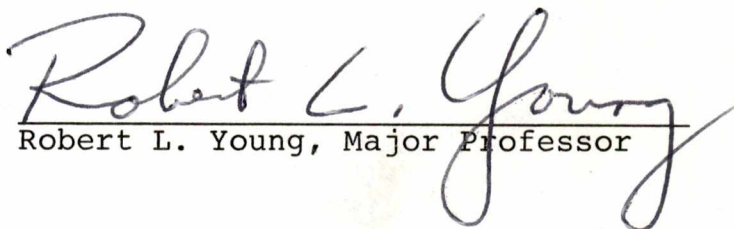
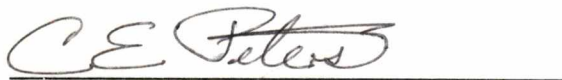


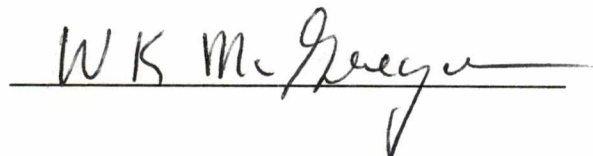
To the Graduate Council:

I am submitting herewith a thesis written by Rick A. Gamble entitled "Crushing Strength of Aluminum Oxide Agglomerates." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Mechanical Engineering.


Robert L. Young, Major Professor

We have read this thesis
and recommend its acceptance:





Accepted for the Council:


The Graduate School

CRUSHING STRENGTH OF ALUMINUM OXIDE AGGLOMERATES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Rick A. Gamble

March 1985

ACKNOWLEDGMENTS

The author wishes to thank Dr. Robert Young for serving as thesis advisor and Drs. Wheeler McGregor and Carroll Peters for serving on the thesis committee. Special thanks are extended to Dr. McGregor and Mr. Dave Van Dyke for the guidance and support they provided throughout this effort.

The work reported herein was sponsored by Headquarters, Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 65807F, Contract No. F40600-81-C-0007. The results reported herein were obtained by Sverdrup Technology, Inc. (SvT), a contract operator at AEDC, AFSC, Arnold Air Force Station, Tennessee, under AEDC Project No. D240.

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ABSTRACT

Aluminum oxide, formed during aluminum-based solid propellant combustion, condenses and solidifies in the exhaust flow to form submicron size particles, which may then adhere together to form agglomerates. Particle sampling, required for motor performance or environmental impact investigations, is usually done using a probe placed in the supersonic exhaust flow field. The bow shock at the sample probe inlet will decelerate the gas flow which introduces a large velocity differential between the gas and the particulate. This differential will result in a sudden increase in the aerodynamic drag on the agglomerates which may cause them to shear apart, thus altering the sampled size distribution.

In this effort, aluminum-oxide agglomerates were formed and then crushed in order to estimate the magnitude of the interparticle forces binding the agglomerate together. The agglomerates were formed by tumbling commercially available aluminum-oxide powder in a jar, and strength was determined by measuring the load required to crush the agglomerate between two flat plates. Analysis indicated that rough, uniformly shaped particles formed the strongest agglomerates. The experimentally derived particle binding forces were in agreement with values predicted by the Van der Waals force equation for closely spaced spheres.

Rocket exhaust particulates collected from a test facility exhaust processing system proved to be unusable due to impurities. Further studies are recommended with suitably collected and processed particulates.

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NOMENCLATURE

A_p	Agglomerate cross-sectional area (cm^2) ($=\pi d^2/400$)
a	Particle separation distance ($\text{\AA}$)
B_1, B_2	Constants in London-Van der Waals equations (ergs, erg-cm)
D	Agglomerate drag behind shock (dynes)
d	Agglomerate diameter (mm)
d_o	Unit particle diameter (μm)
F	Particle bonding force function (dynes)
F_e	Electrostatic bonding force (dynes)
F_s	Surface film bonding force (dynes)
F_{v_1}	Van der Waals bonding force ($a < 2,000 \text{\AA}$) (dynes)
F_{v_2}	Van der Waals bonding force ($a > 2,000 \text{\AA}$) (dynes)
k	Constant in Knudsen number function (gm/cm^2)
L	Sample probe diameter (cm)
M_1	Free-stream Mach number
m	Mass of agglomerate (gm)
P	Agglomerate force of adhesion (dynes)
P_o	Stagnation gas pressure (dynes/cm^2)
q	Surface charge density (couls/cm^2)
R	Universal gas constant ($\text{cm}^3\text{-atm}/\text{gmol-}^\circ\text{K}$)
T_o	Stagnation gas temperature ($^\circ\text{K}$)
T_θ	Sutherland's constant ($^\circ\text{K}$) ($=111.3^\circ\text{K}$ for air)

W_b	Particle Weber number
Z	Coordination number
γ	Gas specific heat ratio
δ	Bow shock detachment distance
ϵ	Coulomb's Law constant (dynes-cm ² /coul)
ϕ	Agglomerate solids fraction
ρ_a	Agglomerate solids density (=mass/volume) (gm/cm ³)
ρ_o	Stagnation gas density (gm/cm ³)
ρ_p	Density of aluminum-oxide powder (=3.7) (gm/cm ³)
σ	Standard deviation
σ_w	Surface tension of water (dynes/cm)

CHAPTER I

INTRODUCTION

One of the exhaust products formed during combustion of aluminum-based solid propellant is aluminum oxide which ultimately takes the form of small solid particles. These unit particles may adhere or agglomerate together into larger particles, as indicated by previous analysis of collected particulates [1].¹ The agglomerate formation location in the flow field, however, is not universally accepted to be in one specific region. Various authors have suggested the motor chamber [2], the throat exit [3], or further into the exit cone [4]. The size of these particles is important due to the effects on motor ballistic performance, and, many times, on the surrounding environment. Nonobtrusive sampling techniques are usually ineffective in measuring aluminum-oxide exhaust particulate, because of the very high densities [5]. Sample extraction techniques are therefore required. The common method of injecting a sample probe in the exhaust flow, however, will disturb the flow field and introduce several potential errors in the ensuing data.

¹Numbers in brackets refer to similarly numbered references in the Bibliography.

Girata [1] identified several potential biases in his sampling work. Those associated with the sample probe are: (1) material adhering to the probe inlet or sample lines; (2) agglomerates impacting the probe lip and breaking up; (3) the probe bow shock diverting the smallest particles away from the inlet; and (4) the agglomerates passing through the shock wave and shearing apart. The effects of the first item are determined easily by comparing the size distribution of material taken from the probe inlet to that on the collection medium. Agglomerate impaction on the probe lip should introduce a relatively small bias since the cross-sectional area of the probe lip is small compared to the inlet area. The remaining two items are caused by the sampling probe bow shock, which has an unknown and significant potential for altering the size distribution of the collected material. If the agglomerates do shear apart, then any collected material will falsely represent the actual free-stream conditions. In addition, information on the location of agglomerate formation cannot be obtained from collected particulate until the effects of the sample probe bow shock are fully known.

Forney et al. [6] derived equations which provide insight on the effects of the bow shock on sampling probe collection efficiency and sampling biases. To further define sampling phenomena, experimental data are needed on

the strength of the aluminum-oxide agglomerate bonds and the effects of shock waves on agglomerate size.

This effort is concerned with determining the strength of the interparticle agglomerate bonds, while subsequent work will be conducted on two-phase flow experimentation. The agglomerate generation and agglomerate crushing procedures are derived from previous work by Meissner et al. [7] with zinc oxide. Data are presented and analyzed with applications to solid rocket motor plume sampling in mind.

CHAPTER II

THEORETICAL BACKGROUND

The exhaust products of an aluminum-based solid propellant include aluminum oxide (Al_2O_3) which condenses and solidifies during discharge from the exhaust nozzle. Experimental data [1] indicate that this aluminum-oxide particulate consists of small ($\sim 0.1 \mu\text{m}$), nearly spherical particles that combine to form agglomerates of various sizes (1 to 5 μm). If a sample extraction technique is used to collect these agglomerates for analysis, then the sampling technique may significantly bias the data. A schematic of a sampling probe in a supersonic flow is shown in Fig. 1. The nonuniform agglomerates in the two-phase flow field will respond to the sampling probe and bow shock based on their size, momentum, and strength. The smaller, lighter agglomerates will best follow the stream lines but may collide with and stick to the probe wall, decreasing the small particle concentration in the sample. The larger, heavier agglomerates outside of the entrained flow may have enough momentum to pass through the shock, cross the turning stream lines, and enter the probe, thus indicating a higher large particle concentration than exists in the free stream. While these two possibilities have

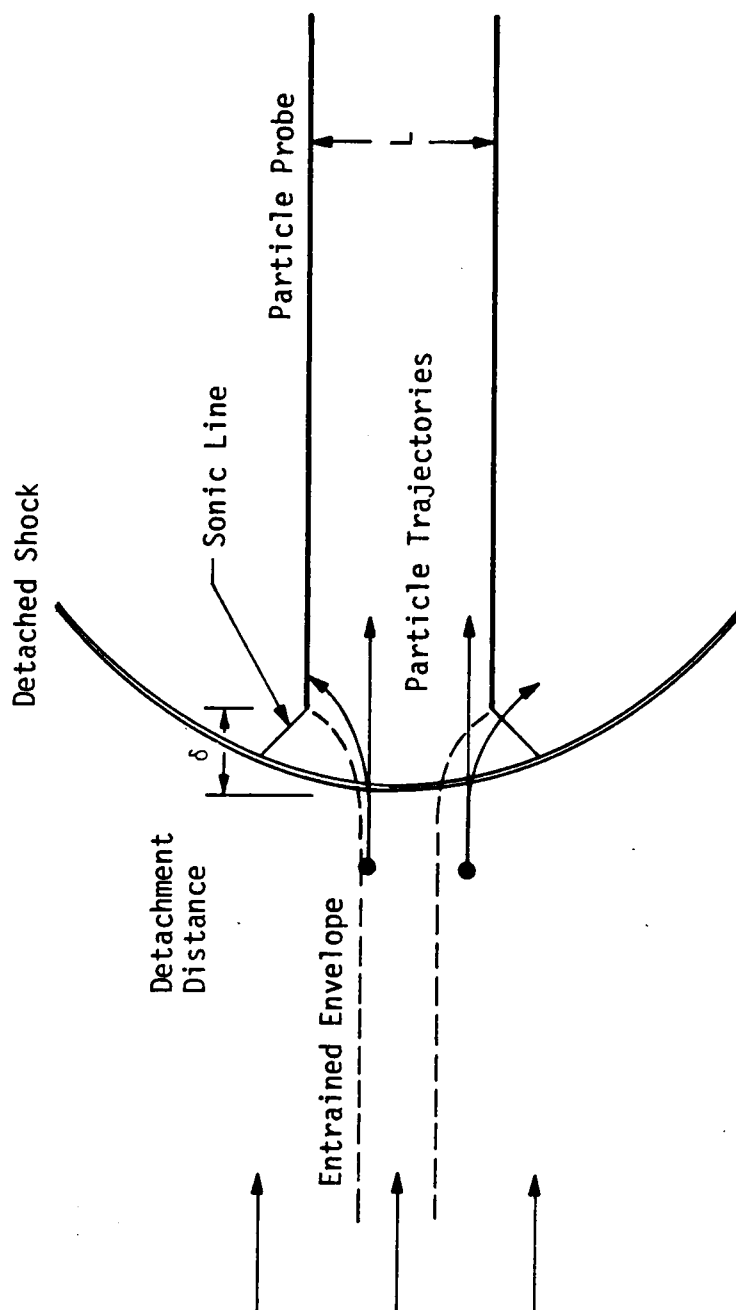


Figure 1. Schematic of Particle Probe in Supersonic Stream.

been addressed previously [8,9,10], the possible disintegration of agglomerates proposed by Girata has not been experimentally investigated.

A supersonic gas stream passing through a normal shock will decelerate to a subsonic velocity. Particulates in the gas stream will pass through the shock wave and suddenly experience a large velocity differential relative to the surrounding gas. The resulting drag on the particulate will be at a maximum immediately downstream of the shock wave and the particle drag will subside as the particle slows and the velocity differential vanishes. Forney calculated the free-stream Mach number which will impose the highest particle drag for a range of gas specific heat ratios. For the specific heat ratio range of 1.16 to 1.4, the maximum drag Mach number is between 2.3 and 2.4.

By definition, an agglomerate will break up if the external forces are greater than the combined interparticle forces binding the agglomerate together. This relationship is expressed as the ratio of the external force to the binding force and is known as the agglomerate Weber number, W_b . If the external forces are in the form of agglomerate drag D and the strength of the agglomerate is P , then,

$$W_b = \frac{D}{P} . \quad (1)$$

The criteria for breakup will be when the Weber number exceeds unity.

Rumpf [11] in his work on granulation of powders defined the strength of an agglomerate composed of small uniform spheres as

$$\frac{P}{A_p} = \frac{\phi Z F}{\pi d_o^2} \quad , \quad \phi = \frac{\rho_a}{\rho_p} \quad , \quad (2)$$

where ϕ is the agglomerate solid to total volume fraction, F is the particle bonding force function, P is the total force of adhesion, A_p is the cross-sectional area of the agglomerate, d_o is the unit sphere diameter, and Z is the coordination number. The derivation of this equation assumes that an agglomerate will fail when a cleavage plane is formed by a unit particle breaking one-half of its contacts with surrounding particles. The coordination number, Z , represents the number of points of contact that each unit particle has with surrounding particles. A coordination number of two would indicate a chain of particles, while higher numbers represent more complex agglomerate structures. Rumpf demonstrates that for common coordination numbers (i.e., 2 to 12), $Z(1-\phi) \simeq 3.1 \simeq \pi$. Equation (1) then simplifies to

$$\frac{P}{A_p} \simeq \frac{\phi}{1-\phi} \frac{F}{d_o^2} \quad . \quad (3)$$

Numerous particle bonding mechanisms have been discovered or invented. The strongest bonds are formed when the particles are heated and the particle surface is melted and fused with surrounding surfaces. Strong bonds are also formed when an adhesive binder is used. Other bonding mechanisms in order of decreasing strength include capillary forces, electrostatic forces, and Van der Waals forces. Figure 2 [12] shows the relative magnitudes of the bonding mechanisms with electrostatic forces included in the Van der Waals force category. Figure 2 was generated from tensile strength test data for various materials. The test procedure consisted of firmly attaching agglomerates to a centrifuge rotor and collecting dislodged particles at various rotation rates. The centrifuge is enclosed and evacuated to eliminate aerodynamic drag with only centrifugal force causing tension on the agglomerates.

The compressive force required to shear an agglomerate will generally be higher than the tensile strength [13]. This results from the unit particles sliding past one another during compression, introducing a friction force. The standard test apparatus for compressive or crushing strength tests consists of a test specimen placed between parallel flat plates. This method will be used in the experiments reported herein, since compressive forces are present on an agglomerate in the decelerating flow field downstream of a normal shock.

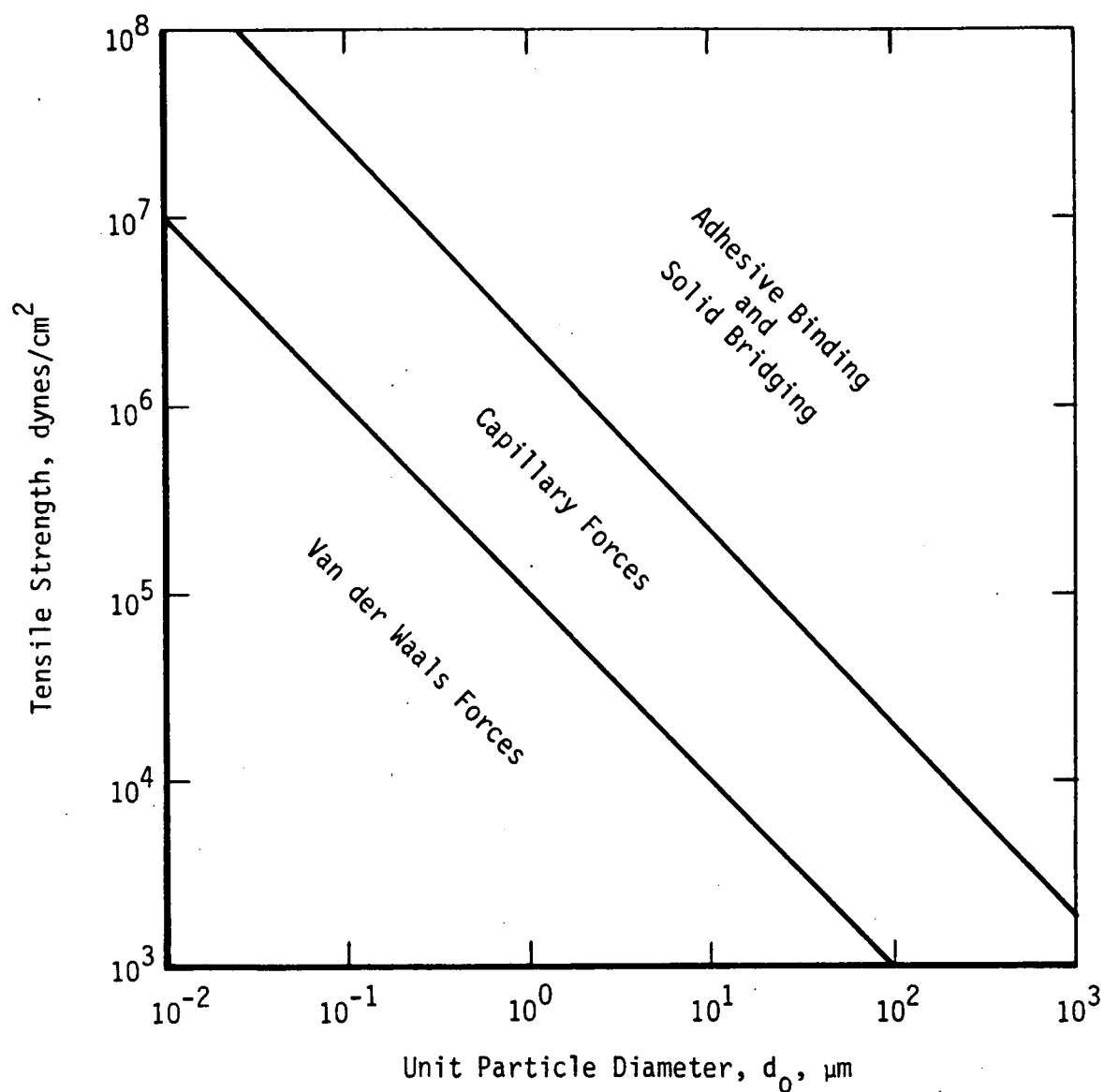


Figure 2. Particle-Size and Agglomerate-Strength Regions in which Various Binding Mechanisms Predominate [12].

Rumpf evaluated and summarized numerous equations pertaining to all types of particle binding. The possible types of forces applicable to aluminum-oxide agglomeration are listed in Table 1, along with definitions, equations, constants, and typical values. Solid bridging of particles was not considered in this instance since Girata's data indicated this type of binding was not present.

Van der Waals forces are due to the interaction of the surface atom electron orbits between adjacent surfaces or particles. As shown in Fig. 2, Van der Waals forces are the weakest of the bonding mechanisms.

London and Heitler [14] derived an expression applicable for small sphere separation distances, while the equations are modified according to Lifshitz [15] for larger distances. These forces are labeled F_{v_1} and F_{v_2} , respectively. An interparticle separation of 2,000 Å (0.2 μm) is the maximum distance for which the London-Heitler derivation applies.

Electrostatic bonding forces are possible when the particles are charged during formation or are exposed to an electron or ion charge after formation (i.e., a charged rocket motor exhaust). Experimental observations have shown that electrostatic forces can have a widely varied effect on the force of adhesion between particles. The magnitude of this effect is further enhanced by irregular particle surfaces and nonuniform charge distributions.

Table 1. Interparticle Bonding Forces

Force of Adhesion	Particle Types Affected	Interparticle Force Equation	Typical Constant Values	Maximum Expected Force ^a
Van der Waals	Clean, dry, uncharged particles			
a) London-Heitler		$F_{V1} = \frac{B1 d_O}{a^2}, a < 2,000 \text{ \AA}$	$B1 = 10^{-12} \text{ ergs}$	$F_{V1} = 8 \times 10^{-3} \text{ dynes}, a = 10 \text{ \AA}$
b) Lifshitz		$F_{V2} = \frac{B2 d_O}{3a^3}, a > 2,000 \text{ \AA}$	$B2 = 10^{-20} \text{ erg-cm}$	$F_{V2} = 1 \times 10^{-10} \text{ dynes}, a = 2,000 \text{ \AA}$
Electrostatic	Particles charged during formation or exposed to ionized gas	$F_e = \frac{\epsilon \pi d_O^2 q^2}{a^2}$	$\epsilon = 9 \times 10^{18} \text{ dynes-cm/couls}$	$F_e = 1.5 \times 10^{-2} \text{ dynes}, 20 \text{ electron charge}, a = 10 \text{ \AA}$
Surface Film	Particles in a condensable vapor	$F_s = 2.2 \sigma d_{wO}$	$\sigma_w = 72 \text{ dynes/cm water at standard conditions}$	$F_s = 1.3 \times 10^{-2} \text{ dynes}$

^a Calculations for a unit particle size of 0.8 μm .

A surface film will develop on a particle when it is in contact with a condensable vapor. Rumpf found that agglomerates of particles can be bonded together through surface fluid bonding or negative capillary pressure in the fluid-filled space between particles. The first method, called the pendular state, assumes that fluid only exists at particle points of contact, while the latter theory assumes that the entire inner agglomerate is fluid-filled. A combination of these two mechanisms, called the funicular state, has gas spaces present in the agglomerate void which are enclosed in a continuous network of liquid. Experimental work with iron ore agglomerates indicates that the funicular state provides the strongest form of liquid bonding.

The equations in Table 1 were derived for bonding forces between smooth, clean spheres. The constants, however, were evaluated from experimental data obtained from work with organic and inorganic particles that were moderately rough and spheroidal in shape. While the exact effects of surface roughness and particle shape are not known, the experimentally derived constants are in acceptable agreement with theoretical values. Experimental measurements for specific applications are still necessary, however.

Meissner [7] experimented with zinc-oxide powders. In his work, he painstakingly filtered the zinc-oxide powders to obtain unit particle sizes of 0.13 and 0.26 μm . These two sizes of particles were tumbled separately for specified time periods to generate agglomerates with repeatable solids fractions. These spherical agglomerates were then crushed using the accepted method of placing the agglomerate between two flat plates. The resulting data are shown in Fig. 3 and are presented using an exponential function of the solids fraction. Meissner's conclusion, which is also imbedded in Rumpf's work, is that the agglomerate strength is a unique function of the unit particle diameter, d_o , the agglomerate diameter, d , and the volume fraction of solids, ϕ .

Aluminum-oxide powder should have a similar function relating d_o , d , and ϕ . Agglomeration experiments were conducted to determine this relationship and to attempt to identify the interparticle forces present in the agglomerates.

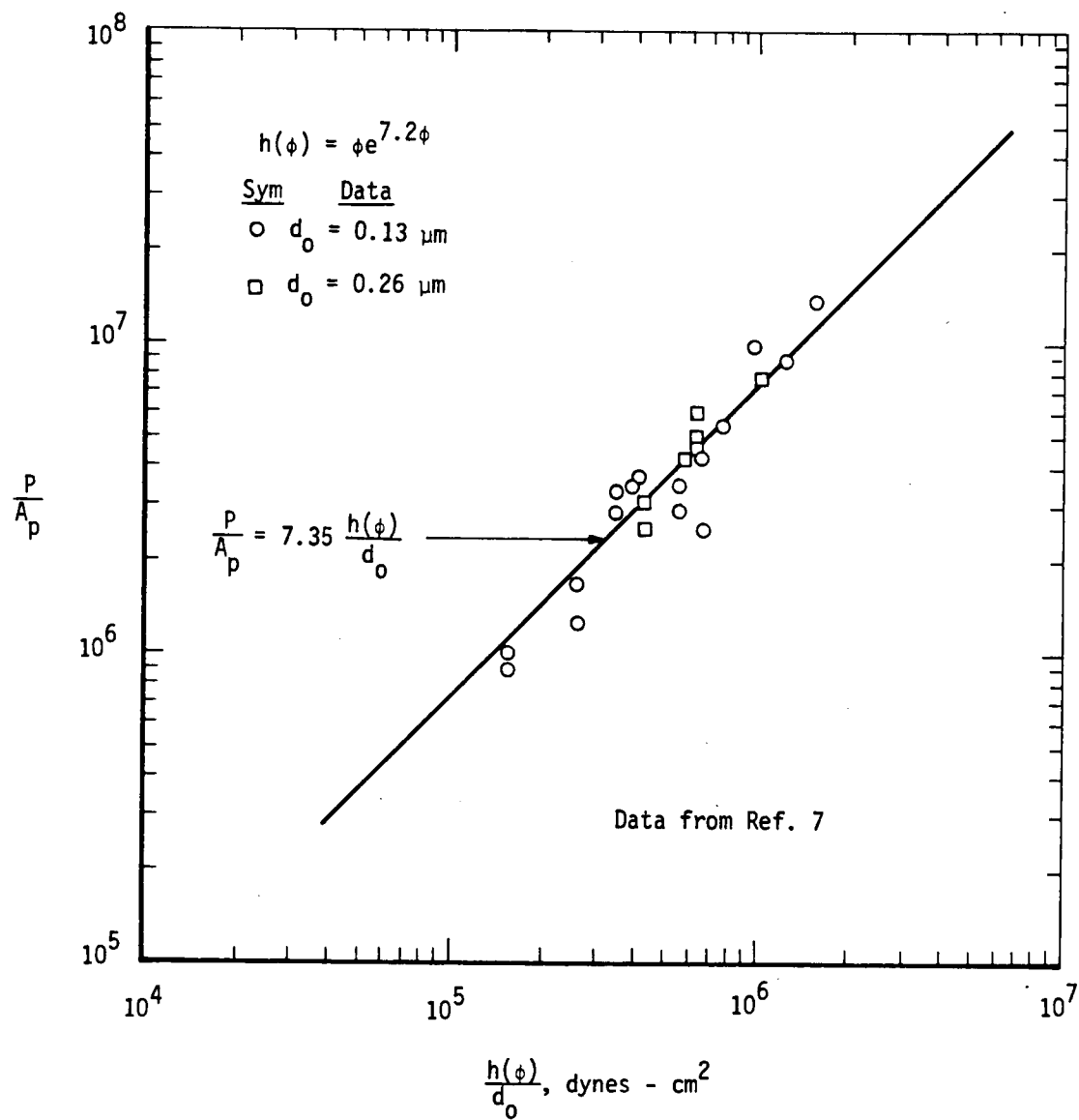


Figure 3. Crushing Strength of ZnO Agglomerates [6].

CHAPTER III

EXPERIMENTAL INVESTIGATION

Agglomerate Generation

The apparatus used to generate the agglomerates is shown in Fig. 4. This apparatus consisted of a two-liter glass bottle and stopper, a four-padded roller support stand, a small drive motor, and a variac for setting the tumbling rates. The drive motor was connected in parallel with the tumbling bottle with an oversize rubber O-ring placed over the midsection of the bottle. A small Teflon support pad was positioned over the bottle stopper to prevent the bottle from moving axially. Bottle rotation speeds were calculated by measuring elapsed time for an arbitrary number of bottle revolutions.

Powder was obtained from several sources. Table 2 identifies the chemical analysis and size range of each of the powders used as advertised by the manufacturer. The RE sample was taken from a collection pit at an AEDC test cell. The material collected was a sample of the remaining particulate from previously tested solid propellant rocket motors. The collected sludge was dried, processed and analyzed at the AEDC Chemical Laboratory. Calcium carbonate was included because it was readily available, appeared similar to the finer aluminum-oxide powders, and would

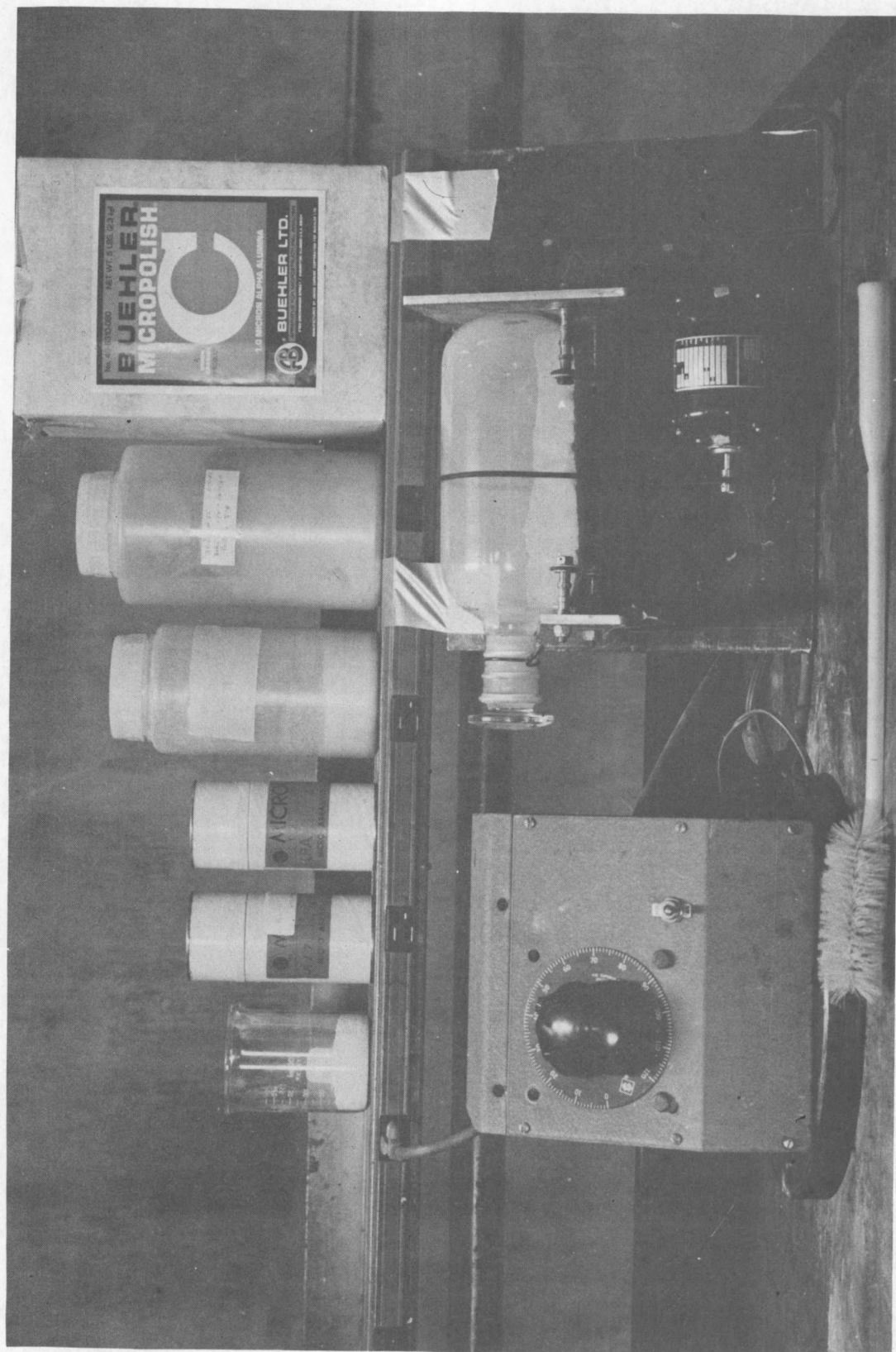


Figure 4. Agglomerate Generation Apparatus.

Table 2. Powders Used in Agglomeration Experiments

Type	Manufacturer	Experimental Designation	Size Range	Chemical ^a Analysis	Agglomeration Achieved
Al ₂ O ₃	Buehler	B-0.05	0.05 μm	99.9% Al	No
Al ₂ O ₃	Buehler	B-0.3	0.3 μm	99.9% Al	No
Al ₂ O ₃	Buehler	B-1.0	1.0 μm	99.9% Al	No
Al ₂ O ₃	Microabrasives	M-1-99	1.0 μm	99.4% Al 0.5% Si	Yes
Al ₂ O ₃	Microabrasives	M-1-97	1.0 μm	97.0% Al 0.2% Si 0.5% Mg	Yes
Al ₂ O ₃	b	RE	60% < 1 μm	86.0% Al 9.0% Fe	Yes
			35% 1-3 μm	1.5% Ca 2.5% Cl	
CaCO ₃	c	C	1.0 μm	99.9% Ca	No

^aAnalysis performed using a scanning electron microscope. Indicated elements are metals or metal compounds.

^bMaterial collected in sludge pit after rocket motor tests.

^cCommercially available ground limestone.

provide an agglomerate strength comparison. Acquisition of a similar size zinc-oxide powder was not possible. Current manufacturers that were contacted could supply nothing in a comparable size range.

Samples of each powder were atomized, placed on a witness stub, and examined and photographed with a Scanning Electron Microscope (SEM). A chemical analysis of each powder was performed by using an energy dispersive spectrometer connected to the SEM.

Agglomerate generation was attempted for each of the powders listed in Table 2. Tumbling rates and duration were varied from 40 to 250 rpm and from 20 minutes to 26 hours, respectively. Best results were obtained by setting jar rotation at 80 to 90 rpm. All powders were tumbled before and after open-air drying on a hot plate in order to determine any noticeable effects of moisture content on agglomerate formation.

Most of the powders tested would not agglomerate. These powders tended to slide on the tumbling jar wall until a "critical" jar rotation speed was reached. At this point, the powder would start to tumble in the jar. One of two events would then occur. Either the powder mass would return to simply sliding on the wall, or the powder would start adhering to the jar wall in increasing amounts until all powder was caked on in a continuous cylinder. This latter event would begin at times varying

from a few seconds to over 30 minutes after tumbling began. The reason for this event is unknown. The caking was not noticeably affected by the pretest drying process. A tesla generator was used on both the interior and exterior surfaces to neutralize any static charge buildup between the jar and powder, but with no apparent effect.

Agglomeration of three of the powder samples was accomplished. These were the Micro-Abrasives samples and the RE material. Of these three, the rocket exhaust residue was the least pure and tended to form the largest, most fragile agglomerates (~6 mm). The agglomerate surface was noticeably rough. The less pure Micro-Abrasives material (M-1-97) contained approximately 3 percent impurities and also formed fragile agglomerates. Attempts to remove many of these two types of agglomerates from the tumbling apparatus ended in their destruction.

The most success was obtained with the M-1-99 Micro-Abrasives sample. At any one time, the number of agglomerates in the previous two materials stayed relatively constant, whereas in the M-1-99 material, the number of agglomerates kept increasing. This held true until all powder had agglomerated, when further tumbling then tended to narrow the size distribution. These agglomerates were smooth spheres or spheroids and dissection indicated a

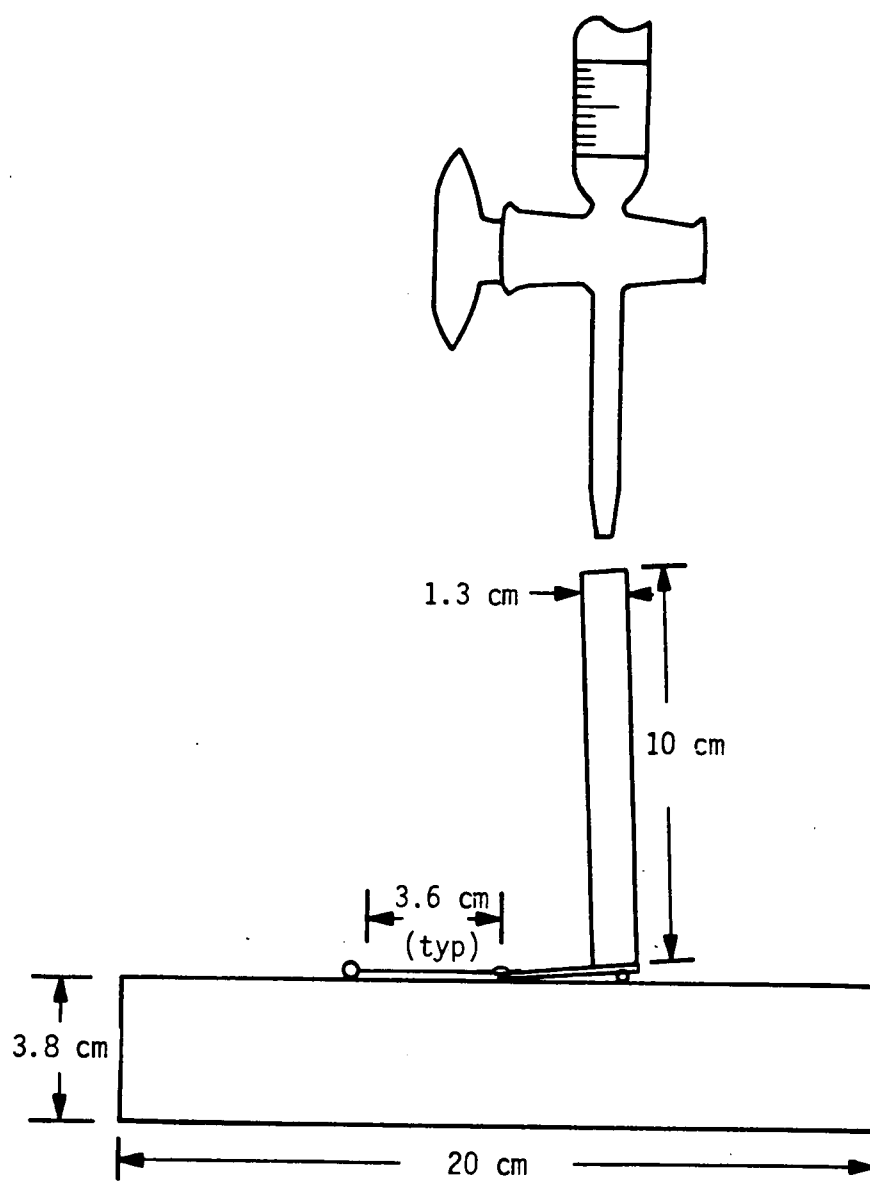
concentric sphere structure with the inner sphere also having a smooth surface.

Crushing Strength Determination

The M-1-99 agglomerates were chosen for crushing strength experiments because they were from the purest powder and had a measurable crushing strength with the apparatus used. It was decided that the RE sample agglomerates were too contaminated to give meaningful results and the M-1-97 agglomerates were too fragile to even handle.

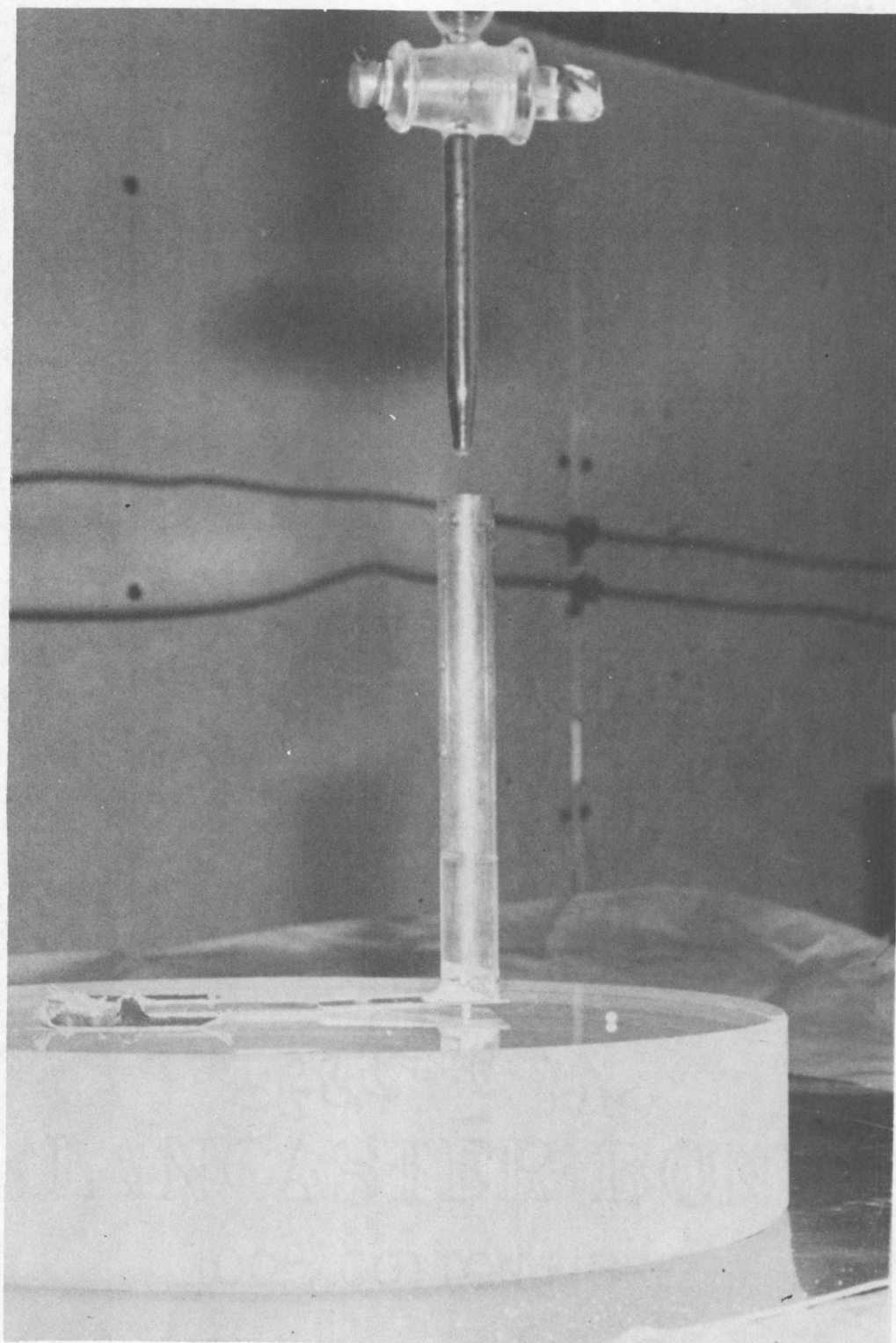
The M-1-99 agglomerates were arbitrarily categorized by size, and several from each category were removed for experimentation. The agglomerates were weighed to the nearest 0.01 mg using a microscale and measured to the nearest 5 μm using a microscope. From these data, the solids fraction, ϕ , of each agglomerate was determined.

A crushing apparatus (Fig. 5) was assembled to load the agglomerates. This apparatus consisted of a thick circular piece of polished glass used as a base plate, two hinged microscope slides, a 10-cm-tall plastic cylinder epoxied to one end of one slide, and a vertically supported graduated burret. Individual agglomerates were placed on the base plate and centered under the slide and cylinder.



a) Schematic

Figure 5. Crushing Strength Apparatus.



b) Photograph

Figure 5. (continued)

The burret stopcock was adjusted so that water would slowly drip from the burret into the open cylinder until the agglomerate failed. Pretest and posttest water levels in the burret provided a measure of the mass of water required to crush the agglomerate. In most cases, preweighed pieces of electrical wire were placed in the cylinder prior to testing in order to avoid filling the cylinder prior to agglomerate failure. In every instance, agglomerate failure occurred suddenly without any premature flattening of the agglomerate. Any prior deformation of the agglomerate would be easily noted in the movement of the relatively long cylinder.

Occasionally, a static charge would build up on the glass base plate and make positioning of the agglomerates difficult. Spray static remover was applied to the glass and slides to alleviate the problem.

A list of the measured parameters of this experiment is shown in Table 3. Also shown in Table 3 are possible factors affecting the accuracy of the measurements along with the maximum estimated error for each factor.

Thirty-eight agglomerates were successfully measured and crushed in this experiment. A larger data base was planned for statistical purposes; however, agglomerate handling during the various processes destroyed many of the agglomerates.

Table 3. Estimated Measurement Errors

Measurement Variable	Possible Causes for Error	Maximum Estimated Error
$d_o, \mu\text{m}$	Monodisperse powder assumption	$\pm 0.4 \mu\text{m}$
d, mm	Measurement uncertainty of microscope	$\pm 0.025 \text{ mm}$
m, mg	Measurement uncertainty of microbalance	$\pm 0.050 \text{ mg}$
P, dynes	Nonvertical loading	600 dynes
	Graduated buret reading	200 dynes
	Water remaining in loading cylinder between tests	100 dynes
	Variations in water density	50 dynes
	Variations in tare due to agglomerate placement	10 dynes

The crushing strength apparatus used here does not duplicate the distributed pressure loading that an agglomerate would actually experience after passing through a normal shock wave. Some previous experiments have used compressive mats to provide a more uniform loading [12]. In either case, failure will occur when a unit particle forms a cleavage plane with surrounding particles, as previously assumed. Evidence for this assumption is provided in the abrupt manner in which the agglomerates fail. The point-loading apparatus will therefore still permit measurement of the interparticle bonding force.

CHAPTER IV

RESULTS

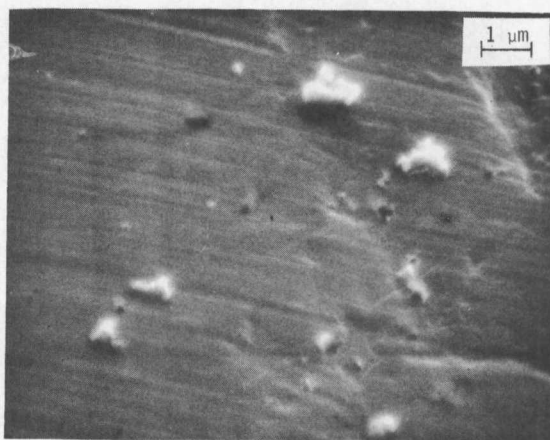
Agglomerate Analysis

The chemical analysis of the powders used in these experiments is included in Table 2, page 17, and a photograph of the typical unit particle shapes for each powder is shown in Fig. 6. Examination of each photograph shows that the particle shapes vary from long spikes to jagged cubes to smooth spheroids. Figures 6a through 6c illustrate the three Buehler powders that would not agglomerate. These unit particles tended to be relatively smoother and uniform compared to the other powders. The calcium carbonate (Fig. 6d) also would not agglomerate even though a wide distribution of particle sizes are evident. The abundance of extremely large particles (3 to 4 μm) may interfere with the agglomeration process in this powder.

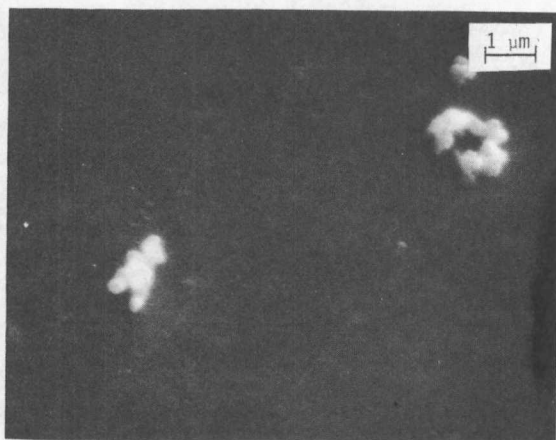
The particles shown in Figs. 6e through 6g are from powders that did agglomerate. Figure 6e shows the unit particles that formed from the strongest agglomerates. These particles appeared to be uniformly sized, similar to the Buehler powders but more varied in shape. It is this variety in shape that may give these agglomerates their strength. The other two agglomerating powders (Figs. 6f and 6g) also have nonuniform shapes but their size



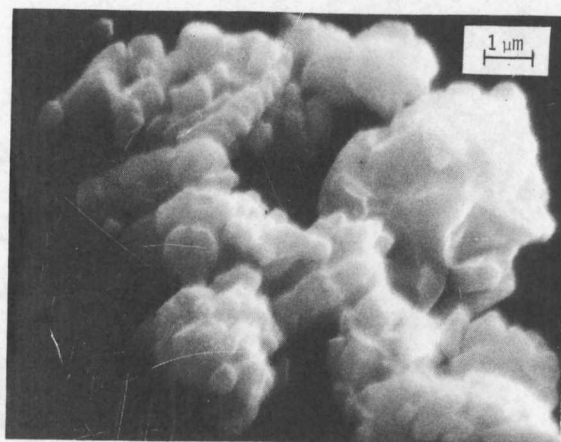
a) 0.005 μm Aluminum-Oxide Powder (B-0.05)



b) 0.03 μm Aluminum-Oxide Powder (B-0.3)



c) 1.0 μm Aluminum-Oxide Powder (B-1.0)

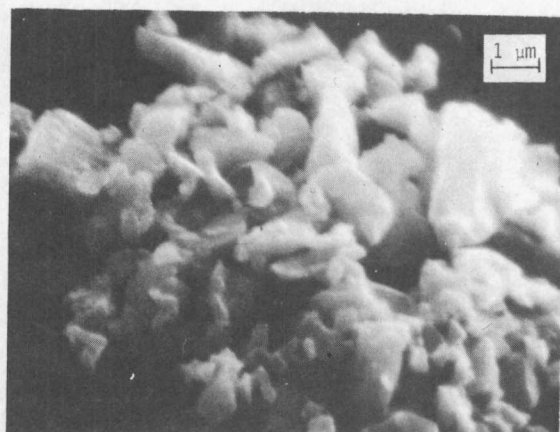


d) 1.0 μm Calcium Carbonate Powder (C)

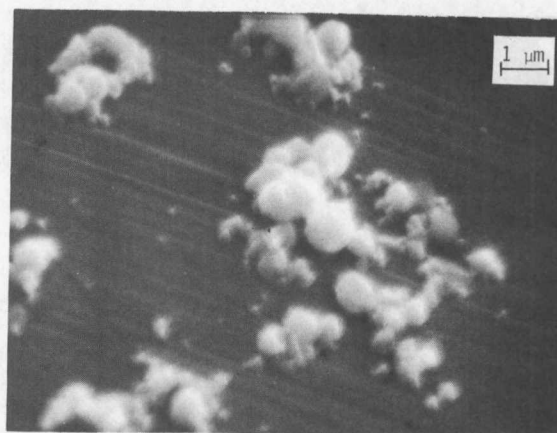
Figure 6. Scanning Electron Microscope Photographs of Unit Particle Shapes.



e) 1.0 μm Aluminum-Oxide
Powder (M-1.0-99)



f) 1.0 μm Aluminum-Oxide
Powder (M-1.0-97)



g) Processed Material from
Rocket Motor Firing (RE)

Figure 6. (continued)

distribution is wider. The chemical analysis of the various powders verified the manufacturer's stated purities. The chemical purity did not appear to affect the agglomeration characteristics of these powders. An exception to this is possible in the RE sample if the interparticle bonding forces were affected by the varied elemental composition.

The size distribution of the agglomerates measured with a microscope and used in the crushing experiment is shown in Fig. 7. There is an unexpected gap in the measured size distribution of these agglomerates. As Fig. 7 shows, most of the agglomerates were fairly evenly distributed in size between 0.8 and 1.4 mm, except for the single agglomerate measuring 1.05 mm. At the beginning of the sample selection process, the agglomerates were crudely sized by sifting through different makeshift sieves and then equal numbers of agglomerates were chosen from each of the four size categories. One of the sieve sizes was slightly over 1 mm. A bias in the size distribution could have been created by separating the 1 to 1.1 mm size agglomerates into two size categories, thereby reducing the probability of that size being chosen.

The solids fraction distribution of the sampled agglomerates is shown in Fig. 8. As in the size distribution, there is a depressed region in the middle of the

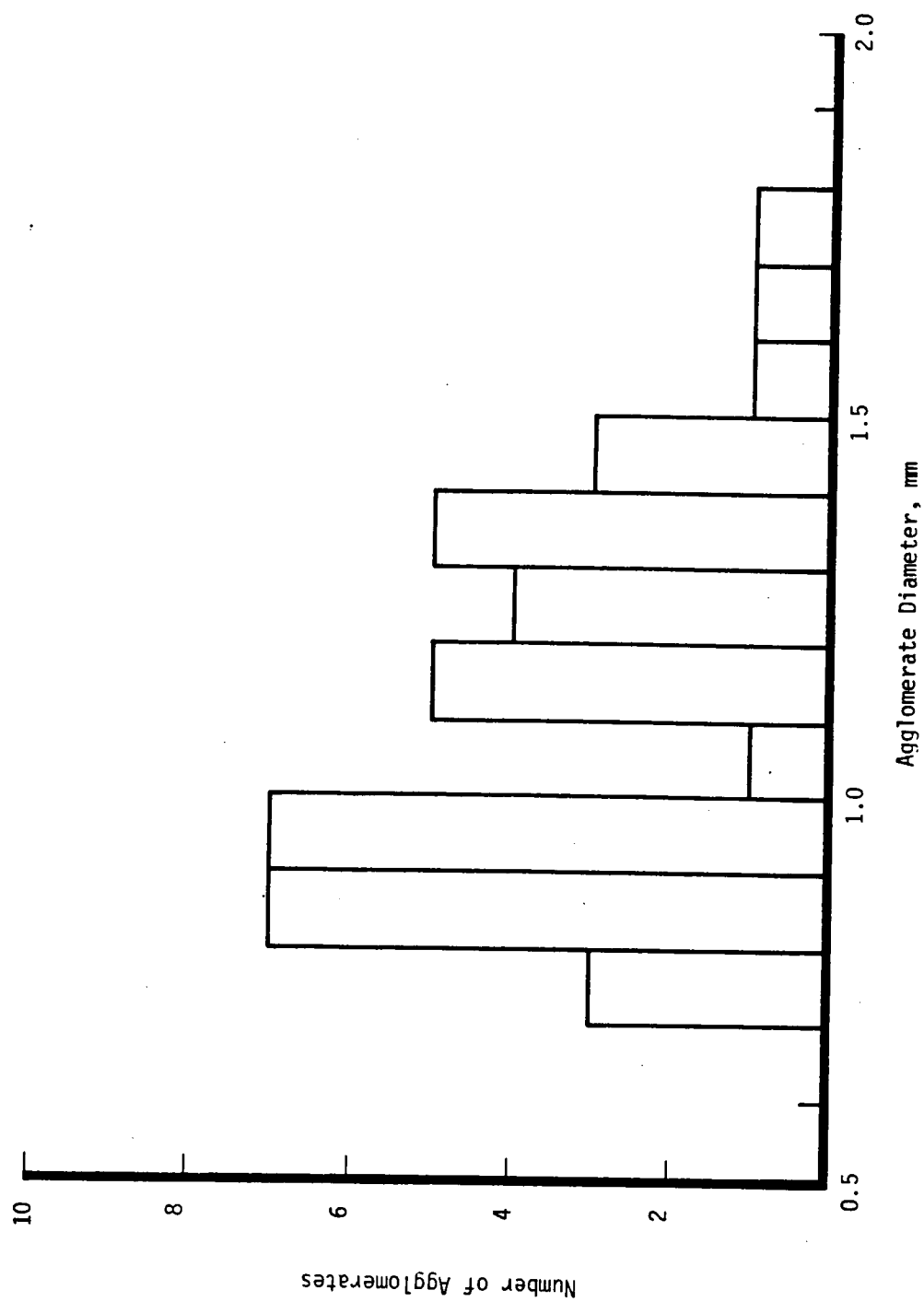


Figure 7. Size Distribution of Agglomerates Tested.

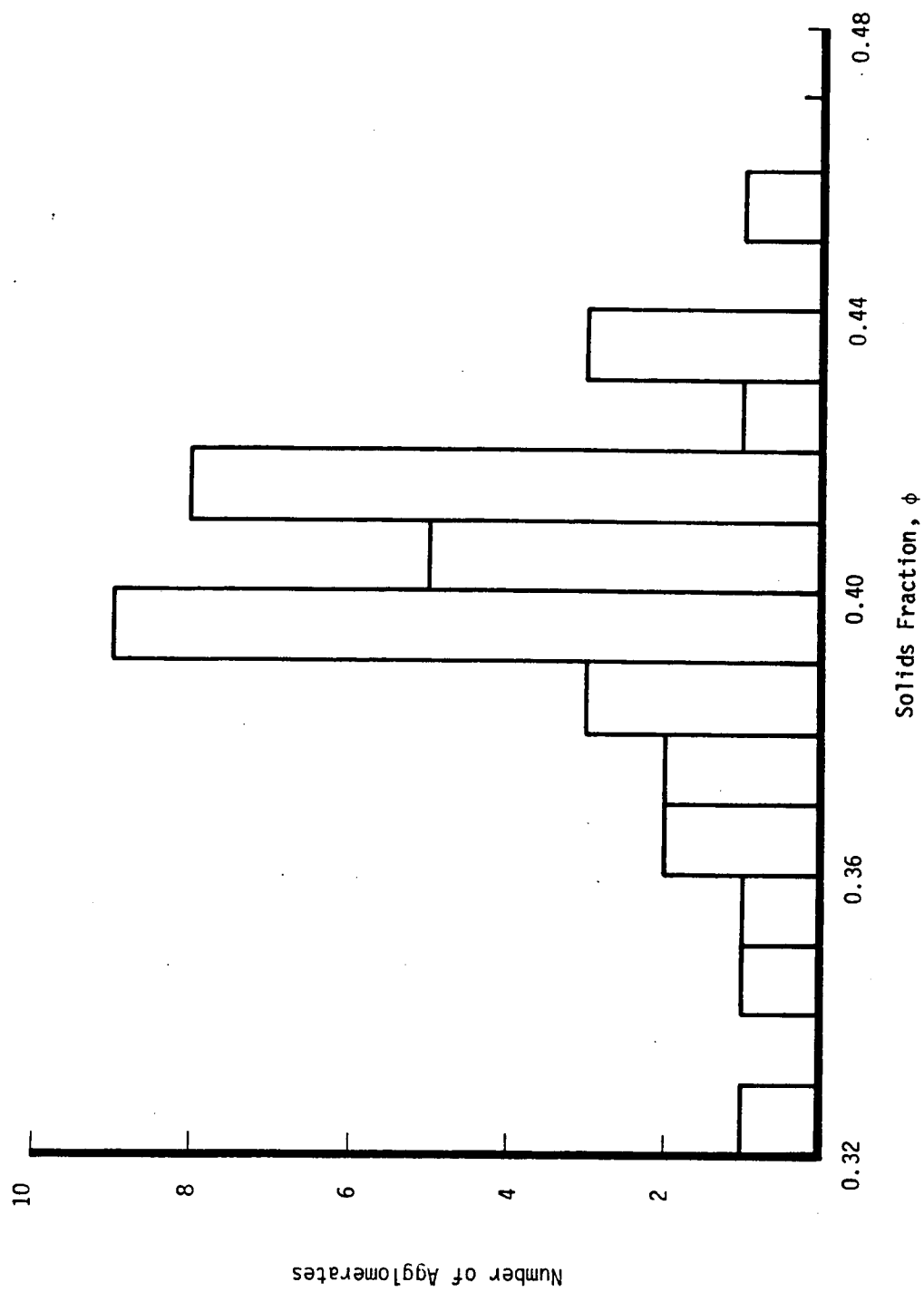


Figure 8. Solids Fraction Distribution of Agglomerates Tested.

distribution. The solids fraction data were plotted against the agglomerate diameter values but no significant trend or correlation was found.

Crushing Strength Analysis

The interparticle bonding force function, F , was calculated for each agglomerate using Eq. (3) and measurement data. A unit particle diameter of $0.8 \mu\text{m}$ was used for all calculations and was based on average particle measurements on the SEM. Figure 9 shows the resulting bonding force function as a function of the agglomerate solids fraction. A least-squares linear fit of the data indicates the trend of decreasing bonding force with increasing solid fraction and constant crushing force. This is expected since a denser agglomerate will have a higher coordination number and each particle bond will be weaker.

The unit bonding force function F/d_o^2 , is plotted for values of the unit crushing force, P/A_c , in Fig. 10. The least-squares linear fit and 2σ confidence bands shown in Fig. 10 indicate that the crushing force and solids fraction data used in Eq. (3) to generate the bonding force function provides a good correlation.

The average value of the bonding force function shown in Fig. 9 is 1.2×10^{-2} dynes. Comparison of this value with the order-of-magnitude predictions by Forney

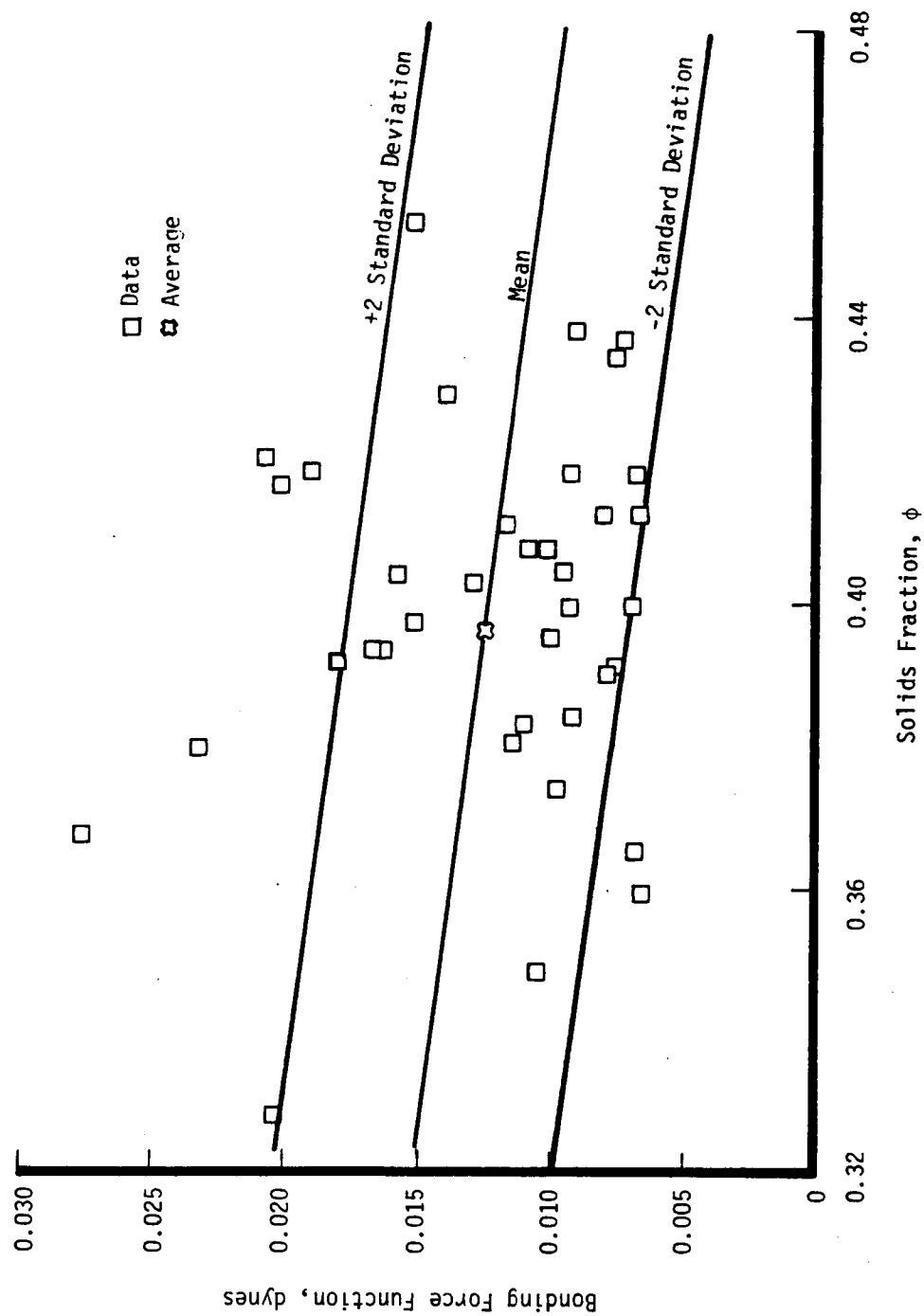


Figure 9. Interparticle Bonding Force Data.

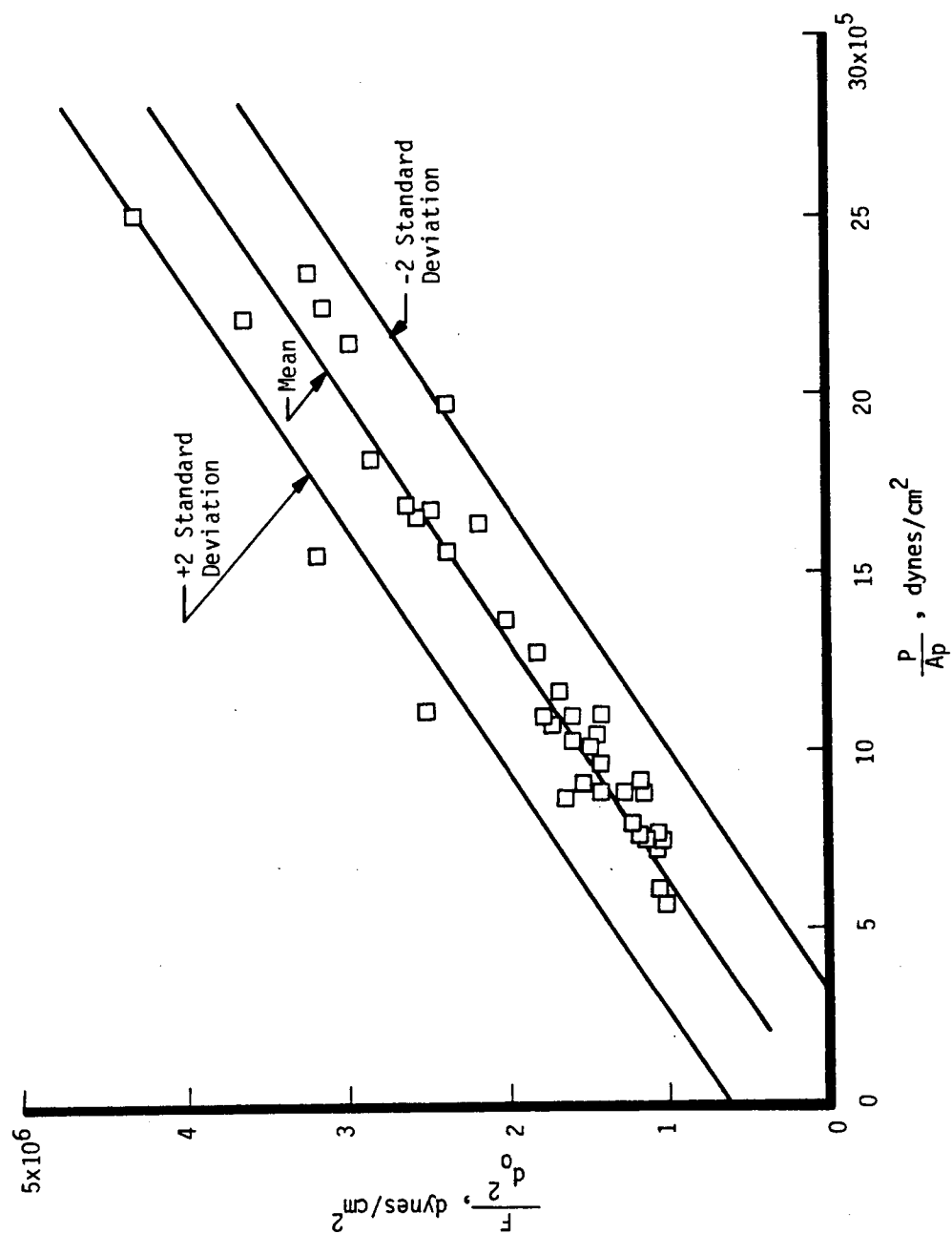


Figure 10. Unit Bonding Force versus Unit Crushing Force.

shown in Table 1, page 11, indicates that any of the types of bonding mechanisms listed could possibly be responsible for the agglomerates' strength. The average value of the unit crushing force data shown in Fig. 10 is 1.4×10^6 dynes/cm². For an agglomerate in tension with 0.8 μ m unit particles, Fig. 2, page 9, incorrectly indicates that the bonding mechanism is due to capillary or surface film forces. Two reasons are given to support this statement. For these two reasons, the writer concludes that capillary forces are not the bonding mechanism in these aluminum-oxide agglomerates.

The first reason deals with the manner in which the agglomerates were formed. The literature addressing the formation of various liquid bonds routinely discusses the addition or removal of liquid during the agglomeration process as the basic factor in agglomerate strength. These aluminum-oxide agglomerates were formed by only tumbling powder in a sealed jar.

The second reason is in the quantity being measured. As previously stated, the compressive strength of an agglomerate is expected to be greater than the tensile strength due to the friction forces between the unit particles. As stated by Rumpf [12], however, this is an unknown nonlinear relationship dependent upon particle size, particle shape, and overall agglomerate strength.

The Van der Waals capillary forces boundary line in Fig. 2, page 9, should therefore be adjusted upward by an undetermined amount.

Electrostatic forces may be the bonding mechanism. A tesla generator was used to discharge a strong electron spark to an agglomerate with no apparent effect. If electrostatic forces were the bonding mechanism, then a strong unipolar charge might have weakened or destroyed the particle bonds. This test is inconclusive, however, since the tesla generator may only affect the surface charge of the agglomerate and not the internal bonding structure.

A test for Van der Waals forces was not devised, so it is unclear as to which type of bonding mechanism is responsible for the strength of the agglomerates. The electrostatic force value shown in Table 1, page 11, is for smooth spheres and, as stated previously, may be increased greatly due to particle surface irregularities. Since these particles have irregular surfaces, electrostatic bonding would produce higher values of bonding force than were determined experimentally. Therefore, London-Heitler-type Van der Waals forces ($a < 2,000 \text{ \AA}$) are the primary binding mechanism.

The experimental data are also presented in the format of Meissner and are included as Fig. 11. The use of an exponential function of the solids fraction is plausible since manipulation of Eq. (3) yields

$$\frac{P/A_c}{F/d_o^2} = \frac{\phi}{1-\phi} , \quad (4)$$

which is an approximation of an exponential term. Various values of the constant in the exponential term were evaluated in an attempt to improve the least-squares fit of the data. The 2σ confidence bands shown in Fig. 11 indicate the ability of the exponential function to fit the data; however, there is a large variance in the slope due to the nature of the data. The scatter in the aluminum-oxide data in Fig. 11 in comparison to the zinc-oxide data in Fig. 2, page 9, is probably due to the differences in the unit particle size distribution and the 15 sample-averaged data points of Meissner compared to the unaveraged data of this work.

The free-stream Mach number which will result in a normal shock strong enough to break these agglomerates is now considered. Forney developed equations for predicting agglomerate breakup in terms of the free-stream Mach number and other gas parameters. Modifying Eq. (1) to account for aerodynamic drag and crushing strength data results in

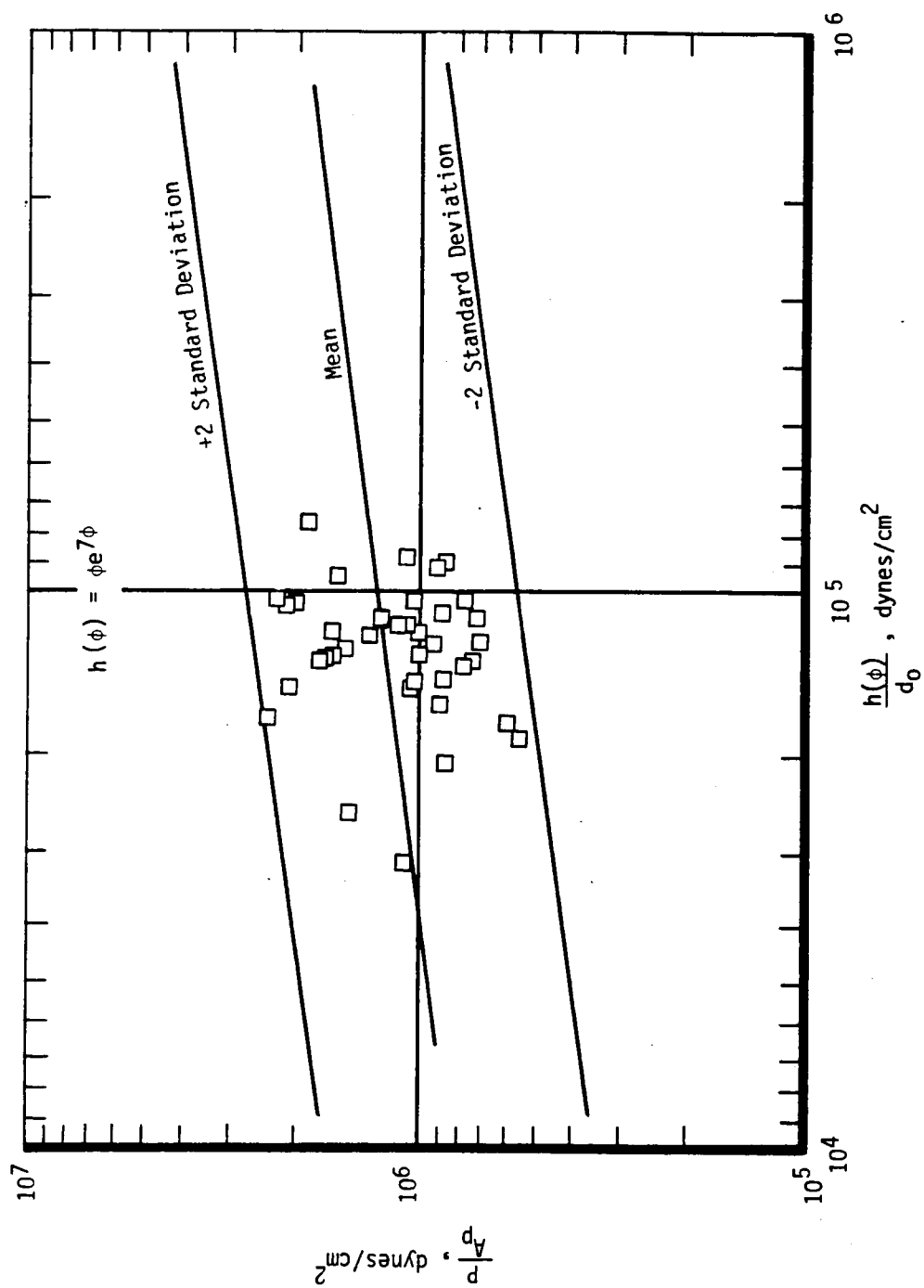


Figure 11. Crushing Strength of Aluminum-Oxide Agglomerates.

$$W_b = \frac{D}{P} = \frac{D/A_p}{P/A_p} = \frac{P_o C_D g(M_1, \gamma)}{P/A_p}, \quad (5)$$

where P_o is the free-stream pressure, C_D is the agglomerate drag coefficient, and $g(M_1, \gamma)$ is a nondimensional function of free-stream Mach number and specific heat ratio relating gas properties across a normal shock wave.

Forney plotted the normalized agglomerate drag, $D/P_o A_p (=C_D g(M_1, \gamma))$, for various values of free-stream Mach number and agglomerate Knudsen number function. The agglomerate Knudsen number is defined as the ratio of the mean free path of the gas to the agglomerate diameter. A complete derivation and description is given by Forney which results in a lumped parameter $d\rho_o/k$, where ρ_o is the gas density and k is a constant (8.46×10^{-9} gm/cm²) calculated from the gas constant, R , and Sutherland's constant, T_θ . This parameter is proportional to the inverse of the agglomerate Knudsen number and is used by Forney as an indicator of normalized agglomerate drag. A set of curves similar to those of Forney is shown in Fig. 12. Curves for higher values of constant $d\rho_o/k$ were added due to the larger agglomerate diameters for this study. By assuming the gas parameter values shown in Fig. 12 and further assuming a free-stream total pressure of 5.5×10^7 dynes/cm² (800 psia), and a Weber number of 1, one can determine a Mach number range which should cause the agglomerate to

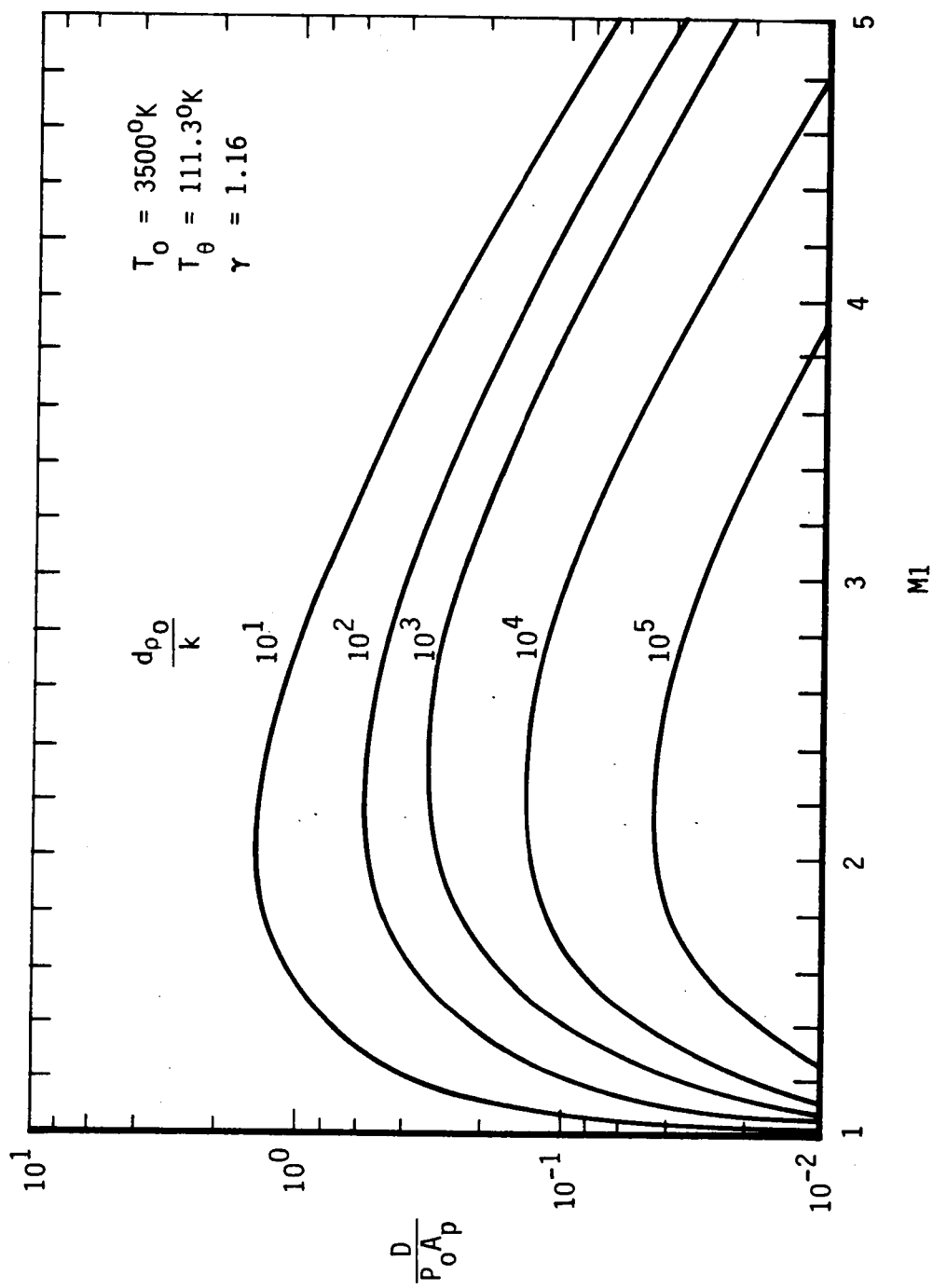


Figure 12. Normalized Agglomerate Drag.

fail. For the assumed conditions, the drag function $D/P_o A_p$ is 2.5×10^{-2} and the value of the lumped parameter, $d\rho_o/k$ is 7×10^4 . From Fig. 12, the corresponding Mach number range for probable agglomerate breakup is approximately 1.4 to 3.4. An experiment to verify this calculation was not performed. The acceleration forces required to establish a supersonic agglomerate velocity would be greater than the agglomerate crushing strength and cause agglomerate failure.

CHAPTER V

CONCLUSIONS

This investigation was conducted to provide experimental data on the strength of aluminum-oxide agglomerates. While the agglomerates studied were not generated by an environment similar to a solid rocket motor firing, the data obtained are unique and provide a basis for further studies. The conclusions are:

1. Based upon SEM photographs and experience, it appears that uniformly sized, rough-edged, unsymmetrical particles form the strongest, most spherical agglomerates. The uniform spherical particles used in this effort would not agglomerate. Agglomerates were randomly selected for crushing strength experiments; however, a preliminary sizing process may have slightly biased the size distribution of the agglomerates used.
2. The interparticle bonding force values were calculated from crushing force, size, and solids fraction data. These force values were in agreement with the predicted estimates by Forney for each of the bonding mechanisms considered; however, Van der Waals forces are

considered the most probable force of adhesion. This is encouraging since the equations and experimental constants were derived for spherical, or nearly spherical, unit particles and the aluminum-oxide particles used here were randomly shaped.

3. A comparison of the crushing strength of these agglomerates with generalized experimental values of tensile strength proved invalid. An experimental program to obtain compressive strength data for direct comparison to Rumpf's tensile strength tests is required.
4. The calculated unit bonding force (F/d_o^2) was favorably correlated with the unit crushing force data (P/A_c). A plot relating the unit crushing force to a function of the solids fraction was generated in an attempt to relate the aluminum-oxide data to previous work with zinc oxide. While similar trends were apparent, the differences in powder preparation and amount of data obtained preclude further comparisons.
5. Further studies are required with characterized agglomerates in a supersonic two-phase flow field to determine experimentally the onset of agglomerate breakup. In addition,

studies with actual rocket exhaust particulate are required. The material for use in these experiments was collected after passing through an iron and cement exhaust diffuser system, and the impurities from these materials substantially weakened the agglomerate bonds. Now that a viable procedure for determining particle bonding forces is available, direct collection of exhaust particulate in the nozzle flow field is warranted. Data from these efforts will then provide a basis for determining the sample distribution bias caused by a sample probe bow shock.

6. A calculation was performed using Forney's equations which compared agglomerate strength to the drag forces present in a decelerating flow field. The calculations indicate that an average agglomerate generated in this study would survive passage through a normal shock, if the free-stream Mach number is less than 1.4 or greater than 3.4, and assuming the agglomerate was initially traveling at the gas stream velocity. The forces required to realistically accelerate such large agglomerates to supersonic velocity, however, would probably cause their destruction.

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VITA

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