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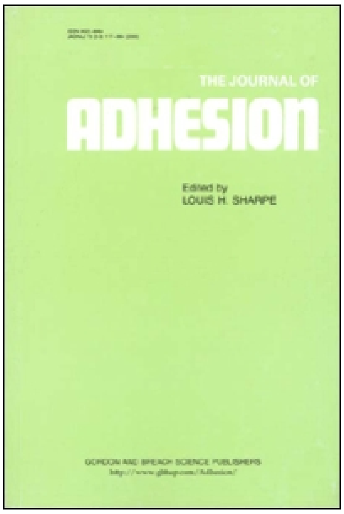

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Adhesion of Micron-Sized Limestone Particles to a Massive Coal Substrate

A. B. Ketkar[a b]; D. V. Keller Jr.[a c]
[a] Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York, U.S.A. [b] Dravo Corp., Pittsburgh, Pennsylvania [c] Materials Science,

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Adhesion of Micron-Sized Limestone Particles to a Massive Coal Substrate

A. B. KETKAR† and D. V. KELLER, Jr.‡
Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York 13210, U.S.A.

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The force of adhesion was measured between limestone (calcite) particles with a mass mean diameter of 1.6 μm resting on a massive coal substrate under ambient conditions where the relative humidity was controlled from test to test between the limits of 18 and 93.5%. The force of adhesion for these particles was less than 0.1 millidyne for relative humidities less than 72% and increased to greater than 0.8 millidyne above 93% relative humidity. A model for this variation is proposed which suggests that the Van der Waal's forces are operative between the particle and substrate below 72% relative humidity and that the adsorbed water film on the limestone interacts with capillary water in the porous coal structure when the relative humidity is above 75%.

INTRODUCTION

The force of adhesion between small particles (50 μm or less in diameter) and particles and substrates has been reviewed in detail by Krupp,[1] Fuchs[2] and Corn.[3] The origin of the forces of adhesion are due to chemical bonding interactions, van der Waal's forces, electrostatics, absorbed liquid layers or combinations of the individual types. In the case of adhesion between limestone, which is a modification of calcite, i.e. calcium carbonate, particles and coal, a hydrogen deficient cyclic hydrocarbon, the existence of chemical bonding forces can probably be neglected which will leave the van der Waal's and electrostatic forces operative when low concentrations of moisture are present. The effects of relative humidity, e.g. the partial pressure of water in

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† Currently of the Dravo Corp., Pittsburgh, Pennsylvania.
‡ Professor Materials Science.

the gas surrounding the adhesion system, on the adhesion forces have been reported by Debye *et al.*,[4] Rumpf,[5] Deryagin,[6] Bohme *et al.*,[7] Bradley,[8] Bikerman,[9] and Corn.[3] Hydrophilic (wateradsorbing) substances such as glass and borax showed an exaggerated effect[8] of relative humidity on the force of adhesion of small particles when compared to much less hydrophilic materials such as quartz. Tomlinson[10] has reported similar observations.

Recently McClure *et al.*[11] used an ultra-centrifuge technique similar to that used in this study to measure the force of adhesion between 2–5 μm diameter coal particles and a coal substrate at a relative humidity of about 20%. The conclusions of this investigation indicated that forces of adhesion due to electrostatic charging was relatively unimportant as was the physical orientation of the substrate relative to the bedding planes of the coal substrate. An increase in surface roughness beyond the cleaved smooth surface increased the force of adhesion of the particles. In any event only a small fraction of the particles were removed before the coal substrate collapsed under the maximum 2.5 mdyne force used to remove the particles.

The purpose of this investigation was to compare the force of adhesion of limestone particles to a coal substrate with McClure's data at a 20% relative humidity and then explore the effects of relative humidity on the adhesion strength of the limestone–coal substrate system.

A brief review of the nature of the two types of adhesion forces which may be operative in this system is as follows:

van der Waal's Forces were described by Krupp[1] as due to the instantaneous dipole fluctuations present in matter and follow the relationship for a spherical particle on a flat substrate

$$F_{\mathrm{vdw}} = \frac{h\bar{\omega}R}{8\pi Z^2} \tag{1}$$

where R = Radius of the particle
Z = Distance from the surface of the particle to the substrate
$h\bar{\omega}$ = Lifshitz constant

The Lifshitz constant, $h\bar{\omega}$, is a material property derived from the frequency dependence of the dielectric constants of both materials. Table I gives values of $h\bar{\omega}$ for different particle substrate systems from the works of Krupp[1] and estimates for the system under investigation.

The values estimated in Table I for $CaCO_3$–Graphite will be used in an attempt to estimate the van der Waal's force of adhesion between limestone and coal substrates. The necessary optical property curves for the absolute determination of $h\bar{\omega}$ values of this system will probably never be made due simply to the heterogeneity of the materials. That is one set of measurements on one volume bears little or no relationship to those on the next because of the complexity of natural coal or limestone. Natural graphite can be assumed to be the final stage of the coalification process, e.g. a hydrogen free organic ring structure. Since the range of $h\bar{\omega}$ values[1] lie from about 0.1 to 10 eV with the metallic materials having values in the range of greater than 8.0 eV, ionic materials with values less than 3.0 eV and covalently bound materials with values between 6–8 eV it seemed realistic to choose the value of graphite ($h\bar{\omega}$ = 7.2 eV) to represent approximately that of coal. Clearly this and the choice of that value of 3.6 eV to represent the limestone–coal system is arbitrary; however, the presence of a water film will cause a reduction in this decision of any known couple value by a factor of ten such that ($h\bar{\omega}$) now is about 0.4 which in any event, cannot exceed 0.5. The discussion below will demonstrate that even with ($h\bar{\omega}$ = 0.5) the van der Waal's forces are not a controlling variable in the adhesion of this system when water is present.

TABLE I

Values of $h\bar{\omega}$ for various systems (in eV)

Particle	Substrate	Medium	$h\bar{\omega}$	Source
Graphite	Graphite	Vac.	7.2	Krupp[1]
KB	KB	Vac.	2.0	Krupp[1]
KB	KB	Water (25°C)	0.2	Krupp[1]
$CaCO_3$	Graphite	Vac.	3.6	Estimated
$CaCO_3$	Graphite	H_2O (25°C)	0.4	Estimated

The electrostatic force of adhesion between a conducting spherical particle and a conducting infinite, flat substrate due to electrostatic charges was also given by Krupp[1] and discussed by McClure.[3] McClure *et al.* observed that electrical charges on the particles of 2–5 μ coal on a coal substrate in a relative humidity of 20%, appeared to be relatively unimportant with respect to forces of adhesion. This is consistent with the observations of Fuchs[2] and others.[3–5] Krupp[1] has also indicated that for non-conducting spherical particles on flat, infinite, conducting substrates, the equilibrium electrical charges on the particles do not contribute very much to the forces of adhesion. On this basis, the authors decided to neglect the effects of electrostatic forces in the system of limestone particles on a coal substrate.

The surface tension force of adhesion (F_{st}) due to the presence of a liquid film on the surface of the particle and/or the substrate was presented by MacFarlane and Tabor[12] as

$$F_{ST} = 4\pi\gamma R \tag{2}$$

where r is the surface tension of the liquid and R is the radius of the particle. This equation provides the maximum value observed for particles larger than

0.01 cm and was given as the relative humidity approached 90%. A review of the problem is given by Fuchs.[2] The density of calcite was given as: 2.710 gm/cc.[13]

TABLE II

Calcite sphere on a graphite substrate where $Z = 4$ Å and $h\bar{\omega} = 0.4$ eV (estimated)

Particle diameter (μm)	F_{vdw} (m dynes)	F_{ST} (m dynes)
1	0.72	45
5	3.60	226
10	7.20	452

F_{vdw} = van der Waal's force.
F_{ST} = Equation 2.
m dynes = 10^{-3} dynes.

EXPERIMENTAL

Krupp[1] and Corn[3] have presented critical reviews of the various techniques used for the measurement of the adhesive forces in a particle-substrate system. Microbalance,[3] pendulum,[14] aerodynamics[15] and an ultracentrifuge[6] are just a few of those techniques considered. The ultracentrifuge method appears to be most suitable for micron-sized irregularly shaped particles and was, therefore, chosen for the system under consideration.[11] The force tending to fracture the particle from the substrate is given by the equation

$$F = \rho V a_c \tag{3}$$

where F = Centrifugal force
ρ = Density of particle
V = Volume of particle
a_c = Centrifugal acceleration

An International B–60 centrifuge with an SB–283 rotor capable of attaining 280,000 g of centrifugal acceleration was used. In the following experiments, the variable position titanium buckets shown in Figure 1 were used to support the samples in the centrifuge. The buckets were designed such as to move from a initial vertical rest position to a horizontal position as the speed or rotation increased. The outer titanium bucket contained an inner removable aluminum holder which housed the coal substrate samples and could be sealed from ambient conditions in order to maintain the required humidity around the sample during the test. An aluminum sample holder was constructed from an aluminum rod approximately 1.2 cm diameter and 5 cm long, which was bored from both ends in order to reduce the mass. An aluminum cap was fitted securely on one end to act as a support for the electron microscope grid. The coal substrate, approximately 0.5 cm × 0.5 cm in area, was cleaved parallel to its bedding planes from a block of medium volatile bituminous Pittsburgh coal. The coal substrate was fixed by means of an epoxy adhesive

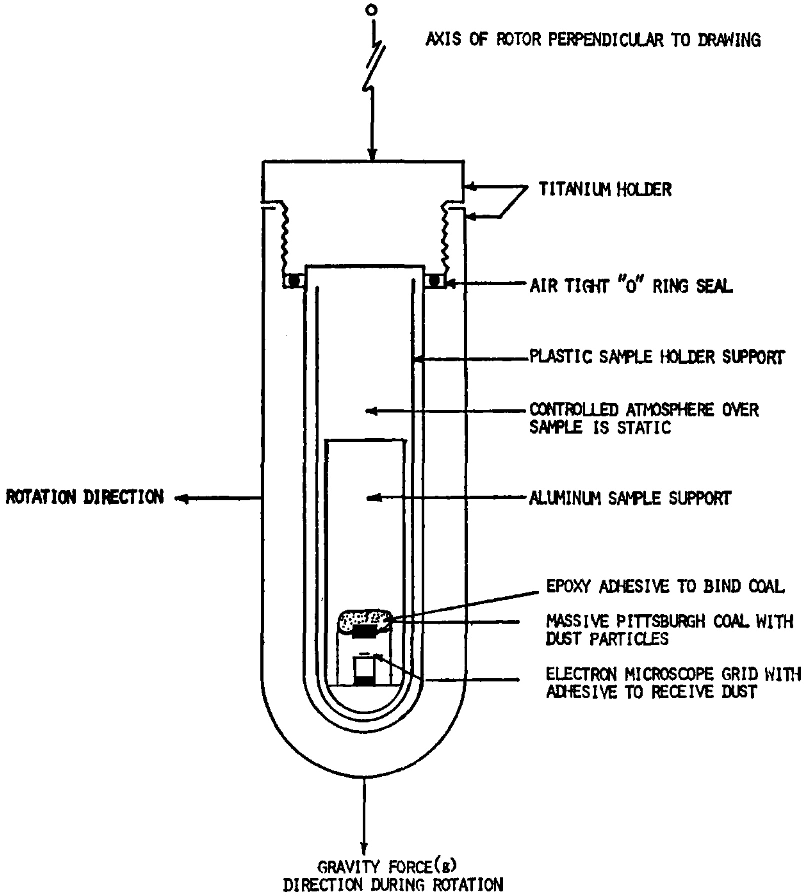


FIGURE 1 Titanium test tube assembly.

to the aluminum holder as shown in Figure 1. The electron microscope grids were 300 mesh copper grids with an overall diameter of 3 mm and were coated with a collodion film. The electron microscope was a model JEM-7A manufactured by Japan Electron Optics Laboratories and capable of attaining a maximum magnification of about 250,000 ×.

PROCEDURE

A constant humidity box was designed to establish the humidity over the samples. The box was isolated from ambient conditions and the air in the box was maintained at constant relative humidity by constantly recirculating the air over a saturated salt solution. The various salts used as given in Table III.

TABLE III

Different saturated salt solutions for constant relative humidity

Salt	Temp. °C	Maximum %RH	Observed %RH
NH_4Cl	20	79.2	72.0
K_2CrO_4	20	88.0	82.5
$Na_2SO_4 . 10\,H_2O$	20	93.0	88.0
H_2O	20	100.0	93.5

% RH = percent relative humidity.

The relative humidity obtained in the box was measured with an Electro Hygrometer Indicator (Model 15–3001, Hygrodynamics Inc.). The limestone dust used in the experiments was 200 mesh × 0 limestone dust, provided by U.S. Bureau of Mines.

Since limestone dust particles tend to agglomerate in a humid atmosphere, the dust was predried for at least 24 hours in a dessicator, and then placed in the round bottom flask shown in Figure 2 and agitated and fluidized by means of completely prefiltered dry air at 7–10 liters per minute. The fluidized particles were allowed to settle down a 6 cm I.D. settling column at ambient temperature and a relative humidity of about 20%. The coal substrate attached to the aluminum holder was placed at the bottom of the 100 cm long settling column such as to receive the dry, deionized limestone dust.

The particle density on the substrates was estimated from four electron microscope grids which were placed adjacent to the coal substrates during the settling procedure. If the particle density was too small, the entire procedure was repeated. When the particle density was satisfactory, e.g. at least one particle per 500 μm^2, the coal substrates were placed in the constant relative humidity box and maintained at desired constant humidity until the system equilibrated. The substrates were then sealed into the titanium centrifuge buckets while in the constant humidity box, so as to retain the same relative humidity ambient around the substrate during the centrifuge test. The titanium buckets with the enclosed substrate were then placed inside the centrifuge and exposed to a known amount of acceleration for about 5 minutes. The temperature was maintained in the centrifuge at about 20°C.

After each acceleration run, the electron microscope grids mounted opposite the coal substrates were removed for observation and a new set of grids were set in their place. This procedure was repeated in detail by steps until a maximum of 142,000 g acceleration was achieved. The coal substrates began to disintegrate at higher g values.[1] All the grids were examined in the electron microscope at a magnification of 3,000 ×, and the per cent area occupied by the particles was counted from the photographs. Several photographs were taken for each grid, and two grids for each acceleration run of a particular substrate. Three different coal substrates were used for each particular relative humidity run. From the initial particle density and the particle density after the test one can calculate particle density due to each acceleration. Figure 3 shows the photographs of limestone dust particles taken with the electron

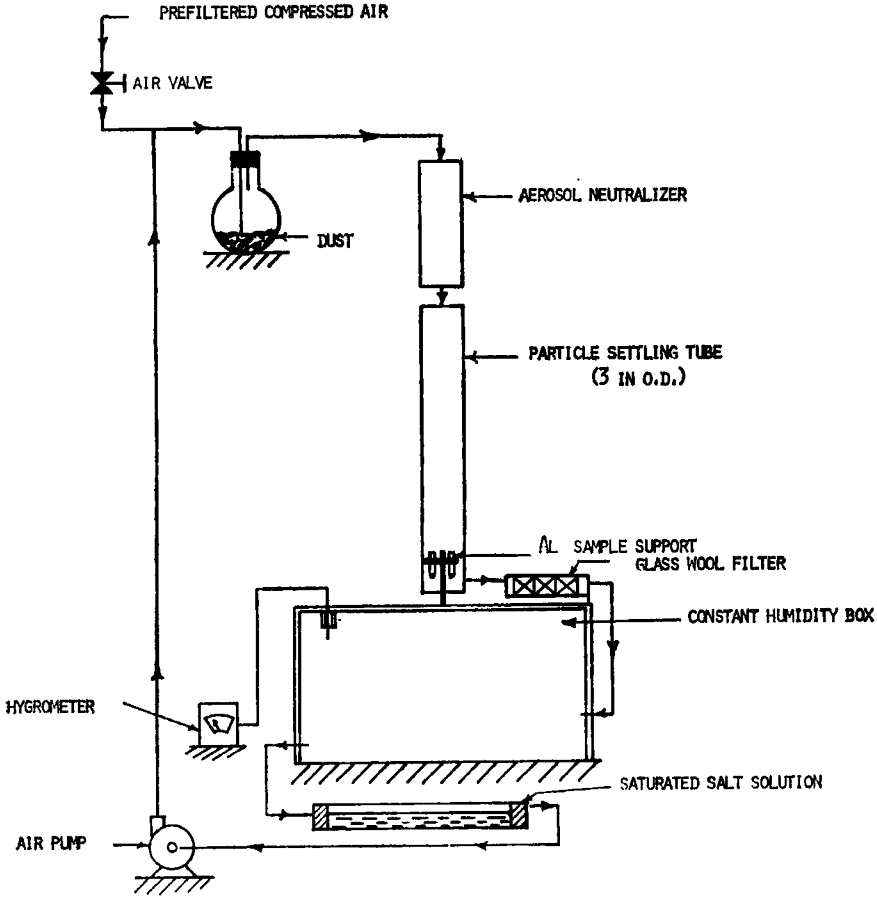


FIGURE 2 Schematic diagram of Particle Settling Apparatus.

TABLE IVa

Particle size distribution before centrifugation (limestone dust)

Size range (μm)	Mass mean (μm)	No. of particles counted	Frequency %	Volume fraction %
0.25–0.5	0.412	67	9.32	0.129
0.5 –0.75	0.649	120	16.69	0.901
0.75–1.0	0.894	145	20.7	2.84
1.0 –1.25	1.14	106	14.74	4.29
1.25–1.5	1.39	70	9.74	5.11
1.5 –1.75	1.64	51	7.09	6.12
1.75–2.0	1.88	53	7.37	9.69
2.0 –2.25	2.13	33	4.59	8.76
2.25–2.5	2.38	25	3.48	9.26
2.5 –3.0	2.77	21	2.92	12.26
3.0 –3.5	3.26	16	2.23	15.23
3.5 –4.0	3.76	5	0.695	7.30
4.0 –5.0	4.55	7	0.974	18.11
	Total	719	100.00	100.00

$d_{\text{mass mean}} = 1.71$ μm [before centrifuging].

Mass mean diameter is calculated as: $d_{mm} = [\phi_1 d_1^3 + \phi_2 d_2^3 + \phi_3 d_3^3 + \cdots + \phi_n d_n^3]^{0.333}$ where d_n's are mass mean diameters of different sizes ϕ_n's are fractional frequencies of the size ranges.

TABLE IVb

Particle size distribution after centrifugation (limestone dust)

Size range (μm)	Mass mean (μm)	No. of particles counted	Frequency %	Volume fraction %
0.25–0.5	0.412	67	11.00	0.195
0.5 –0.75	0.649	162	26.60	1.85
0.75–1.0	0.894	136	22.33	4.05
1.0 –1.25	1.134	70	11.49	4.30
1.25–1.5	1.38	45	7.39	4.99
1.5 –1.75	1.64	30	4.93	5.47
1.75–2.0	1.88	26	4.27	7.22
2.0 –2.25	2.13	26	4.27	10.48
2.25–2.5	2.38	13	2.14	7.31
2.5 –3.0	2.77	16	2.63	14.18
3.0 –3.5	3.26	11	1.81	15.89
3.5 –4.0	3.76	2	0.33	4.43
4.0 –5.0	4.55	5	0.85	19.64
	Total	609	100.00	100.005

$d_{\text{mass mean}} = 1.57$ μm (after CF).
$d_{mm} =$ (before CF) = 1.71 mean
(after CF) = 1.57 1.64 μm
$cF =$ Centrifuging.

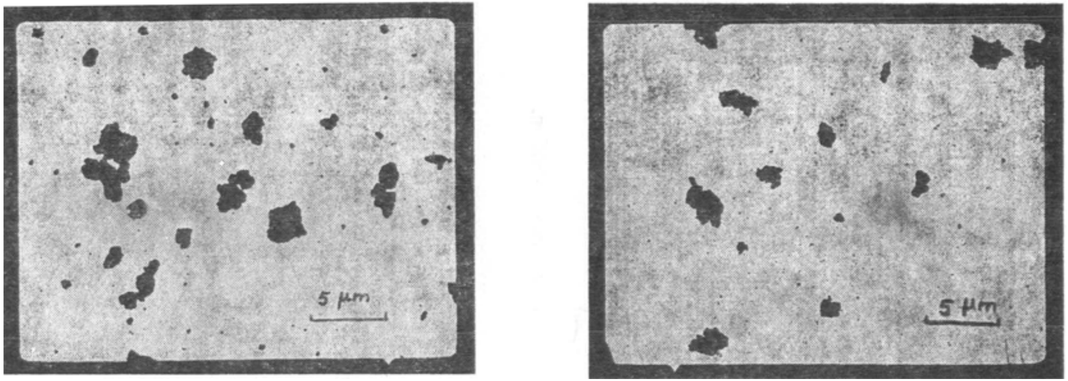
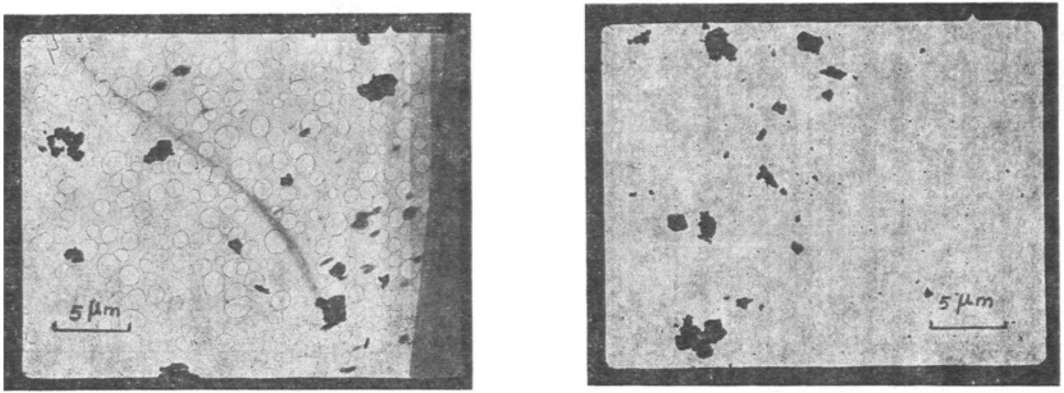


FIGURE 3 Electron micrographs of limestone dust particles before and after centrifugation.



Electron micrographs of limestone dust particles after centrifugation.

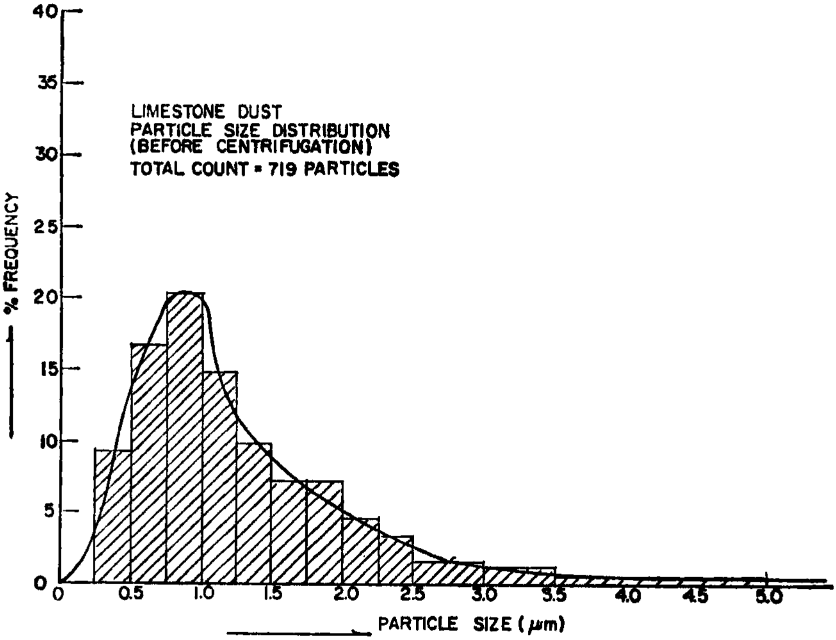


FIGURE 4(a) Limestone particle size distribution before centrifugation.

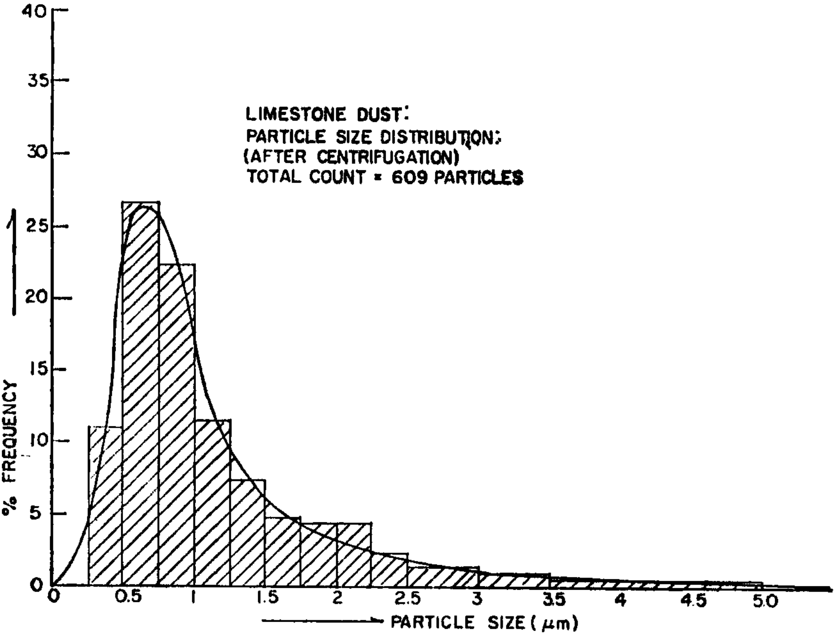


FIGURE 4(b) Limestone particle size distribution after centrifugation.

TABLE V

Limestone dust on coal substrate

Temperature °F	Relative humidity at 74°F %	Substrate number	% Particles retained on substrate at force (mdyne)						
			0.0 (0 g)	0.25 (3,940 g)	0.10 (15,800 g)	0.225 (35,500 g)	0.40 (63,000 g)	0.625 (98,500 g)	0.9 (142,000 g)
74	18	1	100	4.10	4.05	4.00	3.99	—	—
		2	100	3.2	3.1	3.0	3.0	—	—
		3	100	0.51	0.50	0.49	0.48	—	—
74	72	1	100	1.5	1.38	1.38	—	—	—
		2	100	4.31	4.25	4.20	—	—	—
		3	100	1.35	0.0	0.0	—	—	—
76	82	1	100	36.5	33.1	29.7	26.9	22.6	—
		2	100	21.1	17.1	11.9	9.2	6.5	—
		3	100	27.8	24.5	21.0	17.8	15.0	—
74	89.5	1	100	82.2	—	72.8	—	—	—
		2	100	69.0	—	59.9	—	—	—
		3	100	95.5	—	85.0	—	—	—
74	93.5	1	100	96.8	91.4	87.2	—	83.2	81.0
		2	100	95.8	91.6	87.9	—	84.7	82.6
		3	100	93.4	91.2	89.6	—	87.2	85.5

Limestone dust particles have a mass mean diameter of 1.64 μm; as shown in Tables VII and VIII. $\rho_{\text{limestone}} = 2.7$ gm/cc.

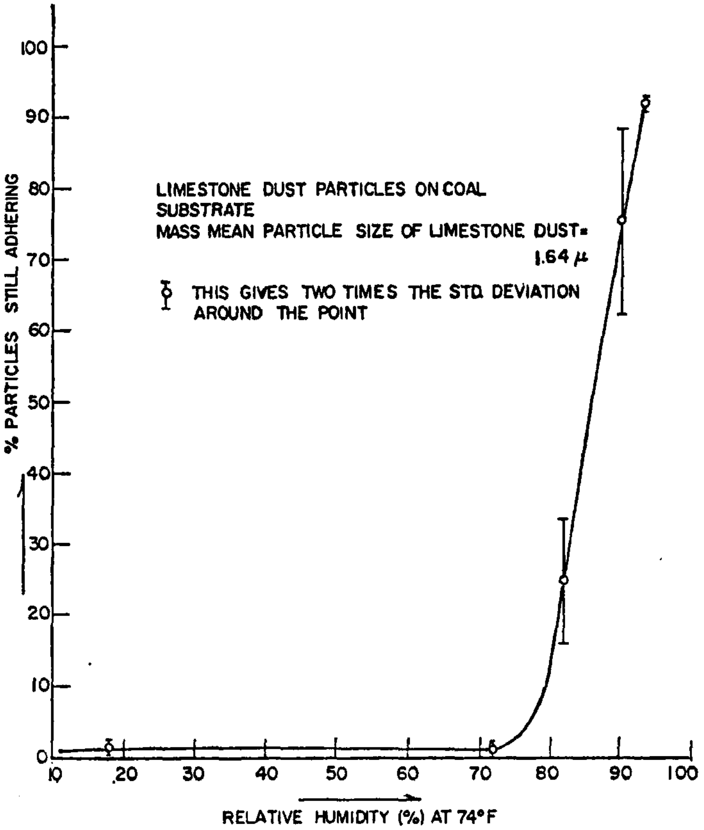


FIGURE 5 Variation of limestone particle adhesion to coal with relative humidity at a particle removal force of 0.1 mdynes.

microscope at a magnification of 3,000 ×. Table IV and Figure 4 show a typical particle size distribution for limestone dust from which we can conclude that the mass mean size (D) for the dust was 1.64 μm. Figure 5 and Table V show the effect of relative humidity on the force of adhesion in the system limestone particles on a coal substrate.

RESULTS AND DISCUSSION

The relatively large scatter shown in Table V from substrate to substrate under similar conditions might be expected when one considers the irregular shape of the particles and the inhomogeneity of the substrates. The data clearly demonstrates, however, that as the relative humidity increases above about 75% the force of adhesion increases dramatically reaching a maximum above 95% relative humidity.

Table VI shows the variation of adhesion with the percent relative humidity at 15,800 g, i.e. a fracture force of 0.1 millidynes on the particles of size 1.64 μm and the respective standard deviations of these values.

TABLE VI

Limestone dust particles in place at 0.1 *m* dyne fracture force

Relative humidity % (at 74°F)	Particles still adhering %			Mean value	Std. deviation
	Sub. #1	Sub. #2	Sub. #3		
18	4.05	3.1	0.5	2.55	0.84
72	1.38	4.25	0.0	1.88	2.17
82	33.1	17.1	24.5	24.9	8.0
89.5	76.0	62.0	89.0	75.7	13.0
93.5	91.4	91.6	91.2	91.4	0.2

Calcite demonstrates a multilayer water adsorption at normal temperatures which follows a typical "sigmoid" type of water adsorption curve that produces a linear BET plot for relative water vapour pressures between about 0.05 to 0.4. From these data provided by Hackerman *et al.*,[16] the constants V_m and c in the BET equation

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m^c} + \frac{c - 1}{V_m^c}\frac{(P)}{P_0}$$

can be evaluated as

$$V_m = 0.135 \text{ cc STP/gm}$$
$$c = 58.3 \text{ (at 25°C).}$$

If we assume that adsorption on a calcite surface is similar to that of a limestone surface the extent of the limestone surface covered with adsorbed water (θ) at given relative humidities can be estimated using the values of V_m and c. Table VII shows the extent of coverage in number of monolayers (θ) of adsorbed water versus the percentage of particles held on the surface at 0.1 millidynes.

TABLE VII

Extent of surface coverage ($\theta = v/v_m$) versus P/P_0

% RH	P/P_0	$v/v_m = \theta$	% Particle adhering after 0.1 mdynes
18.0	0.18	1.13	2.55
72.0	0.72	3.54	1.88
82.0	0.82	5.53	24.9
89.5	0.895	9.5	75.7
93.5	0.935	15.4	91.4

The variation of heat of adsorption of water on calcite indicates that the absorbed water layer becomes essentially "free" water at some point above the adsorption of 5 monolayers.

The data shown in Table VII suggest that there is a stronger adhesive force at 18% relative humidity than exists at 72% relative humidity and in both cases that the force of attraction is much less than one would estimate with the van der Waal's force, Eq. (1), when $h\varpi = 0.4$ eV (water modified) and $Z = 4 \times 10^{-8}$ cm. Since the adsorbed water layer has increased in thickness yet the adhesional bond appears to have decreased in strength between 18 and 72% RH one might suggest that the water layer does decrease the van der Waal's force of attraction even more significantly than previously anticipated.

The effects of the adsorbed water layer on the particle adhesion becomes significant above 72% RH or when the number of monolayers of water exceeds five (assuming that adsorption on limestone is the same as that on calcite). The water meniscus has become the significant factor in the force of adhesion (F_{ST}) as indicated in Eq. (2).

The mean particle diameter was observed as 1.64 μm; therefore those particles having diameters greater than 1.64 μm will experience a centrifugal force proportional to (d^3), whereas the adhesion forces holding these particles is only proportional to "d"; as a consequence, those particles with a diameter greater than 1.64 μm will be removed from the substrate at lower accelerations. If the cut-off point is taken at a mean diameter of 1.64 μm, the number frequency corresponds to a mean diameter of 1.64 μm which is 16.25% of the particles or 83.75% or the particles will still adhere. The force values at the point where 83.75% of the particles still adhere will give us an indication of the adhesion force corresponding to a diameter of 1.64 μm. By the extrapolation of the straight lines observed at a relative humidity of 93.5% (maximum for this study), we find a mean force of adhesion of 0.8 mdynes for three substrates when 83.75% of the particles are still attached to the substrate. The mean force of adhesion values decrease to much less than 0.1 mdynes as the relative humidity decreases below 20%.

Since water is known to reduce the van der Waal's force of adhesion, the observed effect must be due to the presence of a meniscus and as observed should have a value in the range of 0.8 mdynes. A force of adhesion due to surface tension forces as predicted using the MacFarlane–Tabor equations[12] for a particle radius of 8.2×10^{-5} cm is 74.2 mdynes or about two orders of magnitude larger than that observed. It should be recognized that the MacFarlane–Tabor study only included spheres larger than 0.01 cm in diameter and this equation has not been tested for μm diameter particles. A test of Picknett's[17] Eq. (4)

$$F = 4\pi R\gamma \sin^2 \theta + 2\Delta p\pi R^2 \sin^2 \theta \tag{4}$$

as modified for a sphere on a plane where R is the particle radius, γ is the surface tension of the fluid and θ is the angle between the sphere contact normal to the plane and the extent of the meniscus leads to force values between 40–80% larger than those predicted by the MacFarlane–Tabor relationship for angles (θ) between 10°–60°. The consequence is clear that the attractive forces for limestone particles on a coal substrate follow neither the van der Waal's force of attraction as predicted by Eq. (1) nor the equation used to establish the force of adhesion due to meniscus formation in the area of contact.

If we recognize that limestone is hydrophilic (contact angle (θ_1) much less than 90°) and that coal is generally regarded as hydrophobic (contact angle (θ_2) much greater than 90°) a situation considered by O'Brien[18] is approached in which the attractive force was suggested to be

$$F_{ST} = 2\pi R\gamma(\cos \theta_1 + \cos \theta_1) \tag{5}$$

Equation (5) reduces to the MacFarlane–Tabor[12] equation when $\cos \theta_1 \simeq \cos \theta_1$. When θ_1 approaches zero and θ_1 approaches 180° Eq. (5) will approach a value which is 50% of that given by MacFarlane–Tabor equation which for the special case cited above is 37.1 mdynes. On the other hand, if one accepts the high binding forces of water to the limestone (calcite) as shown by Hackerman *et al.*,[16] then one might expect that the solid particle behaves much as a drop of water resting on a hydrophobic substrate offering a minimum of adhesion force.

A slight modification of Eq. (2) was proposed by Schubert[19] where the force of adhesion due to the presence of a meniscus is one quarter of that shown in Eq. (2).

The above analyses have proceeded as if the limestone particles were spherical whereas a careful inspection of the particles shown in Figure 3 indicates that the particles indeed have surface asperities which may in fact impart more control over the adhesion force than does the major radius of curvature of the particle itself. The effect of asperities on micron sized particle adhesion due to van der Waal's and surface tension forces was considered recently by Rumpf.[5] If we assume that the radius of curvature of the limestone asperities was about 0.08 μm as estimated from Figure 3 and that the particles rested in three point asperity contact then according to Rumpf's analysis the van der Waal's force of adhesion for 1.68 μm diameter particles using the variables established above now becomes about 0.8 mdynes which seems to agree quite well with our observations. If we were to presume even smaller asperities (not resolved in Figure 3), the effect would be to reduce the adhesion force by about an order of magnitude for an order of magnitude reduction in the asperity radius of curvature which for the moment appears to be unnecessary.

The effect of the presence of asperities on the forces due to the presence of a water meniscus is not nearly as great as is the case for the van der Waal's forces[5]; that is, using the asperity radius of curvature of 0.08 μm the force due to surface tension is in the range of 10–50 mdynes depending on the meniscus diameter or at least a factor of ten higher than the forces observed.

CONCLUSION

The incorporation of the asperity model did produce theoretical estimates of the force of adhesion of 1.68 μm limestone particles to coal substrates which were more realistic than the non-asperity models; however a problem in analysis still remains. That is, as the relative humidity increases from about 20% to over 90% the force of adhesion increases from less than 0.1 mdynes to in excess of 0.8 mdynes. An adsorbed water layer on the limestone increases in thickness over this same range. The increase in adhesion force with relative humidity must be accounted for through the presence of the water through surface tension forces since the van der Waal's force decreases monatomically with an increase in water film thickness. As a consequence the calculated van der Waal's force of attraction of 0.8 mdynes which agrees with the observed force of 0.8 mdynes at 93% RH must be considered as fortituous since the observed value ought to increase with a decrease in relative humidity.

A possible answer to this dilemma might lie in the structure of the coal itself and the behavior of moisture within the coal structure.[20] Coal is a porous solid with a pore size in the range of 40 Å. The pores are small enough to cause the condensation of water well below the equilibrium condensation point. Such water is often called "inherent" water and under equilibrium conditions can be as high as 38% of the coal mass. The Pittsburgh coal sample used has an inherent water content in the range of 2%; however, this value will increase with the relative humidity surrounding the porous system. This variation may be envisioned as the filling or emptying of the pores in the coal. The solid coal material surrounding the porous system is quite hydrophobic thus an anhydrous particle of coal demonstrates a very high contact angle with water. Once the pores are filled with water, the surface of coal appears to have a zero contact angle, e.g. the advancing contact angle on dry coal is much greater than 90° whereas the receding angle is usually near zero.[21] With these facts in view a new model emerges which suggests that at relative humidities below 70% where the attractive forces are 0.1 or less mdynes the asperity model van der Waal's forces are probably operative and the asperity radii of curvature must be in the range of 10^{-2} μm. The capillaries of the coal are not filled to the point where they can interact with the water film on the limestone. Above 72% RH the capillary water is beginning to interact with the water film on the limestone; and as more capillaries are brought into service the stronger the junction becomes.

In this approach the generation of a meniscus in the early stages, i.e. RH less than 70%, would be against a hydrophobic surface where the contact angle was much greater than 90°. Such a model cannot be interpretated by the MacFarlane *et al.*[12] approach where one must assume very low contact angles. As the capillaries fill up, i.e. RH greater than 80%, the coal surface becomes hydrophilic and a meniscus can exist between the particle and surface. The strength of this junction, however, will be reduced somewhat since some fraction of the free coal surface is hydrophobic which should yield a reduced junction strength relative to a homogeneous hydrophilic surface.

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