mu m) have a tendency to cohere to the flat surfaces of the larger particles (See Figs. 3(a) and 3(b)).

The hydrates, shown in Figs. 3(c) and 3(d), have more rounded morphologies due to their processing from limestones. The individual particles are made up of smaller particles fused together during the hydration process. The results are single particles with rounded surface protrusion or nodules.

**Modeling of Sorbent Contact Geometries (See Fig. 4).**

(1) Contact Geometry Type A

**Description:** Small, approximately spherical sorbent particles (\approx \leq 1 \mu m) attached to flat surfaces of larger particles. Accounts for approximately 6% of the total mass.

**Equation:** The van der Waals force for this contact geometry can be modeled by Eq. (7).

**Sorbent Types:** All carbonates since they are in their original crystalline form. Examples: calcite and dolomite.

(2) Contact Geometry Type B

**Description:** Sphere-sphere contact geometry. Spheres may be of the same or different radius.

**Equation:** The van der Waals force for this contact geometry can be modeled by Eq. (4) where R is the reduced radius for different sized spheres.

**Sorbent Types:** Small (\leq 1 \mu m) particle-particle contact for carbonates. All hydrates for the entire size range.
Figure 4: Sorbent contact geometries.
Surfaces of even the large hydrate particles have rounded protusions, best represented by asphere-sphere contact geometry.

(3) Contact Geometry Type C:

**Description:** Two flat regions in contact.

**Equation:** Van der Waals force for this contact geometry can be modeled by Eq. (8) multiplied by the contacting surface area.

**Sorbent Types:** All carbonates.

(4) Contact Geometry Type D:

**Description:** Two flat regions separated by small particles.

**Equation:** Van der Waals force for this contact geometry can be modeled by Eq. (8) as in Type C except the separation distance will equal the largest diameter of the separating particles.

**Sorbent Types:** All carbonates.

**Sedigraph.** The particle size distributions for the sorbent powders determined from the Sedigraph are shown in Fig. 5. The results indicate that directly comparing aerodynamic diameters of calcite and dolomite is reasonable since the density difference is slight (See Table 1) and the SEM analyses show similar particle morphologies. Therefore, Fig. 5 indicates that calcite and dolomite have comparable median particle sizes and dolomite has a wider size distribution than the calcite.
Figure 5: Sedigraph analyses of four sorbents.
Comparing the Sedigraph results for the two hydrates shows the dolomitic hydrate to be composed of finer particles. Though of similar particle morphologies, the difference in densities is greater between these two sorbents than for the carbonates. The effect of a greater density is to increase the aerodynamic diameter reported for a given size. Therefore, the dolomitic hydrate compared to the hydrated lime has an even finer size distribution than is indicated by the Sedigraph.

**Static Dielectric and Hamaker Constants.** The static dielectric constant of each sorbent material is listed in Table 1.

The Cauchy plots generated from the refractive indices data and Eqn. (7) are shown in Fig. 6 for three of the four sorbent materials and periclase. Table 2 lists the values obtained from the Cauchy plots of the parameters needed for the Hamaker constant determinations. Average values are listed for the uniaxial materials.

The Hamaker constant is calculated for each sorbent material using the values of the parameters in Table 2 combined with Eqns. (3), (4), (5) and (6). For the dolomitic hydrate, Eqn. (7) is solved using refractive indices data for each component, MgO and Ca(OH)$_2$, and the results are used in Eqn. (6) to generate $\varepsilon_1(i\xi)$ and $\varepsilon_2(i\xi)$. Knowing the volume fraction $\phi$, Eqn. (8) is solved for an average $\varepsilon(i\xi)$ at each value of $\xi$. 
Figure 6: Cauchy plots used in the Lifshitz-van der Waals constant determinations.
Table 2: Values of parameters used in the Hamaker constant calculation.

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<th>Material</th>
<th>$\eta^2(0)$</th>
<th>$C_m$</th>
<th>$a_m \times 10^{16}$</th>
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The calculated values of the Hamaker constant for the four sorbent materials are listed in Table 1. Calcite has the highest and hydrated lime has the lowest value of the four sorbent materials.

**Calculation of Interparticle Forces.** A computer program (See Appendix B) is written to calculate the van der Waals, electrostatic and gravity forces for sorbent materials. Inputs include Hamaker's constant, static dielectric constant and density. Figure 7 shows a theoretical force plot for calcite. The other three sorbents have similar plots. The van der Waals equation used in this particular calculation was for a sphere on flat plate, which closely approximates the force for fines in the carbonate materials. For the hydrates, having a more rounded morphology even for the larger particles, the abcissa will correspond to the reduced diameter (See Eqn. (5)).

In Figure 8, the theoretical van der Waals force versus particle diameter for calcite is plotted for the sphere flat plate geometry. The abcissa corresponds to the sphere diameter. The particle diameter range is only up to 1 μm since carbonate sorbents become distinctly angular at higher particle diameters. However, up to 1 μm, this contact geometry should provide a very satisfactory representation of the actual physical condition. The calculations indicate a van der Waals force of agglomeration ranging from $1 \times 10^{-8}$
Figure 7: Theoretical force versus particle diameter for calcite.
Figure 8: Theoretical force versus particle diameter for contact geometry A.
to $1 \times 10^{-7}$ Newtons. The force holding the particles to the surface should lie in this range.

In Figure 9, the theoretical van der Waals force versus reduced radius is plotted for hydrated lime. The reduced diameter covers a range up to 50 μm which is considered the maximum particle size of interest in the sorbents tested. In the submicron range, the force lies between $1 \times 10^{-9}$ and $1 \times 10^{-8}$ Newtons, an order of magnitude less than for a sphere-flat plate geometry. Therefore, we can conclude the fine particle attached to the large, flattened surface (Contact Geometry A) is held much tighter than the particle attached to another particle of similar size (Contact Geometry B). For particle sizes greater than 1 μm, Figure 9 applies only to the spherical-shaped contact regions of the hydrates.

The results in Figure 10 are interesting because they show how drastically the van der Waals force is reduced between two flat surfaces when adhered small particles are present (Contact Geometry D). If the flat surfaces are able to contact (Contact Geometry C), the van der Waals force will be the largest of the contact geometries. This makes sense since the greatest contact surface area is possible with this geometry. However, even the slightest inhomogeneity on the surface will increase the separation and reduce the force of contact. Therefore, it is very important to investigate the condition of the surfaces.
Figure 9: Theoretical van der Waals force for hydrated lime for contact geometry B.
Figure 10: Theoretical van der Waals force versus surface area as a function of separation distance, z.
before assessing the agglomeration potential of a sorbent. This is important for all surface geometries since van der Waals force falls off quickly with distance of separation in all cases.

Figure 11 is comparison in theoretical van der Waals forces for the very fine particle sizes of hydrated lime and calcite. From the sedigraph data for the sorbent materials, calcite consists of a much smaller percent of particles are less than 1\(\mu\)m than hydrated lime. Therefore, it is more likely that a small calcite particle will be adhered to a larger, angular particle (sphere-flat plate) geometry than to a similar small particle (sphere-sphere) geometry. However, the fine particles of the hydrated lime will more likely be adhered to another small particle or to a small nodule of a larger particle (sphere-sphere) geometry. This result indicates the sorbent material (Hamaker constant) and average sorbent contact geometry are both important effects to be considered in powder agglomeration.

Since dispersion is a function of the balance of forces on the agglomerates, the van der Waals forces are compared to drag forces in Figures 12-14. The drag force is determined based upon a simplified model of two contacting spherical particles accelerated in uniform shear flow as shown in Figure 15. The analysis is applicable to turbulent flow. This analysis follows closely the work of Kousaka et. al. (1979).
Figure 11: Comparison between calcite (sphere-flat plate), calcite (sphere-sphere) and hydrated lime (sphere-sphere) van der Waals forces.
Sorbent = Hydrated Lime
Sphere—Sphere Geometry
$U_r = 1.0 \text{ m/s}$
$d = 4.0 \text{ Å}$

Figure 12: Comparison of drag and van der Waals forces at the contact point between two spheres.
Figure 13: Comparison of drag and van der Waals forces at the contact point between two spheres.
Figure 14: Comparison of drag and van der Waals forces at the contact point between two spheres.
Figure 15: A model agglomerate (Kousaka, et. al., 1979).
Based on Stokes' law, the equation of motion can be written for particles A and B

\[ m_A \frac{du_p}{dt} = 3 \pi \mu \ U_r \ d_{PA} - F \quad (29) \]

This analysis is generally valid for the case shown in Fig. 15b. However, in case of Fig. 15a, it is only valid at the onset of acceleration or when the particle just enters the stream. Assuming that density of the particle A and B are the same and is equal to the density of the agglomerate, Eqs. 29 and 30 can be reduced to

\[ F = 3 \pi \mu \ U_r \ d_{PA} \ d_{PB} \ \frac{(d_{PB} - d_{PA})}{(d_{PA}^2 - d_{PA}^2 \ d_{PB}^2 + d_{PB}^2)} \quad (30) \]

where \( U_r \) is the mean air velocity in a pipe or relative velocity as shown in Fig.15.

Figure 12 shows a comparison of van der Waals and drag forces for hydrated lime. The relative velocity is 1.0 m/s. Hydrated lime was chosen for comparison with the drag model since it's particles and agglomerates are close to spherical in shape as shown in the SEM analysis. As seen in Figure 12, the van der Waals force dominates considerable over the drag force. Figure 13 shows a significant increase in drag force with a 100X increase in relative velocity. However, a relative velocity of close to 10,000 m/s is needed to overcome the van der Waals force at the contact point. These results indicate the hydrodynamic force alone is not responsible for dispersion of the sorbents. It is apparent
dispersion be impact is the most important mechanism of dispersion, that is, dispersion be impact of particles upon obstacles in an air stream.

Figure 14 includes the van der Waals force for calcite for a sphere-sphere geometry. In actuality, the van der Waals force will be much higher than shown in the figure since calcite particles cannot be assumed spherical for diameters greater than about 1 μm.

**Powder Dispersion and Transport**

**Dispersion.** The results of the dispersion experiments are shown in Fig. 16. For each sorbent tested, the particle size distributions determined with the Sedigraph and AeroSizer are compared. The results presented for the AeroSizer experiments are representative of the majority of individual runs, each run counting at least 200,000 particles. Repeatability between runs was found to be excellent with this instrument. Also included in Fig. 16 for each sorbent are the two force constants, \( A \) and \( \varepsilon \), as determined in the powder characterization analysis.

The results show that calcite has the least dispersibility, with the majority of the particles having aerodynamic diameters between approximately 15 and 30 μm. For dolomite, the results reveal a greater dispersibility compared with calcite. The hydrates show a very high level of dispersibility. Comparison of the dispersion results for the hydrates indicates that the hydrated lime has a slightly
Figure 16: Comparison of volume distributions between Aerosizer and Sedigraph.
greater dispersibility than the dolomitic hydrate.

**Transport I.** The Transport I results are shown in Fig. 17. The pre- and post-transport size distributions are compared in each graph. The two end points (0% and 100%) are not true data points but are approximated from SEM images.

The distributions presented are the average of three runs with approximately the same mass of solid transported per run. The distributions are averaged in this case to lessen the effect of random deviations due to system variability. Also, since the powder flow is not continuous in this system, a solids flow rate is not reported. Particle deposition on the tube wall was observed for all sorbent materials. The transport tube was cleaned after every run to assure the same probability of adhesion between runs.

Comparing the calcite and dolomite results in Fig. 17, the calcite shows a greater difference between size distributions for pre- and post-transport. Like calcite, dolomitic hydrate also shows a significant loss of fine particles with transport. The hydrated lime shows essentially no loss of fines above 1 μm, and a small loss of fines less than 1 μm. Comparing the hydrates, the dolomitic hydrate has a much greater coarsening of size with transport than the hydrated lime.
Figure 17: Comparison of pre- and post-transport volume distributions for the Transport I experiments.
Transport II. The results for the Transport II system are presented in Fig. 18 in histogram form. The Aerosizer instrument's most detailed analysis is in this format. The results are presented as a number distribution, an instrument option, since the number distribution places more weight on the fine particles which are the most influenced by the solid-solid interaction forces. In other words, by presenting the number distribution, the sensitivity of the results to fine particles is increased. The majority of the particles by number for all sorbent materials are less than 4 μm.

Comparing calcite and dolomite, a similar trend in pre- and post-transport distributions is noted up to the size range 1.2-1.0 μm. For the five ranges between 4.0 and 1.8 μm, the carbonate sorbents show an increase in particle numbers with transport. However, the difference between pre- and post-transport distributions is greater for the calcite. In the ranges below 1.8 μm, the trend reverses in that the post-transport are less than the pre-transport number. This shift to larger particle sizes with transport is indicative of the agglomeration/removal of the fine particles. However, in the 1.2-1.0 and 1.0-0.86 μm size ranges, the calcite shows a much greater loss of fines with transport than the dolomite. Particles having $D_a \leq 0.86$ microns are lost during transport for both carbonate powders.
Figure 18: Comparison of pre- and post-transport volume distributions for the Transport II experiments.
Comparing the hydrates, the dolomitic hydrate, like the calcite, shows a distinct shift toward larger particle sizes with transport. The hydrated lime, on the other hand, shows no clear trend between pre- and post-transport distributions. The results indicate there may even be deagglomeration occurring with the hydrated lime.

E. DISCUSSION

In this section, the results from the dispersion and transport experiments are interpreted with respect to the information obtained from the powder characterization analysis.

Dispersion

The purpose of the dispersion experiments is to determine how the solid-solid interaction forces affect powder dispersibility. First, the effect of the van der Waals forces will be considered. From the powder characterization results, the calcite is found to have the greatest Hamaker constant and shows the lowest dispersibility in Fig. 16. The hydrated lime has the lowest Hamaker constant and shows the greatest dispersibility. However, since contact geometry and particle size also play a role in van der Waals forces, these effects must be considered.

The improvement in dispersibility of the dolomite over the calcite may be attributed to two interparticle force effects: (1) the lower Hamaker constant and (2) the greater
percentage of fine particles. The dolomite has been shown by the Sedigraph analysis to have more fine particles than the calcite. These fine particles are found to cohere to the flat surfaces of the larger particles, as seen in the SEM, acting as spacers between contacting flat surfaces and reducing the van der Waals forces per unit area considerably (as $1/H^3$ for the non-retarded case). The effect is magnified when retardation begins at separations of approximately 0.01 μm, where the van der Waals force decreases as $1/H^4$. Therefore, the differences in dispersibility between the carbonates may be due to two factors, the Hamaker constant and particle size distribution, affecting the relative values of the average van der Waals forces.

The observed difference in dispersibility between the hydrates is slight. The dolomitic hydrate appears to have a slightly lower dispersibility than the hydrated lime. Again the difference in the van der Waals forces may be used to explain this observation. Though the average size of the dolomitic hydrate is smaller, the actual value of $R$ used for the van der Waals force calculation should be based on the curvature at the contact point, not the total particle radius as with the electrostatic forces. As seen in the SEM, both hydrate powders are made up of small rounded particles sintered together in the hydration process. The effect of small radii protrusions on the surfaces of each particle...
particle, such as in Figs. 3(c) and 3(d), results in even smaller average van der Waals forces than if \( R \) is based on the total particle radius. The van der Waals forces for the dolomitic hydrate will be slightly greater than for the hydrated lime due to the higher Hamaker coefficient.

The effects of electrostatic forces on dispersibility are evaluated based on the relative values of the dielectric constants with consideration given to the average particle sizes and morphologies since factors influence the maximum allowable charging. The dielectric constants of the carbonates are not significantly different, especially when the value of \( p \) (See Eqn. (11)), are compared. Since there is little difference in morphology and average size between calcite and dolomite, the electrostatic forces are expected to be similar for these two materials. Therefore, the observed results may be due to the differences in van der Waals forces alone.

The hydrates show a greater difference between static dielectric constants than the carbonates. However, with the hydrates, the difference in the average particle size must be factored into the analysis. The dolomitic hydrate has a smaller average particle size than the hydrated lime which will offset the effect of the higher static dielectric constant on the relative magnitude of the electrostatic forces. Therefore, it cannot be concluded that higher electrostatic forces are responsible for the slightly lower
dispersibility of the dolomitic hydrate.

One other factor that should be mentioned is the effect of inertia on the dispersibility of the sorbents. Greater particle inertia may also play a role in the slightly higher dispersibility of the hydrated lime compared to the dolomitic hydrate since inertia has an \( R^3 \) dependence. For the carbonates, the effect of inertia should be slight when comparing dispersion results since the densities and particle sizes are not significantly different.

Comparing all sorbent materials, it appears the sorbents with the lower average van der Waals forces have greater dispersibility. In addition to the relative magnitudes of the Hamaker constants, differences in contact geometries are suspected of having a significant effect on the relative van der Waals forces. The presence of nodules on the hydrates, as seen in the SEM, result in a reduction of van der Waals forces and increased dispersion is noted. A greater percentage of fine particles for the dolomite, as determined by the Sedigraph, may be a factor in its increased dispersion. The influence of electrostatic forces on dispersion did not seem significant.

**Transport I**

As immediately obvious from the results, the van der Waals forces alone cannot explain the observed differences between pre- and post-transport behavior. The dolomitic hydrate shows as much coarsening with transport as the
calcite though van der Waals forces are lower as indicated by the Hamaker coefficient and contact geometry. Differences in median diameters are no longer a factor as with dispersion since pre-transport results show all powders to have a median size between 10 and 20 μm prior to transport. When density effects are taken into account, since the results show aerodynamic diameters, even smaller differences in median diameters are observed. This unexpected high level of agglomeration/adhesion observed with the dolomitic hydrate may be due to an increased role of electrostatic forces during the transport process. However, considering the higher efficiency of transport of the hydrated lime compared with the calcite though having higher electrostatic forces may indicate that van der Waals forces may also play a significant role in transport processes.

The van der Waals forces for transport now include not only the particle-particle cohesive interactions but also particle-wall adhesive interactions. A particle more tightly held to the tube wall with greater van der Waals forces will have a smaller probability of being reintroduced into the flow stream. The relative effect of the Hamaker constants and contact geometries on the van der Waals forces will remain unchanged for the case of adherence to the tube wall.
The importance of van der Waals forces to transport processes is also reflected in the comparison in the results between the calcite and dolomite. Electrostatic forces are assumed not to be a factor in the observed results based on the similarities in the pre-transport average median diameters and static dielectric constants for the carbonates. Random effects are expected to average out. Therefore, the observed difference appears to be due to the difference in the van der Waals forces between the carbonates.

Transport II

The Transport II results show some similarity to the Transport I results. However, with this system, the differences in pre-transport median diameters are greater than for Transport I. This greater variance is due to the better dispersion obtained with this feeder, with the resulting median diameters closer to the primary size values.

The increased agglomeration/loss of fines for both the calcite and dolomitic hydrate with transport is again noted and, as mentioned previously, could be due to the combined effect of van der Waals and electrostatic forces during transport.

Comparing hydrates, the lack of a distinct trend in the hydrated lime results, also seen in the Transport I, seems to be the effect of lower van der Waals forces reflected in
the lower Hamaker constant. As discussed previously, the presence of nodules on the hydrate surfaces acting as the contact points reduces the effect of differences in measured average particle sizes between hydrates on the van der Waals forces. However, it is interesting to note that the electrostatic forces, which should be based on the total particle size, should be similar if not greater for the hydrated lime compared to the dolomitic hydrate. The larger average pre-transport particle size of the hydrated lime more than offsets the effect of the lower dielectric constant on the theoretically derived equation for the maximum electrostatic forces (Eqn. (13)). This result may indicate another factor influencing the electrostatic interaction between the hydrates such as non-uniformity of surface charge or a stronger dependence of electrostatic forces on the static dielectric constant than indicated in the theoretical development.

The differences between the carbonate results could be attributed to the effect of lower van der Waals forces for the dolomite since electrostatic force effects are expected to not be significantly different.

**F. CONCLUSIONS**

The characterization of powder materials, including particle morphologies, particle size distributions and static dielectric and Hamaker constants, provides insight into the reasons for differences in dispersion and transport
behavior between powders. The theory of interparticle forces indicates that a qualitative comparative analysis of the Van der Waals forces between different powders must not be based on the relative values of the material chemical properties, i.e. static dielectric and Hamaker constants, respectively, alone, but must include the effects of particle size distributions and particle morphologies.

An analysis of differences in van der Waals and electrostatic forces between the sorbent powders indicates that dispersibility may be controlled by van der Waals forces and that during transport, both are significant. For the calcium-based sorbent powders investigated in this study, the powder with the lowest Hamaker constant combined with the presence of small, spherical nodules on the surface gives the best dispersion behavior. For the angular carbonate powders, an increase in the number of fine particles appears to increase both the dispersibility and transport efficiency. The hydrated lime in this study has the best dispersion and transport efficiency of the four sorbents due to having the lowest van der Waals forces. The dolomitic hydrate, on the other hand, has good dispersibility but low efficiency of transport. This result is suspected to be due to higher relative electrostatic forces, reflected in the higher dielectric constant.
G. LITERATURE CITED


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CHAPTER II
REACTIVITY AND FLOWABILITY OF SURFACTANT-MODIFIED HYDRATED LIME POWDERS

A. INTRODUCTION

Solid/gas non-catalytic reactions are subject to unique problems. Since the solid is participating in the reaction, maximizing the utilization of the solid reactant is important economically. A high external surface area of the solid lowers the diffusional resistance to the reaction. Grinding the solid into a powder, therefore, improves the utilization of the solid reactant. The smaller the powder particle size, the greater the surface area. However, the smaller particle size may not result in greater reactivity if the powder cannot be dispersed easily. The finer the powder, the greater the influence of interparticle forces acting between particles, such as van der Waals and electrostatic forces of attraction, and the more difficult to disperse due to the increased cohesion. A powder with highest reactivity will have the optimum combination of high surface area and good dispersion.
Two solid/gas reactions of industrial importance are the reaction of hydrated lime powder with sulfur dioxide (sulfation) and carbon dioxide (carbonation). The sulfation reaction is important in flue-gas desulfurization of coal-fired power plants (Newton, et. al., 1988). At a temperature of 540°C, the hydrated lime calcines, losing water, to form lime (Boynton, 1980). This calcination results in the formation of pores, thereby increasing the available surface area for reaction with SO₂. Duct injection is also employed where the hydrated lime powder reacts directly with the SO₂ below the calcination temperature.

Carbonation of calcium hydroxide is another reaction of interest. Calcium hydroxide reacts readily at room temperature with moisture and carbon dioxide in the atmosphere to form calcium carbonate. For applications where calcium hydroxide is used for another reaction, such as in sulfation, the carbonation side reaction is undesirable as it leads to a decrease in the reactivity of the solid (Theocharis and Yeates, 1991; Jozewicz and Gullet, 1991; Gullet and Blom, 1987). In some applications, such as in fruit preservation, carbonation is the desired reaction path.

Calcium hydroxide powders are formed when limestone is calcined to CaO (lime) and subsequently hydrated. The reaction involves a change from the cubic structure of CaO
to the hexagonal close-packed polar structure of Ca(OH)$_2$ (See Figure 19). Hydration of lime is a strong exothermic, reversible reaction (Boynton, 1980):

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{heat}$$

(31)

An excess of moisture over the theoretical amount is essential to achieve complete hydration since some water will be lost through evaporation due to the heat of hydration. Also, to some extent, there is free water that is not chemically combined but that envelops the hydrate particle as a film of adsorbed water. The purity of the lime and the method of hydration will effect the physical properties of the resulting hydrate. High chemical purity and smaller CaO particle size abets rapid hydration as do higher temperatures. Excess water retards the rate of hydration and improves the dispersion of the hydrate particles, contributing to finer particle size. Insufficient water causes an irreversible agglomeration of fine hydrate particles by the formation of phase contacts, lowering the chemical reactivity.

Studies on the effect of particle size on the reactivity of calcium hydroxide sorbents reveals a relationship between the measured particle diameter and conversion. The reactivity is found to increase inversely with particle diameter to the 0.22-0.32 power in the sulfation reaction at high temperature (Gullet, 1987). This increase in reactivity is thought to be mainly due to the
Figure 19: Unit cell of calcium hydroxide.
increase in surface area per volume for the smaller particles and the lower resistance to diffusion of \(SO_2\) through the pores. The formation of agglomerates decreases the reactivity though the size of the constituent particles influences this effect. Smaller constituent particles is found to increase the intra-agglomerate diffusion of \(SO_2\). Studies have shown that surfactant-modified hydrates have 15-20\% more reactivity to sulfation compared to the unmodified hydrates (Jozewicz and Kirchgessner, 1989; Kirchgessner and Lorrain, 1987). Modified hydrates were produced by dissolving sufficient calcium lignosulfonate, an anionic surfactant, in the water of hydration to yield up to 4.0\% on a mass basis of lignosulfonate in the product hydrate. Reactivity of the hydrates to \(SO_2\) was determined in a flow reactor at a temperature of 1000°C and a sorbent residence time of 1 second. Results showed an optimum sorbent reactivity at approximately 1.0\% calcium lignosulfonate by mass in the final product. The increased reactivity was thought to be due in part to a decrease in the primary particle size combined with a decrease in the tendency to agglomerate.

The dispersing properties of a surfactant enable it to adsorb onto a solid particle and to produce by this adsorption energy barriers of sufficient height to disperse the particle. The properties of the surfactant, medium and the solid particle determine the best combination for
maximum dispersion. Ionic dispersing agents having ionic groups distributed over the entire surfactant molecule and hydrophobic groups containing polarizable structures such as aromatic rings or ether linkages are best for dispersing polar solids in an aqueous medium (Rosen, 1987). Lignosulfonate salts are surfactants that fulfill these requirements.

Lignosulfonates are a waste product from the pulp and paper industry. In the Kraft pulping process, wood chips are cooked at elevated temperatures and pressures, using a mixture of sodium hydroxide and sodium sulfide. In this process, phenolic hydroxyl groups and carboxyl groups are inserted into the lignin structure, which is made up of phenylpropane units. Sulfonate groups are introduced into the alpha positions of the phenylpropane units (Sjöström, 1981). The resulting ionic molecule will contain more than one sulfonate group (See Fig. 20).

The dispersing action of lignosulfonate can be due to a number of factors. The molecules adsorbed to the solid surface may cause the formation of electrical barriers to aggregation due to the repulsive force felt between the ionic charges of similar sign on adsorbed molecules. The ionic groups also permit extension of the surfactant molecule into the aqueous phase thus creating a steric barrier to coalescence.
Figure 20: A Sodium Lignosulfonate Molecule.
Whether the adsorption of the lignosulfonate molecule takes place on the crystal faces or edges seems to depend on the prevailing pH conditions (Theng, 1979). Under acidic conditions, studies with clays have shown that adsorption occurs at cations exposed at crystal edges. In alkaline media, adsorption of lignosulphonate occurs predominately at the external basal surfaces of the crystals by hydrogen bonding between hydroxyl groups on the polymer and water molecules in the primary hydration shell of the exchangeable cation.

Qualitative electrophoretic measurements indicate that even in an acid medium the electrostatic surface forces are predominantly repulsive (Beeckman, 1962). The effect of a decrease in pH should, therefore, favor the adsorption process by increasing the number of available unionized sulphonic acid groups in the polyelectrolyte capable of hydrogen bonding with oxygen atoms in the surface of the solid, and by reducing the mutual repulsion between polyelectrolyte segments.

Beeckmans (Beeckman, 1962) conducted adsorption isotherm experiments of lignosulfonate/kaolin and lignosulfonate/titanium dioxide aqueous systems. Adsorption was found to be rapid, irreversible and independent of temperature in the range 25°C to 35°C. Isotherms were linear when plotted according to the Langmuir or modified Langmuir equation. The mechanism of adsorption was
considered to be basically similar to that of the adsorption of a non-ionic polymer but modified by the presence of electrostatic forces between the polyion and the solid surface, and by the intra- and inter-molecular forces between the charges on the polyions. An estimate of the quantity of lignosulfonate adsorbed at surface saturation was made based on the assumption of spherical, impenetrable spheres of molecules of radius R and molecular weight M of total projected area per unit area of surface of θ from:

\[ \frac{\Gamma_m}{A} = \frac{M \theta}{4R^2 N_o} \]  \hspace{1cm} (32)

N_o being Avogadro’s number and A the specific surface area of the adsorbent. If the value of R^2 is taken as the root mean square distance of the polymer segments from the center of gravity of the molecule, \( \bar{S}^2 \), the ratio of M to \( \bar{S}^2 \) was found to be a constant value of 21.9x10^16 g cm^-2mole^-1 for lignosulfonates in the molecular weight range 4,000-19,000 when checked by means of intrinsic viscosity versus number-average molecular weight data. Substitution of this value and \( \pi/4 \) for θ in Eqn. (32) leads to a constant value 7.15x10^-8 for \( \Gamma_m/A \).

The flow characteristics of a dry powder can be described with properties such as compressibility, dispersibility and cohesion (Carr, 1962). Percent
compressibility computed for flow evaluation will be:

\[ 100 \frac{(P - A)}{P} = \% \text{compressibility} \quad (33) \]

where \( P \) is the packed density and \( A \) is the aerated density. The more compressible a material is, the less flowable it will be. Percentage compressibility indirectly gives a picture of: (1) uniformity in size and shape, (2) deformability, (3) surface area, (4) cohesion and (5) moisture content.

Dispersibility is a direct measurement of the ability of a material to flood or be fluidized. Carr (Carr, 1962) describes a simple procedure to determine dispersibility. A pre-weighed sample of powder is dropped "en masse" through a cylinder onto a pre-weighed watch glass. Material remaining on the watch glass is weighed, any loss having been dispersed during the fall.

Carr describes the cohesion of a powder as the forces between the atoms and molecules existing on the surfaces of fine particles. One procedure for finding the apparent surface cohesion involves determining retention of material on a nest of mesh screens. The screens are vibrated for a set time that depends on the bulk density of the material. The amount of material left on each screen is then weighed and rated in points (%) accordingly. If the entire mass of powder goes through the highest mesh number screen (smallest openings), the cohesion is zero. This test is a direct
determination of the amount of energy necessary to pull apart aggregates of cohesive particles in a specified time.

In these experiments, the effect of mass % calcium lignosulfonate in the final product on the structure and surface area of laboratory-made Ca(OH)$_2$ is investigated. Also, the reactivity of the laboratory-made hydrates to carbonation is tested. Bulk flow properties of the hydrates as a function of % lignosulfonate are tested using four commercial hydrates obtained from Dravo Lime Company.

B. EXPERIMENTAL

Laboratory-made hydrates.

Hydrates are made in the laboratory using 2 grams of reagent-grade (high purity) CaO and 20 ml distilled water per batch. This volume of water gives 30X the theoretical amount needed for complete hydration. In making the hydrates, the CaO powder is placed in a beaker and the distilled water in the temperature range 70-80°C is added while stirring. The beaker is then placed in a vacuum oven at T = 50°C for 24 hours. The dried cake is then ground in a mortar and pestle. A portion of the powder samples are filtered after the drying process with distilled water (T = 70-80°C) and re-dried.

The calcium lignosulfonate used in these studies is made by Pfaltz & Bauer, Inc. and contains 80% calcium lignosulfonate, 9.2% sugars and 1% insolubles. For the modified hydrates, the necessary mass of calcium
lignosulfonate to equal the final product mass percent is dissolved in the water of hydration prior to adding it to the CaO. The mass percentages of calcium lignosulfonate in the final product investigated are 0.0%, 0.38%, 0.75%, 1.13%, 1.5%, 3.7% and 7.1%. The pH of the calcium lignosulfonate solutions are measured to be approximately 5.

Differences in the morphology of the dried powders are determined using a scanning electron microscope. A chemical surface analysis of the dried powders (ESCA) is also performed. Surface areas of the resulting hydrates are measured using the nitrogen adsorption/desorption BET method.

The reactivity of the hydrates is tested at room temperature using the carbonation reaction. Carbonation is chosen as the reaction due to the ease and safety of the experiments. It is suspected that sulfation will yield similar results. To conduct the experiments, the powdered hydrates are placed in petri dishes and set in an evacuated chamber at room temperature. Carbon dioxide from a gas cylinder is bubbled through water before entering the chamber. The pressure in the chamber is adjusted to equal atmospheric. The hydrates are exposed to the CO₂ and moisture for 12 hours. The extent of carbonation of the hydrates is measured using thermogravimetric analysis (TGA) with a Perkin-Elmer TGA 7 instrument.
Flowability Analysis.

To measure differences in dry powder flow as a function of % lignosulfonate (LS) added, commercial hydrates provided by Dravo Lime Company are used. Commercial hydrates are used for these experiments since large quantities are required. The hydrates used are from the Black River quarry. Pure Black River hydrate (BRH) is tested along with three lignosulfonate-modified BRH’s or lignohydrates. The lignohydrates contain 0.5% LS (LH-109), 1.0% LS (LH-108) and 1.3% LS (CH-3-L).

The equipment used to test these hydrates is the Hosokawa Powder Tester made by Hosokawa Iron Works, LTD in Osaka, Japan (See Figure 21). This equipment is based on the research performed and published by Ralph L. Carr, Jr. (Carr, 1965). The Powder Tester reduces human error involved when manually testing for the flowability of dry powders. The properties of interest in this study are dispersibility, compressibility and cohesion. This instrument is used to compare the differences in these properties with the addition of calcium lignosulfonate to the hydrate.

The dispersibility is determined by placing a pre-weighed watch glass under the Dispersing Measuring Unit. The watch glass is centered carefully with the aid of a spacer ring. Ten grams of powder is weighed out and placed in the container above the glass tube. A lever opens the
Figure 21: Hosokawa Powder Tester.
damper and allows the powder to fall through the glass tube and onto the watch glass. The watch glass and powder are weighed and the dispersibility is obtained by the following:

\[(10 - \text{Weight of powder on watch glass}) \times 10 = \% \text{Dispersibility.}\]

This measurement is repeated three times and the results averaged.

Compressibility, C, is calculated from the aerated (A) and packed (P) bulk densities using Eqn. (33). The aerated bulk density is determined by placing powder on a screen which is then vibrated at a controlled flow rate into a pre-weighed cup of volume 100 cm\(^3\). Once the powder fills and overflows the cup, the vibration is stopped and the powder mound is leveled with a scraper. The leveled cup is weighed and the difference between the full container and empty container divided by 100 gives the aerated bulk density in g/cc. This measurement is repeated 3 times to obtain an average figure.

The packed bulk density is then measured by taking the sample in the aerated bulk density measurement and placing it in an automatic tapping device. A cup extension is placed on top of the cup which is filled to the top with more powder. The tapping device is activated and the tapping is made 180 times. During the tapping, more powder is added if the level drops below the rim of the cup. When the tapping is stopped, the cup is again leveled with the scraper and weighed. The packed bulk density is then
determined in the same way as the aerated bulk density.

The cohesion is measured by vibrating 2 grams of powder through a series of screens. The time of the vibration is pre-set depending on the properties of the powder. When the vibration stops, the amount of powder on each screen is weighed. The % cohesion is determined by adding the percentage of powder on each screen.

Cohesion is also measured using the Ajax - W.S.L. Cohesion Tester manufactured by Ajax Equipment (Bolton) Ltd (See Fig. 22). This instrument is designed to measure directly the cohesive strength of samples of powders which are prepared in various states of compaction. The samples are prepared by filling the sample container with powder and preloading the surface to give a stable compact of known bulk density. The powder compact is then sheared by embedding the radially finned cell into the sample. The handle of the loading screw is then turned carefully until the powder surface is seen to slip. The value of the counter is then recorded. Using the counter number, a value of the cohesive stress in g/cm² can be obtained from a company-provided graph relating this number to the cohesion.

C. RESULTS AND DISCUSSION

**Scanning Electron Microscopy.**

Scanning electron micrographs of the laboratory-made hydrates are shown in Figures 23-30. Comparing the micrographs between the pure hydrate and the 1.5% LS-
Figure 22: Ajax Cohesion Tester.
Figure 23: SEM micrograph of pure laboratory-made Ca(OH)$_2$. 
Figure 24: SEM micrograph showing phase contacts between hydrate particles.
Figure 25: SEM micrograph of laboratory-made 1.5% lignohydrate.
Figure 26: SEM micrograph of laboratory-made 1.5% unfiltered lignohydrate at low magnification.
Figure 27: SEM micrograph of 1.5% lignohydrate particle at high magnification.
Figure 28: SEM micrograph of laboratory-made 1.13% lignohydrate at low magnification.
Figure 29: SEM micrograph of filtered 1.5% lignohydrate, low magnification.
Figure 30: SEM micrograph of filtered 1.5% lignohydrate, high magnification.
modified hydrate shown in Figures 23 and 25, a change in the
crystal morphology is noted. All the hydrates formed in the
presence of lignosulfonate show the formation of hexagonal
single crystals. The pure hydrate shown in Figures 23 and
24, however, looks to be made up almost entirely of tiny
spherical crystals fused together into agglomerates. The
hexagonal-shaped particles, on the other hand, appear as
single crystals, that is, not agglomerated to other
particles. Also noted is an increase in the size and
quantity of the hexagonal single crystals with an increase
in the % lignosulfonate in the final product.

This change in morphology indicates that the basal
planes of the developing hydrate crystallites have been
"poisoned." In other words, the lignosulfonate molecules
have preferentially adsorbed to the basal planes, thereby
preventing further growth in this crystal direction. The
increase in number of the hexagonal single crystals with
increase in % lignosulfonate is the result of more
surfactant available to adsorb to the developing
crystallites. The larger size of the crystal plates at
higher lignosulfonate concentrations may be due to the
interference of the large lignosulfonate molecule with the
nucleation process. Therefore, existing particles will grow
larger since less nuclei are present.
Micrographs of the 1.5% unfiltered hydrate are shown in Figures 26 and 27. The presence of large agglomerates is evident. However, these agglomerates are found to be very weakly bonded, breaking apart with any slight disturbance (See Figure 27). On the other hand, the laboratory-made filtered hydrates show more agglomeration than the unfiltered samples (See Figures 28 and 29) and the agglomerates do not break apart. At high magnification (See Figure 30) these agglomerates show the presence of the hexagonal single crystals. There seems to be a greater tendency for agglomeration with the filtered hydrates.

**BET Analysis.**

Results of the surface area analyses are listed in Table 3. The BET results are shown graphically in Figure 31 for the filtered and unfiltered hydrates up to 1.5% lignosulfonate. The surface area steadily increases with an increase in % lignosulfonate for both the filtered and unfiltered hydrates up to 1.5%. However, the filtered hydrates consistently lower surface areas compared to the unfiltered hydrates.

For the lignohydrates of higher than 1.5% lignosulfonate, the surface area of the unfiltered hydrates decreases (See Table 3). There appears to be a critical percentage of lignosulfonate that leads to an increase in surface area. The increase in surface area is thought to be due to the lignosulfonate molecules adsorbing to the
Table 3: Surface Area and % Conversion data for laboratory-made hydrates.

<table>
<thead>
<tr>
<th>% Lignosulfonate</th>
<th>Surface Area (m^2/g)</th>
<th>% Carbonation</th>
<th>% Γ_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.60</td>
<td>23.0</td>
<td>N/A</td>
</tr>
<tr>
<td>0.38, unfiltered</td>
<td>7.70</td>
<td>25.1</td>
<td>0.55</td>
</tr>
<tr>
<td>0.38, filtered</td>
<td>4.27</td>
<td>16.6</td>
<td>0.31</td>
</tr>
<tr>
<td>0.75, unfiltered</td>
<td>11.81</td>
<td>24.2</td>
<td>0.84</td>
</tr>
<tr>
<td>0.75, filtered</td>
<td>8.60</td>
<td>22.7</td>
<td>0.61</td>
</tr>
<tr>
<td>1.13, unfiltered</td>
<td>26.17</td>
<td>30.5</td>
<td>1.87</td>
</tr>
<tr>
<td>1.13, filtered</td>
<td>17.42</td>
<td>29.4</td>
<td>1.25</td>
</tr>
<tr>
<td>1.5, unfiltered</td>
<td>32.46</td>
<td>39.8</td>
<td>2.32</td>
</tr>
<tr>
<td>1.5, filtered</td>
<td>20.63</td>
<td>31.6</td>
<td>1.48</td>
</tr>
<tr>
<td>3.7, unfiltered</td>
<td>25.47</td>
<td>25.3</td>
<td>1.82</td>
</tr>
<tr>
<td>7.1, unfiltered</td>
<td>27.09</td>
<td>25.6</td>
<td>1.94</td>
</tr>
</tbody>
</table>
Figure 31: Surface Area versus Mass % Lignosulfonate added to final product hydrate.
surfaces of the forming Ca(OH)$_2$ crystals. The large molecule sterically hinders the close approach of other crystallites in the solution that would otherwise agglomerate and eventually sinter as seen in the pure hydrate. Another factor that may be occurring is the electrostatic repulsion between lignosulfonate molecules adsorbed on separate crystals acting to prevent agglomeration. The decrease in surface area at the higher lignosulfonate concentrations may be due to the effect of lower nucleation and, therefore, larger particles.

**Carbonation Experiments.**

The results of the carbonation experiments are shown in Table 3. For the unfiltered hydrates, the % carbonation shows little change until 1.13% lignosulfonate in the final product. At this percentage, the % carbonation shows a large increase indicating a much greater reactivity with 1.13% and 1.5%. At percentages of 3.7 and 7.1%, the reactivity returns to a value similar to the lower percentages.

The filtered hydrates showed lower reactivity than the unfiltered with a similar trend. This effect appears to follow, at least to some extent, the changes in surface area. It is expected that a loss in surface area will lead to lower reactivity.
Figure 32 shows both the changes in surface area and conversion with the % lignosulfonate in the product hydrate. This graph shows the similar trend between these two factors.

**Powder flow experiments.**

The results from the Hosokawa Powder Tester are shown in Table 4. BET measurements are also listed. The highest surface area is noted with 0.5% lignosulfonate in the final product. This difference compared with the laboratory-made hydrates may be due to differences in purity between reagent grade CaO used in the laboratory-made hydrates and the CaO produced from the calcination of BRH. In addition, differences in purity and molecular weight of the calcium lignosulfonate will effect the final percentage.

These results are shown graphically in Figures 33-35. Figure 33 shows the change in compressibility with the % lignosulfonate. The compressibility initially increases with the addition of 0.5% lignosulfonate and then decreases at the higher concentrations. Figure 34 shows the results of dispersibility with % lignosulfonate. The dispersibility appears to increase with increasing % lignosulfonate past 0.5%. Both of these results indicate an increase in the hydrate flowability at 1.0% and 1.3% LS concentrations. It is interesting to note that the unmodified BRH shows better flowability properties than the 0.5%L-BRH (See Table 4). The almost doubling in surface area with the 0.5%
Figure 32: % Conversion and Surface Area versus Mass % Lignosulfonate for the unfiltered hydrates.
Table 4: Results of Hosokawa Powder Tester for commercial hydrates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Area (m²/g)</th>
<th>Compressibility (%)</th>
<th>Cohesion (%)</th>
<th>Dispersibility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black River Hydrate (BRH)</td>
<td>13.02</td>
<td>49.2</td>
<td>13</td>
<td>34.0</td>
</tr>
<tr>
<td>0.5%L-BRH</td>
<td>22.81</td>
<td>52.7</td>
<td>54</td>
<td>30.0</td>
</tr>
<tr>
<td>1.0%L-BRH</td>
<td>9.54</td>
<td>49.5</td>
<td>25</td>
<td>37.8</td>
</tr>
<tr>
<td>1.3%L-BRH</td>
<td>9.02</td>
<td>47.5</td>
<td>16</td>
<td>48.5</td>
</tr>
</tbody>
</table>
Figure 33: % Compressibility versus mass % lignosulfonate for commercial hydrates.
Figure 34: % Dispersibility versus Mass % Lignosulfonate for the commercial hydrates.
Figure 35: % Cohesion versus Mass % Lignosulfonate for the commercial hydrates.
lignosulfonate may be responsible. The higher surface area results in greater contact between particles, increasing the van der Waals forces and the cohesion. Also, the lower concentration of lignosulfonate means less is present on the surfaces to cause electrostatically repulsion between particles.

Figure 35 shows the results for the cohesion tests. The % cohesion is seen to increase dramatically with 0.5% LS and then decrease at the higher percentages. It is interesting to note that the % cohesion is the lowest for the unmodified BRH and yet it's dispersibility is much lower than the 1.3%L-BRH which has a slightly greater cohesion value. The cohesion appears to be related to the surface area of the hydrate whereas the dispersibility seems more dependent upon the % lignosulfonate present.

Figure 36 shows the results for the Ajax Cohesion Tester for the BRH and the 1.3%L-BRH. The results are presented as cohesive stress versus bulk density. Though the results show much scatter due to the high sensitivity of the instrument to slight variations in experimental procedure, the trends show very interesting phenomena. Again the cohesion is higher for 1.3LS-BRH compared to the BRH. However, with an increase in bulk density for the 1.3%LS-BRH, the cohesive strength decreases and approaches the value for BRH. This relationship is opposite of what is normally expected since an increase in bulk density normally
Figure 36: Results from Ajax Cohesion Tester.
leads to closer packing of the particles and greater van der Waals forces. The van der Waals forces will always be attractive between like materials. Therefore, another, stronger repulsive force must be acting to counteract the van der Waals forces. If the particles have similar charge or charged groups on the surface, the repulsive electrostatic forces would become stronger at closer separation \( F_e \propto \frac{1}{d^2} \). These results again indicate that the lignosulfonate molecules on the surface of the dry particles electrostatically repel each other.

**D. CONCLUSIONS**

The addition of calcium lignosulfonate to the water of hydration appears to improve both the dispersibility and reactivity of the resulting product hydrate. Increased reactivity is closely tied to available surface area for reaction, as expected. The increase in dispersibility is suspected to be due to the electrostatic repulsion between lignosulfonate molecules on the surfaces of the dry powder particles.

In applications where powder flowability becomes important, such as in the use of hydrate in flue-gas desulfurization, a balance between the flowability and surface area must be considered. If the powder has poor flowability, the added surface area may not be utilized.
The lignosulfonate appears to increase the surface area at a critical concentration, this concentration depending upon the CaO and surfactant purity. However, above this critical concentration the dispersibility continues to rise which may offset the effect of the decrease in surface area at the higher concentrations.
E. LITERATURE CITED


CHAPTER III
THE EFFECT OF A THIN INSULATING COATING
ON THE ADHESION OF PARTICLES
TO A GROUNDED, CONDUCTIVE SURFACE

A. INTRODUCTION

The adherence or 'sticking' of powder particles to surfaces is a common occurrence in pneumatic powder processes. Unwanted effects of adhesion are material losses and clogging of conduits and screens. Beneficial applications of adhesion include the use of powders as coating materials (Cross, 1975) and filtration (Wang and Kasper, 1991).

The equation of motion for very slow flow of a spherical, accelerating spherical powder particle in a gas is (Hinze, 1959; Brodkey, 1967)

\[
\frac{\pi}{6} d^3 \rho_p \frac{dU_p}{dt} = -3\pi \mu_d (v_p - v_g) - \frac{\pi}{6} d^3 g (\rho_p - \rho_g)
\]  

(34)

The term on the left is the force to accelerate the particle. The first term on the right-hand side is the viscous resistance force according to Stokes' law. The second term is the force of gravity. In particle adhesion, two extra forces not included in Eqn. (34) will be
responsible for particle acceleration as it adheres to the surface, i.e., the van der Waals and the electrostatic forces of adhesion.

For a sphere/flat plate geometry, the van der Waals force between a sphere of material 1 and a flat plate of material 2 will be

$$F_{\text{VDW}} = \frac{A_{12}R}{6z^2}$$  \hspace{1cm} (35)

where $A_{12}$ is the Hamaker constant for the van der Waals interaction between the sphere and flat plate and $z$ is the separation distance. Equation (35) describes the non-retarded van der Waals interaction, that is, for separation distances $z \leq 500\text{Å}$ (Israelachvili and Tabor, 1972). In terms of the Hamaker constants of the pure materials, $A_{12}$ can be calculated as

$$A_{12} = \sqrt{A_{11}A_{22}}$$  \hspace{1cm} (36)

For distances $z > 500\text{Å}$, the van der Waals forces become retarded and the force falls off to the third power of the separation distance.

The effect of a thin coating applied to a plate on the van der Waals forces will be a function of the distance of the particle from the surface. At distances greater than the coating thickness, the effect of the coating will be to decrease the attraction between the particle and the base plate material by increasing the separation distance. At separation distances on the order of the coating thickness,
the van der Waals interaction will be determined by the particle and coating properties. The value of $A_{12}$ will be calculated based on the particle and coating Hamaker constants.

If a particle is charged and the plate is conductive and grounded, the particle will be attracted to the plate by its image charge. The charged particle induces an equal and opposite charge on the surface and the charges will be separated at equal distances from the surface. The Coulomb interaction may be expressed as (Zimon, 1969):

$$ F_{im} = \frac{1}{4\pi \varepsilon_0} \frac{Q^2}{l^2} \quad (37) $$

where $Q$ is the charge on the particle, $\varepsilon_0$ is the permittivity of free space and $l$ is the distance between the centers of the charges and is expressed as

$$ l = 2(R + z + \frac{\delta}{2}) \quad (38) $$

where $\delta$ is the thickness of any insulating layer applied to the conductive plate. Equation (37) neglects any particle deformation at contact and charge displacement due to $F_{im}$.

Once a charged particle adheres to a grounded, conductive surface, the rate at which the charge "relaxes" with time is a function of the particle material. If the particle is conductive, the charge leakage to ground takes place in a fraction of a second and the image forces and hence adhesion will tend to zero. Only insulating or
semiconductive particles retain their charge, the time of action dependent on the intrinsic resistivity of the particle and the state of the medium (humidity, temperature) and the presence of adsorbed layers on the surface (Zimon, 1969).

Understanding the factors that control particle adhesion as well as determining ways to alter it are important in many pneumatic powder processes. One method of controlling adhesion is to change the condition of the surface that the particles are adhering to. If a thin coating of a new material is applied, changes will be made in both the electrostatic and van der Waals forces of adhesion. For example, applying a non-conductive coating to a grounded, conductive material will change the electrostatic force that is due to the image charge. Also, van der Waals forces will be altered since the Hamaker constant is material dependent. Caution must be exercised, however, when applying insulating layers to conductive surfaces due to the possibility of a dangerous propagating brush discharge (Zimon, 1969).

In this study, the adhesion of spherical glass particles to a grounded, conductive plate is video recorded and the particle trajectories presented using a Particle Image Velocimetry (PIV) visualization system. Particle adhesion events are video recorded for two cases; a graphite plate/glass sphere and graphite plate/12,000Å vitreous
silica coating/glass sphere combinations. The first combination is an example of adhesion of insulating particles to a grounded, conductive surface. The second combination is studied to show the effect of a thin insulating coating on particle adhesion to a grounded, conductive surface.

B. MATERIALS AND METHODS

Materials

The graphite plate material is supplied by Tokai Carbon Co. Ltd., Japan, G-152, manufactured for electrode use. The resistivity of electrode graphite is given as $1 \times 10^{-5}$ ohm-m (Smithsonian Physical Tables, 1954). The tetraethoxysilane (TEOS) used in the glow discharge deposition of vitreous silica on the graphite plate is supplied by Shinetsu Chemicals, Co., LS-2430, Japan. The resistivity of fused silica is given as greater than $2 \times 10^{12}$ ohm-m (Smithsonian Physical Tables, 1954). The glass particles are supplied by Jaygo, Inc. of size range 1-20 μm, $\rho = 2.55$. These particles, manufactured as grinding media, are chosen due to their small size and spherical shape (See Fig. 37). The composition of the particles is >67% silica (crystalline), <10% Na$_2$O, <7% K$_2$O, <6% BaO, <5% CaO, <2% BoO, <1% MgO and <1% Al$_2$O$_3$. The resistivity of these particles is not known exactly but is estimated as in the same range as the value for plate glass or 0.2 ohm-m.
Figure 37: SEM micrograph of glass particles.
Hamaker Constant

Graphite has one of the highest Hamaker constants reported. The value of $47.0 \times 10^{-20}$ J is determined using the macroscopic approach (Lifshitz, 1956), considered as one of the more accurate methods (Visser, 1972). The Hamaker constant for vitreous silica is reported in Hough and White (1980) as $6.50 \times 10^{-20}$ J using the macroscopic approximation. The Hamaker constant for the glass particles used in this study is determined from index of refraction data measured experimentally and using the macroscopic approximation. The value is determined as $6.34 \times 10^{-20}$ J.

For the van der Waals interaction between the graphite plate and the glass particles, the Hamaker constant from Eqn. (36) is $17.26 \times 10^{-20}$ J. Similarly, for the vitreous silica coating and the glass particles van der Waals interaction, the Hamaker constant will be $6.42 \times 10^{-20}$ J.

CVD Procedure

The amorphous silica coating is applied to the graphite plate by chemical vapor deposition from the decomposition reaction of tetraethoxysilane (TEOS) under plasma discharge at ambient temperatures:

$$Si(O\ell_2H_5)_4 \rightarrow SiO_2 + 4C_2H_4 + 2H_2O \quad (39)$$

A schematic of the CVD process is shown in Fig. 38. The reactor is a Pyrex tube 250 mm high by 28 mm in diameter. Prior to reaction, the reactor is evacuate for 1 hour with a rotary pump. A measured mass of TEOS is put in a small
Figure 38: Schematic of Silica CVD Process.
glass tube and set into a water bath for evaporation. The TEOS gas is mixed with oxygen and argon in the feed line. A radio frequency (RF)-plasma of the feed gas mixture is generated with a crystal-controlled power unit, RF-500 with frequency 13.5 MHz (Pearl Kogyo Co., Japan). The discharge coil is a 4 mm o.d. copper tube wound 6 turns around the outside of the reactor. The RF power is fixed at 150 W and the pressure in the reactor kept at 300 Pa during the reaction. Prior to the deposition, the graphite surface is etched with oxygen to remove impurities.

The reaction involves first the intermediate of TEOS adsorbing on the graphite plate. The adsorbed compounds are completely decomposed on the plate to silica film. The average deposition rate is 10 \( \text{Å/s} \) and the deposition time is 20 minutes.

Scanning tunneling microscopy images of the silica coating are shown in Fig. 39. The micrographs give an indication of the uniformity and smoothness of the coating. Fig. 39(a) shows a three-dimensional image of an area on the plate of 1250nm x 1250nm. Fig. 39(b) shows a two-dimensional view of the region along with a depth bar ranging from 0 to 3000 nm.

These micrographs shows the presence of depressions of approximately the thickness of the coating. These "pits" are probably due to impurities on the graphite surface at
Figure 39: STM micrographs of silica-coated graphite surface.
the time of the coating. The regions between the pits are relatively smooth and uniform.

**Visualization Experimental System**

A schematic diagram of the visualization experimental system is shown in Figure 40. A 2cm x 2cm piece of graphite is suspended from a grounded wire into the column. The base of the column is fitted with a porous plate so that the gas essentially fluidizes the glass powder. As the particles are lifted out of the bed and rise up the column, the region adjacent to the underside of the graphite plate is video recorded (See Fig. 41).

The charge existing on the particles in the column will be generated through triboelectrification. The extent of charge will depend on the means of dispersion (Kunkel, 1950). In this study, the dispersion of the particles is achieved by quickly opening the flow meter at maximum until the particle bed is bubbling violently. A cloud of particles is generated immediately above the bed. Once this cloud forms, the gas is shut off and the particles are allowed to drift up the column. Particles entering the interaction region are then recorded.

**Laser Sheeting**

The laser used in this study is a Lexel 3500, 4 watt Argon Ion laser system. FlowView optical accessories consisting of a 10-foot long fiber optics cable, adapters and a cylindrical lens, are used for generating the laser
Figure 40: Schematic of Visualization Experimental System.
Figure 41: 2-D cross section showing video recorded interaction region.
sheet. The thickness of the laser sheet is about 2 mm.

The laser sheet is positioned to illuminate the middle underside section of the graphite plate. The camera is focused on this region of illumination. The middle plate region, where the effect of flow around the edges of the plate is the least, provides for best interaction viewing.

**Video Camera Recording**

A high resolution Pulnix TM-845 frame transfer CCD array is the camera used in this study. During recording, the camera/lens system is tilted slightly upward so that the underside of the graphite surface is recorded.

**Image Processing**

Particle image velocimetry (PIV) interrogation software is used for a frame-by-frame analysis of the particle trajectory during a recorded adhesion event. A Data Translation DT-2861, 512x480x8 bit frame grabber board is used to digitize the RS-70 analog voltage output from the camera. DT-2861 provides 256 grey levels with a maximum frame grabbing speed of 1/30 second. Each frame consists of two interlaced video fields with an interval of 1/60 second. After acquiring the frame sequence of the adhering particle, grey level thresholding (both high and low pass filtering) is used to remove background and electronic noise for each frame in an effort to improve image quality. Also, any material other than the particle of interest is cut out of the screen except identifying objects used to determine the
location of the plate.

The size of the particle is determined from the frame or frames of best focus. In some frames, the particle is out of focus (indicated by an increase in image size), and these frames are not used for particle size determination. The software determines the particle size by performing an image boundary search in a clockwise manner to find the upper right, lower right, lower left and upper left corners of the particle image. An integration along the x and y axes is performed inside the identified boundary of the particle image. The centroid of the particles is then calculated from the projection. The mean radius of each particle image is calculated and, with the pre-calibrated scale factor, the actual size of the particle is obtained.

C. RESULTS AND DISCUSSION

The forces that are considered in this analysis of particle adhesion are the electrostatic, van der Waals and gravity forces. The viscous drag term is considered negligible at such low particle velocities compared to the other forces.

Figure 42 shows the results of theoretical adhesion force calculations for the two cases investigated. The y-axis equals the total adhesion force, that is, the sum of electrostatic and van der Waals forces minus the gravity force. The total adhesion force is plotted as a function of separation distance, z, for an 8 µm diameter particle.
Figure 42: Plot showing the effect of an insulating coating on the theoretical adhesion force for an 8 μm diameter particle with surface charge $Q = 1.8 \times 10^{-16}$ C.
The van der Waals force is determined using Eqn. (35) for separation distances less than 500 Å. For separation distances greater than this, the van der Waals forces fall off to the third power of the distance of separation and are considered inconsequential compared to the electrostatic forces. Therefore, the van der Waals forces are set equal to zero for these separations.

Equations (37) and (38) are used for calculating the electrostatic force contribution to the total adhesion force. For the calculation, Q is arbitrarily set equal to $1.8 \times 10^{-16}$ C, a charge measured for 10 µm particles suspended in air (Zimon, 1969). For glass (nonconductive) particles, the charges will be located at the surfaces of the particles so R is set equal to zero in Eqn. (38) for both cases. For the uncoated graphite plate/glass case, $\delta$, the coating thickness, equals zero. For the silica-coated plate in this study, $\delta$ equals 12,000 Å.

For the no coating case, the adhesion forces are greater by as much as three orders of magnitude compared to the coated case for separations less than approximately 100 Å. The adhesion force for the uncoated case is due mainly to the electrostatic interaction. For the coated case, van der Waals forces are significant to the total adhesion when they come into play at separations of 500 Å. Actual measurements show that the transition from non-retarded to retarded dipole-dipole interactions occurs gradually from
120 to 500 Å separation (Israelachvili and Tabor, 1972). Therefore, the total adhesion force will be theoretically overestimated in this range of separation.

The total adhesion force equals the gravity force at a value of $6.7 \times 10^{-12}$ N for an 8 μm particle. The total adhesion force becomes negative and, therefore, the curves are terminated at this value. The separation distance at which the gravity force dominates over the theoretical adhesive force is around $2 \times 10^{-4}$ Å for this particle.

Photographs taken directly from the video screen of recorded adhesion events of particles to the plate are shown in Figures 43-46. A comparison of the plate surfaces in Figures 43 and 45 for the graphite plate/glass particle case and the graphite/silica/glass particle case, respectively, show a much greater amount of adhesion of particles to the uncoated graphite plate compared to the coated graphite plate. The uncoated graphite plate was found to be covered with particles immediately upon suspending it in the column. The silica-coated graphite plate, on the other hand, remained relatively clean throughout all the experiments, with only a few adhered particles observed.

Particles trajectories, consisting of particle images with associated velocity vectors, obtained from the frame-by-frame PIV analysis and are shown in Figs. 47-50. Figures 47-50 illustrate particle trajectories corresponding to the
Figure 43: Photograph taken from video screen of two particles (12 and 8 μm) adhering to the uncoated graphite surface.
Figure 44: Photograph taken from video screen of one 10 μm particle adhering to the uncoated graphite surface.
Figure 45: Photograph taken from the video screen of a 10 μm particle in the vicinity of the silica-coated graphite surface.
Figure 46: Photograph taken from video screen of an 11 μm glass particle in the vicinity of the silica-coated graphite surface.
Figure 47: Particle trajectories analyzed by the PIV software for the 12 and 8 μm diameter particles in Figure 43.
Figure 48: Particle trajectory analyzed by the PIV software for the 10 \( \mu \text{m} \) diameter particle in Figure 44.
Figure 49: Particle trajectory analyzed by the PIV software for the 10 μm diameter particle in Figure 45.
Figure 50: Particle trajectory analyzed by the PIV software for the 11 \(\mu\text{m}\) diameter particle in Figure 46.
particles pointed out in Fig. 43-46, respectively. Tables 5 through 9 contain the numerical data generated by the PIV software for the trajectories shown in Figs. 47-50, respectively.

Note that for one specific particle trajectory shown in Figs. 47-50, the size of the image associated with that particle changes and is dependent upon the different degrees of focus between frames. This is due to the particle moving in and out of the plane of focus. Also, as the particle approaches the plate, the reflection of the laser off the plate makes it more difficult to pinpoint the particle location. Therefore, the particle images near the plate surface tend be larger than those removed from the plate.

The field of view of the PIV-generated trajectories correspond to that on the video screen or approximately 1.6 mm width x 1.5 mm length. The frame frequency varies and is indicated on each figure. For example, a frame grabbing speed of 1/5 means 1 frame is recorded every 5 seconds. Therefore, the particle positions recorded on a single image are separated by 5 seconds.

Figure 47 shows the adhesion of two particles to the uncoated graphite plate, with little deviation from the vertical. Figure 48 shows another particle trajectory for the uncoated case where the deviation of the particle from its original path becomes more pronounced the closer the particle is to the plate. In Fig. (48), a gap in the
Table 5: Data obtained from PIV frame-by-frame analysis for the 8 μm particle in Figure 47. Frame frequency is 5 Hz.

<table>
<thead>
<tr>
<th>Pos. #</th>
<th>X Coordinate ((X \times 10^4 \text{ m}))</th>
<th>Y Coordinate ((X \times 10^4 \text{ m}))</th>
<th>X Velocity Component ((X \times 10^{-4} \text{ m/s}))</th>
<th>Y Velocity Component ((X \times 10^{-4} \text{ m/s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.90</td>
<td>3.87</td>
<td>0.58</td>
<td>4.01</td>
</tr>
<tr>
<td>2</td>
<td>11.03</td>
<td>4.27</td>
<td>0.00</td>
<td>4.01</td>
</tr>
<tr>
<td>3</td>
<td>11.14</td>
<td>4.66</td>
<td>-0.58</td>
<td>3.86</td>
</tr>
<tr>
<td>4</td>
<td>11.16</td>
<td>5.07</td>
<td>-0.77</td>
<td>2.93</td>
</tr>
<tr>
<td>5</td>
<td>11.15</td>
<td>5.45</td>
<td>-0.77</td>
<td>1.70</td>
</tr>
<tr>
<td>6</td>
<td>11.10</td>
<td>5.67</td>
<td>-0.58</td>
<td>1.70</td>
</tr>
<tr>
<td>7</td>
<td>11.05</td>
<td>5.81</td>
<td>-0.97</td>
<td>2.78</td>
</tr>
<tr>
<td>8</td>
<td>11.04</td>
<td>6.04</td>
<td>-0.97</td>
<td>3.09</td>
</tr>
<tr>
<td>9</td>
<td>10.94</td>
<td>6.40</td>
<td>-0.39</td>
<td>2.31</td>
</tr>
<tr>
<td>10</td>
<td>10.94</td>
<td>6.85</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Table 6: Data obtained from PIV frame-by-frame analysis for the 12 μm particle in Figure 47. Frame frequency 5 Hz.

<table>
<thead>
<tr>
<th>Pos. #</th>
<th>X Coordinate (X 10^4 m)</th>
<th>Y Coordinate (X 10^4 m)</th>
<th>X Velocity Component (x 10^4 m/s)</th>
<th>Y Velocity Component (x 10^-4 m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.62</td>
<td>5.21</td>
<td>-0.21</td>
<td>3.67</td>
</tr>
<tr>
<td>2</td>
<td>6.64</td>
<td>5.22</td>
<td>-0.62</td>
<td>3.58</td>
</tr>
<tr>
<td>3</td>
<td>6.58</td>
<td>5.57</td>
<td>-0.67</td>
<td>3.27</td>
</tr>
<tr>
<td>4</td>
<td>6.52</td>
<td>5.93</td>
<td>-0.58</td>
<td>2.62</td>
</tr>
<tr>
<td>5</td>
<td>6.44</td>
<td>6.23</td>
<td>-0.48</td>
<td>1.98</td>
</tr>
<tr>
<td>6</td>
<td>6.40</td>
<td>6.46</td>
<td>-0.14</td>
<td>1.60</td>
</tr>
<tr>
<td>7</td>
<td>6.34</td>
<td>6.62</td>
<td>0.07</td>
<td>1.73</td>
</tr>
</tbody>
</table>
Table 7: Data obtained from PIV frame-by-frame analysis for the 10 μm particle in Figure 48. Frame frequency is 5 Hz.

<table>
<thead>
<tr>
<th>Pos. #</th>
<th>X Coordinate (X $10^4$ m)</th>
<th>Y Coordinate (X $10^4$ m)</th>
<th>X Velocity Component (x $10^{-4}$ m/s)</th>
<th>Y Velocity Component (x $10^{-4}$ m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.97</td>
<td>4.27</td>
<td>2.42</td>
<td>0.88</td>
</tr>
<tr>
<td>2</td>
<td>10.47</td>
<td>4.45</td>
<td>2.31</td>
<td>0.82</td>
</tr>
<tr>
<td>3</td>
<td>10.94</td>
<td>4.63</td>
<td>2.18</td>
<td>0.69</td>
</tr>
<tr>
<td>4</td>
<td>11.40</td>
<td>4.78</td>
<td>2.10</td>
<td>0.77</td>
</tr>
<tr>
<td>5</td>
<td>11.81</td>
<td>4.90</td>
<td>2.01</td>
<td>0.79</td>
</tr>
<tr>
<td>6</td>
<td>12.24</td>
<td>5.09</td>
<td>1.69</td>
<td>0.68</td>
</tr>
<tr>
<td>7</td>
<td>12.61</td>
<td>5.22</td>
<td>1.51</td>
<td>0.79</td>
</tr>
<tr>
<td>8</td>
<td>12.91</td>
<td>5.36</td>
<td>1.50</td>
<td>0.71</td>
</tr>
<tr>
<td>9</td>
<td>13.22</td>
<td>5.53</td>
<td>1.29</td>
<td>0.67</td>
</tr>
<tr>
<td>10</td>
<td>13.51</td>
<td>5.65</td>
<td>1.10</td>
<td>0.70</td>
</tr>
<tr>
<td>11</td>
<td>13.74</td>
<td>5.80</td>
<td>1.00</td>
<td>0.71</td>
</tr>
<tr>
<td>12</td>
<td>13.95</td>
<td>5.92</td>
<td>0.79</td>
<td>0.66</td>
</tr>
<tr>
<td>13</td>
<td>14.14</td>
<td>6.08</td>
<td>0.58</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Table 8: Data obtained by PIV frame-by-frame analysis for the 10 μm particle shown in Figure 49. Frame frequency is 3 Hz. X-axis parallel to the plate surface.

<table>
<thead>
<tr>
<th>Pos. #</th>
<th>X Coordinate (X 10⁻² m)</th>
<th>Y Coordinate (X 10⁻² m)</th>
<th>X Velocity Component (x 10⁻² m/s)</th>
<th>Y Velocity Component (x 10⁻⁴ m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.42</td>
<td>8.67</td>
<td>-4.07</td>
<td>0.70</td>
</tr>
<tr>
<td>2</td>
<td>8.93</td>
<td>8.82</td>
<td>-4.03</td>
<td>0.46</td>
</tr>
<tr>
<td>3</td>
<td>7.79</td>
<td>8.96</td>
<td>-2.63</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>7.31</td>
<td>9.00</td>
<td>-2.34</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>6.75</td>
<td>9.11</td>
<td>-1.64</td>
<td>0.38</td>
</tr>
<tr>
<td>6</td>
<td>6.37</td>
<td>9.17</td>
<td>-1.33</td>
<td>0.27</td>
</tr>
<tr>
<td>7</td>
<td>6.09</td>
<td>9.26</td>
<td>-0.84</td>
<td>0.34</td>
</tr>
<tr>
<td>8</td>
<td>5.85</td>
<td>9.28</td>
<td>-0.35</td>
<td>0.34</td>
</tr>
<tr>
<td>9</td>
<td>5.71</td>
<td>9.42</td>
<td>0.51</td>
<td>0.56</td>
</tr>
<tr>
<td>10</td>
<td>5.76</td>
<td>9.61</td>
<td>0.86</td>
<td>0.22</td>
</tr>
<tr>
<td>11</td>
<td>5.91</td>
<td>9.63</td>
<td>1.34</td>
<td>0.29</td>
</tr>
<tr>
<td>12</td>
<td>6.10</td>
<td>9.70</td>
<td>1.53</td>
<td>0.32</td>
</tr>
<tr>
<td>13</td>
<td>6.44</td>
<td>9.76</td>
<td>1.49</td>
<td>0.55</td>
</tr>
<tr>
<td>14</td>
<td>6.74</td>
<td>9.87</td>
<td>1.75</td>
<td>0.56</td>
</tr>
<tr>
<td>15</td>
<td>7.31</td>
<td>10.02</td>
<td>1.83</td>
<td>0.48</td>
</tr>
<tr>
<td>16</td>
<td>7.92</td>
<td>10.24</td>
<td>1.63</td>
<td>0.21</td>
</tr>
<tr>
<td>17</td>
<td>8.53</td>
<td>10.34</td>
<td>1.39</td>
<td>0.22</td>
</tr>
<tr>
<td>18</td>
<td>9.00</td>
<td>10.38</td>
<td>1.44</td>
<td>0.23</td>
</tr>
<tr>
<td>19</td>
<td>9.46</td>
<td>10.49</td>
<td>1.36</td>
<td>0.41</td>
</tr>
<tr>
<td>20</td>
<td>9.96</td>
<td>10.53</td>
<td>1.33</td>
<td>0.21</td>
</tr>
<tr>
<td>21</td>
<td>10.36</td>
<td>10.75</td>
<td>1.31</td>
<td>-0.03</td>
</tr>
<tr>
<td>22</td>
<td>10.84</td>
<td>10.67</td>
<td>0.94</td>
<td>0.43</td>
</tr>
<tr>
<td>23</td>
<td>11.23</td>
<td>10.73</td>
<td>1.02</td>
<td>0.25</td>
</tr>
<tr>
<td>24</td>
<td>11.48</td>
<td>10.96</td>
<td>0.96</td>
<td>-0.04</td>
</tr>
</tbody>
</table>
Table 9: Data obtained from PIV frame-by-frame analysis for the 11 μm particle in Figure 50. Frame frequency is 5 Hz. X-axis is parallel to plate surface.

<table>
<thead>
<tr>
<th>Pos. #</th>
<th>X Coordinate (X $10^{-4}$ m)</th>
<th>Y Coordinate (X $10^{-4}$ m)</th>
<th>X Velocity Component ($x 10^{-4}$ m/s)</th>
<th>Y Velocity Component ($x 10^{-4}$ m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.54</td>
<td>9.89</td>
<td>1.69</td>
<td>0.81</td>
</tr>
<tr>
<td>2</td>
<td>4.08</td>
<td>9.95</td>
<td>1.63</td>
<td>0.21</td>
</tr>
<tr>
<td>3</td>
<td>4.66</td>
<td>10.01</td>
<td>1.38</td>
<td>0.27</td>
</tr>
<tr>
<td>4</td>
<td>5.16</td>
<td>10.09</td>
<td>1.51</td>
<td>0.19</td>
</tr>
<tr>
<td>5</td>
<td>5.58</td>
<td>10.19</td>
<td>1.90</td>
<td>0.02</td>
</tr>
<tr>
<td>6</td>
<td>6.18</td>
<td>10.22</td>
<td>1.63</td>
<td>0.17</td>
</tr>
<tr>
<td>7</td>
<td>6.85</td>
<td>10.20</td>
<td>1.63</td>
<td>0.21</td>
</tr>
<tr>
<td>8</td>
<td>7.26</td>
<td>10.32</td>
<td>1.94</td>
<td>0.07</td>
</tr>
<tr>
<td>9</td>
<td>7.93</td>
<td>10.34</td>
<td>2.06</td>
<td>0.09</td>
</tr>
<tr>
<td>10</td>
<td>8.56</td>
<td>10.38</td>
<td>2.00</td>
<td>0.08</td>
</tr>
<tr>
<td>11</td>
<td>9.31</td>
<td>10.39</td>
<td>2.05</td>
<td>0.13</td>
</tr>
<tr>
<td>12</td>
<td>9.90</td>
<td>10.43</td>
<td>2.21</td>
<td>0.30</td>
</tr>
<tr>
<td>13</td>
<td>10.68</td>
<td>10.49</td>
<td>1.99</td>
<td>0.17</td>
</tr>
<tr>
<td>14</td>
<td>11.37</td>
<td>10.63</td>
<td>2.24</td>
<td>0.12</td>
</tr>
</tbody>
</table>
trajectory is seen close to the plate and is due to the particle moving out of the plane of focus until the instant of adhesion, corresponding to the particle image seen contacting the plate. The less direct approach to the surface of the particle in Fig. (48) compared with those in Fig. (47) may be due to differences in surface charge.

Two captured trajectories of particles near the silica-coated plate are shown in Figs. (49) and (50). The particle in Fig. (49) shows a change in direction and a slow approach to the plate. From the values for the Y component of the velocity vector (the component perpendicular to the plate surface) in Table 8, the particle shows very low velocities in the direction of adhesion and no apparent acceleration to the plate can be deduced. The particle disappeared under the plate and whether the particle actually adhered to the plate is unknown. From Fig. (50) and Table 9, the second trajectory captured near the silica-coated plate shows similar behavior in that no distinct attraction toward the plate and very low velocities are observed in the direction of adhesion.

The numerical values of the velocity vectors and distances for the particle trajectories provided by the software can only be used as approximations due to the three-dimensional motion of the particles and the slight tilting of the camera. However, it is interesting to determine an approximate adhesion force obtained
experimentally and compare it with the other forces needed to produce it. For this analysis, the trajectory corresponding to the 8 \( \mu \text{m} \) diameter particle in Fig. (47) is used to analyze the adhesion force acting on the particle.

Table 5 gives the data obtained from the PIV software for this particular particle. The axes are rotated 10 degrees clockwise to the bottom left-hand corner of the image so that the x-axis is parallel to the plate surface. From particle positions 1 to 5, the particle slows down as it approaches the surface. For positions 6, 7 and 8, the particle is accelerating to the surface. Position 9 shows a decrease in the particle velocity toward the surface possibly due to the adverse pressure gradient immediately below the plate. At position 10, the particle is on the plate surface.

For example purposes, the adhesion force is determined for the 8 \( \mu \text{m} \) particle from Position 6 to Position 7. The left side of Eqn. (35) gives an adhesion force of 3.9 \( \times 10^{-16} \) N (\( \frac{dU_p}{dt} = \frac{((U_{p,7} - U_{p,6})}{(1/5 \text{ sec})} \)). The separation distance from the plate is determined from the Y coordinates listed in the table and an average value for the two positions is 92.5 \( \mu \text{m} \). Since the separation is much greater than 500 \( \AA \), van der Waals forces are not considered in this analysis. The gravity force is constant and equals 6.7 \( \times 10^{-12} \) N. Since the adhesion force is so small, the electrostatic force should be only slightly greater than the
gravity force. For an electrostatic force on the order of the gravity force, Eqn. (37) gives a charge on the 8 μm particle of approximately $5.0 \times 10^{-15}$ C. This value is not unreasonable as Zimon (1969) reported a value of $1.8 \times 10^{-16}$ C for a 10 μm particle suspended in air. Due to the high degree of turbulence in the bubbling bed prior to dispersion, the particle charging should be higher. Using the numerical values of the particle velocities obtained from the PIV analysis verifies the assumption of negligible viscous drag force, e.g., on the order of $10^{-15}$ for the 8 μm diameter particle.

D. CONCLUSIONS

Visualization experiments show that particle adhesion is reduced for the coated case. Theory shows that the adhesion forces are reduced by up to three orders of magnitude for the case of the coated graphite for an 8 μm diameter glass particle. The range of the adhesion force is dependent upon the electrostatic forces since they act at greater separations. From the theoretical analysis, the electrostatic forces are greatly reduced for the silica-coated sample.

These experiments give visual proof that the adhesion of charged dielectric particles to a conductive surface will decrease with the addition of an insulating coating. It should be mentioned, however, that it is suspected this effect will no longer hold if the coating itself has static
charges. Also, if the coating becomes charged, there is the danger of a brush discharge. Therefore, this approach to control adhesion should be used with caution.
E. LITERATURE CITED


APPENDIX A

COMPUTER PROGRAM FOR CALCULATING THE HAMAKER CONSTANT
HAMAKER.FOR - Program for calculating Hamaker constants

The program interactively prompts for:
   Powder name
   X-ray diffraction indices NC, ND, ND
   Powder density (RHO)
   Powder molecular weight

The program calculates the Hamaker constant A and stores the
inputs and results in a disk file named "HAMAKER.DAT".

The user is prompted with '(C)ontinue or (Q)uit?'.
Type a 'C' and hit ENTER to make another
calculation.
Results of subsequent calculations are appended to the
output data file.
Type a 'Q' and hit ENTER to end the program.

WARNING! The output file HAMAKER.DAT is overwritten
each time
the program is started. Be sure you have printed out
the file's contents prior to using the program again.

IMPLICIT DOUBLE PRECISION (A - H, M - Z)
CHARACTER*20 POWDER
CHARACTER*1 ANSWER

calculation constants

E = 1.6021E-19
ME = 9.109E-31
BIGNO = 6.023E23
PI = 3.1416
H = 6.626E-34
VF = 38.07E28
VD = 25.91E28
VC = 20.91E28
CONV1 = 8.9875E15
CONV2 = 8.9875E9

create output data file

OPEN(6, FILE = 'HAMAKER.DAT', STATUS = 'NEW')

calculation loop entry point

200 CONTINUE
C prompt user for input data
C
WRITE(*,7)
7 FORMAT(1X, 'Powder = ') READ(*,8) POWDER
8 FORMAT(A20)
WRITE(*,2)
2 FORMAT(1X, 'NC = ') READ(*,1) NC
WRITE(*,3)
3 FORMAT(1X, 'ND = ') READ(*,1) ND
WRITE(*,4)
4 FORMAT(1X, 'NF = ') READ(*,1) NF
WRITE(*,5)
5 FORMAT(1X, 'RHO = ') READ(*,1) RHO
WRITE(*,6)
6 FORMAT(1X, 'Mol. Wt. = ') READ(*,1) BIŒfW
1 FORMAT(F10.4)
C write user inputs to data file
C
WRITE(6,20) POWDER
20 FORMAT(1X, 'POWDER = ', A20)
WRITE(6,21) NC
21 FORMAT(1X, 'NC = ', F10.4)
WRITE(6,22) ND
22 FORMAT(1X, 'ND = ', F10.4)
WRITE(6,23) NF
23 FORMAT(1X, 'NF = ', F10.4)
WRITE(6,24) RHO
24 FORMAT(1X, 'RHO = ', F10.4)
WRITE(6,25) BIŒfW
25 FORMAT(1X, 'Mol. Wt. = ', F10.4)
C calculate Hamaker constant
C
XC = ((NC * NC) + 2.0) / ((NC * NC) - 1.0)
XD = ((ND * ND) + 2.0) / ((ND * ND) - 1.0)
XF = ((NF * NF) + 2.0) / ((NF * NF) - 1.0)
C
SUMY = XC + XD + XF
SUMX = VC + VD + VF
SUMXY = (XC * VC) + (XD * VD) + (XF * VF)
SUMX2 = (VC * VC) + (VD * VD) + (VF * VF)
C
SMALLM = ((3.0 * SUMXY) - (SUMX * SUMY)) / ((3.0 * SUMX2) - (SUMX * SUMX))
\[
\text{SMALLB} = \frac{\text{SUMY}}{3.0} - \left(\frac{\text{SMALLM \times \text{SUMX}}}{3.0}\right)
\]

\[
C = \frac{\left(\frac{E \times E}{\text{BIGNO} \times \text{RHO}}\right)}{(\text{BIGMW} \times 3.0 \times \pi \times \text{ME})} \times \text{CONV1} / 1.0E3
\]

\[
S = -1.0 \times \left(\frac{1.0}{C \times \text{SMALLM}}\right)
\]

\[
\text{CHARV} = \left(\text{SMALLB} \times C \times S\right)^{0.5}
\]

\[
\text{BIGB} = \left(\frac{3.0 \times H \times (E^{4.0}) \times (S \times S)}{(64.0 \times (\pi^{4.0}) \times (\text{ME} \times \text{ME}) \times (\text{CHARV}^{3.0}))}\right) \times (\text{CONV2} / \text{CONV2})
\]

\[
\text{BIGN} = \frac{\text{RHO} \times 1.0E3 \times \text{BIGNO}}{\text{BIGMW}}
\]

\[
A = (\pi \times \pi) \times (\text{BIGN} \times \text{BIGN}) \times \text{BIGB}
\]

write results to screen and data file

\[
\text{WRITE(*,10)} \, A
\]

\[
\text{WRITE(6,10)} \, A
\]

10 FORMAT (IX, 'A = ', E15.4)

add an extra line

\[
\text{WRITE(*,11)}
\]

\[
\text{WRITE(6,11)}
\]

11 FORMAT(A1)

prompt user to continue with another calculation or quit program

250 WRITE(*,12)

12 FORMAT(IX, '(C)ontinue or (Q)uit?')

READ(*,13) ANSWER

13 FORMAT(A1)

IF ((ANSWER .EQ. 'C') .OR. (ANSWER .EQ. 'c')) THEN

GOTO 200

ELSEIF ((ANSWER .EQ. 'Q') .OR. (ANSWER .EQ. 'q')) THEN

GOTO 300

ENDIF

if entry wasn’t C or Q, go back and try again

GOTO 250

exit point if Q is entered

300 CLOSE(6)

STOP

END
APPENDIX B

COMPUTER PROGRAM FOR CALCULATING
GRAVITY, ELECTROSTATIC AND VAN DER WAALS
FORCES ACTING ON A POWDER PARTICLE
PARFORCE.FOR - Program for calculating interparticle forces

The program interactively prompts for:
Output file name
Powder name
k
Hamaker constant
Powder density (RHO)
Particle separation (Z)

The program calculates the electrostatic, gravity and van der Waals forces and stores the results in user named disk file created to be compatible with the Grapher program as follows:

| Dia. (microns) | Fel | Fg | Fvdw | Fel+Fvdw | Fel+Fvdw+Fg |

The user is prompted with '(C)ontinue or (Q)uit?'. Type a 'C' and hit ENTER to make another calculation.

WARNING! The output file is overwritten each time if the user enters a duplicate file name. Be sure you save each file using a unique name.

IMPLICIT DOUBLE PRECISION (A - H, O - Z)
CHARACTER*20 POWDER, FILENAME
CHARACTER*1 ANSWER

calculation constants

G = 9.8
PI = 3.1416

calculation loop entry point

200 CONTINUE

prompt for name of output data file

WRITE(*,9)
9 FORMAT(I9, 'Output file name = \')
READ(*,8) FILENAME

open output data file
OPEN(6, FILE=FILENAME, STATUS='NEW')

prompt for input data

1 FORMAT(F12.4)
WRITE(*,7)
7 FORMAT(IX, 'Powder = ')
READ(*,8) POWDER
8 FORMAT(A20)
WRITE(*,2)
2 FORMAT(IX, 'k = ')
READ(*,1) SMALLK
4 FORMAT(F10.4)
WRITE(*,3)
3 FORMAT(IX, 'A(E-20) = ')
READ(*,1) A
WRITE(*,5)
5 FORMAT(IX, 'RHO = ')
READ(*,1) RHO
WRITE(*,6)
6 FORMAT(IX, 'Particle separation, Z(E-10) = ')
READ(*,1) ZIN

Z = ZIN * 1.0E-10

WRITE(*,30)
30 FORMAT(A1)
WRITE(*,31)
31 FORMAT(IX, 'The program calculates 100 data points.')
WRITE(*,32)
32 FORMAT(IX, 'Enter a starting diameter (in microns) /
and')
WRITE(*,33)
33 FORMAT(IX, 'interval step size to obtain the desired /
range.')
WRITE(*,30)
WRITE(*,34)
34 FORMAT(IX, 'Starting diameter (microns) = ')
READ(*,1) START
WRITE(*,35)
35 FORMAT(IX, 'Ending diameter (microns) = ')
READ(*,1) FINAL

calculate for particle sizes specified by user

DO 100 I= 0,99

set particle size

STEP = (FINAL-START)/100.0
D = (START + (REAL(I) * STEP)) * 1.0E-6
C calculate electrostatic force
P = (3.0 * SMALLK) / (SMALLK + 2.0)
FEL = 1.0E3 * P * ((D ** 2.0) / 4.0)

C calculate gravity force
FG = RHO * G * ((PI * (D ** 3.0)) / 6.0)

C calculate van der Waals force
BIGA = A * 1.0E-20
FVDW = (BIGA * D) / (12.0 * (Z **2.0))

C calculate total forces
FTOT1 = FEL + FVDW
FTOT2 = FEL + FVDW + FG

C write results to output file
BIGD = D * 1.0E6
WRITE(6,15) BIGD, FEL, FG, FVDW, FTOT1, FTOT2
15 FORMAT(IX, 6E13.4)

100 CONTINUE

C prompt user to continue with another calculation or quit program
250 WRITE(*,12)
12 FORMAT(IX, ' (C)ontinue or (Q)uit?')
READ(*,13) ANSWER
13 FORMAT(A1)
   IF ((ANSWER .EQ. 'C') .OR. (ANSWER .EQ. 'c')) THEN
      GOTO 200
   ELSEIF ((ANSWER .EQ. 'Q') .OR. (ANSWER .EQ. 'q')) THEN
      GOTO 300
   ENDIF

C if entry wasn't C or Q, go back and try again
GOTO 250

C exit point if Q is entered
CLOSE(6)

STOP
END
C PARFORCE.FOR - Program for calculating interparticle forces
C
C The program interactively prompts for:
C  Output file name
C  Powder name
C    k
C  Hamaker constant
C  Powder density (RHO)
C  Particle separation (Z)
C
The program calculates the van der Waals and drag forces as a function of particle diameter and stores the results in user named disk file created to be compatible with the Grapher program as follows:

Dia. (microns) | Fvdw | Fd |

The user is prompted with '(C)ontinue or (Q)uit?'. Type a 'C' and hit ENTER to make another calculation.

WARNING! The output file is overwritten each time if the user enters a duplicate file name. Be sure you save each file using a unique name.

IMPLICIT DOUBLE PRECISION (A - H, K - Z)
CHARACTER*20 POWDER, FILENAME
CHARACTER*1 ANSWER

C calculation constants
C
G = 9.8
PI = 3.1416
MU = 184.6E-7

C calculation loop entry point
200 CONTINUE

C prompt for name of output data file
C
WRITE(*,9)
9 FORMAT(IX, 'Output file name = '
READ(*,8) FILENAME

C open output data file
C
OPEN(6, FILE=FILENAME, STATUS='NEW')
C prompt for input data

1 FORMAT(F12.4)
WRITE(*,7)
7 FORMAT(1X, 'Powder = \')
READ(*,8) POWDER
8 FORMAT(A20)
4 FORMAT(F10.4)
WRITE(*,3)
3 FORMAT(1X, 'A(E-20) = \')
READ(*,1) A
WRITE(*,6)
6 FORMAT(1X, 'Particle separation, Z(E-10) = \')
READ(*,1) ZIN
WRITE(*,20)
20 FORMAT(1X, 'Db is how many times Da?\')
READ(*,1) XDA
WRITE(*,21)
21 FORMAT(1X, 'The relative velocity, Ur (m/s) = \')
READ(*,1) UR
C
Z = ZIN * 1.0E-10
C
30 FORMAT(A1)
WRITE(*,30)
31 FORMAT(1X, 'The program calculates 100 data points.\')
WRITE(*,31)
32 FORMAT(1X, 'Enter a starting diameter (in microns) /and\')
WRITE(*,32)
33 FORMAT(1X, 'interval step size to obtain the desired /range.\')
WRITE(*,33)
34 FORMAT(1X, 'Starting diameter (microns) = \')
READ(*,1) START
WRITE(*,34)
35 FORMAT(1X, 'Ending diameter (microns) = \')
READ(*,1) FINAL
C
calculate for particle sizes specified by user
C
DO 100 I= 0,99
C
c set particle size
C
STEP = (FINAL-START)/100.0
DA = (START + (REAL(I) * STEP)) * 1.0E-6
DB = (XDA*DA)
C
calculate van der Waals force
BIGA = A * 1.0E-20
DR = ((DA*DB)/(DA + DB))
FVDW = ((BIGA * DR) / (12.0 * (Z**2.0)))

calculate drag force

FD = ((3.0 * PI * MU * UR * DA * DB)*(DB - DA)) /
   6 ((DA**2.0) - (DA*DB) + (DB**2.0))

write results to output file

DB = DB * 1.0E6
DA = DA * 1.0E6
RA = DA/2.0
RB = DB/2.0
RR = (2.0*RA*RB/(RA + RB))

WRITE(6,15) A, UR, DA, DB, RR, FVDW, FD
15 FORMAT(1X, 7E13.4)

100 CONTINUE

prompt user to continue with another calculation or quit program

WRITE(*,12) '(C)ontinue or (Q)uit?')
12 FORMAT(*,13) ANSWER
13 FORMAT(A1)
   IF ((ANSWER .EQ. 'C') .OR. (ANSWER .EQ. 'c')) THEN
      GOTO 200
   ELSEIF ((ANSWER .EQ. 'Q') .OR. (ANSWER .EQ. 'q')) THEN
      GOTO 300
   ENDIF

if entry wasn't C or Q, go back and try again

GOTO 250

exit point if Q is entered

300 CLOSE(6)

STOP
END
APPENDIX D

RAW DATA FOR AEROSIZER EXPERIMENTS
Figure 51: Pre-transport Aerosizer data for calcite.
Figure 52: Pre-transport Aerosizer data for calcite.
Figure 53: Post-transport Aerosizer data for calcite.
Figure 54: Post-transport Aerosizer data for calcite.
Figure 55: Pre-transport Aerosizer data for dolomite.
Figure 56: Post-transport Aerosizer data for dolomite.
Figure 57: Post-transport Aerosizer data for dolomite.
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>DOLomitIC HYDRATE</th>
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</thead>
<tbody>
<tr>
<td>DENSITY</td>
<td>2.60</td>
</tr>
<tr>
<td>PMT VOLUME (ml/s)</td>
<td>1360.0</td>
</tr>
<tr>
<td>LEVER INTENSITY</td>
<td>1.0</td>
</tr>
<tr>
<td>DROPLET FREQUENCY</td>
<td>4.0</td>
</tr>
<tr>
<td>DROPLET SIZE</td>
<td>2024.06</td>
</tr>
<tr>
<td>LOWEST SIZE LIMIT</td>
<td>6.50</td>
</tr>
<tr>
<td>FINAL SIZE</td>
<td>4.8</td>
</tr>
<tr>
<td>STANDARD DEVIATION</td>
<td>1.37</td>
</tr>
</tbody>
</table>

<table>
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<th>UPPER</th>
<th>LOWER</th>
<th>UPPER</th>
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<th>UPPER</th>
<th>LOWER</th>
<th>UPPER</th>
<th>LOWER</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIZE</td>
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<td>SIZE</td>
<td>SIZE</td>
<td>SIZE</td>
<td>SIZE</td>
<td>SIZE</td>
<td>SIZE</td>
<td>SIZE</td>
<td>SIZE</td>
</tr>
<tr>
<td>1.00</td>
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<td>20.0</td>
<td>0.005</td>
<td>50.0</td>
<td>0.005</td>
<td>180.0</td>
<td>0.005</td>
<td>160.0</td>
<td>0.005</td>
</tr>
<tr>
<td>1.46</td>
<td>0.52</td>
<td>1.52</td>
<td>0.52</td>
<td>2.52</td>
<td>0.52</td>
<td>4.6</td>
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<td>0.52</td>
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<tr>
<td>1.87</td>
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<td>0.67</td>
<td>2.93</td>
<td>0.67</td>
<td>3.97</td>
<td>0.67</td>
<td>4.97</td>
<td>0.67</td>
</tr>
</tbody>
</table>

**Figure 58:** Pre-transport Aerosizer data for dolomitic hydrate.
Figure 59: Pre-transport Aerosizer data for dolomitic hydrate.
Figure 60: Post-transport Aerosizer data for dolomitic hydrate.
**Figure 61:** Pre-transport Aerosizer data for hydrated lime.
Figure 62: Pre-transport Aerosizer data for hydrated lime.
Figure 63: Pre-transport Aerosizer data for hydrated lime.
Figure 64: Post-transport Aerosizer data for hydrated lime.
<table>
<thead>
<tr>
<th>Material</th>
<th>Hydroclime</th>
<th>Sintered Control</th>
<th>Sinter</th>
<th>Sinter</th>
<th>Sinter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>2.74</td>
<td>2.74</td>
<td>2.74</td>
<td>2.74</td>
<td>2.74</td>
</tr>
<tr>
<td>Flow Rate (g/min)</td>
<td>1100.0</td>
<td>1100.0</td>
<td>1100.0</td>
<td>1100.0</td>
<td>1100.0</td>
</tr>
<tr>
<td>Lower Limit</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Upper Limit</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Figure 65: Post-transport Aerosizer data for hydrated lime.
Figure 66: Post-transport Aerosizer data for hydrated lime.
APPENDIX E

TGA RESULTS FOR HYDRATE POWDERS
Figure 67: TGA curves for Dravo 1.3% lignohydrates showing loss of surface area with pre-carbonation.
Figure 68: TGA curves for reagent-grade CaO carbonated 12 hours (top) and calcium lignosulfonate (bottom).
Figure 69: TGA curves for 0.38% lignohydrate, unreacted (top) and carbonated 12 hours (bottom).
Figure 70: TGA curves for 0.75% lignohydrate, unreacted (top) and carbonated 12 hours (bottom).
Figure 71: TGA curves for 1.13% lignohydrate, unreacted (top) and carbonated 12 hours (bottom).
Figure 72: TGA curves for 1.50% lignohydrate, unreacted (top) and carbonated 12 hours (bottom).
Figure 73: TGA curves for 3.7% lignohydrate, unreacted (top) and carbonated 12 hours (bottom).
Figure 74: TGA curves for 7.1% lignohydrate, unreacted (top) and carbonated 12 hours (bottom).
Figure 75: TGA curves for pure Ca(OH)$_2$, unreacted (bottom) and carbonated 12 hours (top).
Figure 76: TGA curves for filtered 0.38% (top) and 0.75% (bottom) lignohydrates, carbonated 12 hours.
Figure 77: TGA curves for filtered 1.13% (top) and 1.50% (bottom) lignohydrates, carbonated 12 hours.
BIBLIOGRAPHY


Lodge, J. P. and T. L. Chan, eds., Cascade Impactor, Sampling and Data Analysis, AIHA, Akron, Ohio (1986).


