FUNDAMENTAL MECHANISMS IN FLUE GAS CONDITIONING

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Todd R. Snyder, Principal Investigator
P. Vann Bush, Program Manager

SOUTHERN RESEARCH INSTITUTE
2000 NINTH AVENUE SOUTH
P.O. Box 55305
BIRMINGHAM, ALABAMA 35255-5305

Prepared for

Felixa Eskey, Project Manager
UNITED STATES DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center
Post Office Box 10940, MS 922-206
Pittsburgh, Pennsylvania 15236-0940

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INTRODUCTION

This project is divided into four tasks. Task 1 is the Development of a Management Plan. Task 2, Evaluation of Mechanisms in FGD Sorbent and Ash Interactions, focuses on the characteristics of binary mixtures of these distinct powders. Task 3, Evaluation of Mechanisms in Conditioning Agents and Ash, is designed to examine the effects of various conditioning agents on fine ash particles to determine the mechanisms by which these agents alter the physical properties of the ash. Tasks 2 and 3 began with an extensive literature search and the assembly of existing theories. The results of the work performed under Tasks 2 and 3 will be included in a Flue Gas Conditioning Model that will be issued under Task 4. The Final Report for the project will also be prepared under Task 4. This quarterly report covers four months in order to synchronize the reporting periods for this project with U.S. Government quarters.

Work performed on the project during the past quarter consisted almost entirely of the review of literature pertaining to the objectives of Tasks 2 and 3. The primary results of that review are discussed at length in Topical Reports 1 and 2, submitted January 9, 1992. As a consequence of the work described in the topical reports, several of the project’s Measures of Success that were described in the first quarterly report have been achieved. This quarterly report will discuss these achievements.

DISCUSSION OF THE MEASURES OF SUCCESS

The Measures of Success listed in Table 1 have been accomplished during the past quarter. Measures S3 through S7 were met as part of the preparation of Topical Reports 1 and 2. Brief summaries of S3 through S7 are included in this quarterly report; however, full details of these topics are contained in the two topical reports. The development of a plan for initial laboratory work provided the specific information necessary to complete S8.

Each of these measures is discussed in detail below.
DEVELOPMENT OF A COMPREHENSIVE DESCRIPTION OF ASH AND SORBENT SURFACE CHEMISTRY BASED ON FINDINGS FROM THE LITERATURE SEARCH (MEASURE OF SUCCESS S3)

The results of the literature review relative to ash surface chemistry are discussed below under Measure of Success S4. The following discussion pertains to the results of the literature review relative to sorbent surface chemistry. The sorbent particles that are present in an ash-sorbent mixture adsorb water vapor and sulfuric acid vapor from the flue gas in the same manner that ash particles adsorb these vapors. In the case of ash particles, the adsorbed vapors are retained on the particle surface as a thin film. When two or more particles come into contact, these adsorbed films may form bridges that increase the cohesivity of ash layers and dust cakes. The adsorbed films can also reduce ash resistivity by making the particle surfaces conductive. The adsorbed water vapor and sulfuric acid are most effective in reducing resistivity and increasing cohesivity when they are retained on the particle surface. Because of the extensive pore structures in many sorbents, the water that is adsorbed on a sorbent particle may be drawn into the particle interior by capillary action. Adsorbed sulfuric acid may also be drawn into the particle and converted into calcium sulfate when it contacts unreacted lime inside the particle. These capillary action and chemical reaction mechanisms tend to make sorbents more difficult to condition than most fly ashes. These mechanisms are probably responsible for the very low cohesivities of certain ash/sorbent mixtures produced by low-temperature sorbent injection. They may also explain
why SO$_3$ conditioning fails to reduce the very high resistivities of certain ash-sorbent mixtures produced by high-temperature sorbent injection.

In the case of high-temperature sorbent injection, there is strong evidence that the sorbent reacts with the ash to form a cementitious material. The ash-sorbent mixtures from furnace sorbent injection are typically very cementitious; they can be mixed with water and cured to produce structural shapes with considerable compressive strength. Ettringite, an essential ingredient of high-quality cement, has been identified as a component of ash-sorbent mixtures from furnace sorbent injection. In low-temperature sorbent injection, there is no chemical reaction between the ash and sorbent, and the ash/sorbent mixtures are not cementitious. The ash-sorbent mixtures from low-temperature sorbent injection are essentially heterogeneous mixtures of distinct ash particles and sorbent particles.

**Compilation of a List of Elements, Oxides, and Compounds Known to Exist on Fly Ash Particle Surfaces and Their Known Reactivities with Flue Gas Constituents (Measure of Success S4)**

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 tend 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 sulfur and calcium indicate that more sulfur is 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$_2$SO$_4$ (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.
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.

IDENTIFICATION OF THE PRIMARY FORCES AND/OR MECHANISMS CONTROLLING THE REACTIONS BETWEEN ASH PARTICLES, SORBENTS AND ASH PARTICLES, WATER AND ASH OR SORBENT PARTICLES, AND OTHER CONDITIONING AGENTS AND ASH PARTICLES (MEASURE OF SUCCESS S5)

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 2. In this regime, 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 μm, 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).

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. If adsorbed layers are extensive enough, they 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).
Table 2
Primary Interparticle Forces

<table>
<thead>
<tr>
<th>FORCE</th>
<th>EFFECTIVE RANGE</th>
<th>SIGNIFICANT FEATURES</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>3 to 500 Å</td>
<td>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).</td>
</tr>
<tr>
<td>electrostatic</td>
<td>contact</td>
<td>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 &gt;10⁵ charges are on particles (Keller, 1973)</td>
</tr>
<tr>
<td>ionic</td>
<td>≤ 2 lattice spacings</td>
<td>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)</td>
</tr>
<tr>
<td>adsorbed layers</td>
<td>&lt;5 Å to contact</td>
<td>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)</td>
</tr>
<tr>
<td>capillary (liquid bridges)</td>
<td>contact</td>
<td>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 &amp; Harnby, 1978)</td>
</tr>
<tr>
<td>solid bridges</td>
<td>contact</td>
<td>dissolving a water-soluble salt and then evaporating the water can leave a solid bond 10⁴ times stronger than before the salt was dissolved (Williams &amp; Nosker, 1983)</td>
</tr>
</tbody>
</table>
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. Chemical properties of particle surfaces also affect the adsorption of gases (Fuller & Thompson, 1987). Chemical adsorption is usually limited to a monolayer, and creates stronger bonds than do physically adsorbed gases (Rietma, 1984).

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). 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. 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. 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). 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.
IDENTIFICATION OF EXISTING MATHEMATICAL EXPRESSIONS DEFINING THE PRIMARY FORCES AND/OR MECHANISMS (MEASURE OF SUCCESS S6)

For the purposes of this project we want to produce some means of modeling the affects that sorbent particles or conditioning agents or flue gas modifications have on the bulk properties of particulate matter entering a control device. The first step we have taken in the formulation of a model is the assembly of existing equations that describe the forces that govern bulk particulate interactions. The forces and the ranges over which the forces are in effect are given in Table 2. Numerous equations describing interparticle forces are reported in the literature. It is our purpose to distill the various equations enough to pick out the predominant variables. The key variables for these forces have been discussed in Topical Report No. 2. Some of the formulæ are given in the following paragraphs.

Hobbel (1988) has listed the 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 \[ E \propto \frac{z_1 z_2}{4\pi \varepsilon_0 R} \]  
- ion/dipole \[ E \propto \frac{z_1 \mu_2}{4\pi \varepsilon_0 R^3} \]  
- dipole/dipole \[ E \propto \frac{\mu_1 \mu_2}{4\pi \varepsilon_0 R^4} \]  
- ion/induced dipole \[ E \propto \frac{z_1 I a}{4\pi \varepsilon_0 R^4} \]  
- dipole/induced dipole \[ E \propto \frac{z_1 I \cdot a}{4\pi \varepsilon_0 R^6} \]  
- induced dipole/induced dipole \[ E \propto \frac{I^2 \cdot \mu^2}{4\pi \varepsilon_0 R^8} - \frac{1}{R^8} - \frac{1}{R^{10}} \]

for which \( z \) is the ion charge, \( \mu \) is the dipole moment, \( I \) is the ionization potential, \( a \) is the polarizability, and \( R \) is the radius of the 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.
As particles are brought into close proximity (< 500 Å) van der Waals forces exert an attractive force. A conventional expression of the van der Waals energy between two spherical particles is

\[ E = -\frac{AR}{12d} \]  

(7)

in which A is the Hamaker constant, and d is the separation distance (Zimon, 1982). The Hamaker constant is dependent on the material properties, and is defined by Lifshitz to be equal to

\[ A = \frac{3}{8\pi} \frac{h \omega}{\epsilon} \]  

(8)

where \( h \) is Planck’s constant, and \( \omega \) is the average frequency of photon energy obtained from the optical reflectance of the substance (Krupp et al, 1972). Since force, F, is given by

\[ F = \frac{\partial E}{\partial d} \]  

(9)

the van der Waals force between two particles with radii \( R_1 \) and \( R_2 \) can be calculated using equations (7) and (8) as follows:

\[ F_{vdw} = -\frac{h \omega}{16\pi^2d^2} \frac{R_1R_2}{R_1 + R_2} \]  

(10)

in which d is the separation distance between particles, and \( h \omega \) is the Lifshitz-van der Waals coefficient (characteristic of the electromagnetic properties of the material, and varies over a range of \( 10^{-18} \) to \( 10^{-21} \) J or 6.25 to 0.00625 eV).

These equations are typical of all fundamental equations of interparticle interaction in that the simplest case is modeled; for example, perfectly smooth surfaces of perfect spheres having predictable electromagnetic properties. Van der Waals forces are additive, and complex geometries and surface properties present formidable, if not impossible systems to model. Visser (1974) stated that quantitative assessment of the van der Waals forces for particles in contact is not 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. What we do know is that dielectric properties and the morphology of the surface of particles govern the magnitude of van der Waals forces. Increasing the total proximate or contact area of particles or decreasing their separation (by decreasing size, adsorption of vapors, increasing surface roughness, or increasing compaction) will tend to increase van der Waals forces.
As particles come into contact the general form of the force of adhesion is

$$F_c = 4\pi r\gamma_s$$  \hspace{1cm} (11)

in which \(r\) is the radius of the projections on the particle surface at the point of contact (Fuks, 1956), and \(\gamma_s\) is the surface tension at the point of contact. The force due to a liquid bridge between two particles is dominated by the liquid/vapor surface tension. The force due to surface tension is

$$F_c = 4\pi R\gamma_L \cos \theta$$  \hspace{1cm} (12)

in which \(\gamma_L\) is the surface tension of the liquid, and \(\theta\) is the contact angle of the liquid as shown in the figure below. The contact angle will depend on the material and liquid compositions and the amount of liquid at the contact point.

Equations (11) and (12) indicate that not only is the particle morphology important, the chemical and physical affinity to vapors that may be adsorbed onto the particle surfaces is critical, as are the quantity and properties of the adsorbed vapors. Thus, we need to characterize as many of these parameters as possible in order to interpret the interactions of particles.

COMPLETION OF THE TWO TOPICAL REPORTS (MILESTONES 2 AND 3)
(MEASURE OF SUCCESS S7)

On January 9, 1992, copies of Topical Reports 1 and 2 were distributed according to the requirements of Contract No. DE-AC22-91PC90365. Following introductory comments, each of these two reports contain an overall summary of the information obtained during the review of articles pertaining to the specific area of interest of the topical report. The specific search procedures used in the literature review are also presented in both reports, along with
a comprehensive bibliography of all the sources of information used in the generation of the reports. In addition, each topical report includes reviews of all articles located in the literature search that were found to contain information applicable to the scope of this project. Topical Report No. 1 contains summaries of 42 specific articles and reports. 84 individual summaries are contained in Topical Report No. 2.

Topical Report No. 1 divides the discussion of the implications of sorbent applications on fine particle collection into high-temperature sorbent injection processes and low-temperature sorbent injection processes. Recommendations for further work in these two areas are presented at the end of the main body of the report. Topical Report No. 2 contains descriptions of the types of forces and interactions that occur between fine particles, as well as descriptions of coal fly ash particles. The chemical makeup of the surfaces of fly ash particles is given specific attention because of the roles surface chemicals can play in generating strong bonds between particles. Topical Report No. 2 concludes with a brief discussion of how particle characteristics, interparticle forces and flue gas environment may affect the collection of fine particles.

IDENTIFICATION OF SPECIFIC TESTS TO EVALUATE EACH OF THE PRIMARY FORCES/MECHANISMS (MEASURE OF SUCCESS S8)

The laboratory tests that will be used in the assessment of interparticle forces consist of various measurements of the behavior of bulk samples of ashes, powders and sorbents. The models to be developed in Task 4 of the collection of fine particles from sorbent injection processes and the collection of conditioned fly ash are intended to be practical guides to improving the collection of these materials. Therefore the laboratory investigations will be directed toward bulk behavior, not quantification of the primary forces active in interparticle bonding. However, a basic understanding of these forces and the regimes in which they act is required to guide and interpret laboratory measurements.

The forces controlling the strength of interparticle attraction and bonding are in turn controlled by such factors as particle morphology, total contact area, and other surface characteristics of the particles (chemical compounds, adsorbed water, etc.) By selectively varying these factors and performing selected analyses of bulk samples, it should be possible to identify the key particle properties controlling the primary forces, and the relative importance of different forces in the overall determination of the strength of interparticle bonds. Measurements of tensile strength, porosity, and cohesivity are some of the primary means that will be used to assess the characteristics of bulk samples. For example, measurements of the tensile strengths of dessiccate samples compressed to varying degrees should reveal the importance of total contact area to total interparticle bonding. Contact area is known to be a key determinant of van der Waals attraction.
The forces of interparticle attraction due to these presence of adsorbed layers and liquid bridges can be assessed by measurements of cohesivity and tensile strength made in environments with varying partial vapor pressures of the adsorbed compound(s). The most common material responsible for these adsorbed layers and liquid bridges is water, making relative humidity a key experimental parameter. Electrostatic forces are so rapidly dissipated in particle collection processes that extensive efforts will not be pursued to measure their contribution to overall particle bonding. Ionic forces may be assessed with parametric tests with particles composed of different materials. One limitation of this approach is that as the particles comprising different materials often have fundamentally different morphologies.

Since solid bridges between particles are generated by the concentration of soluble compounds at points of contact, samples of ashes and powders can be washed to remove these compounds from the samples. Measurements of cohesivity and tensile strength can then be used to compare these washed samples with unwashed samples. In addition, chemical analyses of the solvent extract should reveal the particular compounds responsible for the solid bridges formed between the particles. As with other applications of cohesivity and tensile strength measurements, environmental conditions (temperature, relative humidity) will be carefully controlled.
REFERENCES


