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FINAL REPORT OF EXPERIMENTAL LABORATORY-SCALE BRITTLE FRACTURE STUDIES OF GLASSES AND CERAMICS

by

L. J. Jardine, W. J. Mecham, G. T. Reedy, and M. J. Steindler

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L. J. Jardine, * W. J. Mecham, G. T. Reedy, and M. J. Steindler

Chemical Engineering Division

October 1982

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ABSTRACT

An experimental program was conducted to characterize the fragments generated when brittle glasses and ceramics are impacted. The direct application of the results is to radioactive waste forms for which the effects of accidental impacts must be known or predictable. Two major measurable experimental responses used for characterization of these effects are (1) the size distribution of the fragments, including the sizes that are respirable, and (2) the increase in surface area of the brittle test specimen. This report describes the glass and ceramic materials characterized, the procedures and techniques used for the characterization of size distributions and surface areas, and the results of the two key responses of the impact tests. Five alternative methods of determining size distributions were compared. Also examined were the effects of diametral and axial specimen impact configurations and the use of mechanical stops to eliminate secondary crushing during testing. Microscopic characterizations of Pyrex and SRL 131 simulated waste glass and SYNROC fragments were also performed.

Preliminary correlations of impact energy with key sizedistribution parameters, fragment surface areas, and respirable fines were proposed as useful for future verification and for use with modeling and scale-up studies of brittle fracture of larger realistic waste forms. The impact fragments of all specimens could be described by lognormal size distributions.

I. INTRODUCTION

Solid waste forms under development to immobilize high-level radioactive wastes are brittle and thus are subject to fracture during handling and transportation accidents. Fracture of a solid waste form causes an increase in the surface area potentially available for leaching while generating fragments small enough to be airborne and respirable.

Dispersion mechanisms of waste forms into pathways potentially leading to exposure of mankind must be sufficiently characterized via future risk analyses for successful licensing of waste handling, transportation, and disposal schemes. Water poses the most universally recognized pathway for dispersion of waste since water can dissolve or leach the exposed surfaces of breached canisters, overpacks, or other barriers. Airborne pathways in the plant must also be assessed, as well as transportation accident scenarios. The consequences of brittle fracture of solid waste forms can be evaluated if sufficient characterization measurements exist of (1) the increase in surface area of impact fragments and (2) the size distribution of the impact fragments. Focusing experimental measurements on these two measurable responses greatly simplified the scope of the experiments. However, applying laboratoryscale experimental responses to actual large-scale canistered radioactive waste forms requires that a theoretical basis be developed that is sufficient to at least determine scaling-laws of test data. A previous report [MECHAM, ANL-81-27] described such a proposed theoretical basis along with the results of initial experimental measurements.

This final report describes the experimental results of a brittle fracture program terminated in FY 1982. The goal of the program was to develop the necessary models, engineering correlations, scaling laws, and experimental characterization methods required to assess the two measurable responses discussed above for large canisters of radioactive waste forms. Sets of standardized laboratory-scale impact tests and characterization procedures were defined, developed, and used to measure particle size distributions and surface areas. The results were used to develop modeling methodologies, as well The direct applicability of the current test as preliminary correlations. results to full-scale waste forms is not now obvious since scaling-law tests for larger systems have not yet been performed. However, the present results do have merit for making comparative material evaluations. In fact. a comparative testing program on eight high-level waste forms was conducted and reported [JARDINE], to aid in the selection of superior waste forms for further development.

This report has been structured around the experimental results. Reference is made to detailed modeling methodologies developed as an integral part of this program and reported elsewhere. Experimental details are presented concerning the materials tested, the impact apparatus, and impact fragment characterization methods. The results are presented and illustrations made as to how the results have potential application to waste management concerns via future risk analyses. Alternative characterization methods and test configurations were also examined and are reported.

II. EXPERIMENTAL: LABORATORY-SCALE IMPACT TESTS

This section describes the details of the types of materials examined in this program and the impact test device, as well as characterization techniques and procedures used to determine the fragment size distributions and fragment surface areas. Some information on the methods of calibrating the various techniques is also given.

A. Specimen Descriptions--Procurement and Preparation

Glass, crystalline ceramics, and concrete were either procured from commercial vendors or were supplied by the developers of alternative waste forms for the High Level Waste Program, then managed by the Savannah River Laboratory for the Department of Energy. The nominal compositions of materials examined in this work are given in Table 1. Additional properties of these test materials are described below. Other materials tested previously have been reported [MECHAM ANL-81-27].

			Simulated			Crye	talline (Ceramics	Concrete
Constituent	SRL 131	High Silica	Alkoxide Waste	PNL 76-68	Pyrex	SYNROC B	SYNDROC D	Tailored Ceramic	FUETAP
\$102	41.7	54.9	37	41	81	-	0.5	1.4	28*
B203	10.6	3.3	10	9.0	13	-	-	-	-
T102	0.7	-	-	3.0	-	59.4	18.7	2.0	-
A1203	3.0	8.0	22.6	0.6	2	6.5	19.9	52	1.8
L120	4.1	-	-	-	-	-	-	-	-
Na ₂ 0	13.3	2.0	14.9	11.3	4	-	3.4	4.6	1.3
Ma2SO4	0.4	-	0.1	-	-	-	0.6	0.4	0.2
Ce 70	-	0.1	0.1	1.1	-	-	0.3	-	-
MEO	1.4	-	-	0.1	-	-	-	-	-
CeO	1.0	0.6	0.9	2.2	1	15.2	4.7	0.8	0.5
SrO	-	0.1	0.1	0.4	-	-	0.4	-	0.2
BaO	-	-	-	0.5	-	8.0	1.4	-	-
ZrO	0.4	0.01	-	1.8	-	10.9	4.9	-	-
Feg03	13.9	14.5	9.8	9.5	-	-	24.2	12.6	9.4
Ha07	3.7	4.3	2.3	0.06	-	-	7.5	10.4	2.6
NIO	1.6	1.9	1.1	0.2	-	-	3.1	1.8	1.2
LapOn	0.4	-	-	4.1	-	-	-	7.2	-
CeO ₂	-	1.1	0.8	0.8	-	-	0.4	-	0.4
G4203	-	-	-	0.02	-	-	0.4	-	0.4
Md203	-	0.4	0.3	1.5	-	-	0.4	-	-
Eu 203	-	-	-	0.005	-	-	0.4	-	-
U02	-	-	-	-	-	-	2.1	ь	-
P205	-	5.0	-	0.7	-	-	-	-	-
Zeolite	2.7	-	-	-	-	-	-	7.3	1.6
Flyash ^C	-	-	-	-	-	-	-	-	52C
Other	-	-	-	7	-	-	-	-	-
Waste Totals	27	30	30	33	0	0	64	85	20
Matrix Total	6 73	70	70	67	100	100	36	15	80

Table 1. Nominal Compositions (in weight percent) of Alternative Waste Forms Used in Comparative Impact Study Tests

"FUETAP used Ottawa sand as \$102.

^bThree wt X UO₂ was replaced with 3 wt X Al₂O₃.

Cincludes flyash, 11%; coment, 22%, water, 18%; and water reducer, 1.25%.

1. Glasses

Five types of borosilicate glasses were used in our studies. Pyrex^{*} glass was purchased from a commercial vendor as rod stock in sizes of 1.2-cm(1/2-in.) OD to 3.8-cm $(1\ 1/2-in.)$ OD. Specimens for testing were cut from rod stock into appropriate lengths and were then annealed, using standard procedures, prior to testing. Pyrex glass contained no waste additives but was used as a reference material for our tests because of its ready availability and known material properties.

Of the simulated waste borosilicate glasses, the SRL 131 glass was studied the most. Its composition is shown in Table 1. The SRL 131 glass

*Trademark of the Corning Glass Works.

contained no uranium or minor additives but was loaded with 27 wt % simulated SRL TDS calcine. The glass (~ 200 lb) was supplied by SRL from their pilot one-third scale continuous melter. Specimens for impact testing were prepared by remelting the SRL 131 glass in stainless steel crucibles at 1100°C for $\sim 1/2$ h under a nitrogen purge, annealing the glass at 550°C for several hours, and then core drilling to obtain specimens with diameters of ~ 12 mm, ~ 25 mm

The composition of a simulated high-silica glass waste form containing 30 wt % SRL waste is also given in Table 1. Two specimens were received from Catholic University (CU). Specimens of ~2.5-cm diameter x 2.5-cm had been core-drilled from a larger piece of the high-silica glass, which had been formed by sintering powders in a crucible for four hours at 1250°C in a vacuum. The material was tested as received. It appeared to be heterogeneous, with zones of different colors. No analysis of the microstructure was available.

Two core-drilled specimens of simulated alkoxide waste glass were received from Westinghouse. The glass contained 30 wt % SRL simulated waste with the nominal composition given in Table 1. The specimens were 25.4-mm OD x 25.4 mm long.

A 10-kg batch of a simulated commercial waste glass containing 33 wt % waste, PNL 76-68, was received from the Materials Characterization Center (MCC) at Battelle Pacific Northwest Laboratory (PNL). Specimens for testing were prepared by remelting the glass at 1050° C for several hours in stainless beakers. Specimens with diameters ranging from 12 mm to 38 mm were core-drilled from the remelted glass after annealing.

2. Ceramics

Three types of SYNROC ceramics and a tailored ceramic waste form were procured for testing. SYNROC was studied the most. SYNROC B, containing no waste, and SYNROC D, loaded with ~64 wt % simulated SRL waste containing 2 wt % UO₂, were two ceramic materials supplied by Lawrence Livermore Laboratory (LLL). The ceramic compositions are shown in Table 1. The SYNROC B material was prepared by hot pressing at 1200°C and 13.8 MPa (2000 psig) for five minutes in a graphite die to a density of 4.2 g/cm³ (96% T.D.). Specimens for impact testing were prepared by core-drilling specimens to 26.8-mm OD x 25.85 mm from a 566.8-g stock sample. The SNYROC D was prepared by hot pressing at 1100°C and 27.6 MPa (4000 psig) for five minutes in a graphite die. The final material density was 3.96 g/cm³ (99% T.D.). At LLL, specimens 25.4-mm OD x 27.3-mm were prepared by core drilling for impact testing. Two cylindrical specimens of SYNROC C containing 10 wt % PW-4b simulated commercial waste were obtained from the Materials Science Division (MSD) of ANL [MECHAM, ANL-81-35, ANL-81-13]. The SYNROC C specimens were made by cold-pressing and sintering at 1300°C for three hours in an atmosphere of CO/CO2. Their geometric density was 4.26 g/cm^3 .

Some simulated hot-pressed tailored ceramic was obtained from Rockwell International (RI). The tailored ceramic was loaded to ~85 wt % simulated high-aluminum SRL waste but did not contain any uranium; the nominal composition is given in Table 1. The material was prepared by hot pressing in graphite at 1300°C and 27.6 MPa (4000 psig) for one hour. Specimens for impact

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testing (<u>e.g.</u>, 26.8-mm OD x 18.15 mm long) were prepared by core drilling. The thickness of the materials supplied did not allow production of a coredrilled specimen having a length-to-diameter ratio of approximately unity, as was accomplished for other waste forms.

3. Concrete

Two types of FUETAP concrete simulated waste form specimens were supplied by ORNL; the composition is summarized in Table 1. The FUETAP contained no uranium but was loaded with v20-25 wt % modified, SRL simulated waste. The two types of FUETAP specimens differed slightly in diameter and each had been prepared by different processing conditions. Lot 1 had a 2.54-cm diameter; processing conditions included curing at 100°C and 0.1 MPa (~15 psig) followed by dewatering at 250°C, each for 24 h. Lot 2 had a diameter of 2.65 cm; processing conditions included curing at 250°C and 6.1 MPa (~100 psig) followed by dewatering at 250°C, each for 24 h. The ORNL-supplied specimens were prepared for impact testing by cutting the specimens into 25.5-mm lengths, using a low-speed Isomet saw equipped with a diamond blade and saturated limewater coolant. The cut specimens were then dewatered a second time for 24 h at 120°C in a vacuum oven.

B. Impact Test and Apparatus

An impact test consisted of placing a single cylindrical specimen on its side between two hardened tool steel plates (Rockwell C58) inside a sealed chamber. A sketch and a photo of the impact chamber are given in Fig. 1. Each specimen received a dynamic diametral impact by a weight, normally 9.9 kg, dropped from a preselected height onto the upper hardened plate. A plexiglass tube was used to guide the delivery of the dropped weight. The initial height of the dropped weight was selected so that the available impact energy per unit volume of the specimen (calculated from potential energy and ignoring any losses) ranged from ~ 0.2 to 150 J/cm^3 , with most tests in the range of 1 to 10 J/cm^3 . Variations in the heights of the weight drops were used to define the test conditions, once a test specimen energy density was selected. For example, to achieve the required 10 J/cm^3 for a 25.4-mm-OD x 25.4-mm-long specimen, a drop height of 1.34 m produces a potentially available impact energy of 131 J or 10 J/cm^3 .

During and immediately after the impact, the 12.7-cm-dia chamber remains sealed by a metal bellows (Fig. 1) which is welded to the the upper hardened steel plate and the upper removable cover. The brittle specimens absorb impact energy during loading until fracture occurs (in $\sim 100 \ \mu$ s). The fracture fragments are contained within the chamber, allowing subsequent size and/or surface area characterization.

High-speed photographs (5000 frames/s) were taken in mock-ups of the impact process. Pyrex specimens (38-mm OD x 64 mm long) were used in these mock-ups. Figure 2 shows the sequence of events in one test during the first 1300 µs of the impact. Cracks appeared within the first 150 µs, which is the resolving time (or frame spacing) of the photographs. As the weight continued to drop, the glass specimen fragmented and the fragments were "blown-away" from the hardened steel plates. Experiments described in Section III.E indicated that no important secondary crushing of the specimen occurred as the weight



Fig. 1. Bellows Chamber for Impacting Brittle Specimens. ANL Neg. No. 308-81-39

continued to fall and came to rest on the fragments of the specimen. Figure 3 shows the first ${\sim}\,300~\mu s$ of the impact events in two diametral and one axial tests.

C. Impact Fragment Characterization Methods

Both the particle size distributions and the surface areas of the impact fragments were measured.





t = 152 µs



t = 304 µs





Scale 10 mm





t + 912 µs







Fig. 2. End View of a 91-J Diametral Impact of a Solid Cylindrical Pyrex Specimen (Diameter, 3.81 cm; Length, 6.41 cm). ANL Neg. No. 308-80-342K

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Fig. 3. 91-J Impacts of Solid Cylindrical Pyrex Specimens. ANL Neg. No. 308-80-341K. (A) Side View of a Diametral Impact. (Diameter 3.81 cm, Length 6.41 cm) (B) Side View of an Axial Impact (Diameter 3.81 cm, Length 3.81 cm) (C) Angle View of a Diametral Impact. (Diameter 3.81 cm, Length 6.41 cm)

1. Particle Size Analyses

After impact, fragments were collected by introducing water into the impact chamber through a valve assembly (not illustrated in Fig. 1) that penetrated the upper flange. A slurry of fracture fragments was formed, and after removal of the upper chamber flange, the slurry was transferred directly to a 90- μ m sieve. The bellows was then cleaned, and fragments in the cleaning water were collected by water washings over the 90- μ m sieve. By additional washings of the material collected on the 90- μ m sieve, two size fractions were separated and collected: <90 μ m and >90 μ m. These steps are illustrated in Fig. 4.

In the normal procedure for partitioning between particles to be counted in the Coulter counter and particles to be sized by sieving, the fine particles for the Coulter counter are washed through a $90-\mu m$ sieve into a slurry. It was found that even after thorough washing of the material retained



Fig. 4. Procedure Used to Characterize the Fragments Generated in the Impact Tests

on the sieve, if the sieve was shifted during handling after the sieve and its contents had been dried, additional particles originally retained on the sieve would quickly pass through. An examination of the size distribution of the particles that passed through the sieve was made with the Coulter counter. Results for glass fragments are shown in Fig. 5. When the dried particles are added to the slurry of particles passing through the wet $90-\mu m$ sieve, the particle size distribution (Fig. 5C) shows continually increasing mass fractions up to the $90-\mu m$ cutoff. This observation strengthens confidence in the present technique of particle size analysis using the Counter counter.

The $\langle 90 - \mu m$ fraction in the slurry was then sampled and analyzed into sixteen size fractions (equivalent spherical diameter) from 4 to 90 μm using a Coulter counter (Model TA-II) equipped with a 280- μm aperture tube.

This instrument determines the number of individual particle fragments as a function of particle volume. The individually measured particle volumes are counted in 16 size ranges and are automatically converted to equivalent spherical diameters. The instrument is calibrated using two sizes of latex monospheres supplied by the vendor. If the densities of all fragments (of a given homogeneous material) are assumed to be the same, the relative (fractional) volume distributions are equivalent to relative mass distributions as a function of fragment size.

The relative mass distributions were renormalized, and absolute cumulative mass distributions were calculated based on (1) a measured aliquot from the $\langle 90 \ \mu m \ slurry \ that \ had \ been \ evaporated \ and \ weighed \ and \ (2) \ the \ original$



Fig. 5. Coulter Counter Mass Frequency vs Size Distributions of Glass Fragments

specimen mass. The alternative normalization of cumulative mass distributions based on the difference between the initial specimen mass and the $\geq 90 \ \mu m$ mass measured on the 90- μm sieve was used in only very few early experiments. Another method of obtaining the normalization mass is to calculate it from the particle-count data recorder in the registers of the Coulter counter.

It should be pointed out that the Coulter counter can introduce an error into the cumulative mass-fraction data because of limitations on the discrimination of smaller particles by the pulse electronics. For example, the 280-µm aperture tube counts fragments between ~4 to 5 µm in the first channel, fragments between ~5 to 6 µm in the second channel and so on. Fragments with sizes below 4 µm produce pulses that are not registered in any channels. If cumulative lognormal linear plots of the Coulter counter data are made, the first data point at 4 µm is extraneously low. The values of successive data points also are low, but progressively less so as the cumulative mass increases. After the fifth data point at ~13 µm, the missing contribution to the cumulative distribution makes no difference in the fitted plots.

To minimize this problem in the analyses, the general data-fitting procedure consisted of including all points above $~8 \mu m$ in fits of the cumulative data. Extrapolation of the fitted curve can be used to establish sizes smaller than 8 μm . Plots of the cumulative size data presented in this report are generally straight lines determined by using raw Coulter counter and sieving data for all particles in the size range of 8 μ m to 2000 μ m. In some few early tests, the points shown had the extrapolated value of the cumulative mass for sizes less than 4 μ m artificially added to the raw data before plotting.

Successively smaller orifices than the standard 280- μ m orifice were also used to measure the distribution to \sim l μ m in order to verify that these deviations are indeed an artifact of the Coulter counter.

The ≥ 90 µm fraction remaining on the sieve was dried in a vacuum oven at 120°C and sized into seven size fractions (sieve mesh openings) of 90-125 µm, 125 µm, 250 µm, 500 µm, 1000 µm, 2000 µm, and 4000 µm, using a Sonic ATF-L3P sifter. The collected sieve fractions were then weighed. These masses were then converted to cumulative mass fractions based on the starting specimen mass and the Coulter counter analyses of the <90 µm fragment fractions.

Two sieves used in particle size analyses were calibrated against National Bureau of Standards (NBS) Standard Reference Material 1018a. This material consists of glass beads with a known particle size distribution. By sieving this material by the routine procedure and comparing the cumulative percent mass that passes through each sieve to the known distribution determined by the NBS, the effective sieve openings (μ m) can be established. Due to the limited range of NBS Reference Material 1018a particle sizes (225 to 780 μ m), only the 250- and 500- μ m sieves were calibrated. The sieve data are reported in Table 2.

	Sieve Time, min				
Sieve Size, µ∎	12	24	36	48	
500	99. 98	99.96	99.98	99.97	
250	43.97	52.27	52.82	53.14	
125	12.85	13.64	13.72	13.74	

Table 2. Sieve Calibration (cumulative mass % on each sieve) with NBS Standard. Reference Material No. 1018a

The upper sieve $(250-500 \ \mu\text{m})$ was heavily loaded with over 40 g of material. This can be seen in Fig. 6 where, after 12 min of sonic sifting, the 500- μ m sieve is nowhere near its sieve endpoint. There is little difference between the 36- and 48-min data. The data taken after 48 min is believed to be closest to the sieving endpoint, and so these data points have been used in the calibration. By comparing the cumulative mass percentages observed to the known NBS distribution, the sieve openings were determined to be 252 μ m and 508 μ m.



Fig. 6. Progress in Sieving NBS Standard Reference Material 1018a as a Function of Sieve Time

When the NBS material was transferred back into a bottle, many beads were stuck in the sieve openings. These beads were photographed under a microscope and measured. The mean particle sizes with a 95% confidence factor were determined to be 258.2 \pm 9.3 μ m and 501.3 \pm 17.4 μ m. These values support the NBS calibration.

2. Surface Area Measurements

Surface areas of impact fragments were measured using the BET gas adsorption technique [JAYCOCK]. To collect fragments for surface area measurements, the wet-collection procedure outlined in Fig. 4 was modified. No water was used to collect fragments from the impact chamber. Instead, the fragments were brushed from the impact chamber surfaces and loaded directly into standard 15-mL BET tubes for measurements. The use of water to collect glass fragments as a slurry followed by evaporation of water was found to be unsatisfactory. The water caused surface reactions (verified by SEM photographs of the fragments) which produced BET surface areas two to eight times greater than the surface areas of fragments that never contacted water.

The initially unsuccessful procedure for BET measurements was done by the standard methods used for routine particle size distributions (Fig. 4), with the following add-ons: First, the size fraction >90 μ m was passed over a 2-mm sieve to obtain fragments larger than 90 μ m but smaller than 2000 μ m, which were loaded into a BET tube. Secondly, the <90 μ m fraction contained in the Coulter counter alurry fraction was evaporated to dryness in a beaker during a 24-28 h period, weighed to obtain the normalizing Coulter counter mass fraction, and then transferred to the BET tube--either with the larger fractions or into a separate tube. A surface area determination of this entire fraction <2000 μ m was then done by the BET method.

In one example, the BET surface area measured for a 2.5-cm x 2.5-cm Pyrex specimen (Run No. PD50-53) impacted at 10 J/cm³ was found to be 3.27 m² (i.e., 3.0 m² for the sizes smaller than 90 μ m and 0.27 m² for the sizes larger than 90 μ m but smaller than 2000 μ m). A previous BET measurement (Run No. PD136) of a similar impacted 2.5 x 2.5-cm Pyrex specimen impacted at 10 J/cm³ that was dry-transferred (i.e., no water was contacted with the fragments) immediately after impact and sieved to remove all fragments larger than 2000 μ m was found to have a surface area of 0.77 m² for all sizes smaller than 2000 μ m. Thus, these two procedures resulted in the BET surface areas differing by a factor of v4.2.

To examine the effect of water contact on these Pyrex fragment surfaces, SEM-EDAX electron microscope examinations were performed for the two size fractions of BET-measured fragments and for newly prepared Pyrex fragments never exposed to water. Both the $\langle 90 \ \mu m$ fragments and the $\rangle 90$, $\langle 2000 \ \mu m$ fragments exposed to water were observed to have pitted and roughened surfaces in comparison to the non-water-exposed fragments. These roughened surfaces were not always uniformly distributed on the fragments and were localized at times. The <90 um fraction had more surface reacted than did the >90 um fraction. The >90 μ m fraction was observed to have many small (~1 μ m) particles adhering to them. Also observable in the samples were agglomerates of fragments. These had the appearances of a hydrated jell mass that had formed during evaporation, then cracked during drying. Also, after the BET measurements, the Coulter counter size distribution of the Pyrex fragments was remeasured. There was no change in the mass/volume distributions. All of these observations are consistent with the BET surface area measured for Pyrex fragments exposed to water followed by the evaporation recovery procedure being about four times larger than for glass never exposed to water.

It is concluded that BET surface areas measured for impacted fragments that have been exposed to water, using our standard procedure for particle size determinations, are significantly different from surface areas of fragments not exposed to water. No change in the masses of the fragments was measurable. The use of water to collect glass fragments for surface area measurements is not satisfactory; dry transfers should be used.

Considerable effort was also spent to examine the consistency of BET results for the rather low specific surface area samples. These efforts included establishing correlations of measured BET surface areas with reasonably well-known geometrically calculated surface areas. In particular, BET surface area measurements were made to establish if our Micrometrics Model 2100D BET analyzer could measure samples having total surface areas as low as tenths of a square meter. BET measurements are normally performed on highspecific-surface-area materials and thus on samples with total surface areas of many square meters. The brittle fracture program experiments generated simulated waste glass and ceramic fragments samples of very low specific surface areas and very low $(\sqrt{1/2} m^2)$ total surface areas; BET surface area measurements of these samples were required. The performance of the BET instrument on such samples was not known, and so measurements (described in more detail below) were undertaken to establish the performance by bounding both the probable accuracy of BET measurements and the precision of BET measurements in the sample size range of 0.1 m² to $\sqrt{3} m^2$ total surface area.

It should be noted that no materials are available for establishing the absolute calibration of BET surface area devices. This is due to the lack of smooth materials that can serve as calibration standards (<u>i.e.</u>, of materials having no surface roughness on a scale of Angstroms, since BET measurements depend on monolayers of krypton gas adsorption). Hence, the approach discussed below was defined and used in our brittle fracture studies to estimate the accuracy and to determine the precision of BET measurements of samples of $v0.1 \text{ m}^2$ to 4 m^2 .

a. Introduction

Materials were sought that could be used as stand-ins for nonexisting calibration standards for the Micrometrics 2100D BET analyzer. The initial requirements for these materials were that they have shapes whose geometric surface area could be calculated and be of a reasonably high specific surface area such that material with about 0.1 m² of surface area could be fitted into a 15-cm³ standard BET measurement tube. The diameters of the particles also had to be smaller than about 2 mm for the particles to fit into standard BET tubes. Three different types of glasses, each consisting of particles of $\langle 120-\mu m$ diameter and having various degrees of sphericity, were identified and procured.

Various amounts of these three materials were then used as "quasi standards" for BET measurements. Comparisons of the measured BET surface areas with calculated geometric surface areas based on measurements of different masses of the materials of assumed specific (geometric) surface areas allowed the establishment of correlations of the BET with the geometric surface areas.

Two other materials were identified and used to establish the typical precision of the BET device for samples in the operating range of 0.1 m^2 to 4 m^2 . One material was a ZnO powder with a well-characterized specific surface area. Also, glasses were used to establish the BET measurement precision in two ways: (1) by performing measurements of the same Pyrex fragments at ANL and at an off-site laboratory (Micrometrics) and (2) by performing replicate BET measurements of the same glass samples at ANL. Details are presented below.

b. <u>Surface Area Correlations for Glass Monospheres:</u> <u>BET (Measured) vs. Geometric (Calculated)</u>

Two sizes of single-size glass microspheres, whose BET surface areas could be measured and whose geometric surface areas could be calculated, were obtained from Duke Scientific Corporation. The uniform spheres, having a density of 2.45 g/cm³, were of two different diameters, 50.7 \pm 1.2 µm (stock No. 299) and 120 \pm 3 μ m (stock No. 150). For these two sizes, specific geometric surface areas were calculated to be 0.052 m²/g and 0.021 m²/g, respectively. These values neglect any surface roughness.

The masses of samples of the $50.7-\mu m$ glass spheres ranging from ~ 2 to 19 g were measured and the samples transferred into standard BET tubes. The corresponding range of geometric surface areas was $\sim 0.1 m^2$ to $\sim 1.0 m^2$. Table 3 summarizes these values and the corresponding measured BET surface areas. Comparison of these data shows that the BET surface areas were larger

Sample		Surface		
ID	Mass, 8	Calculated, ^a m ²	Measured, ^b z ²	Calculated Deviation, ^C X
50.7 ± 1.2	um spheres			
122-7	1.90	0.098	0.10	0
122-8	2.76	0.14	0.17	22
122-9	3.80	0.20	0.20	0
122-10	5.62	0.29	0.33	14
121-8	8.56	0.45	0.47	5
122-11	13.4	0.70	0.83	19
124-2	19.0	0.99	1.13	14
				ll ± 9 average
120 ± 3 µm	sphere			
122-12A	2.44	0.05	0.06	20
122-13	7.47	0.16	0.21	31
120-12B	8.89	0.19	0.24	26
124-1	14.4	0.30	0.36	20
				24 ± 6 average

Table 3. Comparison of Measured BET Surface Areas with Calculated Geometric Surface Areas for Glass Microspheres of Uniform Size

and for 120-µm spheres it is 0.021 m²/g. ^bMeasured with Micrometrics Model 2100D BET device, using krypton; background of 0.02 m² subtracted from all runs. Background has been corrected.

^C(Measured - calculated) divided by calculated, times 100.

than the geometric, being on the average $11 \pm 9\%$ larger. These data are also plotted in Fig. 7 and suggest a linear correlation. A solid line, denoted "theory," has also been included which corresponds to the line which would be obtained if the BET surface area equals the geometric surface area. In no cases are the measured BET points smaller than the calculated geometric surface areas. It should be noted that several measurements were made of blanks (<u>i.e.</u>, with no material in the BET tube) to establish the BET tube background surface areas as 0.02 m^2 , which was then subtracted from all the measured BET surface areas reported. Thus, surface areas approaching 0.1 m^2 had a $\sim 20\%$



Fig. 7. Correlation of Measured BET Surface Area of Glass Microspheres with Calculated Geometric Surface Area

Masses of $120-\mu m$ glass spheres ranging from $\sim 2 1/2$ to ~ 14 g were also weighed, loaded, and their surface areas measured with the BET device. Because of the small specific surface area and the limited quantities of spheres, the range of the measured geometric surface areas was only 0.05 to 0.3 m². Results are given in Table 3 and are also plotted in Fig. 7. The correlation again appears to be linear over the limited range studied. The BET surface areas were always larger (the average being $24 \pm 6\%$ larger) than the geometrically calculated areas. SEM examinations of a sample of the microspheres showed them to have minor surface imperfections, which makes plausible the BET surface areas being larger than geometric surface areas. As shown in Fig. 7, the correlations are nearly linear for both sizes of spheres over the entire measured range of 0.1 m^2 to $\sim 1 \text{ m}^2$. A least-squares fit of these data generated the following correlation relations for the two sizes:

 $A_{BET} = 1.16 A_{Geo} = 0.015$ (50.7-µm spheres) $A_{BET} = 1.20 A_{Geo} + 0.008$ (120-µm spheres)

where A_{BET} is the measured BET surface area in m^2 and A_{GeO} is the geometric surface area that neglects any surface roughness.

It is concluded from these results that the BET surface areas are consistently larger by 10 to 30% than surface areas calculated from geometric factors. A linear correlation was measured over the range of 0.1 m^2 to $\sim 1 m^2$. The surface roughness on the scale of tens of Angstroms cannot be estimated. However, as an explanation of the 10-30% deviations, there must be

roughness since the size of krypton atoms is ~ 3 Å. Currently, nothing can be stated about the accuracy of these results. No measurements of precision were attempted with this material.

c. Precision of BET Measurements

To establish the precision of the BET measurements over the range of 0.1 to 4 m^2 , a source of ZnO (stock No. 208) having a known specific surface area of 0.63 ± 0.03 m^2/g was procured from Duke Scientific Corporation. The ZnO is used for determining the precision of BET measurements, but not their accuracy. The specific surface area of the ZnO was established to $\pm 5\%$ by a series of round robin measurements using several types of BET instruments.

The procedure used to determine BET measurement precision was, first, to weigh out different amounts of the ZnO powder. From the mass of ZnO, the surface area of a sample in the BET tube was determined. Masses were selected to provide samples having 0.06 m^2 to 4 m^2 total surface area since the objective was to define the precision over this measurement range. More data points were obtained for amounts of ZnO where surface areas approached the BET instrument background (established in blank runs) or 0.02 m^2 .

Results are shown in Table 4 for (1) the measured surface areas and (2) the surface areas calculated from the masses of ZnO used and the ZnO specific surface area furnished by the vendor. The same data have been plotted in Fig. 8.

These results show a precision of about $\pm 6\%$ if the single point of 0.05 m² is excluded. (This exclusion might be justified since the BET instrument background correction of 0.02 m², applied to all points, is a $\sim 30\%$ correction for this one datum point.) This precision is the same as the given specific surface area uncertainty of $\pm 5\%$. Hence, it is concluded that BET precision is $\pm 6\%$ when measuring surface areas of ZnO over the range of 0.1 to $4 m^2$.

Sam	ple	Surfac	Calculated	
ID	Mass, g	Calculated, ^a m ²	Measured, ^b	Deviation, ^C %
121-2	0.093	0.059	0.05	-17
121-9	0.16	0.10	0.10	0
121-3	0.24	0.15	0.14	-7
121-10	0.32	0.20	0.20	0
121-1 1	0.49	0.31	0.31	0
122-5	0.79	0.50	0.48	-4
122-6	1.08	0.64	0.65	+2
121-4	1.59	1.0	0.94	-6
-	6.04	3.81 ± 0.18	3.84	+2
				-3 ± 6 average

Table 4. Comparison of Measured BET Surface Area with Calculated Geometric Surface Areas for ZnO to Establish Precision

^aCalculated surface area based on measured mass and vendor-supplied specific surface area of 0.63 \pm 0.03 m²/g.

b. Measured with Micrometrics model 2100D BET device, using krypton; background of 0.02 m² subtracted from all runs.

c(Measured minus calculated) divided by calculated, times 100.

To provide another estimate of the precision of determining BET surface areas, two Pyrex specimens (3.8-cm OD x 6.3 cm long), identified as samples 108-A and 108-B, were each impacted in a separate test with an energy of 181 J (2.4 J/cm³ energy density) in the sealed drop-weight chamber. fragments were collected, using dry transfers, and were sieved. The Two size fractions collected from specimen 108 A (165.8 g total initial specimen) were a size fraction smaller than 125 μ m (labeled 108 A-1) and a size fraction larger than 125 μ m but smaller than 500 μ m (labeled 108 A-2). These two size fractions were then measured by BET analyses by R. Malewicki of the Chemical Engineering Division-Analytical Chemistry Laboratory (CEN-ACL), after which they were removed from the CEN-ACL BET tubes, loaded directly into bottles, and sent offsite to Micrometrics for independent BET measurements to establish that site's measurements of the BET surface areas of these samples. The two size fractions from specimen 108-B (158.2 g total initial specimen) were labeled 108 B-1 (<125 µm) and 108 B-2 (>125 µm but <500 µm).



Fig. 8. Correlation of Measured BET Surface Area of Zinc Oxide Powder with Geometric Calculated Surface Area to Establish Precision of BET Measurements

The results of these measurements are shown in Table 5. The Micrometrics measurements (108 A-1R and 108 A-2R) were done on different sample masses from those of CEN-ACL (108 A-1 and 108 A-2). The resulting measured specific surface areas and sample masses were used to calculate comparable surface areas (assuming that representative samples were taken). Surface areas of the total specimens are compared in the extreme right-hand column of Comparison of the ANL and Micrometric surface areas shows that the Table 5. two size fractions agree within %3% for the larger size fraction and within 76% for the smaller size fraction. This comparison is also a measure of the precision of performing BET measurements at different sites with the same model of BET instrument. However, the uncertainties related to whether representative samples were obtained, when the entire sample was not measured, do not permit firm conclusions. The use of either of the glasses discussed below in Section II.C.2.d or the ZnO (described above) gives better, more direct measures of the precision of BET measurement. However, it is gratifying that these two results for Pyrex agree and that the precision is within the same %6% established from the ZnO measurements.

The Micrometrics BET measurements for specimens 108 B-1 and 108 B-2 also are shown in Table 5. If the two separate 2.4 J/cm^3 impacts and the particle collection methods at the two sites were reproducible, run 108 A-1

	Site ^a	Sample Measured ^b						
Specimen		Mass, g	Specific Surface Area, $\frac{m^2}{g}$	Surface Area, ^c m ²	Total Sp S Mass, g	Specim Surfa Area, m ²	en Values ce c	
Size <125 µm								
108 A-1R	Micro	2.176	0.21	0.46	2.263	0.48	0.51±0.03d	Avg
108 A-1	ANL	2.249	0.24	0.54	2.263	0.54		
108 B-1	Micro	2.194	0.27	0.59	2.3116	0.62		
Size <500 µm,	>125 µm							
108 A-2R	Micro	3.180	0.044	0.14	8.291	0.37	7 0.36±0.01 ^d 6	Avg
108 A-2	ANL	8.304	0.043	0.36	8.291	0.36		
108 B-2	Micro	2.69	0.041	0.11	7.968	0.33		

Table 5. BET Surface Area Results for Pyrex Specimens (3.8-cm OD × 6.3 cm long) Impacted with 181 I (2.4 J/cm³).

^aThe site performing a BET measurements using krypton was either Micrometrics (Micro) or the Analytical Chemistry Laboratory of this Division.

^bFor some samples, only a part was measured. The actual sample sizes and their specific surface areas are given. From these, surface area may be calculated.

^cIncludes a background subtraction of 0.01 m^2 from Micrometrics values and a 0.02 m^2 subtraction from ANL values.

^dThe same material from an impacted specimen was measured at two different sites; comparison of results showed that results agreed within ±6% or ±3%.

surface area should agree with that of run 108 B-1 (likewise for runs 108 A-2 and 108 B-2). However, there is an apparent 15% disagreement when these comparisons are made. This type of comparison has less dependence on good sieving separation but is still dependent on the impact test itself. From these results, it is concluded that the two separate impact tests generated the same surface area within about $\pm 12\%$ for all fragments collected that are smaller than 500 μ m.

Estimates of the precision were also made by performing repeated measurements of the same material in the same BET tube, on different days, employing no sample transfers; the BET operators were not informed of the replications. The precision of BET measurements was found to be ±2% for samples with 1 m^2 and 4 m^2 surface areas. Such a precision is claimed also by the BET instrument manufacturer. This precision is smaller than 16%, determined with the ZnO powder over a much wider range of surface areas, <u>i.e.</u>, 0.1 m^2 to 3 m^2 . However, the quoted uncertainty in the ZnO specific surface area itself was ±5%, which means that a ±2% precision may be achievable in BET measurements.

d. Other Materials Examined For Surface Area Calibration Correlations

Glass beads (NBS Standard reference material 1003) in the size range 5-30 μ m were procured from the National Bureau of Standards (NBS). The microscopically characterized glass beads were intended for calibrating equipment and methods for sizing particles in the range, 5-30 μ m. The use of these beads for BET measurements is not recommended by the NBS. However, these beads were studied by BET measurements since they represented a source of glass fragments whose shapes are somewhat geometrically characterized. Of the beads, 96% were stated to be spheres, with an average specific gravity of 2.39 ± 0.01 g/cm³. The specific surface area based on NBS microscopic measurements was stated to be 0.173 ± 0.005 m²/g, and there were between 500,000 and 600,000 beads per milligram. Some of the beads contained gas voids (<u>i.e.</u>, were partially hollow) according to the NBS literature.

Eight samples weighing from 0.7 to 18 g were put into standard BET tubes, and their surface areas were measured. The calculated surface areas (based on the NBS specific surface area provided) ranged from 0.1 m^2 to 3 m^2 .

SEM examinations of this material revealed that many spheres were hollow and broken, perhaps as a result of the thermal cycling used in the BET measurements (i.e., heating to outgas and cooling with liquid nitrogen). The SEM observations are consistent with (1) larger BET surface areas than would be based on the single NBS specific area value and (2) a larger deviation than that determined for the uniform microspheres described in subsection a above.

These BET data did not allow any final determination to be made on the accuracy of the BET measurements. A linear correlation was established over the entire measured range of 0.1 m^2 to 3 m^2 , but the BET-measured surface areas were consistently $\sqrt{30-40\%}$ larger than the calculated geometric surface areas.

Reportedly spherical glass beads of optical glass were procured from Potters Industries. They were type "H" series spheres of sizes -200 mesh or <75 μ m (stock No. H-002). The density of the beads was 4.493 g/cm³. The beads were mechanically sieved into three size fractions of 20-30 μ m, 45-53 μ m, and 63-75 μ m. The corresponding specific surface areas were calculated from average diameters of these three size fractions as 0.054 m²/g, 0.0276 m²/g and 0.0196 m²/g, respectively.

Different masses of these different fractions of sieved glass beads were then weighed out and loaded into standard BET tubes for surface area measurements. The 20-30 µm spheres were measured to have surface areas ranging from 0.1 m² to 0.9 m². The measured BET surface areas were uniformly larger (an average of 12 \pm 3% larger) than the values based on the calculated (geometric) specific surface areas.

In the measurements of various quantities of 45-53 μ m spheres, the surface areas range from 0.1 m² to vl.3 m²; krypton was used for the BET determinations. The results show that the BET surface areas are consistently v30% larger than the geometrically calculated surface areas and are uniform over this entire range.

There were only two samples of 63-75 μ m fraction beads, one of 0.1 m² and one of 0.6 m². These limited data gave measured BET surface areas $\sim 60\%$ larger than the geometrically calculated surface areas.

From microscopic observations, broken and undersize beads were observed in all three size fractions. In the 20-30 μ m size fraction sample, v8% by number count were either broken or undersize. In the 45-53 μ m size fraction sample, v28% by number count were either broken or undersize. Such an observation is consistent with the smaller deviation from the calculated surface areas for the 20-30 μ m sizes (±12%) than for the 45-53 μ m sizes (±30%).

From all of these data, it is concluded that the BET measurements are consistently larger than the geometrically calculated surface areas by 12 to 60%, depending on the size fraction examined. Microscopic examinations show the smaller size fractions having the smallest deviations.

e. Summary and Conclusions

BET surface area measurements were performed on glass samples of reasonably well-characterized geometric shapes and with geometric surface areas of 0.1 m² to 4 m². The BET surface areas were consistently higher by about 10 to 30% than the geometrically calculated surface areas, depending upon the material. Smooth linear correlations of BET-measured surface areas with calculated geometric surface areas were observed. The precision of determining BET surface areas in the above range was measured to be ± 2 to 6% (i.e., better than $\pm 6\%$ and perhaps as good as $\pm 2\%$). The accuracy of performing BET measurements could not be defined because of the lack of standards. However, the results for three of the materials, based on the suppliers' material characterizations, coupled with our microscopic characterizations of the materials, indicate that the accuracy is probably in the range of ± 10 to 20%.

It is concluded that the CEN-ACL Micrometrics Model 2100D BET device using krypton adsorbate performs BET surface area measurements to a precision of ± 2 to 6% on glass samples having total surface areas ranging from 0.1 m² to 4 m².

D. Reference Test Conditions--Material Properties Comparisons

For the purpose of facilitating comparisons of material properties of simulated waste forms, a set of standardized impact test conditions was defined and used in some experiments. Only a minimum of variables were selected for the standardization because of the limited availability of many test materials. The reference test conditions specified were: an impact
weight of 9.9 kg; 2.54-cm (1-in.) specimen OD; specimen length to diameter ratio of about unity; diametral impact configurations; and input energy density of 10 J/cm³ (<u>i.e.</u>, calculated maximum impact energy per specimen volume). The height of fall of the 9.9-kg weight was varied according to the actual specimen size so as to provide an energy density of 10 J/cm³. The impact velocity was about 1 m/s.

The procedures used to characterize the impact fragments and the methods of analysis for particle size distribution and surface area are described above.

III. RESULTS

Impact tests reported here are focused on defining some of the material properties of alternative waste forms. To narrow the field of possible experimental measurements, two measurable responses of materials properties were assumed to be of most interest for waste management applications. These two responses are (1) the particle size distributions of the impact fragments, with emphasis on the respirable sizes (i.e., <10 μ m) and (2) the surface area of the fragments (for potential water leaching scenarios). A previous report [MECHAM, ANL-81-27] summarizes the literature pertaining to impact tests for waste management applications and to the dynamic brittle fracture process. In addition, the results of some initial impact tests of laboratory-scale Pyrex, quartz, UO₂, nepheline syenite and sandstone specimens were reported.

One objective of the experiments reported here was to perform comparative measurements of different materials and waste forms, using a set of standardized test conditions. Standardized test conditions (as defined in Section II.D) were used to minimize many sources of unknown errors and to help produce a data set from which initial comparative rankings of performance could be made based on the two measurable responses. An impact test on coal was performed (Appendix A) to examine the applicability of the impact test conditions described above to brittle materials of other Division programs.

A limited number of comparative impact tests of borosilicate glass and SYNROC were also done using a set of impact test conditions that differed from that used by the Australians [RAMM]. The effects of using test conditions other than the standardized conditions are reported in Section III.B below.

A. Particle Size Distributions--Reference Test Conditions

The cumulative size data of measured fragments from all impact tests were analyzed and fit with a lognormal distribution, using a computer regression analysis. The results are summarized in Table 6 and are shown graphically in Fig. 9. All materials were found to have fracture particulate sizes that are accurately described by a lognormal size distribution over the measured size range of ~ 5 to 2000 µm, as illustrated by the linear fit of the data over the entire range. The fracture particles smaller than 2000 µm contain >95% of the total surface area and so the departure from linearity for particles larger than 2000 µm has no practical consequence.

						Partic Distri Lognormal	le-Size bution: Parameters	
		Size Spec:	of Cylind imen Impac	lrical ted	Total	Mean Diameter	Standard	Fracture Particles:
Material	Source Laboratory	Dia, mm	Length,	Mass, g	Energy, J	Drameter, Dg, mm	Deviation, ^o g	Respirable Size Fraction, wt % ^b
Glasses								
SRL 131 (1)	SRL	25.5	27	39.7	146	2.6 ± 0.4	6.4 ± 0.2	0.14 ± 0.02
SRL 131 (2)	SRL	25.4	29.1	40.7	148	2.6 ± 0.2	6.6 ± 0.4	0.18 ± 0.05
High silica	CU	28.1	28.9	47.2	178	3.7 ± 0.7	8.5 ± 0.3	0.29 ± 0.03
Alkoxide	WE ST	25.7	25.4	33.2	131	2.2 ± 0.6	7.0 ± 0.3	0.27 ± 0.05
PNI. 76-68	PNL	25.4	25.2	37.7	128	2.3 ± 0.3	6.5 ± 0.3	0.17 ± 0.04
Pyrex	ANL	25.0	25.8	28,0	127	1.4 ± 0.2	6.0 ± 0.2	0.27 ± 0.03
Ceramics								
SYNROC B	LLL	26.8	25.9	60.5	146	4.2 ± 0.8	7.6 ± 0.3	0.15 ± 0.02
SYNROC D	LLL	25.4	27.3	53.5	138	4.7 ± 0.7	8.1 ± 0.3	0.16 ± 0.02
SYNROC C ANL (1)	ANL	20.7	20.4	29.9	69	6.4 ± 2.4	8.2 ± 0.5	0.15 ± 0.03
SYNROC C ANL (2)	ANL	20.7	19.9	28.4	67	10 ± 3	9.6 ± 0.9	0.13 ± 0.03
Tailored	ROCK	26.8	18.2	40.8	102	13.7 ± 2.1	9.3 ± 0.3	0.06 ± 0.01
Concrete								
FUETAP	ORNL	25.4	25.5	23.0	131	2.3 ± 0.3	7.9 ± 0.2	0.43 ± 0.04

Table 6. Summary of Results of Standardized Comparative Impact Tests^a at Constant Input Energy Density of 10 J/cm³

^aA further description of materials and test conditions is given in the text.

^bThis is the cumulative weight percent (\leq 10 µm in diameter) of the initial specimen mass.



Fig. 9. Computer Regression Analysis Plots of P(%), the Cumulative Lognormal Mass Distributions (in mass percent of initial specimen mass) of Fragments vs D(m), the Measured Fragment Diameters from 10 J/cm³ Impact Tests of (1) Glasses (Upper Plot) and (2) Crystalline Ceramic and Concrete Simulated Waste Forms (Lower Plot). The shaded areas correspond to potentially respirable particles (i.e., (10 um)

The amount of respirable particles (<10 μ m) and the standard computer fitting errors are shown in the rightmost column of Table 6. The two parameters describing the lognormal distribution, <u>i.e.</u>, the standard deviation σ_g and the geometric mean diameter D_p , are also given in Table 6.

Two different groupings ($\sqrt{0.15}$ and 0.3 wt %) of respirable sizes were observed for the glasses, as summarized in Fig. 10. The SRL 131 and PNL 76-68 glasses resulted in the same quantities of respirable particles (about 0.15 wt %) which were about one-half those of the high-silica, alkoxide, or Pyrex glasses at $\sqrt{0.3}$ wt %. Duplicate runs of the SRL 131 glass provided an estimate of the precision of the method--about 30%.

Two different groupings (0.06 and 0.15 wt %) were also observed for the crystalline ceramics, as summarized in Fig. 11. The quantity of tailored ceramic respirable materials (0.06 wt %) was a factor of two lower than for either the SYNROC or glasses. The four SYNROC specimens resulted in the same quantity of respirable sizes; this implied that the quantity of respirable particles was independent of composition, processing parameters, and modest specimen size variations. Such observations, in addition to independence of grain size, were also reported by [RAMM] for similar impact tests of smaller specimens but at an energy density of $\sqrt{140} \text{ J/cm}^3$.

Tests of two ANL SYNROC C specimens were used to estimate test reproducibility; it was $\sim 20\%$. The SYNROC results were essentially the same as those measured for the SRL 131 and PNL 76-68 waste glasses.



Fig. 10. Summary of Respirable Fines Produced for Glasses at Impact Energy Density of 10 J/cm³



Fig. 11. Summary of Respirable Fines Produced for Ceramics at Impact Energy Density of 10 J/cm³

Of the materials tested, the FUETAP concrete produced the largest amount of respirable particles (~0.4 wt %), but this quantity was only a factor of two higher than the quantities for SYNROC or glass waste forms.

A summary of the production of respirable sizes for all alternative waste forms is shown in Fig. 12.

Preselected standardized test conditions (described above) were used to facilitate comparison of results. Specimen sizes varied slightly (because of limited availability of materials), but the impact energy density was held constant at 10 J/cm³. Such conditions were selected a priori from previous test experience in order to generate measurable masses and surface areas.

The standardized diametral impact tests at the same impact energy per specimen volume provided a direct comparison of properties of the materials tested. Tests showed that SRL 131 and PNL 76-68 glasses, SYNROC B, SYNROC C, and SYNROC D ceramics generated the same mass fraction of respirable material. The tailored ceramic waste form generated four-tenths as much respirable material. The mass fraction of respirable material generated by the FUETAP waste form was 2 1/2 times the mass fraction generated by the SRL 131 and PNL 76-68 glasses or the SYNROC. The alkoxide, high-silica, and Pyrex glasses generated about 50% larger mass fractions of respirable material than did the SRL 131 or PNL 76-68 glasses. All impact fragments were found to follow lognormal particle size distributions. The quantity of respirable sizes was not strongly dependent on the brittle material tested. Such results



Fig. 12. Summary of Respirable Fines Produced for All Alternative Waste Forms at 10 J/cm³. Comparative Impact Tests. Note: SYNROCS MSD1 and MSD2 are identified as SYNROC C ANL (1) and (2) in Table 6.

suggest it may be possible to characterize and model one waste form to establish a brittle fracture methodology and data base that are also applicable to other brittle waste forms with similar mechanical properties.

Some diametral tests were done with (2.5-cm-OD x 2.5-cm-long) SRL 131 and Pyrex glass specimens at three different energy densities other than 10 J/cm³ to examine the sensitivity and variation of the respirable sizes and lognormal parameters at other than the standardized conditions. The results, obtained by the same characterization procedures and computer analyses as are discussed above, are given in Table 7 and Figs. 13 and 14. The respirable fraction increased linearly as the energy density was increased. Pyrex seemed to consistently generate more material of respirable size than did the SRL 131 glass. Such observations may be associated with the elastic properties of the materials and the impact loading failure mechanisms. Error bars are from the computer regression analysis of the respirable fraction from particle size data in a single test. The datum point for Pyrex at 1.2 J/cm^3 probably reflects the variability of physical effects at low energy density (near threshold for fracture); additional tests would be necessary to determine statistical significance.

The mass mean diameter, D_g , decreased linearly as the energy density was increased and was essentially the same for Pyrex and SRL 131 glass (Fig 14).

Glass Material	Energy Density, J/cm ³	D _g ,	σg	Respirable Fraction (<10 µm), wt X
SRL 131	10	2.7 ± 0.6	6.8 ± 0.4	0.16 ± 0.05
	5	5.4 ± 1.7	6.1 ± 0.4	0.087 ± 0.018
	2.4	5.0 ± 1.7	7.5 ± 0.5	0.031 ± 0.008
	1.2	9.5 ± 2.5	6.7 ± 0.4	0.016 ± 0.004
Pyrex	10	1.7 ± 0.5	6.3 ± 0.4	0.27 ± 0.04
	5	3.4 ± 0.7	6.7 ± 0.4	0.11 ± 0.02
	2.4	6.9 ± 1.4	7.3 ± 0.5	0.052 ± 0.007
	1.2	11.0 ± 3.0	8.7 ± 0.5	0.067 ± 0.010

Table 7. Variation of Fraction of Respirable Particles and Lognormal Parameters with Energy Density. Specimen Size: ~25-mm OD x 25 mm



Fig. 13.

Plot of Respirable Sizes (in weight percent of initial specimen mass) for Impact Tests of Pyrex and SRL 131 Glass Specimens as Function of Impact Test Energy Density.



Fig. 14.

Variation of Two Lognormal Parameters, D_g and σ_g , with Energy Density of Specimens

The standard deviation remained relatively constant and independent of type of material over the range of energy densities used. Extrapolation of these laboratory-scale results to larger waste forms cannot currently be justified because of the lack of proven scaling laws. However, the results from such standardized tests are assumed to be useful for comparing properties of the materials.

When the consequences of generating respirable particles are further assessed, the waste loading in a given waste form must also be considered. For example, for a given accident scenario, waste forms with higher waste loadings may pose more of a hazard than those with lower loadings if each generates the same amount of respirable particles.

To summarize, with increasing impact energy density, the absolute amounts of respirable particles were found to increase linearly while the mass mean diameter of the lognormal distribution decreased. The standard deviation remained fairly constant. However, scaling laws have not been established for extrapolation of these laboratory test results to full-scale waste forms.

B. Particle Size Distributions-Other Test Conditions

Experiments were also done to obtain data that could be compared with the results reported for the brittle fracture of SYNROC in a paper by [RAMM]. In that work, the authors axially impacted 12.5-mm-dia by 12.5-mm-long specimens (various forms of SYNROC and waste glass), using a hardened steel punch-and-die device of a type used by PNL [BUNNELL] with a total impact energy of 217 J. This corresponds to an energy density of 141 J/cm^3 . The higher energy density, different impact chamber, and smaller specimen size represent test conditions guite different from those used in the experiments reported above. The method of preparing the specimens varied with respect to the presence or absence of simulated waste, the use of hot pressing or sintering, and the use of an air or a CO/CO₂ atmosphere during sintering. Scanning electron micrographs were used to obtain an estimate of the grain size in the specimens and to check for grain boundary or transgranular fracture in the fragments. Size analyses of the fragments were obtained by the use of sieves for particles larger than 63-um sieve size and the use of a Sharples micromerograph (a Stoke's law sedimentation apparatus) for particles smaller than 63 µm.

The conclusion of the studies by Ramm and Ferenczy was that the impact behavior of SYNROC is insensitive to the presence or absence of simulated waste, the sintering atmosphere, and the annealing time, as well as grain size variation within the range, 4 to 34 μ m. Neither fracture at the grain boundary nor transgranular fracture predominated.

The particle size distributions for three types of SYNROC (SYN 1, SYN 2, and SYN 3) were presented graphically in their paper [RAMM]. These plots were read to two significant figures. The data are replotted on lognormal coordinates in Fig. 15 with a computer regression analysis. The computer fit parameters are given in Table 8. A better lognormal fit was obtained when the two points representing the largest-size particles, 1 and 2 mm, were excluded from the linear regression. The lognormal analysis was based on eight data points in the range of 5 to 500 µm. From Fig. 15, it appears that the size distributions of the fracture particulate of the two sintered specimens were in very close agreement, showing that there was no effect of waste addition. The hot-pressed material (containing no waste) had a significantly different fracture behavior, showing a higher impact resistance, as indicated by the smaller amount of respirable-size particles (Table 8). By extrapolation of data for Pyrex and SRL 131 glass in Fig. 13, it is estimated that the impact strength of these two glasses (as measured by the amount of respirable-size particles) is about the same as that of SYNROC.

To examine these results further, the brittle fracture characteristics of four materials in the form of 1.25-cm (0.5-in.) diameter by 1.25 cm (0.5 in.) long cylinders were measured in the laboratory with our impact chamber. The measurements were made on (1) Pyrex cut from an annealed Pyrex rod; (2) Savannah River Laboratory frit, SRL 131 simulated waste glass; (3) SYNROC B from Lawrence Livermore Laboratory (LLL), a ceramic waste form, free of waste; and (4) SYNROC D from LLL, the same waste form as SYNROC B, but with added



Fig. 15. Cumulative Volume Fractions of Particles (Australian SYNROC Data), Replotted on Lognormal Coordinates [RAMM]

Table 8. Lognormal Analysis of Three Types of Australian SYNROC 12.5-mm x 12.5-mm Cylinders Impacted Axially at 141 J/cm³

	1250°C, Hot-Pressed; No Waste Added; SYN 1	1300°C, Sintered in CO-CO ₂ ; No Waste Added; SYN 2	1300°C, Sintered in CO-CO2; 10% Waste Added; SYN 3
D _g , mm	0.41 ± 0.14	0.65 ± 0.22	0.66 ± 0.48
σg	4.8 ± 0.2	7.3 ± 0.4	7.4 ± 0.9
Respirable Fraction,			
P _V (<10 μm)	0.91 ± 0.24	1.8 ± 0.4	1.8 ± 0.8

synthetic waste including uranium. Compositions were given in Table 1. The specimens were impacted diametrally inside a bellows-sealed chamber. The particles were washed from the chamber with water onto either 90- or $63-\mu m$ sieves. The particles passing through the sieves were analyzed for size in the size range, 4 to 102 μm , using a Counter counter; the material remaining on the sieve was dried in a vacuum oven and size-analyzed by sieving. The results of computer regression analyses of the particle size analyses are plotted in Fig. 16 and are summarized in Table 9.



Fig. 16. Diametral Impact in ANL Impact Chamber of 1.3-cm-OD × 1.3-cm-Long Specimens at 141 J/cm³ of SYNROC, SRL 131 Simulated Waste Glass, and a Pyrex Standard

Further comparisons of our results with the independent Australian results are given in Table 10. The results of impact studies on hot-pressed SYNROC conducted here and in Australia are in remarkable agreement. The extent of the agreement perhaps should not be overly surprising, however, when account is taken of the fact that the tests were made with very similar apparatus, the specimen sizes were the same, and the calculated impact energy was the same. One major difference between the two sets of experiments was that the fine particles were measured by different techniques: our (ANL) method utilized the Coulter counter; theirs (AAEC) utilized the Sharpes micromerograph.

C. Surface Areas Generated in Impact Tests

Another measurable response of major interest in relation to the impact resistance of brittle materials and waste forms is the surface area of the

···	d	Impact Fper		Lognormal Pa	arameters ^C	Respirable Size ^d (<10 μm),	
Material	Size	Mass, g	Impact Energy, ^a J	Density,b J/cm ³	D _g , mm	σ _g	wt % ^e
Pyrex	12.65-mm OD × 13.33 mm	3.716	236	141	0.18 ± 0.02	4.7 ± 1	3.2 ± 0.2
SRL 131 Glassf	12.78-mm OD × 12.70 mm	4.465	230	141	0.32 ± 0.08	5.2 ± 0.2	1.7 ± 0.3
SNYROC BS	12.78-mm OD × 13.96 mm	7.422	253	141	0.59 ± 0.05	5.4 ± 0.1	0.76 ± 0.1
SYNROC D ^h	12.84-mm OD × 13.14 mm	6.693	240	141	0.52 ± 0.03	5.9 ± 0.1	1.2 ± 0.1

Table 9. High-Energy-Density Impact Tests at ANL of Four Brittle Materials--Diametral Impacts

^aImpact energy is maximum available, as delivered by dropping a v9.9 kg weight onto a sealed chamber from a v1.3-m height.

^bEnergy density calculated from the maximum available impact energy and the initial specimen dimensions.

^cLognormal parameters of fracture particulates obtained by computer regression analysis of measured particle size data. D_g is mass mean diameter and σ_g is geometric standard deviation of measured particle size distribution. Errors are from best fit of data with a regression analysis.

dRespirable size is arbitrarily defined for this study as the amount of all cumulative particles smaller than 10-µm diameter as measured by Coulter counter and mechanical sieving procedures.

eValue is obtained from computer analysis of data from one impacted specimen and is illustrated by data in Fig. 22 (presented in a later section of this report). The wt % refers to the total initial specimen mass.

^fSRL frit 131 specimens (28 wt% simulated waste) were core-drilled from an annealed piece of SRL 131 simulated waste glass that had been remelted.

SSYNROC B (containing no waste) was core-drilled from a bulk piece supplied. Density was reported to be 4.2 g/cm³ (96% T.D.).

hSYNROC D (containing 64 wt% waste) was core-drilled from a bulk piece by LLL. Density was reported to be 3.96 g/cm³ (99% T.D.).

Specimen		Prep. Conditions	D _g , am	σg	<10 µm, wt %
ANL					
SNYROC B		(LLL Hot Pressed)	0.59	5.4	0.8 ± 0.1
SYNROC D		(LLL Hot Pressed)	0.52	5.9	1.2 ± 0.1
SRL 131		-	0.32	5.2	1.7 ± 0.3
Pyrex		(Standard)	0.18	4.7	3.1 ± 0.2
AAEC					
SYNROC)		(Hot Pressed)	0.41	4.8	0.9 ± 0.2
SYNROC	w/o Waste	(CO/CO ₂ Sintered)	0.65	7.3	1.8 ± 0.4
SYNROC)		(Air Sintered)			2.04
SYNROC		(Hot Pressed)			1.1 ^a
SYNROC	w/waste	(CO/CO ₂ Sintered)	0.7	7.4	1.8 ± 0.8

Table 10.	Comparison of the Results of Impact Tests at ANL with those of	
	[RAMM] (Australia, AAEC) under Conditions of 140 J/cm ³ Impact	
	Energy and 12.5-mm-OD x 12.5-mm Sample Size	

^aObtained directly from a table in [RAMM].

fragments produced by an impact. To characterize this effect, a series of impact tests were performed on specimens of simulated waste SRL 131, Westinghouse alkoxide glass, PNL 76-68 glass, and Pyrex. After impact in the same sealed impact chamber as was used in other tests, fragments were collected using dry techniques, and all fragments ≤ 2 mm were transferred into standard 15-cm³ BET tubes for surface area measurements.

Results of the measured BET surface areas for three different sizes of specimens of these materials at different total impact energies (or energy densities) are summarized in Table 11. Only fragments passing through 2-mm sieves were put into BET tubes. The fractions of the surface area associated with fragments ≥ 2 mm were not measured. However, these missing fractions of surface area were determined from the lognormal parameters obtained from particle size measurements of other specimens under the same test conditions, and the fractions (1.e., "factors") of the areas associated with the fragments ≥ 2 mm were estimated to be generally less than 10% of the total surface area, except for the lower energy density tests, and were used to calculate the "corrected"

Specimen		Calculated	BET Surface Area				
Size	Identification	Material	Energy Density, ^b J/cm ³	Total J	Measured, m ²	Factor ^C	Corrected,d m ²
1-in.	OD x 1 in.:						
	133	Pyrex	1.2	16	0.12	0.82	0.15
	Z92A	SRL 131	1.2	16	0.10	0.82	0.12
	134	Pyrex	2.4	32	0.28	0.91	0.31
	Z89	SRL 131	2.4	32	0.20	0.91	0.22
	135	Pyrex	5	64	0.51	0.95	0.54
	Z88	SRL 131	5	64	0.33	0.95	0.35
	136	Pyrex	10	130	0.78	0.97	0.80
	Z96	Pyrex	10	125	1.02	0.97	1.05
	Z76A	Pyrex	10	125	1.04	0.97	1.07
	Z76B	SRL 131	10	151	0.74	0.97	0.76
	Z92B	SRL 131	10	128	0.60	0.97	0.62
	Z92C	SRL 131	10 ^e	121	0.55e	0.97 ^e	0.57e
	Z85	alkoxide	10	130	0.76	0.97	0.78
	Z81	PNL 76-68	10	130	0.67	0.97	0.69
	107AB	SYNROC B	10	146	0.87	0.97	0.90
	107CD	SYNROC D	10	107	7.47	0.97	7.7
	110AB	SYNROC D	10	109	7.36	0.97	7.6

Table 11. Summary of BET-Measured Surface Areas of Impacted Pyrex, Simulated Waste Glasses, and SYNROC Ceramics

Specimen		Calculated	BET Surface Area				
Size	Identification	Material	Energy Density,b J/cm ³	Total J	Me as used, m^2	Factor ^c	Corrected, ^d
1 1/2	in. OD x 2 1/2 in	•:					
	132	Pyrex	0.21	15	Did	not break	
	131	Pyrex	0.43	32	0.33	0.7	0.47
	125	Pyrex	1.2	90	0.57	0.82	0.70
	126	Pyrex	1.2	90	0.58	0.82	0.70
	Z102AB	Pyrex	1.2	88	0 .76	0.82	0.93
	Z100ABC	SRL 131	1.2	84	0.48	0 . 82	0.59
	127	Pyrex	2.4	180	1.36	0.9	1.5
	Z102CDE	Pyrex	2.4	177	1.17	0.9	1.3
	297AB	SRL 131	2.4	170	0.98	0.9	1.08
1/2-in	• OD x l in.:						
	137	Pyrex	10	32	0.22	97	0.23
	138	Pyrex	50	161	0.81	99	0.81
	129	Pyrex	100	319	1.45	99	1.45

Table 11. (contd)

^aCalculated from height and mass of drop-weight.

^bCalculated from measured specimen volume and calculated impact energy.

^CThis is the fraction of cumulative surface area for all fragments <2 mm, based on lognormal parameters obtained from measured cumulative mass distributions of fragments.

^dSince only fragments passing a 2-mm sieve were measured in the BET surface area device, the measured BET surface area were corrected using the fractions calculated from lognormal parameters.

This is the best estimate of the surface area of the fracture fragments.

^eThis was an axial impact test; all others were diametral impacts.

total BET surfacea areas for all fragments, as shown in the rightmost column of Table 11; the latter surface areas are assumed to best represent the total surface areas generated in the impact tests.

Plotted in Fig. 17 are the corrected surface areas from Table 11 of the $25-mm-OD \times 25-mm-long$ specimens. These results show that the surface area increases relatively smoothly with increasing impact energy. The results for Pyrex and SRL 131 bound all the measured surface areas. The surface area increases for SRL 131 glass are $\sim 20-30\%$ less than for Pyrex over the eightfold energy range tested. Previous measurements showed that SRL 131 waste glass generated only $\sim 50-60\%$ as much respirable particles as Pyrex did. The alkoxide and PNL 76-68 waste glasses also generated $\sim 20-30\%$ less surface area than did Pyrex (or essentially the same amount of surface area as SRL 131 glass) at the 10 J/cm³ standard test conditions. Impact of the SYNROC B ceramic may have produced slightly more surface area than did impact of the waste glasses, but less surface area was produced than by Pyrex.



Fig. 17. Measured BET Surface Areas vs Impact Energy for 25-mm-OD x 25-mm-Long Specimens of Various Materials. The alkoxide, PNL 76-68, and the SYNROC B each have only one datum point.

The two SYNROC D specimens listed in Table 11 represent a special case and are not plotted in Fig. 17. In two tests with SYNROC D specimens, surface areas were eightfold those produced by a SYNROC B specimen and by the simulated glass waste forms.

SEM examinations were made of fragments of both SYNROC D and SYNROC B from the BET tests. The fracture surfaces of SYNROC D fragments of 100 μm

were noticeably rougher, and seemingly more porous, than the SYNROC B fragments. This observation is consistent with the BET measurements. The characterizations of the SYNROC (done by LLL) indicated that the SYNROC D material (LLL specimen S2OSO3a HP2A) had a relatively low density of 3.76 g/cm^3 (94% T.D.) while the SYNROC B material (LLL specimen Mll HP3A) had a higher density of 4.02 g/cm^3 (96% T.D.). These LLL characterizations are also comsistent with BET surface area measurements. Thus, it is concluded the high BET surface area measurements of the SYNROC D material occurred because of the lower density and higher porosity of the SYNROC D specimens.

Previously, particle size distributions were measured for SYNROC D (LLL specimen S2OSO3a HPIA) and SYNROC B (LLL specimen M11 HP3A) fragments. The SYNROC D material had a density of 3.95 g/cm^3 (99% T.D.), but no BET measurements were performed since only one specimen was available. The particle distribution measurements showed no difference of the SYNROC D and SYNROC B materials and were lognormal.

Plotted in Fig. 18 are the corrected BET surface areas for three different sizes of Pyrex specimens as a function of impact energy. Over the range tested, there is probably no significant difference between the 25-mm-OD x 25-mm and the 38-mm-OD x 63-mm specimens. However, the smaller (13-mm-OD x 25-mm) specimens may produce, for a given impact energy, less surface area than the larger specimens. Further tests are needed to establish any significant differences or definite patterns. It is concluded that the effect of the Pyrex specimen size studied does not introduce changes in the surface area of impact fragments by more than a factor of two for comparative impact tests in this size range.



Fig. 18. Measured BET Surface Areas vs Impact Energy for Pyrex Specimen of Sizes Indicated. (Specimen dimensions in inches.)

Figure 19 plots the measured BET surface area for two different sizes of Pyrex and SRL 131 glass as a function of impact energy. As is discussed for Fig. 17 for 25-mm-OD \times 25-mm specimens, for the larger (38-mm-OD \times 63-mm) specimens, SRL 131 glass produces, at a given impact energy, less surface area than does Pyrex. Further tests are needed to establish definite correlations.



Fig. 19. Measured BET Surface Areas <u>vs</u> Impact Energy for Two Different Sizes of Pyrex and SRL 131 Glass Specimens. (Specimen dimensions in inches.)

D. Comparison of Axial and Diametral Impacts

The standard drop-weight impact test consisted of a diametral impact of a cylindrical specimen with an approximately 10-kg dropped weight at an energy density of 10 J/cm³. An axial impact test (PD106A) of a Pyrex specimen was made under otherwise identical conditions, and the fracture particulates were measured in the standard manner by sieving and Coulter counter analyses, in addition to some BET surface-area measurements. The objective of this work was to determine if any significantly different results could be obtained for different impact configurations. To allow comparison, the results for an axial impact test of a 2.5-cm-dia \times 2.5-cm-long specimen are shown in Table 12, along with results of two diametral impacts. The values of σ_g of the replicate diametral impacts agree within 10%, the D_g within about 25%, and the respirable fraction P_v(10 µm) within about 3%.

The two diametral impacts agree closely with each other with respect to particle size distribution. This can be seen from the plots of all three size

Parameter ^a	Axial (PD106A)	Diametral (PD128C)	Diametral (PD280/50-53)
Specimen Volume, cm ³	12.9	12.9	12.9
Input Energy, J	129	129	129
Mean Diameter, D _g , mm	1.1 ± 37%	2.1 ± 15%	1.6 ± 11%
Std. Deviation, og	5.6 ± 5%	6.9 ± 3%	6.3 ± 2%
Respirable Size Fraction, wt %	0.30 ± 27%	0.28 ± 10%	0.29 ± 8%
Mass Balance Loss			
ng wt X	189 0.67	163 0.56	165 0.6

Table 12. Particle Parameters for Axial and Diametral 10 J/cm³ Impacts of 2.5-cm by 2.5-cm Pyrex Specimens

^aD_g and σ_g determined for specimen volume using all data points for particle sizes between 8 µm and 1000 µm, inclusive.

distributions in Fig. 20; in this plot, only the data points for the axial test are shown; for the diametral impact tests, the previously fitted lines are shown.

For the axial impact test and the diametral tests, the parameters for the respirable fraction agree, but those for D_g and σ_g differ significantly (Table 12). Possibly, a more uniform initial stress distribution in the axially impacted specimen results in a smaller σ_g . More experiments are needed to resolve this issue.

E. Comparison of Impact Tests with and without Mechanical Stop

The Materials Characterization Center (MCC) at the Pacific Northwest Laboratory has proposed [MERZ] a standard drop-weight impact test, MCC-10, for brittle waste materials. The test proposes axial impaction of a specimen of well-defined cylindrical shape and size. In the absence of a mechanical stop, fracture may consist of two stages: (1) a primary impact compression fracture and (2) a secondary crushing stage due to just the mass of the dropped weight. For an impact test of type MCC-1, a mechanical stop is specified that prevents the dropped weight from coming to rest on the particles formed in impact fracture. The mechanical stop limits the maximum axial compression to ~30% of the height of the specimen and provides a narrow range of loading rates during the compression stage of impact. The specimen was specified to be ~12.7 mm in diameter and ~31.8 mm long. A massive tup (225 kg) dropped from a height of 30.5 cm is proposed to generate a large input energy and ensure fracture for even the strongest brittle material.



Fig. 20. Cumulative Volume Fractions and Surface Area Fractions for Axial (PD 106A) and Diametral (PD 128C and PD280/50-53) Impacts at 10 J/cm³ of 25-mm x 25-mm Pyrex Specimens

In our impact tests to examine the effects of using a mechanical stop, the standard 10 J/cm³ drop-weight apparatus was used to study impacts of 25-mm by 25-mm Pyrex cylinders. The mechanical stop allowed a maximum of 27% linear compression before stopping the 10-kg weight. The stop consisted of a 19-mm-long piece of 3-in. schedule 40 stainless pipe; the specimen was centered inside the stop and impacted axially. (Axial and diametral tests with no mechanical stop present are reported above.)

In our 10 J/cm^3 test, the calculated maximum dynamic compressive stress is 1.2×10^9 Pa, and the maximum force is 5.8×10^5 N. The gravitational force exerted by the mass of the dropped weight on the fragments is negligibly small: the force is 98 N for our 10-kg tup, though in the proposed MCC test, it would be proportionally higher for the >23 times more massive tup. The 10 J/cm^3 energy input limits the calculated compressive strain to 1.7%, which is far less than the $\sim 30\%$ compression provided by the mechanical stop. The ratio of gravity force (of just the weight of the tup) to maximum dynamic compressive force in a 10 J/cm³ impact is $98/(5.8 \times 10^5) = 1.7 \times 10^{-4}$ or 0.017%. Therefore, it is unlikely that crushing by gravity would alter the overall results of impact fracture. If some residual kinetic energy of the weight after fracture is allowed, such as the dropping of a 10-kg mass on the specimen from a height of 2.5 cm, this residual energy is ~2.5 J; this energy may be compared with the energy input of standard tests of 10 J/cm^3 , which is 129 J. This residual energy input is thus only about 2% of the total input energy. Therefore, a secondary crushing effect is not expected to be significant. It may also be assumed that compressed glass fractures explosively by the propagation of shock waves traveling at about 5000 m/s, so that fracture results do not depend on the loading rate for impacts of practical interest.

The particle size distributions for two axial impacts, one with and one without the stop, may be compared in Fig. 21; lognormal parameters for the particle-size data are summarized in Table 13. It appears that the absence of a stop does not affect the size of the respirable fraction nor does it



Fig. 21. Particle Size Distributions for 10 J/cm³ Axial Impacts of Pyrex with (PA1095) and without (PD106A) a Mechanical Stop

Parameter, unit	W1 thout Stop	With Stop		
Respirable fraction, wt %	0.30 ± 0.08	0.29 ± 0.09		
Standard deviation, og	5.6 ± 0.3	6.7 ± 0.5		
Geometric mean diameter (mass distribution) D _g , mm	1.1 ± 0.4	1.9 ± 0.8		
Mass balance loss				
ng vt X	189 0.67	49 0.17		

Table 13.	Lognormal	Parameters	for Axial	Impact	of	Pyrex	with	and
	without a	Mechanical	Stop					

make much difference in the lognormal parameters, D_g and σ_g . Additional replicated tests are required to further compare effects with a stop present and absent. However, it is not obvious that a stop is necessary since, in our tests, the stop did not make a significant difference in particle sizes (Table 13).

F. <u>Comparison of Six Alternative Methods of Measuring Small</u> Particle Size Distribution

To determine the extent to which measured particle size distributions are dependent upon specific measurement technique, portions of a sample of simulated-waste glass particles were sent to various laboratories for different methods of analysis. The results of these analyses were used to show discrepancies between the analyses obtained in various laboratories using different techniques. The primary objective was to determine if our particle size measurements (obtained using a Coulter counter) differ appreciably from those obtained by sedimentation rate measurements and other techniques. No significant differences would be expected between measurements made by various techniques if the particles measured were spherical. However, for particles of irregular shape such as our glass fragments, the results obtained by different techniques differ somewhat since the particles are not examined in the same way nor are exactly the same parameters measured.

A large sample of approximately 16 g of SRL 131 simulated-waste glass particles in the size range between 90 μ m and 1μ m was prepared by separately impacting at 10 J/cm³ in our sealed impact chamber ten specimens of waste glass in the form of cylinders 2.5 cm in diameter by 2.5 cm long. The particles were collected using dry techniques, combined in a single container, carefully mixed, then apportioned into six small vials, one for Coulter counter analysis in our laboratory and five for shipment to and analyses at various vendor laboratories. The results of these analyses were used to determine the extent of agreement or disagreement of techniques and to identify any systematic differences in size distributions reported that can be explained in terms of the specific measurement technique being used.

The five alternative methods to Coulter counter analysis are discussed below.

1. A micromerograph analyzer was used by the Val-Dell Company of Norristown, Pennsylvania. This method is based on Stoke's law of sedimentation velocity in gas. A sample of about 0.1 g is deagglomerated and allowed to fall through a 3-m column of nitrogen to an electronic servo-balance at the bottom. The relative size distribution of the sample is determined from the record of mass accumulation as a function of time. This method was also used to obtain the reported size distribution of the fracture particulate of Australian SYNROC [RAMM].

2. A PMS-2000 analyzer was used by Fluid Energy, Inc. of Hatfield, Pennsylvania. This method is based on Stoke's law of sedimentation in liquid and on the measurement of suspended particle concentrations by photoextinction. A 10-cm test cell is filled with liquid in which the sample particles are suspended initially at a 0.05% weight concentration. A light beam and associated instrumentation monitor the progress of sedimentation at intervals of one second. A microprocessor calculates the particle size distribution and produces a tabular or graphical output. 3. A HIAC PA-70 analyzer was used by the HIAC/ROYCO Division of the Pacific Scientific Company, Menlo Park, California. This instrument measures the projected area of individual particles as they pass through an orifice past a light beam. The suspending medium can be an aqueous or organic liquid or a gas; the medium used was water with Ethomeen C-15 dispersant. This is a counting method, as is the Coulter counter, but it is not required that the suspending medium be an electrolyte. Both types of counter must cope with the highly irregular shapes of glass particles.

4. A Sedigraph analysis was performed by the Micromeritics Instrument Corporation, Norcross, Georgia. This method is based on sedimentation rate in liquid, as is the Fluid Energy PMS-2000 instrument, except that the Sedigraph uses an X-ray source and a scintillation detector to measure suspended particle concentration in a liquid as a function of time.

5. An ELZONE analysis was conducted by Particle Data Laboratories, Elmhurst, Illinois. This instrument measures the displacement volume of individual particles suspended in an aqueous electrolyte as they pass through an orifice. This principle is much like that of the Coulter counter, except that the ELZONE instrument measures a voltage, rather than a current pulse as is used in the Coulter counter. Also there are some differences in the way samples are handled in the two instruments.

The particle size distributions for the sample described above, measured with our Coulter counter and the five other particle size analysis instruments are presented in Tables 14 through 19. The cumulative volume (mass) percent for all particles smaller than a given size is shown, based on renormalization of the data from the sample size to the total mass of the 25-mm-OD x 250-mm impacted specimen. The cumulative volume percentages based on sample size are plotted on linear coordinates in Fig. 22. The cumulative volume percentages, renormalized to the impact specimen volume, are plotted in Fig. 23. The solid line (<u>i.e.</u>, curve) in Fig. 23 represents data obtained in an impact test at 10 J/cm³ of a 25-mm x 25-mm specimen, using mechanical sieving and Coulter counter analysis in the size range of $\sqrt{8} \mu m$ to 2 mm. These data were fit to the particle size distribution defined by the lognormal parameters D_g = 2.6 ± 0.2 mm and $\sigma_g = 6.6 \pm 0.4$; the respirable fraction was 0.18 ± 0.05 wt X, as reported in Table 6.

The insensitivity of the Coulter counter to particles smaller than 5 μ m is responsible for the deviation in Fig. 22 of the raw Coulter counter data points at <20 μ m. This is discussed in Section II.C.1. The ELZONE instrument has an insensitivity to particles smaller than 10 mm, similar to (but less pronounced than) that for the Coulter counter. By the use of multiple and smaller orifices, a Coulter counter could be used to collect data into successively smaller sizes, using a multitube orifice overlap method to verify that the deviation shown in Fig. 22 is an artifact of the method.

In comparison to the other methods, the micromerograph appears to overestimate the smaller sizes. Reasons are unknown, but could be the effective diameter differing from the effective diameter for other methods. The only practical method of measuring submicron particles is electron microscopy. This is discussed in Section III.G.

Upper D, μm	Sample, cumulative vol %	Cumulative vol % Normalized to V _O		
8.0	0.3	0.014		
10.1	0.8	0.037		
12.7	1.9	0.087		
16.0	3.9	0.18		
20.2	6.9	0.32		
25.4	11.2	0.51		
32	17.9	0.82		
40	27.4	1.3		
51	41.0	1.9		
64	58.7	2.7		
80	82.0	3.8		
102	99.9	4.6		

Table 14. ANL Coulter Counter Measurements of Particles from Impacted SRL 131 Glass Specimen

Table	15.	PMS 2001 Measurement by Fluid Energy,
		Inc., of Particles from Impacted
		SRL 131 Glass Specimen

Upper D, μm	Sample, ^a cumulative vol %	Cumulative vol % Renormalized to Initial Specimen Volume
5	2.05	0.094
10	4.06	0.19
15	12.8	0.54
20	19.0	0.87
25	26.6	1.22
30	35.3	1.6
40	49.5	2.3
50	63.0	2.9
60	77	3.5
70	88	4.0
80	98.1	4.5
90	100	4.6

^aAs reported by Fluid Energy, Inc.

Upper D, ^a µm	Sample, ^a cumulative vol %	Cumulative vol X Renormalized to Initial Specimen Volume	
3.0	0.0	0	
5.0	1.0	0.046	
10	7.8	0.36	
20	21	0.97	
30	40	1.8	
35	50	2.3	
40	60	2.8	
50	77	3. 5	
60	91	4.2	
70	97	4.5	
80	100	4.6	

Table 16. Sedigraph Analysis of Particles from Impacted SRL 131 Glass Specimen at Micromeritics Instrument Corp.

^aRead to two significant figures from a vendor-supplied graph.

Table 17.	Micromerograph Analysis of Particles from
	Impacted SRL 131 Glass Specimen at
	Val-Dell Co.

Upper D, μm	Sample, ^a cumulative vol X	Cumulative vol X, Renormalized to Initial Specimen Volume	
2.4	0	0	
4.0	5.6	0.26	
6.0	9.0	0.41	
10	22	1.0	
20	49	2.2	
30	68	3.1	
40	75	3.4	
50	84	3.9	
60	89	4.1	
80	97	4.5	
90	100	4.6	

^aRead from a vendor-supplied graph to two significant figures.

Upper D, ^a µm	Sample, ^a cumulative vol %	Cumulative vol % Renormalized to Initial Specimen Volume	
4.86	0.1	0.0046	
6.61	1.0	0.046	
12.25	6.0	0.28	
23.57	22	1.0	
40.41	50	2.3	
64.15	78	3.6	
90.73	94	4.3	
128.31	99	4.6	
181.66	99.9	4.6	

Table 18. Measurement by ELZONE Method of Particles from Impacted SRL 131 Glass Specimen at Particle Data Laboratories

^aTaken from tabular data supplied by vendor.

Table	19.	HIAC Anal	lysis of	E Particl	es from	Impacted
		SRL 131 (Glass Sp	pecimen a	t PSA Lá	aboratory

Upper D, ^a µm	Sample, ^a cumulative vol %	Cumulative vol %, ^b Renormalized to Initial Specimen Volume		
2.7	0.10	0.046		
3.2	0.28	0.013		
3.8	0.42	0.019		
4.5	0.79	0.036		
5.3	1.32	0.061		
6.2	2.02	0.093		
7.4	3.15	0.14		
8.7	4.79	0.22		
10.2	7.08	0.33		
12.1	10.12	0.47		
14.3	14.04	0.65		
16.3	19.24	0.91		
19.9	26.35	1.2		
23.4	33.84	1.6		
27.6	43.98	2.0		
32.6	54.48	2.5		
38.5	66.40	3.0		
45.4	78.06	3.6		
53.6	88.57	4.1		
63.2	95.64	4.4		
74.6	99.21	4.6		
88.1	99.83	4.6		
103.9	100.00	4.6		

^aTranscribed from tabular data of vendor. ^bRenormalization factor: 0.046.



Fig. 22. Qumulative Volume Percentages Based on Specific Sample Size Used by Vendors to Determine Size Distribution of Impact Fragments of SRL 131 Glass

In the absence of an absolute standard, the methods whose data points lie close to the lognormal straight line are assumed to be the most reliable in this size range. These are the ELZONE, PMS 2001, Sedigraph, and HIAC methods, although the HIAC method seems to produce higher values than the other methods for particle sizes above about 50 µm (Fig. 22). Our experience has shown that when the appropriate corrections are made to the Coulter counter data, this method agrees with the other four methods. Overall, the agreement seems quite remarkable for characterizing particles so irregular in shape as those produced by impact fracture of glass because the methods all determine different characteristic size dimensions. The maximum deviation of the methods in determining sizes of $\ll 10 \ \mu m$ is about a factor of five. Thus. it appears that several methods are available to be used in conjunction with sieving data to establish the size distribution of impact fragments of inter-More experiments are needed to properly define the limitations and est. reproducibilities of the methods.



Fig. 23. Particle Size Distributions of Impact Fragments Determined by Six Measurements Normalized to the Initial Volume of 25-mm-OD × 25-mm-Long Impacted SRL 131 Glass Specimens

G. Microscopic Characterization of Impact Fragments

1. SRL 131 Simulated Waste Glass

Fragments of SRL 131 glass from a 10 J/cm³ standard impact test were partially characterized using optical microscopy. Micrographs of typical fragments (Fig. 24) show that smaller particles (<10 μ m) are attached to the larger particles. After impact, these fragments had been collected from the sealed chamber, using water, and had been wet sieved.

The sample was examined to determine if smaller particles ($\langle 10 \ \mu m \rangle$) were strongly attached to the larger ones. Roughly one-third to one-half of the small particles (fines) could not be detached. This indicates a very strong binding mechanism, probably surface welding or fusion. Attachment was seen to occur preferentially on the flat surfaces of the particles. Stepped surfaces, irregular topography, or conchoidal fractures with high surface relief showed little evidence of attachment. It is not uncommon to find surface fusion, especially on clean, freshly exposed surfaces which result from the grinding of glass. The particles are of like chemistry, have no precisely defined melt point (since glass has a liquid structure at normal temperature), and do not require preferred orientation to effect fusion (in





100 MICROMETERS

Fig. 24. Fragments of SRL 131 Glass from 10 J/cm³ Impact Tests, Showing Small Particles (<10 µm) Attached to Larger Particles

constrast to crystalline materials). Then, too, there is the possibility of locally high temperatures as the particles collide during the drop-weight impact. This latter possibility has been examined theoretically in Appendix B, on the basis of the conversion of elastic strain energy into heat.

2. SYNROC B Ceramic Waste Form

A preliminary SEM examination of impacted LLL SYNROC B fragments was made.^{*} The objective was to photograph the fragments and to use EDAX/SEM to establish if any significant elemental concentration differences could be identified in different fragment sizes, especially in particle sizes approaching the individual grain size of ~1 µm.

Five separate SEM specimens in size ranges of $125-150 \mu m$, $38-53 \mu m$, $20-38 \mu m$, $10-20 \mu m$ and $<10 \mu m$ were prepared. Photographs were taken of each size range to record the fragment shapes. EDAX spectra examinations were also taken on about five particles in each size range. The gold coating required for SEM specimens prevented observation of any zirconium; a different coating material should be used in any future work with SYNROC.

In general, all particles larger than 20 μ m examined showed the same EDAX spectra. For particles smaller than 20 μ m, several seemed to show possible variations in elements. However, more work is required to resolve if there is really a variation. Use of this SEM approach with another coating material was judged to be reasonable to accomplish the original objectives, if detailed characterization of ceramic fragments is needed in future work.

3. Pyrex--North Carolina State University

a. Introduction

A study was carried out at North Carolina State University $(NCSU)^*$ to apply computer-based stereometric and statistical analysis methods to scanning electron microscope (SEM) and optical microscope images. The objectives were to characterize the surface area, shape, and volume distributions for impact-induced fracture fragments of Pyrex glass. The Pyrex specimens (38-mm OD x 63 mm long) were impacted at ANL, and fragments were collected using dry transfer techniques. Fragments collected and passing through a 2-mm sieve were then sent to NCSU for characterization analysis. No further analyses were conducted on the >2 mm fragments remaining at ANL, but the impact conditions used corresponded to those for which fragments of other specimens were previously characterized completely at ANL.

b. Experimental Procedures

To obtain reliable large-number statistics for particulate materials spanning wide ranges of sizes, shapes, etc., it is necessary to utilize specimen-preparation procedures which reasonably assure (a) representative sampling, (b) good dispersion, (c) a reasonable concentration of particles within a given microscope field, and (d) freedom from random or tramp impurities and/or other method-induced artifacts. The procedures utilized in this study are summarized in Fig. 25 and are briefly discussed below.

The dispersion method, developed by Thaulow and White [THAULOW], makes use of a eutectic mixture of two volatile organic solids (camphor and naphthalene). This waxy dispersing medium has a controllable, temperaturedependent viscosity, does not react with the inorganic glass materials being dispersed, and can be readily removed after dispersion has been achieved by sublimation at room temperature in vacuo.

As noted above, fragments of impacted Pyrex glass samples, 2-mm and finer, were prepared at Argonne National Laboratory. Two specimens (38-mm diameter x 63 mm long) were impacted in the sealed bellows chamber by diametral impacts of 90 J (sample AR-1) and 20 J (samples AR-2' and AR-2), respectively. A third specimen (AR-3) of the same size was prepared by dropping (free fall) the specimen from a height that would produce 30 J of kinetic energy upon impact onto an unyielding surface. In all cases, the fragments were collected, and all recovered fragments smaller than 2 mm were loaded into a container for shipment to NCSU. The percentage of fragments lost varied from 0.05 to 0.4 wt %, as summarized in Table 20; the largest losses occurred in the free-fall drop tests because of the difficulty of recovering fragments in the absence of a sealed bellows chamber. Additional losses occurred at NCSU (as indicated in Table 20) during subsequent analyses.

^{*}The principal investigators were Hayne Palmour, III, John C. Russ, and Thomas M. Hare. The results of their study, summarized in this report section, are based on a final report.





Flow Diagram for Preparation of Scanning Electron Microscope Specimens of Impact-Produced Glass Fragments, after (THAULOW)

Since their downward range of sizes was very broad, it was deemed necessary, in order to facilitate precise dispersion and counting of fragments and to permit effective focusing and magnification, to separate the sample into nearly uniform groupings of reasonably similar particles. Thereafter, the reduced data for separate fractions were summed statistically over the entire spectrum of sizes.

Carefully cleaned Tyler Standard series screens--76-mm dia 80-mesh ($\langle 175 \mu m \rangle$, 100-mesh ($\langle 147 \mu m \rangle$, 150-mesh ($\langle 104 \mu m \rangle$, 200-mesh ($\langle 74 \mu m \rangle$, 250-mesh ($\langle 55 \mu m \rangle$, 325-mesh ($\langle 47 \mu m \rangle$, and 400-mesh ($\langle 37 \mu m \rangle$)-were utilized to make sieving separations. The as-received weights and the percentages of weights retained for various size fractions are given in Table 20. The weight-loss figures represent those particles which were retained within screen meshes or remained as adherent dust after screening, and which had to be removed by subsequent cleaning. Typical sieving losses were small, in the range 0.5-1.6% of the total, depending inversely upon the quantity of $\langle 2 mm$ particles received. The source of losses in transferring fragments from the shipping container is unknown, but this raised the total loss to 2.1% in the case of AR-3.

	- •	-		_	
Sample					
ANL Identification		2519F-101	2519F-106A	2519F-111	2519F-106B
NCSU Identification		AR-1	AR-2	AR-2 '	AR-3
Mass Balances					
ANL					
initial mass, g		164.0997	164.1256	162.1614	164.3409
mass >2 mm, g		124.0601	150.4869	148.3195	144.9516
mass <2 mm (loade	d), g	39.9232	13.5604	13.7099	16.2311
mass lost, g		0.116(0.07%)	0.078(0.05%)	0.132(0.08%)	0.640(0.4%)
NSCU					
mass recovered (b	ottle), g	38.6334	13.5376		16.2150
mass after sievin	g, g	38.4672	13.4333		15.9540
mass lost (sievin	g), g	0.166(0.43%)	0.104(0.77%)		0.261(1.6%)
Combined ANL and NC	SU				
total mass loss,	g	1.57 (0.96%)	0.205(0.12%)		3.43(2.1%)
Sieve Analyses					
Hadaba Distrikution	(Norinol				
by Size Fraction	(NOMINAI Mech Size)				
190 mach	(\175m)	94 019	92 319		95.47%
-90 ± 100 mean	$(/1/3 \mu m)$	0.79%	0.9%		0.42%
-100 ± 150 mesh	$(<1/5, >1/4, \mu m)$	1.42%	2.25%		1.20%
-150, $+200$ mesh	$(\langle 104 \rangle, \rangle 104 \mu m)$	0.85%	1.42%		0.59%
-200 + 250 mesh	$(\langle 74, \rangle 55 \text{ um})$	0.21%	0.54%		0.20%
-250, $+325$ mesh	(<55, >47 um)	0.77%	0.26%		0.18%
-325, $+400$ mesh	(<47, >37 um)	0.54%	0.45%		0.06%
-400 mesh	(<37 µm)	0.98%	1.1%		0.26%
Subtotal, recovered	weight	99.57%	99.23%		98.39%
Weight Loss. %		0.43	0.77		1.61

Table 20. Summary of Mass Balances and Tyler Screen Analyses of 2-mm and Finer Size Fractions from Three Specimens of Impact-Fractured Pyrex Borosilicate Glasses The <175 μ m particles were counted from photomicrographs obtained using a scanning electron microscope, while >175 μ m (+80 mesh) particles were counted on enlargements of photographs.

For completeness, those descriptions of materials and work not necessary for this discussion are presented in Appendix C. Representative scanning electron microscope photomicrographs are shown in Figs. 26a, b, c, and d. Figures 27a and b show typical optical macrography fields of +80 mesh particles for specimens AR-1 and AR-2, respectively.

c. Measurement and Data Reduction

The SEM photomicrographs of dispersed particles, enlarged 2.5 times,^{*} were placed on a "digitizer pad" or "graphics tablet" connected to our laboratory microcomputer (Apple II with 48K memory, extended Basic, two disk drives, a thermal printer, and other peripherals). By use of this tablet, which is a commercially available program designed for the stereometric measurement of particles and subsequent statistical analysis, the perimeter of each particle was traced and the digitized information stored on a disk. The number of particles counted within each size range was recorded for each sample. The total numbers of such particles are summarized in Table 21.

The resolution of the graphics tablet is 180 points per inch, so that in effect each particle was considered to be a many-sided polygon, with the points specified by the continuous motion of a hand-held stylus. Examination of the stylus markings on the photographs confirms the accuracy of the method: we are confident that no consistent errors or bias were introduced by use of this technique. There were a few cases where some portion of the periphery of a particle was obscured, <u>e.g.</u>, by wax or another particle. Reasonable judgment was applied in these cases, but they were so few that they were unimportant in the total statistical analysis.

From the series of points defining the periphery of the particle, the projected area of the particle (A), the perimeter (P), the maximum diameter (D_L), and Feret's diameters (D_{fx}, D_{fy}) in two directions were obtained as primary variables. The symbol definitions, which are shown in Table 22, are used throughout this report section for the defined and derived quantities. The maximum diameter is the distance between those two points on the periphery of the particle which are farthest apart. The Feret's diameters are the projected dimensions of the particle in two orthogonal directions, which are arbitrary with respect to the particle and correspond to the random orientation of the photograph. The unit of all linear parameters is μ m. Area is in μ m², and the form factor is dimensionless.

With these data stored on disks for each of the various samples and size ranges, a further set of derived parameters was computed, using the program's capability of transforming a new parameter from any combination (algebraic and/or logical) of existing ones. Each is mathematically defined as in Table 22 with additional comments below.

^{*}The total magnification, SEM plus enlarger, determined from the NBS reference standard, was used to obtain actual linear dimensions.



Fig. 26a. Typical SEM Photograph of Pyrex Fragments for Sample AR-1 after Treatment by the Dispersion Procedures Described in Text. -80 mesh (<175 μ m) at X135 magnification.



Fig. 26b. Typical SEM Photograph of Pyrex Fragments for Sample AR-1 after Treatment by the Dispersion Procedures Described in Text. -400 mesh (<37 µm) at X1080 magnification.



Fig. 26c. Typical SEM Photograph of Pyrex Fragments for Sample AR-1 after Treatment by the Dispersion Procedures Described in Text. -400 mesh (<37 µm) at X1080 magnification.


Fig. 26d. Typical SEM Photograph of Pyrex Fragments for Sample AR-1 after Treatment by the Dispersion Procedures Described in Text. -400 mesh (<37 µm) at X1080 magnification.</p>



Fig. 27a. Typical Optical Microscope Photograph of Fragments >175 µm (+80 mesh) for Specimen AR-1 at 17.5X magnification.



Fig. 27b. Typical Optical Microscope Photograph of Fragments >175 µm (+80 mesh) for Specimen AR-2 at 17.5X magnification.

Sample	Size (Mesh) Range	Number of Particles Counted
AR-1	+80 (>175 µm)	349
	-80 +100 (175-104 µm)	151
	250 ++400 (5537 µm)	214
	-400 (<37 µm)	452
AR-2'	+80 (>175 µm)	215
	-80 +400 (175 to 37 µm)	150
	-400 (<37 µm)	174
AR-3	+80 (>175 µm)	103
	-80 +400 (175 to 37 µm)	150
	~ 400 (<37)m)	142

Table 21. Summary of the Number of Particles Individually Measured for the Three Samples Used in this Work.

- (1) Form Factor (F) is equal to 1 for a circle, the maximum possible value. The form factor decreases as the ratio of the perimeter to the area of the particle projection increases, and so very elongated or very rough particles have low form factors.
- (2) <u>Minimum Diameter</u> (D_S) : The minimum diameter is the length of the minor axis of an ellipse that has the same area and maximum diameter as does the particle projection.
- (3) Ellipsoidal Volume (V_e) is the volume of an ellipsoid (in this case, a prolate spheroid) with axes D_L , D_S , and D_H to be taken to be a good estimate of the particle volume where the particle height, D_H (not directly observed), is given the value D_S and is assumed to be the same as D_S .
- (4) <u>Mass</u> (M): The mass is calculated from the assumed density of the Pyrex glass (taken to be 2.23 g/cm³ for all samples).
- (5) Equivalent Spherical Diameter (D_{se}): This is the diameter of a sphere equal in volume to the computer particle ellipsoidal volume. This is a convenient linear dimension that is used for the plotting of results.
- (6) Ellipsoidal Surface Area (S_e) : The surface area of the ellipsoid of volume V_e defined above. It may underestimate the actual surface areas of the particles (see Table 23 for a further illustration of this). The method of computing the surface area of a prolate spheroid is described in Appendix C.

Symbol	Name	Description
Defined Q	uantities	
A	Area	Projected Area of Particle
P	Perimeter	
D _{fx}	Feret's Diameter (x direction)	Length of projection onto the x-axis
D _{fy}	Feret's Diameter (y direction)	Length of projection onto the y-axis
DL	Maxinum Diameter	
Derived Q	uantities	
F	Form Factor	4 mA/P ²
DS	Minimum Diameter	4A/ #DL
۷ _e	Ellipsoidal Volume	D _L D _S /6
D _{se}	Equivalent Spherical Diameter	$(6V_{e}/\pi)^{1/3}$
Se	Ellipsoidal Surface Area	$(\pi/2) \cdot (D_S^2 + D_L^2 \tan^{-1}(e)/e),$ $e = (D_L^2 - D_S^2)$ (see Appendix C)
S _{ef}	Adjusted Surface Area	S _e /F
M	Мавя	ρV _e , where ρ = density

Table 22. List of Symbols Used in this Section

(7) <u>Adjusted Surface Area</u> (S_{ef}): This gives the most reliable simple estimate of the actual surface area of the particle.

The adjustment of surface area was applied particularly so that the surface areas of rough, irregular particles would not be seriously underestimated. A rough sphere with a surface area twice that of a smooth sphere would have a form factor considerably below 1, using its two-dimensional projection. Dividing the computed ellipsoid surface area by the form factor appropriately increases the surface area estimate to account for roughness.

The results of using the volume and surface estimates obtained from various 2-D projections of regular 3-D solids are shown in detail in Table 23. It is concluded that for prismatic or cylindrical particles with

		e = edge					_			
								Fraction Error (calc - true)/true		
2-D Particle Projection	F	3-D Shape	True V	ve	True S	Se	S _{ef}	٧ _e	Se	S _{ef}
Circle r = 1	1	Sphere r = 1	0.5232	0.5235	3.142	3.142	3.142	0.0	0.0	0.0
	-	Cvlinder h = 1	0.7855	0.5235	4.712	3.142	3.142	-0.33	-0.33	-0.33
		Cylinder $h = 0.5$	0.3977	0.5235	3.142	3.142	3.142	+0.32	0.0	0.0
	0 786	Cube e = 1	1,0000	0.6000	6.000	3.557	4.529	-0.40	-0.41	-0.25
Square s = 1	0.700	Plate $(1 \times 1 \times 0.5)$	0.5000	0.6000	4.000	3.557	4.529	+0.20	-0.11	+0.13
		h = 1	0.8550	0.6000	4.712	3.557	4.529	-0.29	-0.29	-0.04
Pootonalo	0.698	$(1 \times 1 \times 2)$	2.0000	1.5184	10.00	6.854	9.818	-0.24	-0.31	-0.02
1×2	0.070	$(0.5 \times 1 \times 2)$	1.0000	1.5184	6.000	6.854	9.818	+0.52	0.14	0.64
Trianale	0.605	Prism h = 1	0.4330	0.1591	3.866	1.502	2.484	-0.63	-0.61	-0.36
	0.005	Prism h = 0.5	0.2165	0.1591	2.366	1.502	2.484	-0.27	-0.37	0.05
5 - 1		Tetrahedron	0.1179	0.1591	1.732	1.502	2.484	0.35	-0.13	0.43
Wavy Circle	0.66	Bumpy Sphere ^a	0.5235	0.5253	4.712	3.142	4.712	0	-0.33	0
-										

Table 23. Computation of Ellipsoidal Volumes and Surfaces for "Ideal" Shapes

r = radius h = height s = side

^aBumpy sphere defined as a sphere covered with surface hills and valleys such that the volume is equal to that of a smooth sphere, but the surface area is 1.5 times that of the smooth case. A projection will have a form factor, F, approximately equal to that indicated, depending on the exact nature of the bumps. heights approximately equal to the diameter of the 2-D projection, the volume is underestimated 33-64%, with the worst case being the triangular prism. The surface area for these types of particles is also underestimated by about the same amount when S_e is used. When S_e is divided by the form factor to obtain S_{ef} , the error is considerably reduced in some cases.

For particles which are more plate-like (those having a height = 0.5), the errors in the volume and surface estimates are in the other direction. The only error which could be serious is the type of particle represented by a rectangular prism having dimensions in the ratio, $0.5 \times 1 \times 2$, but seen as a 1×2 rectangle. In this instance, using S_{ef} to estimate the surface area overestimates the surface area by 642.

Summarizing, particle shapes which could lead to erroneous measurements (worse than 50% error) are:

- (1) Prismatic or "tall" particles.
- (2) Platey or thin particles with a height somewhat less than one-half the maximum diameter.
- (3) Very angular or concave particles, which would particularly affect volume calculation.

Very few of these types of particles were observed, leading to confidence that the error in measurement is manageable, with errors probably less than $\pm 33\%$ on the average, and varying between over- and underestimation. Because of this and the fact that the observed form factor is reasonably large (0.6-0.7), this approach is believed to be justified.

d. Results

(1) Particle Shape

In the handling of specimen AR-1, measurement of several intermediate sieve splits (+400 -250 and +100 -80) was attempted to fill in the size distribution; however, examination in the SEM showed that these splits contained significant amounts of smaller size particles which had not passed through the screens. This made it impossible to weigh them and obtain distribution plots from their masses. The total mass contained in these intermediate sizes was fortunately so small that there was no need to subdivide a sieve split by measurement in any case. Measurements of these intermediate sizes were used only to characterize particle shape.

Consistency of shape from sample to sample and from size range to size range is important in the assumptions previously described for estimating surface area. It is also of significance in assessing fracture mechanisms, as discussed in Section III.E and in assessing the surface area to volume shape factor defined in Section III.1. For these Pyrex glass samples, it was found that the consistency of shape in different size ranges was most easily demonstrated by making histograms of the form factor and the max/min diameter ratio, which are shown in Figs. 28 and 29.



Fig. 28. Histograms of Form Factor for Particles in Each Fraction. Each plot covers the range, 0-1 (horizontal scale) in 0.1 steps. The vertical scale is the relative number of particles in each segment.

a) Sample AR-1 +80f) Sample AR-2' -80 +400b) AR-1 -80 +100g) AR-2' -400c) AR-1 -250 +400h) AR-3 +80d) AR-1 -400i) AR-3 -80 +400e) AR-2' +80j) AR-3 -400

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Fig. 29. Histograms of Max Diameter/Min Diameter Ratio for Particles in Each Fraction. Each plot covers the range 1-6 in N 0.5-steps.

- a) Sample AR-1 +80
- b) AR-1 -80 +100
- c) AR-1 -250 +400
- d) AR-1 -400 e) AR-2' +80

f) Sample AR-2' -80 +400

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- g) AR-2' -400
- h) AR-3 +80
- 1) AR-3 -80 +400
- j) AR-3 -400

The overall average form factor was determined from each size range to be 0.663, with those for individual samples (Fig. 28) AR-1, AR-2', and AR-3 equal to 0.651, 0.695, and 0.657, respectively. The averages for +80 (>175 µm) and -400 (<37 µm) fractions were 0.642 and 0.688, respectively. These values, and the others for the individual fractions and various combinations, show no clearly discernible trend as a function of particle size. It is concluded on the basis of these results that the shape factor does not depend significantly on particle size. The relationships of the maximum diameter, perimeter, and form factor are shown in Table 24.

Table 24. Relationships of D_L, P, and F

 From	the	definitions:	
	F =	4πA/P ²	(1)
	D _S =	= 4A/πDL	(2)
	D S -		(2)

Dividing Eq. 2 by Eq. 1

$$D_{S}/F = P^{2}/\pi^{2}D_{L}$$

 $F = D_{S}D_{L}\pi^{2}/P^{2}$ (3)

$$F/D_L^2 = \frac{D_S}{D_L} \frac{\pi^2}{P^2}$$
 (4)

if
$$D_S/D_L$$
 = constant (d)

$$F = \frac{D_L^2}{P^2} d\pi^2$$
 (5)

From Eq. 5, it can be seen that only if D_L/P is constant will F be uniquely determined by d (the D_S/D_L ratio).

Similarly, for the max diameter/min diameter ratio, the global mean is 2.22, and for the individual samples (Fig. 29), the averages are 2.17, 2.21, and 2.36, respectively. Averages for the +80 (>175 μ m) and -400 (<37 μ m) fractions are 2.16 and 2.24, respectively. Again, all of the individual values seem to fit into a single population, implying no dependence of particle shape on particle size.

Finally, the linear correlation coefficients (max/min diameter ratio vs. form factor) were examined for individual size ranges of particles. Figure 30 shows plots of these parameters for the individual



Fig. 30. Plots of Max Diameter/Min Diameter Ratio (Horizontal Scale, Range 1-6) Against Form Factor (Vertical Scale, Range 0.2-1) for Particles in Each Fraction.

> a) Sample AR-1 +80 b) AR-1 -80 +100 c) AR-1 -250 +400 d) AR-1 -400 e) AR-2' +80



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- h) AR-3 +80
- i) AR-3 -80 +400
- j) AR-3 -400

particles. The linear correlation coefficients are given in Table 25. It is clear that these parameters are highly correlated, even though the relationship between the variables is not linear. These nonlinear relationships are given in Table 24.

Sample	Size (Mesh) Range	Linear Correlation Coefficient	Number of Pairs
AR-1	+80 (>175 µm)	-0.546	349
	-80 +100 (175-104 μma)	-0.718	151
	-250 +400 (55-37 μm)	-0.638	214
	-400 (<37 μm)	-0.633	452
AR-2 '	+80 (>175 μm)	-0.699	215
	-80 +400 (<175 to >37 μm)	-0.903	150
	-400 (<37 μ m)	-0.619	174
AR-3	+80 (>175 μm)	-0.764	103
	-80 +400 (175 to 37 μm)	-0.875	150
	-400 (<37 μm)	-0.727	142

Table 25. Summary of Linear Correlation Coefficients (Maximum to Minimum Diameter Ratio vs Form Factor) for Different Size Ranges of Fragments for the Three Samples

(2) Distribution of Volume and Surface Area

By use of the equivalent spherical diameter obtained from the ellipsoid volume, V_e , as a sorting parameter, the individual particle volumes and surface areas, computed as described above, were sorted into groups. For samples AR-2' and AR-3, all sieve fractions were actually sampled and measured, while for sample AR-1, the fractions from 400 mesh ($\langle 37 \ \mu m \rangle$) to 80 mesh (175 μm), which represented only 19.3% by weight of the sample submitted (4.5% of the total sample), were represented only by the sieve results themselves. Since the -400 mesh ($\langle 37 \ \mu m \rangle$) sieve fraction represents the bulk of the surface area and since the sieve sizes are very close together in this narrow range, this portion of the cumulative curve, in any case, is still well defined.

Bin sizes were arranged logarithmically with a ratio of upper to lower limit of 1.18921 (fourth root of 2). Within each bin or group, the number of particles, and the sum of particle volumes and surface areas were accumulated. The individual distributions of these parameters and their cumulative totals are shown in Appendix C for each sample (AR-1, AR-2', AR-3). The partial distributions in Appendix C are of little meaning by themselves, since they must be combined in proportion to the weight of each sample fraction. At this time, the rather narrow bin widths were also combined to produce groups differing by a factor of 2 in linear dimension.

Tables 26, 27, and 28 show the cumulative volume (μm^3) and surface area (μm^2) data for samples AR-1, AR-2', and AR-3. Based on the weight in each sieve fraction, the cumulative mass distribution is shown, and is also expressed as a fraction of the whole sample (taken as 164.0997 g for AR-1; 162.1614 g for AR-2'; and 164.3409 g for AR-3). The surface areas are also accumulated, using a nominal value of 2.23 g/cm³ for the density of Pyrex. For sample AR-1, the surface areas in the intermediate sizes are estimated from the volume, as described above (although so little material is involved that the overall curve depends but little on this estimate).

Direct comparison of these microscopic cumulative distributions with those obtained from sieving and Coulter counter analyses must be considered with extreme caution since current data are at times incomplete and do not allow definitive conclusions to be made. Plots of the cumulative volume fractions of Tables 26, 27, and 28 suggest that some type of calibration difference, or error, in size (or ESD) may exist between SEM and optical microscopic results. These data do not form a single smooth straight line at lognormal distribution. Also, the mass balances showed that the masses lost were relatively large (e.g., 1-3%); nothing is known about the distribution of these losses. As a result, no conclusions are possible that would relate these NCSU data to the fragment data for Pyrex presented elsewhere in this report.

The cumulative surface area distributions have the same uncertainties as the cumulative volumes. Thus, it is probably only fortuitous that the cumulative surface area for sample AR-1 is calculated to be 0.99 m^2 , which agrees relatively well with the measured BET surface area of 0.76 m^2 (run Z102AB, Table 11) for an equivalent impact test (90 J). The calculated surface area for AR-2 of 0.19 m^2 agrees reasonably well with the BET surface area of 0.33 m^2 measured for a 30-J impact test (run 131, Table 11).

H. Experimental Mass Balances

A primary measurable response of impact test experiments is the absolute amount of respirable sizes in the brittle fragments. Since the size distribution results are generally reported as weight percent of the initial specimen mass, it is important to know the amount of materials lost during the impact test and analysis procedures. Ideally, the size distribution of the material unaccounted for is also desired.

To begin to address these concerns, material balances were made for our impact tests used for both particle size analyses and surface area analyses. These current material balances provide information only on the mass of material lost during either the impact test or the analysis procedures. Nothing quantitative is known about the size distribution of the lost mass of fragments nor at what point after impact the fragments were lost. Future work is needed to determine where the losses occur and the size distribution of the losses.

Table 29 summarizes the mass balances obtained from many tests and analyses made in this study. These experiments are classified by specimen size

	Volume			M	A 8 8		Surface Area			
Size, ^a µm	-400, µ = 3	From Sieve, 8	+80 , بشر	Total, 8	% of Original, ^b wt %	-400, μæ ²	From Sieve, µm ²	+80, µ■ ²	Total,	
0.125-0.25	0.0195			1.45E-8	7.01E-9	2.286			5.77 E-7	
0.25-0.5	0.2028			1.194E-7	7.31E-8	12.194			3.0 8E-6	
0.5-1	3.476			2.046E-6	1.25E-6	86.54			2.19E-5	
1-2	46.42			2.733E-5	1.67E-5	627.7			1.59E-4	
2-4	1856			1.093E-3	6.69E-4	8861			2.24E-3	
4-8	14665			8.633E-3	5.28E-3	40403			1.02 E-2	
8-16	80 2 82			4.726E-2	2.89E-2	1.481E5			3.74E-2	
16-32	4.959E5			0.2919	0.1786	4.341E5			0.1097	
32-64	6.431E5	0.506		0.8846	0.541	5.117E5	6.090E-2		0.1902	
64-128	6.431E5	1.464		1.8426	1.128	5.117E5	0.1103		0.2396	
128-256	6.431E5	1.769	7.096E6	2.153	1.318	5.117E5	0.1211	6.267E5	0.251	
256-512	6.431E5	1.769	6.940E9	7.419	4.54	5.117 E5	0.1211	2.74 9 E8	0.459	
512-1024	6.431E5	1.769	3.039E10	25.230	15.44	5.117E5	0.1211	7.905E8	0.851	
1024-2048	6.431E5	1.769	4.781E10	38.467	23.54	5.117E5	0.1211	9.763E8	0.992	

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Table 26. Cumulative Volume, Mass, and Surface Area Distribution Calculated for Sample AR-1

^aSize is equivalent to spherical diameter (ESD).

^bThe initial sample mass was 164.0997 g.

	Volume			Ma	ass		Surface Area			
Size, ^a µm	-400 (0.107g), μm ³	+400 -80 (0.77g), μm ³	+80 (12.79g), μm ³	Total, g	% of Original, ^b wt %	-400, μ ^{m2}	+400 -80, μm ²	+80, μm ²	Total, m ²	
0.25-0.5	0.0102			9.054E-9	5.58E-9	0.0365			1.449E-8	
0.5-1.5	0.0102			9.054E-9	5.58E-9	0.0364			1.449E-8	
1-2	41.24			3.661E-5	2.26E-5	373.7			1.487E-4	
2-4	982.4			8.720E-4	5.38E-4	3097.5			1.555E-3	
4-8	5450	507.1		4.854E-3	2.99E-3	13854	905.6		5.527E-3	
8-16	28020	19834		2.557E-2	0.0158	46203	20184		1.868E-2	
16-32	120550	142322		0.1116	0.0688	1.07892	78103		4.408E-2	
32-64	120550	4.593E6		0.2564	0.1581	1.07892	1.627E6		6.667E-2	
64-128	120550	2.368E7		0.8770	0.5408	1.07892	4.692E6		0.1114	
128-256	120550	2.368E7	2.756E7	0.8802	0.5428	1.07892	4.692E6	1.671E6	0.1115	
256-512	120550	2.368E7	3.212E9	1.252	0.7718	1.07892	4.692E6	1.112E8	0.1172	
512-1024	120550	2.368E7	1.733E10	2.898	1.787	1.07892	4.692E6	4.090E8	0.1328	
1024-2048	120550	2.368E7	8.093E10	10.315	6.361	1.07892	4.692E6	1.159E9	0.1720	
2048-4096	120550	2.368E7	1.097E10	13.66	8.427	1.07892	4.692E6	1.437E9	0.1865	

Table 27. Cumulative Volume, Mass, and Surface Area Distribution Calculated for Sample AR-2'

^aSize is equivalent to spherical diameter (ESD).

^bThe initial sample mass was 162.1614 g.

Volume		Ma	88		Surface Area				
Size,ª µm	-400 (0.0159g), β∎μ	+400 -80 (0.3756g), μm ³	+80 (15.4687g), μm ³	Total, 8	X of Original, ^b wt X	-400, μ <mark>ω</mark> 2	+400 -80, μ= ²	+80, μm ²	Total,
2-4	6.8			2.1471E-7	1.310E-7	155.6			2.203E-6
4-8	1151.5	188.1		3.9649E-5	2.419E-5	4263.6	320.4		6.288E-5
8-16	58770	8749.3		2.0117E-3	1.227E-3	802 68	14149		1.247E-3
16-32	503557	1.1104E5		1.7840E-2	1.088E-2	398110	84 591		6.300E-3
32-64	503 557	4.1348E6		8.8147E-2	5.378E-2	398110	1.706E6		1.901E-2
64-128	503557	2.1496E7		0.3915	0.2389	398110	5.246E6		4.674E-3
128-256	503557	2.1496E7	2.0514E7	0.4042	0.2466	398110	5.246E6	1.850E6	4.708E-2
256-512	503557	2.1496E7	1.2696E9	0.9182	0.5602	398110	5.246E6	6.143E7	5.817E-2
512-1024	503557	2.1496E7	1.3394E10	5.9481	3.629	398110	5.246E6	4.175E8	U.1244
1024-2048	503557	2.1496E7	3.7287E10	15.8602	9.676	398110	5.246E6	7.0 80E8	0.1785

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Table 28. Cumulative Volume, Mass, and Surface Area Distribution Calculated for Sample AR-3

^aSize is equivalent to spherical diameter (ESD).

^bThe initial sample mass was 164.3409 g.

			Calculat Impact En	ed ^b ergy		·		
	Specimen		Energy		Mass Measurements ^d			
Size	ID ^a Material		Density, ^c J/cm ³	Total, J	Initial Specimen, g	Lost, mg	Lost, wt %	
25-mm OD	x 25 mm						·	
	133-PS	Pyrex	1.2	16	28.8	31	0.10	
	133-SA	Pyrex	1.2	16	28.4	115	0.40	
	Z92A-SA	SRL 131	1.2	16	36.4	31	0.09	
	Z93-PS	SRL 131	1.2	16	35.8	91	0.25	
	134-PS	Pyrex	2.4	32	28.1	95	0.34	
	134-SA	Pyrex	2.4	32	28.6	126	0.44	
	Z89–SA	SRL 131	2.4	32	35.7	15	0.04	
	Z94-PS	SRL 131	2.4	32	34.8	39	0.11	
	135-PS	Pyrex	5	64	28.1	199	0.71	
	135-SA	Pyrex	5	64	28.4	139	0.49	
	Z88–SA	SRL 131	5	64	35.7	48	0.13	
	Z95-PS	SRL 131	5	64	35.2	101	0.29	
	136-SA	Pyrex	10	130	28.9	219	0.78	
	Z96-SA	Pyrex	10	125	27.9	93	0.33	
	Z76A-SA	Pyrex	10	125	28.0	126	0.44	
	Z50 - PS	Pyrex	10	127	28.0	165	0.59	
	128-PS	Pyrex	10	130	29.2	163	0.56	
	Z106-PS	Pyrex	10	126	28.1	189	0.6	
	Z108-PS	Pyrex	10	127	28.3	40	0.14	
	Z109-PS	Pyrex	10	127	28.2	49	0.17	
	Z46-PS	SRL 131	10	146	39.7	140	0.35	
	Z82-PS	SRL 131	10	146	40.7	42	0.10	

Table 29.	Summary of Mass Balances Obtained after Completion of All Procedures Required for Either	
	Particle Size Analyses or BET Surface Area Measurements	

Table 29. (contd)

		Calculat Impact En	ed ^b ergy				
Greetman		Energy		Mass Measurements ^d			
Specimen		Density, ^C	Total,	Initial Specimen,	Lost,	Lost,	
Size ID ^a	Material	J/cm ³	J	8	mg	vt X	
276B-SA	SRL 131	10	151	41.5	72	0.17	
Z92B-SA	SRL 131	10	128	35.2	75	0.21	
Z92C-SA	SRL 131	10 ^e	121	33.3	156	0.47	
Z84-PS	alkoxide	10	131	33.2	46	0.14	
Z85-SA	alkoxide	10	130	33.0	70	0.21	
Z81-SA	PNL 76-68	10	130	38.2	58	0.15	
Z80-PS	PNL 76-68	10	128	37.7	60	0.16	
Z60-PS	high silica	10	1 78	47.2	126	0.27	
Z48-PS	tailored						
	ceramic	10	102	40.8	16	0.04	
Z62-PS	SYNROC C	10	69	29.2	87	0.03	
Z68–PS	SYNROC C	10	67	28.4	133	0.47	
Z107AB-SA	SYNROC B	10	146	60.4	105	0.17	
Z244-PS	SYNROC B	10	146	60.5	73	0.12	
Z107CD-SA	SYNROC D	10	107	42.2	178	0.42	
Z110AB-SA	SYNROC D	10	109	42.2	110	0.26	
Z42-PS	SYNROC D	10	138	53.5	76	0.14	
38-mm OD x 63 mm							
132-SA	Pyrex	0.21	15	did 1	not break		
131-SA	Pyrex	0.43	32	167.3	69	0.10	
125-SA	Pyrex	1.2	90	158.3	229	0.14	
126-SA	Pyrex	1.2	90	163.2	326	0.20	
Z102AB-SA	Pyrex	1.2	88	163.9	256	0.16	
Z100ABC-SA	SRL 131	1.2	84	192.1	187	0.10	

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		• • • •	Calculat Impact En	ed ^b ergy		<u> </u>		
			Energy		Mass Measurements ^d			
Size ID ^a	Material	Density, ^c J/cm ³	Total, J	Initial Specimen, g	Lost, mg	Lost, wt %		
	127–SA	Pyrex	2.4	180	158.6	416	0.26	
	Z102CDE-SA	Pyrex	2.4	177	164.1	380	0.23	
	Z105-PS	Pyrex	2.4	177	164.7	295	0.18	
	297AB-SA	SRL 131	2.4	170	195.4	225	0.11	
<u>13-mm 0</u>	D x 13 mm				• •			
	Z66-PS	Pyrex	141	217	3.72	44	1.2	
	Z64-PS	SRL 131	141	217	4.46	83	1.9	
	Z56-PS	SNYROC B	141	217	7.42	33	0.44	
	Z54–PS	SYNROC D	141	217	6.69	51	0.75	
<u>13-mm 0</u>	D x 25 mm							
	137-SA	Pyrex	10	32	7.2	156	2.2	
	138-SA	Pyrex	50	161	7.2	210	2.9	
	129-SA	Pyrex	100	31 9	7.1	240	3.4	
	299-PS	Pyrex	50	157	7.0	42	0.6	

Table 29. (contd)

^aID includes code that data were used for either surface area (SA) or particle size (PS) analyses. The IDs with prefix Z are from experiments using the most developed procedures; the IDs with no Z prefix are the initial scouting experiments and thus have larger and more variable losses.

^bCalculated from height and mass of drop-weight.

^cCalculated from measured specimen volume and calculated impact energy.

^dThe mass balances were computed from the differences between the starting masses and the total masses recorded after sieving and Coulter counter or BET analyses. These losses occurred somewhere in the impact test or analysis procedures and thus contribute to the overall uncertainty of the measured values of mass fractions.

^eAxial impact test; all others are diametral impact tests.

(or mass), material, energy density, and total impact energy. For each particle size experiment, a mass balance was determined from the difference between (1) the combined measured masses of the sieve fractions and the mass of fragments measured in the Coulter counter slurry after evaporation and (2) the initial specimen mass. For each surface area measurement, a mass balance was determined as the difference between (1) the sum of the masses of fragments loaded into the BET tubes and the fragments >2 mm not used for BET analyses and (2) the initial specimen mass. These results, expressed as both mg of material lost and weight percent lost, are shown in Table 29.

These data should be grouped into two classes for any further comparisons. Specimen IDs not preceded by a Z ($\underline{e \cdot g} \cdot$, 133-PS) are the earliest generation tests and using the least-developed procedures and typically show the largest losses. Specimen IDs preceded by Z ($\underline{e \cdot g} \cdot$, Z92A-SA) are from the latest generation tests and analysis procedures and thus tend to have smaller losses; these data represent more-optimized procedures and experience.

The losses obtained by the optimized procedures generally are relatively constant and smaller than 100 mg. The losses do not seem to depend on whether wet particle size analysis or dry BET surface area analyses were used. For the standard 25-mm OD x 25-mm specimen, the losses each represent several tenths of a weight percent, which is of the same magnitude as the amount of material measured as $\leq 10 \ \mu m$. However, in the absence of knowledge of the size distribution of these losses, no meaningful conclusions can be drawn as to increased uncertainty in the amount of respirable particles generated.

In general, the absolute amount of material lost seems to be somewhat independent of the test conditions and specimen mass. However, the weight percent losses are increased to several percent for the 13-mm-OD specimens, which have a smaller total mass than other specimens. Thus use of larger specimens acts to reduce the uncertainty in the respirable sizes and may be preferable in future testing.

As a conclusion from these mass balance results--experiments designed to characterize the size distribution of the lost material are needed. The relatively constant amount of mass lost, 100 mg, in comparison with largely varying values of particle size distributions and surface areas, provides hope that such characterizations are achievable.

I. Preliminary Correlations Derived from Initial Impact Tests

A methodology of characterization of the impact fracture of brittle waste materials has been partially developed during the course of this program. The principal features are: (1) a standard drop-weight impact test of approximately laboratory-scale cylindrical specimens with a (10-kg) weight [ANL-81-27, p. 27]; (2) determination of the lognormal particle size parameters, D_g and σ_g , from linear regression analysis by computer fitting the size distribution obtained by combining sieving data and Coulter counter data of the fracture particulate in the range, $\sqrt{8}$ -2000 µm; (3) BET measurement of the total surface area of the fracture particulate to define the effective impact strength of the material (as J/m^2) and the mean surface area/volume shape factor, α (dimensionless), for the given D_g and σ_g ; (4) finite-element modeling of the dynamic stresses in a glass or ceramic specimen as a function of time during the compression stage of impact. This latter modeling is a key element of this approach and defines strain-energy density, mean stress, and impulse as the impact-severity parameters to be correlated with particle-size parameters for various impact conditions and body sizes. The model is needed to transform (<u>i.e.</u>, scale) laboratory-scale results to large actual waste forms and is discussed in more detail in Appendix D.

In principle, a complete characterization of the impact fracture of brittle waste materials in accidents could be provided by such an approach. That is, from calculations of impact severity parameters for accident conditions, particle size and surface area parameters evaluated in small-scale tests could be used to predict accident behavior. Since the required correlations are empirical generalizations, experimental confirmation over the range of conditions of practical interest is required to confirm their reliability. Although the preliminary laboratory-scale results obtained indicate the utility and economy of this approach, additional experimental evidence with larger-size specimens is required to establish the reliability of the overall correlations for use in accidents. Examples are given below of preliminary correlations to illustrate the proposed methodology for future accident analyses.

Many standard drop-weight impact tests have been made of Pyrex and SRL 131 simulated waste glass specimens over a range of energy densities from 1 to 100 J/cm^3 , as discussed elsewhere in this report. Three different sizes of cylindrical specimens have been used: 13-, 25-, and 38-mm diameters and 13-, 25-, and 62-mm lengths. The principal parameters of concern here are: the impact surface area, the respirable fraction, the geometric mean particle size (D_g) , the geometric standard deviation (σ_g) , and the mean surface area to volume shape factor (a) defined for the lognormal particle size distribution defined by D_g and σ_g . To illustrate potential correlations, the behavior of these parameters describing the particle sizes and shapes as a function of energy or energy density is examined. Plots of these parameters for Pyrex and SRL 131 simulated waste glass are shown in Figs. 31-40.

These graphs are largely self-explanatory, but a few generalizations are given below before they are discussed further. To gain a perspective of these tests, it should be pointed out that the mean energy density of a body with a density of 5 g/cm³ falling a height of 10 m to an unyielding flat surface is about 0.5 J/cm³; our standard impact test condition was 10 J/cm³, except that in some tests the range was tenfold higher or lower.

The two principal measures of impact strength are the surface area generated in the impact (i.e., ratio of impact energy to surface area, γ_f/ϵ , and the respirable fraction, as shown in Figs. 31, 32, 33, and 34. The geometric mean (Dg) of the lognormal distribution is approximately inversely proportional to energy density; the respirable fraction is approximately directly proportional to energy density. Both the dimensionless standard deviation, σ_g , of the lognormal distribution and the dimensionless surface area/volume shape factor, α , are nearly invariant with energy density.

Figures 31 and 32 show the measured BET surface areas, S_n , vs impact energy, W_i , for a variety of specimen sizes for Pyrex and SRL 131 glass, respectively. In general, a straight line can be drawn through the data points to provide an approximate correlation. The slope of the line is





Pyrex Surface Area vs Impact Energy for Diametral Impact. c = energy efficiency. yf = impact strength







Fig. 33. SRL 131 Simulated Waste Glass: Weight Percent Respirable Fraction vs Impact Energy Density



Fig. 34. Pyrex: Weight Percent Respirable Fraction vs Impact Energy Density



Fig. 35. Pyrex: Geometric Mean of Particle Size, Dg, vs Impact Energy Density



Fig. 36. SRL 131 Glass: Geometric Mean of Particle Size, Dg, vs Impact Energy Density





Fig. 37. Pyrex: Geometric Standard Deviation, σ_g , <u>vs</u> Impact Energy Density



Fig. 38. SRL 131 Simulated Waste Glass: Geometric Standard Deviation, σ_g , vs Impact Energy Density



Fig. 39. Pyrex: Mean Surface Area to Volume Shape Factor, α , <u>vs</u> Impact Energy Density, Calculated from BET Surface Area Measurements. V_o = volume of original specimen. σ_{g} = geometric standard deviation



α, vs Impact Energy Density, Calculated from BET Surface Area Measurements

the term, ϵ/γ_f , where $\gamma_f(J/m^2)$ is some measure of the impact strength of the brittle material and ϵ is the efficiency ($\epsilon \leq 1$) relating the maximum available impact energy, W_i , to the actual energy available to create new surface area. Previous reports such as [MECHAM, ANL-81-27] have discussed the proposed relation as

$$\varepsilon W_i = \gamma_f S_n$$

More experiments are required to establish whether there is a definite dependence of these results on specimen size, as suggested by these data and the other plots (Figs. 18 and 19).

The amounts of respirable fractions (in wt %) as a function of impact energy density for impact tests with different sizes of Pyrex and SRL 131 waste glass specimens are given in Figs. 33 and 34. The SRL 131 results suggest a nearly linearly relation. The Pyrex data are not as convincing, especially at the lower energy densities. The cause of the large scatter in the Pyrex energy density tests of 1 J/cm³ is not really known. The scatter is probably due to the use of some earlier generation analysis procedures, the lack of Coulter counter data (<u>i.e.</u>, respirable sizes determined by extrapolation of sieve data only) in some cases, and the as-yet-unknown effects as test energies approach the undetermined threshold for fracture, or a combination of all three. More data are needed to resolve the scatter of these data. However, it is clear that the respirable fraction increases with increasing energy density.

Figures 35 to 38 summarize the two lognormal parameters, i.e., the mass mean diameter D_g (mm) and the geometric standard deviation, σ_g , as a function of impact energy density for various specimen sizes of Pyrex and SRL 131 glass. These two parameters were obtained by linear regression analyses. The mass mean diameter, D_g , is observed to vary inversely with the energy density for both materials and all specimen sizes. The geometric standard deviation is relatively invariant with energy density for both materials.

Another parameter of interest in characterizing the fracture particulate is the surface area to volume shape factor, α . For a complete lognormal distribution defined by D_g, σ_g , and volume V (or mass if the density is known), the cumulative surface area S_n to cumulative volume ratio of the distribution of fragments can be shown [HERDAN] to be

$$\frac{S_n}{V_n} = \frac{\alpha \sigma_g^{0.5 \ln \sigma_g}}{D_g}$$

The term, α , is dimensionless and is defined here as the surface area to volume shape factor. The value of α can be determined for fragment distributions of known mass with known D_g and σ_g if the surface area is experimentally measured and equated to S_n. This is

$$\alpha = \frac{S_n}{V_n} D_g \sigma_g^{-0.5 \ln \sigma}$$

where S_n is defined as the BET-measured surface area. This has been summarized for impact tests of Pyrex and SRL 131 glass specimens of different sizes (Figs. 39 and 40). These results show that the shape factor so derived is relatively invariant at about 20. Further work is needed to relate a to other parameters of interest and to establish whether a varies with either particle size or brittle material.

IV. CONCLUSIONS AND SUMMARY

This work is incomplete in the sense that it was terminated prior to full completion of the long-range goals of this program. However, impact testing procedures, fragment characterization methods, and a modeling methodology required to characterize dynamic impacts resulting in brittle fracture were developed to various degrees. This report describes the results obtained for impact testing procedures and fracture characterization methods. The modeling methodology will be reported separately.

Standardized diametral impact tests, useful for material properties comparisons, at the same impact energy per specimen volume showed that SRL 131 and PNL 76-68 glasses, SYNROC B, SYNROC C, and SYNROC D ceramics each generated the same mass fraction of respirable material. The tailored ceramic waste form generated two-fifths as much respirable material. The FUETAP waste form generated 2 1/2 times as much respirable material as the SRL 131, PNL 76-68 glasses, or SYNROC. The alkoxide, high-silica, and Pyrex glasses generated (~50%) greater mass fractions of respirable material than did the SRL 131 or PNL 76-68 glasses. All impact fragments were found to follow lognormal particle size distributions. The quantity of respirable sizes was not strongly dependent upon the brittle material tested. Such results suggest that it may be possible to characterize and model one waste form to establish a brittle fraction methodology and data base that are also applicable to other brittle waste forms.

The absolute amounts of respirable sizes were found to increase linearly with increasing impact energy density. However, no scaling laws have been established for extrapolation of these laboratory test results to full-scale waste forms.

Impact tests were performed on three sizes of laboratory-scale specimens of simulated SRL 131, PNL 76-68, alkoxide waste glasses, SYNROC B, and Pyrex to measure the BET surface areas of the fragments. The surface areas increased smoothly with increasing impact energy. The surface areas of all other materials were bounded by the surface areas of Pyrex and SRL 131 glasses, with the SRL 131 glass surface area increases being ~20-30% less than those of Pyrex over an eight-fold energy test range. Surface area increases differed slightly for different specimen sizes, indicating a minor dependence on specimen size.

Uniform glass microspheres (50.7 μ m and 120 μ m) were used as quasistandards and the probable accuracy of BET measurements of surface areas was estimated to be ±10 to 30% for glass samples of 0.1 m² to $\sqrt{3}$ m² total surface area. The precision of BET measurements was determined to be ±2-6%, using glass materials and ZnO material; the precision measurements included comparisons with measurements by one off-site independent laboratory. Optical microscope observations of $\sim 100-\mu m$ SRL 131 glass fragments showed that the smaller fragments, $\langle 10 \ \mu m$, were readily attached to larger particles by some type of bonding mechanism during or after impact.

An optical and SEM characterization study of the fragments of Pyrex was subcontracted to NCSU. Their results showed that the surface area to volume shape factor, α , did not depend on fragment size over the range of ~ 0.1 to 1000 µm. Poor mass balances indicated material losses, preventing definitive conclusions in which the cumulative mass fractions and surface areas obtained from the microscopic methods would be compared with those obtained from sieving/Coulter counter and BET analyses.

The two lognormal parameters, the surface area increases, and the respirable fraction obtained from standard impact tests on Pyrex and SRL 131 waste glasses have been summarized and correlated with energy density over the range of 1-100 J/cm³ for three laboratory-scale specimen sizes. The geometric mean diameter, D_g , varied inversely with energy density; the standard deviation was nearly invariant. The amount of respirable particle sizes was directly proportional to energy density. The dimensionless surface area to volume ratio shape factor, α , derived from the two lognormal distribution parameters and the measured BET surface areas, was also found to be nearly invariant at a value of ~ 20 for both glasses.

Samples of impact fragments of SRL 131 glass smaller than 90 μ m were sent to five different laboratories for size analyses by five different methods. The reported cumulative volumes for particles smaller than a given size were lognormal and showed some variations among the different methods. However, the overall means agreed closely with the values of the two lognormal parameters obtained by Coulter counter measurements at ANL. Thus, the measurement of small particle sizes was not greatly dependent upon the method used for characterization.

Standard impact test conditions of 10 J/cm^3 were used to compare diametral impacts with axial impacts of 25-mm-OD x 25-mm specimens. The standard deviation of the lognormal distribution for axial impact was ~ 10 to 20% smaller than for diametral impacts. This result is consistent with the stresses being more uniform in axial impacts than in diametral impacts.

Drop-weight impact tests done with a mechanical stop (to prevent secondary crushing) showed that the mechanical stop was not really necessary in our test apparatus.

Impact tests of SYNROC B, SYNROC D, and SRL 131 glass were made at the very severe test conditions of 141 J/cm³ used in Australia on $13-mm-0D \times 13-mm$ specimens. The size distributions of fragments were lognormal. The respirable sizes measured in our tests agreed with those reported in Australia, where different analysis methods and different types of SYNROC were used.

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APPENDIX A

IMPACT TEST OF COAL

To examine the applicability of our impact test procedure to brittle materials of other Division programs, several 25-mm-ID (1-inch) cylindrical specimens were core-drilled from chunks of coal. The coal was obtained from the ANL Power Plant stockpile. A procedure was developed of core-drilling coal without splitting its layered structure (which would ruin the coredrilled specimen). Apparently, drilling at too fast a rate generates enough heat to turn the water coolant into steam, fracturing the layered coal specimen.

A 16.8-g dried specimen (25.3-mm OD x 26.0 mm long) was impacted at room temperature with v131 J in a sealed drop-weight chamber. This corresponded to an impact energy density of 10 J/cm³. The fragments were collected with water and were washed on a 63- μ m sieve. The sizes larger than 63 μ m were dried in a vacuum oven at 50°C, then sieved on a Sonic sifter into seven fractions. The <63 μ m fraction, still in water, was analyzed with a Coulter counter. After the Coulter counter analyses, the <63 μ m fraction was evaporated to dryness to determine the mass of those fragments.

The cumulative particle size distribution was then plotted and was fit with a lognormal distribution. The results are shown in Fig. A-1. The two lognormal parameters are D_g , 2.5 ± 0.5 and σ_g , 7.0 ± 0.2. The amount of coal fragments smaller than 10 µm is 0.22 ± 0.03 wt % or 37 mg. SEM examinations of coal fragments sized into the ranges, <10 µm, 10-50 µm, and >50 µm, were also performed. Maceral (plant) phases in the fragments were not easily identified. The mass balance losses were 112 mg or 0.6 wt %, but nothing is known about the distribution of the losses.

These results are comparable with those for glass and ceramic type materials that have been impacted under similar conditions and whose fragments have been characterized in this report. It is concluded that the fracture of coal occurs similarly to other brittle materials--resulting in lognormal fragment distributions.



Fig. A-1. Size Distribution of Fracture Particulates from Coal (from ANL Power Plant) Impacted at 10 J/cm³

APPENDIX B

EVIDENCE AND ANALYSIS OF FUSION OF GLASS PARTICLES FORMED BY MECHANICAL IMPACTS

SUMMARY

A method of characterizing impact fracture of simulated waste glass and other brittle materials has been applied to the conditions under which fusion of glass particles was observed in standard drop-weight impact tests of small glass specimens. Calculations predict that particles smaller than 4 μ m can be heated to a temperature of 500 °C or more during impaction of a borosilicate waste glass at an impact energy density of 10 J/cm³ of specimen volume. The mass fraction of particles smaller than 4 μ m was 0.03%. This particle size is the same as that of fused particles observed in calibrated microphotographs. The characterization method described in this appendix is applicable generally to a large range of impact conditions.

1. Introduction

One feature of impact fracture of brittle materials that should be understood is the tendency of input kinetic energy to be converted into heat. If there is sufficient heating, partial fusion of the fractured material can occur. This aspect was analyzed as part of the overall characterization of impact fracture of brittle materials since one consideration is the quantity of respirable fines generated in the event of a mechanical impact which fractures a brittle body. Fusion affects the quantity of respirable fines, since small particles are the most susceptible to fusion. Some evidence of impact fusion is cited here. Also, mathematical analysis is presented predicting the conditions under which impact fusion could occur for a particular borosilicate glass.

2. Observations of Fusion of Glass Particles in Impact Tests

In a study of brittle fracture of various simulated waste glasses, a standard impact test was used in which small cylindrical specimens were impacted by dropping a 10-kg steel bar from a predetermined height [MECHAM-1981]. The range of impact energy densities was varied from about 0.5 J/cm³ of specimen to 100 J/cm³. In some tests at the higher energy densities, glass particles found under the steel bar appeared to be consolidated into lumps rather than to be independent particles. The appearance of these lumps suggested that partial sintering had occurred.

A sample at SRL-131 simulated waste glass^{*} from the impact test (10 J/cm³) was anchored to a slide using double-sided-adhesive tape to immobilize the larger particles. Particles were photographed by optical microscopy [BAYARD]. Three views of fragments on a microscope slide are shown in Fig. 24 (p. 51). As seen, small glass particles (smaller than 10 μ m) remained attached to the relatively flat surfaces of the larger particles (about 50 μ m) during the

^{*}The SRL 131 simulated waste glass has properties similar to Pyrex, but the softening temperature is lower.

preparation of the microscope slide. A number of instances of small particles being attached to large particles were examined with a tungsten needle (tip radius of about 1 μ m) to see how strongly the small particles were attached. In nearly one-half of these examinations, the small particles resisted detachment to the extent that compression welding or fusion was indicated. The remainder of this paper describes a mechanism by which such attachment by fusion could occur.

3. Surface-Energy Correlations for Fracture Particulates

In drop-weight impact tests of brittle waste materials, the total fracture surface area of all particles, S_n (m²), correlates with the energy dissipated in the total volume, V_n (m³), of the brittle material.^{*} The input kinetic energy, W_i , is converted chiefly into heat, as shown by impactcalorimeter studies [ZELENY]. The global energy-surface correlation is

$$\varepsilon W_i = \gamma_f S_n$$
 (B-1)

where γ_f (J/m^2) is a strength property of the material and ε is an efficiency factor ($\varepsilon < 1$; in typical tests, $\varepsilon \sim 0.5$.). In the cited impact-calorimeter work, ε was determined, and it was shown that γ_f is a constant, 77 J/m², for Pyrex and quartz over a 24-fold range of energy density (0.60 J/cm³ to 15 J/cm³), which is the input kinetic energy per unit volume or energy density of brittle material, W_i/V_n . In our (noncalorimetric) work, we correlate the combined factor (γ_f/ε) with energy density and relate the overall surface/ volume ratio to energy density:

$$\frac{\mathbf{r}_{\mathbf{f}}}{\epsilon} \left(\frac{\mathbf{S}_{\mathbf{n}}}{\mathbf{V}_{\mathbf{n}}} \right) = \frac{\mathbf{W}_{\mathbf{i}}}{\mathbf{V}_{\mathbf{n}}} \tag{B-2}$$

4. Lognormal Size Distributions of Fracture Particulates

Impact-fracture particulates have size distributions that can be approximately described by the lognormal probability parameters: the geometric mean diameter, D_g , and the geometric standard deviation, σ_g [MECHAM-1980]. These parameters are determined from particle size analyses and correlate with energy density. A typical linear-regression fit of the data plot for a 10 J/cm³ diametral impact of a (2.5-cm x 2.5-cm) SRL 131 simulated waste glass cylinder is shown in Fig. B-1. The cumulative volume fraction, V(D)/V_n, and the calculated cumulative surface area fraction, S(D)/S_n, are shown. Volume, V_n, is the total volume of the original specimen (12.9 cm³), and S_n is the total surface area of the fracture particulate (0.63 m²) based on a BET surface-area measurement.

When the parameters, V_n , S_n , D_g , and σ_g , are known, the cumulative volume V(D) and the cumulative surface area S(D) can be found graphically (from Fig. B-1) or they can be calculated for particles smaller than any size D, as shown in the Addendum to this appendix. The calculated values of the mean surface/ volume ratio as a function of particle diameter, D, for a given fracture particulate are summarized in Table B-1, for values of D from 1 μ m to 2048 μ m.

^{*}Symbols are defined on the Nomenclature page at the end of this appendix.


Fig. B-1. Cumulative Volume Fraction and Calculated Cumulative Surface Area Fraction of the Fracture Particulate Formed from SRL 131 Simulated Waste Glass Impacted at 10 J/cm³

Also shown in the table are the energy density and the temperature rise as a function of particle size, D. The energy density as a function of D is calculated from the relation between energy density (W_i/V_n) and the surface/ volume ratio (S_n/V_n) shown in Eq. B-2, using the measured value of (γ_f/ϵ) . (Mathematical details are given in the Addendum.) Note that the surface/volume ratios in Table B-1 are higher for smaller values of D. Values of energy density in the table are based on the assumption that (γ_f/ϵ) is the same for the local energy density as that experimentally determined for the global energy density (W_i/V_n) .

The temperature rise as a function of size D was calculated on the assumption that the energy represented by the energy density in Table B-1 was converted into heat at the average heat capacity, $C_v = 2.2 \text{ J/cm}^{3\circ}C$, for simulated waste glass. (Heat capacities for simulated waste glass [CORNMAN] and for Pyrex [HUTCHINS] are shown in Table B-2.) From these heat capacities, the temperature rise, $\Delta T(^{\circ}C)$, as a function of D is given for consistent volume units by

 $\Delta T = \frac{\text{energy density}}{C_{u}(J/cm^{3} C)}$

Particle Dia, µm	Cumulative Volume Fraction, V(D)/V _n	Surface/ Volume Ratio, ^a m ⁻¹	Energy Density, ^b J/cm ³	Temperature Rise, ^C °C
1	1.89 x 10 ⁻⁵	2.1×10^7	4.3×10^3	2.0×10^3
2	8.50 x 10 ⁻⁵	1.1×10^7	2.3×10^3	1.0×10^{3}
4	3.37×10^{-4}	5.3 x 10 ⁶	1.1×10^3	49 0
8	1.18 x 10 ⁻³	2.7 x 10 ⁶	554	252
16	3.68×10^{-3}	1.3 x 10 ⁶	266	121
32	1.04×10^{-2}	6.5 x 10 ⁵	133	61
64	0.0256	3.3 x 10 ⁵	68	31
128	0.055 9	1.6 x 10 ⁵	33	15
256	0.109	8.2 x 10^4	17	7.6
512	0.194	4.1×10^4	8.4	3.8
1024	0.308	2.1 x 10^4	4.3	2.0
2048	0.442	1.0×10^4	2.0	0.93

Table B-1.	Calculated Properties of a Fracture Particulate Formed
	from SRL 131 Simulated Waste Glass Impacted at 10 J/cm ³

^aCalculated from Eq. B-9 in the Addendum of this appendix. ^bEnergy density = $(\gamma_f/\epsilon) \times (\text{surface/volume ratio}); \gamma_f/\epsilon$ is defined in Eq. B-2 above.

^CSee following text for details.

	C _p ,cal/g°C		C _v , J/cm ³ °C ^a	
	at 25°C	at 500°C	at 25°C	at 500°C
Simulated Waste Glass	0.19	0.28	1.8	2.6
Pyrex	0.17	0.28	1.6	2.6

Table B-2. Heat Capacities for SRL 131 Simulated Waste Glass [CORNMAN] and Pyrex [HUTCHINS]

 $^{\rm a}{\rm Calculated}$ from ${\rm C}_{\rm p}$ to give appropriate units for Pyrex and simulated waste glass.

The calculated temperature rise is plotted as a function of particle size (Fig. B-2). The calculated points plotted on logarithmic coordinates all fall on a straight line.





Calculated Temperature Rise as a Function of the Size of Glass Particles Produced by Impact Fracture (based on Table B-1)

Since glass has no definite melting point but has a measurable decrease in viscosity as temperature is increased, the temperature at which fusion can occur is somewhat arbitrary. From available information on the softening temperature of glasses (HUTCHINS, CORNMAN), it is assumed that fusion in impact compression can only occur when the local temperature is 500° C or higher. From Fig. B-2, this is seen to occur for a particle size of 4.0 µm or smaller. For the given impact conditions, the volume fraction for particles of this size range is 3.4×10^{-4} or 0.03% as shown by Fig. B-1 and Table B-1. For impacts with larger energy density, the critical diameter for impact fusion will be larger, as will the volume fraction of sizes of particles that can fuse.

5. Conclusion

On the assumption of conservation of energy in the conversion of elastic strain energy to heat in impact fracture, the calculated temperature rise from the impact of waste glass (calculated using an empirical surface-energy correlation) predicts the maximum size of small particles firmly attached to large particles. This result supports the utility of the lognormal method for characterizing the results of brittle fracture. Our literature review has not revealed a previous observation of this model of particle fusion.



ADDE NDUM

The following mathematical definitions are discussed in detail in [HERDAN].

The cumulative lognormal probability function, P(u), and the corresponding probability density (frequency) function p(u) are substitution instances of the basic normal probability law, also known as the error function and the Gaussian distribution. The mathematical definitions are:

$$P(u) = \int_{-\infty}^{u} p(u)du; \ p(u) = \frac{1}{\sqrt{2\pi}} e$$
 (B-3)

In the application of the normal probability function to small-particle statistics, the experimental cumulative volume fraction as a function of particle size (D) is equated to the lognormal distribution according to volume:

$$\frac{V(D)}{V_n} = P(u_v); \ u_v = \frac{\ln D}{\ln \sigma_g} - \frac{\ln D}{\ln \sigma_g}$$
(B-4)

For a lognormally distributed particulate, the cumulative surface area distribution has the same geometric standard deviation, σ_g , and has a related variate, u_g

$$\frac{S(D)}{S_n} = P(u_s); u_s = u_v + \ln \sigma_g \qquad (B-5)$$

By definition, the derivatives of Eqs. B-4 and B-5 are

$$du_{v} = du_{g} = \frac{d \ln D}{\ln \sigma_{g}}$$
(B-6)

$$\frac{dV(D)}{du_{v}} = V_{n} \frac{d P(u_{v})}{du_{v}} = V_{n} P(u_{v})$$
(B-7)

Note that $p(u_v)$ is defined by Eq. B-3. The derivative of Eq. B-5 is:

$$\frac{dS(D)}{du_{g}} = S_{n} \frac{dP(u_{g})}{du_{g}} = S_{n} p(u_{g})$$
(B-8)

By combining Eqs. B-7 and B-8 and substituting $u_v + \ln \sigma_g$ for u_s :

$$\frac{dS}{dV} = \frac{S_n}{V_n} \frac{p(u_v + \ln \sigma_g)}{p(u_v)}$$
(B-9)

The physical meaning of dS/dV in Eq. B-9 is the surface/volume ratio of all particles of exactly size D. The mathematical form of Eq. B-9 allows us to calculate dS/dV for any particle size, D, from known values of the lognormal

parameters, D_g and σ_g . The overall surface/volume ratio, S_n/V_n , for all possible D at a given D_g and σ_g is defined by the ratio of the second and third moments of the lognormal distribution of D:

$$\frac{S_n}{V_n} = \frac{\alpha \sigma_g^{0.5 \ln \sigma_g}}{D_g}$$
(B-10)

where α is a dimensionless mean shape factor determined by an experimental measurement of surface area, as described in the text above. Note that S_n/V_n is also related to the energy density (W_i/V_n) by Eq. B-2 in the text.

NOMENCLATURE $C_{\rm p}$ = specific heat capacity, cal/g °C C_v = heat capacity, J/cm^{3} °C D = particle size D_g = geometric mean diameter (mass median), m p(u) = normal probability density function P(u) = cumulative lognormal probability function S(D) = cumulative surface area of a particulate, for all particles smaller than size D, m^2 S_n = total surface area of the fracture particulate, m^2 ΔT = temperature rise, °C u = standard normal variate $u_s = u$ defined for particle distribution by surface area $u_v = u$ defined for particle distribution by volume or mass V(D) = cumulative volume of a particulate, for all particles smaller than size D V_n = total material volume of the fracture particulate, m^3 Wi = input energy density to impact, J $\frac{W_1}{V_2}$ = overall energy density, J/m^3

Greek Letters

 α = mean surface/volume shape factor γ_f = impact strength of material, J/m² ϵ = efficiency of utilization of energy for brittle fracture σ_g = geometric standard deviation

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APPENDIX B

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APPENDIX C

PREPARATION AND MICROSCOPIC CHARACTERIZATION OF PYREX IMPACT FRAGMENTS AT NORTH CAROLINA STATE UNIVERSITY (NCSU); COMPUTATION OF SURFACE AREA FOR A PROLATE SPHEROID; DISTRIBUTION PLOTS

1. Preparation and Characterization of Pyrex Fragments

a. Riffling of Samples

To provide representative small samples from various screen size fractions, a small riffle splitter was designed and fabricated in NCSU shops. The milled brass splitter provides five equal, 45° sloped channels directing particles to the left, and a similar number of channels directing particles to the right. Top edges of the dividing walls between adjacent left and right channels are knife-edged and beveled. A stainless steel hopper/cover is closely fitted over the milled brass block, and stainless steel pouring and receiving pans of suitable sizes are also fitted for use with the splitter.

For coarse fractions (+80 mesh) >175 μ m, the splitter was used directly. For smaller screen sizes, where the weight fraction recovered was usually also small, an added fabric diffuser (-70 mesh nylon screen) was stretched across the hopper of the splitter. By use of a rectangular funnel, small quantities of finer mesh materials were scattered on the screen while the whole assembly was vibrated by the shaker table. This ensured rather uniform particle distributions over the full screen area, with the probability that the sample would split evenly between left and right channels.

Careful preliminary evaluations carried out gravimetrically with mock-up or dummy samples of crushed Pyrex glass confirmed that the riffle splitter were very effective in producing two representative smaller samples, each having approximately 50% of the total weight initially introduced. Successive splittings of a given material produce representative smaller samples having a weight ratio of $(1/2)^n$, where n represents the number of successive splits.

Because large dilution factors (typically, dilution factors of 75:1, 150:1, or even 300:1), are required to achieve proper dispersion of particles in the "wax" (Fig. 25), the actual quantity of a given representative sample required is quite small, typically in the range of 25-35 mg. Depending on the total weight of the initial size fractions, the sampling procedures may require 2, 3, 4, or even 5 successive splits (<u>1.e.</u>, to 1/4, 1/8, 1/16, or even 1/32 of initial weight). For the samples being characterized, the actual splitting process was closely monitored gravimetrically.

b. Dispersion of Samples

To achieve a dilute uniform particle/dispersant mixture, a small plastic packet containing a weighed quantity of specimen and a proper quantity of dispersant "wax" to achieve a predetermined dilution ratio (typically 150:1) was heat-sealed (Fig. 25). After sealing, the material was kneaded and thoroughly mixed within the packet to achieve a fine, uniform dispersion of sample particles within the somewhat grainy organic "wax." Since the specimen particles were well diluted by the softer "wax" and were also kneaded with gentle finger pressure only, the probability that additional fracturing of significant numbers of glass fragments would occur was considered to be acceptably small.

The virtue of using a sealed plastic packet is obvious: it protects against contamination, it facilitates manual kneading and visual observation of progress toward uniformity, and importantly, it retains volatile organic constituents, thereby maintaining the proper dilution ratio. When material is to be removed, the packet is opened with scissors and the necessary quantity is removed. The entire packet can again be heat-sealed to retain the volatiles and maintain the integrity of the mix more or less indefinitely.

c. Removal of Dispersant

In preparing a substrate-supported dispersion of particles for observation and photomicrographs in the scanning electron microscope, the sample-"wax" mix was dispersed uniformly on a 2.5-cm x 7.5-cm x 0.1-cm glass microscope slide. The slide, containing a small quantity of the mix, was transferred onto the hot plate, the mix was lightly leveled with the spatula, covered with a second slide (or cover glass) to provide uniform leveling, and brought to a temperature just above the melting point of the wax ($\sqrt{32^{\circ}C}$), causing the dispersant to flow out uniformly.

After cooling, the upper slide was separated from the substrate by use of a razor blade.

The dispersant camphor-naphthalene eutectic sublimes at room temperature in vacuo, but a period of several hours was normally required for complete removal of the waxy substance. A facility consisting of a mechanical vacuum pump, a freon-chilled cold trap and a small bell jar was assembled to sublime the eutectic mixture. During pumping, some condensation of the waxy material was observed within hoses upstream from the cold trap. This created some difficulties in removing the mixture in the initial samples. After overnight pumping, some specimens were still not fully wax-free. Some of these incompletely sublimed preparations were utilized for SEM photographs and subsequent counting. For any further work, a well-designed permanent sublimation facility (e.g., featuring closely connected, cleanable metal components, readily arranged for washing with alcohol between runs) is recommended.

d. Coating of Particles

A conventional vacuum evaporator was used to deposit ~ 200 Å of gold coating omnidirectionally on dispersed, wax-free particles. The purpose of the gold coating was to provide a conductive thin film to minimize charging of particles under the SEM electron beam. After coating, prepared specimens were stored in clean, covered petri dishes prior to SEM examination.

e. Examination in Scanning Electron Microscope

For scanning electron microscopy (SEM), a prepared particle-bearing substrate (microscope slide) was slipped beneath the clips of a special low-form stage and was inserted in the low stage position in a JEOL JSM-2 scanning electron microscope, yielding an effective working distance of 26.5 mm. All SEM micrographs were taken at that working distance, with zero tilt angle, at 25-kV accelerating voltage, and with a constant (small-spot, high-resolution) condenser lens setting. Magnifications were varied to best image the particles in a given field. Considerable operator patience, skill, and judgment were required in randomly locating fields, selecting appropriate magnifications, adjusting photographic contrast/brightness conditions, and maintaining accurate specimen identity and magnification records.

Fields of view were selected by a random method. The operator initially set the X and Y specimen drives at zero. If particles were present, they were photographed at one of six appropriate magnification settings. After photographing, or if no particles were present, the operator moved the Y-drive 0.25 mm or 1/2 turn (at the end of travel in the Y direction, the X-drive was shifted 0.25 mm and the Y-drive reset to zero), ascertained a new field, and again photographed at one of six appropriate magnification settings, repeating this stepwise process until more than 300 particles had been photographed.

The film used was Polaroid type 665. Negatives were processed in 12% sodium sulfite, then washed and dried according to the manufacturer's standard recommendations.

The specimen stage was custom-machined to produce a central cavity with a depth that permitted the top surface of a SEM calibration standard (NBS Standard Reference Material 484, Serial LJ 148555) to be adjacent to, parallel to, and at the same working distance from the objective lens as the top plane of the glass slide substrate. In accordance with NBS recommendations, the calibration standard was photographed at each of six magnification settings. The normal range of magnifications for the reference is X1000 to X20,000. To check the accuracy at low magnifications, a particle was found on the standard and photographed at the three lowest magnification settings.

All photographic negatives (for sample particles and the calibration standard) were enlarged, at a constant enlargement factor of X2.5, to about $20 \times 25 \text{ cm}$ ($\sim 8 \text{ in. } \times 10 \text{ in.}$). A "witness print" of the calibration scale built into the negative carrier of the Durst S-45 EM enlarger was produced at the beginning and end of each such set of enlargements to record the accuracy and consistency of the overall darkroom photographic process.

f. Examination by Optical Macropgraphy

As shown in the flow diagram in Fig. 25, the +80 mesh (>175 μ m) fraction was split to obtain a small representative specimen (on the order of 1 g) which was manually spread (principally by tapping) on a black matteboard substrate for optical macrography. A copystand-mounted 35-mm SLR camera (Canon AE-1) equipped with an extension bellows-mounted 50-mm macrolens was used to image the particles, and a millimeter scale was employed as a direct calibration standard. Both the reference scale and a number of randomly selected fields of the particles from each sample were photographed. Photographic enlargements to λ X17.5 (full frame, nominal 20 x 25 cm or 8 in. x 10 in. format) of the reference scale and the particles were prepared for subsequent electronic digitization and counting.

8. Modified Sieving Procedure

After this complete procedure was followed for the first sample, AR-1, and the measurements and calculations described below were performed, it became apparent that a simpler and better procedure could be employed. The sieve screen sizes from 400 mesh $(37 \ \mu m)$ to 80 mesh $(175 \ \mu m)$ differ little; on a logarithmic scale, they cover comparatively little of the range of interest, particularly when only a tiny fraction of the sample is involved. In addition, not only does the additional handling of the material afford many opportunities for contamination, but also retention of some of the fine particles with coarser fractions has been observed. This makes it difficult to quantitatively combine size measurement distribution data from different sieve fractions, unless all fractions are measured. However, if all sieve fractions are measured, the need for complete sieve sorting disappears, and only enough separation of coarse from fine is required to facilitate the sample preparation and examination steps.

Accordingly, samples AR-2' and AR-3 were combined and resieved into only four splits: +80 mesh (>175 μ m), -80 mesh (<175 μ m), +400 mesh (>37 μ m), and -400 mesh (<37 μ m). The weight of each split was recorded (see Tables 26, 27, and 28) and used to combine the distribution measurements from the different samples, all of which were measured. This not only simplifies the procedure, but makes the resulting total distribution a more reliable estimate of the specimen.

2. Computation of Surface Area (S_e) for a Prolate Spheroid (from Chemical Rubber Handbook (CRC) math tables)

$$S_e = 2\pi b^2 + 2\pi \frac{ab}{\epsilon} \sin^{-1} \epsilon$$

$$\epsilon = \frac{\sqrt{a^2 - b^2}}{a}$$

 ε = eccentricity

a = minor semi-axis

$$a \int_{\theta} \sqrt{a^2 - b^2} \qquad \theta = \sin^{-1} \sqrt{\frac{a^2 - b^2}{a}}$$

$$\theta = \tan^{-1} \frac{\sqrt{a^2 - b^2}}{b}$$

$$S_e = 2\pi b^2 + \frac{2\pi a^2 b}{\sqrt{a^2 - b^2}}$$
 $\tan^{-1} \frac{\sqrt{a^2 - b^2}}{b}$

Using our notation,

$$b = D_{g}/2, a = D_{L}/2$$

$$S_{e} = \frac{\pi D_{g}^{2}}{2} + \frac{\pi D_{L}^{2} D_{g}}{2 \sqrt{D_{L}^{2} - D_{g}^{2}}} \tan^{-1} \frac{\sqrt{D_{L}^{2} - D_{g}^{2}}}{D_{g}}$$

3. Distribution Plots (Figs. C-1 to C-3)

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Fig. C-1. Distribution Plots for Sample AR-1

- a) Sample AR-1 +80. Number of particles in 16 logarithmic groups with equivalent spherical diameters from 128 to 2436 μm.
- b) Same as C-la but summed volume in each group.
- c) Same as C-la but cumulative summed volume.
- d) Same as C-la but summed area in each group.
- e) Same as C-la but cumulative summed area.
- f) Sample AR-1 -400. Number of particles in 35 logarithmic groups with equivalent spherical diameters from 0.125 to $64 \mu m$.
- g) Same as C-lf but summed volume in each group.
- h) Same as C-lf but cumulative summed volume.
- i) Same as C-lf but summed area in each group.
- j) Same as C-lf but cumulative summed area.



Fig. C-2. Distribution Plots for Sample AR-2'

- a) Sample AR-2' +80. Number of particles in 18 logarithmic groups with equivalent spherical diameters from 128 to $3444 \mu m$.
- b) Same as C-2a but summed volume in each group.
- c) Same as C-2a but cumulative summed volume.
- d) Same as C-2a but summed area in each group.
- e) Same as C-2a but cumulative summed area.
- f) Sample AR2' -80 +400. Number of particles in 21 logarithmic groups with equivalent spherical diameters from 4 to 181 µm.

- g) Same as C-2f but summed volume in each group.
- h) Same as C-2f but cumulative summed volume.



Fig. C-2 (cont'd)

- i) Sample AR-2' -400. Number of particles in 28 logarithmic groups with equivalent spherical diameters from 0.25 to 38 µm.
- j) Same as C-2i but summed volume in each group.
- k) Same as C-2i but cumulative summed volume.
- 1) Same as C-2i but summed area in each group.
- m) Same as C-2i but cumulative summed area.



Fig. C-3. Distribution Plots for Sample AR-3

- a) Sample AR-3 +80. Number of particles in 12 logarithmic groups with equivalent spherical diameters from 256 to 2436 µm.
- b) Same as C-3a but summed volume in each group.
- c) Same as C-3a but cumulative summed volume.
- d) Same as C-3a but summed area in each group.
- e) Same as C-3a but cumulative summed area.
- f) Sample AR-3 -80 +400. Number of particles in 21 logarithmic groups with equivalent spherical diameters from 4 to 181 µm.
- g) Same as C-3f but summed volume in each group.

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h) Same as C-3f but cumulative summed volume.



Fig. C-3 (cont'd)

- i) Same as C-3f but summed area in each group.
- j) Same as C-3f but cumulative summed area.
- k) Sample AR-3 -400. Number of particles in 13 logarithmic groups with equivalent spherical diameters from 4 to 45 µm.
- 1) Same as C-3k but summed volume in each group.
- m) Same as C-3k but cumulative summed volume.
- n) Same as C-3k but summed area in each group.
- o) Same as C-3k but cumulative summed area.

APPENDIX D

SCALE-MODELING OF IMPACT SEVERITY FOR BRITTLE FRACTURE

ABSTRACT

Geometric modeling of elastic deformation during the compression stage of impact has been used as a basis for calculation of the stress-time relations that characterize the severities of particular cases of mechanical impacts with respect to fracture effects for brittle bodies of various sizes and shapes. Such calculations provide impact-severity parameters which can be correlated with parameters describing the fracture particulates. The overall correlations provide a nearly complete characterization of impact fractures of brittle materials. In particular, the time-dependent nature of crack propagation is critical for scaling the results of laboratory impact tests.

1. Introduction

Mechanical impacts of sufficient severity cause a brittle body to fracture into particles of widely varying size and shape. A review [MECHAM-1981] of the technical literature did not disclose practical generalizations of the scaling laws of impact fracture, which are required in order to use smallscale tests to predict accident behavior. If known, such scaling laws would greatly reduce the cost of experiments to establish the fracture behavior of brittle waste forms.

In earlier reports [MECHAM-1980, -1981], a method of characterizing impact-fracture particulates was developed, using the two parameters of the lognormal probability function: the mass median particle diameter (D_g) and the geometric standard deviation (q_{g}) . A mean value of the dimensionless surface/volume shape factor (a) was determined for given values of D_g and σ_g by the direct measurement of particle surface areas by the BET gas adsorption method. A complete description of the fracture particulate was made in terms of the cumulative volume (or mass) fraction of particles smaller than size D, $V(D)/V_n$, and the corresponding cumulative surface-area fraction, $S(D)/S_n$. The total surface area, Sn, of the lognormally distributed fracture particulate is mathematically related to the total volume, V_n , in terms of D_g , σ_g , and α . In standard drop-weight (DW) impact tests of small ($\sqrt{2}$ cm) cylindrical specimens of representative vitreous and ceramic materials, it was found that the standard deviation, σ_{g} , and the shape factor, α , were nearly invariant with input impact energy, while the mean size, D_g , and the -10 μ m fraction were, respectively, inversely and directly proportional to the input energy density (that is, the energy per unit volume of the specimen).

The extent of fracture is measured by the total surface area of the fracture particulate, S_n . This surface area has been empirically correlated with the energy dissipated in the brittle material in a series of impact tests using a dual pendulum impacting device in conjunction with an impact calorimeter [ZELENY]. The correlation was based on the relation^{*}

^{*}Symbols are defined in the Nomenclature list of the end of this appendix.

$$\varepsilon W_{i} = \gamma_{f} S_{n} \qquad (D-1)$$

where S_n is the surface area measured by the BET method, W_i is the input kinetic energy, ε is an efficiency factor (about 50% in standard tests), and γ_f is the impact-strength property of the material. The value of γ_f was reported to be a nearly constant 77 J/m², measured for small specimens of Pyrex and crystalline quartz over a 20-fold range of impact energy density [ZELENY].

In the present paper, geometric models of the elastic deformation of brittle bodies in impacts are used to define parameters measuring the severity of impacts with respect to the particulate mode of fracture observed in impact tests of brittle materials. From presently available data, these impactseverity parameters appear to correlate well with particle-size parameters and thus provide a quantitative basis for interpreting impact data and for predicting the results of postulated accidental impacts from material properties measured in small-scale impact tests.

2. Fracture Mechanics of Brittle Materials

Elastic stress (more precisely, local tensile strain) is the direct cause of crack propagation and body cleavage of brittle materials in impacts. There appears to be a maximum velocity of crack propagation (about 40% of the acoustic velocity, or about 2000 m/s in typical glass). This velocity is independent of the stress level [DOREMUS]. The crack velocity is, however, dependent on crack size: microcracks propagate at velocities at least one order of magnitude slower than those of millimeter dimensions. These facts account for the highly irreversible and catastrophic nature of brittle fracture: crack propagation is a time-dependent, accelerating "chain reaction." Furthermore, the propagation of the first crack destroys the continuous stress field and makes classical continuous mechanics useless for describing the fracture process itself.

The characterization of impact fracture proposed here relies on the statistical uniformities of the particulate and on the general principles of dimensional analysis and geometric modeling [LANGHAAR]. Specifically, energy and force balances are constructed as functions of time during the compression stage of impact fracture, noting the dimension of stress:

$$STRESS = \frac{FORCE}{AREA} = \frac{ENERGY}{VOLUME}$$
(D-2)

The energy/volume parameter (energy density) is directly related to elastic compression by the local strain energy density defined in terms of the local stress, σ , as $\sigma^2/2E$, where E is Young's modulus for the material. That is, the unidirectional application of force results in local strain energy, which integrates over the whole body volume, V_n , to give the total compression energy (work), W(X), defined for the overall linear compression, X:

$$W(X) = \int_{V_n} \frac{\sigma^2}{2E} \, dV. \qquad (D-3)$$

Equation D-3 is well established in elastic theory as Saint-Venant's principle [TIMOSHENKO]. It is also well established that the elastic compression wave travels at a speed that depends only on the material properties, E, and

density, ρ , namely, \sqrt{E}/ρ , independently of the stress level of the wave. The actual motion of the material itself, dX/dt, has a much lower velocity, and is proportional to the stress level, σ ; this material motion is that initially imparted by the collision velocity u_0 in impacts:

$$u_{o} = \left(\frac{dX}{dt}\right)_{o} = \frac{\sigma}{\sqrt{E\rho}}$$
 (D-4)

For free-fall impacts from 10 m, the collision velocity is about 14 m/s, and the stress σ is about 2 x 10⁸ Pa (3 x 10⁴ psi), which is below the fracture threshold. Therefore, the primary stress waves in practical impacts do not produce fracture, but only serve to increase the stress level in the body generally. Of course, the magnitude of the stress in the "wave" decreases as the bodily motion decreases during impact deceleration.

3. Axial Compression of a Cylinder in a Drop-Weight Impact

A rigorous analysis can be made for the dynamic stresses in a drop-weight (DW) axial impact of a cylinder, shown in Fig. D-1.



Fig. D-1. Drop-Weight Axial Impact of a Cylinder

In this ideal case, a uniform compressive stress, σ , is generated in the brittle body by the compression force F(X) and strain X/L:

$$F(X) = A\sigma = AE \frac{X}{L}.$$
 (D-5)

The elastic deformation is essentially planar, and the maximum elastic work, W(X), is related to input energy, W_1 :

$$W_{i} = W(X_{m}) = \int_{0}^{X_{m}} F(X) dX = \frac{\sigma^{2}}{2E}.$$
 (D-6)

The strain energy can be considered unidirectional along the force axis by Saint-Venant's principle, as discussed above. (The transverse strain energy, as calculated by Poisson's ratio, is small generally, and for typical glass is particularly small, about 4% of the total.)

The deceleration force, F(t), allowing for the negative value of the deceleration, du/dt, is given by

$$F(t) = -M\frac{du}{dt} = -M\frac{d^2X}{dt^2}.$$
 (D-7)

By a force balance, F(t) = F(X),

$$\frac{du}{dt} = \frac{d^2x}{dt^2} = -\left(\frac{EA}{ML}\right) X = -B^2X, \qquad (D-8)$$

which integrates over the boundary conditions to

$$X(t) = \frac{u_0}{B} \sin (BT)$$
 (D-9)

$$u(t) = \frac{dX}{dt} = u_0 \cos (BT) = u_0 \left[1 - \frac{W(X)}{W_i}\right]^{1/2}$$
 (D-10)

$$t(X) = \frac{1}{B} \arcsin (BX/u_0).$$
 (D-11)

For full compression,

$$W_{i} = 0.5 Mu_{o}^{2} = W(X_{m})$$
 (D-12)

$$t_{m} = t(X_{m}) = \frac{\pi}{2} \left(\frac{M}{V_{o}}\right)^{1/2} E^{1/2} L$$
 (D-13)

$$\frac{\mathbf{X}_{\mathrm{m}}}{\mathrm{L}} = \left(\frac{\mathbf{W}_{\mathrm{1}}}{\mathrm{V}_{\mathrm{o}}}\right)^{1/2} \left(\frac{2}{\mathrm{E}}\right)^{1/2}.$$
 (D-14)

Of particular interest is impulse I(t), the integral of force over time:

$$I(t) = \int_{0}^{t} F(t)dt = Mu_{0} - Mu.$$
 (D-15)

If the loss of kinetic energy is completely converted into compression energy in the brittle body, there is a direct relation of impulse to compression energy:

$$W(X) = u_0 I(t) - \frac{I^2(t)}{2M}$$
 (D-16)

The above analysis provides a mathematically rigorous complete description of the stress and energy as function of time. For free-fall impacts and for other impact configurations (e.g., diametral), such a rigorous analysis is not possible and geometric modeling together with numerical integration is required. The above mathematical relations provide a check of numerical calculations for particular modeled cases of DW axial impact.

4. Modeling Free-Fall Impacts

When a cylinder is impacted axially in free fall to an essentially unyielding flat surface, the external compression force, F(X), is applied to only one end of the cylinder, as in Fig. D-2. The overall energy balance in terms of input energy density (J/m^3) is

$$\frac{W_{1}}{V_{0}} = 0.5 \ \rho u_{0}^{2} = 9.8 \ \rho H = \frac{\sigma^{2}}{2E}$$
(D-17)

where ρ is the body density (kg/m^3) , H(m) is the free-fall distance, and σ_m is a mean stress over body volume, V_0 , at full compression, defined as in Eq. D-6. This equation provides a scaling law for impact stress. However, the material at the impact surface is compressed more than is the surface at the free end. This stress gradient can be defined in terms of a disk model described below.



Fig. D-2. Free-Fall Axial Impact of a Cylinder Showing the Force Gradient

As shown in Fig. D-2, the analysis of a free-fall (FF) impact can be made by assuming that the cylinder as a whole consists of a number of equal-sized coaxial disks. Each disk has its own force and energy balance. For disk 1, the compression force F_1 is balanced by the internally generated deceleration force:

$$F_1 = m_1 \frac{d^2 X_1}{dt^2},$$
 (D-18)

where m_1 is the mass and X_1 the linear compression for this disk. For disk 2,

$$F_2 = F_1 + m_2 \frac{d^2 x_2}{dt^2},$$
 (D-19)

and so on. The total force, F(X), on the load-bearing surface area, A, is

$$F(X) = F_7 + m_8 \frac{d^2 x_8}{dt^2}$$
 (D-20)

The overall linear compression, X, is formed from the sums of X_1 , X_2 , etc.:

$$x = \sum x_i; \frac{dx}{dt} = \sum \frac{dx_i}{dt}; \frac{d^2x}{dt^2} = \sum \frac{d^2x_i}{dt^2}.$$
 (D-21)

For this case, there is a linear gradient of force and stress during impact compression, and the maximum force and stress are twice the mean value defined by Eq. D-5 above. The mean values are the ones which are defined for the overall energy balance, in Eqs. D-6 and D-12.

5. Modeling Diametral Impacts

A general method of modeling elastic deformations of convex surfaces can be illustrated for the practical case of diametral impact in a drop-weight (DW) test. The circular cross-sectional area of the brittle cylinder impacted by steel surfaces is shown in Fig. D-3. There are two load-bearing surfaces, A(X), and two flattened zones described by the chord, C, and the circularsegment area, A_a . By geometry,



Fig. D-3. Diametral Compression of a Cylinder in a Drop-Weight Impact Test

$$C(X) = 2X^{1/2} (D - X)^{1/2}$$
(D-22)

$$A_{s}(X) = \int_{0}^{X} C(X) dX$$

$$= \frac{D^{2}}{4} \arcsin (C/D) - \frac{CD}{4} \left(1 - \frac{2X}{D}\right) \cdot$$
(D-23)

Each load-bearing surface area is A(X):

$$A(X) = LC(X). \qquad (D-24)$$

The deformation volume of each zone is V(X):

$$V(X) = LA_{s}(X). \qquad (D-25)$$

The maximum linear deformation in each zone is X and the mean \overline{X} at the surface A(X) is

$$\overline{X} = \frac{V(X)}{A(X)} \cdot (D-26)$$

The mean stress, $\sigma(X)$, at A(X) for the superimposed strains is

$$\sigma(X) = E \frac{2\overline{X}}{D} = \frac{F(X)}{A(X)}, \qquad (D-27)$$

which defines compression force F(X). The total compression energy, W(X), is the sum of each zone:

$$W(X) = 2 \int_{0}^{X} F(X) dX = 2 \int_{0}^{X} \frac{2E}{D} V(X) dX.$$
 (D-28)

Equation D-28 cannot be integrated analytically, but it can be integrated numerically for small time increments, using the general equation for dX/dt, as previously given for the axial impact in Eq. D-10:

$$u(t) = 2 \frac{dX}{dt} = u_0 \left[1 - \frac{W(X)}{W_1} \right]^{1/2}$$
 (D-29)

Equation D-29 is general and is independent of the body shape or impact configuration. The numerical integration starts by defining the initial state: $t_1=0$, $u_1=u_0$, $X_1=0$, $F_1=0$, $\sigma_1=0$, $I_1=0$, W_10 . In the first time increment, Δt , there is an increment of linear compression, X_1 . The calculation proceeds:

$$\Delta X_{1} = \frac{u_{0}}{2} = \Delta t; \quad X_{2} = X_{1} + \Delta X_{1}; \quad t_{2} = t_{1} + \Delta t$$

$$F_{2} = \frac{2EV(X_{2})}{D}; \quad \sigma_{2} = \frac{F_{2}}{A(X_{2})}$$

$$\Delta W_{1} = 2F_{2}\Delta X_{1}; \quad W_{2} = W_{1} + \Delta W_{1}$$

$$\Delta I_{1} = F_{2}\Delta t; \quad I_{2} = I_{1} + \Delta I_{1}$$

$$u_{2} = u_{0} \left[1 - \frac{W_{2}}{W_{1}} \right]^{1/2}$$

$$\Delta X_{2} = \frac{u_{2}}{2} \quad \Delta t; \quad REPEAT.$$

The calculation is repeated for additional Δt increments until velocity u falls to zero. A simple FORTRAN program was written to perform this calculation. Equal increments of Δt were used, and the Δt was chosen (by trial and error) so that the number of iterations was between 50 and 100. With this number of iterations, the time, t_m , for full compression and the other parameters were within about 5% of the rigorous calculation made for the axial DW impact.

The above numerical method can be used for any impact configuration for which the geometric functions A(X) and V(X) are defined. Cases were calculated for the following impact configurations:

- 1. axial impact of a flat-end cylinder;
- 2. axial impact of a cylinder with its ends formed into hemispheres;
- 3. axial impact of a cylinder with its ends formed into 90° cones;
- 4. diametral impact of a cylinder;
- 5. impact of a flat-end cylinder on its corner, with the cylinder aligned so that its center of mass is directly above the impact point on the force axis.

The end shapes were chosen to illustrate different stress configurations over the range of practical interest and to be convenient for the preparation of glass test specimens.

6. <u>Results of Calculations of Stress and Time Parameters</u> in Free-Fall Impacts

For free-fall (FF) impacts of a given configuration from a given height, the stress distributions are the same, independent of body size. This is evident from Eq. D-17. The maximum compression energy, $W(X_1)$, and maximum impulse, $I(t_m)$, are similarly independent of body shape. The time for full compression, t_m , is directly proportional to linear body size or to $M^{1/3}$, as shown by Eq. D-13. These predictable results were borne out by numerical calculations for the five impact configurations described above, for a freefall height of 10 m for a body with the properties of Pyrex glass. Calculations were made for three diameters (0.5 m, 0.1 m, and 0.0254 m), each at two L/D ratios (2 and 5). This is a mass (volume) range of about 10⁴. For the time increments used, the axial-flat-end impact cases agreed with the rigorous analytical calculations within about 5%. The relative mean stresses, at full compression for the five different impact configurations, normalized to the axial flat-end impacts, are:

	Relative Mean	Stresses in 10-m Drop
Impact Configuration	$\frac{L}{D} = 2$	$\frac{L}{D} = 5$
Axial-Flat	1.0	1.0
Diametral	0.51	1.4
Corner	2.1	0.67
Axial-Hemisphere	2.4	1.9
Axial-Cone	18	12

These results indicate that the FF impact severities for the axial-flat and diametral FF impacts are comparable (within a factor of 2), but that the cone-end case is in a class by itself.

The times for full compression as a function of body mass in the 10-m drop are shown in Fig. D-4. At a given body mass, there is about a 10-fold range of values of t_m for the various impact configurations. Axial-flat and diametral impacts vary by a factor of only about 1.5 with respect to the time to reach full compression, for the cases calculated.

7. <u>Results of Calculations of Stress and Time Parameters</u> for Drop-Weight Impacts Tests

In drop-weight impact tests, a steel striker bar, or tup, is dropped on small cylindrical specimens. Calculations were made for two tup masses, two



Fig. D-4. Time, t_m (µs), for Full Compression for a 10-m Free Fall of a Pyrex Cylinder for Various Impact Configurations as a Function of Body Mass (kg).

impact configurations, and three energy densities for flat-end Pyrex cylindrical specimens. These cases were chosen because they were conditions for which experimental tests have been carried out. The results are summarized in Table D-1. The data follow the predictable pattern and are largely selfexplanatory. Of course, the peak force, such as would be measured by a force transducer, is related to both the stress and the impulse.

8. Application of Stress-Time Calculations

It was observed in preliminary impact tests that the fracture threshold for impact fracture increased when a 1-kg tup was substituted for the 10-kg tup in DW diametral impact tests. It was also observed that a 160-g hemisphere-end glass cylinder (L/D = 2) bounced off a massive steel plate in a 10-m drop, rather than fracturing. From Fig. D-4, the times associated with these impact conditions are approximately 40 µs and 20 µs, respectively. The full-compression time for the 10-kg impact test was about 100 µs (Fig. D-4). It appears that times of less than about 50 µs are not long enough for microcracks to develop the high crack-propagation velocities that are effective in shattering glass. This observation is consistent with available data on crack propagation rates. The effects and the general principles of time scaling are important in predicting accident effects from test data.

High-speed motion pictures and high-speed force measurements are two well-developed methods for observing the course of impact fracture. The relations of stress, time, energy, and impulse provide a means of evaluating the various options for conducting efficient standard tests for the impact resistance of various materials.

Table D-1. Calculated Time, Calculated Maximum Stress, and Calculated Maximum Impulse for Full Compression, in Drop-Weight Impacts Tests of Cylindrical Pyrex Specimensa

	Note: Impulse = \int_{0}^{t} (Force)dt = change of momentum = $\Delta(Mu)$				
Input Energy Density, J/cm ³	Parameter	Axial Impact 81-kg Tup	Axial Impact 10-kg Tup	Diametral Impact 10-kg Tup	
1	Max. Stress (Pa)	3.70×10^8	3.70×10^8	7.18 x 10 ⁸	
1	Time (µs)	356	125	345	
1	Impulse (N·s)	42	14.7	14.5	
10	Max. Stress (Pa)	1.17×10^9	1.17×10^9	1.80×10^9	
10	Time (us)	356	125	270	
10	Impulse (N·s)	133	46.7	45.0	
100	Max. Stress (Pa)	3.69×10^9	3.69×10^9	7.18 x 109	
100	Time (us)	356	125	215	
100	Impulse (N·s)	420	147	145	

^aPyrex cylinders, all 2.54-cm diameter and 2.54-cm length.

It has not been possible within the scope of the present brittle fracture studies to make experimental tests validating the methodology for scaling test data, as outlined here for characterization of impact-fracture effects. However, in the course of this study, the consistency of these principles with fracture mechanics, glass science, and elastic theory was maintained. In conjunction with the lognormal particle parameters describing the fracture particulates, these impact-severity parameters provide a basis for more efficient and therefore more economical characterization of impact-fracture effects.

APPENDIX D

NOMENCLATURE

A, A(X) = 1 oad-bearing surface of impacted body, m^2 $A_s(X)$ = area of segment of a circle, m² (Fig. D-3) $B = a \text{ constant}, s^{-2}, \text{ defined by Eq. (8)}$ C(X) =length of chord of circle (Fig. D-3), m D = cylinder diameter, mE = Young's modulus of elasticity, Pa F_1 , F(t), F(X) = force, N H = height of free-fall drop, m I, I(t) = impulse, N·s L = length of cylinder, mM = deceleration mass, kg m_1 , m_2 , etc. = mass, Eq. (D-18) S_n = total surface area of fracture particulate, m^2 t = time, s $u, u_0 = velocity, m/s$ V_n , V_o = total volume of fracture particulate of impacted body, m^3 V(X) = displacement volume of elastic deformation, m³ W_i = input energy density to impact, J W(X), W_1 , etc. = elastic compression energy, J X, X_m , X_1 , etc. = linear elastic deformation, m \overline{X} = mean value of X, m
APPENDIX D

NOMENCLATURE

Greek Letters

$$\begin{split} \gamma_{\rm f} &= {\rm empirical\ fracture\ strength,\ J/m^2} \\ \varepsilon &= {\rm efficiency\ of\ input\ energy\ dissipation\ in\ brittle\ fracture,\ \%} \\ \sigma,\ \sigma_{\rm X} &=\ {\rm stress,\ Pa} \\ \sigma_{\rm m} &=\ {\rm maximum\ value\ of\ stress\ at\ full\ compression,\ Pa} \\ \rho &=\ {\rm density,\ kg/m^3} \end{split}$$

APPENDIX D

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