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FUNDAMENTAL MECHANISMS IN FLUE GAS CONDITIONING

Topical Report No. 2

**Literature Review and Assembly of Theories on the Interactions of Ash and
Conditioning Agents**

**By
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January 9, 1992

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INTRODUCTION

This is one of two special topical reports issued concurrently under DOE Contract No. DE-AC22-91PC90365. The Department of Energy's Pittsburgh Energy Technology Center (DOE/PETC) has sponsored a number of research and development activities in fine particulate control technology. Because of this emphasis on fine particle collection, and the potential of flue gas conditioning to increase the effectiveness of this collection, DOE/PETC is funding this investigation into the fundamental mechanisms involved in the conditioning and subsequent collection of fine particles by electrostatic precipitators (ESPs) and fabric filters. An initial review of existing literature, summarized in these two topical reports, will be followed by laboratory and pilot-scale testing to evaluate the fundamental mechanisms involved in sorbent injection and flue gas conditioning processes. This report summarizes the existing literature that describes how ash particles are modified by interactions with flue gas conditioning processes and how the mechanisms controlling these interactions affect fine particle collection. Topical Report No. 1 (issued under separate cover) contains a review of literature describing the mechanisms governing interactions of sorbents and ash particles and how these mechanisms may affect the collection of fine particles.

A substantial body of research results have been published describing the factors that influence the effectiveness of conventionally operated electrostatic precipitators (ESPs) and fabric filters. Much of the research into the factors determining ESP and fabric filter performance has been directed toward the characterization of fly ash particles and bulk fly ash behavior. The fundamental characteristics of fly ash can be expressed in terms of particle morphology (including size distribution, shape, surface area, pore geometry and particle agglomeration), chemical makeup of the particles, and the environment immediately surrounding the particles (adsorbed water or other compounds, gaseous compounds, temperature, and the concentration of surrounding ions).

ESP performance has been shown to depend on the inlet particle size distribution, the relative dielectric constant of the ash particles, and the fly ash resistivity (White, 1963). Fly ash resistivity has, in turn, been shown to depend on coal chemistry, ion mobility, and flue gas temperature, as well as the concentration of H_2O , O_2 and SO_3 in the flue gas (Bickelhaupt, 1985). The wide range of sorbent injection processes currently in use are capable of modifying all of these important parameters. Various flue gas conditioning

agents, which have been widely used to enhance ESP performance, also have the capability of modifying these parameters.

Similarly, the filtering pressure drop and collection efficiency of fabric filters have been shown to be strongly dependent on characteristics of the filtered particulate matter. The resistance of the dustcake to the passage of flue gas depends on coal and ash chemistry, flue gas temperature and viscosity, and particle size distribution and morphology (Bush, et al, 1989). Poor filtration efficiency has been associated with ashes having extremely low cohesivity (Felix and Merritt, 1986). As with ESPs, sorbent injection processes can modify all of these determining factors. Other baghouse conditioning agents, although not widely applied, have shown promise for enhancing fine particle collection in specific baghouse applications (Bush, et al, 1991).

No significant interactions between particles occur until the particles are initially collected. The concentrations of particles in typical inlet flue gases are far too low for substantial interactions between suspended particles. (There are, of course, reactions between entrained particles and various flue gas constituents.) Particles collected on the grounded electrode in an ESP or on the dustcake in a fabric filter form layers or agglomerates that exhibit characteristics that strongly influence the effectiveness of the overall particle collection process. In ESPs, bulk ash resistivity is the most important ash characteristic determining collection performance (White, 1963). The effect of resistivity on ESP performance has been extensively studied. Standardized laboratory and in situ measurement apparatus and procedures have been developed to quantify the resistivity of ash. For fabric filter applications, the cohesivity of the ash collected in the dustcake is a key determinant of collection efficiency and filter cleanability (Bush, et al, 1989). The study of the effects of cohesivity on fabric filter performance is relatively immature, and there are no standard measurements to quantify cohesivity.

Resistivity and cohesivity are derived from the characteristics of the entrained fly ash particles and the flue gas environment. In some cases the mechanisms by which these properties influence fine particle collection have been identified, while in other cases proposed mechanisms are based primarily on empirical evidence. Although many programs have successfully demonstrated the advantages of flue gas conditioning for improving particulate collection, most of the fundamental mechanisms involved in these processes remain poorly understood. The development of conditioning processes for the enhancement of fine particle collection is hampered by a lack of a comprehensive

understanding of these mechanisms. Flue gas conditioning involves the modification of one or more of the parameters which determine the magnitude of the forces acting on the fly ash particles, and can take place through many different methods. Modification of particulate properties can alter ash resistivity or ash cohesivity and result in improved control device performance. The modification can be caused by changes to the flue gas, addition of particulate matter such as flue gas desulfurization (FGD) sorbents or the addition of reactive gases or liquids. Also it may be possible to modify the operating parameters of the ESP or fabric filter to match the characteristics of the particles to be collected. If the mechanisms by which conditioning agents and FGD sorbents react with fly ash particles can be better understood, selective application of appropriate conditioning agents may result in significantly improved fine particle collection at lower capital and operating costs.

SPECIFIC OBJECTIVES

The overall goal of this research project is to formulate a mathematical model of flue gas conditioning. This model will be based on an understanding of why ash properties, such as cohesivity and resistivity, are changed by conditioning. Such a model could serve as a component of the performance models of particulate control devices where flue gas conditioning is used. There are two specific objectives of this research project, which divide the planned research into two main parts. One part of the project is designed to determine how ash particles are modified by interactions with sorbent injection processes and to describe the mechanisms by which these interactions affect fine particle collection. The objective of the other part of the project is to identify the mechanisms by which conditioning agents, including chemically active compounds, modify the key properties of fine fly ash particles.

The study of fine particle collection in sorbent injection processes has the potential to affect the broad implementation of technologies currently available or under development to control SO₂ emissions. The investigation of flue gas conditioning agents is designed to provide for the effective development of advanced approaches to flue gas conditioning of fine fly ash particles. In both cases, the focus of the research will be on an evaluation of the fundamental mechanisms that are responsible for controlling or changing the key physical properties of the particulate matter. This evaluation will require theoretical development to describe the relationships between interparticle forces and the characteristics of the particles, and empirical trials to assess the relative magnitudes of these forces.

The literature searches, reviews of existing data, and the two topical reports are designed to provide accurate, timely information describing the state of the existing knowledge. This design ensures that the subsequent laboratory and pilot-scale studies will address those issues that are still not fully understood and that will yield the greatest benefit for the stated objectives of the project.

GOALS OF THE LITERATURE REVIEW AND TOPICAL REPORTS

The literature review was performed in order to determine the current state of knowledge with regard to the type of interactions that are likely to affect the collection of fine fly ash and/or sorbent particles. Since much of the prior research into these types of interactions was directed toward topics other than the collection of particulate matter from coal-fired sources, the literature review was not limited to this field. The literature review was designed to provide a general overview of pertinent material to the reader and to help in the development of a suitable series of tests for the investigations to be performed in the laboratory.

The two topical reports are intended both as references for use during this current project and as stand-alone documents that should be useful to other researchers working in these same areas. For this reason, some of the background information and parameters used in the literature search are presented in both topical reports. Additional articles located during the remainder of this project, but too late to be included in either of the two topical reports, will be summarized in the final report for this project. (According to the current schedule, this final report is to be issued in September, 1994.)

LITERATURE REVIEW METHOD

SEARCH PROCEDURE

An abstract search was performed through the DIALOG Information Services. This computer-based service was used to access the National Technical Information Service (NTIS), COMPENDEX PLUS, and Chemical Abstracts data bases. The NTIS data base consists of unclassified government-sponsored research, development and engineering reports, and other analyses prepared by government agencies. The COMPENDEX PLUS data base provides coverage of the worlds significant engineering and technical literature. This data base corresponds to the printed publication "Engineering Index", plus additional conference records from the Engineering Meetings file. The Chemical Abstracts data base provides the most current indexing and abstracting of the major chemical literature. Complete details of the search procedure are presented in Appendix A.

Over 35,000 abstracts were returned from this search and examined. We selected 136 articles and reports that appeared to contain information describing the factors involved in either the interactions of ashes and sorbents or in the general conditioning of ash or other fine particles. Many of these articles and reports were obtained from the holdings of Southern Research Institute's Library. The other articles and reports selected were ordered through NTIS and various interlibrary loan services.

REVIEW PROCEDURE

Thorough reviews were conducted to assemble and reconcile the theories and data applicable to the objectives of this project. The results of the laboratory studies and the articles obtained in the literature reviews performed under Contract No. DE-AC22-88PC88868 and Contract No. DE-AC22-88PC88851 were also included in this review. In addition to the information obtained through these literature reviews and abstract searches, operating experiences with ash conditioning were assembled for analysis. These field data will be especially useful in the development of meaningful test programs.

Each article or report received was read, and a summary was written. The summaries of the articles are intended to extract the parts of the article that apply to the objectives of this project. Summaries were not written for articles or reports that were found to contain no

information applicable to project objectives. The summaries of the articles and reports were grouped according to their applicability to sorbent or general conditioning applications. Appendix B in this report contains the complete summaries of articles dealing with general conditioning applications or fundamental particle-to-particle interactions. Articles dealing with sorbent conditioning applications are summarized in Topical Report No. 1. In some cases the reader of the summary has been directed to access the complete article in order to obtain the full range of information and comments presented by the author(s).

SUMMARY OF THE REVIEW

This section of the report contains a discussion of mechanisms that govern the relationships between particles in a bulk agglomerate, including descriptions of the fundamental interparticle forces and how they are related. Emphasized in the discussion are those forces dominant in the regime of particles having the properties of fly ash. Several paragraphs are devoted to descriptions of the surface chemistry of fly ash. Then there is a discussion of what the mechanisms and fly ash properties suggest can be accomplished to modify particulate properties to improve their collection.

MECHANISMS

Interactions of particles and interparticle forces are relevant at the collecting surfaces of particulate control devices: electrostatic precipitator plates, cyclone walls, or baghouse filtering fabric. At these surfaces, characteristics of the particles, the surfaces, and their environment yield a conglomerate of particles with resultant bulk properties that govern the performance of the particulate control device. Chemical reactions and physical forces will dictate the nature of the conglomerate.

Mechanisms by which particles interact define the applicable forces, and formalize the relationships between these forces, the effective range of the forces, the relative magnitudes of the forces, and the influences that can be applied to modify the strengths of the forces. Understanding these mechanisms will enable us to predict bulk particulate properties, to modify bulk particulate properties, and ultimately to improve the performance of particulate control devices.

Interparticle Forces

Forces that apply to particles in the size range of fly ashes have been listed by numerous authors. Forces that should be considered of influence in the regime of fly ash particles are listed in Table 1.

Table 1
Primary Interparticle Forces

FORCE	EFFECTIVE RANGE	SIGNIFICANT FEATURES
van der Waals	3 to 500 Å	very important because of the relatively long range of action; interparticle forces for particles of one micron diameter are four to six orders of magnitude greater than the gravitational force on the particles (Jayasinghe, 1972; Keller, 1973; Rumpf, 1972).
electrostatic (in the absence of an external electric field)	contact	quickly dissipated by grounded surfaces or humidity; greater than van der Waals forces only if particles exposed to corona charging (Visser, 1974); a small factor for particles 1 to 10 μm diameter unless $>10^5$ charges are on particles (Keller, 1973)
ionic	≤ 2 lattice spacings	10 times stronger than van der Waals force, but charges quickly cancel at distance (Hobbel, 1988); initial layer(s) of adsorbed water may form hydrogen bonds that can contribute 99% of the total adhesive force (van Oss, 1988)
adsorbed layers	<5 Å to contact	increases adhesion due to van der Waals forces by as much as 5 times up to several layers of adsorption (Visser, 1974); chemisorbed vapors are usually a monolayer thick, whereas physisorbed vapors, less tightly bound, can be many layers thick (Hench, 1971; Rietma, 1984)
capillary (liquid bridges)	contact	stronger than van der Waals forces, depending on tensile strength of the adsorbed film and the solid/liquid contact angle (Luckham, 1989); develop above a critical humidity (Coelho & Harnby, 1978)
solid bridges	contact	dissolving a water-soluble salt and then evaporating the water can leave a solid bond 10^4 times stronger than before the salt was dissolved (Williams & Nosker, 1983)

In the particle size regime of coal fly ash, van der Waals forces are generally considered the most fundamental of the interparticle forces. Other forces are usually subsidiary; that is, they become important after the van der Waals forces have attracted particles close enough together for the shorter-range forces to participate in the adhesion. At this point, the subsidiary forces may become dominant, as in the case of capillary forces, for example.

Particle size, shape, and surface roughness (traits that combine to describe particle morphology) govern the van der Waals forces. Since the distance over which these forces have significant influence is less than $0.05\ \mu\text{m}$, particle shape and the surface roughness have a large effect on the van der Waals forces. In fact, the intensity of the van der Waals force is proportional to the radii of curvature of surface asperities at the contact points (Donsi & Masimilla, 1974). Particle morphology combined with external forces applied to the particles (electrical or fluid dynamic forces) determine the number of contacts, or points of close proximity, each particle has with neighboring particles or surfaces. Adhesive forces increase with increasing proximate or contact area (Visser, 1974). Thus, decreasing particle size, particle sphericity, or particle surface smoothness will generally increase the strength of adhesive forces between particles.

Physical adsorption of gases is attributed to van der Waals forces and depends largely on particle morphology. Geometry of the particles near the contact point will promote adsorption and condensation of molecules from the gas phase (Hobbel, 1988). Adsorption will occur even when the concentration of gas molecules is far below the level for condensation. Physical adsorption can result in multiple layers of adsorbed molecules on the surface of particles. The adsorbed layers increase the area over which the interparticle forces are acting, effectively decrease the separation distance between particles, and, if extensive enough, can lead to the formation of liquid bridges between particles. Adsorbed layers may increase adhesion due to van der Waals forces by as much as a factor of five (Visser, 1974).

Only the first atomic layers on the surface of particles interact in van der Waals forces, so surface chemistry is important in determining adhesion (Lauga *et al*, 1991). However, compared to the morphology the chemical nature of the particle surface is of secondary importance for van der Waals forces (Luckham, 1989). The surface chemistry is a governing feature for some shorter-range forces. Work functions of materials, zeta potentials, and oxidation states are properties that can generate electrostatic and ionic bonds between particles.

Chemical properties of particle surfaces also affect the adsorption of gases (Fuller & Thompson, 1987). (This is, of course, the guiding principle in the development of specific sorbents to collect gaseous pollutants.) Chemical adsorption is usually limited to a monolayer, and creates stronger bonds than do physically adsorbed gases (Rietma, 1984). These strong chemical bonds normally involve ionic-covalent interactions (Hench, 1971), as is often the case with adsorbed water. The hydrogen-bonding component of interactions with adsorbed water generally makes a far greater contribution to the adhesion than the change in van der Waals forces (van Oss & Good, 1988).

Adsorbed water is almost a universal factor in the interaction of particles, even in cases of very low relative humidities (Gillespie, 1987). Monolayer coverage of adsorbed water is reported to occur at 10% relative humidity for most oxides (Fuller & Thompson, 1987). Adsorption of water is specifically pertinent in the case of fly ash under virtually all flue gas conditions (Rothenberg, 1980). The literature is extensive in its treatment of the effects of adsorbed water on interparticle adhesion. Water can be present in different forms: adsorbed monolayers or multilayers on particle surfaces, 'free' mobile water on the surface, physically adsorbed within pores in the particles, or strongly bound by chemisorption (Khan & Pilpel, 1986). The form of the water depends on the relative humidity of the gas, the morphology of the particles, the geometry of the contact points, and the surface chemistry of the particles. For a hydrophilic powder there are binding sites all over the surface allowing the formation of a monolayer and then subsequent multilayers of water; there would be many particle-to-water bonds and water-to-water bonds formed. For a hydrophobic particle surface there may be only a few sites suitable for water binding, which when saturated act as anchor points for adsorbed droplets (Buckton, 1990). Net adhesive force can vary by an order of magnitude depending on whether the particle surface is hydrophobic or hydrophilic (Leong *et al*, 1981). Agents can be applied to particles to alter the affinity of their surfaces to water, and thereby affect the adhesion.

Adsorbed water will form liquid bridges between particles when the relative humidity (RH) exceeds some critical level for condensation to occur at contact points, reported to be between 65 and 80% RH (Coelho & Harnby, 1978). A meniscus forms around the point of contact between particles, and surface tension of the liquid exerts a capillary force between the particles. The solid/liquid contact angle and the principle radii of curvature of the liquid bridge, together with the liquid surface tension, determine the magnitude of the

capillary force, and depend on the surface chemistry. There is typically a peak in the adhesive force associated with adsorbed water near 90% RH.

Drying surfaces after liquid bridges have been formed can leave residual solid bridges between particles. Any water-soluble salt can act as an adhesive in this way (William & Noker, 1983). Hydroxides of the alkali metals, abundant in fly ash and in FGD sorbents, are very soluble in water. Sulfur oxides are prevalent on the surface of fly ash particles and can yield salts upon reaction with water. Solid bridges are the strongest of interparticle bonds. Conventional particulate control devices typically operate in such a way as to systematically, or occasionally create liquid and consequential solid bridges between collected particles.

In summary, van der Waals forces, adsorption, and liquid and crystalline bridges all intimately depend upon the nature of the particle surface. The morphology of particles, their surface chemistry, and the adsorption of vapors (in particular, water vapor) determine the forces of interaction among particles. The physical and chemical nature of the surfaces of fly ash particles is a primary determinant of the types of interactions that occur between fly ash particles, or between fly ash particles and conditioning agents. In the case of fly ash, the morphology and surface chemistry of the particles are generally a consequence of the chemical composition, preparation, and combustion of the coal. Adsorption of vapors onto the fly ash is dependent on the composition and temperature of the flue gas. The following section briefly describes the surface chemistry of fly ash particles.

CHEMICAL CHARACTERISTICS OF THE SURFACES OF FLY ASH PARTICLES

The mineral core of ash particles is generally composed of an aluminosilicate glass along with the minerals quartz, mullite, hematite, and magnetite, although ashes from lignite and subbituminous coals tended to have more and different crystalline phases than these four mineral types (Buck *et al*, 1983). Because of the mechanisms involved in fly ash particle formation, the chemical environment on the surfaces of fly ash particles is relatively complex. Surface enrichment of many trace elements results in concentrations up to 75 times greater than those measured for bulk ash samples. Elements concentrated on the particle surface include As, Cd, Cu, Cr, Ga, Mo, Na, Ni, Pb, S, Sb, Se, Tl, and Zn (Klein *et al*, 1975; Davison *et al*, 1974). Natusch (1978) determined that an outer layer, 50 to 300 Å thick, is the region where the many different trace elements that are volatilized in the

combustion process reside as sulfate salts on the fly ash particles. This layer is completely soluble in water, but accounts for only 2 to 3% of the total weight of the ash.

In addition to the condensation of species on the surface of particles, vapors are adsorbed on the particle surfaces. Sulfur exists primarily as a surface layer a few nm thick on the mineral core (Mamane *et al*, 1986). The relative amounts of S and Ca indicate more S present than can be accounted for by CaSO_4 . Some of the sulfur on the particle surface is the result of adsorption of SO_2 , SO_3 , or H_2SO_4 (Natusch, 1978; Kaufherr *et al*, 1985). Analyses show a correlation between the amounts of residual sulfur and calcium in dustcake ash (Bush *et al*, 1989). There is no such correlation for ash that does not have prolonged exposure to the flue gas. These results suggest that calcium and other alkalis on the fly ash surface can continue to combine with adsorbed sulfur oxides until the available alkali is completely reacted. Sulfur adsorbed in excess of this amount is then present on the surface in other forms. Time resolved surface leaching (TRSL) techniques demonstrated that surface sulfur is present exclusively in the +6 oxidation state. TRSL also suggests that, although Ca is distributed more or less uniformly throughout fly ash particles, it may be present in a different, more soluble form near the particle surface (Natusch *et al*, 1980). Ca and Mg are probably present as soluble oxides or hydroxides on the surfaces of fly ash particles (Tidy, 1986). Surface iron is primarily in the +3 oxidation state, although the iron distributed throughout the bulk of the fly ash particles has an oxidation number of +2.

Water is readily adsorbed on fly ash particles, and its presence may increase rates of adsorption and oxidation of SO_2 by several orders of magnitude over the rates associated with a gas-solid reaction. Even at temperatures as high as 400°F, appreciable amounts of water are still chemically adsorbed on the surface of ash particles. As the temperature of the gas surrounding the fly ash particles is reduced, multimolecular layers of water rapidly develop. As is the case with the micropores on many other adsorbates, the adsorption and desorption of water to or from the micropores on fly ash particles occurs very slowly, usually requiring more than a minute to equilibrate at typical flue gas temperatures (Rothenberg, 1980). The amount of water adsorbed on ash particles depends on the relative humidity, and also on the chemical makeup of the ash particles. Ashes high in silica and alumina are difficult to wet (Harker & Pimparker, 1988).

The mineral constituents and the condensation and adsorption of volatile species determine the surface chemistry of fly ash particles. We know, mainly from empirical correlations, that certain constituents of the ash surface chemistry are controlling factors in

particulate control device performance. Key constituents on the surface include sulfur, alkali metals (calcium and sodium, in particular), and water. The following paragraphs discuss implications for particulate collection of the relationship between these surface constituents and the interparticle forces.

IMPLICATIONS FOR PARTICULATE COLLECTION

The synergism between the inherent properties of fly ash particles and the flue gas environment determines the resistivity and cohesivity of the bulk ash collected in ESPs and fabric filters. These two bulk properties, as discussed in the Introduction, are determinants of the performance of the particulate control devices.

Effects of various flue gas desulfurization processes on particulate properties and control device performance are discussed at length in the companion Topical Report No. 1. The reader is referred to that volume for a thorough treatment of that specific modification of the particulate properties and flue gas environment.

Modifications to the inherent properties of the particles generally requires the addition of material into the furnace with the coal, changes in the fineness of the coal injected into the burners, or alteration of the combustion temperature/residence time history of the particles. Some particulate additives have been injected into furnaces or upstream of particulate control devices to affect the bulk properties of the collected material. Sodium sulfate is added to coal having low sodium content to provide an enriched sodium concentration on the surface of fly ash particles. Sodium ions serve as the principal charge carriers in fly ash at elevated temperatures (Bickelhaupt *et al*, 1984). In ESPs operated at 700 to 800°F these charge carriers can become depleted in the layer of ash contiguous with the collecting electrode because of the high mobility of the sodium ions at these temperatures. The addition of sodium to the ash provides sufficient charge carriers to keep the ash resistivity from becoming so high as to degrade ESP performance.

There has been little use of particulate additives to improve fabric filter performance. Several products are offered for use as "precoat" materials: they are to be applied to new bags to provide a protective filtering dustcake. Aluminum silicate, diatomaceous earth, limestone, and coal ash are the most common materials used for this purpose. Limited tests have shown that precoating bags can improve fabric filter performance (Snyder *et al*,

1990; Carr *et al*, 1991; Merritt *et al*, 1991). Particles can also be added continuously to the gas stream to modify the filtration performance of the fly ash. Fine particles can be added in concentrations as low as 0.1% by weight to ash to reduce the cohesivity of fly ash (Snyder *et al*, 1991). These particulate additives primarily decrease van der Waals forces by increasing the ash particle separation distances and contact area.

Though primarily a function of the coal chemistry, the flue gas environment offers the best opportunity to affect the particle properties and interparticle forces through changes in the adsorption on particle surfaces.

Altering the flue gas environment through gaseous additives is a common technique to improve ESP performance. Resistivity of fly ash is controlled by the characteristics of the surfaces of the ash particles at temperatures below 400 to 450°F. Since surface chemistry controls ash resistivity, the physical and chemical processes that control the nature of the particle surfaces and their surrounding environment ultimately determine ESP performance. Alkali metal ions, which serve as charge carriers, are mobilized on the glassy surfaces of fly ash particles by water and acid (Bickelhaupt, 1975). As SO_3 , H_2SO_4 , $\text{NH}_2\text{SO}_2\text{OH}$, or NH_3 are adsorbed onto ash particles in increasing amounts, the resistivity drops until the surfaces of the particles are effectively saturated with the adsorbed compound, at which point resistivity remains constant with additional adsorption of conditioning compound. Higher particle surface area and lower temperature, both factors that influence adsorption, result in lower resistivity. Bickelhaupt (1975) suggests that the relationship between resistivity and temperature may result from more water molecules being present on a given amount of surface area at lower temperatures. Adsorption of water can be limited by the surface chemistry of the ash (high silica and alumina content, for example), which can limit the effectiveness of water conditioning for resistivity reduction.

Modifying the flue gas environment has also been demonstrated to change the cohesivity of ash. NH_3 alone or in conjunction with SO_3 injected into the flue gases entering ESPs diminish rapping emissions (Dalmon & Tidy, 1972; Dismukes, 1975). This effect is attributed to an increase in the cohesiveness of the ash collected on the grounded plates in the ESP. Solid bridges, postulated to be ammonium sulfate, have been observed between particles that were exposed to NH_3 injection. Ash cohesivity has been altered in tests of NH_3 and SO_3 injection into flue gases entering fabric filters. Felix *et al* (1986) and Miller & Laudal (1987) reported significant improvement in particle collection as a result of the

changes in ash cohesivity caused by NH_3 and SO_3 . The mechanism by which these chemicals alter ash cohesivity has been postulated to be sequential adsorption of the gases on the particle surfaces, creating liquid bridges of ammonium bisulfate between particles that can become solid bridges of ammonium sulfate, given adequate concentrations of reactants and sufficient reaction time (Snyder *et al*, 1990).

The addition of water to the flue gas has been demonstrated to reduce pressure drop in fabric filters (Ariman & Helfritch, 1977; Snyder *et al*, 1990). The pressure drop is reduced because the dustcake formed by the ash has a higher porosity, resulting from a higher ash cohesivity. Increasing the humidity of the flue gas increases the amount of adsorbed water on the particles. Increased van der Waals forces, hydrogen-bonding of adsorbed water on neighboring particles, capillary forces due to liquid bridges, and formation of solid bridges from the dissolution of surface salts may all result from the increased surface water. These changes in interparticle forces increase the adhesion of particles and the bulk ash cohesivity.

Other types of flue gas additives to alter interparticle adhesion are suggested by the review. Since adsorbed water is a critical component of the particle surface, injecting agents to moderate the particle's affinity to water should change the bulk particulate properties. Silanizing agents and other hydrophobic agents (for example, certain carboxylic acids such as stearic acid) can inhibit or even preclude the formation of liquid bridges (Karra & Fuerstenau, 1977), which would lower particulate cohesivity. Surfactants such as lignosulfonate have been used to decrease particle adhesion by decreasing the surface tension of water, and thus weakening the liquid bridges between particles. Trials of anionic and cationic surfactants have been suggested for this purpose (Snyder *et al*, 1990). Deliquescent materials, with their high affinity for water, can promote adsorption and the consequential formation of liquid bridges with their capillary forces. This action would increase particulate cohesivity.

The above synopsis provides an overview of the existing knowledge regarding the mechanisms controlling bulk particulate properties, the relationships between the particulate properties and control device performance, and the approaches that have been

tried or proposed to modify particulate properties to enhance collection efficiency. This base of knowledge provides the setting and direction for theoretical and empirical development of a comprehensive description of the factors affecting particulate properties, and guidelines for modifying particulate properties through flue gas conditioning to improve fine particle control.

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Yeh, J. T., C. J. Drummond, J. I. Joubert, D. M. Tulenko, R. R. Crynack, and M. L. Hochhauser. Performance of a Spray Dryer/ESP Flue Gas Cleanup System During Testing at the Pittsburgh Energy Technology Center. Presented at the Ninth Symposium on Flue Gas Desulfurization. Cincinnati, OH (1985).

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APPENDIX A

DETAILED DESCRIPTION OF SEARCH PROCEDURES

The literature review included a search of abstracts performed through the DIALOG Information Services. This computer-based service was used to access the National Technical Information Service (NTIS), COMPENDEX PLUS, and Chemical Abstracts data bases. The search terms used are presented in table A-1. About 35,000 abstracts were returned from this search which was performed on July 29, 1991.

Table A-1
Terms Used in Abstract Search

Set	Items	Description
1	127886	powder? or particle? or particulat? or sorbent? or ash?
2	127886	S1/ENG,NPT
3	120912	S2 not (Chromatog? or extract? or soil? or virus?? ? or viral? or pollen? or pharmaceut? or drug?)
4	6789	S3 and (inject? or spray()(dry? or drie?) or hydroxide? or reentrai? or cohesi? or adhesi? or adsor?)
5	16328	S3 and (propert? or interpartic?)
6	21722	S4-S5
7	7195	S3 and (propert? or interpartic?)
8	13463	S4 or S7

APPENDIX B

SUMMARIES OF PERTINENT ARTICLES

Albanese, V.M. Resistivity Modification for High Sulfur Coal Fired Boilers by Flue Gas Conditioning: Implications for Particulate Emissions Reduction, 75th Annual APCA Meeting (1982).

The author investigated the effects of an unnamed solid additive (probably some type of sodium compound) on ash resistivity. He points out that in some cases it is advantageous to increase resistivity. He also conjectures that chemical additive solids may well react with SO_3 before the SO_3 adsorbs on the fly ash.

American Society of Mechanical Engineers. Determining the Properties of Fine Particulate Matter, ASME Power Test Codes (1965).

This document contains useful descriptions of ASME standard methods for powder analyses. These methods will not be reproduced here.

Anonymous. Evaluating the Use of Coal, Ash Analyses for Predicting Fabric-Filter Performance, Power 125:2 (1981).

In an early review of fabric filter experiences and means for predicting fabric filter behavior, the author states several trends about the primary factors that correlate (or possibly help cause) differences in fly ash particle size. The author claims that fly ash particle size can vary up or down from the average of 13 μm MMD with coal source, moisture, sodium, sulfur, and ash contents. Fine particle sizes are associated with finely pulverized eastern coals, coarsely pulverized western coals, high total moisture, low ash content, and low sulfur content. The author states that the sodium that vaporizes in the boiler later condenses onto the fly ash particles (probably as sodium sulfate).

Ash, S. G., D. H. Everett, and C. Radke. Thermodynamics of the Effects of Adsorption on Interparticle Forces. *J. Chem Soc. Faraday Trans. 2*, 69(1973).

The authors describe a general thermodynamic analysis of the influence of adsorption on the force between particles whether in gas or immersed in a liquid. The development depends on a qualitative separation of the forces in energetic and entropic terms.

For particles in a gas, the basic equations of force are taken from the well-known Hamaker and Lifshitz theories, which depend on the dielectric properties of the particles. The effect of adsorption can be studied by measuring adsorption isotherms over a range of particle separation. Two opposing effects arise when the separation distance is decreased. Adsorption fields of the two surfaces overlap increasingly, so that each element of volume between the surfaces makes an increasing contribution to the total adsorption. At the same time, the volume between the surfaces decreases, and this tends to reduce the total adsorption. If moving the surfaces closer together causes a larger number of molecules to be accommodated at the lower potential energy of the adsorbed state, then there will be an attraction between the surfaces; whereas, if moving the surfaces together reduces the volume of the adsorption space, and "squeezes molecules out", then there will be a tendency to repulsion. These may be generally considered the energy and entropy effect respectively.

The authors show that in porous media the conventional models indicate that adsorption will always lead to swelling of the solid. However, contraction at low adsorptions have been observed. Contractions in porous solids have been explained to result from bridging of adsorbed molecules across pores, or hydrogen bonding between molecules adsorbed on opposing surfaces. Using the above-mentioned energy and entropy effects, the contributions of adsorption may be attractive or repulsive, and so cause contraction or swelling. Furthermore, there is a contractile force resulting from the decreased pressure in capillary condensed liquid.

Baker, J.W. and K.M. Sullivan. Developments in the Electrical Testing of Fly Ash in Relation to Electrostatic Precipitation, Proc. International Clean Air Conference, Brisbane, Australia (1978).

The authors compared the resistivity and other electrical properties of simulated fly ash generated from the laboratory combustion of coal with actual fly ash generated from the full-scale combustion of that same coal. The effects of particle size were closely examined in these studies. The ash resistivity and other electrical properties were found to vary with particle size. These differences were found to relate to the chemical composition of different size fractions of ash.

Benson, S.A, D.K. Rindt, G.C. Montgomery, and R.D. Sears. Microanalytical Characterization of North Dakota Fly Ash, Ind. Eng. Chem. Res. Dev. 23 (1984).

SEM/microprobe, ESCA, X-ray diffraction, and X-ray fluorescence (XRF) were used to characterize sized ash fractions from the combustion of high-sodium lignite coal. Elemental trends determined by XRF analysis show increasing concentration of Na_2O and

SO₃ and decreasing SiO₂, CaO, Fe₂O₃, and MgO with decreasing particle size. The authors conjecture that the relatively more volatile sodium salts may sublime to form very small particles of pure salt or they may condense on the surfaces of other particles such as aluminosilicates originating from clay minerals of the coal.

Bickelhaupt, R.E. Effect of Chemical Composition on Surface Resistivity of Fly Ash, EPA-600/2-75-017 (1975).

Resistivity data were taken between 60 °C and 250 °C in an environment of air containing approximately 9 % water by volume. Chemical transference experiments were conducted for two ashes having substantially different chemical compositions. Chemical analyses of the transference specimens revealed a pronounced migration of the alkali metal ions toward the negative electrode. The author observed that the surface resistivity was proportional to the concentration of these ions and that the iron concentration influenced particularly the participation of potassium. The author states that surface resistivity is sensitive to the chemical composition of fly ash because the alkali metals serve as charge carriers. It was concluded that the attack of the glassy surfaces of the fly ash particles by water and acid mobilizes the alkali metal ions. The author also observed that the measured resistance of ash layers were inversely proportional to a parameter defining the surface area of the ash when surface conduction is important. Decreases in resistivity were correlated with increased surface area and lower temperatures. The author states the rationalization for this as the tendency for more water molecules to be present on a given amount of surface area at lower temperatures.

Bridgewater, J. and I. Tranter. The Effect of Interstitial Liquid on Inter-Particle Percolation. *J. of Powder & Bulk Solids Tech.*, (2)1978.

Millimeter-size particles were allowed to percolate through a packed bed with and without the pores of the bed saturated with oil. Nothing applicable to our work was derived from this paper.

Brown, T.D., G.K. Lee, J. Reeve, and N. Sekhar. Improved Electrostatic Precipitator Performance by use of Fly Ash Conditioning Agents, *Journal of the Institute of Fuel* 51:409 (1978).

The authors evaluated the use of various conditioning agents for resistivity reduction. They postulate that surface adsorption and/or reaction of the conditioning agent reaches a saturation level producing a saturation resistivity. The acidic conditioning agents (SO₃,

H₂SO₄, and NH₂SO₂OH) were found to produce significantly greater reductions in resistivity than NH₃.

Buck, A.D., T.B. Husbands and J.P. Burkes. Studies of the Constitution of Fly Ash Using Selective Dissolution, Army Corps of Engineers, miscellaneous paper SL-83-5 (1983).

The authors detail methods for dissolving the glassy products out of fly ash particles, thereby allowing better resolution (using XRD or optical microscopy) of the crystalline phases within the particles. The best method evaluated involved the use of fluosilicic acid, and the second best method used sodium hydroxide. Several ashes obtained from operating ESP's installed on pulverized-coal-fired power plants burning different types of fuels were characterized following the dissolution process. Some of the ashes contained appreciable amounts of titanium, barium, strontium and manganese. Ashes from lignite and subbituminous coals tended to have more and different crystalline phases than the quartz, mullite, hematite, and magnetite common to almost all ashes.

Buckton, G. Contact Angle, Adsorption and Wettability - A Review with Respect to Powders. *Powder Technology*, 61(1990).

The original equation on which the theory of the contact angle was based was reported by Young (1805):

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

in which θ is the contact angle and γ_{SV} , γ_{SL} , and γ_{LV} are the interfacial free energies between the solid and liquid, the solid and vapor, and the liquid and vapor, respectively.

According to BET theory, it is the first layer of adsorbed molecules that is most significant in terms of the powder/liquid interaction. Subsequent adsorption is more like condensation, and immersion of the vapor-laden particle will require only a re-ordering of the adsorbate molecules to allow the 'condensed' outer adsorbed layers to fit in with the structure of the bulk liquid.

By use of multitemperature isotherms, it is possible to calculate the isosteric thermodynamic functions for adsorption. The isosteric heat of adsorption is related to the differential heat of adsorption, which is the heat change occurring with an infinitely small change in the amount of vapor adsorbed. However, isosteric measurements do not differentiate between the binding energies of different molecules of the adsorbate.

The favored method to measure powder vapor interactions is microcalorimetry to directly determine the enthalpy of adsorption. Combination of one adsorption isotherm and one heat of adsorption allows the calculation of the thermodynamic functions of adsorption. You can discriminate different ways vapor/liquid is binding to the powder with microcalorimetry.

The Gibbs free energy, obtained from vacuum microbalance measurements, and the microcalorimetric data allow the calculation of the entropy of adsorption.

The values for the calorimetric enthalpies of adsorption are inversely related to perceived wettability. The calorimetric values for the entropy of adsorption do rank with the wettability of the powders, suggesting entropy is the dominant factor in the wetting process.

For a hydrophilic powder it is assumed there are binding sites all over the surface allowing the formation of a monolayer and then subsequent multilayers. In such a case, many powder/water bonds and water/water bonds are formed. For a hydrophobic powder there may only a few sites suitable for water binding, which when saturated will act as anchor points for adsorbed droplets. Molecules of water must be correctly aligned with the sparse binding sites before they can bind to the hydrophobic surfaces.

The vapor load on a powder will change from day to day unless the environment is controlled.

Dielectric Spectroscopy is a method to study the mechanism of powder/water interactions. The resulting frequency response curve provides information on the freedom of movement of dipoles in the powder to align with the impose AC field. Again, 'loosely bound' water can be distinguished from 'tightly bound' water. Dielectric spectra support the calorimetric adsorption data, suggesting that water adsorbs readily over the surface of hydrophilic powder and is to some extent free to move (reduced entropic hindrance).

Two different factors can influence the surface energy of a powder; the chemical nature and physical treatment. Compensation analysis, which looks for relationships between two thermodynamic parameters, can be used to study physico-chemical phenomena: for example, enthalpy/entropy compensation analysis.

Coelho, M.C. and N. Harnby. The Effect of Humidity on the Form of Water Retention in a Powder, Powder Technology 20 (1978).

This article is the first part of a two part article that covers the effects of water on particle surfaces. At low relative humidities, the moisture associated with the particles of a powder is adsorbed water vapor. As the relative humidity increases, the thickness of the adsorbed

layer also increases, until eventually condensation occurs at the contact points, generating liquid bridges. The boundary between the two forms of water retention is determined by the stability of the liquid bridges, and occurs at a value of the relative humidity that can be derived from the BET isotherm for the adsorption of water vapor on the solid surface. The authors stress that the relative humidity is the variable that defines the boundary condition rather than the moisture content of the powder. Liquid bridges co-exist with adsorbed layers, but their contribution to the moisture content of the powder is usually much greater. There is therefore a critical value of humidity at which condensation first occurs. The authors reference G.A. Turner (Powder Technology 10 (1974)) who presents values from 65% to 80% for this critical humidity.

A liquid bridge will only be stable if its tendency to evaporate equals the tendency of water vapor to condense on it. This equilibrium can be expressed in terms of the Kelvin equation:

$$p = p_0 \exp [-(M\Delta P)/(\gamma RT)]$$

where p is the partial pressure of water vapor over the bridge, p_0 is the vapor pressure of water at the same temperature, M is the molecular weight of the vapor, γ is the density of the liquid, R is the gas constant, T is the absolute temperature, and ΔP is the pressure difference across the liquid surface. From this relation, it follows that there is a critical value of the humidity below which it is no longer possible to have stable liquid bridges.

The authors point out that application of these relationships to porous particles is basically valid, although it is no longer possible to guarantee that inside the pores liquid water cannot exist. It is indeed likely that it should, and the humidity of the air entrapped between the powder particles could be much greater than the humidity of the gas surrounding the powder. Such a situation is not an equilibrium one. The diffusion involved in this situation is a slow process, and the moisture within the powder has a buffer reaction on the entrapped air.

Coelho, M.C. and N. Harnby. Moisture Bonding in Powders, Powder Technology 20 (1978).

The authors provide an excellent summary of the critical parameters involved in the effects of bonding between unequal spherical particles (including discussions of roughness) due to the presence of varying amounts of adsorbed or condensed water on the surfaces of the particles. This article is the second part of a two part article that covers the effects of water on particle surfaces.

Moisture will be present as adsorbed vapor if the humidity is below a critical value, and as liquid bridges for higher humidities. Adsorbed layer bonding is caused by the overlapping of the adsorbed layers of neighboring particles, and its strength will therefore be proportional to the area of contact and to the tensile strength of the adsorbed film. The tensile strength of an adsorbed water film has been calculated by Rumpf to be 9.8 N/m^2 . Knowledge of the area of contact along with this value allows the interparticulate force to be calculated. Since real particles always exhibit a degree of surface roughness, the bulk of the particle surfaces will be maintained apart at a spacing approximately equal to the average peak-to-trough height of the surface irregularities. For the contribution of interacting adsorbed layers to be significant for the interaction of particles with surface regularities, the thickness of the adsorbed layers must exceed a certain minimum value. Below this value interactions are limited to the peaks of roughness.

The thickness of an adsorbed monolayer of water is given to be $\sim 3.5 \text{ \AA}$. The value of b , the BET constant, associated with the solid-water adsorption is a key factor determining the strength of the interaction between adjacent adsorbed layers of water. An increase in β means a stronger solid-vapor interaction. The minimum value of relative humidity below which no significant interaction occurs between adsorbed water layers, $H_{\min}$, is strongly dependent on β while the surface roughness is small, but rapidly loses its dependence on β as the surface roughness of the particles increases. $H_{\min}$ increases as surface roughness increases because the total surface area of interaction of the adsorbed water layers becomes progressively smaller. In fact, for sufficiently rough particles, the value of $H_{\min}$ may be equal to or greater than the critical humidity, H_c , and thus no adsorbed layer interaction will occur for such powders. (H_c is defined in the discussion of reference article above.) As soon as the critical humidity is reached, conditions are met for condensation to occur at the contact points between particles, thus generating liquid bridges.

The authors discuss the structure and geometry of liquid bridges, noting that for the same solid-liquid pair, at the same temperature, the size of the liquid bridge is a function of humidity alone. The authors discuss the components that determine the overall strength of a liquid bridge, with the resultant binding strength of the bridge decreasing with increasing humidity, until a sudden drop occurs at a value very near saturation.

Coelho and Harnby review the nature of the attractive forces that exist between particles in equilibrium with a dry atmosphere. As is commonly stated, van der Waals forces arise from the interaction of dipoles in the molecules and will only be significant for very fine powders. Because van der Waals forces vanish very rapidly with distance, they are very sensitive to surface roughness, which tends to keep particles apart. Electrostatic forces are dependent on the nature of the solid, and should also be reduced by surface roughness, as edges and corners tend to assist discharge from particles. Forces of friction and particle interlocking react to the movement of particles. Increased surface roughness greatly increases these

forces. Chemical forces result from hydrogen bonding or chemical reaction between the particles. Magnetic forces, mentioned by the authors, are not expected to be of significance in this project.

The effect of adsorbed moisture on van der Waals forces is to increase their value, as the adsorbed layers may be considered as part of the particles and a decrease in interparticle distance occurs with adsorption of moisture. Moisture in the gas around the particles rapidly decays electrostatic forces by conducting the charge away from the particles. Adsorbed moisture should also reduce mechanical forces by acting as a lubricant, and decreasing the chances for stable interlocking of particles.

The authors state that the value of $H_{\min}$ should not be considered as a sharp boundary, but rather as being a turning point at which the contribution of adsorbed layer attraction should be substantially increased. The authors cite Rumpf, who suggested that whereas, for particle sizes below $1\ \mu\text{m}$, adsorbed layers should take over from van der Waals forces, for coarser particles van der Waals interaction should be negligible and hence adsorbed layer bonding should become the main component of interparticulate forces. Rumpf also stated that this effect should be most marked for particle sizes greater than $100\ \mu\text{m}$.

Coluccia, S., S. Lavagnino, and L. Marchese. Adsorption and Dissociation of Ammonia on the Hydroxylated Surface of Magnesium Oxide Powders. *J. Chem. Soc., Faraday Trans. I*, 83(1987).

The value of this paper is the evidence that it provides that infrared spectroscopy can be used (with a great deal of interpretive skill) to determine the types of molecular bonds formed by molecules adsorbed on particle surfaces. The case studied in this paper is of limited specific interest. They noted that most adsorbed species are produced by interaction of NH_3 molecules with cations $\text{Mg}_{\text{LC}}^{2+}$ and anions $\text{O}_{\text{LC}}^{2-}$ exposed on the surface of the particle.

The authors note that excess molecular water is mostly removed from MgO particle surfaces by outgassing at 373 K, with the last traces being removed at 473 K. Surface hydroxyl groups are gradually removed as the outgassing temperature is increased up to 1073 K. All of the tests they conducted were in the absence of surface water molecules.

Dahneke, B.E. Retention Kinetics of Solid Particulates on Solid Surfaces, Special Report CRDC-SP-84021 U.S. Armament, Munitions and Chemical Command (1986).

Although this report deals with relatively large particles ($> 25\ \mu\text{m}$), and primarily with particle bounce (in the absence of induced charges and electric fields), the author does

include some useful information for adhesion and reentrainment of particles. In particle bounce and particle reentrainment processes, particle adhesion forces act to hold the particles on the surface while aerodynamic and/or inertial forces act to dislodge them. Because of the finite time required to completely dissipate the collision energy, newly collided particles that have not yet relaxed to the minimum in the interaction potential well require a smaller removal force compared to adsorbed particles that have completely relaxed to the bottom of the interaction potential well and are experiencing maximum attractive interaction. The author summarizes the action of van der Waals forces in the following way. van der Waals forces are due to induced electric dipoles. When two atoms are in close proximity, the distribution of electrons in their electron clouds fluctuate in a cooperative way to cause oscillating, induced dipoles that attractively interact to lower the system energy.

When the separation between two interacting atoms or molecules becomes small enough that their electron clouds overlap, a strong repulsive force results. This force depends strongly on separation; therefore, it is negligible at separations greater than 4 or 5 Å, and dominates at separations less than 4 Å. Thus, bodies can experience local elastic deformations (flattenings) at the point or points of contact. The author also discusses the effects of surface roughness on adhesion. When surface roughness acts to reduce the amount of material in close proximity, adhesion force and energy are reduced below the sphere-flat case. When roughness acts to increase the amount of material in close proximity, adhesion force and energy are increased. Capillary forces should not influence particle bounce because the bounce process is too short-lived; however, the effects of these capillary forces can affect the reentrainment of particles.

Dahneke states that when the particle is non-spherical or the surface rough, the interaction mechanics can be complex. It is generally not possible to obtain the large amount of detailed descriptions of the interacting surfaces for successful modeling of collision processes. He points out that the adhesion energies of all but the simplest particle-surface geometries are not accurately known.

Dahneke discusses the capture limit velocity, and notes that it is not strongly influenced by variations in surface composition. Likewise, the capillary condensation of vapors or material creep during particle-to-surface collisions are not expected to significantly influence the adhesion energy of the capture limit velocity because the duration of contact is too short. However, liquid layers already condensed or otherwise applied can strongly influence sticking probability. In general, such liquid layers strongly promote particle capture as they allow the collision energy to be dissipated through viscous resistance. The effectiveness of this capture mechanism depends on the viscosity and surface tension of the liquid and the velocity and incidence angle of the particle.

In his summary, Dahneke notes that in characterizing the collection of particles by several disparate mechanisms (interception, impaction, sedimentation and diffusion), one can generally calculate the collection by each individual mechanism and approximate the total collection as the sum of these components. Such an approach is valid because there is negligible interaction between the mechanisms in a typical aerosol system. In contrast, the mechanisms of particle reentrainment (aerodynamic drag, scouring, diffusion, vibrations and shock waves) are all strongly coupled.

Davison, R.L., D.F.S. Natusch and J.R. Wallace. Trace Elements in Fly Ash Dependence of Concentration on Particle Size, *Environmental Science and Technology* 8:13 (1974).

The authors utilized spark source mass spectroscopy, optical emission spectroscopy, atomic absorption spectroscopy, and X-ray fluorescence spectroscopy to determine that concentrations of Pb, Tl, Sb, Cd, Se, As, Zn, Ni, Cr, and S increased with decreasing particle size.

Deryagin, B.V., V.M. Muller, Y.P. Toporov, I.N. Aleinkova and G.I. Scherbina. Mechanism of Influence of Pressing on Adhesion of Elastic Particles, *Colloid Journal of the USSR* 49:4 (1987).

The authors note that the elastic deformation of a spherical particle after its contact with a rigid plate is accompanied by an increase in the adhesive forces. They show that the increase cannot be due to molecular forces, but rather must be attributed to electrostatic forces. These electrostatic forces appear as a result of the electric double layer formed at the contact.

Do, D.D. Effect of Surface Barrier on the Sorption of Gases in Microporous Solids. *AIChE Journal*, 35(1989).

The article describes a matrix of adsorption models and their domains of validity. The models are:

- Macropore-micropore diffusion-surface barrier
- Macropore-micropore diffusion
- Macropore diffusion
- Micropore diffusion
- Micropore diffusion-surface barrier
- Surface barrier
- Macropore diffusion-surface barrier

The author investigates the dependences of the models on particle size and temperature. The three basic components of these models are well-known, and the author illustrates the application of the six degenerate models to specific cases in which the diffusivities and rate constants of adsorption are known or estimated. The analyses show which mechanism of adsorption is dominant.

Do, D. D., and P.L.J. Mayfield. A new Simplified Model of Adsorption in a Single Particle. *AIChE Journal*, 33(1987).

This paper describes a new model for calculating the adsorption in a single particle with improved accuracy for fractional uptake over the linear driving force model. There is, in fact a quadratic form of the concentration driving force in the simplified model. The new model equations have two manifestations depending on whether the pore diffusion model or the solid diffusion model applies. For the case of pore diffusion the equations are

$$\frac{0.046}{n^{1.47}} (9 + 9.37n) = \ln \left[\frac{C_0}{C_0 - C} \right]$$

$$\frac{dC}{dt} = \frac{3(n+3)D_e}{R^2(\epsilon_p + \rho_p K) \left[1 + \frac{(n+3)D_e}{k_m R} \right]} (C_0 - C)$$

and, for solid diffusion the equations are

$$\frac{0.046}{n^{1.47}} (9 + 9.37n) = \ln \left[\frac{C_0}{C_0 - \frac{q}{K}} \right]$$

$$\frac{dq}{dt} = \frac{3(n+3)D_s}{R^2 \left[1 + \frac{(n+3)K\rho_p D_s}{k_m R} \right]} (KC_0 - q)$$

in which

C = intraparticle concentration

C_0 = bulk concentration

D_e = effective diffusivity

D_s = surface diffusivity

k_m = external mass transfer coefficient

$n = 0.123\tau^{-0.638}$

τ = nondimensional time = $\frac{D_e t}{R^2(\epsilon_p + \rho_p K)}$ for pore diffusion model, and = $\frac{D_s t}{R^2}$ for solid diffusion model

q = mean adsorbed concentration
 R = particle radius
 ρ_p = particle density

Donsi, G. and L. Massimilla. Particle to Particle Forces in Fluidization of Fine Powders, Fluid Ses Appl. Conference (1974).

The majority of this paper is strictly limited to the fluidization of powder beds, however the authors do state that the interparticle forces of concern are van der Waals forces and capillary forces. The presence of surface asperities is the major determining factor of the magnitude of these forces. The authors state that the intensity of these forces is proportional to the radius of curvature of particle asperities at the points of contact.

Dutta, A. and L.V. Dullea. A Comparative Evaluation of Negatively and Positively Charged Particles as Flow Conditioners for a Cohesive Powder, AIChE Symposium Series 86:276 (1990).

The authors added aluminum oxide (AOC), and Aerosil 200 (A200), a high purity silica, in their optimum amounts as flow conditioners to a cohesive powder composed of a phosphate based nonporous material. The AOC has a strong affinity for positive charges, while the A200 tends to develop a overall negative charge. The optimum amount of either additive is a small fraction of a monolayer. The authors state that charge effects, rather than spacer or ball bearing effects, govern the operation of these flow conditioners. The reasoning they use is that the optimum conditioning amounts of these two additives are so small that there seems, from SEM observations, to be too few conditioning particles to successfully separate the host particles.

The A200 was a more effective flow conditioner than the AOC. At $199 \text{ m}^2/\text{g}$, the A200 has over twice the specific surface area as the AOC ($84.2 \text{ m}^2/\text{g}$). The surface of the AOC contains both Al-OH and Al-O-Al bonds. The surface of the A200 has both siloxane and silanol groups, giving the surface a hydrophilic nature. In an introductory discussion about the ability of conditioners acting as spacers between host particles to reduce van der Waals attraction, the authors state that adsorbed gas molecules could also act as spacers.

Everett, D.H. The Effect of Adsorption on the Interaction Between Solid Particles, Pure and Applied Chemistry 48 (1976).

The author develops a unifying thermodynamic framework for the determination of the effects of adsorption on the interaction between particles. He addresses the problem of

particles in a liquid and particles in a gaseous environment. In his discussion of the gas/solid system, Everett notes how the attractive forces between two particles with adsorbed layers in close proximity can be enhanced or diminished according to their separation distance. The theoretical treatise in this article is highly idealized, and probably will not be directly applicable to the experiments or models developed as part of this project.

Fleer, G.J. and J.M.H.M. Scheutjens. Interaction between Adsorbed Layers of Macromolecules. *J. Colloid and Interface Sci.*, 111(1986).

This paper describes a theory for the interactions of polymers in colloidal suspension with a solvent between two surfaces. The theory does not apply directly to other systems. Several properties of the adsorbed layer (such as the adsorbed amount, the average extension of the polymer from the surface, and the distribution of trains, loops, and tails) can be predicted. Entropic effects and energetic factors are accounted for, and full equilibrium and restricted equilibrium conditions are modelled. The theory depends on considering the space between two surfaces as a semicrystalline lattice, with all the lattice sites occupied by either a polymer segment or a solvent molecule.

Fletcher, H.G. Coal Selection and Dual Flue Gas Conditioning to Aid in Meeting Air Pollution Control Regulations, 78th Annual APCA Meeting paper 53.1 (1985).

The author recounts the experiences of Detroit Edison's Monroe Plant with NH_3 and SO_3 conditioning for improved ESP operation. Prior to the installation of these conditioning systems, low ash resistivity (1×10^8 ohm-cm) produced heavy fly ash reentrainment losses as the electrical holding forces at the collection plates were either very low or even negative. After the installation of an NH_3 injection system between the preheater and the ESP a strong space-charge effect was observed in the inlet fields of the precipitator. This was due to the introduction of a fume of fine ammonium sulfate or ammonium bisulfate particles in the interelectrode space. The ammonium sulfate or bisulfate was also responsible for an increase in ash cohesivity which in turn reduced reentrainment. Ammonia conditioning did not change fly ash resistivity or promote particle agglomeration prior to collection.

Fletcher, H.R. Operating Experiences at Detroit Edison with Various Flue Gas Conditioning Systems, 75th Annual APCA Meeting (1982).

The author recounts conditioning experiences with combined SO_3 and NH_3 , and with sodium carbonate. The explanations of the residual effectiveness of the latter application are covered, but are available in greater detail elsewhere.

Fraioli, A.V. Mass Transfer Mechanisms for Water Adsorbed on Silica Gel, Report # CONF-871234-13 ASME Winter Meeting (1987).

In his evaluation of silica gels for water adsorption, the author used and describes humidistat tubes which employed saturated salt solutions to maintain final equilibrium partial pressures of water vapor over the adsorbent samples. He proposed that at or about 40% relative humidity, pore flooding on the external surface creates a meniscal force imbalance with respect to the menisci adjacent to unfilled voids within the interior of the particle. At this point and beyond to saturation, fluid flow in a manner analogous to wicking saturates the particle, and appears to be responsible for the appearance of the second knee in the observed classical BET Type IV isotherm. In his introduction Fraioli presents a very readable summary of the origin of the five primary types of classical BET isotherms. Type I behavior is characteristic of strongly interacting systems, where the bonding energies of the gaseous adsorbate to the adsorbent surface are much greater than those involved in the bonding of the adsorbate molecules to each other in the liquid phase. In other words, for Type I behavior, the heat of adsorption in the first layer is much greater than the heat of vaporization of the bulk liquid at the temperature of the measurement. Heats of adsorption in Type I systems range from 10 to 100 Kcal/mol., and are indicative of chemisorption, with chemical bonding to the surface.

Physical adsorption is reflected in Type II behavior and represents about 98% of the isotherms reported in the technical literature. The forces responsible for physical adsorption are the van der Waals forces created by dipole-dipole interaction of the real (if only instantaneous) dipole of the adsorbent molecule with its mirror-image-induced dipole in the adsorbent surface. Because of the heterogeneous nature of most high surface area materials undergoing Type II physical adsorption, the most energetic sites are occupied with the adsorbed polar gas molecules localized at that site; near neighbor localized adsorptions provide sites which promote lateral interactions within the partially formed film to incoming adsorbate molecules and can lead to cluster-film growth. Ultimately these regions are saturated at multilayer coverage, and a nearly asymptotic approach to a limiting adsorption at saturation is achieved by condensation forces in the bulk, now liquid-like film.

An example of a Type III isotherm for a polar adsorbate is exhibited by water on graphite. It appears that adsorption on these surfaces is de-localized by virtue of the mono-energetically uniform surface. In extreme cases the sub-monolayer film has two dimensional gas characteristics which delay the onset of lateral interactions within the film until near mid-range equilibrium adsorption pressures ($\sim 0.4 P_0$) are reached.

Type IV and V isotherms are exhibited by gases on highly porous adsorbent particles. Isotherms of types IV and V have the first layer energetics of Types I and II, respectively. They are therefore special cases of the non-porous Types differentiated by the large internal surface areas and pore size distributions which dominate the upper ends of their respective isotherms.

Fuller, E.L., Jr. and K.A. Thompson. Chemical and Geometric Factors in Physical Adsorption/Desorption of Gases and Solids. *Langmuir*, 3(1987).

This article describes analytical techniques for interpreting sorption isotherms to distinguish the pore structure and type of adsorption (capillary, monolayer, multilayer) as well as surface area of sorbents. Many of the data were obtained from tests done with a modified, automated, computer-controlled volumetric sorption apparatus (Micromeritics Model 2500) and some from tests with a vacuum microbalance. Analytical techniques include the autoshielding potential theory, which provides an adjustable extensive energy term, $E(O)$, and an intensive capacity term, $N(ASP)$, comparable to the equivalent terms from the BET theory, $C(BET)$ and $N(BET)$, respectively.

The sorption processes are strongly influenced by the chemical nature of the sorbate and sorbent as well as by the pore size and pore shape of the sorbent. Micropores are defined as those pores < 2 nm across, and mesopores are 2 to 100 nm. Monolayer formation, generally considered to be formed near $0.1 P_0$ for most oxides, involves structuring of the bound sorbate appreciably more stringent than the loss of two degrees of translational freedom for minimal association. Classically, this involves an energy change of $E(*) = RT$ and can be envisioned to occur at 1.5 monolayer coverage. This state prevails at $P/P_0 = 1/e = 0.36778...$

$$N(ASP) = \frac{2 g(a) \ln \left[\frac{E(O)}{RT} \right]}{3}$$

$$g(a) = E(*) \cdot \left[\frac{dE(*)}{dN(a)} \right]^{-1}$$

in which $E(*) = -RT \ln(P/P_0)$, and $N(a)$ is the amount sorbed.

Significant numbers of open-ended mesopores increase hysteresis in the adsorption/desorption isotherm. The surface tension effects that become important as the dimensions approach the colloidal range (~ 2.0 to 100 nm) can be used to evaluate the size and shape of mesopores through thermochemical reactions to the sorption potential $E(*)$.

Using the autoshielding theory, one can extrapolate to the behavior of a chemically identical nonmesoporous material and the pressure of experimental points on the sorption isotherm and estimate the uptake occurring in pores whose dimensions and shapes are estimated by the Laplacian/Young relationship

$$E(*) = -RT \ln \left[\frac{P}{P_0} \right] = (s) V \left[\frac{1}{r(1)} + \frac{1}{r(2)} \right]$$

in which (s) is the surface tension at the gas/liquid interface, V is the molar volume of the liquid sorbate, and r(1) and r(2) are the principal radii of curvature required to define the menisci of interest.

The sorption data plotted using the autoshielding model fit a straight line. Linearity prevails up to the range of $0.70P_0$, where the inherent bed porosity becomes significant as cavities between the crystallites. This range is far beyond the $0.35P_0$ range, which is the upper limit for the BET equation.

Gillespie, T. The Contribution of Electrostatic Induction to the Long Range Forces between Solid Particles. Particulate and Multiphase Processes: Vol. 3 Colloidal and Interfacial Phenomena.

Electrostatic effects have been reported to cause some large long-range forces between solid surfaces. These forces generally can be reduced by orders of magnitude by ionizing the air or the molecules. After ionization, a weak long-range force remains which is not diminished by prolonging the ionization. This is attributed to an inductive force that is a function of the static dielectric constant of the surfaces, the separation distance, and the number of ions on the surface per unit area. For a separation distances greater than 200 Å the force calculated by kinetic analysis is on the order of 10^{-19} J/m.

The author states that contamination of surfaces by adsorbed water is difficult to prevent or remedy. Even at high temperatures there may be an increasing amount of water generated by dehydroxylation. Therefore you must assume surface water is an intervening medium. Electrostatic inductive forces will depend on the difference between the dielectric constant of the solid surfaces and the dielectric constant of the intervening medium.

(Water was apparently eliminated in one set of experiments by flushing the apparatus with air that had been dried by passing it through sulfuric acid and sodium pentoxide.)

Using the equation for the force between two cylinders in contact, $F = 4\pi R\gamma$, where R is the radius and γ is the surface tension of water, calculated forces are much larger than any

electrostatic force due to distributed surface ions. Thus, when solids are in intimate contact the intermolecular forces are much larger than the electrostatic forces.

Good, R.J. Fundamental Research on Surface Science of Coal in Support of Physical Beneficiation of Coal, DOE Contract No. DE-AC22-87PC79905 Quarterly Technical Progress Report # 5 (1988).

The author developed a theoretical model of liquid bridging for spherical particles with concave liquid bridges having nonzero contact angles. Stability analysis with this model indicates that, as the contact angle increases, the critical distance of separation increases. This result suggests more stable liquid bridges for higher contact angles.

Görner, Peter, and Josef Pich. Generalized Theory of Dispersion Forces. J. Aerosol Science, 20(1989).

This paper presents a generalized theory to calculate the dispersion forces for sphere-sphere and sphere-plate systems over all radii and separation distances. This is accomplished by exact analytical integration of the Overbeek potential for two interacting bodies. The rigorous integration and appropriate selection of dimensionless parameters allows the development of the generalized theory.

The theory reduces to the Hamaker theory of small distance interactions (where the particle radii are much greater than the separation distance), and to the Van Silfhout expression for long-range interactions. In the Van Silfhout theory a retarded Hamaker constant is used to express the diminished interaction energy. The Generalized Theory derives the relation between the retarded and non-retarded Hamaker constant:

$$B = A 2.45\lambda(40\pi^2)^{-1}$$

in which B and A are the retarded and non-retarded Hamaker constants, respectively, and λ is the London wavelength corresponding to the chief dispersion frequency ν of the interacting atoms ($\lambda = c/\nu$, where c is the speed of light).

$$A \sim 10^{-19} \text{ J} \text{ and } \lambda \sim 10^{-7} \text{ m. } \therefore B \sim 10^{-28} \text{ J} \times \text{m}$$

The theory shows that the retardation effect on the interaction energy is not only a function of particle distance, but a function of their sizes.

Gröbner, O. Dielectric Properties of Adsorbed Gas Molecules, Journal of Chemical Physics 46:11 (1967).

The author discusses a method whereby the dielectric properties of adsorbed gas molecules can be compared. Work on this subject has shown, at least for acetylene molecules, that chemically absorbed molecules exist on the surface of alumina particles in a completely different orientation than physically absorbed molecules. The data presented supports the much stronger bonding that exists for the chemically adsorbed molecules.

Harker, J.H. and P.M. Pimparker. The effect of Additives on the Electrostatic Precipitation of Fly Ash, *Journal of the Institute of Energy* 61:448 (1988).

The authors tested ferric sulfate, phosphorous pentoxide, sulfamic acid, ammonia, sulfur trioxide, sulfur dioxide and moisture as conditioning agents in an ESP collecting reinjected fly ash suspended in a flue gas stream generated from the combustion of natural gas. The authors cite prior work of Busby and Darby who found that water conditioning is optimized at water additions of 0.008 - 0.015 kg/m³ gas, although such large amounts of water can generate condensation problems. These studies also showed that ashes that are high in silica and alumina are difficult to wet and that therefore conditioning with water does not always promote enhanced collection efficiencies. Harker and Pimparker feel that economic considerations limit the choice of conditioning agents to SO₃, H₂SO₄, and (NH₃)₂SO₄.

Hench, L. L. Characterization of Powder Surfaces - Chapter 16 of Ceramics published by Marcel Dekker. 1971.

This chapter provides a summary of the types of analytical techniques that are available to characterize the surfaces of ceramics. Surface characteristics determine agglomeration and aggregation of powders, and the reactivity of powders. Nevertheless, the author states that "the understanding of powder surfaces is perhaps the least developed of any field of science and technology".

The analytical methods for powder surface characterization include direct means which are variations of microscopy (TEM, SEM, Auger spectroscopy, Field Emission Microscopy, Field Ion Emission Microscopy, scanning electron diffraction, and low energy electron diffraction). Of these TEM comes closest to analyzing powder surface structures, but has formidable sampling problems, limited resolution, and is especially difficult for amorphous or disordered surfaces.

There are a number of indirect means for characterizing powder surfaces. Most of these have to do with adsorption measurements (interactions of the powder with liquids or gases). The experimental methods may be straightforward, but the interpretive models are difficult and/or controversial. The author reviews the nature of surface forces that are the

bases for models of powder interactions. Electrostatic potential energies, London-van der Waals dispersion forces, covalent bonding, etc. within a solid particle can extend to atoms or molecules in the proximity of a particle and result in monolayer chemisorption or physisorption at the particle surface. These are short-range forces acting only over distances of atomic and molecular radii (a few angstroms).

Chemisorbed species form a chemical bond nearly as strong as the substrate, and normally involve ionic-covalent interactions. Physical adsorption species are more weakly bonded and involve electronic interaction energies. Physisorption can occur on top of a chemisorption layer.

Two particles need only come within a distance of separation of approximately the diameter of the particles in order to be bonded by dispersion forces. These forces depend on the material Hamaker constant ($H = \frac{3}{4} \pi^2 n^2 h \nu_0 \alpha^2$ which is on the order of 10^{-13} erg), the particle radius, and the separation distance. Although only weaker bonded agglomerates arise from such interactions, additional shorter range interactions become more favorable as the particles are attracted together by the dispersion forces.

The author discusses methods for measuring surface energies. These range from simple mechanical measurements (the energy required to fracture a solid, crack propagation, crushing, drilling, bending) to a variety of thermodynamic methods (contact angle, heat of immersion, heat of solution). Of these, the critical angle of wetting is considered the most accurate. [Reduction in surface energies by as much as a factor of 5 are caused by adsorption of water layers on ceramics.]

Techniques for measuring the volume of gas sorbed on particles are used to characterize the powder-gas interface. Direct measurements of adsorption isotherms is most common, but dielectric losses, capacitance, conductance, NMR, and IR can be used for this measurement.

A physisorbed gas is bonded to a particle by London-van der Waals dispersion forces with a bond strength of approximately 7 kcal/mole or less. Chemisorbed species will have developed a strong chemical bond with the surface of 10 to 40 kcal/mole or more. Physisorption is rapid, and reversible, and may form multiple layers. Chemisorption is stable, may take a long time though the reaction rate may be much greater at higher temperatures, and is usually limited to a monolayer.

Hobbel, E.F. Cohesion and Interparticle Forces. Dissertation, 1988.

In Chapter 2 of this thesis the author describes a mathematical procedure to model the morphology of particles. This approach to describe particles was developed because characterizing particles on the basis of their interaction with their environment is does not

provide a general description of the morphology. (We need to be sensitive to this in our studies.) Different processes and different scales can yield different interactions, obscuring the physical properties of the particles. The author's objective was to investigate and interpret cohesion by relating the effects of morphology on adsorption of water, on interparticle force, and on the formation of contact areas.

(For an explanation of the mathematical procedure for describing the morphology of particles, and its relative merit, see Chapter 2 of the thesis.)

Chapter 3 discusses the forces of interaction between individual particles, and provides the most pertinent material for our purposes. The forces are divided into adhesion and friction, or normal and tangential forces respectively.

Molecular Forces of Interaction. The energy of interaction is mainly dependent on the distribution of electrons on the molecules. The forces are due to the following interactions:

ion/ion	$E \propto \frac{z_1 \cdot z_2}{4\pi\epsilon_0 R}$
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ion/dipole	$E \propto \frac{z_1 \cdot \mu_2}{4\pi\epsilon_0 R^3}$
------------	--

dipole/dipole	$E \propto \frac{\mu_1 \cdot \mu_2}{4\pi\epsilon_0 R^4}$
---------------	--

ion/induced dipole	$E \propto \frac{z_1 \cdot I}{4\pi\epsilon_0 R^4}$
--------------------	--

dipole/induced dipole	$E \propto \frac{z_1 \cdot I \cdot a}{4\pi\epsilon_0 R^6}$
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induced dipole/induced dipole	$E \propto \frac{I^2 \cdot a^2}{4\pi\epsilon_0 R^6} - \frac{1}{R^8} - \frac{1}{R^{10}}$
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for which	z = ion charge
	μ = dipole moment
	I = ionization potential
	a = polarizability
	R = radius of particles

The last in this list is the London-van der Waals force, which is the weakest in magnitude but is effective over longer distances than the others. For this reason, the other forces are usually neglected, and only the van der Waals forces are considered.

The van der Waals force is proportional to the inverse of the separation distance to the 7th power $\left[F_{vdw} \propto \frac{1}{r^7} \right]$. This expression is valid for distances from 3 to 4 Å up to 500 Å.

Forces Between Particles. The following classification of particle forces was taken from Rumpf:

Attractive forces without contact

- van der Waals forces
- electrostatic forces
- magnetic forces

Attractive forces with contact

- liquid bridges with a mobile interface
- viscous binders
- solid bridges

The total force between two particles is found by summing all individual interactions of the molecules and adding the Coulomb forces. All properties of an adsorbed layer are strongly influenced by the molecular interactions with the material in the neighborhood, which also means that the geometry of the neighborhood (e.g. curvature of the interface) can have a definite effect.

At a large distance (up to 500 Å) the forces between the particles are dominated by the van der Waals forces. The attractive forces can be calculated using the Hamaker solution. If the particles are rough, care must be taken to substitute the appropriate mean radius of the sphere, or use the radius of the approaching asperities. The large exponent of the van der Waals forces causes the material nearest to the area of contact to be dominant and small asperities may dominate completely.

Electrostatic attraction may occur when one or both particles are charged or when double layers are present. A net charge develops through breaking, rubbing, or collision when the resistivity is so high that on separating the contact between two parts the charge differences cannot equalize in time. This charge leaks away through the air, especially if there is humidity. Electrical double layers are created when the work potentials of touching particles are unequal.

Ionic interactions are stronger than the van der Waals forces (about 10 times greater) but the positive and negative charges quickly cancel each other at distance. These forces are only important at close approach of about 2 lattice spacings.

Captured molecules, e. g. water molecules, influence the interfacial properties of contacting particles. The geometry of the solid phase near to the contact will promote adsorption and condensation of molecules from the gas phase. When the molecules adsorb, the forces between the particles are influenced in two opposing ways:

The molecules increase the interfacial area and enlarge the forces between the particles by bridging and other interactions. Water may promote ionic/dipole forces and may also form hydrogen bonds between the crystal faces.

The dielectricum between the particles is changed and the dispersion forces (van der Waals forces) may be shielded by this, thus decreasing their contribution.

The overall behavior of particles is subject to the local geometry of the contacts. This geometry is completely controlled by asperities and by interference from small, adhering particles. The final contact geometry may be a network of more or less ellipsoidal capillaries running through the interfacial area. The capillaries will preferentially adsorb molecules from the gas and water may influence the separation force even at low relative humidities.

The adsorption of water on the contact area is controlled by a complex potential field. The near vicinity of the solid at the contact line and in the network of pores in the contact area itself will promote preferential adsorption of molecules. In general, pores are classified into three categories: macropores $> 100 \text{ \AA}$, mesopores $100\text{-}10 \text{ \AA}$, and micropores $< 10 \text{ \AA}$. Condensation in micropores and ultrafine pores occur at relative humidities far below the saturation point. At the contact line itself preferential adsorption will start at very low humidities. As the humidity increases this adsorption continues and the angle of contact fills.

Weak contacts have large pores and condensation does not occur easily. Strong contacts have no pores and condensation can only occur at the line of contact. The majority of contacts have meso- and micro-capillaries and condensation will influence the separation forces greatly.

The saturation pressure for a conical microcapillary is calculated from Kelvin's law:

$$\ln \left(\frac{p}{p_s} \right) = - \frac{2 \nu \tau}{r R T} \cos \delta$$

in which r = radius of curvature and τ = surface tension. This approximation is valid if the liquid bridge is at least 7 molecular layers thick. Substituting a radius of 7 atoms we find a corresponding humidity of 80%. Extrapolating to smaller radii, a thickness of 2 layers coincides with 30% RH. Since the interaction of the solid walls is neglected the actual thickness of the layer will be larger, making condensation more likely at low humidities.

When humidity rises it may be more favorable for some materials to adsorb water onto the entire surface of the contact area. In that case the particles lose contact. Thus, the distance between the particles is increased, causing a decrease in the contribution of the van der Waals force. The dielectric properties of the space between the particles changes and the van der Waals forces are shielded. On the other hand, the force is enlarged by a strong interaction between the solids and the water layer due to the van der Waals forces and the ionic forces and hydrogen bonding. Between 30 and 60% RH the normal separation force increases more or less abruptly, increasing further with the humidity until a maximum is reached, after which the force drops suddenly. In one reported experiment, the mean separation force at 58% RH was twice as high as that at 5% RH, reducing at higher humidity. At 80% RH the force was about 1.5 times as high as at 5% RH.

Chapter 4 of the thesis provides a mathematical development of a description of a packing and resultant forces in multi-particle systems. Chapter 5 discusses shear and tensile strength measurements of yield in multi-particle systems.

Jayasinghe, S.S. The Cohesion and Flow of Particulate Solids, Process Technology International 17:11 (1972).

The author reviews a variety of sources and provides a brief discussion of the roles of van der Waals forces and liquid bridges in the attraction and cohesion of particles. He notes that particles with a mean diameter smaller than 80 μm adhere to a wall due to van der Waals attraction, and that the binding force of a 1 micron particle is nearly 10000 times larger than its weight. When discussing the effects of moisture and humidity on cohesion, the author notes that:

$$\partial H / \partial \ln p = (pd/2v)(a-2h)$$

where $\partial H / \partial \ln p$ is the variation of particle adhesion with change in vapor pressure, and

d = the diameter of the particles

v = the molar volume of liquid

a = the distance apart of particles

h = the thickness of the adsorption layer

This relationship suggests that if $a > 2h$ the force of adhesion should grow with increasing vapor pressure, while if $a < 2h$ the adhesion force decreases on approaching saturation. The author states that bulk powders have a critical moisture content which if exceeded will result in a reduction in strength.

Kanellopoulos, N.K., J.K. Petrou, and J.H. Petropoulos. Realistic Modeling of the Interaction of Vapors with Densely Packed Spherical Particles (Parts I and II), *Journal of Colloid and Interface Science* 96:1 (1983).

The hypothetical packings of uniform spheres utilized by the authors are too idealistic and too densely packed to apply to ESPs or fabric filter dustcakes. The authors do base their calculations on a model of the interparticle pores as spherical voids, not as cylindrical pores, as has been more commonly done. They discuss their rationale for this approach, which has some advantages.

Karra, V.K. and D.W. Fuerstenau. The Effect of Humidity on the Trace Mixing Kinetics in Fine Powders, *Powder Technology* 16:1 (1977).

By examining the effectiveness of the mixing of fine powders under different levels of humidity, the authors found that 80% relative humidity was a critical level for altering powder behavior. When this humidity was reached or exceeded, the powder particles aggregated significantly. Hydrophobic coating agents such as magnesium stearate or stearic acid negated these effects. Other authors were cited for their identification of palmitic acid as a hydrophobic conditioner. The authors conclude that the level of humidity at which a powder would aggregate and the level at which it would flow relatively freely are related directly to water vapor adsorption.

Kaufherr, N., M. Shenasa, and D. Lichtman. X-ray Photoelectron Spectroscopy Studies of Coal Fly Ashes with Emphasis on Depth Profiling of Submicrometer Particle Size Fractions, *Environmental Science and Technology* 19:7 (1985).

The authors reviewed several fly ashes and found that, of the elements Si, Al, O, Fe, Ca, S and Na, S and Na were surface enriched. Although S is surface enriched, 50% or more of the S was still present 180 Å below the particle surface. The amount of S vs. Ca exceeds that corresponding to CaSO_4 , suggesting adsorbed sulfur oxide. Their studies found that the main components of fly ash are in their highest oxidation state.

Keller, D.V., Jr. et al. Investigation of Physics of Adhesion of Coal Aerosols. Bureau of Mines Report 16-75. October 1973.

The authors investigated the adhesion of limestone dust and coal dust to coal substrates as a function of relative humidity. This was of interest since limestone is used in coal mines, in which humidity is often high, to keep coal dust from being resuspended in the air and ultimately inhaled.

The authors state that the forces of adhesion between particles a few microns in diameter can exceed the weight of the particle by four to five orders of magnitude (elsewhere, reported to differ by 10^6). Also, they say that smoother, naturally cleaved surfaces give rise to smaller forces of adhesion than those measured on rough abraded surfaces. (The scale of roughness for which this conclusion is valid is not provided and would certainly affect this result.) They authors claim that in their tests the average surface asperities found on the coal substrate are at least 50 times larger than the average diameter of deposited limestone dust particles ($1.6 \mu\text{m}$).

At high relative humidities, the surface tension of adsorbed surface films can make a significant contribution to adhesion. This is in addition to van der Waals forces, chemical bonding interactions, electrostatic forces, etc. Other researchers reported hydrophilic substances showed a greater effect of relative humidity on adhesion than hydrophobic quartz.

Van der Waals and electrostatic forces determine the initial size of the contact area. Then shorter-range interactions (chemical bonds, hydrogen bonds, sintering, alloying) can become important. Unless the charge on each particle is large ($>10^5$ charges), the contribution of electrostatic forces to particle adhesion is small. If there is an adsorbed water film on the particle and substrate, the meniscus between the particle and the substrate contributes a force of adhesion equal to

$$F_T = 4 \pi \gamma r$$

in which r is the radius of the meniscus (cm), and γ is the surface tension of the adsorbed film (dynes/cm). Whenever there is a considerable water film between the substrate and the particle, the force due to the surface tension of water is expected to be a significant factor in the total force of adhesion.

The authors tests were conducted with an ultra-centrifuge described in the paper. They exposed the dust and substrate in controlled humidity conditions for only 30 minutes before conducting the tests. Nevertheless, they found that the force of adhesion of limestone particles exhibited a strong dependence on relative humidity at values of RH above 72%. Coal dusts did not have such a dependence. The conclusions of the authors were that the limestone (mostly calcite, an ionic solid with Ca^{++} ions and CO_3^{--} ions placed alternately

on the corners of a rhombohedron) is hydrophilic and water molecules adsorb strongly in multiple layers. The average thickness of one layer of water on calcite is 3 Å. The adsorption of water on calcite follows a 'sigmoid' curve indicating multilayer formation. Surface coverage is low up to about 65-70% RH and rises rapidly after about 80% RH toward an asymptote at 100% RH. The authors suggest 5 layers of water are tightly bound on the limestone particles, and the 6th layer is 'free' water.

In contrast to the limestone, coal adsorbs water only at the hydrophilic sites and does not show any signs of multilayer adsorption behavior. Again this behavior is deduced from adsorption isotherms.

For limestone particles, surface tension of adsorbed films can be the dominant contribution to adhesive forces. Without the same meniscus formation with the coal particles, the adsorbed water makes much less of a contribution to adhesion as compared to the van der Waals force.

A general conclusion drawn by the authors is that in any system of particle-substrate adhesion, the adsorption data of water on the particle material and on the substrate material is important in the determination of the effect of RH on adhesive forces in the system. Also evident is the need for a better analytical method to measure adhesion. The electrostatic tensiometer may be very well suited for the task.

Khan, F. and N. Pilpel. The Effect of Particle Size and Moisture on the Tensile Strength of Microcrystalline Cellulose Powder, Powder Technology 48 (1986).

Although the powder treated in this article is not one that directly applies to the objective of this project, the authors cover the analyses and theories dealing with the effects of size and moisture on the powder in a complete and systematic way. The discussions contained in this article are therefore potentially very valuable in designing and interpreting analyses of moisture on fly ash and sorbents. Some of the general comments of the authors are presented below. Water can be present in powders in different forms; as adsorbed monolayers or multilayers on the surfaces of the particles; as an actual water layer on the surface capable of forming pendular bonds between the particles; as physically absorbed water within the particles; or as strongly bound chemisorbed water. The distribution of water in these various forms depends on the amount present, the chemical nature of the powder and on its physical state, particularly particle size and porosity. The authors used measurements of tensile strength to measure how additions of water alter some of the fundamental properties of Avicel, such as the surface energy of the particles, and the forces that act between them. They state that tensile strength is a function of particle size, packing fraction, and moisture content. Additional comments and equations from the article are presented below.

Tensile Strength T of a packed bed of powder:

$$T = \frac{ab}{2\bar{v}} \cdot c \bar{s} \rho_f h \cdot \left\{ t_0 - \frac{\bar{d}}{3} \left(\frac{\rho_f}{\rho_0} - 1 \right) \right\}$$

in which $a = \frac{\text{number of particles per unit area}}{\text{number of particles per unit volume}}$

$b = \frac{\text{true area of contact per particle}}{\text{surface area per particle}}$

$c = \text{mean co-ordination number}$

$h = \text{interparticle force per unit area (Nm}^{-2}\text{)}$

$t = \text{interparticle separation } (\mu\text{m})$

$t_0 = \text{value of } t \text{ when } T = 0$

$\rho_f = \frac{\text{bed density}}{\text{particle density}}$

ρ_0 is the value of ρ_f at $T = 0$

$\bar{d}$, $\bar{s}$, and $\bar{v}$ are effective particle diameter (μm), surface area (μm^2), and volume (μm^3), respectively.

ρ_0 are obtained by extrapolation of graphs of measured tensile strength against ρ_f .

Plot $\frac{1}{F} = \frac{\bar{s}}{2\bar{v}T} \rho_f$ versus $G = \frac{\bar{d}}{3} \left(\frac{\rho_f}{\rho_0} - 1 \right)$ to obtain t_0 at $\frac{1}{F} = 0$.

Enthalpy of vaporization of free water is 41 kJ/mole. Energy of hydrogen bonds is ≈ 20 kJ/mole. Differential Scanning Calorimetry can be used to discriminate the water 'strongly bound' by hydrogen bonds to hydroxyl groups and weakly bound water. There is a threshold of water content above which weakly bound water, in excess of the water attached by hydrogen bonds, can form pendular bonds (liquid bridges) between particles, and thus increase the interparticle force. The strength of these bonds (from Cheng) is

$$I = \frac{T}{w^{0.955}} \cdot \frac{1 - \rho_f}{\rho_f}$$

in which w is the weight fraction of moisture, the interparticle separation t being given by

$$t = \left(\frac{\rho_0}{\rho_f} \right)^{1/3} w^{0.4} (\bar{d} + t_0)$$

Plot t versus $\frac{t}{t_0}$ fits a single line through the data.

RESULTS

Increasing particle size decreases tensile strength because there are fewer sites for liquid bridges to form.

Increasing the packing density creates more contacts between particles and sites where the liquid bridges form.

Particle size has less effect on tensile strength than packing density.

Klein, D.H. et al. Pathways of Thirty-seven Trace Elements Through Coal-Fired Power Plant, *Environmental Science and Technology* 9:10 (1975).

Coal, fly ash, slag, and combustion gases from a large cyclone-fed power plant were analyzed for a suite of elements. Mass balance calculations show that most Hg, some Se, and probably most Cl and Br were discharged to the atmosphere as gases. As, Cd, Cu, Ga, Mo, Pb, Sb, Se, and Zn were quite concentrated in the ash discharged through the stack compared with that collected by the precipitator. The authors propose the following scheme to describe the fate of trace elements during the coal combustion process. 1) Trace elements in coal are present in aluminosilicates, as inorganic sulfides, or as organic complexes. 2) On combustion the aluminosilicates are not decomposed. Rather they melt and coalesce to form the slag and fly ash. 3) During the initial stages of combustion, the conditions in a coal particle and within its immediate vicinity are probably reducing and under these conditions the chemical bonding between metallic elements and sulfur in sulfide mineral inclusions or between the elements and the organic matrix is broken, and these elements form volatile species. If the elements are dispersed in the coal organic matrix, they become initially dispersed in the gas stream when the coal is burned. Thus even those elements that are not as stable as the vapor at the combustion temperature initially enter the flue gas stream as the vapor. 4) The elements initially volatilized or dispersed in the flue gas stream may then be oxidized to form less volatile species which then may condense or be adsorbed on the fly ash as the temperature of the flue gas drops. 5) Since the slag is in contact with the flue gas for a short time, and at a high temperature, condensation of volatiles on the slag is minimal.

Knight, P.C. and S.H. Johnson. Measurement of Powder Cohesive Strength with a Penetration Test. Powder Technology, 54(1988).

This is a description of a crude method to use in place of the shear cell. The technique is of questionable accuracy and utility.

Kono, H.O., C.C. Huang and M. Xi. The Effect of Flow Conditioners on the Tensile Strength of Cohesive Powder Structures, AIChE Symposium Series 85:270 (1989).

The authors mixed small amounts of calcium stearate and polysaccharide with Pittsburgh coal powder. Measurements indicated significant reductions in tensile strength for the conditioned mixtures. The authors quote prior studies that state that this type of tensile strength reduction is generated by the conditioning powders that are deposited between the host particles according to three different mechanisms. The conditioning particles 1) act as a physical barrier between the host particles thus reducing the contact forces between the host particles, 2) act as lubricants to reduce the friction between host particles, or 3) act as neutralizers of electrostatic charge. The authors address the situation where less as little as a 0.1% mixture by wt. of conditioning particles with the host particles results in a significant reduction in tensile strength. They suggest that the few conditioning particles create scattered weak points throughout the powder structure. Shearing fractures are initiated at these weak points. The authors determined that there is an optimum amount of calcium stearate to add to the coal powder to reduce tensile strength. Beyond this amount, the calcium stearate agglomerates and tensile strength increases.

Kono, H.O., C.C. Huang, and M. Xi. Function and Mechanism of Flow Conditioners Under Various Loading Pressure Conditions in Bulk Powders. Powder Technology, 63(1990).

Tensile strengths and plastic deformation coefficients of bulk powders were measured as a function of compressive pressures in the range of 10 to 2000 kPa. The host powder was pulverized coal, and fine starch and calcium stearate were used as flow conditioners.

In general, flow conditioners are very fine powders with a primary particle size on 0.1 to 30 μm . When a bulk powder becomes finer than 40 μm , the interparticle force plays an important role, so that the bulk powder forms a certain packing structure. The mechanism of flow conditioners was found to depend on the structure of the fine bulk powders in which the flow conditioners were dispersed. The structure of fine bulk powders is generally determined by the prevailing compressive pressure and the rheological properties of the powders.

Two types of flow conditioners were identified, based on the properties of the conditioner (certainly size relative to the host particles, and perhaps adhesion of conditioner particles to one another). Flow conditioners were added in concentrations from 0.1 to 5% by weight. Flow conditioners do not change the macroscopic structural properties (porosity) of bulk powders.

Tensile strength and plastic deformation coefficient show similar and very sensitive changes with respect to the concentration and type of flow conditioner. For the flow conditioner that is much finer than the bulk powder, the host particles are coated so that the contact points between particles have been replaced with flow conditioner. After sufficient concentration of the flow conditioner is added the conditioner particles begin to agglomerate and the effect of the flow conditioner is rapidly diminished. There is a sharp minimum in the tensile strength and in the plastic deformation coefficient.

For the flow conditioner that is similar in size to the host particles, there is a rapid reduction in tensile strength and plastic deformation coefficient that does not recover with the addition of conditioner. The explanation given is that the adhesion of the conditioning particles to any other particles is lower than the adhesion of the host particles to one another, so that the greater the number of flow conditioner particles that are added the larger the number of weak bonds in the bulk powder. The data illustrate the importance of tensile strength as a measure of bulk powder cohesivity.

H. Krupp, W. Schnabel, and G. Walter. The Lifshitz-Van der Waals Constant: Computation of the Lifshitz-Van der Waals Constant on the Basis of Optical Data. J. Colloid and Interface Sci., 39(1972).

Based on the calculation of the Lifshitz-Van der Waals constant $\pi \bar{\omega}$ using $\epsilon_i''(\omega)$, the imaginary part of the complex dielectric constant of media i ($i = 1, 2, 3$; medium 3 lies between media 1 and 2), tabulated results for several adhering solids separated by vacuum and by water are given. In the case of a vacuum between solids: $\epsilon''(\omega) = 1$; ω is the angular frequency of photon energy E ($E = \hbar \omega$); h is Planck's constant ($\hbar = h/2\pi$). The ϵ'' values are calculated from optical reflectance measurements with the aid of the Kramers-Kronig analysis.

For homogeneous and heterogeneous material combinations with a vacuum between the adherents, the $\pi \bar{\omega}$ values obtained range from 1 to 12 eV. If the adherents are separated by a third medium (e.g., water, polystyrene) the $\pi \bar{\omega}$ values vary between about 0 and 9 eV. { $\pi \bar{\omega}(\text{H}_2\text{O}) = 1.14 \text{ eV}$ }

Lauga, C., J. Chaouki, D. Klvana and C. Chavarie. Improvement of the Fluidisability of Ni/SiO₂ Aerogels by Reducing Interparticle Forces, Powder Technology 65 (1991).

Much of the most useful information in this article is derived from the authors' review of references. Some of this information follows. For a powder in a dry gaseous environment and having an average particle diameter of the order of tens of microns, the dominant interparticle force is the van der Waals force. The equation that describes the adhesion forces due to van der Waals force (F_1) for two smooth spheres of radius R at a separation distance H is

$$F_1 = \{(\hbar\omega R/(8\pi Z^2))\} \{1 + \hbar\omega/(8\pi^2 Z^2 H)\}$$

in which $\hbar\omega$ is the Lifshitz-van der Waals coefficient (characteristic of the electromagnetic properties of the material) and H is the hardness of the softer of the two spheres.

Only the first atomic layers on the surface are responsible for the van der Waals attractive forces. Thus, the chemical character of the surface layer is expected to induce a specific behavior of the powder. For example, particles covered with an oxide may behave differently than those with a metallic surface or covered by adsorbed water molecules. Another important factor influencing the van der Waals force is the hardness of the particles (H), which is larger for harder bodies.

The authors' work with humidified environments indicated that the total interparticle forces (which are predominantly due to van der Waals forces in a dry environment), are increased by capillary forces. The authors suggest an adsorbed layer of H₂O molecules is present at the particle surface. Since the Lifshitz-van der Waals coefficient is only 1.43 eV for water, the van der Waals force is reduced.

Leong, K.H., J.J. Stukel, and P.K. Hopke. Effects of Surface Properties of Collectors on the Removal of Charged and Uncharged Particles from Aerosol Suspensions, EPA Report EPA-600/7-82-006 (1981).

The authors include an extensive review of the types of forces and existing theories and equations for the adhesion of particles on a solid substrate and collection of particles by droplets. They note serious shortcomings in the existing theories for these phenomena, especially with respect to the determination of microscopic surface roughness on particle adhesion to solid substrates, and the effects of particle wettability on particle collection by droplets. They state that no adequate model exists to explain the observed behavior of a charged or uncharged particle coming into contact with a charged or uncharged droplet.

The role and effectiveness of surfactants in the wet collection of particles is also poorly understood.

In discussing the relative importance of forces, the authors state that for wettable or partially wettable particles, capillary forces, if present, are dominant. Otherwise, van der Waals and electrical double layer forces are dominant. For solid-to-solid contacts, surface roughness can increase or decrease the adhesion forces, depending on the nature of the roughness and the rigidity of the particles. Surface roughness becomes secondary when wettable particles are collected by droplets. According to the authors there is a substantial difference of about an order of magnitude in the net adhesion force between the case of a hydrophilic particle and a hydrophobic particle. The report concludes with a discussion of proposed studies and the experimental apparatus required to carry out these studies.

Liberti, A., D. Brocco and M. Possanzini. Adsorption and Oxidation of Sulfur Dioxide on Particles, *Atmospheric Environment* 12 (1978).

Although the authors cover particles emitted from stacks and particles collected from ambient locations, some of the general conclusions of the work apply to coal ashes. They studied the adsorption and desorption of SO_2 on a variety of particles. The following discussion contains selected conclusions from their work. The interactions between SO_2 and particles can occur through two processes: adsorption and conversion to sulfate. The extent of these processes depends upon the particles, chemical composition, and their nature, which can be defined in terms of pH, titratable acidity, surface area, humidity and degree of surface coverage by adsorbed components. Higher humidity increases the adsorption of SO_2 . Chemical bonding is the predominant mechanism (vs physical bonding) for particles collected directly from stacks. Conversion of SO_2 to sulfate occurs at a very high rate for particles coming from industrial emissions, with the alkaline reaction being the determining factor. Increased alkaline content speeds the reaction. The authors used differential thermal analysis and X-ray photo-electron spectroscopy to support these conclusions.

Lu, G.Q. and D.D. Do. Adsorption Properties of Fly Ash Particles for NO_x Removal from Flue Gases, *Fuel Processing Technology* 27 (1991).

Although most of this article deals with material not of particular interest to this project, the authors do present some data describing the measured specific surface areas and carbon contents of size-classified (sieved) fly ash. This data follows below:

Size (μm)	Carbon(%)	Surface area (m^2/g)
-63	1.57	0.99
-63-75	2.67	1.37
+75-150	4.90	1.78
+150-178	12.87	4.34
+178-211	24.09	6.74
+211-564	43.84	9.35

These data demonstrate that the unburned carbon remaining in the fly ash particles contributes the main surface area to the fly ash particles.

Luckham, P.F. The Measurement of Interparticle Forces. (An Invited Review) Powder Technology, 58(1989).

Principally a discussion of the experiments conducted with a device to measure the forces between two flat surfaces of mica as a function of their separation down to separations of the molecular scale ($<1 \text{ nm}$). The device, experimental procedure, and analytical methods used in the measurements are described. The author stated that the chemical nature of the surface is of secondary importance, with the surface smoothness being of primary importance, and suggests that the results with mica will be similar to any other surface (particularly hydrophilic surfaces).

As two surfaces are brought together they start to experience van der Waals attractive forces. Theoretically, the van der Waals energy E_a is given by

$$E_a = - \frac{A_{sv}}{D^2}$$

in which A_{sv} is the Hamaker constant between the mica surface and air (vapor), and D is the separation distance. At separations $>10 \text{ nm}$ the force law has a lower dependence on the separation distance due to the time taken for the transient dipole/induced dipole to develop. This interaction is known as the retarded van der Waals interaction:

$$E_a = - \frac{A'_{sv}}{D^3}$$

There is a transition regime in which the dependence on separation distance varies from second power to third power. In the reported tests the transition was between $\approx 10 \text{ nm}$ and 75 nm . { $A_{sv} = 1.35 \times 10^{-19} \text{ J}$ and $A'_{sv} = 0.97 \times 10^{-28} \text{ J}$ for mica in air. }

Condensible vapors, such as water, can increase the force of adhesion because the surface tension of the capillary condensate formed around solid-solid contact regions is often dominant. When the two mica sheets were brought together into adhesive contact by the van der Waals forces, vapor condensed at the annulus of the two surfaces over a period of 10 s. The surface geometry in the reported experiments was equivalent to a sphere on a plate, for which the general formula for the adhesive force F is

$$F = F(\Delta P) + F(S-S) + F(\gamma_{LV})$$

in which $F(\Delta P)$ is the force due to the Laplace pressure ΔP , $F(S-S)$ is the force due to direct solid-solid interactions, and $F(\gamma_{LV})$ is the resolved force due to the liquid/vapor surface tension γ_{LV} .

$$F(\Delta P) = 4\pi R \gamma_{LV} \cos \theta$$

$$F(S-S) = 4\pi R \gamma_{SL}$$

$$F(\gamma_{LV}) = 2\pi R \gamma_{LV} \sin \phi \sin(\theta + \phi)$$

in which R is the radius of the sphere, θ is the solid/liquid contact angle, γ_{SL} is the solid/liquid interfacial free energy, and ϕ is the angle from the center of the sphere to the edge of the annular ring of liquid.

In most cases, ϕ is small and

$\sin \phi \sin(\theta + \phi) \ll 1$ so that $F(\gamma_{LV})$ is negligible. Thus

$$F = 4\pi R \gamma_{LV} \cos \theta + 4\pi R \gamma_{SL}$$

The Laplace pressure $\Delta P = \gamma_{LV} / r$ as $r \rightarrow 0$ was measured to determine the applicability of bulk thermodynamics to menisci. Tests determined at which partial pressure of liquid and hence r the adhesion force F was *not* described by $4\pi R \gamma_{LV} \cos \theta$ but by $4\pi R \gamma_{SL}$. This depended on the liquid. For cyclohexane bulk thermodynamics applies to menisci as small as 1 nm representing only one or two molecules, while for water bulk thermodynamics only applies for $r > 5.0$ nm which is ~ 20 water molecules. This was attributed to hydrogen bonding in water although trace organic impurities would alter γ_{LV} and hence the adhesion.

Results have shown that for dry surfaces the interactions between solid surfaces in air are well described by van der Waals forces. By simply knowing the Hamaker constants of the solid surfaces the form of the force profile between the surfaces may be calculated. In the presence of a vapor of condensible liquid the adhesion between the surfaces increases. Thermodynamic treatment used to predict particle adhesion forces are valid for very thin liquid films.

The van der Waals energy between two planar surfaces immersed in a continuum liquid is

$$E_a = - \frac{A_{SL}}{12\pi D^2}$$

in which A_{SL} is the Hamaker constant for the interaction of the solid across the liquid. Until the separation exceeds the thickness of one molecule the van der Waals interaction is actually across a vacuum, i.e.

$$E_a = - \frac{A_{SV}}{12\pi D^2}$$

in which A_{SV} is the Hamaker constant for the interaction across a vacuum. Generally $A_{SV} > A_{SL}$ (typically $A_{SV} \approx 10^{-19}$ J while $A_{SL} \approx 10^{-20}$ J).

The measured adhesion on the separation of surfaces that have a condensed vapor between them is predicted by the Young/Laplace equation

$$\Delta P = \frac{\gamma}{r}$$

in which ΔP is the pressure of adhesion, γ is the surface tension and r is the radius of curvature of the meniscus formed at the contact interface.

Malabrel, C.A., P. Somasundaran, and N.J. Turro. In Situ Kinetics Measurements of the Surfactant Adsorption on Colloidal Alumina using ESR Spectroscopy. *J. Colloid and Interface Sci.*, 137(1990).

The authors propose the use of electron spin resonance (ESR) spectroscopy to monitor the adsorption kinetics of polymers and surfactants in colloidal suspensions. The ESR data provide greater temporal resolution of adsorption than measurements of changes in the composition of liquids passed through packed beds, the standard technique to study adsorption kinetics. Analysis of anisotropic features of the ESR spectra provides information on the rotational mobility of the probe from which probe characteristics can be deduced: this can indicate the adsorption in a flat conformation, or in a stretched dangling configuration.

Mamane, Y., J.L. Miller and T.G. Dzubay. Characterization of Individual Fly Ash Particles Emitted from Coal- and Oil-Fired Power Plants, Atmospheric Environment 20:11 (1986).

The authors used SEM in combination with an energy dispersive X-ray spectrometer (EDX) and determined several characteristics of coal ash particles. Sulfur appeared as a surface layer (a few nm thick) on the mineral core. Abundances of Fe and S were highly variable. The Al/Si ratio was fairly constant for most of the spheres, but not for the relatively few Fe-rich or non-spherical particles. Particles were either typical aluminosilicates, Ca-rich, or Fe-rich.

Mann, R.M., R.A. Magee, R.V. Collins, M.R. Fuchs and F.G. Mesich. Trace Elements of Fly Ash: Emissions from Coal-Fired Steam Plants Equipped With Hot-Side and Cold-Side Electrostatic Precipitators for Particulate Control, EPA/908/4-78/008 (1978).

Arsenic, nickel, copper, and zinc were more concentrated on smaller particles collected from both hot- and cold-side ESP's. The cold-side ESP also showed increased concentration of cadmium, chromium, and manganese for smaller particle sizes. Only the hot-side ESP showed increased concentration of selenium on the smaller fly ash particles. The cold-side and hot side ESP's were operated at different plants burning different coals. Generalization of these results is probably not justified.

Martin, C.M., M. Ghadiri, U. Tüzün and B. Formisani. Effect of the Electrical Clamping Forces on the Mechanics of Particulate Solids, Powder Technology 65 (1991).

This paper analyses the mechanisms of interactions between the electrical and mechanical forces between particles and between particles and walls. The electrical clamping forces are produced in a porous bed of particles by the current flow through the bed, and are due to current constriction at contact points. The authors note that it has been suggested that the adhesion of a deposited dust layer to the passive electrode in an ESP is brought about by the electroclamping forces. The additional details presented in the bulk of the article are not specifically useful to the objectives of this project.

McKay, G., S. McKee, and H.R.J. Walters. Solid-Liquid Adsorption Based on External Mass Transfer, Macropore and Micropore Diffusion. *Chemical Engineering Science*, 42(1987).

This paper describes the development of a model and computer program to predict concentration decay curves for batch adsorption systems, incorporating three mass transport rate controlling steps:

- 1) external mass transfer,
- 2) diffusion in the adsorbent macropores, and
- 3) diffusion in the adsorbent micropores.

The four major variables are

- EK_f , the external liquid film mass transfer coefficient
- D_s , the surface diffusion coefficient
- EK_b , the branched pore rate coefficient,
- and f , the fraction of total adsorptive capacity in the macropores.

The incorporation of the micropore diffusion step is new to this model, and allows the accurate prediction of concentration decay over very long times. The model is based on the "Branched Pore Kinetic Theory" and includes the basic equations developed by Peel *et al.*

There are a number of limitations to the model described in the paper, but nothing fundamental, as evidenced by the very accurate modelling of adsorption for two sets of experiments reported in the paper. The concept of a two resistance intraparticle mass transfer mechanism appears very useful for modelling the concentration decay curve at long time intervals. The micropore diffusion term explains the long uptake in the latter stages of the adsorption process.

McLean, K.J. Cohesion of Precipitated Dust Layer in Electrostatic Precipitators, *JAPCA* 27:11 (1977).

The author establishes, using an idealized system, that one of the important cohesive forces acting on the precipitated layer in an electrostatic precipitator is that due to the effect of the electric field established in the air gaps between the adjacent particles by the corona current as it flows through the layer. McLean finds an approximately linear relationship between the cohesive force and the applied electric field. He concludes that in an ESP, the electric field E_a is the main factor which determines the magnitude of the cohesive force holding the particulate to the collecting plate. This field, however is given by $E_a = J\rho$, where J is the corona current at the surface of the dust layer and ρ is the layer's effective resistivity. Since J is reasonably constant in practice, and resistivity may vary by many

orders of magnitude, it is mainly the resistivity of the dust which determines E_a and hence the cohesive force.

Midkiff, L.A. Flue Gas Conditioning Upgrades Performance, Cuts Down Size of Precipitators, Power 123:4 (1979).

Written in 1979, this review of ESP conditioning theory and methods provides basic information about the mechanisms involved in resistivity and cohesivity modification. Some of the comments of the author are included below. Resistivity is virtually zero at the acid dewpoint. The resistivity of typical fly ash is at a maximum at about 300 °F. Above this temperature resistivity drops due to volume conduction, which varies with the chemical composition of the flyash, especially the presence of the alkali metals: sodium, lithium and potassium. Free SO_3 raises the acid dew point of the flue gas, enabling the dust particles to adsorb more water. If a large portion of the SO_3 in high-sulfur ash appears as calcium sulfate, it will produce an ash with uncharacteristically high resistivity.

If the resistivity of the particles collected on the plate is low enough, a current can begin flowing through the dust layer to the grounded electrode. This leaves the surface of the dust layer positively charged (in conventional polarity ESPs), and some of the particles can be attracted by the discharge electrode and drawn back into the gas stream. Midkiff also notes that chemical conditioning of a flyash alters its resistivity by means of a surface coating adsorbed onto the dust particles, the resistivity of the treated ash approaches a final value that does not depend on the resistivity of the treated particle.

Natusch, D.F.S. Characterization of Fly Ash from Coal Combustion, NTIS # COO-4347-4 Workshop on measurement technology and characterization of primary sulfur oxides emission from combustion sources, Southern Pines, NC, USA April 1978.

The author studied fly ash particles and determined that an outer layer, 50 to 300 Å thick, is rich in many trace elements in the form of simple and complex sulfates. This layer, which is soluble in water, contains essentially all of the particulate sulfur present in fly ash in the form of sulfate. The author identifies three primary ash particle morphological types. The first involves solid, or slightly voided, spheres and accounts for most fly ash particles having physical diameters less than about 5 µm. The second type consists of hollow spheres whose interior voids are filled with CO_2 at a pressure of about 0.2 atm. These particles predominate in the physical diameter range 10 µm to 60 µm. The third type consists of hollow particles filled with about 10 to 200 of small solid particles. This encapsulation phenomenon is encountered primarily for particles in the physical diameter range of 20 µm

to 60 μm . Evidence indicates that the encapsulated particles form within their hosts and are therefore unavailable for reaction with external vapors such as SO_2 .

The basic matrix of fly ash particles is composed primarily of an aluminosilicate glass together with small amounts of the minerals a quartz, mullite, hematite, and magnetite. Fly ashes from western coals have some crystalline gypsum and lime. The author notes that, overall, fly ash should exhibit low aqueous solubility. (Only 2-3% of the total mass of fly ash is soluble in water.) However, the author notes that the material present in the region of surface enrichment is readily soluble in aqueous media.

The author presents data illustrating the nearly complete removal of sulfur from fly ash by water washing. These data demonstrate that sulfur is, at most, only a trace constituent in the fly ash matrix. The author believes, although definitive evidence was not available at the time of his work, that essentially all of the elements present in the so-called surface layer of coal fly ash exist in the form of sulfates. The author found no evidence for the existence of free H_2SO_4 in fly ash particles. The author also states that adsorption of SO_2 , SO_3 , or H_2SO_4 is probably responsible for the formation of particulate sulfate salts. He notes that adsorption of SO_2 would require fairly rapid (possibly catalytic) oxidation to the sulfate species.

Natusch, D.F.S., E.R. Denoyer, T.R. Keyser, S.E. Kirton, D.R. Taylor, and M.V. Zeller. Surface Analysis of Particles Emitted to the Atmosphere, AIChE Symposium 201 vol 76 (1980).

The authors review techniques for surface analysis and present some conclusions for coal ash particles. Distinction is made between the use of surface analytical techniques to establish surface composition and so-called surface layer thicknesses on the one hand and to monitor changes in surface characteristics which result from external interactions and chemical reactions on the other. The authors use surface analyses in combination with solution leaching to provide a bridge between surface analysis and bulk analysis. They divide surface analytical techniques into two general types: those which observe the surface itself and those which observe material which is removed progressively from the surface. Techniques of the first type include scanning electron microscopy with associated emission spectrometry (XES), electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES) and ion scattering spectroscopy (ISS). Techniques which observe materials removed from the surface include secondary ion mass spectrometry (SIMS) and time resolved solvent leaching (TRSL). The authors provide some general comments about these different techniques, which are briefly summarized below.

In XES, the analytical volume extends well below the surface region of interest. The lateral resolution of ESCA is about 1 mm, but the depth resolution is limited to 10 to 20 Å. AES has a lateral resolution of about 1 µm. SIMS is very sensitive allowing trace element detection, not possible with the other techniques. The authors note that SIMS destroys the sample as part of the analysis. The authors made extensive use of TRSL. The method involved the exposure of a thin bed of particulate to a solution flowing continuously through it. Various leaching solutions were used. Aliquots of eluent are analyzed continuously for both anionic and cationic species to provide profiles of dissolved species versus time.

The authors note some special problems with surface analyses. They state that since it is difficult to define a precise analytical volume, truly quantitative measurements are extremely difficult if not impossible. The heterogeneity in fly ashes makes it difficult to generalize information from single particle (or small sample) analysis to a larger sample. Finally, since all the techniques (except ESCA) involve bombardment of the sample with charged particles, there is considerable potential for altering the surface and thereby obtaining erroneous information. The authors state that these problems are often encountered for alkali metals and for chlorine and sulfur in environmental samples.

TRSL studies showed that Ca is initially leached quite rapidly in conjunction with sulfate, carbonate and chloride. This behavior suggests that, although more or less uniformly distributed throughout the particles, Ca may be present in a different, more soluble, chemical form near the particle surface. ESCA established that surface sulfur is exclusively present in the +6 oxidation state and that surface Fe is primarily in the +3 oxidation state even though much of the bulk iron is +2. These results, when taken in conjunction with those of bulk analyses, strongly support the hypothesis that elements or compounds which can be volatilized at temperatures encountered during coal combustion (~1600 °C) will exhibit surface predominance.

Neimark, A. V. Theory of Adsorption and Capillary Condensation in Porous Bodies of Corpuscular Structure. Adsorption and Capillary Condensation at the Site of Particle Contact. *Kolloidnyi Zhurnal*, (47)1985.

The author derives a model that provides a synthesis between the two adsorption mechanisms of capillary condensation and polymolecular adsorption (surface adsorption). The model calculates the simultaneous effects of these mechanisms. To use the model for calculation of the volume of adsorbate by either mechanism requires significant simplifying assumptions - monodisperse, spherical particles with a known packing density and packing density distribution. The value of the article is in the general discussion about the need to consider both mechanisms. In porous bodies, there are several contacts per particle. At the sites of each contact, a cup-shaped meniscus is formed. If the points of contact are

sufficiently far apart the menisci do not overlap. Capillary condensation may also occur between particles that are not in contact if the adsorbed films on the particles come into contact. Capillary condensation in gaps is irreversible, and gives rise to the hysteresis in adsorption-desorption isotherms.

Neumann, A.W., S.N. Omenyi, and C.J. van Oss. Attraction and Repulsion of Solid Particles by Solidification Fronts. 3. van der Waals Interactions. J. Phys. Chem., 86 (1982)

This paper is a report of the use of Hamaker coefficients derived for particle-liquid-solid interfaces to predict the repulsion or engulfing of particles in a melt at the solidification front. The change in free energy in such a system is essentially a surface tension effect. The free energy ΔF_{net} is the change in free energy for the process of particle engulfment

$$\Delta F_{\text{net}} = \gamma_{\text{PS}} - \gamma_{\text{PL}}$$

(for materials in this paper ΔF_{net} is on the order of 0.01 to 5.0 erg/cm²)

in which γ_{PS} and γ_{PL} represent the particle/solid and particle/liquid interfacial tension, respectively. For $\Delta F_{\text{net}} < 0$ engulfment is favored, whereas $\Delta F_{\text{net}} > 0$ indicates that, from a thermodynamic point of view, the particle should be rejected.

The links between surface thermodynamics and van der Waals interactions is given by the fact that van der Waals attractive or repulsive forces, integrated from infinity to the equilibrium separation, should yield the thermodynamic free energy of adhesion

$$\Delta F_{\text{PLS}}^{\text{adh}} = \gamma_{\text{PS}} - \gamma_{\text{PL}} - \gamma_{\text{SL}}$$

It should therefore be possible to determine material parameters in the theories of van der Waals interactions from interfacial tensions and the underlying contact angles. It is these tensions that give rise to the total macroscopic interactions.

Assuming the solid-liquid interface is a plane and the particle positioned at the interface is spherical of radius R, the appropriate Hamaker expression for the interaction energy for a minimum separation distance $d_{0\text{PLS}}$ in a third medium L, is

$$\Delta F^{\text{sph}}(d_0) = - \frac{A_{\text{PLS}} R}{6 d_{0\text{PLS}}}$$

in which A_{PLS} is the combined Hamaker constant for the particle, liquid, and solid.

If the interaction energy $\Delta F^{ph}(d_0)$ is positive, there will be mutual repulsion between the particle and the interface; i.e., the particle will tend to separate from the interface. Hence, mutual repulsion (particle rejection) will exist between particle and interface when

$$A_{PLS} < 0$$

Conversely, a particle will tend to be attracted to the interface and may be engulfed for

$$A_{PLS} > 0$$

A_{PLS} is a material constant independent of geometry. The expression for the interaction energy between two half-spaces in the presence of a third medium is

$$\Delta F_{PLS}^{adh}(d_0) = - \frac{A_{PLS} R}{12\pi d_{0PLS}^2}$$

So the Hamaker coefficient can be calculated

$$A_{PLS} = - 12\pi d_{0PLS}^2 (\gamma_{PS} - \gamma_{PL} - \gamma_{SL})$$

The more accurate macroscopic approach of Lifshitz states

$$A_{PLS} = \frac{3}{4\pi} \hbar \bar{\omega}_{PLS}$$

in which $\hbar$ is Plank's constant divided by 2π and $\bar{\omega}_{PLS}$ is the average frequency obtained from the optical properties of substances P, L, and S.

The authors point out that Lifshitz theory and Hamaker's microscopic theory do not disagree. The difficulty with the Hamaker theory is in the determination of the minimum separation. For a number of materials, both solid and liquid, Hamaker coefficients A_{ij} were calculated as a function of d_0 , using experimental data for γ_{LV} and values of γ_{SV} obtained from contact angles and the equation of state approach. Irrespective of whether they were liquids or solids, d_0 was close to $2 \text{ \AA}$, with the mean value of $d_0 = 1.82 \text{ \AA}$.

Using these values, effective Hamaker coefficients, A_{PLS} , can be calculated. It is apparent that A_{PLS} can be positive as well as negative (the negative values of the Hamaker coefficients indicate repulsion). Repulsive van der Waals interactions are by no means rare and unusual occurrences.

$$\Delta F^{adh} = \Delta F_{net} - \gamma_{SL}$$

As ΔF_{adh} is proportional to A_{PLS} , the essential difference between the two approaches centers around the solid/liquid interfacial tension γ_{SL} . The largest value of γ_{SL} in this paper was $1.44 \text{ erg}\cdot\text{cm}^{-2}$.

Ondov, J.M., A.H. Biermen, R.E. Heft, and R.F. Koszykowski. Elemental Composition of Atmospheric Fine Particles Emitted from Coal Burned in a Modern Electric Power Plant Equipped with a Flue Gas Desulfurization System, American Chemical Society Meeting (1980).

The authors obtained samples from a spray tower scrubber installed at two conventional pulverized-coal-fired power plants. Many elements (especially selenium) were found to be concentrated on smaller particles. The authors state that the action of the scrubbing tower may account for some of this enrichment. The spray becomes highly acidic after contacting the flue gas, thus dissolving many minor and trace elements from particle surfaces. As the spray solution is recycled in the scrubber, the concentration of these trace and minor elements in the solution increases. On contact with the hot flue gas, the water evaporates from some of the aerosolized droplets. The trace elements may deposit on fine particles, or the evaporation of the water may form highly enriched submicron particles. If the mechanism of vapor deposition on existing particles is accurate, the concentration of trace elements on the surfaces of these fine particles may contribute to an surface enrichment factor as large as 75 times greater than in the bulk ash samples.

Otsuka, A. Recent Advances in Research on Powder Mechanical Properties in Japan, Society of Powder Technology Conference (1981).

The author employed various techniques to measure the adhesive force of several kinds of standard powders. Large increases in tensile strength and cohesive force were measured with decreasing porosity.

Otsuka, A. and K. Danjo. Influence of Humidity on Compaction of Quartz Powder, Journal of Powder and Bulk Solids Technology 3:3 (1979).

Four quartz powders produced from ground quartz sand were compacted under varying conditions of relative humidity (RH). Porosity increased with decreasing particle size, and showed a minimum between the region of 20 - 40% RH, and a maximum around 70% RH. This minimum porosity condition corresponded to the existence of a monolayer of adsorbed water. Adsorbed water levels correlated well with porosity measurements. In the stage of adsorption from dry powder up to a monolayer of water, a decrease in adhesion force with

increasing moisture adsorption occurred. This is supposed to be caused by a decrease in the surface energy of particles with moisture adsorption. When the amount of adsorbed water lies in the region between the monolayer value and the bimolecular value, the adhesive force increased with increasing adsorbed water. The authors believe this result is due to a decrease in mean separation distance between particles, because the adsorption of water molecules may take place on the uneven surface of irregularly shaped particles without changing the conditions at each point of microcontact. In this region, capillary condensation would not occur. When RH reached 70%, the moisture adsorption increased markedly and the adsorbed water would condense at contact points between particles and affect the adhesive force between them. However, water gain at 90% RH was only about 0.1% by weight, so the authors concluded that agglomerates were formed. These agglomerates were postulated to decrease the real number of contact points on a plane of breakage of a powder mass, leading to a decrease in the tensile strength of the powder bed.

Pahl, M.H. and B. Bogenschneider. Forces of Adhesion in Compacted Bulk Materials, Aufbereitungs Technik 7 (1988).

Although the experimental work was performed with 74 μm particles, and is therefore not too useful for this project, some of the information presented by the authors is pertinent. Drawing from references, the authors list the following binding mechanisms for agglomerates:

- Solids material bridging
 - sintering
 - chemical reaction
 - adhesion of melting, cold welding
 - hardening binding agents
 - crystallization of dissolved substances during drying
- Liquid surface
 - capillary forces of adhesion
 - highly viscous binding agents, adhesives
 - adsorption layers
- Forces of attraction between solid particles
 - van der Waals forces
 - electrostatic forces
 - magnetic forces
- Binding due to locking or clamping
 - sticking, entangling

The authors also note that for sufficiently large liquid bridges, the influence of roughness for real particles can be allowed for by a corresponding increase of distances. In these cases, the roughness elements become completely engulfed within the liquid bridges.

Pope, M.I. The Physical Adsorption of Gases on Solids. Calculation of Physico-Chemical Data from Sorption Measurements, Education in Chemistry 3:6 (1966).

The author provides a review of the development of basic sorption theory along with the following definitions:

monolayer capacity (x_m) - x_m is the mass of adsorbate taken up by 1 gram of adsorbent, when its surface is just covered by a single monolayer of adsorbed molecules. The monolayer capacity has units of g/g and its value is proportional to the specific surface of the solid.

specific surface (S) - S is the total surface accessible to gas molecules exposed by 1 g of adsorbent.

molecular area (A_m) - A_m is the area occupied by an individual molecule of adsorbed vapor, when present in the first monolayer covering the surface of the solid.

The relation between these quantities is: $S = NA_mx_m/M$,

where N is Avogadro's number, and M is the molecular weight of the adsorbate.

Pope notes that the specific surface of a powder may be as low as 0.01 m² or as high as 1000 m².

Radford, C.D. and R.T. Fowler. A Review of Variables Affecting the Flowability of Bulk Granular Solids: Part 2 - The Effect of Moisture upon the Adhesive and Cohesive Properties, Australian Chemical Engineering 13:8 (1972).

The authors noted experimental results that determined that there is an exponential decay in the molecular interaction between particles due to the presence of water. With a film of three layers of water on the surface of a solid, the water film may be considered to possess the properties of liquid water to within 4.5%, and at the fourth layer to within 0.81%. Thus the authors state that the adhesion between two particles would decrease exponentially as water vapor condenses on their surfaces. The adsorbed layers are usually classified into three types: (i) the monolayer, (ii) films thicker than a monolayer but thinner than duplex

films, and (iii) duplex films, where the film is sufficiently thick to give complete independence between the energy of the solid surface and that of the interface. The interacting solids are usually classified as hydrophilic or hydrophobic. The authors state that because of the complex interaction of the nature of the vapor, the relative vapor pressure, the temperature, and the nature of the solid surface, the adhesion of a bulk solid cannot be accurately predicted from the humidity of its surrounding atmosphere.

Adsorption isotherm hysteresis is often explained by the capillary condensation theory. This theory is based on using the differing angles of contact of advancing and retreating films to describe the adsorption and desorption isotherms. The authors reference Bowden and Throssell who determined the effects of degassing of foil surfaces on water adsorption. Degassed foils adsorbed two molecular layers at 95% humidity, while foils that were not degassed adsorbed 20 molecular layers at his same humidity. This increase was attributed to the adsorbed gases on the surface of the foil.

At zero humidity the adhesion between the particles is simply the surface energy of the solid surfaces. As the humidity increases from zero, the adhesion decreases markedly as the moisture forms first a chemisorbed monolayer. As following layers are physically absorbed, adhesion decreases until at saturation the adhesion is equivalent to the surface energy of the liquid surfaces plus the surface energy of any remaining solid-to-solid contacts.

Rendall, H. M. and A. L. Smith. The Adsorption of Ionic Surface Active Agents. Surface Active Agents, a Symposium, (1979).

In this article the authors show that the adsorption energy at a solid-liquid interface should include a mean potential contribution as well as "chemical" term associated with a reduction in available adsorption sites. This is the Stern-Langmuir isotherm for the adsorption of ions, including surfactants. The authors show that the mean potential term should be included for low or high coverage of adsorbed ions.

Rietma, K. Powders, What Are They?, Powder Technology 37 (1984).

This paper covers a broad range of powder types. Some of the author's comments about fine particles like the ones covered in this project are presented below. There is a general consensus of opinion that cohesion of dry powders is mainly due to van der Waals forces. Physical adsorption of gases is attributed to van der Waals forces as well, and its bonding is much weaker than that of chemically adsorbed gases. Hence, physically adsorbed molecules can be expected to have a higher mobility on the surface and may be active at the

contact area between two solid particles more or less similar to that in which thin liquid films are active, and thus increase the cohesion force between these particles. The cohesion due to these physically adsorbed gases increases when the gas pressure is increased.

Robens, E. The Measurement of Specific Surface Area and Pore Size Distribution of Powders, Powder Metallurgy International 18:1 (1986).

Robens reviews the definition of surface area and the variety of methods and applications for its determination. He points out that the resolution of the sizes of the surface pores that are included in the measurement is limited by the measuring unit of the measurement method. Reducing the size of the unit increases the resulting surface area. The unit of a microscope is the wavelength of the radiation used. The unit of an adsorption method is the cross-sectional area of the adsorbed molecule. Robens also presents the IUPAC definition of pores based on their pore width d , which is included below:

macropores	$d > 50 \text{ nm}$
mesopores	$50 \text{ nm} > d > 2 \text{ nm}$
micropores	$2 \text{ nm} > d > 0.6 \text{ nm}$
ultramicropores	$0.6 \text{ nm} > d$

Rothenberg, S.J. Coal Combustion Fly Ash Characterization: Adsorption of Nitrogen and Water, Atmospheric Environment 14 (1980).

The author points out that the presence of adsorbed water on fly ash particles may increase rates of reaction for the adsorption and oxidation of sulfur dioxide by several orders of magnitude over the rates associated with a gas-solid reaction. Adsorption of water may also prevent the adsorption of other species, which is called "competition". Outgassing of samples at 200 °C removes physically adsorbed water but does not remove chemically bound surface hydroxyl groups. Rothenberg's data indicate that most fly ash samples adsorb appreciable amounts of water at 200 °C. In his analysis of the rates of adsorption and desorption of water, the author notes that the times required to reach desorption equilibrium at 0 °C were many hours in some cases. Rates of moisture loss were also low at 20 and 50 °C, but samples did reach a constant weight when heated under vacuum for 16-20 hours at 200 °C. In summary, Rothenberg states that fly ash samples are "active" solids with specific surface areas greater than 1 m²/g. All the fly ash samples adsorbed more than a monolayer of water at water vapor pressures above 0.4 Torr at 0 °C. The author believes that fly ash particles are covered by a monolayer of water under most conditions of environmental interest. This monolayer may prevent adsorption of polycyclic aromatic hydrocarbons by competition. Filling and emptying of micropores by water is slow, and this

characteristic has been demonstrated for many other adsorbates. Rate data obtained (0-300 °C) for the interaction of water vapor and fly ash demonstrate that times taken to reach adsorption or desorption equilibrium normally exceed a minute, and may exceed a day.

Schubert, H. Principles of Agglomeration, International Chemical Engineering 21:3 (1981).

Schubert summarizes many of the principles involved in the adhesion of particles to other particles and to flat plates. He states that if a liquid bridge is extended by increasing the distance between the particles, the bridge becomes unstable at reaching some critical distance, and finally breaks. The instability sets in earlier the smaller the bridge is. When discussing van der Waals forces, he notes that these forces have a significantly greater range than the attraction forces between molecules, and therefore are of greater significance for particle adhesion.

Schubert uses a sphere/flat plate model system for most of his discussions of adhesive forces. Within this framework, he makes the following comments for spheres with diameters less than 100 μm . The adhesion due to liquid bridges is the greatest. However, all the adhesion forces are large compared with the particle weight. With the exception of particles that act as electrical insulators (for which the adhesion force increases quadratically with the sphere diameter, the adhesion forces all increase linearly with the sphere diameter.

For a sphere/flat plate system with a 10 mm diameter sphere, Schubert notes the differences in adhesion due to the size of the liquid bridge. When the angle of the bridge is 20°, the effects of particle/ plate separation distance become relatively insignificant. He notes that a 20° liquid bridge breaks down and cannot be maintained at a separation distance of about 2.5 μm . The small liquid bridges arising from capillary condensation at a relative humidity of 50% break at even smaller increases of the separation. The range of these adhesion forces is therefore extremely small.

From the separation dependence of the adhesion forces the following important consequence is noted by Schubert: if it is necessary to capture particles from distances greater than about 2.5 μm , only the electrostatic attraction of charged particles remains for practical consideration. However, if already captured particles are to remain agglomerated, liquid bridges and van der Waals adhesion are particularly important.

Schubert also considers the effect of surface roughness on particle-to-plate adhesive forces. The keys to the magnitude of the van der Waals force for rough particles are the size of the particle, size of the asperity, and the separation distance between the flat plate and the tip

of the asperity. He also notes that adhesion forces can be significantly amplified by deformation at particle contact points. A large increase in adhesion force can be attributed to the reduction in separation as a result of very small roughness elements.

In his summary, Schubert includes the following conclusions: a) In general, the adhesion forces decrease in the following order: solid bridge forces, liquid bridge forces, van der Waals forces, and electrostatic forces; b) The van der Waals adhesion and the forces caused by very small liquid bridges react very sensitively to changes of separation. These forces are therefore decisively influenced by the mostly unknown surface structures of the particles. As a result of this, more or less wide distributions of adhesion forces can result depending on the points of contact that come into play; c) Electrostatic (Coulomb) forces and also interactions based on large liquid bridges are only sensitive to separation or the size of the rugosities to a very small degree.

Schubert, H. Capillary Forces - Modeling and Application in Particulate Technology, Powder Technology 37 (1984).

Properties and behavior of particulate systems can be substantially controlled by capillary forces. If a liquid of low viscosity forms a bridge between two particles, a force F_H acts between them consisting of two components, the surface tension force F_R , and a force F_p due to the difference of the pressure outside and inside the bridge.

$$F_H = F_R + F_p$$

While the surface tension force F_R always brings about an attraction, the capillary pressure p_k , (where

$$p_k = \sigma_{1g}(1/R_1 + 1/R_2), \text{ and}$$

σ_{1g} = the surface tension of the liquid

R_1, R_2 = the principle radii of the curvature of the liquid surface)

can only contribute a positive component to the adhesion force if it produces a pressure deficiency within the bridge. The author goes on to state that when a bulk material is in contact with moist air, water vapor is appreciably adsorbed and forms adsorption layers. If, however, the humidity approaches saturation (60 to 85%), then capillary condensation will occur and moisture will be present mainly in the form of liquid bridges at the contact points between the particles. When liquid bridges exist in combination with adsorbed water layers, the powder is said to be in a pendular state. With increasing moisture, liquid bridges develop more and more in dependence on the material properties and the contact geometries.

Seaverson, L.M., J.F. McClelland, G. Burnet, J.W. Anderegg, and M.K. Iles. Investigation of Water and Hydroxyl Groups Associated with Coal Fly Ash by Thermal Desorption and Fourier Transform Infrared Photoacoustic Spectroscopies, *Applied Spectroscopy* 39:1 (1985).

Thermal desorption spectroscopy (TDS) and Fourier infrared photoacoustic spectroscopy (FT-IR/PAS) have been shown to be useful in combination for the identification of hydroxyl and water species associated with coal fly ashes. The latter technique enabled mid-IR spectra to be measured on samples which had been dehydrated under vacuum to temperatures between desorption peaks determined by TDS without further sample manipulation. A small desorption peak at 50 °C was assigned to physically adsorbed water. A broad desorption band from 180° to 400 °C was assigned to hydrogen-bonded surface hydroxyls in the four fly ashes tested.

Shinohara, K. and T. Tanaka. Ultimate Tensile Strength of Cohesive Powders Based on Non-Uniform Packing Model, *Journal of Chemical Engineering of Japan* 8:1 (1975).

The authors present an analysis of ultimate tensile strength of packed cohesive powders based on their model of non-uniform packing. They note that all the contact points act equally at tensile breakage, the maximum tensile strength is supposed to be obtained. This would be an ideal tensile strength. The actual tensile strength is much less than this ideal strength. The authors also found that theories existing at the time they did this work were unable to account for the large increase in tensile strength with a small decrease in void fraction of a powder. Some data taken with fly ash indicates that the ultimate tensile strength of the ash increased by up to 10 times when the moisture content was increased from 2.1 % to 7.1 % vol H₂O. They authors characterized the ash as having 0.3 m²/g of surface area, a true density of 2.17 g/cm³, and a mean size of 8 μm. This would be a very smooth, spherical fly ash.

Sing, K.S.W. Surface Characterization: Physical, Characteristics of. Powder Surfaces, Conference (1976).

The author provides an extensive review of then current techniques and algorithms involved in the determination of powder specific surface area, and the interpretation of pore and surface structures of powders. He defines terms, and discusses at length the limitations and applications of specific interpretations of adsorption isotherm data. This review is worthwhile for its completeness of the subjects covered. Therefore, a more detailed summary of this work will not be included here.

Smith, D.M., G.P. Johnston, and A.J. Hurd. Structural Studies of Vapor-Phase Aggregates via Mercury Porosimetry, *Journal of Colloid and Interface Science* 135:1 (1990).

The authors inferred from BET and mercury porosimetry measurements of Cab-O-Sil fumed silica (EH5 and L90D) that surface roughness increased as particles sizes decreased. They also examined fine carbon black powders.

Tagawa, M., K. Gotoh, M. Yokokura, A. Syutoh, and S. Takechi. Influence of Surface Properties of Particles on their Adhesion and Removal, *Colloid Polymer Science* 267 (1989).

The adhesion and removal phenomena of particles to and from a flat substrate in aqueous solutions are expected to depend on the particle size and shape, the surface potentials, the overall Hamaker constant, the surface roughness, and the presence of adsorbed layers. The authors calculate Hamaker constants for nylon and quartz for their experimental setup.

Terashita, K., T. Kimura, H. Kimura, and K. Miyunami. Computer-Aided Measurement of Breakup Processes and Tensile Strengths of Powder Beds, *Bulletin of the University of Osaka Prefecture Series A* 37:2 (1988).

The authors identify two primary mechanisms of tensile strength breakdown in packed powder beds. Depending on the degree of compaction, the beds underwent primary particle breakup or aggregate particle breakup. In the latter mechanism, the shear layers were formed between aggregates of particles, while in the former mechanism, the layers formed between discrete particles. The authors also noted the increase in tensile strength of silica sand as water content was increased from 1.5 to 25 % by weight. The applicability of further results contained in this article is limited due to the types of powders tested.

Tidy, D. A Leaching Technique for Determining the Surface Composition of Pulverized Fuel Ash (PFA), *Journal of the Institute of Energy* 59:43 (1986).

The author describes the rapid leaching method he developed for the determination of the surface chemistry of PFA. He relates his findings to laboratory-measured resistivity values. His technique, and the subsequent data analysis depends heavily on the commonly held assumption that the ash particles are covered by a multimolecular layer of high sulfate content material which contains most of the sulfate in the ash. For the 10 ashes he tested,

the author concluded that Mg and Ca were probably present as oxides or hydroxides, but not bound up in the glassy matrix of the ash particles. He found that K was primarily bound up in the glassy matrix. His surface chemical composition data provided stronger evidence than simple bulk chemical analyses that resistivity decreases with increased Na content. The leaching technique and the data analysis methods Tidy employed are potentially valuable tools for the determination of many different chemical compounds on the surface of ash particles during this project.

van Oss, C. J. and R. J. Good. On the Mechanism of "Hydrophobic" Interactions. *J. Dispersion Science and Technology*, 9(1988).

The authors show that "hydrophobic" interactions arise out of a combination of Lifshitz-van der Waals forces and hydrogen bonds, where the contribution of the latter is by far the greatest. The free energies of cohesion and adhesion are the sum of the Lifshitz-van der Waals component and the Lewis acid-base (or hydrogen-bonding) component. The acid-base interactions depend on the electron-donor-electron-acceptor interactions.

Ideally, 99% of the total interfacial attractive energy is imputable to the hydrogen-bonding part of the cohesive energy of water. (The surface tension parameters, polar interactions, for water are $\gamma^{\oplus} = \gamma^{\ominus} = 25.5 \text{ mJ/m}^2$.) In less than ideal cases, where the hydrophobic surface still has some polar properties, the polar interaction energy between the solid and water must be subtracted from the ideally obtainable "hydrophobic" attraction energy.

The strong (polar) attraction between water molecules pushes the other molecules or particles together. The apolar component of the "hydrophobic" attraction (van der Waals force) is usually very slight in water, because the values of these forces for water and most low-energy materials are rather close. The polar component is therefore the dominant one.

Visser, J. Adhesion of Colloidal Particles. Manuscript for Surface and Colloid Science.

This manuscript provides an excellent survey of the state of development of theories and experimental evidence for adhesion between particles in vacuo and in immersions. The forces in effect are described and their domain of operation given.

The author attributes most of the adhesion to van der Waals forces. In simplified systems, the derivations of Hamaker and Lifshitz (microscopic and macroscopic models of interparticle interaction, respectively) are shown to be correct. This reference provides a tabulation of Hamaker and Lifshitz-van der Waals constants for several materials.

Practically, quantitative assessment of the van der Waals forces for particle in contact is not generally feasible because surface roughness, size of contact area, distance of closest approach, and effects of moisture and electric charges are not known in adequate detail.

Surface asperities, or gross sphericity of the particles in contact will directly bear on the strength of the adhesive forces. As particle sphericity increases the adhesive force diminishes as a result of the reduction in actual contact. But adhesion decreases as the particle surface roughness increases until the macro-roughness become on the same order of magnitude as that of the particle dimensions. This phenomenon is explained in terms of the total contact area: adhesion increases with increasing contact area. Any parameter, such as load, load duration, temperature, time of contact, that tends to increase the effective area of contact will increase the force of adhesion. (At elevated temperatures, the mobility of the atoms in the adherents increases so that mass transport occurs due to surface tensions. As a result, the dimensions of the contact area will change.)

Electrostatic forces have been shown to change the adhesive force by as much as a factor of 2, without changing the van der Waals interaction. This effect arises when dissimilar materials are in contact, and electrons from the material with the lower work function are transferred to the material with the higher one. Electrostatic forces may also arise from Coulombic interaction, when a charged particle creates an image charge in a substrate. This interaction exceeds the ordinary adhesive force only if particles are charged in corona discharge systems, and if there is no charge leakage through grounded surfaces or ionization of the gas.

There is considerable discussion of the electrostatic double-layer interaction for immersed systems. All solid materials in an aqueous environment attain a surface charge due to preferential adsorption or dissociation of surface groups (related to the zeta-potential of the material). This charge manifests itself by a displacement of positively charged particles to a negatively charged electrode (and vice versa) if an electric field is imposed. This charge is balanced by a counter-charge via ions that are oppositely charged. In this way, a double layer is established.

The reason this discussion is of interest is that some of the relations observed in experiments may be pertinent in the case of ash and sorbent materials in the presence of adsorbed water. (This postulate was not made by the author, and the degree to which electrostatic double layer forces are applicable in cases of multilayered adsorption of water on particles was not discussed. Therefore, I mention the following cases for the purpose of providing a hypothesis to evaluate in the laboratory.) In immersed colloidal systems, the adhesive force depends on the pH of the medium. In alkaline medium ($\text{pH} = 8-10$), particles are far more easily removed than in distilled water ($\text{pH} = 5-7$), whereas in acid medium ($\text{pH} = 2.5$) particles are slightly more easily removed than in a neutral medium.

The reduction in adhesion at increasing pH is assumed to result from electrostatic double layer repulsion forces.

A reduction in adhesion has been observed by adding CaCl_2 to distilled water. Non-ionic surfactants can markedly decrease adhesion, but this is probably an entropic effect instead of electrostatic.

Ion bonding can influence adhesion. The presence of ions between the adherents may be due to an equilibrium between repulsive and attractive forces. Attractive forces are the van der Waals and electrostatic forces due to mobile adsorbed ions. The repulsive forces are from water layers bound to the surfaces and around the ions adsorbed on these surfaces. Polyvalent ions may bridge between particles and surfaces. Calcium bridges are an example of this type of bonding. The role of ion deposition can be explained along the same lines as the swelling of clay, the role of the interlayer cation being the neutralization of the two interacting surfaces of like charge, opposite to that of the cation. Particles deposited in the presence of calcium ions (in pH 10 environment) were much more difficult to remove from the substrate than particles deposited in the presence of sodium ions. Calcium ions probably were not acting as bridging ions between negatively charged groups on the surface of the particle and substrate, but neutralized two neighboring groups of negative charge on one surface, thus making it possible for the particle and surface to come much closer together, resulting in a higher adhesive force.

Liquid films increase adhesion. In the presence of half a monolayer of water on a gold substrate, the adhesion increased by a factor of 5, possibly due to the decrease in the work function of gold. Capillary force is the predominant force contributed by liquid films of greater thickness. Capillary forces have their greatest effect on a hydrophobic surface. Particle interaction forces induced by wetting and adherence of wet powders to surfaces can be reduced by hydrophobization of the particles and surfaces (reduced by a factor of 2 and by a factor of 25 to 30 respectively). In general, the difference between capillary forces and the other contributions to the adhesive force are particularly appreciable for particles more than $10\text{ }\mu\text{m}$ diameter. In various cases reported, adhesion increased at relative humidities above 65%, at humidities between 20 and 50%, and between 20 and 90%.

Humidity eliminates or greatly reduces the effect of electrical forces. When the liquid film in the gap between the adherents contains electrolyte, evaporation of the liquid may produce crystals and possibly crystal bridge formation.

Williams, R. and R.W. Nosker. Adherent Dust Particles, RCA Engineer 28:1 (1983).

The authors discuss the effect of deliquescence on particle adhesion to a surface. The relative humidity was allowed to exceed the critical value for placing a salt into solution next a particle adhered to a surface. After the humidity was subsequently reduced to its original value, the force required to remove the particle from the surface increased by a factor of 10000. The authors point out that when the conditions are right, any water-soluble salt can act as an adhesive.

Wood, P.A. Fundamentals of Bulk Solids Flow, IEA Coal Research Report # ICTIS/TR31 (1986).

The author touches briefly on many of the aspects of bulk solids behavior, with particular emphasis on the transport of pulverized coal. The discussions that cover fly ash particles are limited, but the author does include some useful information. Details that have been fully covered by other authors are well referenced. Wood states that ash particle shapes are primarily determined by time and temperature exposure conditions in the combustion chamber. He also discusses intraparticle porosity and its effects on moisture adsorption characteristics and particle density. Wood stresses the need for the development of better methods for identifying the shape and roughness of particles.

Yamamoto, H. Relationship Between Adhesive Force and Dispersability of Sub-Micron Particles, ICHIME 5th International Symposium on Agglomeration (1989).

The author measured the adhesive forces of sub-micron particles of limestone and silica by using a split-cell type tester (Hosokawa Micron Cohetester) under various vapor pressures of water, ethanol and ether. His results indicate that the initial cohesion of the powder can be minimized by reducing the surface tension of the adsorbed layers. Another critical factor is the contact angle between adsorbed solvent and the particle surface. These factors are the primary determinants of the strength of the liquid bridges between the particles. The author concludes that the tensile strength of a powder is a good indicator of the forces that will be needed to disperse it. Therefore any preconditioning of the powder which can reduce the tensile strength will aid the powder dispersion. He also states that there are at least two factors that can be manipulated to minimize the initial tensile strength of the powder: avoid exposure of the powder to high humidities; and reduce the surface tension of the adsorbed layer on the particle surface by adsorbing different solvents onto the powder.

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