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ZIRCONIUM POWDER CHARACTERIZATION AND PROCESS IMPROVEMENT FOR THERMAL BATTERIES

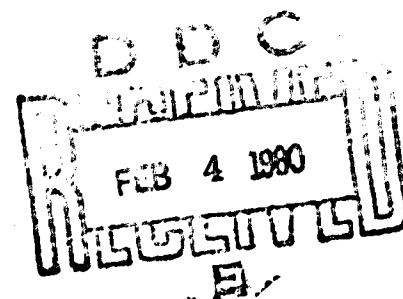
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K. S. Mazdiyasni

Metals and Ceramics Division

November 1979

TECHNICAL REPORT AFML-TR-79-4069

Final Report for Period 1 Sep 75 - 1 Dec 76



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This technical report has been reviewed and is approved for publication.


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FOR THE COMMANDER


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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFML-TR-79-4069	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ZIRCONIUM POWDER CHARACTERIZATION AND PROCESS IMPROVEMENT FOR THERMAL BATTERIES		5. TYPE OF REPORT & PERIOD COVERED Final Report. Sep 75-Dec 76
7. AUTHOR(s) Robert F. Geisendorfer K. S. Mazdidasni		8. CONTRACT OR GRANT NUMBER(s) N00073500142 01
9. PERFORMING ORGANIZATION NAME AND ADDRESS Processing and High Temperature Materials Branch Air Force Materials Laboratory Wright-Patterson AFB, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 73500142
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory, AFML/LLM Wright-Patterson AFB OH 45433		12. REPORT DATE November 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 128
		15. SECURITY CLASS. (of this Report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Zirconium Powder Thermal Battery Zirconium Dioxide Zirconium Silicate (Zircon)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The inhouse program has resulted in a survey and characterization of existing production raw materials and product Zr metal powder as a heat source in the AF Maverick thermal battery. The variables most likely causing inconsistency and ignition sensitivity of zirconium metal powders are identified. The criteria for design and safety requirements for a laboratory scale zirconium-reduction-leach facility were established. The reduction and leach-wash cycle parameters		

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20. Abstract (Continued)

were optimized to produce consistent quality fine particle 1-2 μ m zirconium powder. The reduction scale up (400 grams per batch) was achieved in order to produce sufficient quantities of Zr metal powder for performance tests and to evaluate variables. The technology was transferred to the industry for production of 50 lbs/batch Zr metal was accomplished.

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FOREWORD

The research work described in this final report was performed under an in-house work unit directive 73500142. Mr. K. S. Mazdiasni of the Processing and High Temperature Materials Branch, Metals and Ceramics Division was the WUD leader and principal investigator. Mr. Robert F. Geisendorfer of the Systems Support Division was the research engineer.

The authors would like to express their appreciation to Mr. Robert Sweeney of Westinghouse Research Laboratory for his assistance in the preparation of Zr metal powder and Miss Sonya Nash, a summer co-op student, for leaching experiments and Mr. Adolf Biermann of the University of Dayton for the scanning electron microscopy work. The technical assistance of Mr. James Muntz of the Analytical Services Division, AFML, for help in powder analysis, and Dr. Bert Werbel of U. S. Armament Research and Development, and Lt. David C. Ferguson of the Air Force Rocket Propulsion Laboratory for the burn rates experiments and Mrs. Kayann Cornish, AFML/LLM for preparation of this technical report is acknowledged.

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SECTION I

INTRODUCTION AND BACKGROUND

A thermal battery is a rapidly-activated single-usage, short-life electrical energy source, which is used to power most United States missiles. The battery achieves its high operating temperature by oxidizing fine particulate zirconium powder.

Production problems have occurred recently in the manufacture of fast rise time (to operating voltage) thermal batteries used in missiles such as the AF Maverick. According to the battery manufacturer,* the problem is due to variability of zirconium powder in the heat paper used as the heat source to melt the electrolyte and thus activate the battery resulting in a fire hazard during its production, as well as poor battery performance. The problem, as identified by the battery manufacturer, is variability of the commercially available zirconium powder** used in the heat paper. Currently, two types (particle sizes) of powders are produced using different sources of the zirconia starting material. The problem is associated with the finer material (1-2 μm) identified as Type II. The basic requirement of the Type II Zr metal powder is to provide a heat source for thermal batteries which permits attainment of full operating voltage in a maximum time of 550 milliseconds at -65°F without degrading the useful life of the battery. The Air Force Materials Laboratory was designated as the lead laboratory of the Joint Deputies for Laboratories Committee's on Thermal Batteries which had the responsibility to define the problem(s), to obtain a timely solution, and to develop long-range plans to ensure an adequate supply of consistent, high quality zirconium powder. Other laboratories supporting this effort were AFAPL, AFRPL, AMMRC, Picatinny Arsenal, and Harry Diamond Laboratory.

This research was directed toward the development of a powder preparation process specifically the reduction method of zirconium

*Eagle-Picher, Joplin, Mo.

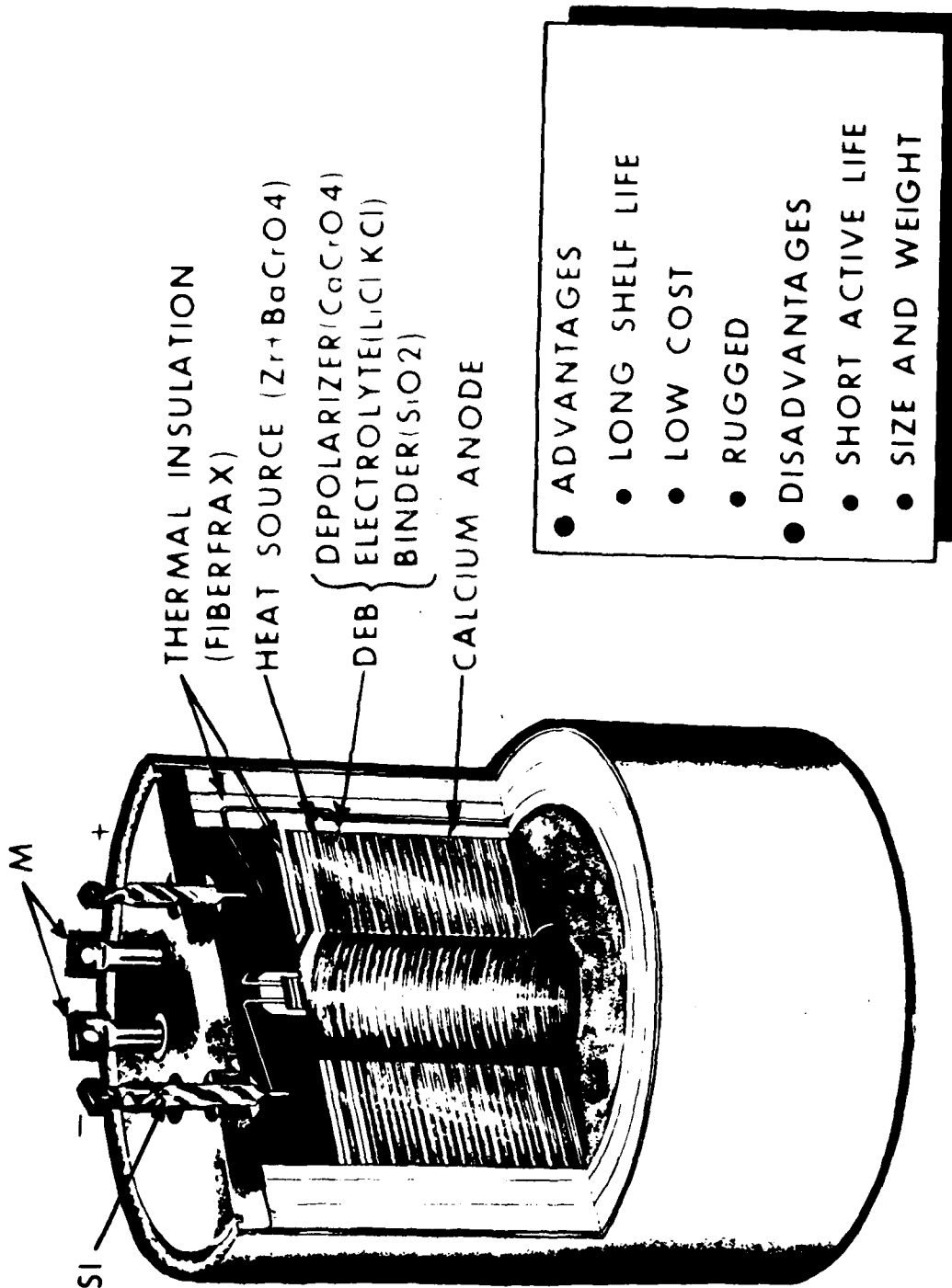
**Ventron Corporation, Beverly, Ma.

dioxide (ZrO_2) by magnesium (Mg) to form Zr metal powder, a process similar to that described by J. W. Marden (Reference 1).

The first part of this report covers the sources and availability of Zr ore, the production of ZrO_2 powders, the characterization of these powders, and the selection of suitable raw materials for production of the Type II Zr metal powder. Additionally, the characterization of the commercial Zr powder is reported. The last part of this report describes in detail the apparatus and experimental procedures developed to produce consistent quality Zr metal powder. The unique characteristics of powders made under various time, temperature and atmospheric conditions as well as leaching procedures for the reaction product have been included. Microstructural characterization and chemical analysis of the zirconium powders were combined with their performance evaluation, namely ignition sensitivity and burn rates, to establish an acceptable process specification for manufacturing reproducibility and reliability for use in AF Maverick thermal batteries (Figure 1).

It should be noted that zirconium powder for the aforementioned application is currently being provided with the following performance requirements:

Open Train Burn Time	4.0 Sec./Ft. Max.
Ignition Gain	30.0 w% Minimum
-120 Mesh	99.5 Minimum
Average Particle Size	1.5 - 2.0 Microns
Particle Distribution	
0.75 Microns	10-24%
3 Microns	65-92%
9 Microns	90-100%
Chemical Composition (wt.%)	
Total Zirconium	95.5% Minimum
Calcium	.05 Maximum
Iron	.10 Maximum
Aluminum	.10 Maximum
Hydrogen	.20 Maximum



● ADVANTAGES

- LONG SHELF LIFE
- LOW COST
- RUGGED

● DISADVANTAGES

- SHORT ACTIVE LIFE
- SIZE AND WEIGHT

Figure 1. Air Force Maverick Thermal Battery

SECTION II

ZIRCONIUM ORES AND ZIRCONIA

The most important zirconium mineral is zircon, a zirconium silicate with varying amounts of hafnium (References 2, 3). Zircon is by far the most abundant zirconium ore occurring in extensive littoral and placer deposits intimately associated with ilmenite, rutile, monazite, and other minerals. The world supply of zircon is almost wholly obtained from beach sands. Most of the production of zircon comes from Australia at points along the coast of New South Wales and Queensland (References 2, 3, 4), from Florida (Reference 5), and from Travancore, India (Reference 6). An important coastal deposit of zircon sand with monazite and rutile occurs near Victoria in the State of Espirito Santo, Brazil (References 3, 7).

The best known deposits of zircons and zirconium bearing rocks in the Soviet Union are those of Northern Kirgizia and the Kola Peninsula. They have been described by Kosterin et al. (Reference 8) and by Gerasimovskii et al. (Reference 9).

The commercial deposits of zircon in the United States are treated in detail by Mertie (Reference 5) in Geological Survey Bulletin 1082-A. The potential production in the United States is probably as great as that of Australia. Principal domestic sources of zircon now being mined are the ilmenite-rutile-zircon places of Florida, near Jacksonville in Duval County, along Trail Ridge in the western part of Clay County and Panama City in Walton County. Promising deposits have been identified in Charlton County, and Cumberland Island, Georgia. Table 1 lists the major impurities found in the Florida and Australia zircon.

1. SYNTHESIS OF ZIRCONIA POWDERS

Depending on the kinds of raw material and ore processing used, various grades, particle sizes, and particle morphologies of monoclinic ZrO_2 are manufactured. To obtain synthetic zirconia of reasonable purity it is first necessary to concentrate the naturally occurring zircon ore

TABLE 1
ANALYSES OF AUSTRALIA AND FLORIDA ORES

Impurities	ZrSiO ₄			Method
	Florida Sand Dupont Stark wt%	E. Australia Rutile wt%	W. Australia Elminite wt%	
ZrO ₂	66.3	67.1	66.8	
HfO ₂	2.2%	2.2%	2.2%	
Nb ₂ O ₅	0.007	0.007	0.007	Emin. Spec.
Ta ₂ O ₅	0.012	0.012	0.012	Emin. Spec.
Al ₂ O ₃	1.5	0.041	0.25	Chem.
Fe ₂ O ₃	0.092	0.039	0.28	Emin. Spec.
CaO	0.028	0.032	0.038	Emin. Spec.
TiO ₂	0.36	0.07	0.32	Chem.
SiO ₂	Quartz 0.80	0.49	0.78	Chem.
TiO ₂	0.055	.016	0.017	Chem.
Y ₂ O ₃	0.077	0.089	0.14	Chem.
U ₃ O ₈	0.025	0.028	0.233	
P ₂ O ₅	0.095	0.12	0.080	Chem. & X-Ray

by electrostatic and electromagnetic separation. According to Blumenthal (Reference 10), a zircon concentrate of about 99% purity can be isolated from the commonly associated minerals, such as quartz, rutile, ilmenite, and monazite.

The zircon concentrate is then decomposed by heating it with carbon in an electric arc furnace. In this process SiO_2 , the principal impurity, is volatilized as silicon monoxide and either zirconium carbide or a solid solution of carbon in zirconium metal is formed. In a variation of this process a golden-yellow phase called zirconium cyanonitride is obtained, which is a solid solution of various amounts of carbon, oxygen, and nitrogen in zirconium. These reaction products are then oxidized to yield zirconium dioxide. To obtain a dioxide of greater purity the intermediate reaction products are chlorinated rather than oxidized to yield zirconium tetrachloride. The tetrachloride is further purified by reacting with hydrochloric acid to give zirconium oxychloride which in turn is oxidized to produce zirconia. Zirconium sulphate, basic sulphate, nitrate or organic acid salts, and alkoxide are other intermediate reaction products which by direct ignition or after ammonia precipitation or hydrolytic decomposition result in zirconia. Another technique uses caustic soda for the decomposition of zirconium silicate at a furnace temperature of 650°C . This process, if followed by a series of leaching and purification steps, result in a relatively pure zirconium oxide.

The Zirconium Corporation of America, ZIRCOA*, extracts zirconia from Australian zircon** via the well known dolomite ($\text{CaMg}(\text{CO}_3)_2$) process by mixing the zirconium silicate with dolomitic ground limestone. The pelletized mix is calcined at about 1315°C and the dicalcium silicate formed by this technique is removed by acid leaching. A detailed description of these various synthesis techniques, including furnace constructions, is given by Lustman and Kerze (Reference 11) and by Blumenthal (Reference 10).

*Zirconia Products, Ceramic Product Division, Corning Glass Work

**Milled to -325 mesh, Continental Mineral Processing, P.O. Box 5, Cincinnati, Ohio 45241

a. X-Ray and Emission Spectrographic Analysis

The x-ray powder diffraction patterns of the Zircoa Type A, -325 ZrO_2 powders, used for both the commercial (Ventron Corporation) Type II powder and to prepare fine Zr metal powders in this study indicate that the oxide powders are fully crystalline monoclinic phase. Typical emission spectrographic analysis of several powder lots is listed in Table 2.

Disregarding Hf as a major impurity, it is interesting to note that with the exception of Si (140-1500 ppm) and Mg (40-5000 ppm), the elemental impurities are relatively small and reproducible. None of the unlisted impurities was higher in concentration than those shown in Table 2. The major anion impurities found in the oxides are approximately 0.1 w/o Cl and 0.2 w/o \overline{SO}_4 . The source of chloride is obviously the HCl acid leaching, and the sulfate impurity is probably due to the high-sulfur content fuel used in the burners.

b. Particle Size and Morphology

Particle morphology of the oxide powders was examined by both electron microscopy and scanning electron microscopy. The powders were ultrasonically dispersed in soap-water solutions; a drop or two of the dispersion was then placed in a Freon nebulizer and sprayed onto a carbon substrate on a Cu mesh screen for electron microscopy. For the SEM work, the powders were ultrasonically dispersed in either triply distilled and deionized water or absolute ethyl alcohol; a drop of the dispersion was directly applied on an Al stub coated with isoamylacetate and finally carbon coated for observation.

Representative TEM and SEM micrographs are shown in Figure 2 and Figure 3, respectively. With the exception of a few irregular and elongated particles, the majority of the particles are well defined rounded particles of 1-2 microns diameter. The semi-quantitative analysis of the typical "maple seed" or platelet like particles by Energy Dispersive Analysis X-Ray (EDAX) invariably indicates the presence of

TABLE 2
EMISSION SPECTROGRAPHIC ANALYSIS OF ZrO_2 AND ZR POWDERS*

ELEMENT	LOT NUMBERS									
	AFML Analytical No.	6425	6426	6716	6720	6715	6719	6714	6717	6718
	Ventron or Zircoa No.	12602 + J4878A-3	12602 + J4878A-3	12602 + J4878A-3	10283 + J4863A-1	9396 + J4863A-6	—	J4863A-7		
		ESTIMATED PPM								
Si	140	200	300	600	1000	1000	1500	1500	1500	1500
Mg	40	2700	200	5000	200	5000	200	5000	5000	5000
Mn	<10	50	<10	50	<10	50	<10	50	50	50
S	10	40	2	50	2	50	2	50	50	50
Al	<10	250	50	1500?	50	300	50	300	300	300
Fe	100	1400	200	1500	200	1500	200	1500	1500	1500
Ni	<10	10	<10	30	<10	30	<10	30	30	30
Cu	10	50	<10	30	<10	30	<10	30	30	30
Ti	100	1400	500	1500	500	1500	500	1500	1500	1500
Ca	300	250	500	700	500	700	500	700	700	700
Mo	-	-	<10	30	<10	30	<10	30	30	30
Hf	5000	13,000	-	-	-	-	-	-	-	-
Pb	<10	<10	-	-	-	-	-	-	-	-
Na	10	250	-	-	-	-	-	-	-	-
K	100	<10	-	-	-	-	-	-	-	-

*AFML Sample No.'s 6425 and 6426 analyzed concurrently; likewise for balance of lots.

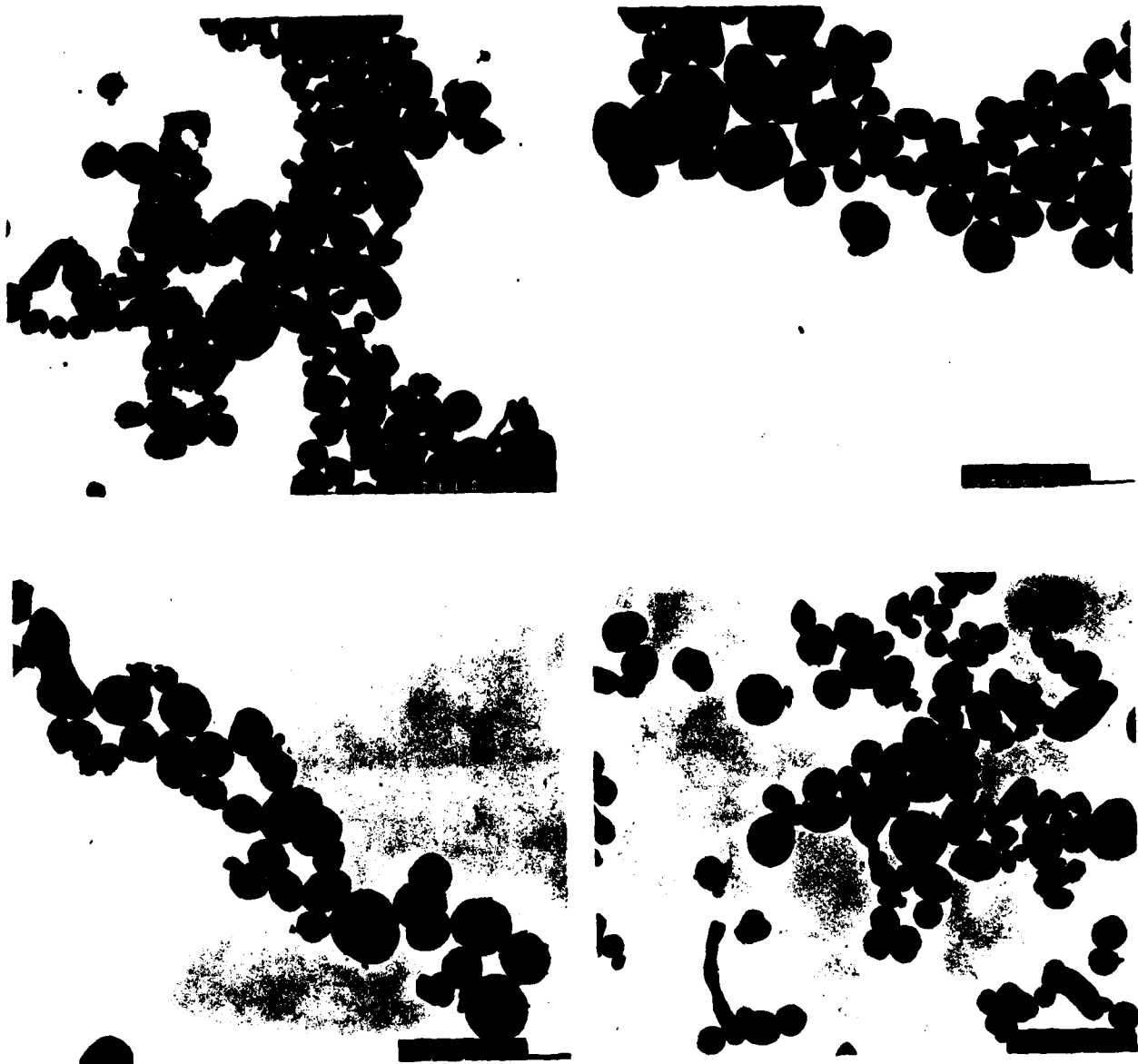


Figure 2. Typical Transmission Electron Micrographs of Zircoa
Type A Zirconia

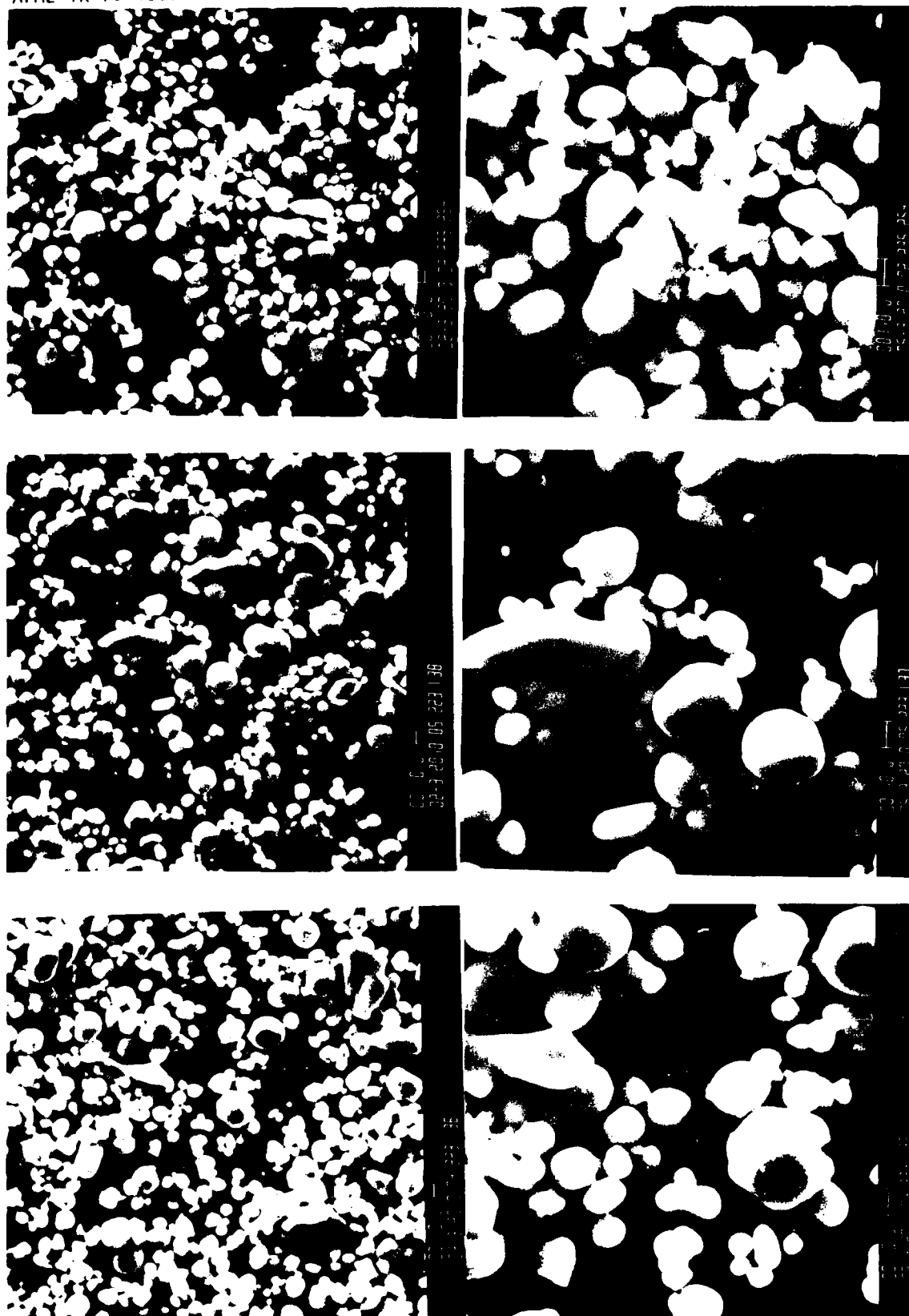


Figure 3. Scanning Electron Micrographs of Zirconia Type A Zirconia

glassy compounds consisting of Ca, Mg and Si, confirming the emission spectrographic analysis data for the same elements as major impurities.

c. Thermogravimetric Analysis

The thermogram (TG) of the as-received powder, in ambient atmosphere from room temperature to 960°C indicated 1-1.5 w/o weight loss in the temperature range of 70-110°C. This amount of weight loss is normal to the fine particle size oxide powders and is attributed to the surface absorbed water.

For the BET surface area measurements and particle size distribution see Appendices A and B respectively.

SECTION III

CHARACTERIZATION OF Zr STOCK

During the course of this research program, several batches of commercial, Type II, Zr metal powders from Ventron Corporation, (Stock #9396, 10283, and 12602) were received and characterized. Also two batches of a reaction product (unleached material Stock #4929A3 and 4929A4) from the Ventron Corporation was received, leached under this program and characterized. It must be emphasized that none of the specific processing procedures for the above batches were previously known or were provided to AFML by Ventron Corporation because of the proprietary nature of the processing and production method for Zr metal powders.

1. PARTICLE MORPHOLOGY

The as received Zr powders were examined both by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The samples were ultrasonically dispersed in a solution of distilled water-soap; a small amount of the dispersion was placed in a Freon nebulizer, and the suspension sprayed onto a carbon substrate on a Cu-mesh screen for the TEM studies. The samples for SEM analysis were ultrasonically dispersed in a solution of absolute ethyl alcohol; a small amount of the dispersion was placed on the sample holder by a dropper, coated with isomylacetate and then air dried. Figures 4 and 5 are typical electron micrographs of the oxide and metal powders, respectively. Figures 6 and 7 are the scanning electron micrographs of the same materials. The figures indicate that the oxide surfaces are smooth, rounded, and of relatively uniform particle size (1-1.5 microns in diameter). However, the Zr metal particle surface is jagged with cusps and nonuniform compared to the oxide starting material. A higher magnification TEM and SEM of a typical metal particle is shown in Figures 8 and 9, respectively. The particle morphology of the metal powder indicate that there are many sharp edges and thin foil like regions about 1000-2000Å thick. These very thin, high surface area regions could be considered potential ignition sites creating a fire hazard when the powder is used in the

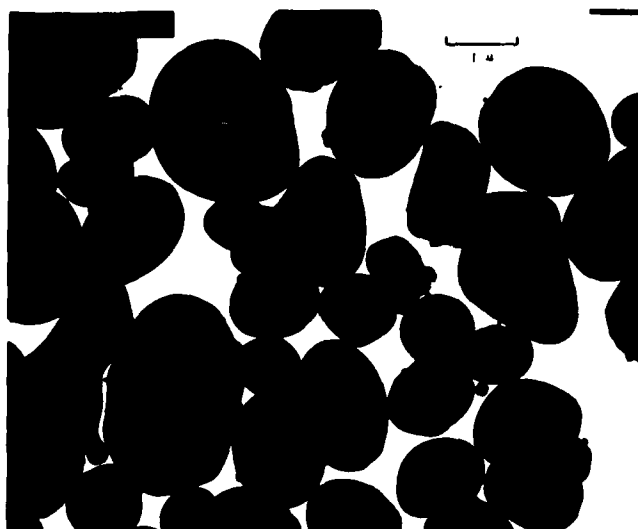


Figure 4. Electron Micrograph of Commercial Zirconium Dioxide



Figure 5. Electron Micrograph of Ventron Zr Metal Powder

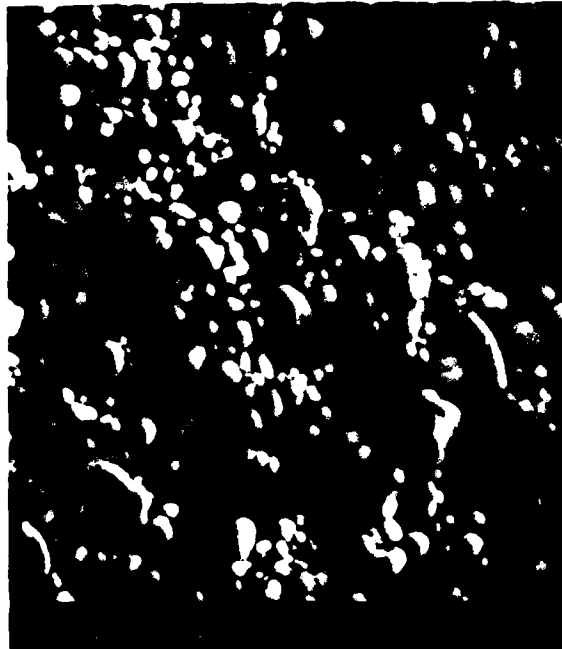


Figure 6. Scanning Electron Micrograph of Commercial Zirconium Dioxide

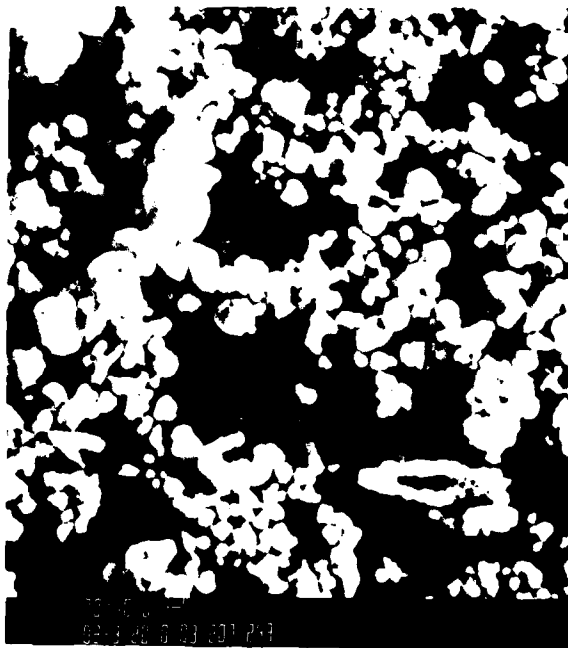


Figure 7. Scanning Electron Micrograph of Ventron Zr Metal Powder



Figure 8. Electron Micrograph of Zr Metal Showing Many Sharp Edges and Thin Foil-Like Regions

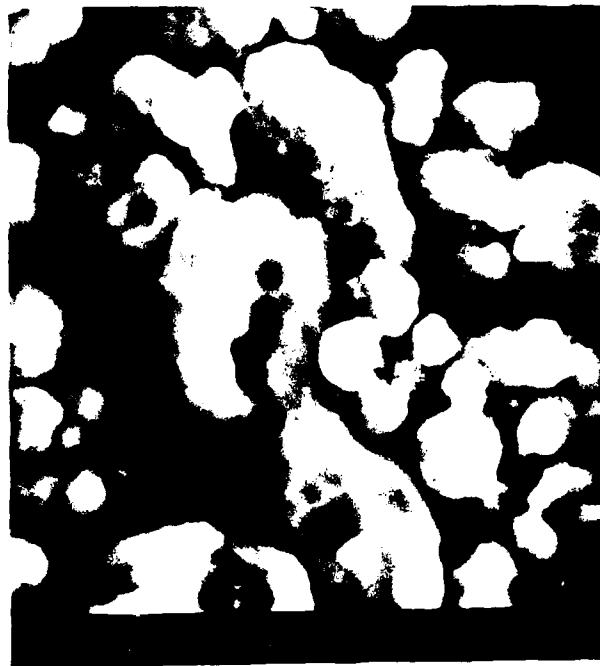


Figure 9. Scanning Electron Micrograph of Zr Metal Particle with Cusps

production of the heat powders or heat papers. Additionally, it should be noted that although the particle size is about 1-2 μm in diameter, the average surface area of such particles far exceed the theoretical or calculated values based on the average particle diameter.

2. X-RAY STUDIES

The x-ray diffraction pattern, using $\text{CuK}\alpha$ radiation of the Zr metal powder indicated highly crystalline about 97%, by peak height determination, alpha phase zirconium metal plus about 3% unreacted ZrO_2 as a minor second phase. These Zr percentages were determined by comparison to the peak heights of a well characterized Zr-standard. The ZrO_2 percentage is by difference.

3. PARTICLE SIZE MEASUREMENTS

The average particle size determination, using three different techniques, for the ZrO_2 and Zr metal powders are shown in Table 3. The results indicate that not only is there direct one to one correlation between the oxide to metal particles but the results are quite reproducible and in good agreement within the experimental error for a given method of analysis.

TABLE 3

COMPARATIVE OXIDE AND METAL PARTICLE SIZE MEASUREMENTS

SAMPLE IDENTITY		AVERAGE PARTICLE SIZE, MICRONS				
		ZIRCOA (FISHER)	VENTRON (FISHER)	AFML (FISHER)	MICROMERITICS (SEDIMENTATION)	AFML (DIRECT)
12602	OXIDE	2.8	2.2	2.4	1.9	1.27
"	METAL		1.5	1.51	2.1	1.32
(J4878A3)						
10283	OXIDE	2.8	2.5	2.54	2.1	1.40
"	METAL		1.6	1.60	2.5	1.45
(J4863A1)						
9396	OXIDE		1.7	2.0 $\pm .05^*$	1.6	1.15
"	METAL		1.5	1.54 $\pm .10$	2.05	1.23
(J4863A6)						

*Reproducibility Checked Using a New 5.6g. Sample for Each Determination.

SECTION IV

EXPERIMENTAL PROCEDURES - ZIRCONIUM POWDER PRODUCTION

1. STARTING MATERIALS

Zircoa Type A, zirconium dioxide, ZrO_2 , and Hummel Chemical Company* - 50+80 mesh magnesium, powder of approximately 98% purity were used.

The Zircoa's Type A ZrO_2 powder characteristics were similar to the powder batches previously received and characterized (see Section III). With the exception of an SEM of the Mg metal powder shown in Figure 10, no additional characterization of the magnesium powder was conducted or considered necessary.

2. APPARATUS

In Figure 11 the apparatus and supporting equipment used in the reduction of the ZrO_2 -Mg mixtures to zirconium powder is shown. The apparatus is shown ready for operation. In addition to the reaction vessel, the following supporting equipment are shown: pH meter, drybox, and drying oven. A high temperature tube furnace 36 cm long by 10.6 cm in diameter, capable of operating up to 1350°C is not shown. The temperature controller and programmer (Data Track) for the tube furnace are shown. The most important and critical part of the equipment, the reaction vessel, is made of 1 1/2" O.D. Inconel 600.

Since the moisture content and other volatiles in the starting blend or charge of ZrO_2 + Mg were initially unknown, the first reaction vessel was conservatively designed to withstand 140 mega pascal (3500 psig) pressure at 1010°C. The volume was calculated to yield approximately 40 grams of zirconium metal powder. Type 304 stainless steel seamless tubing was selected for the inner retort to avoid a eutectic reaction between Mg and the high Ni content of Inconel 600. The construction features of the reaction vessel, inner retort, end-plug and related high

*Hummel Chemical Company, South Plainfield, New Jersey



Figure 10. Scanning Electron Micrograph of Hummel Magnesium Powder

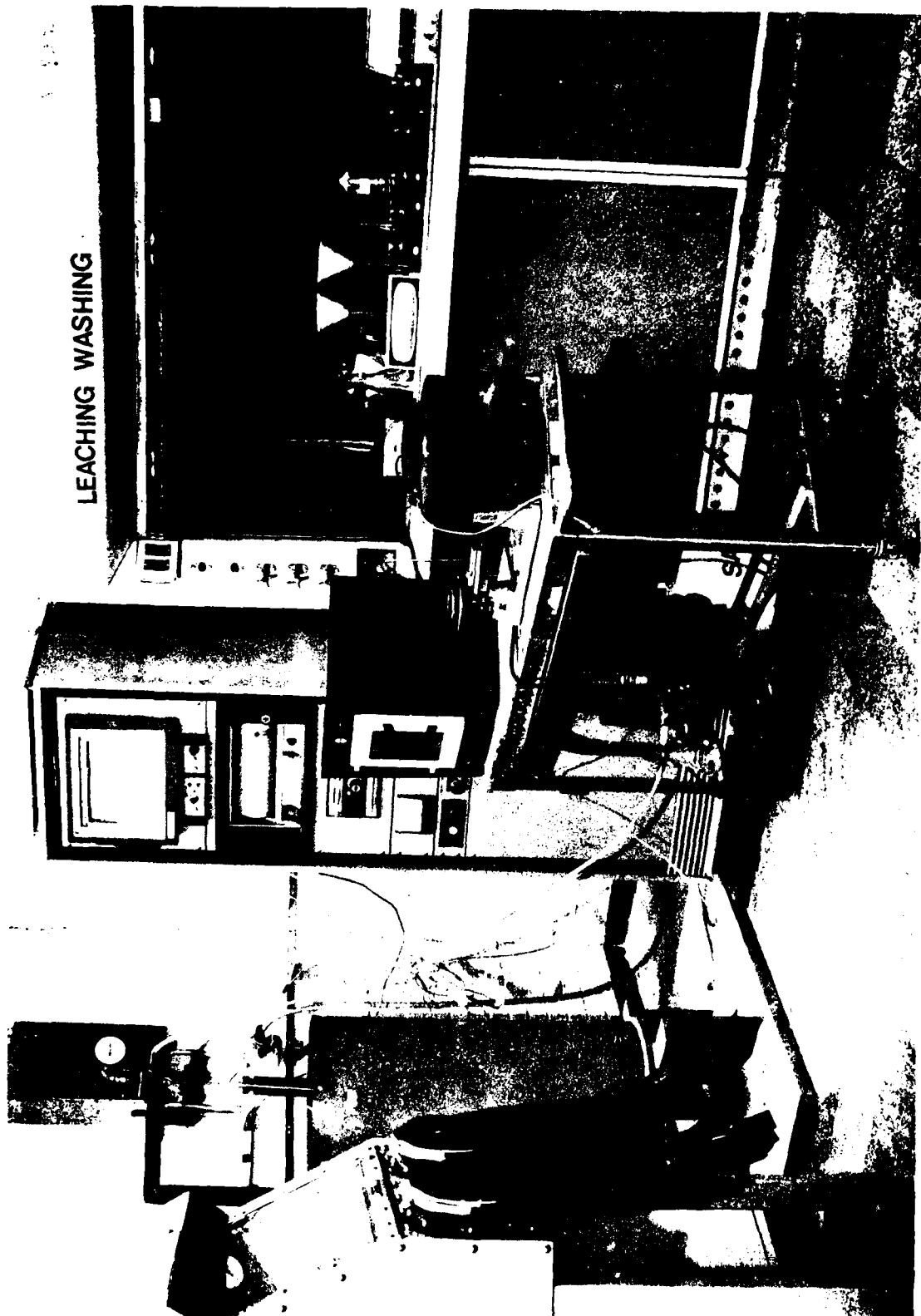


Figure 11. AFML Zirconium Reduction Facility

pressure valving are shown in Figure 12. The valves and high pressure tubing were Type 316 stainless steel, while the end-plug used for the initial runs was Inconel 600 and contained a 0.32 cm diameter hole to provide for evacuation and outgassing of the retort. A pressure gauge that could be isolated from the system in the event of pressure buildup in excess of the gauge capacity was used to monitor internal pressure during the reaction cycle. Very early in the experiments, it was discovered that with repeated use the Inconel 600 end plug would erode by the formation of a Mg-Ni eutectic which resulted in leaking of the inner retort. Subsequent runs were conducted using an end plug of Type 304 stainless steel. Additionally, the greater coefficient of thermal expansion of stainless steel plug with respect to the Inconel tube provided a gas tight seal at the flared area of the retort end plug interface. However, it is to be noted that during cool-down the opposite effect occurred but, excess magnesium vapor usually provided a gas-tight seal as it solidified in the gap formed between the plug and the tube.

The initial series of reduction tests were directed toward the optimization of the reduction parameters. The time and temperature combinations used are listed in Table 4. Later in the program, when the appropriate reduction conditions were established, larger retorts which yielded nominally 400 grams of zirconium powder were used. The larger retort consisted of Type 304 stainless steel seamless tubing, 17 cm long by 7.62 cm in diameter and 0.152 cm thick with 0.735 cm thick alloy end plugs welded at both ends. Additionally, a 25 cm long by 1.27 cm diameter evacuation and fill tube of the same alloy was welded to the end plug as shown in Figure 13. The 1.27 cm diameter tube was in turn connected to the valving and gauge system using high pressure flare fittings.

3. POWDER PREPARATION AND ANALYSIS

The Zr metal powder was prepared by a reaction similar to that described by Marden (Reference 1). Seventy-seven separate reduction

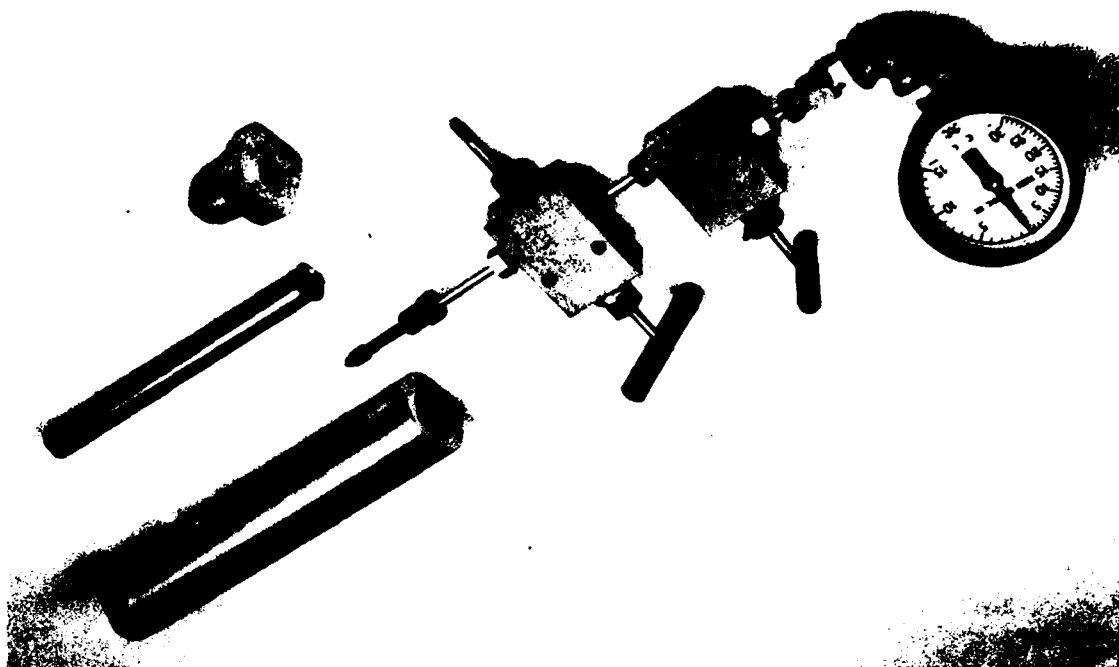


Figure 12. Photograph of the Small Scales (40 Grams ZrO_2 Charge) Reaction Vessel, Showing the Components and a Close-Up View of the Metal-to-Metal Retort

TABLE 4
ZrO₂ REDUCTION TEST MATRIX

TIME, HOURS TEMP, °F (°C)	16	8	4	2	1	.5	.25
1950 (1065)			X	X			
1850 (1010)		X	X ²⁰	X			
1750 (954)	X	X	X ¹⁷	X ¹⁶			X ¹⁵
1650 (900)				X ¹³			X ¹⁴
1550 (843)		X ¹⁹	X ¹⁸	X ¹¹	X	X	X ¹²
1450 (788)				X ⁹			X ¹⁰
1350 (732)				X ⁷			X ⁸
1250 (678)				X ⁴			
1150 (621)			X ⁶	X ⁵			

-MP, MG

runs were made using Zircoa's Type A ZrO_2 . The ZrO_2 powder was mechanically mixed with the required Mg usually in excess of the stoichiometric amount in order to ensure complete chemical reaction, without stratification and reacted in the reaction vessel shown in Figure 13. The chemical reaction, the flow diagram outlining the steps required, and the variable evaluated are shown in Figure 14.

The reaction product which was black consisted of Zr metal, MgO and Mg, (by x-ray), and could be either pored or gently scraped from the retort; depending on the reaction time and temperatures, as well as the amount of excess Mg. Excess Mg, greater than the 14 w%, invariably resulted in considerable agglomeration of the Zr powder and made it more difficult to remove from the retort. It should be noted that the reaction product, a mixture of Zr powder, MgO and Mg is relatively safe to handle and is usually not a fire hazard compared to the leached product. (For the safety requirements and precautionary measures necessary for production and handling of Zr metal powder see Appendix C.)

4. REDUCTION EXOTHERM

The reduction of zirconium dioxide by magnesium to zirconium metal is usually accompanied by an exotherm. The measured exotherm, ΔT , may be used as a reaction indication parameter in the production of the Zr powders. Due to the massive reaction vessel, initially used in this study, no measurable exotherm was observed. However, when it was necessary to scale-up the production quantity, from 40 grams to 400 grams, changes in the design of the reduction vessel were required and resulted in a measurable ΔT . Typical time temperature curves are shown in Figure 15. However, it must be emphasized that no effort was made to quantify the exothermic phenomenon for the purpose of any process specifications under this program.

5. TECHNIQUE FOR X-RAY DIFFRACTION ANALYSIS

Samples for phase identification by x-ray diffraction were prepared by crushing the reaction product in a boron-carbide mortar to -325 mesh

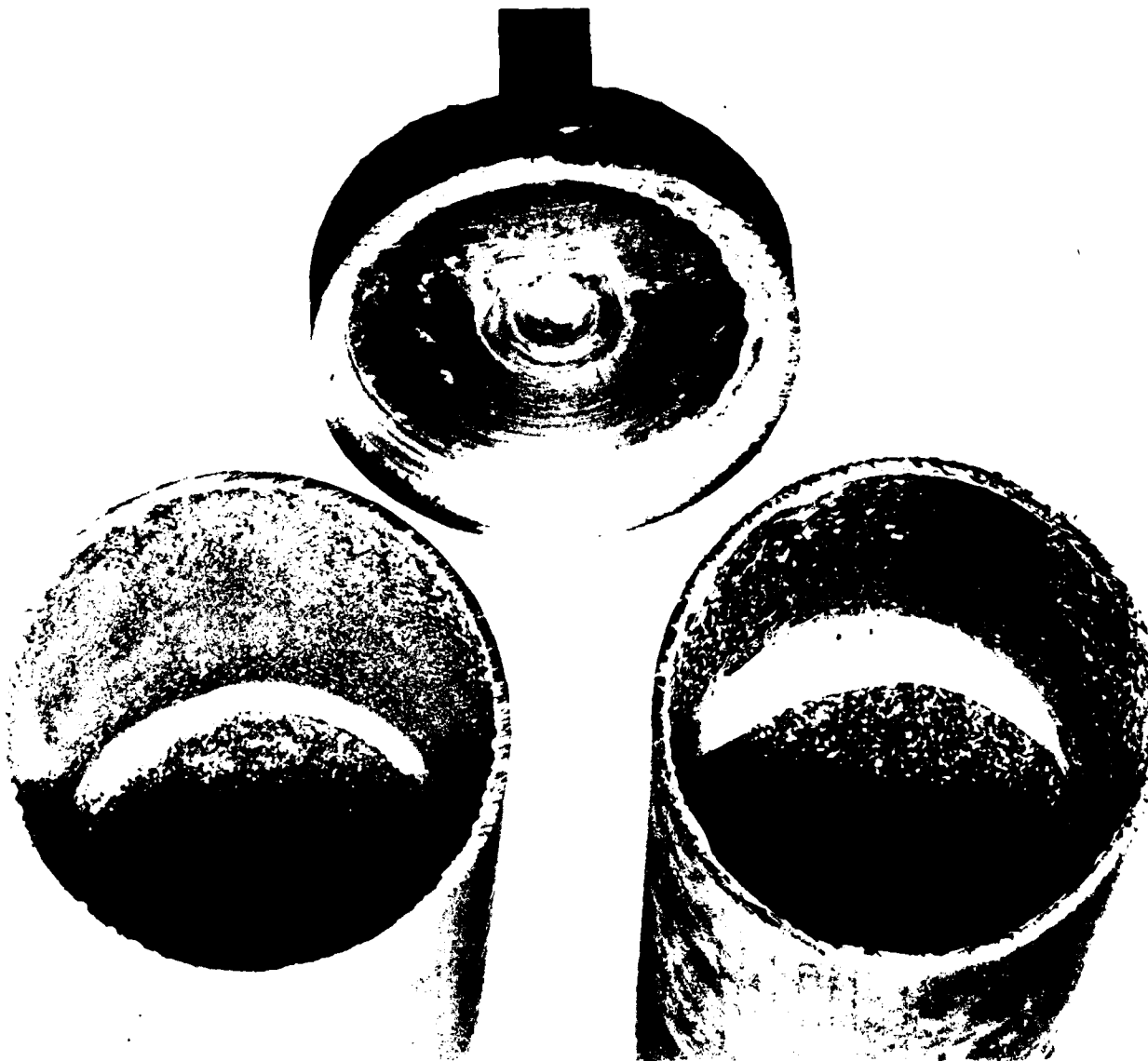


Figure 13. Photograph of the Scaled-up Retort after Removal of the Reaction Product. Mag 1X

REDUCTION OF ZrO_2



VARIABLES-AF INHOUSE EVALUATION

FLOW DIAGRAM

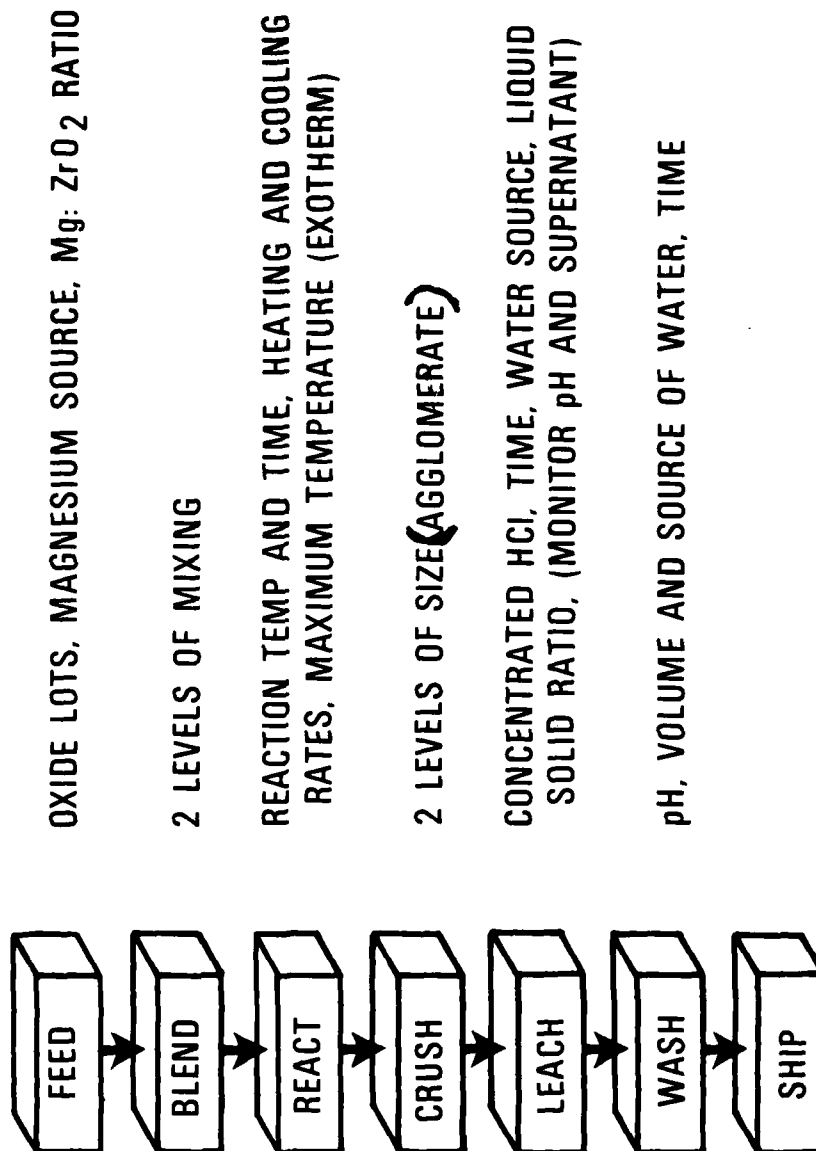


Figure 14. Chemical Reaction and the Flow Diagram Outlining the Steps Required and the Variables Evaluated

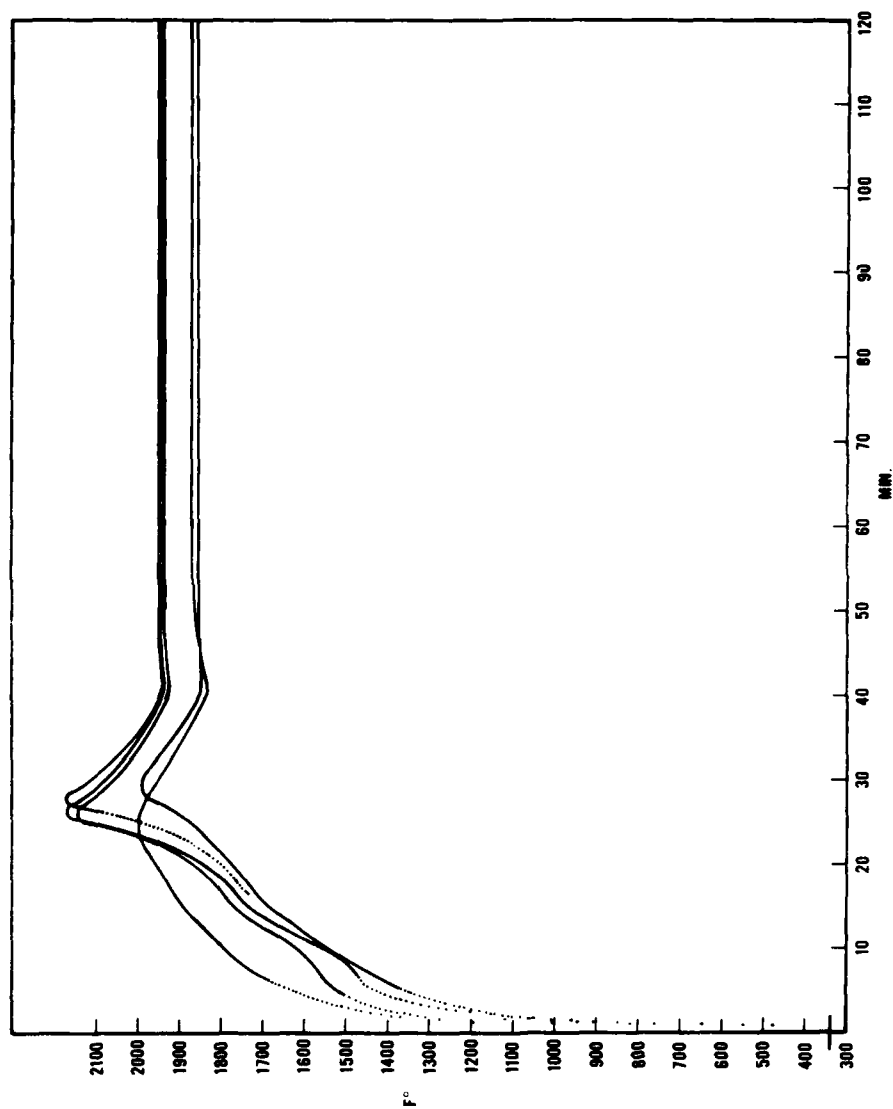
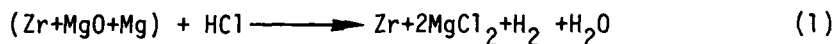


Figure 15. Typical Time, Temperature (Exotherm) Curve Observed when Large (Scaled-Up) Retort Used

particle size. Uniform powder films were obtained by placing a slurry of the powder and 20 vol % collodion amylacetate on a glass slide. Diffraction patterns for phase identification were run at one degree 2θ /min. using Ni-filtered $\text{CuK}\alpha$ radiation. Relative peak heights were used as an indication of the amount of unreacted ZrO_2 in the reaction product. Typical x-ray diffraction patterns indicating the degree of reduction for a given reaction condition are given in Figures 16 A-D. The XRD patterns (Figures 16A & B) show that the chemical reaction has not gone to completion in the given reaction conditions and there are considerable amounts of unreacted ZrO_2 remains in the reaction product. However, the XRD pattern (Figure 16C) indicates that the reaction product is predominantly Zr metal with minor amounts of 3-5 w% ZrO_2 and the XRD pattern (Figure 16D) is ZrO_2 free Zr metal powder. The x-ray analysis of the reaction product could be considered as quality control indicator to predetermine whether or not the final (leached and washed) product is more likely to have the expected powder performance for use in the thermal battery.

6. LEACHING PROCEDURE

Relatively high purity 97% fine particle size 1-2 μm zirconium powders were prepared by the reaction of the reaction product (Equation 1) with calculated amounts of hydrochloric acid in one liter glass beakers with vigorous stirring. The reaction was allowed to go to completion with the evolution of hydrogen while monitoring pH. The liquor was decanted and washed twice with water or when $\text{pH} \approx 7$ was reached.



The settling rate was determined by percent incident light transmission through the sample as a function of time using colorimeter.

Initially, leaching experiments were conducted using available commercial reaction product samples (Ventron lot #J4929A3 and J4929A4).

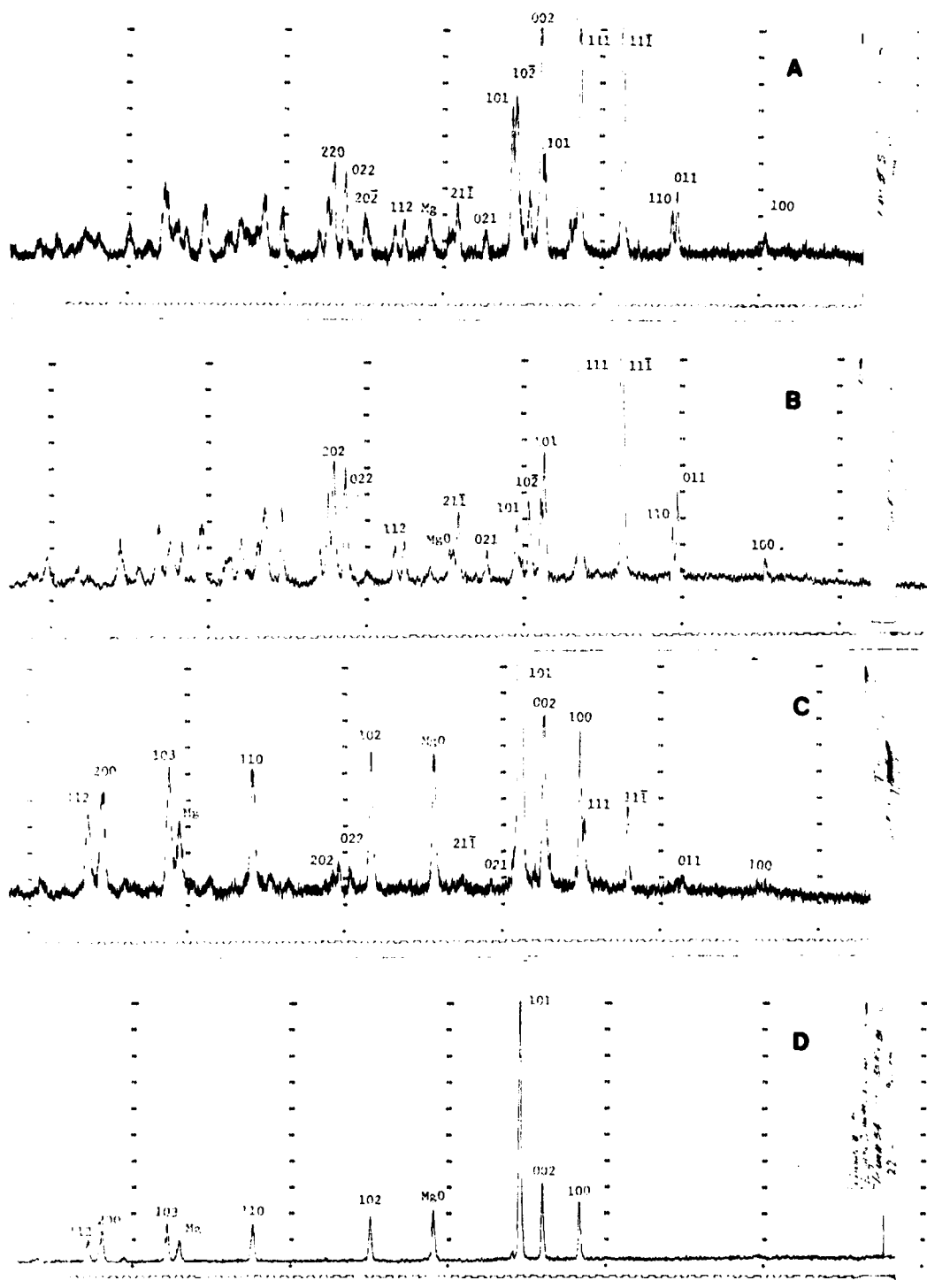


Figure 16. X-ray Diffraction Pattern of Reaction Product Indicating the Degree of Reduction for a Given Reaction Condition

AFML-TR-79-4069

The leaching variables were optimized with respect to the acid concentration and to liquid to solid ratios by evaluating the following sets of parameters:

Liquid/Solid cc/gram	Ventron's Reaction Product lot #J4929A3 gram	HCL Concentration cc in 500 m/H ₂ O
400/1	1.25	3.50
200/1	2.50	7.30
100/1	5.00	18.20
50/1	10.00	36.50
25/1	20.00	73.00

SECTION V

RESULTS AND DISCUSSION

Table 5 contains a summary of reduction conditions and the corresponding zirconium powder characteristics. The results indicate that the purity of the starting oxide has no significant effect on the physical characteristics of the Zr metal powder. Additionally, pre-drying of the oxide powder is unnecessary and the slow heat up and fast quench of the retort during a reduction run has no significant effect on the final product. However, the data clearly indicates that the lowest ignition gain was observed when the system was not outgassed at the beginning of a run or when outgassed it was backfilled after outgassing with 30 psig inert gas such as argon. The best result was obtained when the reduction runs were made with pre-mixed powders plus 14 w% excess Mg in a temperature range 954 - 1065°C for two to four hours under vacuum, 10-15 mm of Hg. And, most importantly, when the reaction product did not contain any ZrO_2 as determined by x-ray. A typical x-ray diffraction pattern of a master lot reaction product to be leached to high purity Zr metal powder is shown in Figure 17.

Table 6 shows the result of the leaching variable study with the corresponding zirconium powder characteristics on the right. The table also includes the powder characteristics of the leached reaction product (Ventron's lot #4929A3) using the standard 4-day leaching cycle developed by AFML. Also the scanning electron micrographs of selected samples (LV-1 through LV-7) are shown in Figure 18. The micrographs show that the surface morphology of the zirconium metal particles are essentially unaffected by the wide range of leaching conditions. This is a significant observation particularly since the performance characteristics are shown in the same table, to vary widely with different leaching conditions. Therefore, the conclusion based on the above observation must be, that the leaching conditions do not affect the external morphology of a particle but are highly significant in determining the performance characteristics of the Zr powder. Indeed, the external morphology is predetermined by the reduction conditions as determined in Figure 19. (788°C for two hours at temperature vs. 954°C for four hours).

TABLE 5
REDUCTION VARIABLE STUDY

REDUCTION CONDITIONS			ZIRCONIUM METAL POWDER CHARACTERISTICS								
OXIDE LOT NUMBER	AFML RUN NUMBER	TEMP/TIME	VARIABLE	BURN SEC/10"	RATE SEC (PIC.)	IGNITION GAIN, WT%	SENS. VOLTS	IGNITION MICRONS	FISHER APS, MICRONS	B.E.T. Mg, m ² /g.	Residual ZrO ₂ X-ray Peak Hgt., Inches
<u>Effect of Starting Oxide</u>											
13382	45-67	1850°F/2 Hrs	oxide lot	2.56	.326	28.2	36	1.71	1.82	1.86	1/3
13276	46-67	1850°F/2 Hrs	oxide lot	2.08	.224	28.6	58.3	1.70	1.75	1.21	1/3
14013	49-67	1850°F/2 Hrs	oxide lot	2.58	.281	28.0	18.7	N.D.	1.90	1.27	1/2
13382	73	1850°F/4 Hrs	oxide lot	3.45	.381	27.30	58	1.64	1.90	2100	
13276	74	1850°F/4 Hrs	oxide lot	3.18	.256	26.82	64.4	1.63	2.05	2100	
14013	72	1850°F/4 Hrs	oxide lot	4.07	.299	27.66	50.	1.68	2.15	1500	
<u>Degree of Charge Mixing</u>											
14013	54-621	1850°F/7-1/2 Hrs	Premixed (spex mixer)	1.53		30.24	55	N.D.	1.8	1.30	3000
14013	55-77	1850°F/7-1/2 Hrs	Not mixed (N ₂ in retort bottom)	2.9	.183	29.33	51.7	N.D.	1.95	1.13	2100
<u>Effect of Heating & Cooling Rate</u>											
14013	56-77	1850°F/7-1/2 Hrs	slow heat up	2.38	.215	29.27	53.1	N.D.	1.78	1.45	3000
14013	59-77	1850°F/7-1/2 Hrs	fast quench	2.93	.271	29.07	32.0	N.D.	1.88	1.69	3000
<u>Effect of Outgassing Procedure</u>											
13459	34	1750°F/2 Hrs	Cont. evac.	N.D.	N.D.	31.35				2100	0
13459	33	1750°F/2 Hrs	No Outgassing	N.D.	N.D.	21.16				1500	0
<u>Effect of Argon Atmosphere</u>											
13459	35	1750°F/2 Hrs	Argon backfilled to 30 psig.	N.D.		21.12				1500	1/2
13459	36	1750°F/2 Hrs	Repeat of 35	not measurable		25.94				45000	1/2
<u>Other Variables</u>											
14013	71a	1850°F/4 Hrs	Predried 1850°F tap water	2.87	.323	29.28	85.8	1.68	2.24	2100	
14013	71b	1850°F/4 Hrs	Predried except distilled H ₂ O + Fe	2.75	.213	28.05	82.5	1.80	2.15	2100	
13382	75	1850°F/4 Hrs	Predried 1850°F/20 min	3.16	.254	31.48	58.4	1.76	1.95	3000	
14013	69-82	1950°F/4 Hrs	Standard conditions	N.M.	.646*	31.05	24.1	1.5	3.2	3000	

* Delayed Ignition - Wide Variability

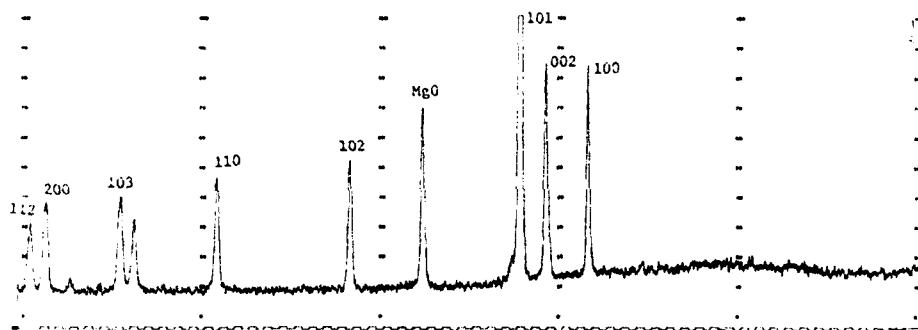


Figure 17. X-ray Diffraction Pattern of a Master Lot for Leaching Experiment

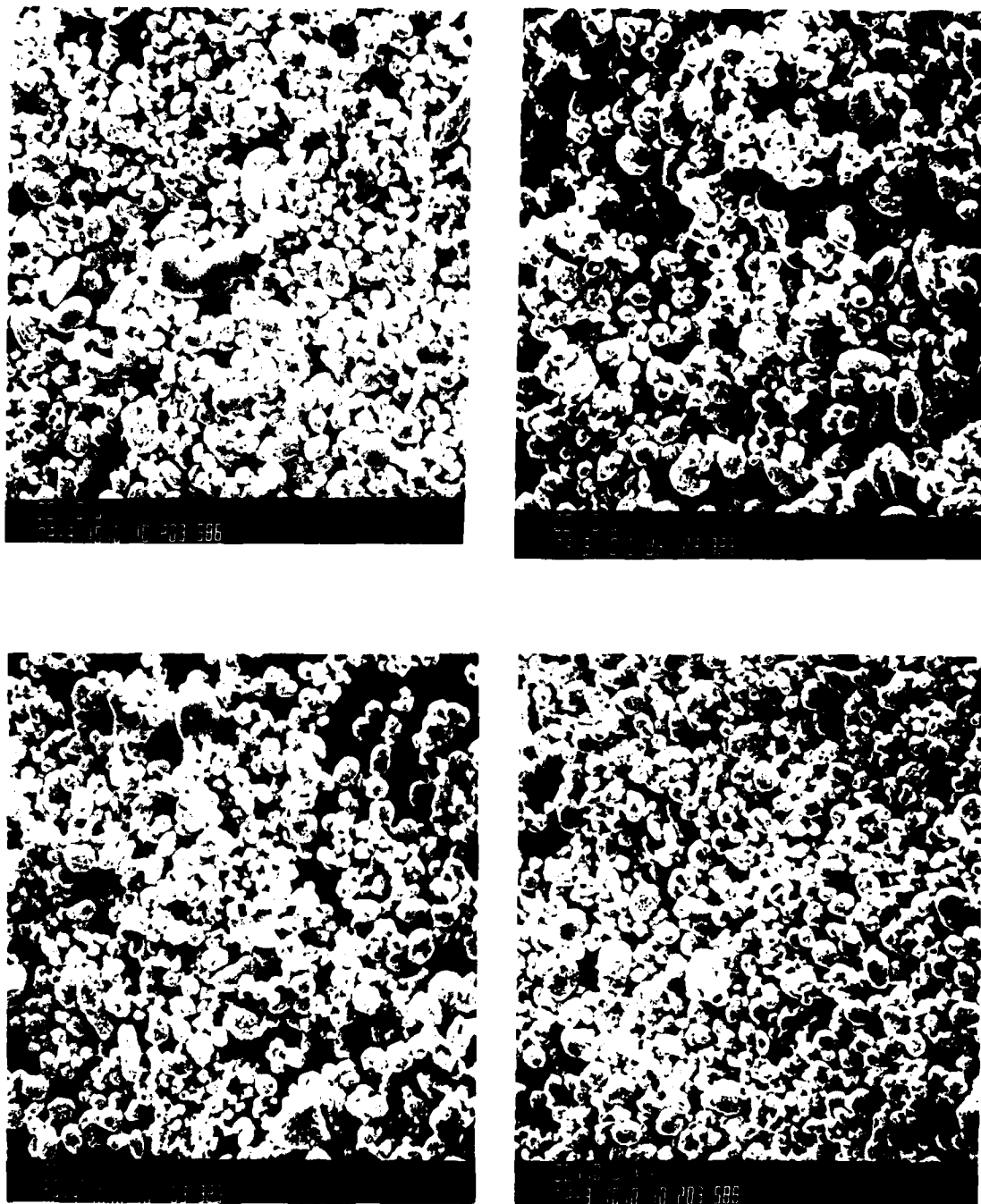


Figure 18. Scanning Electron Micrographs Showing No Change in Surface Morphology of Zr Reaction Product Leached Under Wide Range of Leaching Conditions

TABLE 6
LEACH VARIABLE STUDY

OXIDE LOT NUMBER	AFML NUMBER	VARIABLE	ZIRCONIUM METAL POWDER CHARACTERISTICS					
			BURNING RATE SECONDS PER 10"	SECONDS ¹	IGNITION SENSITIVITY, MINIMUM VOLTS	IGNITION, GAIN Wt %	APS, MICRONS (PICATINNY)	Mg, PPM
14013		Master lot of reaction product, 1850°F/4 hrs, standard reduction procedures.						
			2.37	.224	96.4(114) ²	27.05	1.93	3000
			2.80	.226	77.5(77.8)	27.14	1.98	2100
			0.90	2.93	55.5(55.8)	22.53	1.47	15000
			2.68	.239	56.6(58)	22.33	2.00	2100
			3.36	.273	52.4(51.3)	25.11	2.30	2100
			2.69	.248	23.5(49)	27.73	1.95	2100
	LV-1	Liquid/solid = 10/1	3.09	.249	64.5(64.1)	25.57	1.90 (1.72 AFML)	2100
	LV-2	Liquid/solid = 20/1 (standard cycle)	2.03			30.37		3000
	LV-3	1/2 Amount of HCl						
	LV-4	Mixed by impeller (rather than magnetic stirrer)						
	LV-5	Distilled H ₂ O						
	LV-6	"Short Cycle" (2 days)						
	LV-7	Two (2) washes (1 less than standard cycle)						
Ventron 4929A3 - AFML DATA (Reduction parameters unknown to AFML)								
	4929A3	VENTRON DATA						
	4929A3	REACTION PRODUCT AFML leached using standard cycle	2.76			30.9		4000
			1.85			31.14		2100

(1) 79 w/o BaCrO₄, 21 w/o Zr, .23" dia cylindrical pellet, 1500 mg, compressed at 18,500 psi, tested by Picatinny Arsenal

(2) Indicates maximum voltage attainable without ignition

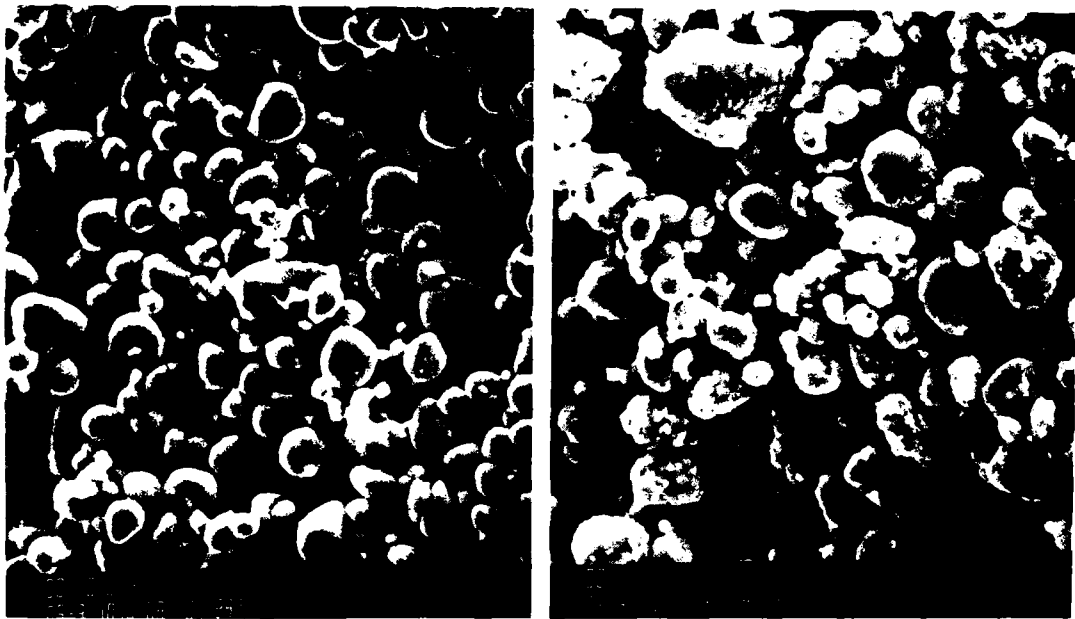


Figure 19. Scanning Electron Micrographs Showing External Morphology as Predetermined by the Reduction Conditions (A) 788°C for 2 hrs., (B) 954°C for 4 hrs

1. POWDER PERFORMANCE

Comparative burn rates for selected samples using two well known burn rate techniques are listed in Table 7. The results are in good agreement with those for commercial powders, Ventron and Foot Mineral, under identical conditions. It is interesting to note that the reduction temperature of 954°C for two hours is not desirable since it resulted in a burn rate below the acceptable minimum value. The result is consistent with the ignition gain values determined previously on samples under somewhat similar reduction conditions. For detailed methods of burn rates and equipment used by AFRPL, see Appendix D.

TABLE 7
COMPARATIVE BURNING RATES

SOURCE/REDUCTION PARAMETERS	(1) AFRPL SEC/10"	(2) PICATINNY SECONDS
AFML/1850°F/8 HRS	1.5	-
" 1850°F/2 HRS	2.6	.28
" 1750°F/2 HRS	4.7	1.83
VENTRON CONTROL	2.1	.22
FOOTE MINERAL	-	.21

(1) CURRENT BATTERY MFG. SPECIFICATION - 3.4 SECONDS (MAX.)
PER 10-INCH POWDER TRAIN

(2) HEAT POWDER (79 w/o BaCrO₄, 21 w/o Zr)

SECTION VI

PROCESS SPECIFICATIONS

The information listed below is based on some 77 reduction runs and several leaching parameter studies conducted over some 12 months at AFML. The specific information and recommendations for scale-up to 50 lb batches are provided below. Standard conditions for reduction and leaching are indicated.

1. STARTING MATERIALS

ZrO₂ Zircoa Type A, run-of-the mill
 31501 Solon Rd

Mg Hummel Chemical Company
 S. Plainfield, NJ
 -50 + 80 Mesh Powder

Charge ratio - 14 wt % excess Mg over that required by the stoichiometry

Method of mixing - Any method giving thorough blending without stratification - Spec mixer, elbow blender, etc.

Predrying - No predrying of the charge is necessary.

2. RETORT MATERIALS

Type 304 stainless steel tubing to match the furnace was used.
(400 series stainless is also acceptable)

3. OUTGASSING, HEATING AND COOLING

The charged retort should be room temperature outgassed by evacuation, suitably sealed (valved off) and placed in a furnace preheated to the desired reduction temperature. Allow the pressure to attain 30 psig, outgas (bleedback) to 25 psig several times until the pressure no longer builds up - let reaction occur for the selected time at temperature. Upon completion of run, remove retort from furnace and allow it to air-cool at room temperature. (The retort is of course kept evacuated.)

4. LEACHING CYCLES

In Common - Total Liquid (c.c.) to solid (reaction product, grams)
ratio of 20/1 to 30/1.

Amount of Acid - Conc. HCl (Reagent grade) =
3.7 c.c./g. R.P. (Based upon 14 w % to excess Mg)

Tap water only

"Standard Cycle" - 4 Days

- a. Acid leach with stirring a minimum of 2 hours
- b. Settle overnight
- c. Decant, add tap water to original volume
- d. Wash with stirring 2 hours
- e. Settle overnight
- f. Repeat steps 3 through 5 for a total of three washes.

"Short Cycle" - 2 Days

- a. 2-3 hour leach with stirring
- b. 4 - hour settle
- c. Decant, fill with tap water, wash 1 hour with stirring,
settle overnight
- d. Decant, fill, wash 1 hour, settle 4 hours, decant, fill,
wash 2 hours, settle overnight.

5. RECOMMENDED REDUCTION PARAMETERS AND VARIABLES FOR SCALE-UP STUDIES

Reduction Temp/Time*

- a. 1750 F - 6 to 8 hours at temperature
- b. 1850 F - 2 hours
- c. 1850 F - 4 hours
- d. 1850 F - 6 hours
- e. 1850 F - 8 hours
- f. 1950 F - 1 hour
- g. 1950 F - 2 hours
- h. 1950 F - 4 hours

*To be conducted using single lots of oxide and magnesium and the procedures given previously.

SECTION VII

SUMMARY AND CONCLUSIONS

Commercially available Zircoa Type A Zirconia was characterized and reduced by magnesium powder to yield consistent quality fine particle 1-2 μm zirconium powder with burn rates and ignition gain values equivalent or better than currently being provided commercially for use as heat source in Air Force Maverick Thermal Battery. The particle morphology most likely causing ignition sensitivity of zirconium powders is identified. Alternate zirconium powder production sources suitable for use in Air Force Maverick Battery in case of emergency or shortages was established. Comprehensive and closely coordinated (Figure 20) technology transferred to the industry was accomplished.

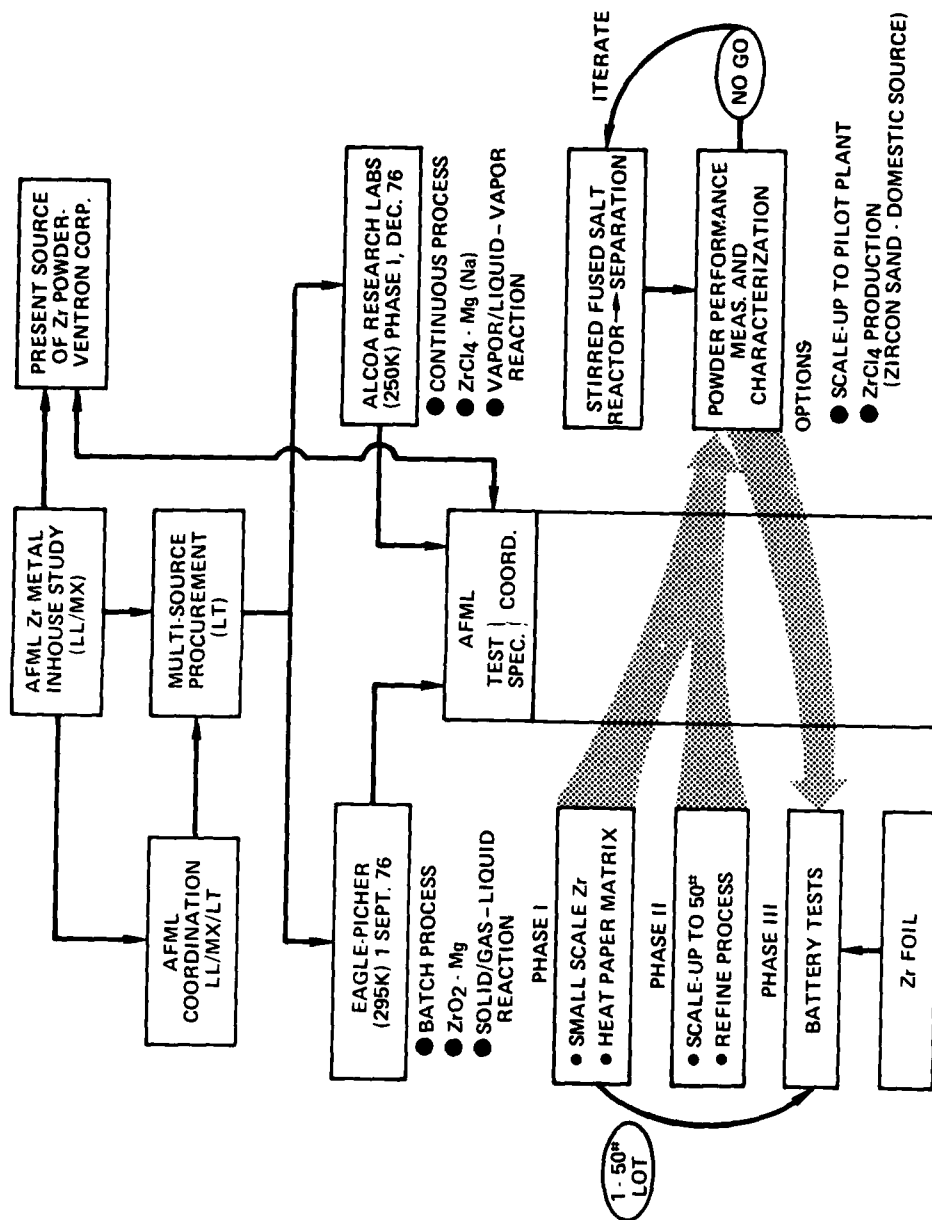


Figure 20. Schematic AFML-Industry Coordinated Programs

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APPENDIX A

PARTICLE SIZE DISTRIBUTION OF ZIRCONIUM AND
ZIRCONIUM OXIDE POWDERS

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I. INTRODUCTION

The reaction of zirconium powders with suitable oxidants produces an exothermic reaction necessary for the operation of thermal batteries used in Air Force systems. The metallic powders are produced by reduction of zirconium oxide powders; careful control over this reduction is necessary for the production of uniform powders. To develop a quality control procedure and to provide monitoring for in-house processing investigations, various powder size measurement techniques were used to establish baseline data.

II. EXPERIMENTAL

Two basic techniques were used and compared, hand measurements with the Zeiss particle size analyzer and an automated procedure using the Micromeritics SedioGraph 5000 Particle Size Analyzer. Powder samples were sent to Micromeritics to be examined directly; the hand measurements were made on images from both transmission and scanning electron microscopes. Size distributions obtained in both cases were then compared to correlate the techniques and obtain source data as to the number of measurements needed to characterize a lot of powder.

The SedioGraph 5000 Particle Size Analyzer measures the sedimentation rates of particles in suspension and automatically presents these data as a cumulative percent distribution in terms of the equivalent spherical diameter.

The instrument determines, by means of a finely collimated beam of X-rays the concentration of particles remaining in suspension at various sedimentation depths as a function of time. The logarithm of the transmitted X-ray intensity is electronically generated, scaled, and presently linearly as "Cumulative Mass Percent Finer" on the Y-axis, see Figure 3. Six batches of powders, 3 oxide and 3 metal, were analyzed by this method (Figs. 3 through 8). Examination of the results show good correlation with hand measurement in the one to five micron range. Above five microns there is a possibility of clumping as more large particles

were measured. Below one micron the use of mass percent makes the determination of absolute numbers difficult as small deviations in the distribution curve can represent a large number of particles.

The Zeiss particle size analyzer measures the diameter of a circular section projected through a photograph. The analyzer is an electron-mechanical device; the operator adjusts a diaphragm to match the image size and hits a switch which marks the particle and records that particle size through a bank of 48 counters. The analyzer will measure diameters (on the photograph) between 1 and 48 mm in normal operation.

A comparison of images from the scanning and transmission electron microscopes was the first phase of operation. TEM images at a variety of magnifications were examined; it was found that the number of particles per image was low (Table I) and clumping of particles made size analysis difficult. Automated particle sizing using the Quantimet 720 was also attempted. The same problem, impinging particles, was encountered and some continued solutions such as scratching the print to produce artificial boundaries were not successful. This instrument could be useful if a rough measure of surface area were required; a perimeter measurement would give some indication of particle surface irregularity.

The SEM images were chosen for final analysis. If particles are well dispersed a clean picture containing a large number of particles is obtained. In this case almost all the particles within the field of view can be measured, even those that are clumped. Of the two magnifications used initially, 2000X was chosen as it provided a maximum number of particles with good resolution. Consequently, all discussion will deal with SEM images at 2000X.

III. RESULTS

A. Sedimentation

The results of this technique are represented by the six plots, Figs. 3 through 8. Using cumulative mass percent allows the mean of the

size distribution to be read directly at 50% but number of particles in this distribution is more difficult to obtain. It is fairly obvious from the higher mass percentage above 10 microns in the metallic powders that some clustering has occurred. Whether this phenomenon is a function of the powder condition or the test method is unclear. To facilitate the comparison of these results with hand measurements, the cumulative mass percent was converted to number of particles. At the time each powder lot analysis cost \$50.00.

B. TEM-Zeiss

Combining the size distributions from several images (459) resulted in very poor cumulative number of particle plots as compared to the SEM results so that no further measurement were made beyond the initial 100 images, Figs. 9, 10 and 11.

C. SEM-Zeiss

Once it was decided to use SEM images on the Zeiss machine a total of ten lots of powder was examined, Figs 12 through 20. Counting statistics on most lots was good, over 1000 particles as an arbitrary minimum, for most lots, Table II. In the cases where oxide and metal data was available for the same lot the distribution curve shapes were quite similar indicating little change in powder size characteristics, Figs. 12 through 17. Almost all particles were spherical. For the few elongated particles an equivalent spherical diameter was calculated by assuming an elliptical shape and measuring major and minor axes. These measurements although precise are tedious and time consuming, an average of 12 hours per image.

IV. DISCUSSION

The good and bad points of all methods examined have been brought out in the previous sections, what remains is direct comparisons between the distributions obtained from sedimentation and SEM images at 2000X using the Zeiss particle size analyzer. As a first step, the cumulative

mass percent and number of counted particles had to be converted using the size distribution breakdown of the Zeiss machine. Volumes were calculated for the midpoint of each particle size range and conversion followed to produce a number of particles distribution for sedimentation and a mass distribution for the particle count. A sample tabulation is included as Figure 21.

When the total range of particle sizes measured by both methods was used for comparison it became apparent that the sedimentation method showed more particles and both ends. It is possible that the sedimentation technique is more accurate for small particles; finer may not be resolved in the SEM or could have been lost in preparation techniques. The large particles shown by sedimentation, particularly in the metallic lots, Figures 6, 7 and 8, could have been produced by clustering.

As a result of these differences it was decided to try a comparison of techniques in the range of one to five microns, the conversions are shown in Figure 21. Figures 23 through 26 show the results of these manipulations, the missing lot was a result of sample mislabeling. The correlation in most cases was excellent. In the one case where matching was not perfect it was carried through both oxide and metal lots.

V. CONCLUSIONS

Both methods are successful for characterizing the size distribution of oxide and metallic powders in the range of primary interest. The sedimentation method is much cheaper considering the time necessary for counting with the Zeiss Analyzer. If a technique such as sedimentation is to be used for quality control a SEM photograph should also be used as a check for nonspherical particles and to provide evidence of sintering of the metallic powder. It is strongly recommended that any control technique be based as a particle size distribution rather than a single average size.

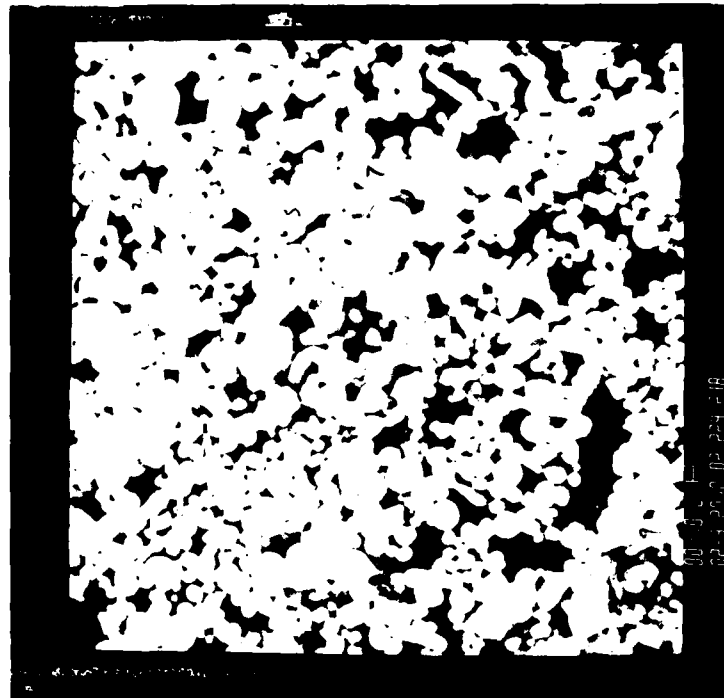


A. TEM, OXIDE

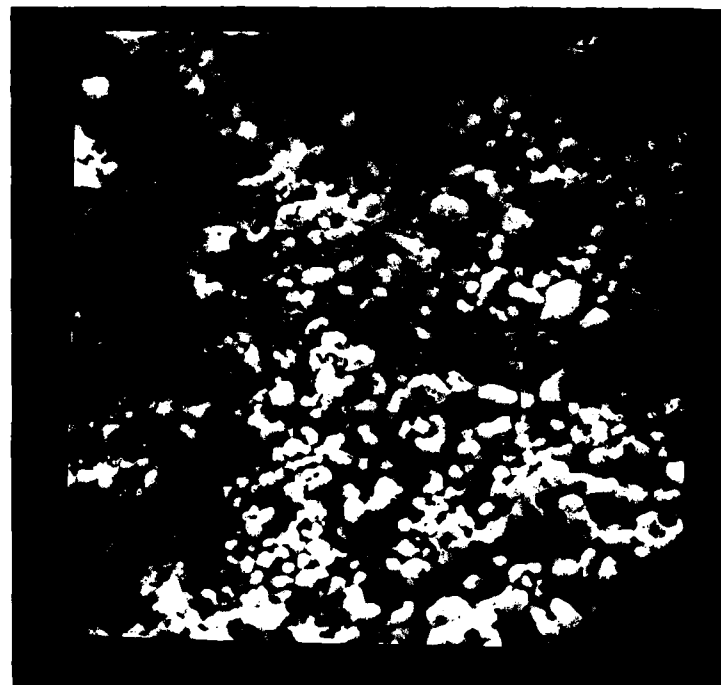


B. TEM, METAL

Figure 1



A. SEM, OXIDE, 2000X



B. SEM, METAL, 2000X

Figure 2

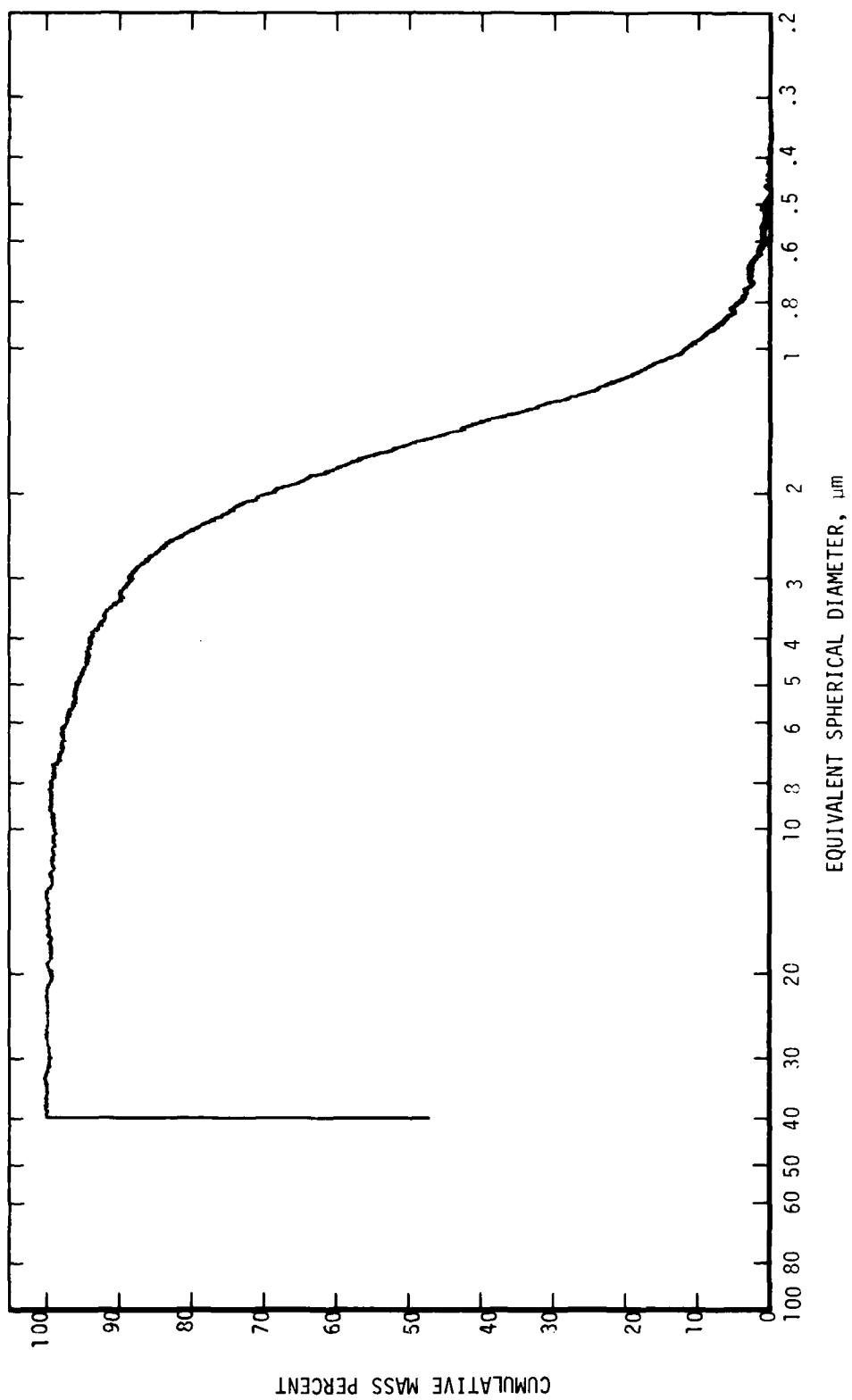


Figure 3

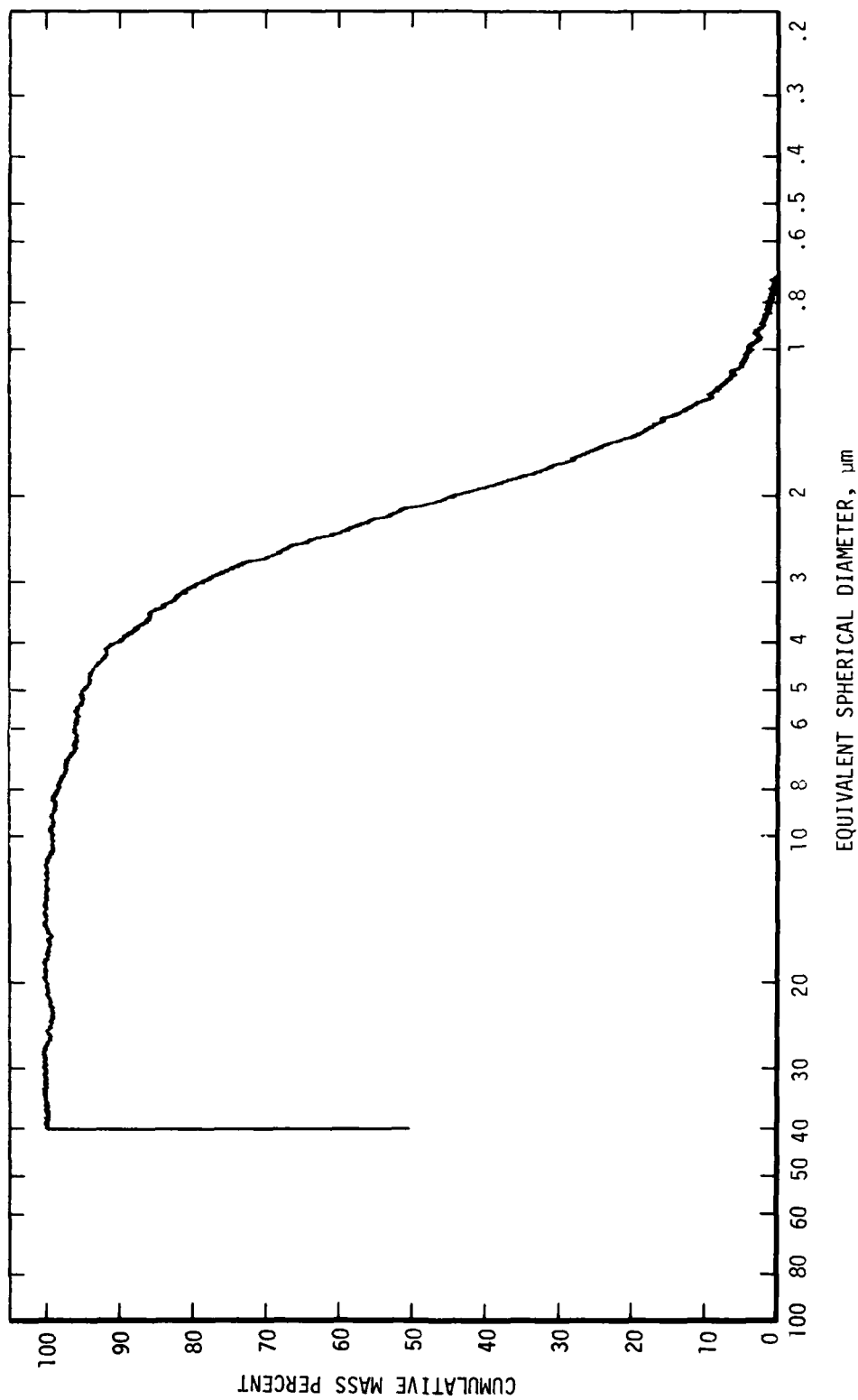


Figure 4

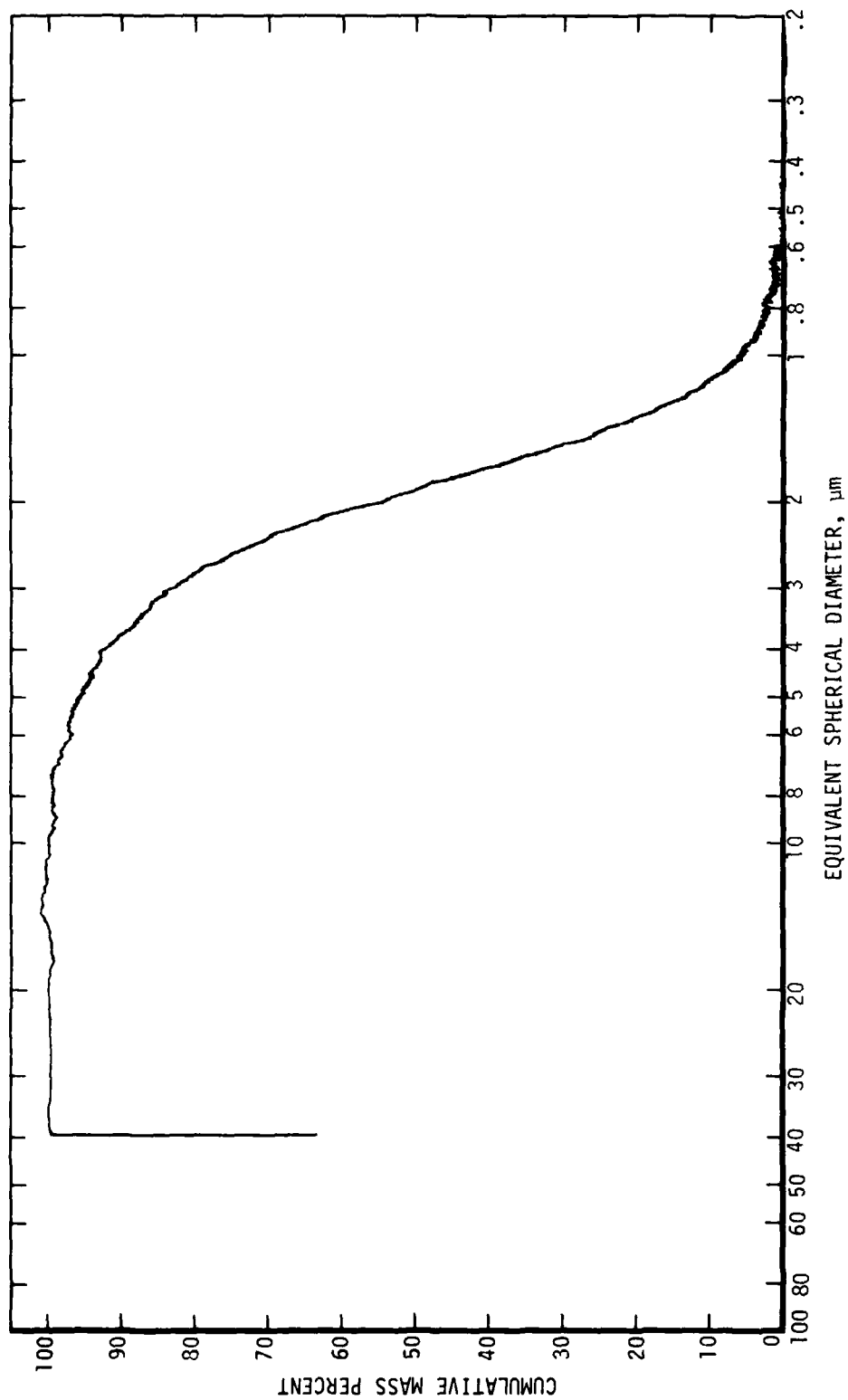


Figure 5

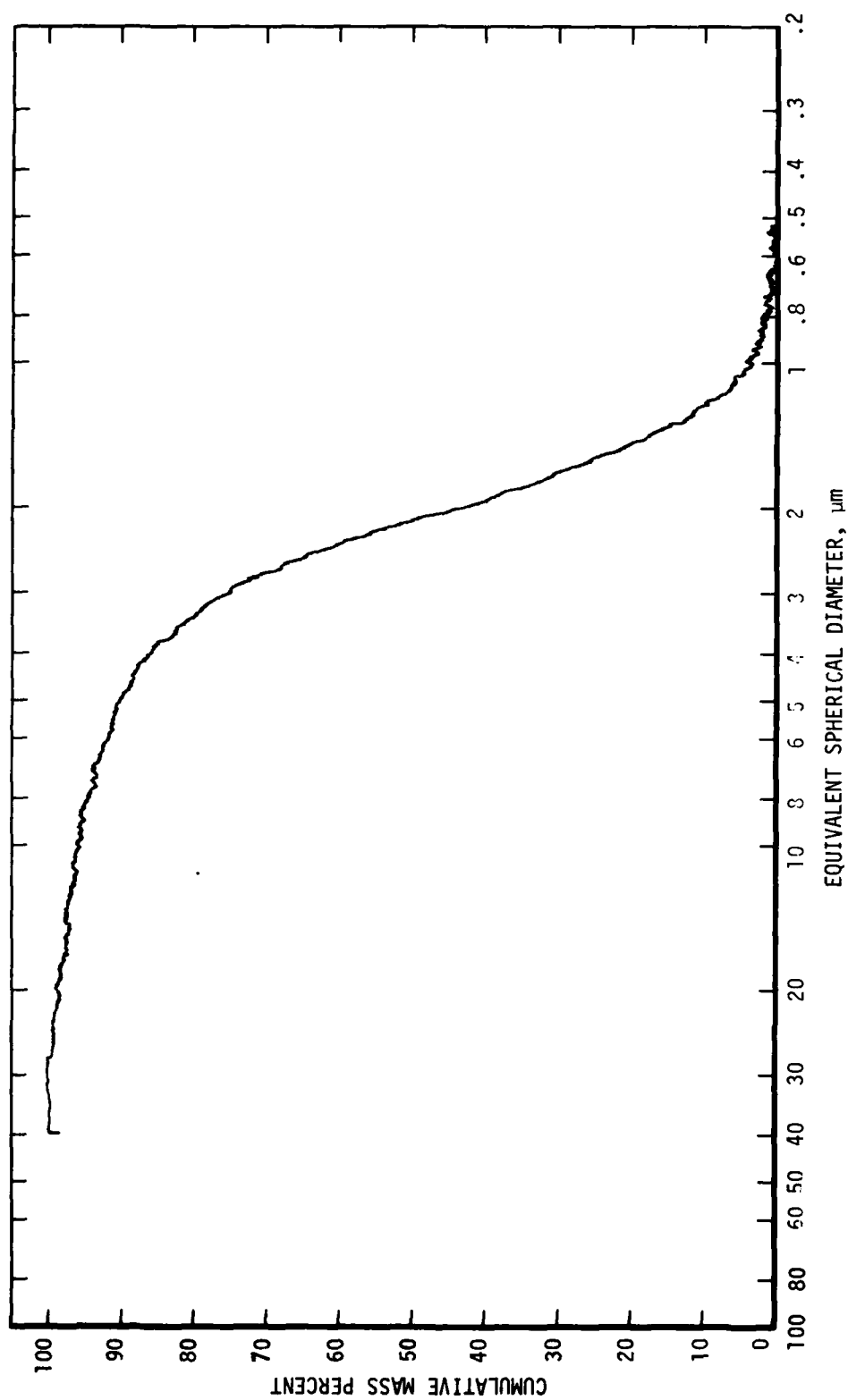


Figure 6

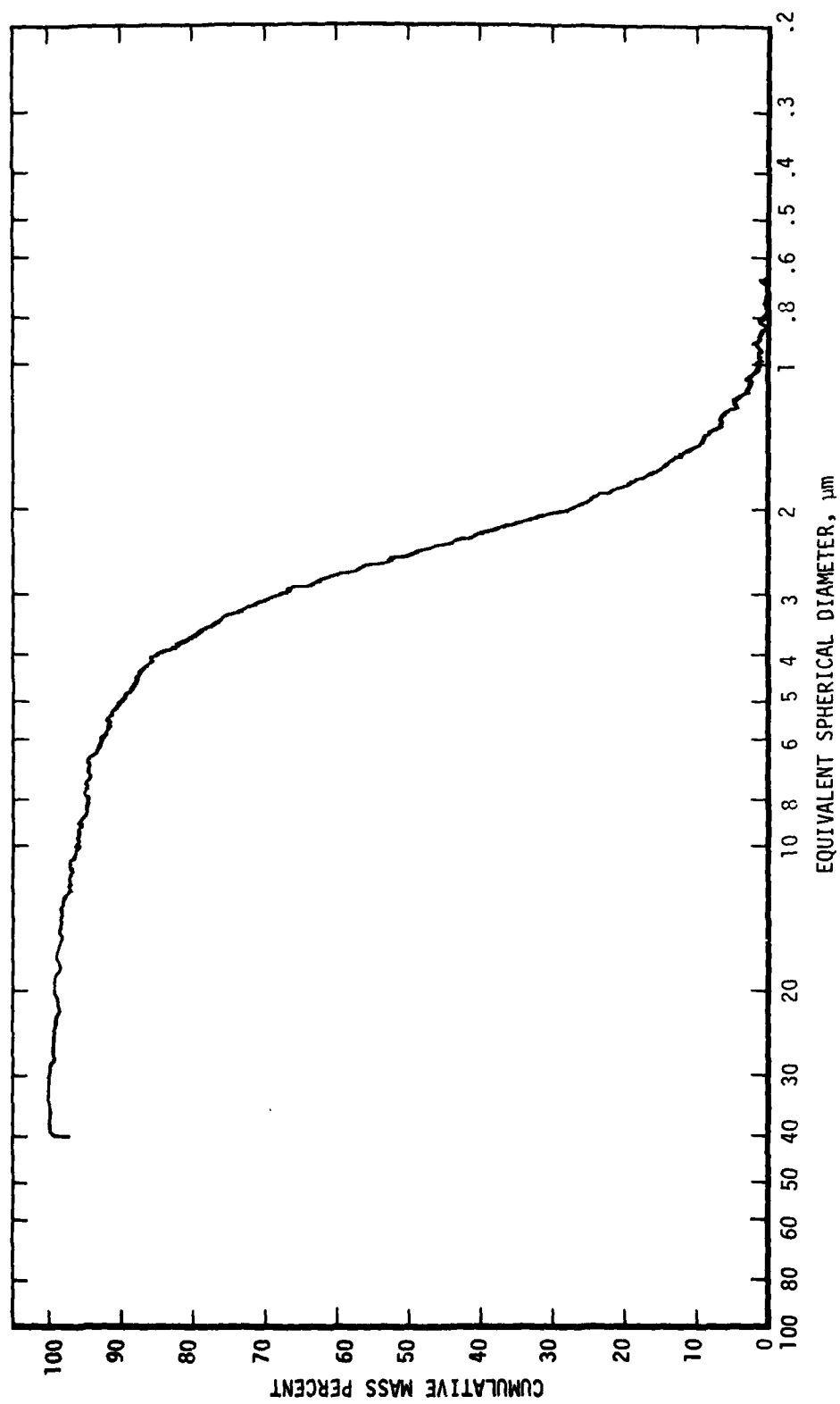


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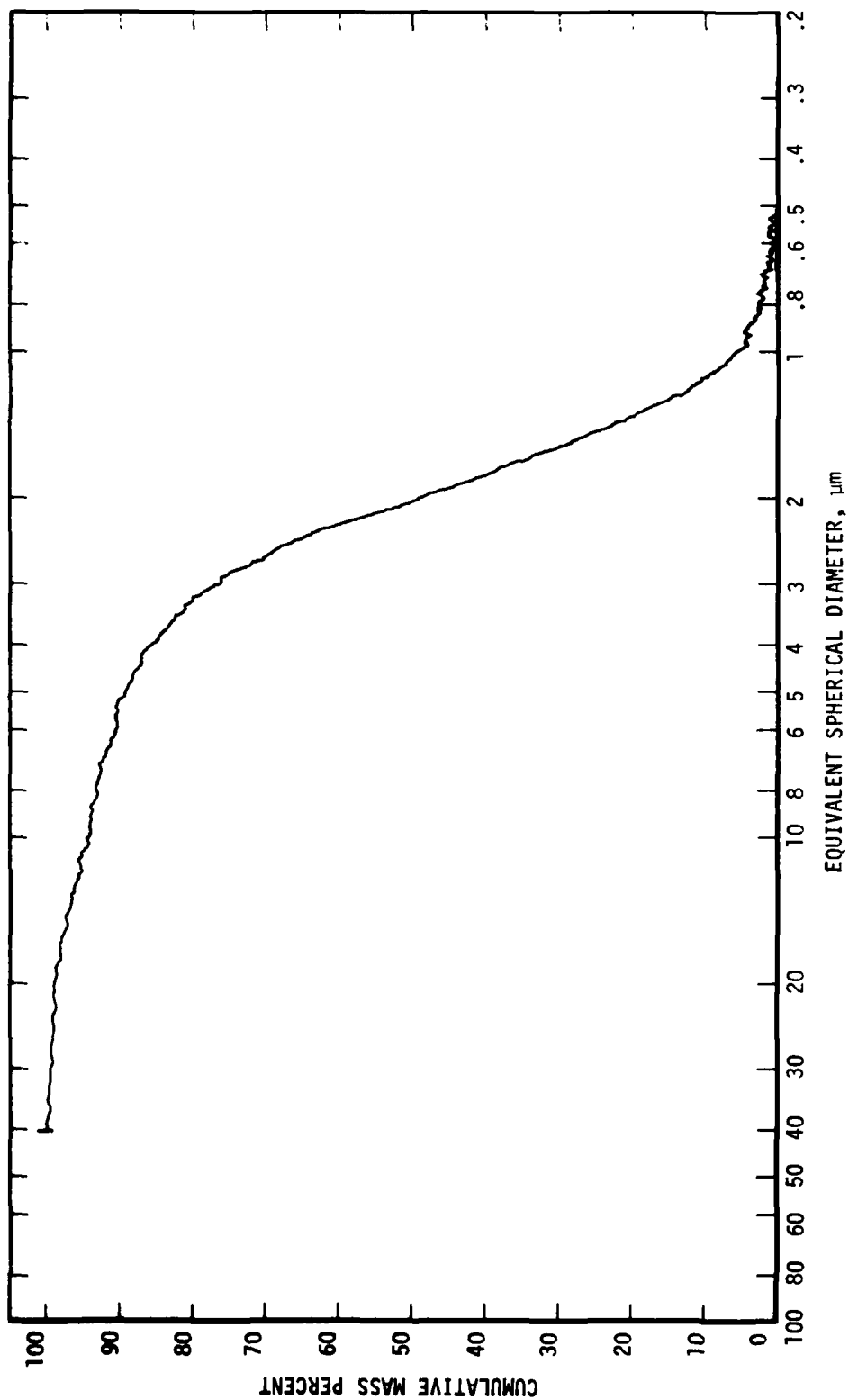


Figure 8

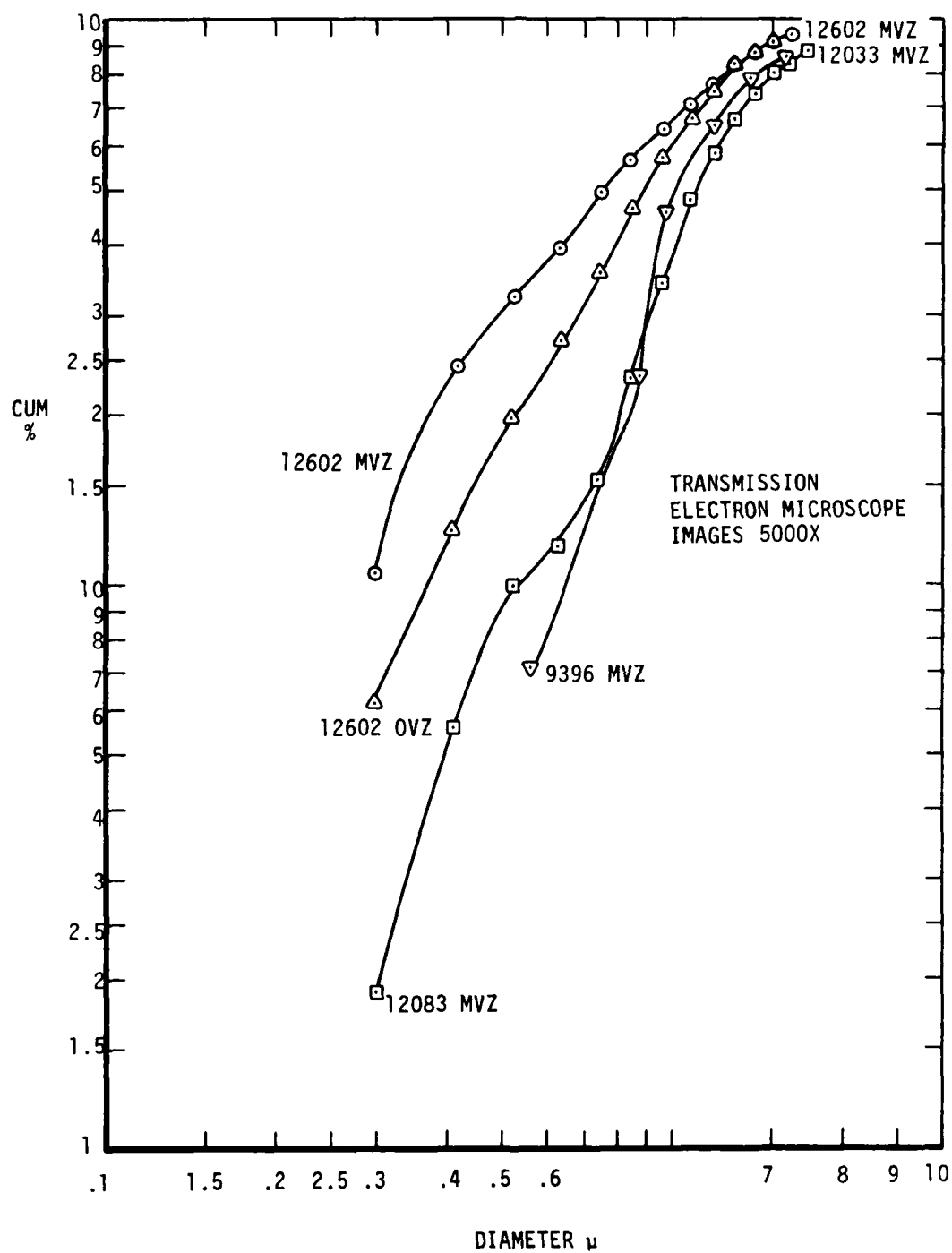


Figure 9

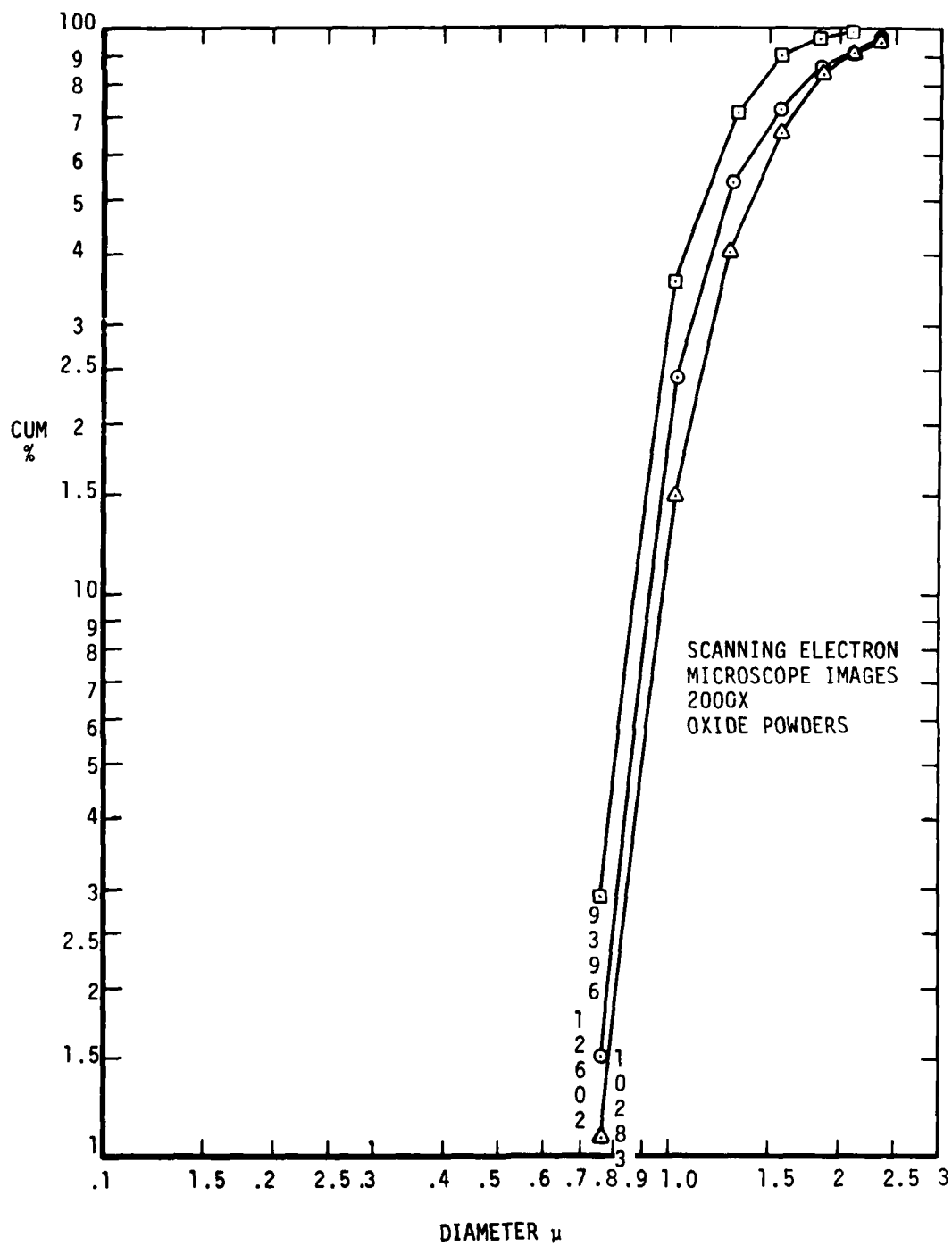


Figure 10

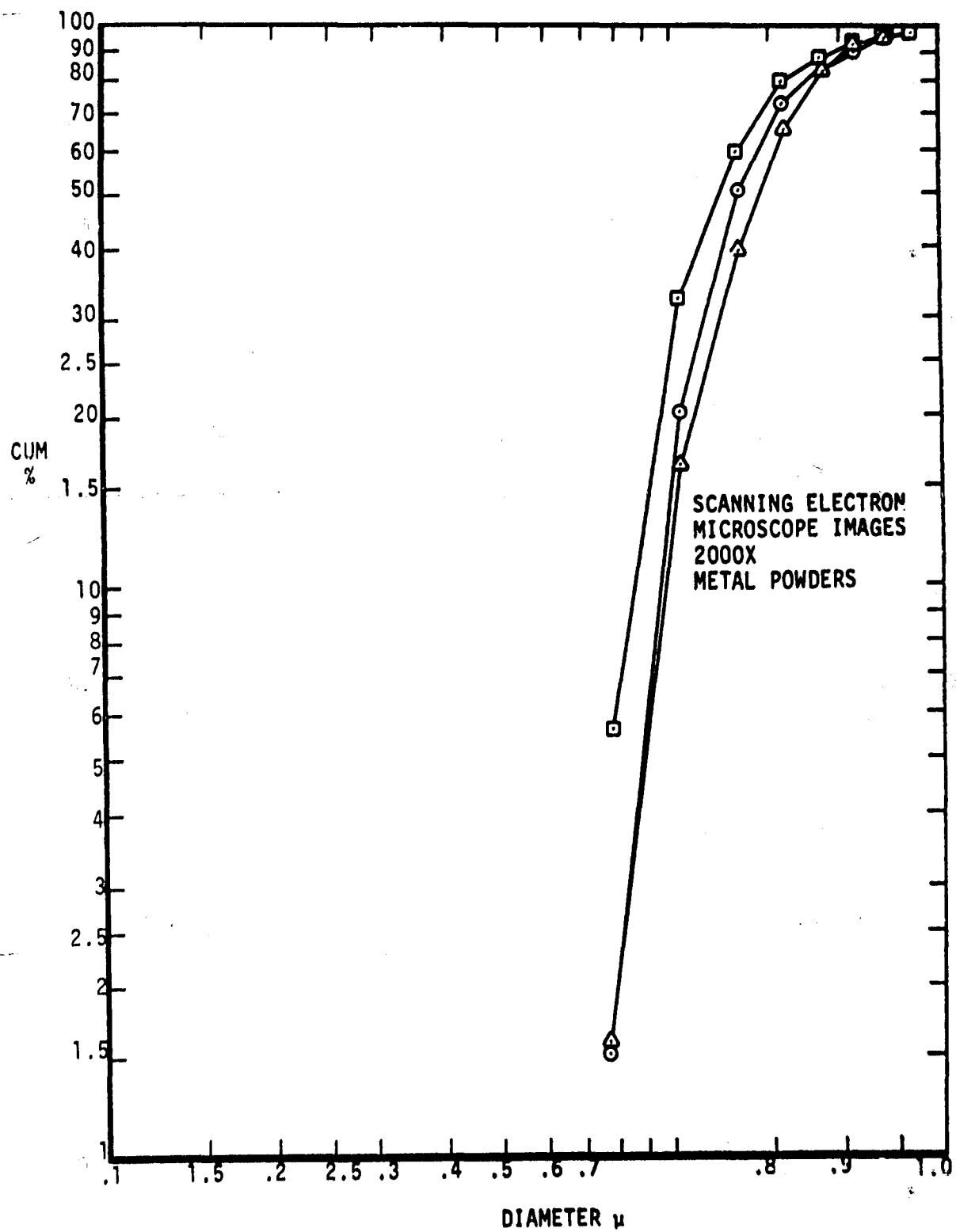


Figure 11

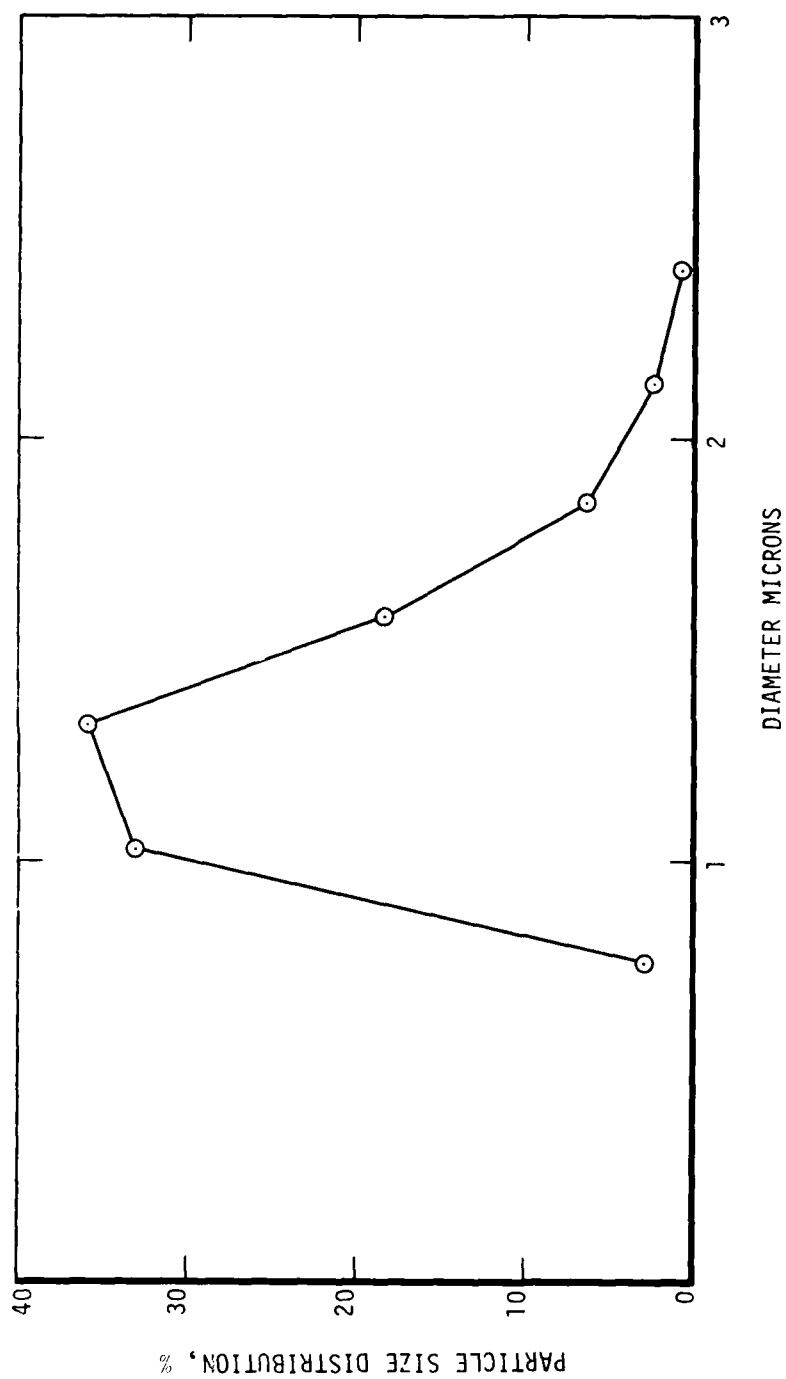


Figure 12. Particle Count Sample 9396 Oxide

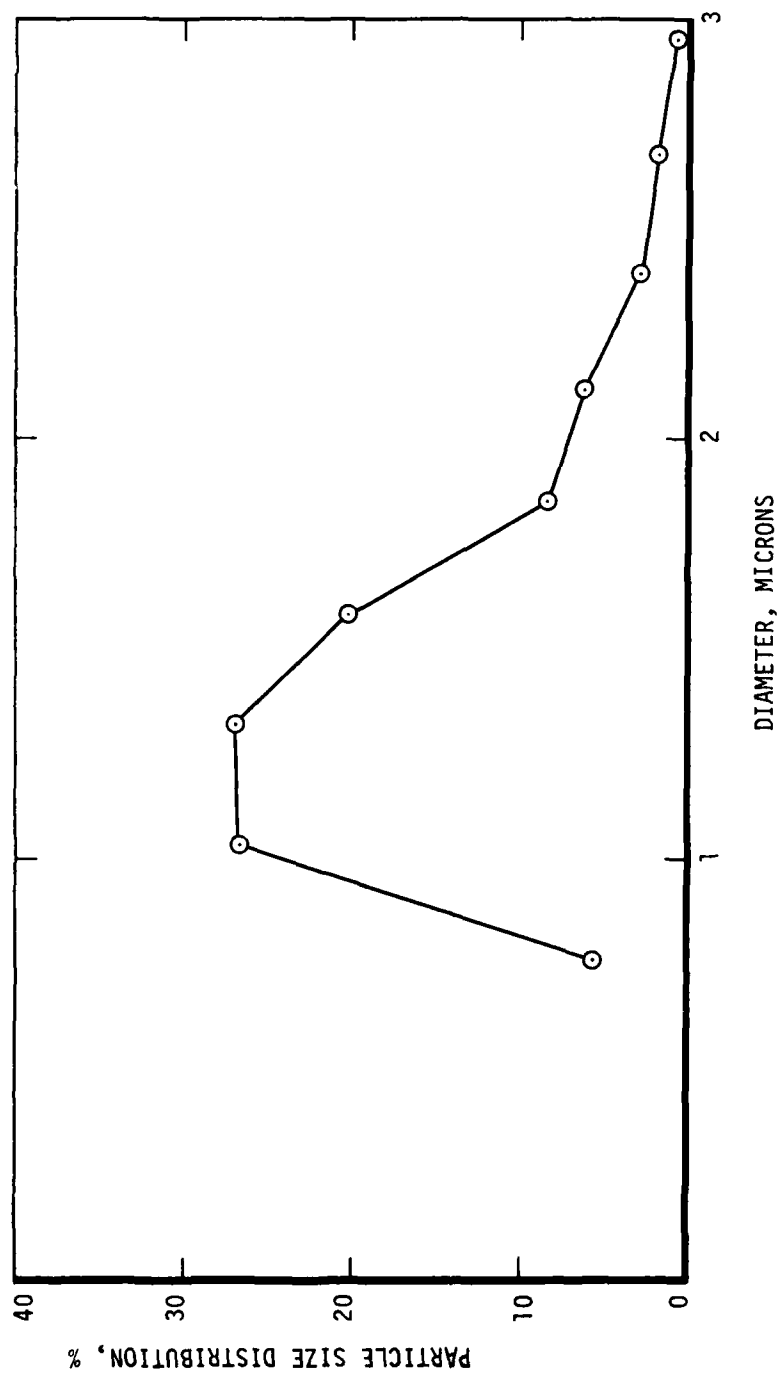


Figure 13. Particle Count Sample 9396 Metal

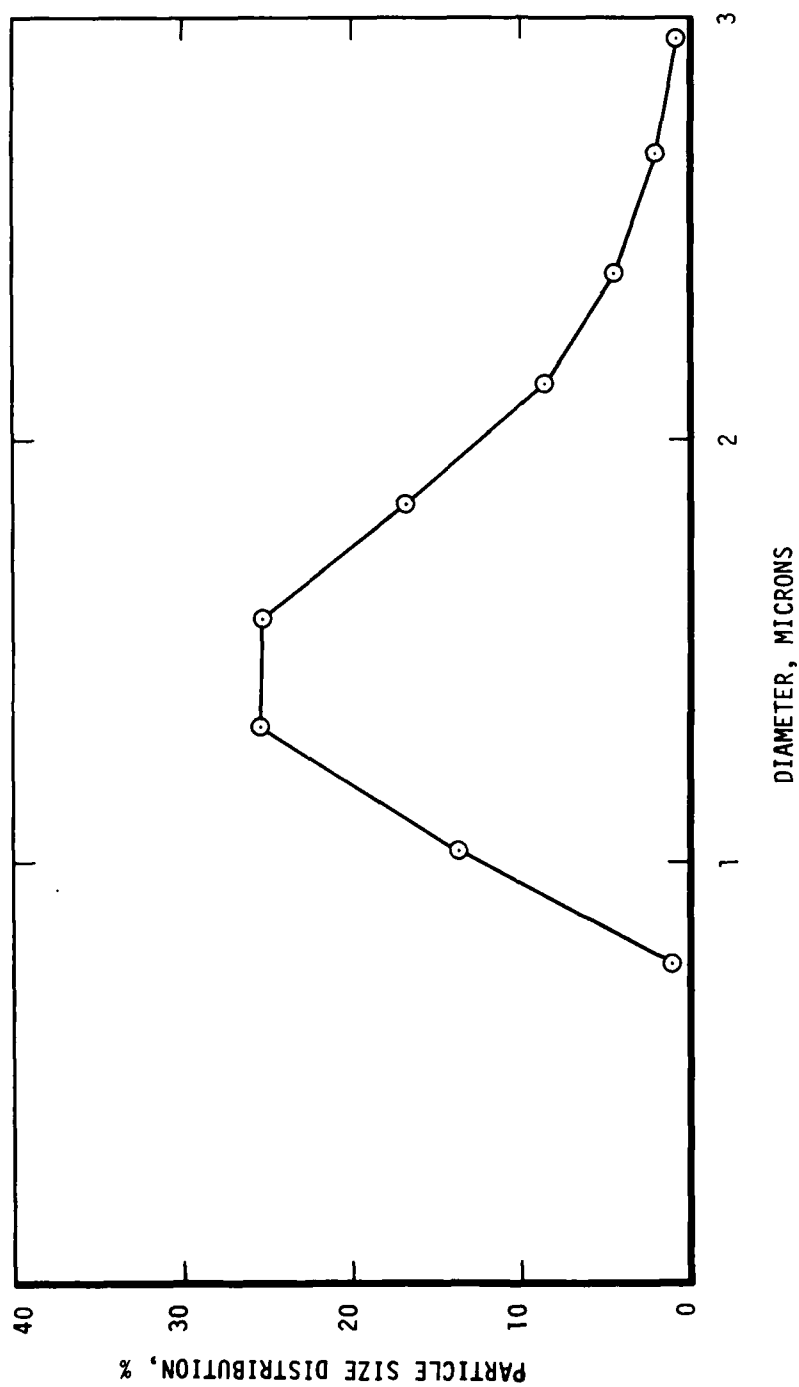


Figure 14. Particle Count Sample 10283 Oxide

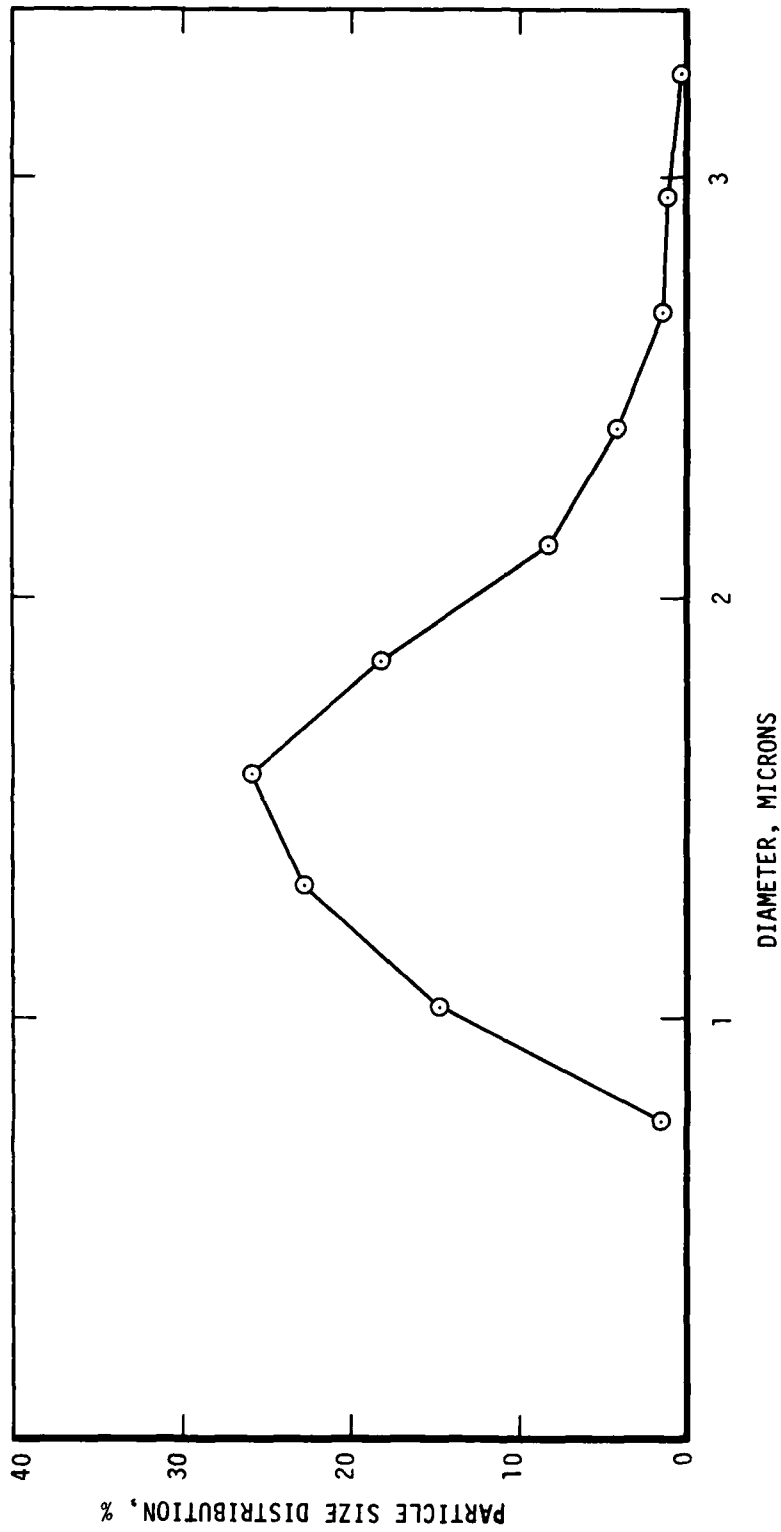


Figure 15. Particle Count Sample 10283 Metal

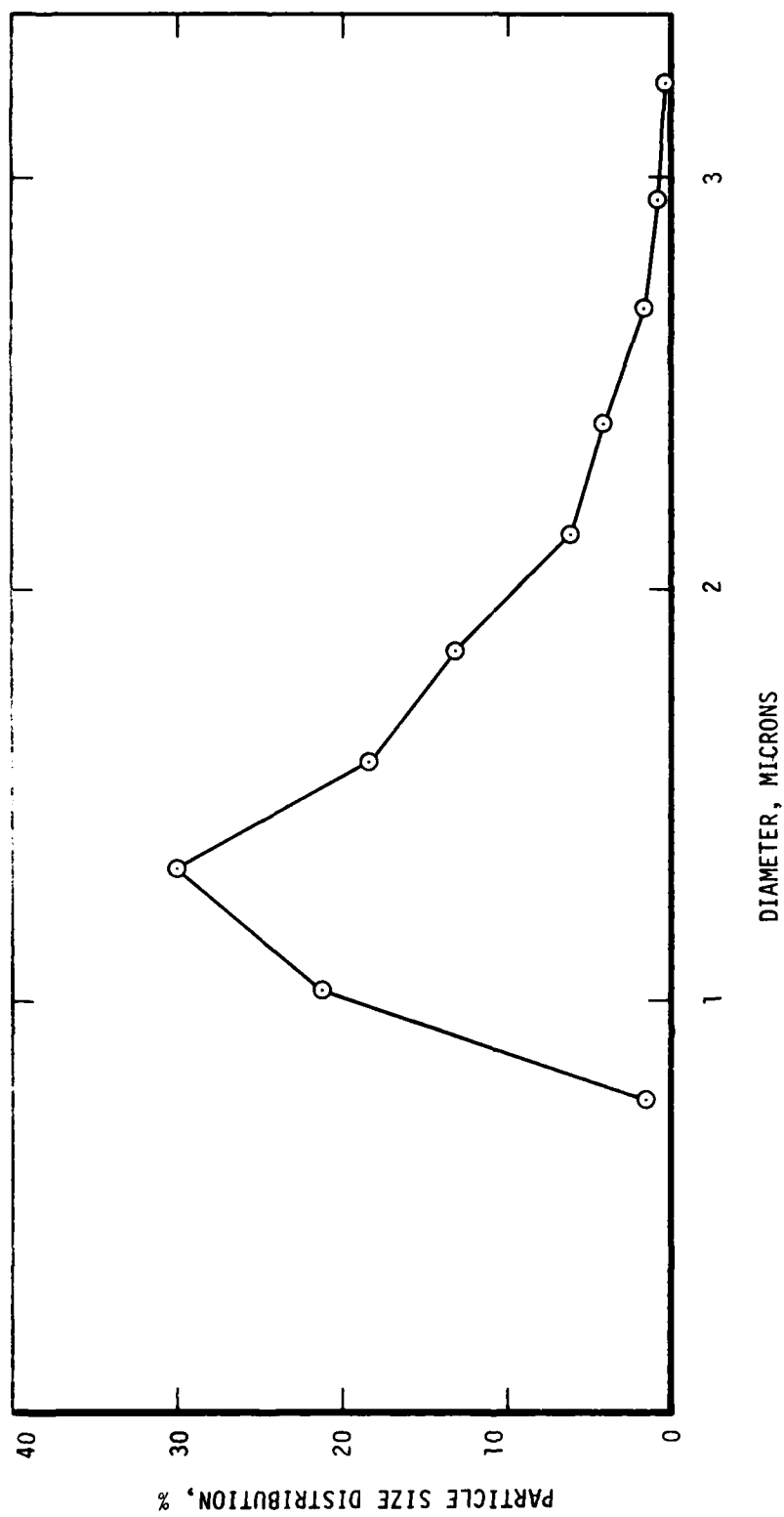


Figure 16. Particle Count Sample 12602 Oxide

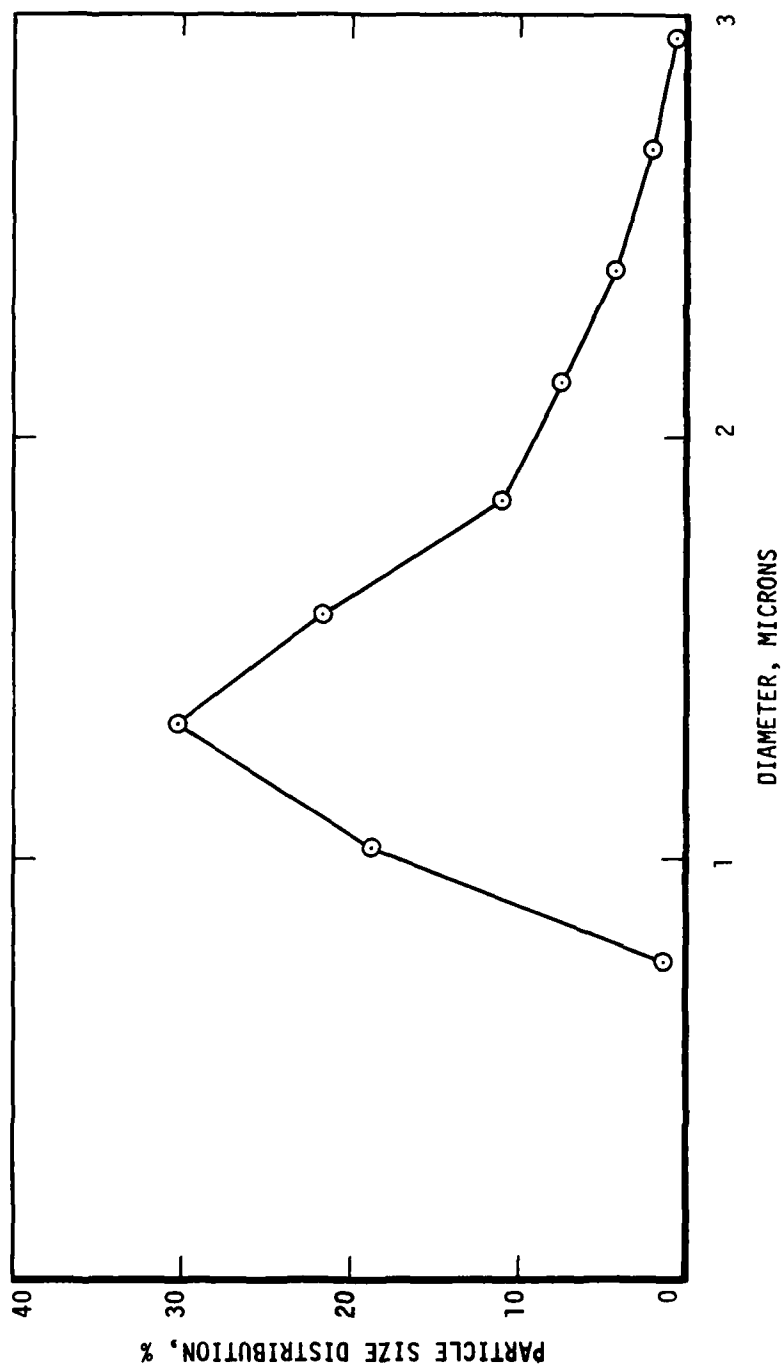


Figure 17. Particle Count Sample 12602 Metal

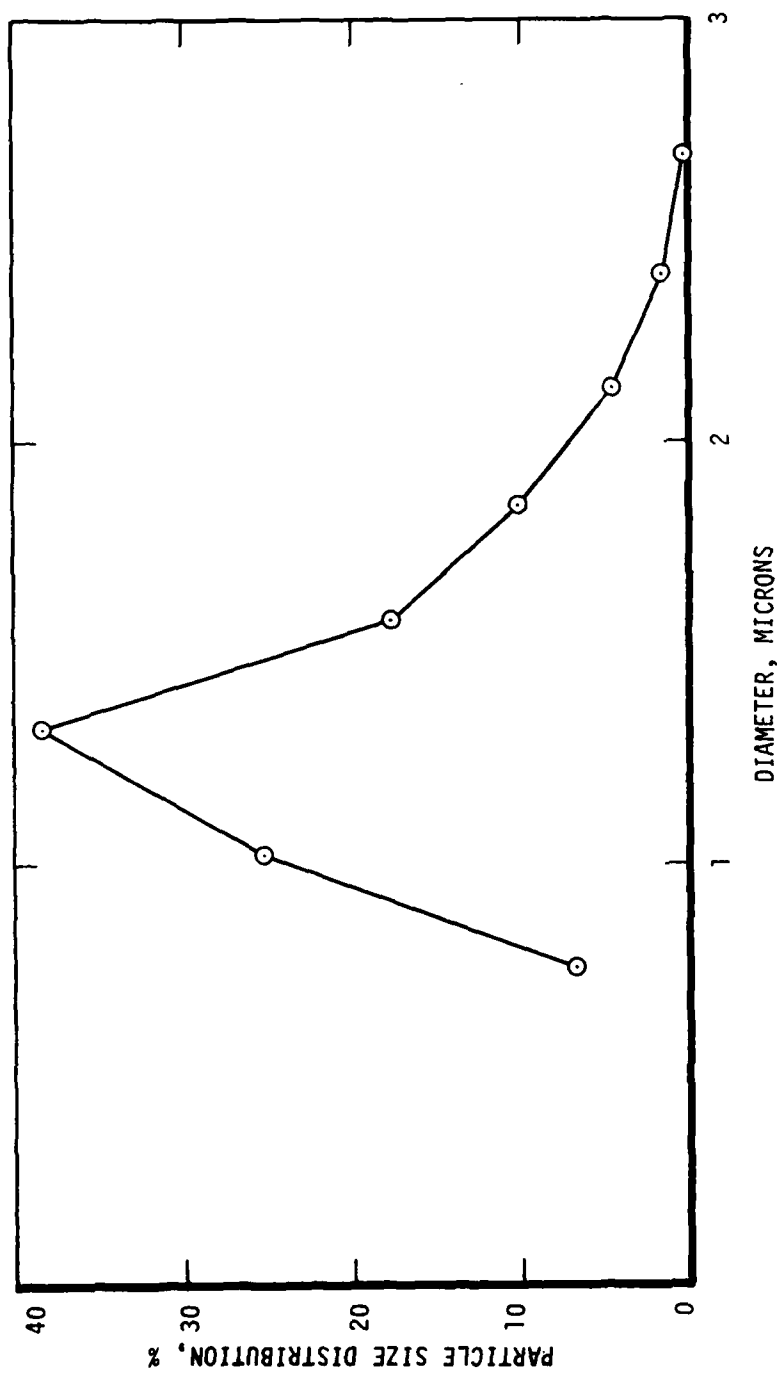


Figure 18. Particle Count Sample 13276 Metal

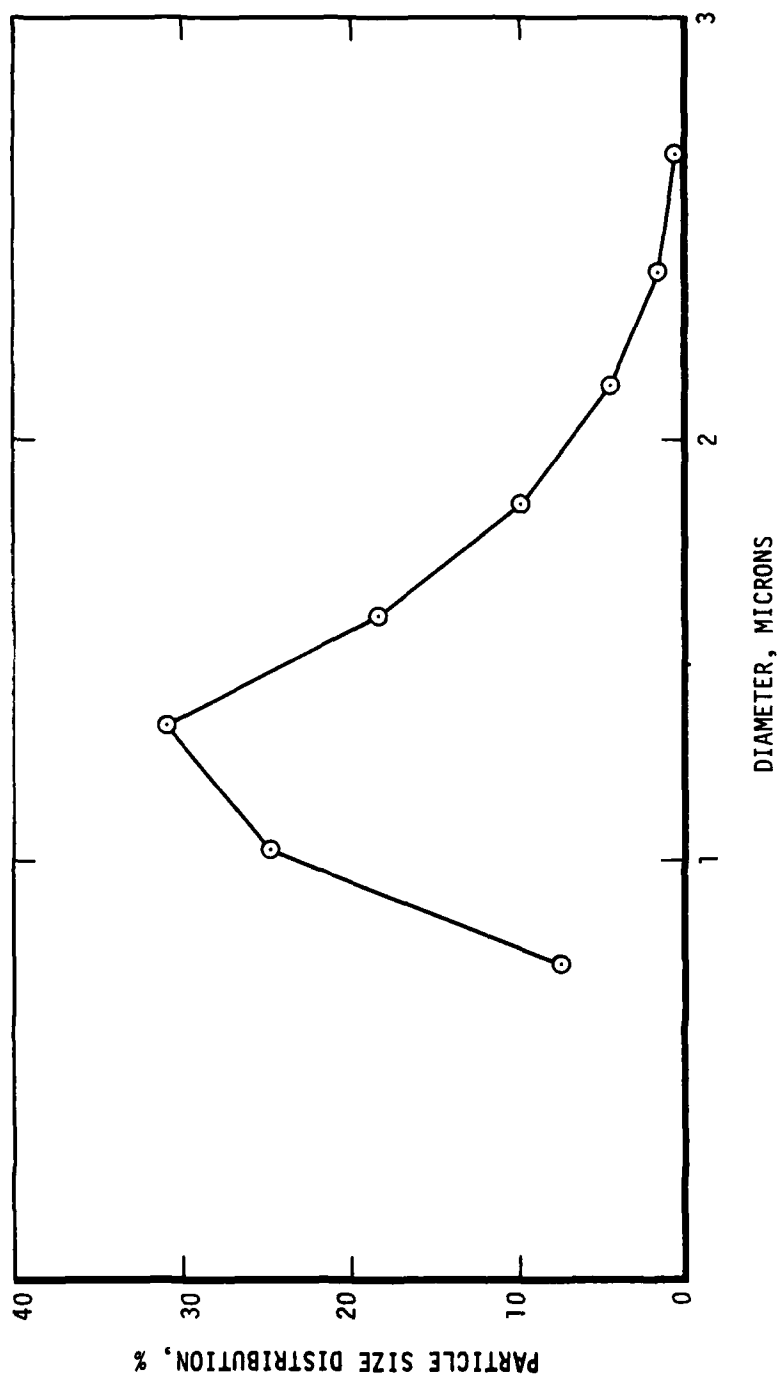


Figure 19. Particle Count Sample 13382 Metal

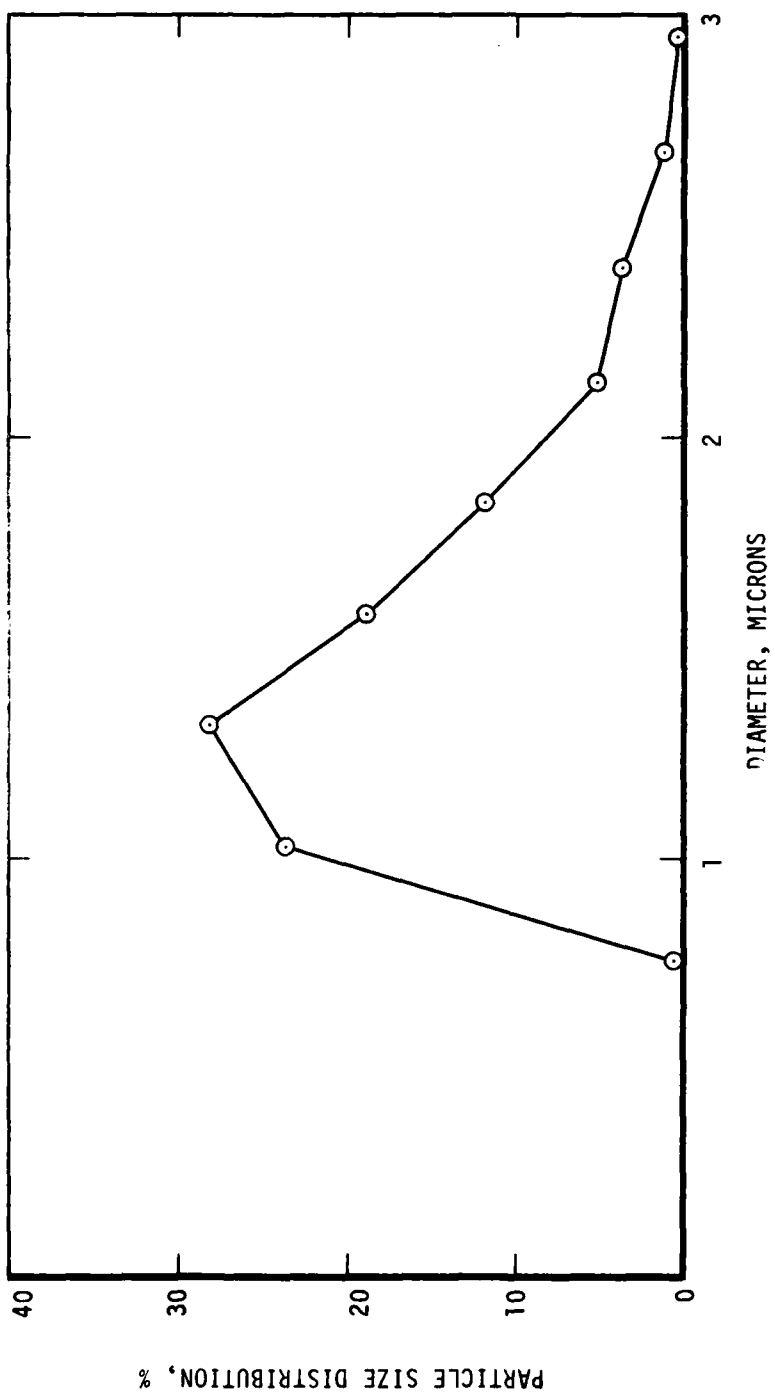


Figure 20. Particle Count Sample 13459 Metal

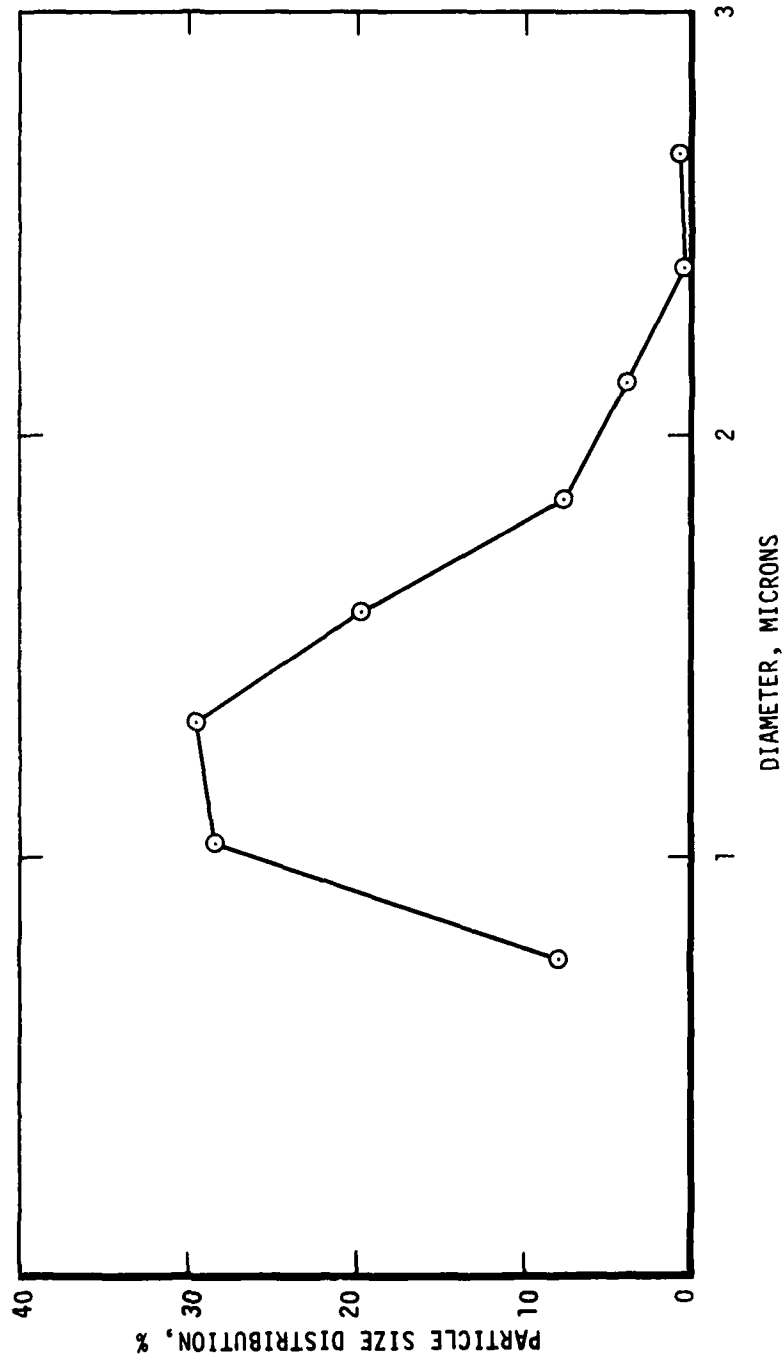


Figure 21. Particle Count Sample 14013 Metal

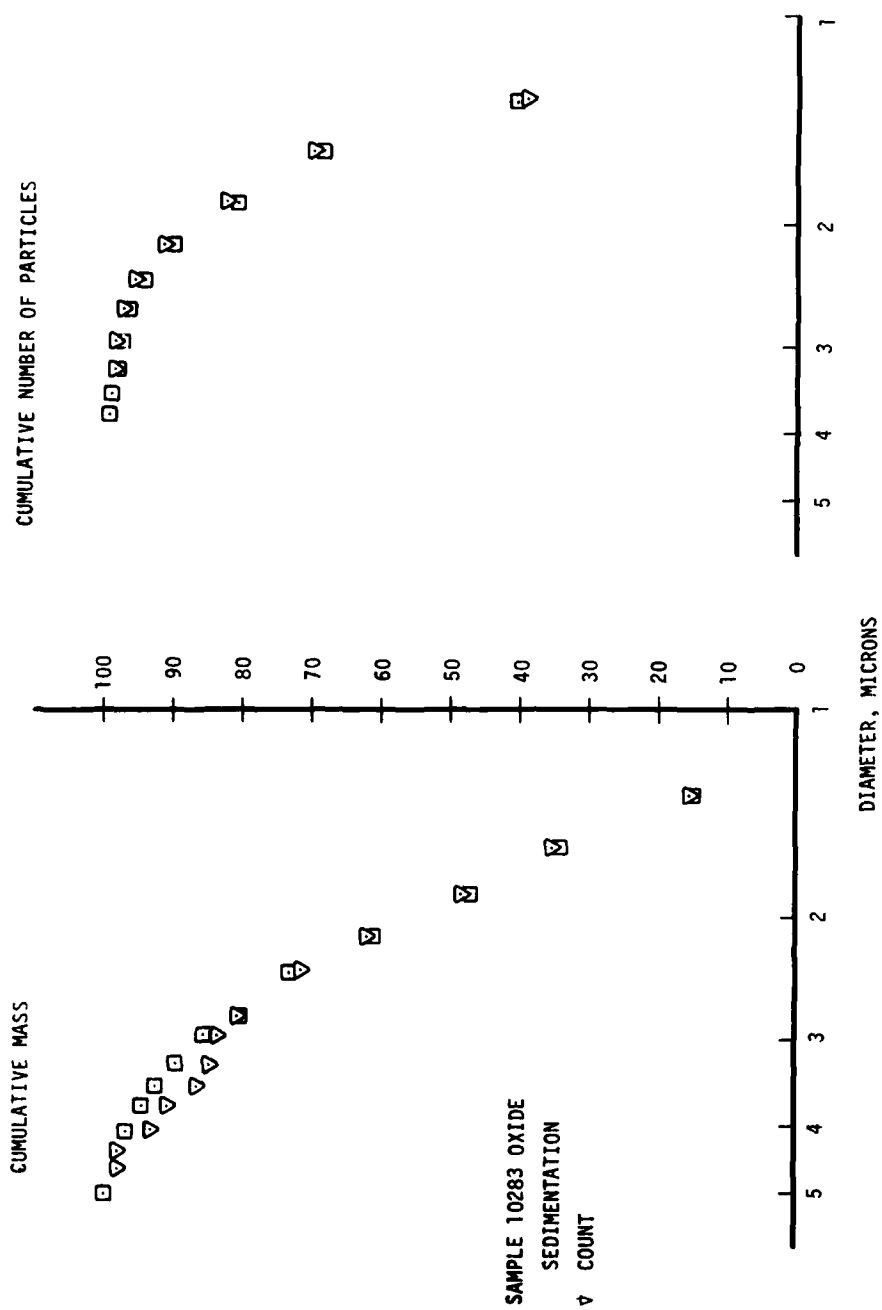


Figure 23

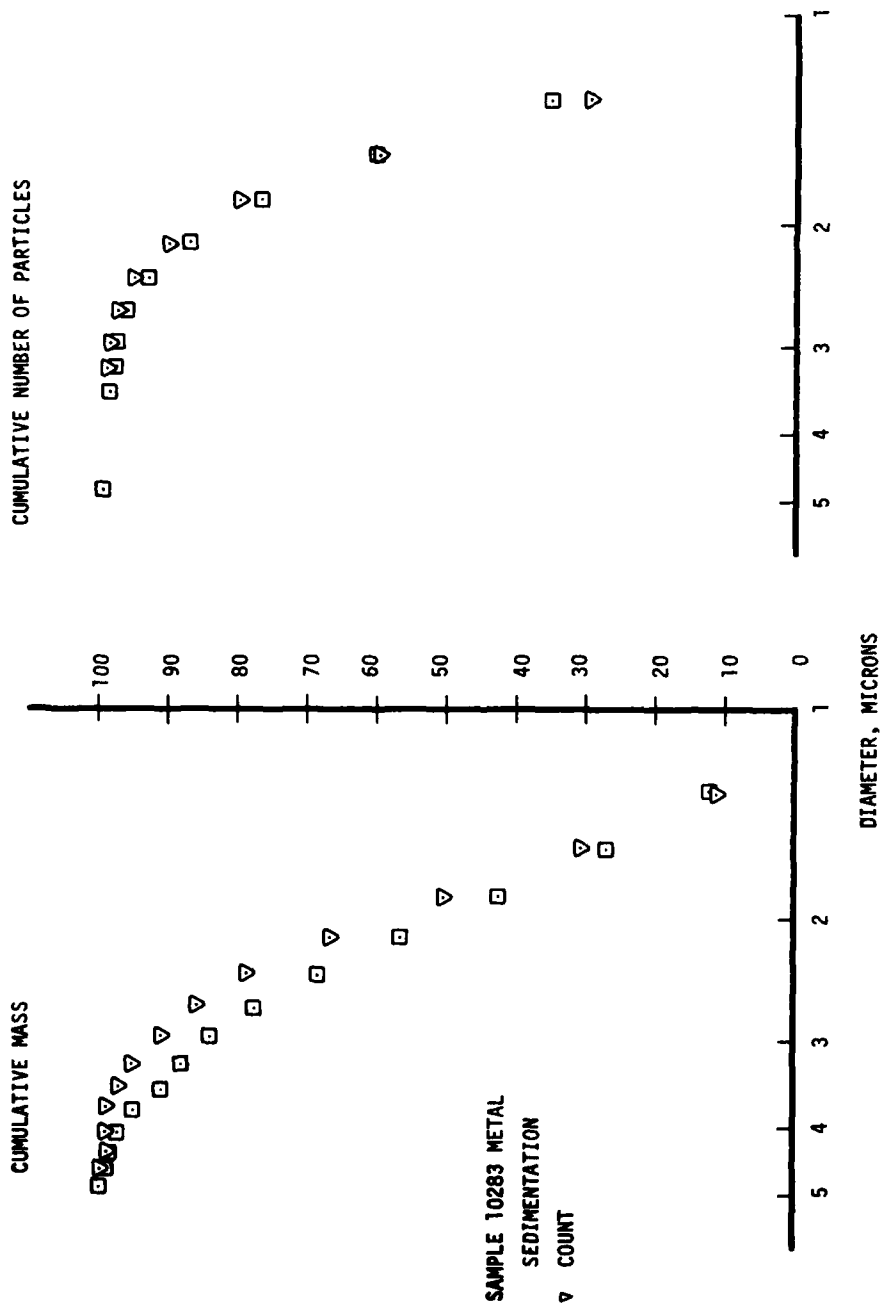


Figure 24

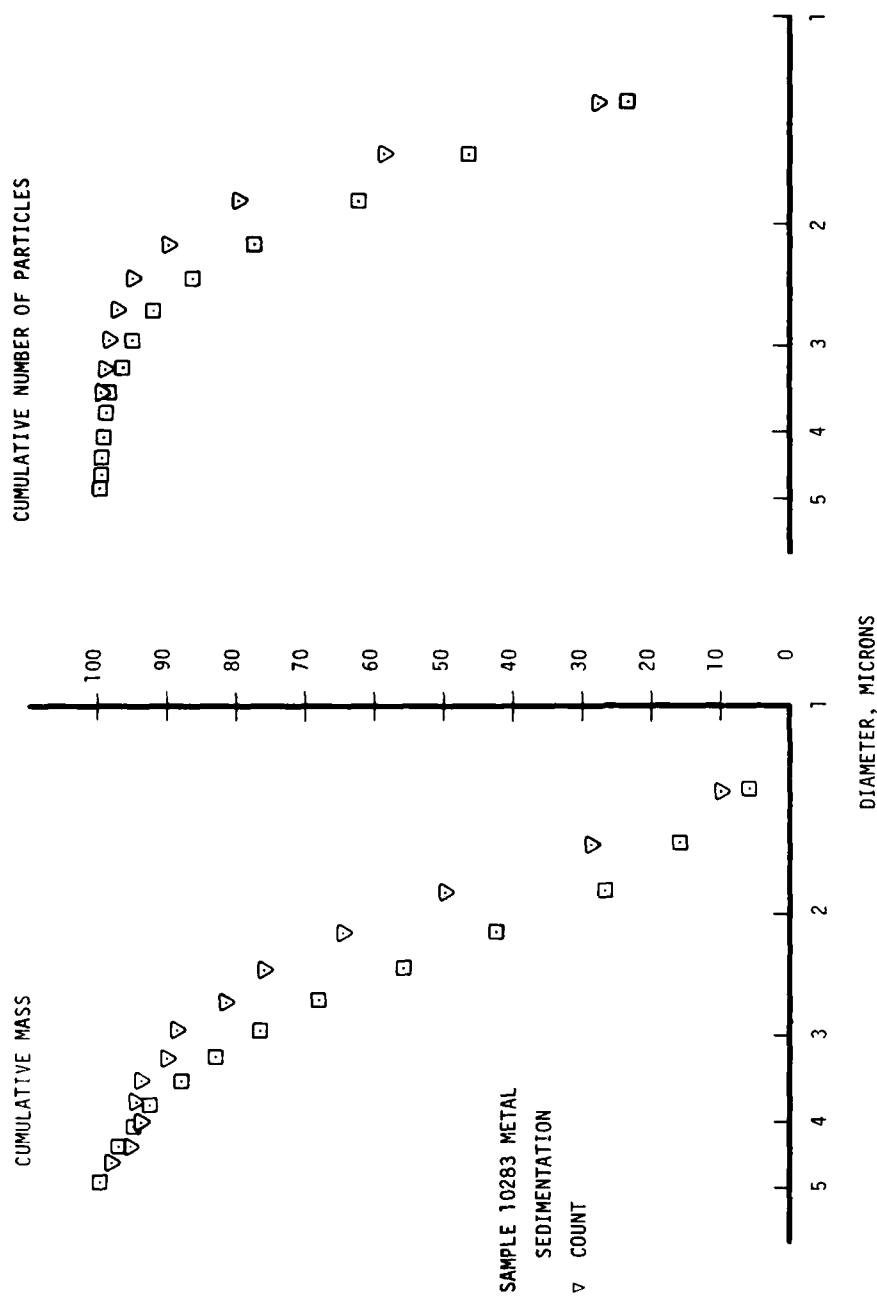


Figure 25

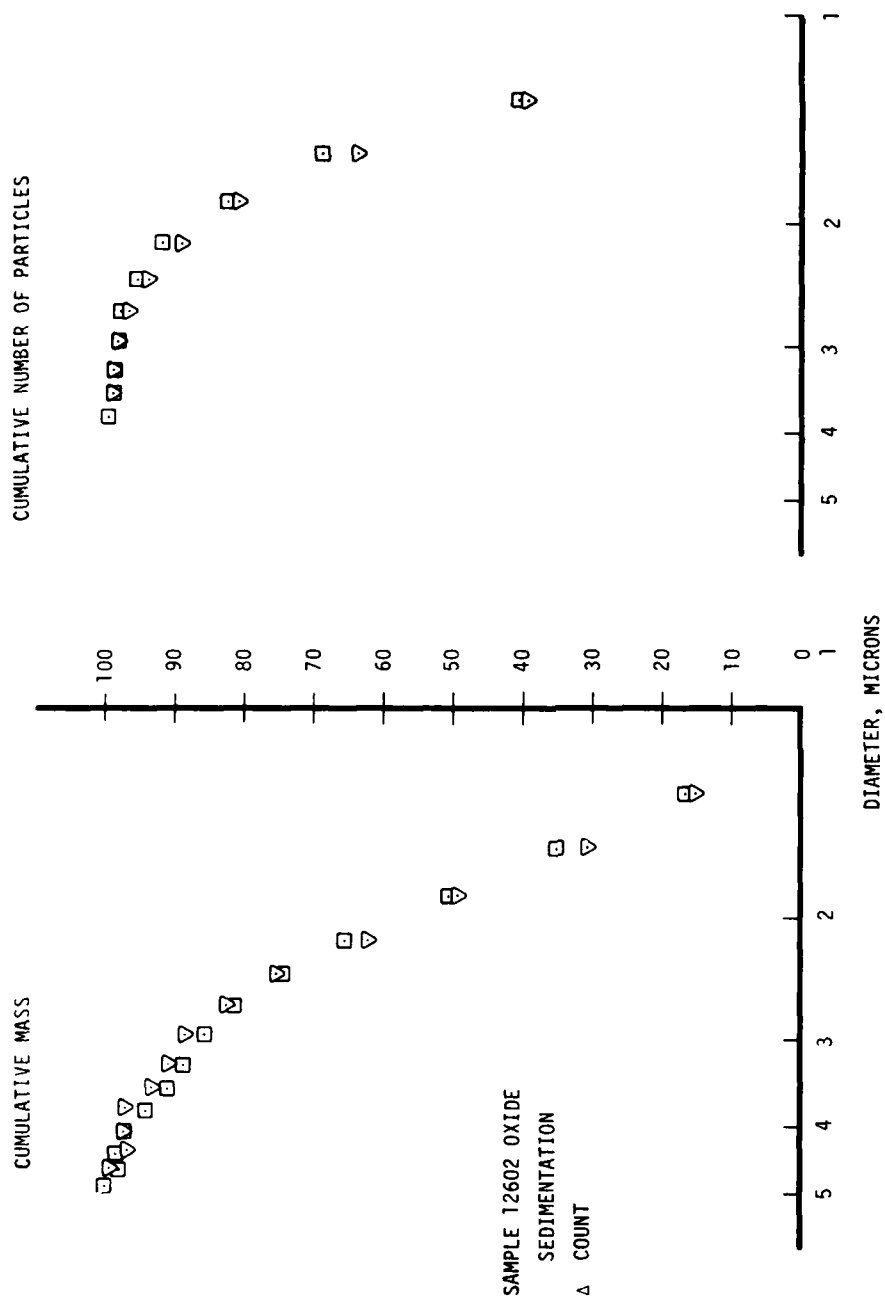


Figure 26

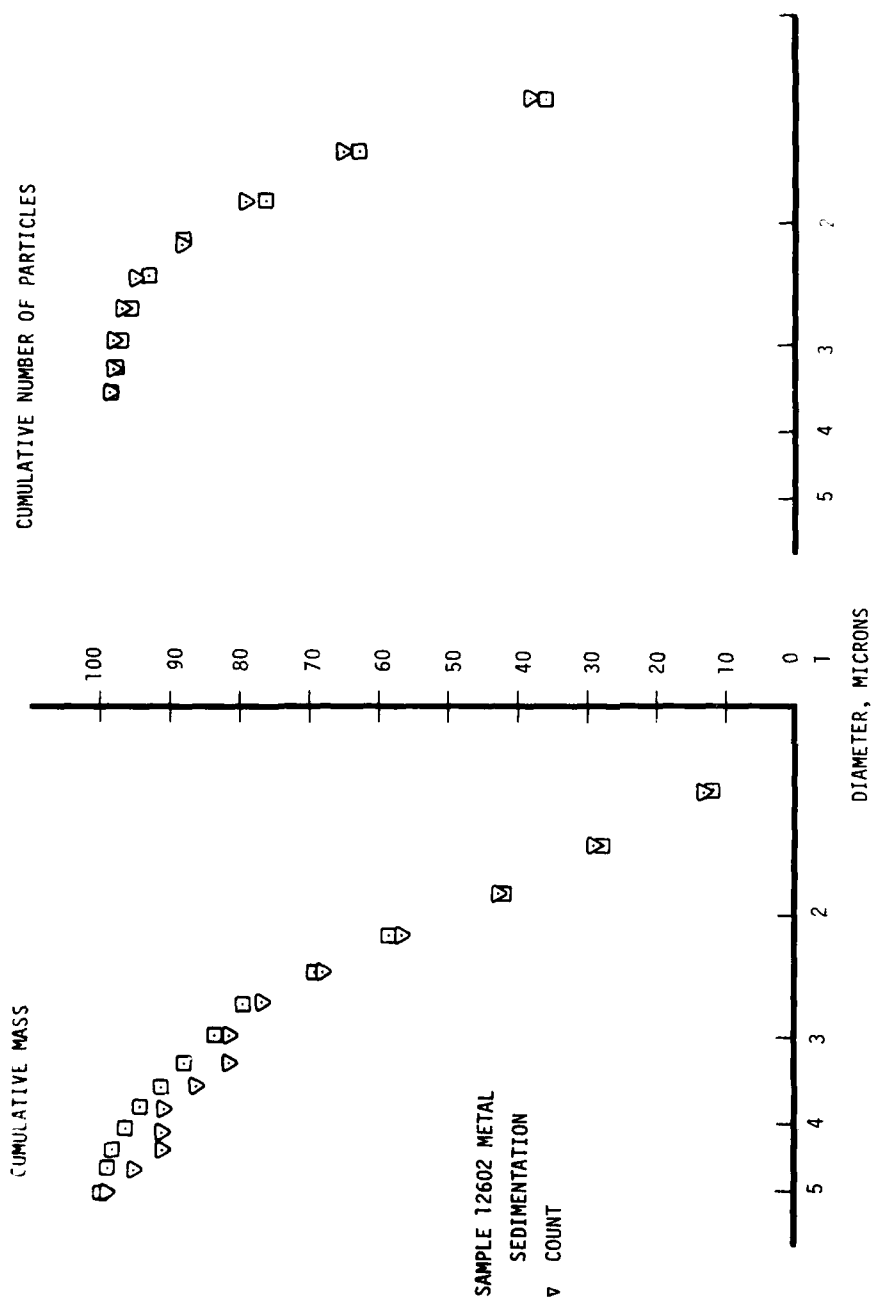


Figure 27

TABLE I
RANGE OF PARTICLE COUNTS IN INITIAL SURVEY

IMAGE	MAGNIFICATION	NUMBER OF PARTICLES PER IMAGE
TEM	5000X	32 to 81
TEM	10400X	11 to 42
SEM	2000X	543 to 829

TABLE II
PARTICLE COUNTS ON SEM IMAGES AT 2000X

LOT #	TOTAL # PARTICLES	# IMAGES
9396 M	1300	2
9396 O	682	1
12602 M	543	1
12602 O	829	1
10283 M	1249	2
102830	1237	2
13276 M	2838	3
13382 M	2723	3
13459 M	1313	4
14013 M	1377	2

APPENDIX B

SURFACE AREA MEASUREMENTS OF ZIRCONIUM OXIDE
AND ZIRCONIUM POWDERS

Capt. L. T. Drzal and Judith A. Mescher

Air Force Materials Laboratory

AFML-TM-MB-76-3

SURFACE AREA MEASUREMENTS OF ZIRCONIUM OXIDE AND
ZIRCONIUM POWDERS

Capt. L. T. Drzal
Judith A. Mescher

March 1976
Project 7350

Approved for public release; distribution unlimited.

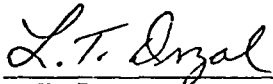
AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.



L. T. Drzal
Project Engineer

FOR THE DIRECTOR



S. W. Tsai, Chief
Mechanics and Surface Interactions Branch
Nonmetallic Materials Division

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

FOREWORD

This report was prepared by the Mechanics and Surface Interactions Branch, Nonmetallic Materials Division under Project 7350, WUD No. 73500142 (administered by R. Geisendorfer).

This report covers work conducted from December 1975 through February 1976. This report was completed by Capt. L. T. Drzal, Mechanics and Surface Interactions Branch and Judith A. Meshcer University of Dayton Research Institute.

This report is reviewed and approved.

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ABSTRACT

This memorandum presents the results of some surface area analysis measurements on low surface area zirconium oxide and zirconium powders being developed by MXE for use in Air Force thermal batteries. The surface area of zirconium reduced from zirconium oxide increases by a factor of six, from one to six square meters per gram. Removal of water by vacuum thermal treatment at 160°C increases the surface area of the zirconium by an additional 0.5 square meters per gram.

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I. INTRODUCTION

The reaction of zirconium powders with suitable oxidants produces an exothermic reaction necessary for the operation of thermal batteries used in Air Force systems. This powder is prepared by reduction of zirconium oxide. Uniformity in operation of these batteries depends upon quality control of the reduction process to produce particles of consistent surface area. A measurement of the surface area of these particles can provide the information necessary to optimize processing parameters. The small surface areas and small batch sizes of these materials however precludes using commercial equipment for these studies. The B.E.T. adsorption apparatus designed for low surface area samples is uniquely suited to this task.

II. EXPERIMENTAL

A. Apparatus

The adsorption measurements needed for this study were taken with a high precision B.E.T. nitrogen adsorption apparatus. The system was of stainless steel construction using bellows valves and an electronic pressure transducer for the pressure measurements providing a clean, oil and grease free, environment. Details of the apparatus and experimental techniques will be described elsewhere (AFML-TR).

B. Sample Preparation

A sample of zirconium oxide, #12602-0VZ-BE-1, and a sample of zirconium powder were obtained from R. Geisendorfer for surface area analysis. The zirconium oxide was dried for 1 hr. at 82°C in an hot air oven and cooled before transfer into a pyrex sample tube and attachment to the adsorption system. The sample was outgassed 1 hr. at 40°C and cooled at liquid nitrogen temperature 2 hrs. before the adsorption run. A minimum of 10 hrs. was necessary to complete the isotherm to saturation.

Due to the pyrophoric nature of the zirconium powder, special precautions were exercised in transferring the powder to the sample tube

for adsorption measurements. First, the water slurry of the zirconium sample plus transfer and weighing equipment were placed in an argon atmosphere glove box. The zirconium slurry sample was then placed in a vacuum desiccator and evacuated overnight to remove all the water. The dried zirconium powder was transferred to the sample tube and weighed by difference in the argon atmosphere. Finally, the sample was immersed in a liquid nitrogen bath until a layer of argon condensed above the zirconium. At this time the sample was removed from the argon atmosphere and immediately attached to the adsorption system while being held at liquid nitrogen temperature. The zirconium was then outgassed 20 hrs. at 40°C and cooled at liquid nitrogen temperature 2 hrs. before the adsorption run.

After these adsorption runs the same zirconium sample was heat treated at 160°C for 1 hr. under vacuum. The temperature was raised gradually while being monitored continuously with a chromel-alumel thermocouple attached to a Leeds and Northrup K-4 potentiometer. Abrupt increases in the volume of desorbing gases were noted at ~105°C and at ~153°C. The sample was allowed to cool to room temperature and then cooled overnight at liquid nitrogen temperature prior to the adsorption run.

III. RESULTS

Nitrogen adsorption isotherms are used to measure surface areas. Nitrogen pressure in the system, with the sample kept at the boiling point of liquid nitrogen, is gradually increased. As the pressure increases more and more molecules of nitrogen adsorb on the sample surface forming a layer one molecule thick. Ideally one monolayer is completed before another is started. A change in slope occurs in the isotherm at this point. A statistical analysis of this data linearizes this portion and allows the value of the monolayer point to be calculated.

Nitrogen adsorption isotherms were obtained on each of the samples described. The results are listed in Table 1 for a representative isotherm on each surface. Plots of this data for zirconium oxide, as

received zirconium and vacuum heat treated zirconium are shown in Figures 1, 2 and 3 respectively. Results are plotted as amount adsorbed in moles per gram versus the nitrogen equilibrium pressure in torr.

Brunauer, Emmett, and Teller developed the B.E.T. analysis of adsorption data which provides a statistical value of the monolayer. This relationship is

$$\frac{P}{V(P_0 - P)} = \frac{C-1P}{V_m C P_0} + \frac{1}{V_m C} \quad (1)$$

where P is the equilibrium pressure in torr, P_0 is the saturation vapor pressure of nitrogen at the adsorption temperature, V is the volume of nitrogen adsorbed per gram of sample at S.T.P., C is a constant for each surface and V_m is the volume adsorbed at the monolayer. A plot of $P/V(P_0 - P)$ versus P/P_0 will give a straight line with $1/V_m C$ as the intercept and $C-1/V_m C$ as the slope allowing the monolayer value V to be determined.

This type of analysis was used to calculate surface areas of these powders. Typical plots are shown in Figure 4. Results of this analysis are shown in Table 2.

IV. DISCUSSION

The isotherms displayed in Figures 1, 2, and 3 show a pronounced decrease in slope of amount adsorbed with pressure around 50 torr. This is approximately the monolayer point. This point occurs at approximately 1×10^{-5} moles per gram for zirconium oxide, 6×10^{-5} for zirconium, and 6.5×10^{-5} for heat treated zirconium. The surface area analysis in Table 2 converts these monolayers points in column 4 to the surface areas in column 3 according to the relationship

$$\Sigma = n_m \sigma N$$

where σ is the molecular area of adsorbed nitrogen at 77°K (0.162 nm^2) and N is Avagadro's number.

Reduction of zirconium oxide increases the surface area by a factor of six. Vacuum heat treatment at 160°C removes all physically adsorbed water yet is low enough to avoid sintering the particles. The additional increase in surface area to 6.5 m²/gm is most probably due to opening of pores, cracks, etc. blocked by adsorbed water. Adsorption-desorption measurements can confirm this. Finally it must be noted that even with these small samples (~3 grams) the surface area values are reproducible to ±3% and make the changes in surface areas significant.

V. CONCLUSIONS AND FUTURE WORK

Reduction of zirconium oxide results in a six and one-half times increase in surface area for zirconium. Approximately 7% of this area is composed of areas inaccessible to nitrogen due to blockage by adsorbed water.

The surface area technique used here is applicable for low area zirconium powders.

Future work will be directed at determining the effect of processing parameter on zirconium surface area and adsorption-desorption measurements directed at estimating pore size and pore size distribution of the powders.

TABLE 1

RESULTS OF ISOTHERM DATA FOR ZIRCONIUM OXIDE AND
ZIRCONIUM POWDER BEFORE AND AFTER HEAT TREATMENTRESULTS OF ADSORPTION RUN NO. 3-41
N2 /ZIRCONIUM OXIDE

TEMP(K) = 77.12

PASS	N(ADS)/W	(P2)*(TT)	P1	P2	TT	TR	TC
1	.6539E-05	.74258E+01	.355E+02	.743E+01	1.000	77.12	313.33
2	.8669E-05	.41026E+02	.752E+02	.410E+02	1.000	77.12	313.29
3	.1013E-04	.87237E+02	.130E+03	.872E+02	1.000	77.12	313.29
4	.1175E-04	.14591E+03	.199E+03	.146E+03	1.000	77.12	313.32
5	.1400E-04	.22704E+03	.301E+03	.227E+03	1.000	77.12	313.30
6	.1745E-04	.34257E+03	.450E+03	.343E+03	1.000	77.12	313.30

RESULTS OF ADSORPTION RUN NO. 3-62
N2 /ZIRCONIUM/AS PEG'D

TEMP(K) = 77.22

PASS	N(ADS)/W	(P2)*(TT)	P1	P2	TT	TR	TC
1	.3108E-04	.35145E+01	.756E+02	.351E+01	1.000	77.26	313.25
2	.4851E-04	.29709E+02	.902E+02	.297E+02	1.000	77.25	313.24
3	.5731E-04	.63572E+02	.111E+03	.636E+02	1.000	77.23	313.28
4	.6290E-04	.92894E+02	.130E+03	.929E+02	1.000	77.23	313.24
5	.6794E-04	.12304E+03	.160E+03	.123E+03	1.000	77.21	313.28
6	.7324E-04	.15737E+03	.200E+03	.158E+03	1.000	77.20	313.25
7	.7930E-04	.19895E+03	.248E+03	.199E+03	1.000	77.19	313.26
8	.8755E-04	.25469E+03	.321E+03	.255E+03	1.000	77.19	313.23
9	.9748E-04	.31848E+03	.396E+03	.318E+03	1.000	77.18	313.25

RESULTS OF ADSORPTION RUN NO. 3-89
N2 /ZIRCONIUM/160C VHT

TEMP(K) = 77.19

PASS	N(ADS)/W	(P2)*(TT)	P1	P2	TT	TR	TC
1	.4219E-04	.34587E+01	.100E+03	.346E+01	1.000	77.21	313.29
2	.6178E-04	.40204E+02	.114E+03	.402E+02	1.000	77.19	313.25
3	.7020E-04	.79279E+02	.130E+03	.793E+02	1.000	77.19	313.23
4	.7570E-04	.11155E+03	.151E+03	.112E+03	1.000	77.19	313.14
5	.7997E-04	.13916E+03	.172E+03	.139E+03	1.000	77.19	313.22
6	.8362E-04	.16413E+03	.194E+03	.164E+03	1.000	77.19	313.24
7	.8724E-04	.18925E+03	.219E+03	.189E+03	1.000	77.19	313.26
8	.9117E-04	.21662E+03	.249E+03	.217E+03	1.000	77.19	313.25
9	.9570E-04	.24964E+03	.287E+03	.249E+03	1.000	77.19	313.23
10	.1017E-03	.28949E+03	.339E+03	.289E+03	1.000	77.19	313.22
11	.1092E-03	.33799E+03	.397E+03	.338E+03	1.000	77.19	313.20

TABLE 2

B. E. T. SURFACE AREA ANALYSIS OF ZIRCONIUM
OXIDE AND ZIRCONIUM POWDERS

Adsorbent	Temp °K	C	$\Sigma \frac{m^2}{gm}$	$n_m \frac{\text{moles}}{gm} \times 10^{-5}$
Zirconium Oxide	77.35	115.6	1.05	1.07
Zirconium Oxide	77.12	56.6	0.99	1.01
Zirconium, as rec'd	77.27	87.4	6.04	6.19
Zirconium, as rec'd	77.22	70.4	5.89	6.04
Zirconium, 160C VHT	77.19	205.5	6.42	6.58

ADSORPTION ISOTHERM NO. 3-41
N₂ /ZIRCONIUM OXIDE
AVERAGE TEMP = 77.120 °K

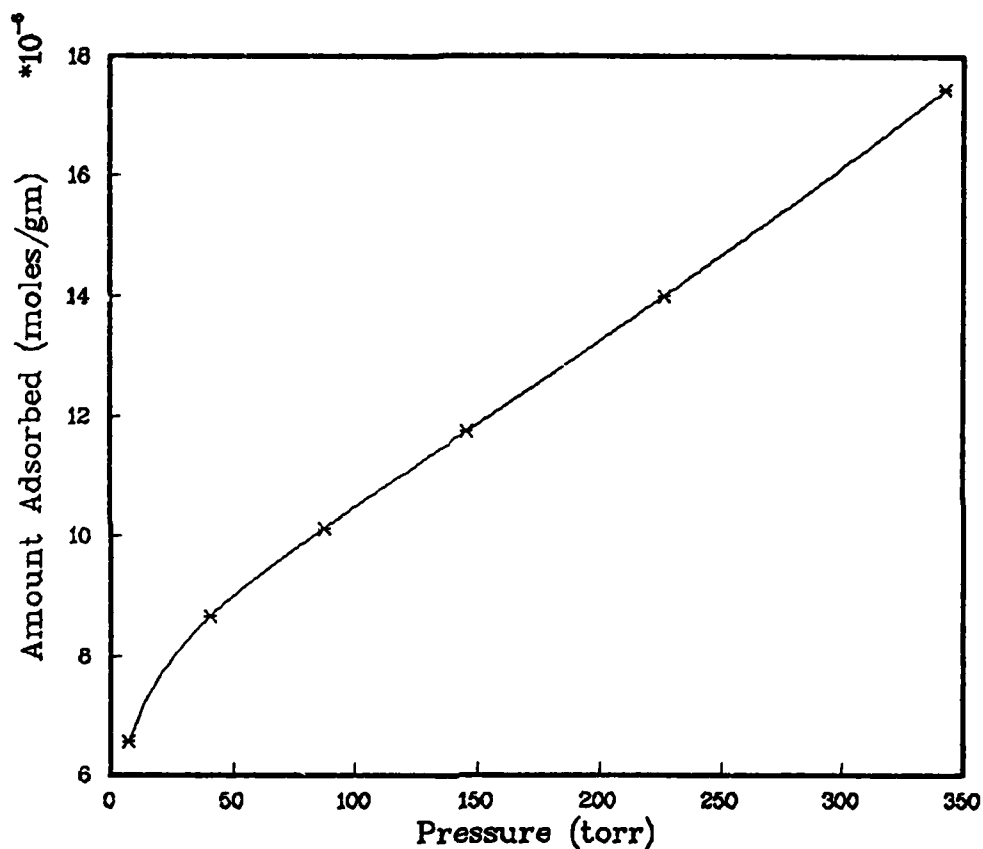


Figure 1. Isotherm for the Adsorption of Nitrogen on Zirconium Oxide

ADSORPTION ISOTHERM NO. 3-62
N₂ /ZIRCONIUM/AS REC'D
AVERAGE TEMP = 77.220 °K

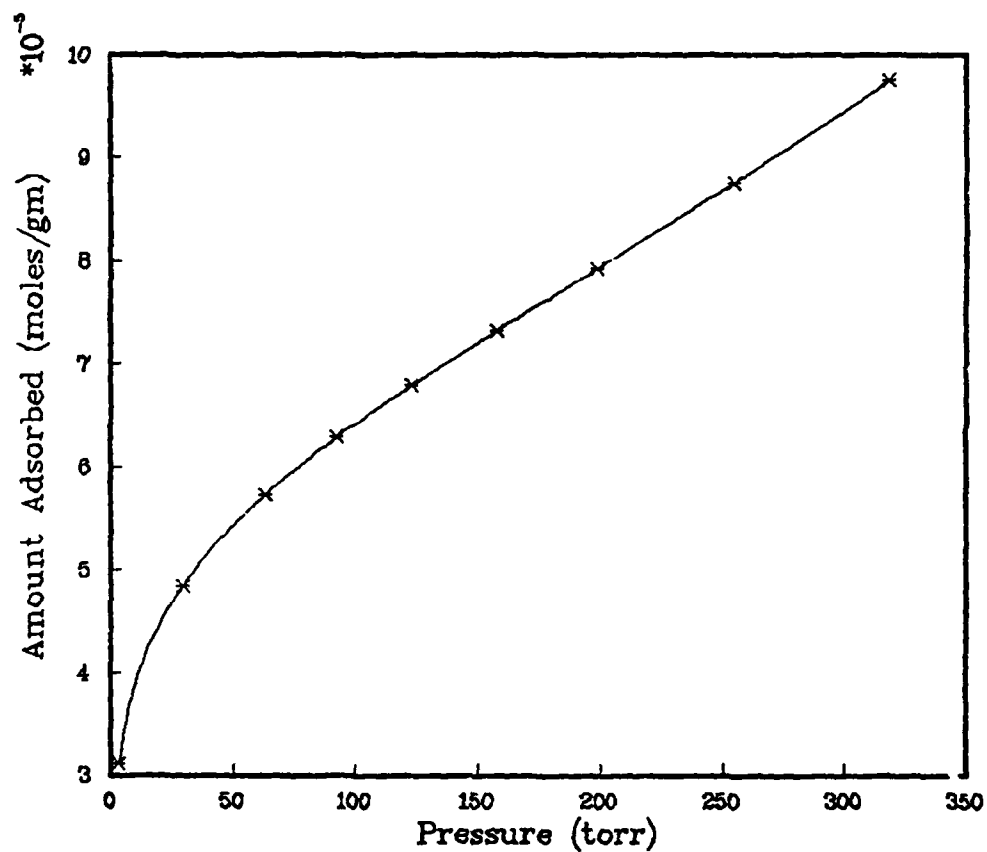


Figure 2. Isotherm for the Adsorption of Nitrogen on Zirconium Powder

ADSORPTION ISOTHERM NO. 3-89
N₂ /ZIRCONIUM/160C VHT
AVERAGE TEMP = 77.190 °K

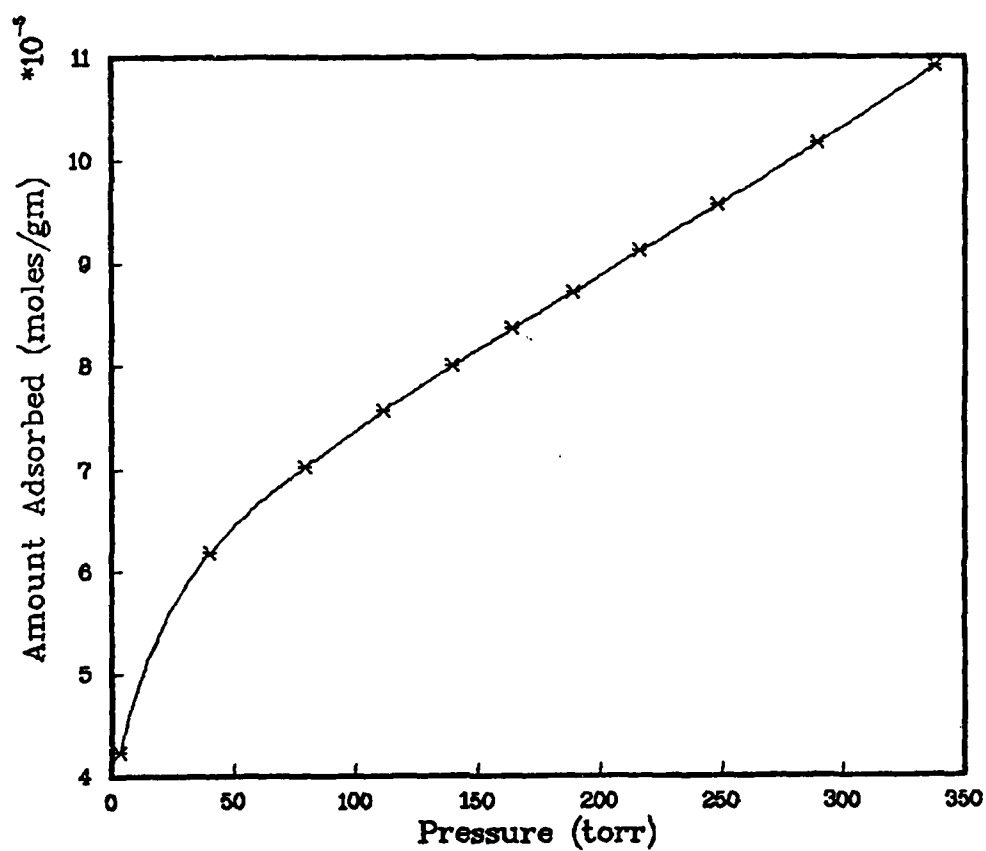


Figure 3. Isotherm for the Adsorption of Nitrogen on Heat Treated Zirconium Powder

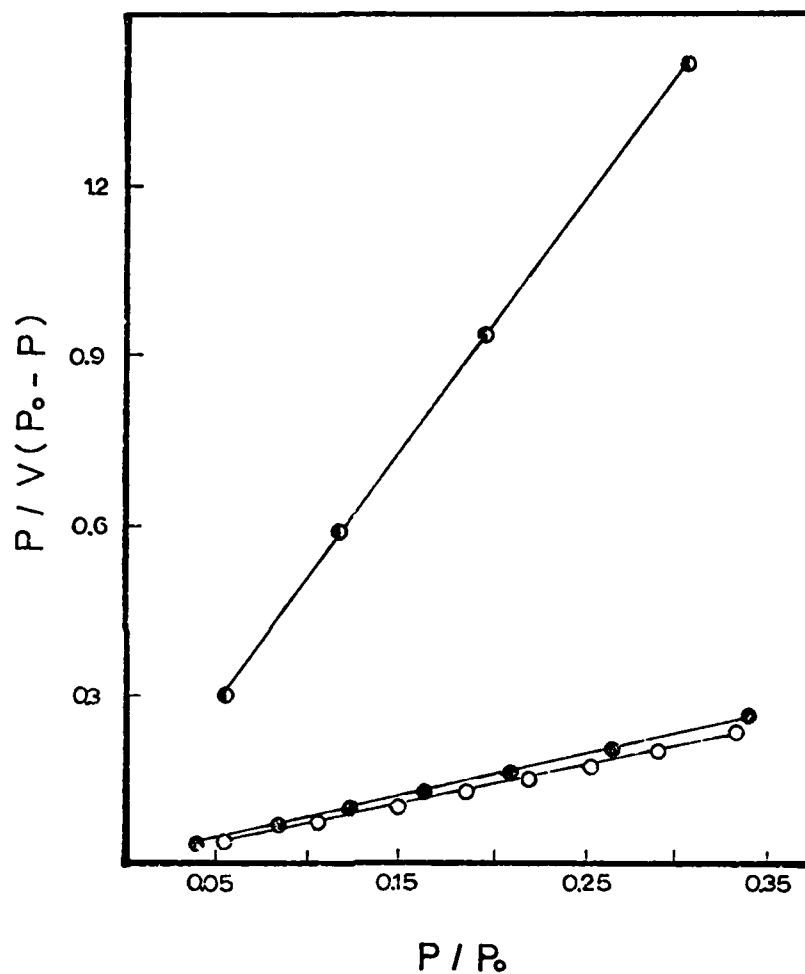


Figure 4. Adsorption of Nitrogen on Several Adsorbents at 77°K, Plotted According to the B.E.T. Equation; Symbols: ● Zirconium Oxide, ● zirconium as Rec'd, ○ Zirconium after Heat Treatment

APPENDIX C

SAFETY INSPECTION AND SAFETY GUIDANCE CONCERNING
LABORATORY SCALE PRODUCTION OF SMALL QUANTITIES
OF ZIRCONIUM POWDER

C. P. Mueller

Universal Technology Corporation

SAFETY INSPECTION AND SAFETY GUIDANCE
CONCERNING LABORATORY SCALE PRODUCTION
OF SMALL QUANTITIES OF ZIRCONIUM POWDER

Request No. ML-116
Contract F33615-74-C-5043
Research Project No. M-357-116

C. P. Mueller

UNIVERSAL TECHNOLOGY CORPORATION
1656 Mardon Drive
Dayton, OH 45432

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I. INTRODUCTION

The Air Force is having a considerable amount of difficulty with reproducibility of the properties of thermal batteries. After a considerable amount of analysis, it was determined that one of the major problems was the zirconium powder used in the manufacture of these thermal batteries.

To attempt to resolve this problem, the Air Force Materials Laboratory is pursuing several courses of action. One of these approaches is to set up a small laboratory scale production unit to produce small batches of zirconium metal powder. This type of facility will permit a systematic evaluation of processing variables for isolating the important parameters required to produce the desired powder characteristics.

One of the concerns about handling zirconium powder is the safety factor. Fine zirconium powder is a very dangerous material to handle because of its pyrophoric nature under a wide variety of circumstances.

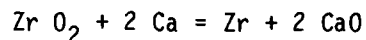
This consultation will address the question of safety as it relates to the manufacture and handling of zirconium powder.

II. MANUFACTURING PROCESS

There are many approaches to preparing zirconium powder including direct reduction of the oxide or tetrachloride, hydride-dehydride and simple attrition. All of these processes contain inherent dangers related to possible fires and explosions. For this reason, a description of the manufacturing process to be employed is necessary prior to establishing preventive measures.

The flow sheet shown in Figure 1 is essentially the process to be employed in the Air Force Materials Laboratory approach to producing zirconium powder. In this technique, the particle size of the starting oxide material is selected based upon past experience, which results in the resultant final powder particle with the desired characteristics. The powder source for thermal batteries has already been established and these experiments will only be directed toward controlling the processing parameters.

After the starting material is selected, the next question is the selection of the desired reductant which can be either magnesium, sodium or calcium, depending upon the desired results and the economic factors. For purposes of this presentation, it is assumed that calcium will be used as the reductant which results in a highly exothermic reaction, as follows



which has a free energy of -45 Kcal. The reaction will not occur spontaneously, but only upon heating of the powder to a suitable reaction temperature. The temperature at which the reaction takes place determines to a great extent the particle size of the resultant material.

Likewise, the amount of calcium chloride added to the reaction mix will help to control the final particle size. The greater the quantity of calcium chloride the finer the particle size of the zirconium powder. Also, the greater the quantity of calcium chloride, the less the reaction

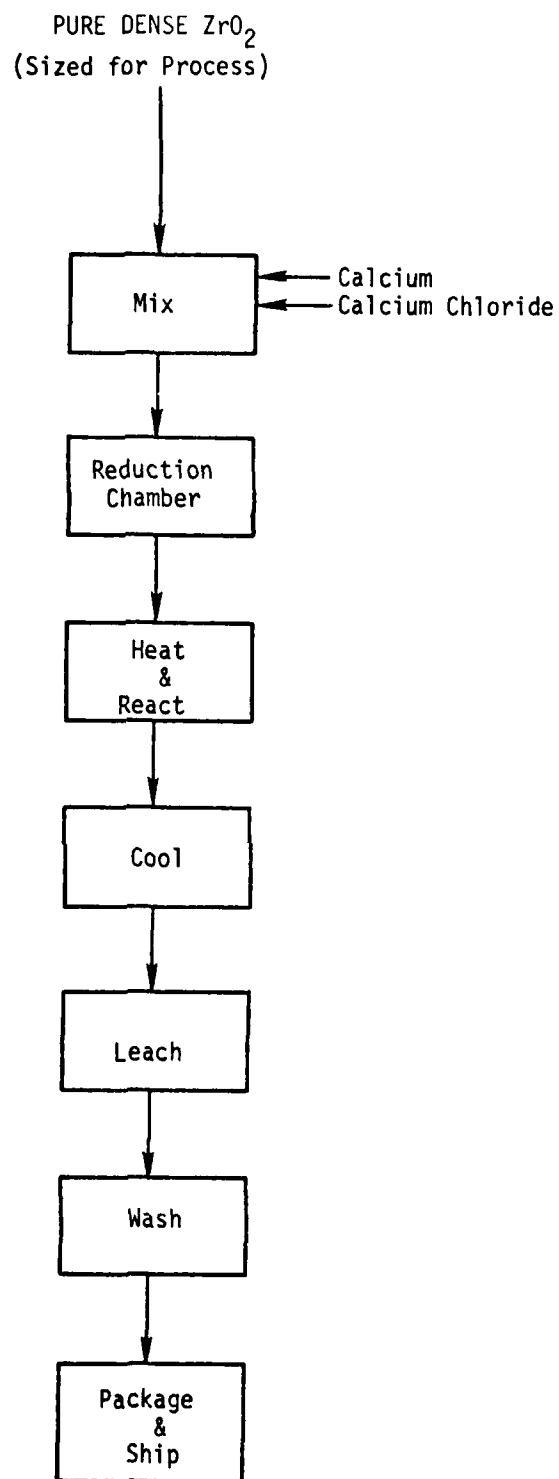


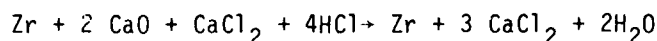
Figure 1. Flow Sheet for the Calcium Reduction of Zirconium Oxide

with the walls of the reaction chamber. In addition to the amounts of calcium and calcium chloride, and their particle size, the thoroughness of mixing and the temperature of reduction will have a significant effect on the resultant zirconium powder particle size.

One very important factor to consider is the fact that the reduction process and all subsequent handling must be undertaken under controlled atmospheric conditions. Zirconium powder will react vigorously with carbon, oxygen, nitrogen and carbon monoxide, depending upon temperature and concentration. For that reason, it is important that a full understanding of the status of the powder is known at all times so that the proper environmental controls can be employed.

Normally, it is satisfactory to protect the powder in an atmosphere of helium or argon. However, it must be remembered that if there are impurities in these gases they will be absorbed by the surface of dry zirconium at ambient temperatures and dissolved by the bulk zirconium at elevated temperatures. The environment in which the reaction takes place is usually high purity argon and helium.

After the reaction has taken place, it is next necessary to cool the resultant product to ambient temperature and then leach out the unwanted calcium chloride and calcium oxide. This is usually accomplished in a dilute solution of hydrochloric acid following the reaction shown below:



Thus, the calcium chloride carried along in the reaction is eliminated at this stage of manufacture. The leached material is then washed with high purity water and is ready for packaging and shipment.

This is obviously not the only approach to the manufacture of zirconium powder, but it does represent a close approximation to the method to be employed by the Air Force Materials Laboratory. It therefore serves as a model for treating the safety aspects of this problem.

III. HAZARDOUS PROPERTIES OF ZIRCONIUM

Zirconium in bulk or massive forms such as ingots, billets, bar and sheet can be handled in air for forging, rolling or other metal working operations at elevated temperature of 1200 C or lower. However, as the surface area increases the danger of ignition of the material increases and caution must be exercised.

Metallic zirconium wires and strips are used in pyrotechnic devices. Some flash bulbs use zirconium strips (slit from strip) as the light emitter because of zirconium's high burning rate. This high rate of combustion of zirconium is especially dangerous when the material is available in the form of chips or turnings. Dry chips or turnings are more difficult to ignite and burn less rapidly than those that are partially wet. Loosely piled, partially wet chips are very susceptible to ignition by a spark, static electricity or other sources of high temperature.

In the early years of zirconium production several people were killed as a result of a spontaneous explosion of a drum containing partially wet, fine zirconium scrap. Sludges from grinding operations can, and have, resulted in spontaneous explosions of unknown origin. The after effects of these explosions and fires usually indicate inadequate knowledge of the cause of the incidents, but do attest to the dangerous nature of finely divided zirconium and draw attention to the need for exerting extreme caution.

Even though wet zirconium chips and turnings are very dangerous and susceptible to spontaneous combustion, it is virtually impossible to sustain combustion of chips and turnings under water. No known example of explosions or self ignition have occurred when stored under water. However, it is not a good practice to accumulate large quantities of wet chips and turnings. Evaporation, as well as leakage of the water can occur and result in highly dangerous, partially wet chips which can start a chain reaction in otherwise water protected surrounding containers.

The self-sustaining combustion of zirconium in air is unattainable at ambient temperatures if the minimum thickness of the zirconium exceeds a value of 1/8 inch. Thus pieces less than 1/8 inch thickness present no known problems.

The combustion characteristics of powder are even more critical than chips or turnings. Zirconium powder and dust ignitions have occurred as low as 151 C and samples of -325 wet powder have ignited at 210 C. A far more serious type of explosion was produced at the Bureau of Mines when a very fine powder was dispersed as a cloud and ignition occurred at room temperature with no apparent source of ignition. Combustion of damp zirconium powder in air should be expected to occur while powder containing sixteen (16) percent moisture is known to have exploded spontaneously while under vacuum.

Undisturbed layers of zirconium powder will also burn vigorously in the absence of air but in the presence of either nitrogen or carbon dioxide. The only known safe atmospheres to handle the powder are dry argon or helium. Powder can also be stored under water, but if ignited under these conditions can continue to burn so that caution must be exercised.

As indicated above, the major concern about fire and explosions when handling zirconium is when the metal is in a finely divided form and is exposed to rapid oxidation, static electricity, sparks from other sources or temperatures above the ignition temperature. Fires have been witnessed that were caused by shearing of square wire and bars. These fires are most dangerous when they occur near machining or drilling operations where an accumulation of partially wet turnings, drilling chips or scrap were present.

Powder is much more of a problem as related to fires, explosions or spontaneous combustion than solid zirconium. The following examples will give some idea of the hazards involved:

a) Zirconium powder of 3.3 micron size ignited spontaneously when blown into the air at 20 C.

b) Zirconium powder of 17.9 micron size did not ignite under similar conditions until heated to 350 C.

c) Zirconium powder of 3.3 micron size did not ignite in carbon dioxide under similar conditions until heated to 650 C.

In atmospheres of helium it was necessary to have at least 5% oxygen present to obtain spark ignition of dust clouds. Numerous instances of explosives and spontaneous ignition of zirconium powder have been reported in the literature. An attempt will be made in the following pages to set forth the means by which such occurrences can be minimized or eliminated.

IV. PREVENTION AND PROTECTION FROM HAZARDS

The most obvious control that can be exercised in the manufacture or handling of zirconium powder is to exercise caution and develop good work habits. The preventing of an accumulation of fine dust or powder is probably the best habit to develop. Routine cleaning of equipment at both the point of dust or powder generation as well as places where it has the opportunity to accumulate must be accomplished.

No storage of other combustibles, such as cardboard boxes, stacks of paper, oils, grease or other material not required in the process, should be stored in close proximity to the zirconium powder manufacturing or storage facility.

All equipment should be routinely inspected to insure safe operating conditions and to prevent breakdowns. All equipment used in the manufacture should be adequately grounded to a common ground to minimize generation of sparks. This includes all equipment used to handle a transfer of zirconium powder. Bearings or all equipment should be sealed so as to prevent accumulation of fine powder and should be periodically checked to determine if they are overheating. Electrical apparatus should be monitored and checked by a competent technician on at least a weekly basis.

All manufacturing operations must be conducted under controlled conditions to prevent dust dispersion. Only small quantities should be handled at one time. In the case of the present manufacturing arrangement the use of inert atmospheres and the quantities of 5 to 10 gm should minimize the problem. Before any powder is removed from the controlled inert environment, it should be completely immersed in an excess of water. There are very real problems associated with rapid oxidation of powder after it has been held in an inert atmosphere and then exposed to air. This is probably the most serious and dangerous step involved in handling zirconium powder and should only be done with small quantities of powder and with personnel protected.

The equipment to be used by the Air Force Materials Laboratory can be adapted to perform the required zirconium powder manufacturing evaluations. However, there are many precautions that should be taken.

a) The walls and floor of the immediate work area should be sealed so as to prevent powder accumulation in cracks and crevices. Even though all work is to be done in controlled atmosphere glove boxes, this precaution will minimize problems.

b) Grounding of all equipment and machinery must be accomplished.

c) All crevices and corners in glove boxes should be minimized and/or periodically cleaned so as to minimize dust accumulation. This cleaning should be done at least weekly.

d) Sand buckets should be available and filled to be used in the event of a fire. As discussed during my visit, it might be advisable to place the glove boxes on sand trays on the benches to prevent burning of the wooden bench top.

e) A criticality chart depicting the quantity of zirconium powder in the area must be established and for the facility in question there should never be more than 250 gms present.

f) Metal containers with grounding clips should be available for transporting the zirconium powder.

g) Exhaust systems must be equipped to adequately handle the powder by dry or wet methods as covered below.

h) Non-flammable clothing should be worn by all people working in the area and they should be thoroughly trained in the handling of zirconium powder and the resultant fires that can occur.

With respect to point (g) above, unless the powder can be collected dry directly at the source, the use of water collectors should be utilized. Attempts to collect dry zirconium dust have not been successful. The possibility of dust clouds and their subsequent ignition by static charges or heating due to rapid surface oxidation exists. Also, dust deposits within duct work can lead to dangerous accumulations and subsequent disastrous fires.

A wet dust collecting system should be designed similar to Figure 2. This system should be located directly above the working area and should have a minimum of duct work leading to it, and preferably none. There should be a liquid level detector to interlock with alarms and operating equipment to insure the presence of water. The sludge should be cleared from the unit in accord with the amount of work being performed. Provisions should be made for washing out the facility as well as the glove boxes.

For fire protection all personnel should be thoroughly briefed in the hazards of working with zirconium powder and the preventive measures to be taken. Additionally, fire detection and alarm devices should be so devised to evacuate the building except for personnel specifically trained to fight this type of fire. Ordinary fire extinguishers are ineffective and should not even be available in the area of the zirconium operations. For the installation in question (which involves only zirconium powder), water should not be used because of its dangerous consequences when admixed with finely divided zirconium. Only dry powders, extinguishers approved for use on combustible metal fires or sand can be used to fight the fires.

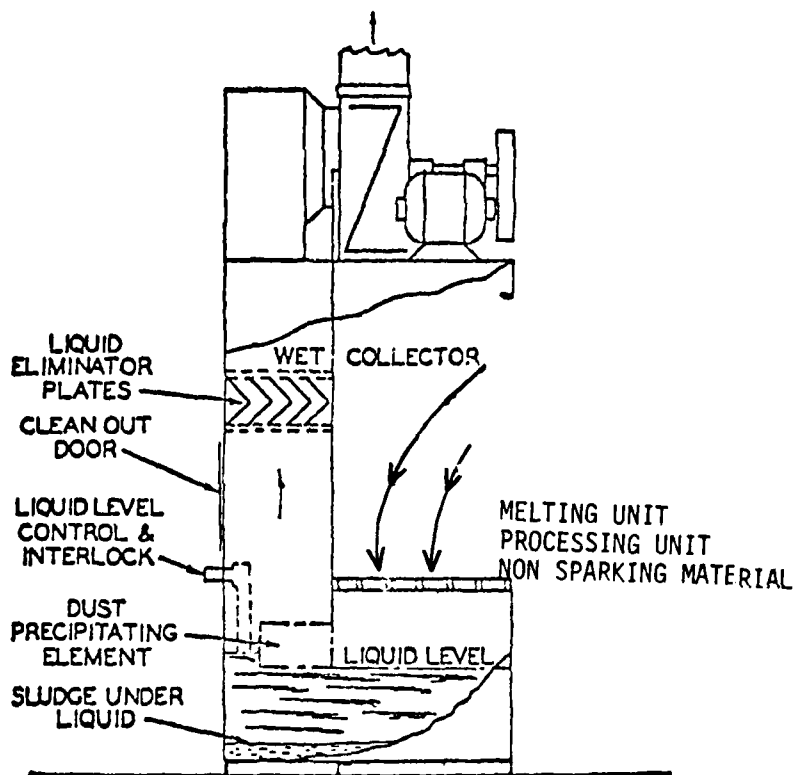


Figure 2. Wet Dust Collecting System
for Zirconium Dust

V. DISPOSAL OF UNWANTED MATERIAL

Zirconium powder should not be stored for extended periods of time because of its potential fire hazard. It should either be used for the intended purpose for which prepared or disposed. This includes sludges, scrap, misruns or partly reduced powder.

The disposal sequence is important in order to minimize damage to the individuals conducting the disposal operation. The powder or other material should be stored under water in metal containers no larger than five gallon drums. These containers should be taken to a remote site and deposited behind barricades. After spilling, the material can be ignited by an oil-soaked rag attached to a fifty foot fuze. All of these operations should be undertaken in remote areas so as not to endanger either people or property.

If powder has become dry the problems of disposal are even more hazardous and additional precautions must be undertaken. In all cases the people handling the material should be protected with suitable protective clothing and stay as far away as possible from the material in question.

VI. CONCLUSIONS

The facility to be used at the Air Force Materials Laboratory assigned to the evaluation of manufacturing parameters to produce zirconium powder can be effectively used if certain precautionary measures are imposed. The most significant item to accomplish is the use of wet dust collection. This is believed necessary to prevent accumulation of dust in a dry collection system.

A significant amount of training needs to be accomplished as regards the operating personnel. This training can be accomplished in a rather short period of time.

APPENDIX D

ZIRCONIUM POWDER ANALYSIS

Lt. David C. Ferguson

Air Force Rocket Propulsion Laboratory (AFSC)

DEPARTMENT OF THE AIR FORCE
AIR FORCE ROCKET PROPULSION LABORATORY (AFSC)
EDWARDS AIR FORCE BASE, CALIFORNIA 93523



REPLY TO
ATTN OF: MKPA (Lt David C. Ferguson, 32250)

MAK 8 1977

SUBJECT: Zirconium Powder Analysis

TO: AFML/MXA (R. F. Geisendorfer)

1. The purpose of this letter is to provide you with the operating procedures for the Powder-Burning Apparatus and the Electrostatic Discharge Sensitivity (ESD) Tester.

2. For the system setup and operating procedures of the Powder-Burning Apparatus, refer to Attachments 1 and 2. There is only one change in this procedure. The three intermediate photocells were not used due to the fact that the only two pulses required were the start and stop. The zirconium powder samples were prepared by gently pouring the dry powder into the groove of the mold bar (1 in. x 5/8 in. x 30 in. with a groove 1/16 in. deep and 1/8 in. wide running the length of the bar) until it is completely filled. The excess is then scrapped off with the edge of a wooden spatula so that the zirconium powder is flush with the top of the groove. Do not pack. Place the micarda board on top of the bar mold. Hold bar mold and micarda board together and invert. Place on bench and tap bottom of bar mold with handle of spatula to loosen sample particles. Remove bar mold. Place start and stop blocks on tray to shield photocells. Attach igniter wire. Ignite powder and record results.

3. ESD Test Procedures - The zirconium powder is placed in a small brass cup (same cup as drop-weight tester). Excess powder is scraped off with a spatula leaving the powder flush with the top of the cup. The sample is placed directly under the needle on the sample stand. The needle is adjusted so that it touches the bottom of the brass cup when completely extended. The capacitor is charged up to the required voltage. Then the needle is brought down to the sample. This disconnects the power supply and discharges the capacitor through the sample. If the test is negative, the voltage is increased until a positive test occurs. If the test is positive, a new sample is prepared, the needle replaced and the voltage lowered.

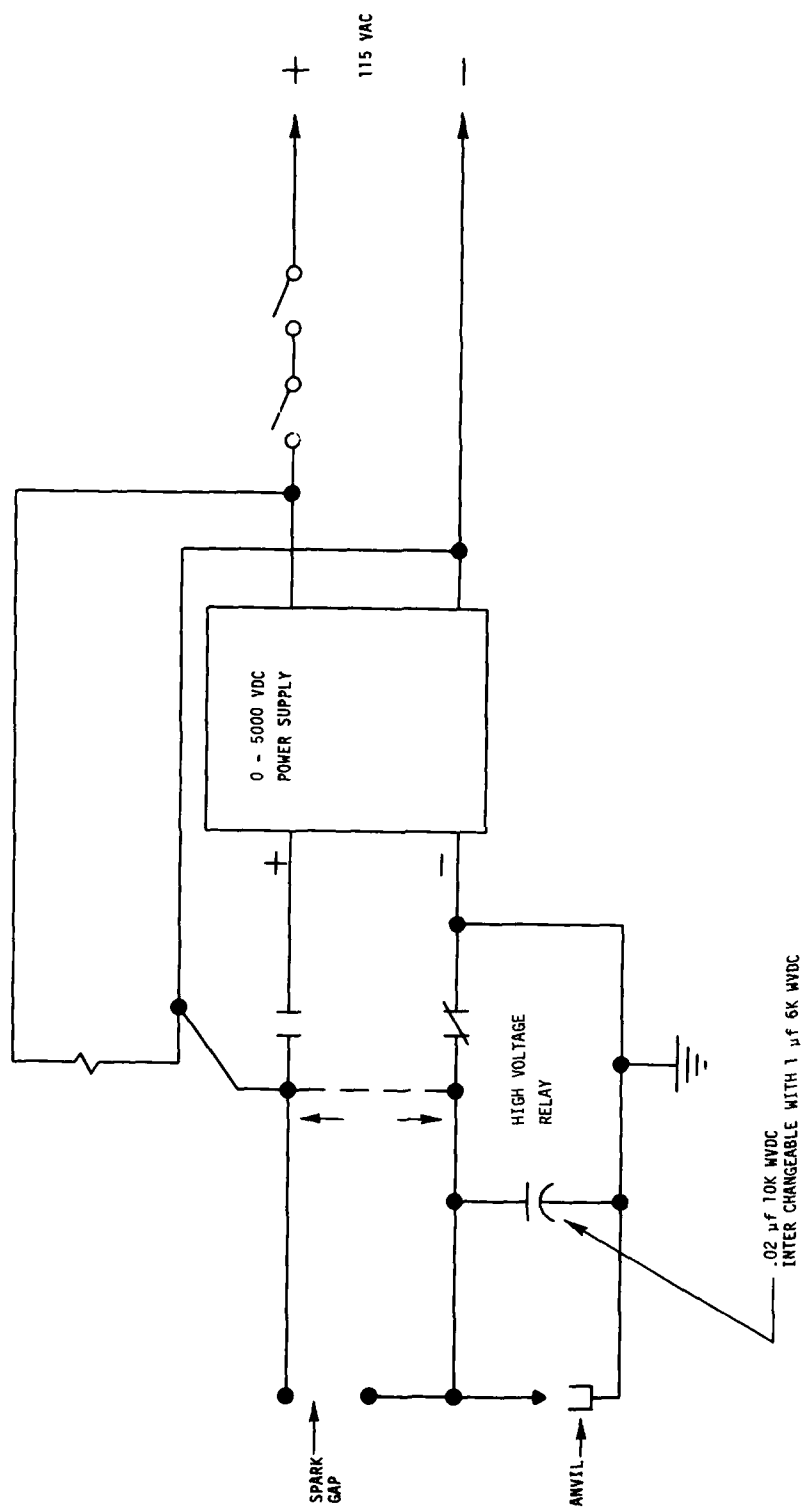
4. If any more information is required, please contact Lt Ferguson (Autovon 350-1110, extension 32250).

FOR THE COMMANDER

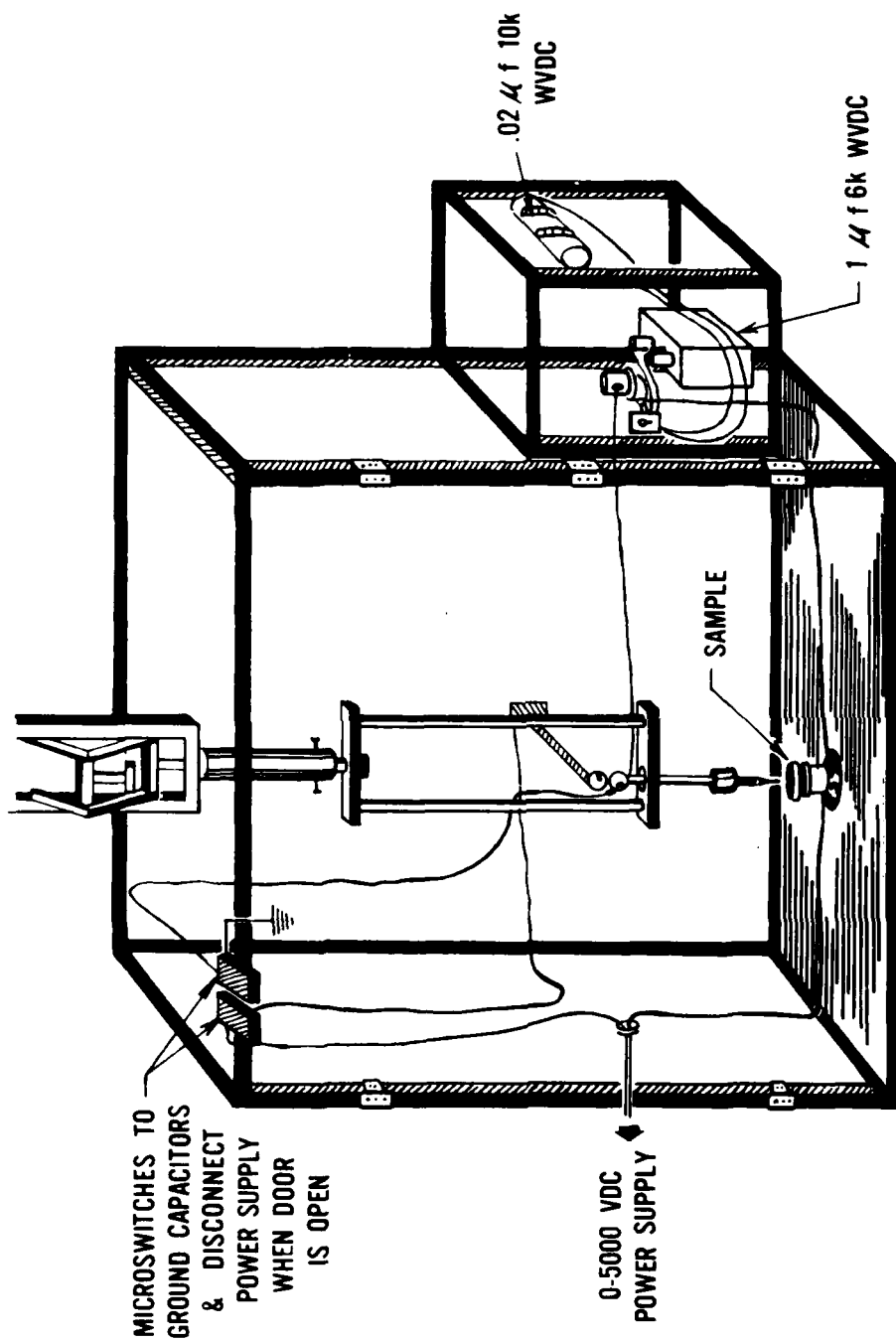
ROBERT L. GEISLER
Chief, Propellant Development Br

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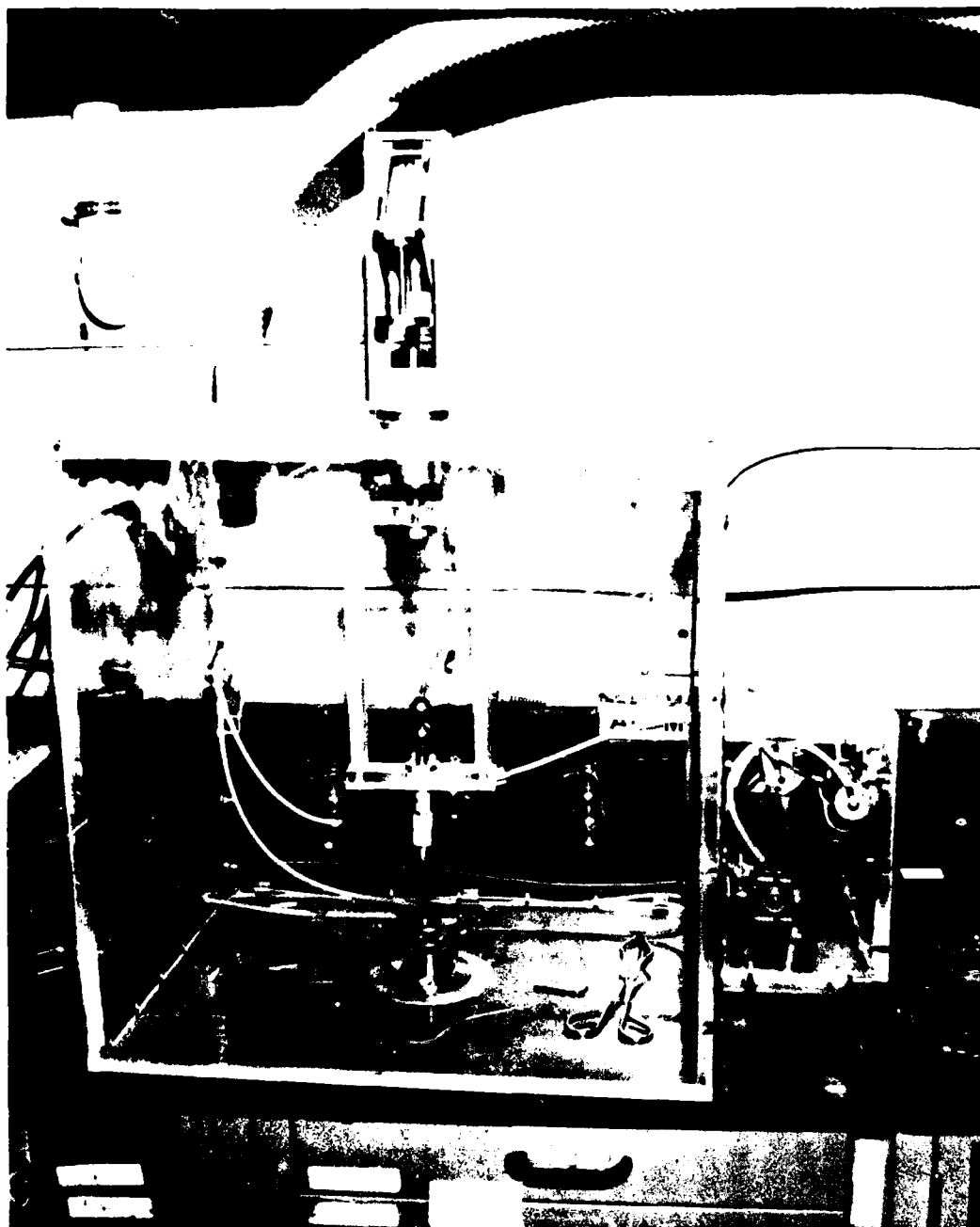
1. Drawing #X7517347
2. ESD Test Data (3 Pages)
3. "b Test Procedures (5 Pages)
4. Drawing - Powder Burning Apparatus
5. Drawing - ESD Tester
6. 8x10 Color Photos (5)



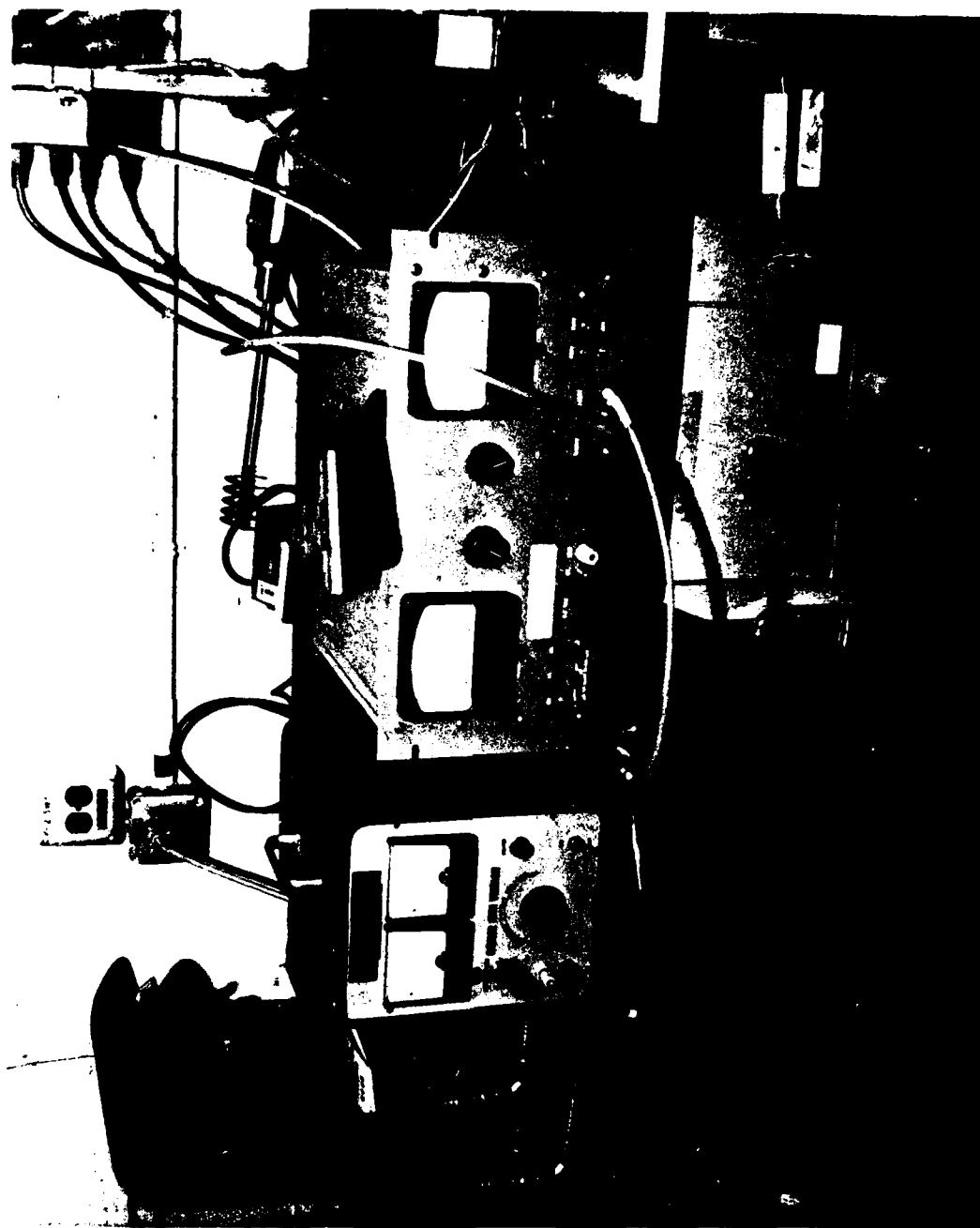
ELECTROSTATIC DISCHARGE SENSITIVITY TESTER



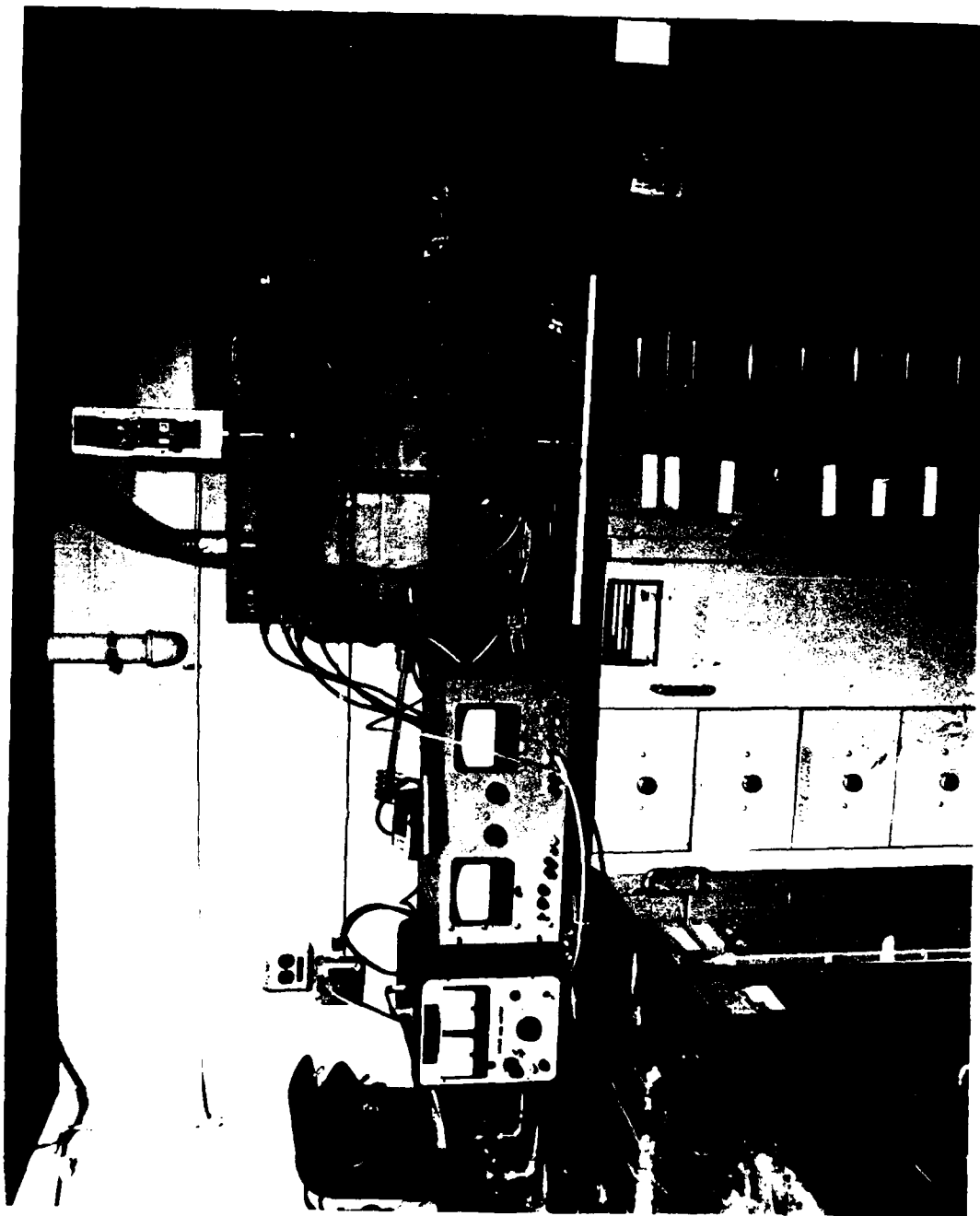
Electrostatic Sensitivity Tester Schematic - 1 - 30



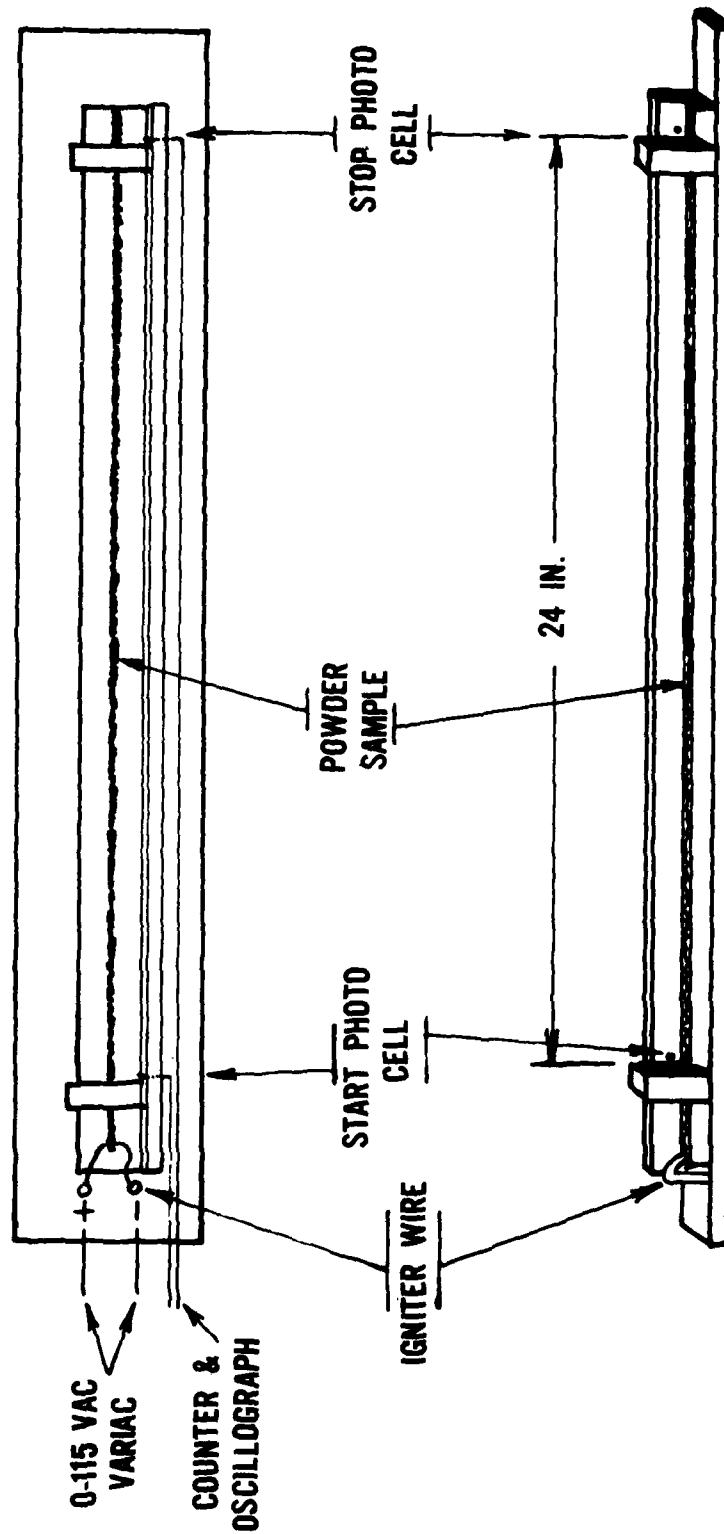
ESD Test Cell

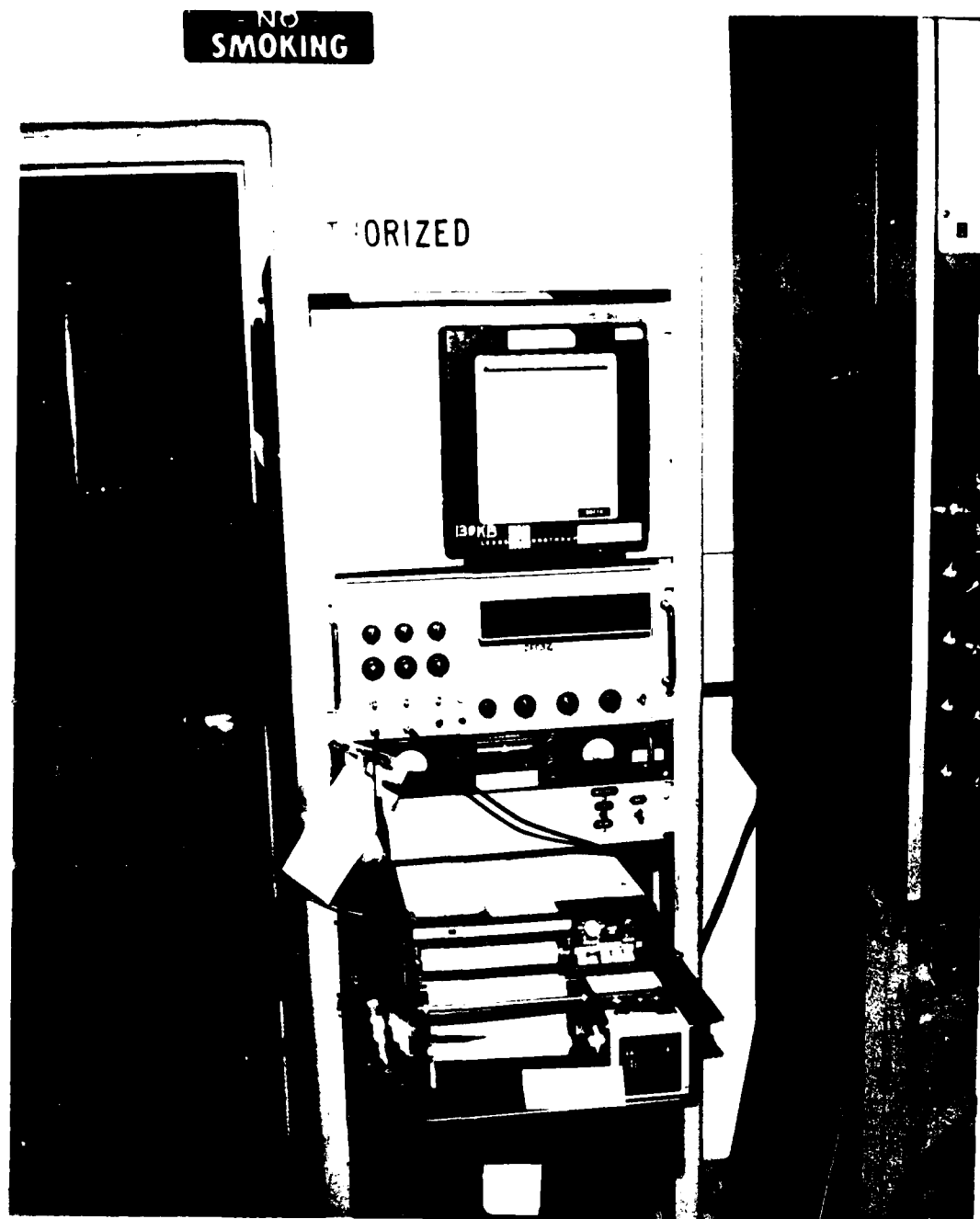


Power Supplies for ESD Tester

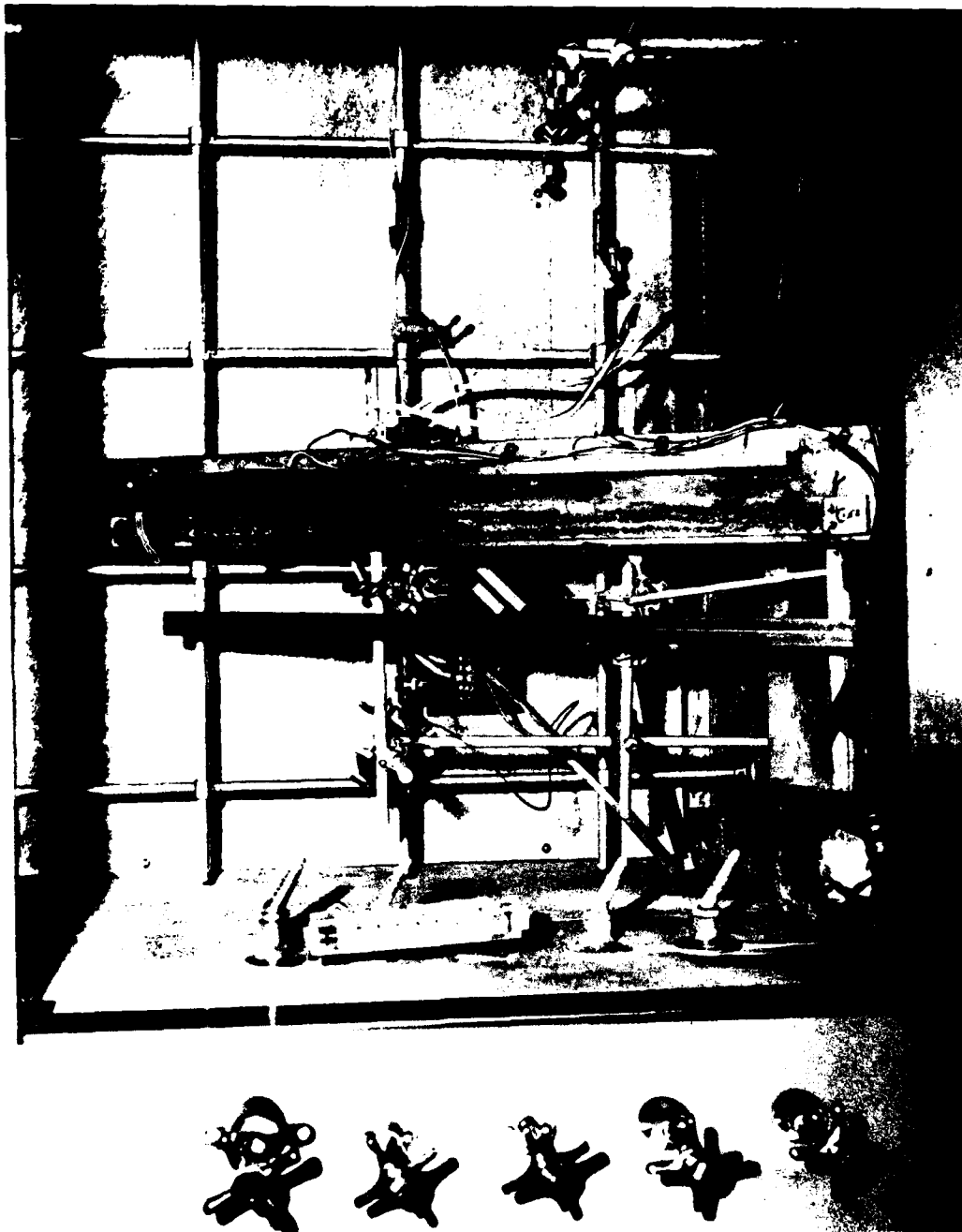


POWDER-BURNING APPARATUS





Burn Rate Tester Sample Mold Test Tray w/Photo Cells



Burn Rate Tester Timer Power Supply Oscilloscope