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FUEL CYCLE PROGRAMS
QUARTERLY PROGRESS REPORT

October-December 1981

by

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Chemical Engineering Division

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ABSTRACT

A method of measuring rates of leaching from simulated waste glasses using neutron activation analysis has been developed. Leaching tests of SYNROC have been completed except for analyses. Also, leach tests qualifying the use of radiotracers in measuring the release from SRL 211**^{*}, SRL 211***^{*}, SRL 131, and SRL 131*^{*} have been completed. Also leached was PNL 76-80 glass containing radiotracers and actinide elements.

Laboratory-scale impact tests of solid alternative waste forms are being performed to obtain a size analysis of the fragments. From this, dispersion from mechanical impacts during normal and accidental conditions of transport can be determined. The particle size distribution of an axially impacted Pyrex cylinder was determined, and a preliminary analysis was made of empirical size distributions for impact fractures of full-size canisters of simulated waste glass.

Logging techniques are being developed to measure the relative amount of residual oil in a depleted oil reservoir by injecting gamma-active solution into it. Some laboratory-scale experiments were completed that showed a 63% variation in gamma signal for oil-containing and oil-free rock cores. The use of surfactant-containing water for improving logging sensitivity is promising.

Work to test the behavior of radionuclides leached from proposed nuclear-waste repositories using laboratory-analog experiments is in progress. Digital equipment to record experimental variables has been assembled, basalt cores prepared, and the laboratory apparatus assembled. Glass has been prepared for a series of analog experiments to measure the migration, through repository components, of radionuclides leached from the glass.

The flow of groundwater through igneous rocks is of considerable interest in connection with storage of high-level radioactive waste in deep geological formations. High potassium levels in crushed granite from a Northern Illinois drill hole are probably derived by the leaching of potassium feldspar.

Testing and development of equipment for the destructive analysis of full-length irradiated fuel rods from the LWBR are in progress. The schedule for this work, in support of the LWBR Proof-of-Breeding Project, has been foreshortened, and the scope of the destructive fuel analysis has been reduced.

SUMMARY

Neutron Activation and Tracer Studies

Leach tests qualifying the use of radiotracers in measuring the release from nuclear waste glasses have been completed, and the data are being compiled. Leach tests demonstrating the use of neutron activation analysis as applied to SYNROC have been completed, and the leachates are awaiting analysis. PNL 76-68 glass containing radiotracers and actinide elements has been leached. Observed in the leachate are ^{85}Sr , ^{133}Ba , ^{137}Cs , ^{237}Np , ^{239}Pu , and ^{241}Am . Weathering tests on glass samples are continuing.

Brittle Fracture Studies

An axial impact test of a Pyrex glass cylinder was made by the standard method, except that a steel ring surrounded the specimen and functioned as a mechanical stop during impact. This ring allowed only a 26% axial compression of the cylinder and prevented the falling weight from coming to rest on top of the glass fragments. A complete size analysis was made by the usual sieving and Coulter counter analysis, and the result, in comparison with a similar impact test made without the mechanical stop, was as expected--no significant difference was found in the particles of respirable size or in the particle size distributions.

A preliminary lognormal analysis was made of empirical particle size distributions reported by the Pacific Northwest Laboratory (PNL) for impact fractures of full-size canisters of simulated waste glass falling distances of 30 m and 9 m. Lognormal analysis was also made of particle sizes reported for thermally induced fracture in the absence of impact. All particles could be described by the two lognormal parameters, as in our small-scale tests.

A preliminary analysis was made of the energy transformations calculated from test data reported by the Materials Characterization Center (MCC). The data consisted of force-time plots for small Pyrex and alumina specimens impacted in a large dynamic loading device, according to a proposed standard impact test (MCC-10) for brittle waste materials. The chief difference between this test and the ones used in our brittle fracture studies is the large involvement of strain energy stored in components of the MCC test machine in the case of the MCC-10 device; the question of how this is related to impact severity could not be resolved with the available data, which did not include particle sizes.

Summary reports are being written for our brittle fracture work, which has been terminated.

As a possible aid in understanding the physical basis for the engineering correlations made in our brittle fracture studies, an analogy has been developed between the random kinetic-energy fluctuations in liquid turbulence and the variations of elastic strain energy during the brittle-fracture process (the latter may be considered a kind of solid-state turbulence). The statistical parameters describing particle size are correlated with the principal parameter (elastic energy density) describing impact severity. The impact conditions and fracture results are described in the form of two dimensionless numbers. In the absence of experimental work verifying the implied scaling laws (*i.e.*, by the application to full-size waste-glass bodies), these correlations can only be applied to small-scale impact tests.

Nuclear Logging of Oil Reservoirs

Work performed this quarter centered on performing core-flood experiments to test the possibility of logging an oil reservoir by the use of a gamma-active fluid. Results of the experiments indicate a great difference in the gamma signals from oil-bearing and oil-free cores. The signal from an oil-free core was 63% higher than that from a core containing oil in 48% of its pore space. This difference is substantial and suggests that oil can be logged accurately by injecting water containing a gamma-emitting radionuclide.

Preliminary analysis of experiments in which surfactant was used suggest that the logging sensitivity can be increased by using a surfactant. The surfactant-containing water entered pores more quickly than did water alone.

Laboratory Analog Program

An experiment was started this quarter to investigate the behavior of radionuclides leached from a borosilicate waste glass as they contact an engineered barrier and basalt rock. Preparations for the experiment, discussed in this report, include (1) assembling digital equipment to record experimental variables, (2) splitting rock cores, (3) designing experimental apparatus, and (4) testing the effects of ionizing radiation and Teflon components on water composition. In addition, details of the composition, preparation, and characterization of a borosilicate waste glass are given. Finally, the stability (resistance to plugging) of a rock fissure while water flowed through it in the initial part of the experiment is discussed.

Trace-Element Transport by Fluid Flow

Additional analyses of soluble salt in crushed granite from Northern Illinois drill hole UPH-3 are presented. The observed high potassium concentrations were probably leached from potassium feldspars.

A novel potentiometric method is presented for locating end points with high accuracy in chloride titrations. This method appears to be an improvement of the Gran method.

Light Water Breeder Reactor Proof-of-Breeding Analytical Support Project

Our responsibility in this project is the destructive analysis of full-length irradiated fuel rods from the LWBR. The results will be used by the Bettis Atomic Power Laboratory (BAPL) in support of their nondestructive assay of the end-of-life (EOL) core to determine the extent of breeding.

Activity is reported on five main sub-activities of this Project: (1) the full-scale shear (FSS), (2) the single-unit or prototype dissolver (SUD), (3) multiple dissolvers needed for the destructive analyses of full-length (about 3-m) irradiated fuel rods for the EOL campaign, (4) scrap/waste disposal, and (5) process control and data management system.

I. NEUTRON ACTIVATION AND TRACER STUDIES (L. J. Jardine and J. K. Bates)

A. Introduction

Dispersion of wastes into the biosphere is the principal potential hazard of nuclear waste disposal. Characterization of waste forms requires the use of sensitive analytical methods to obtain dispersion data for low-rate phenomena. Neutron activation analysis (NAA) has been shown to be one method applicable for measuring leach rates. Alternatively, radioactive tracers can provide sensitive methods for applications in which NAA is not possible or practical. Both methods are likely to be useful also for characterization measurements other than leach rates.

The general objective of this program is to develop techniques and to qualify methods that utilize neutron activation analysis and radioactive tracers for characterizing simulated waste forms. By comparison of characterization test results obtained using these two methods with other existing characterization data, conditions can be specified under which such tests and the resulting data may be extrapolated to fully radioactive specimens. The current focus is on leach-rate characterizations of simulated waste glasses and, to a lesser extent, advanced waste forms.

Major goals are to complete the development of the NAA method for leach-rate determinations and to define the accuracy, sensitivity, and limitations of NAA. Similar goals exist for the development of methods utilizing radioactive tracers.

B. Qualification of Radioactive Tracer Method

1. Introduction

A series of experiments has been completed that qualify the use of NAA and radioactive tracers for the measurement of leach rates from SRL frit 131 and SRL frit 211 simulated waste glasses. Four classes of chemical elements present as minor (<5 wt %) elements in SRL defense wastes and of concern in radioactive waste management have been the focus of the measurements. The four classes are alkali metals (Cs), alkaline earths (Sr and Ba), rare earths (Ce, Eu) and noble metals (Ru). Simulated waste glass containing radioactive tracers has been prepared; this glass was leached directly and also submitted for neutron activation prior to leaching. Leach rates were measured wherever possible, using four different techniques: (1) via conventional chemical solution analysis (ICP,* AA,† DCP,‡ flame emission) of leachates from non-neutron-activated glass, (2) gamma-ray spectroscopy analysis of leachate solutions from neutron-activated glass specimen (A), (3) gamma-ray spectroscopy analysis of leachate solutions from glass specimens containing radioactive tracers (S), (4) gamma-ray spectroscopy analysis of leachate solutions from neutron-activated glass specimens containing radioactive tracers (S/A).

* Inductively coupled plasma emission spectroscopy.

† Atomic absorption.

‡ Direct coupled plasma emission spectroscopy.

The objective of these measurements was to obtain comparative leach rate data in order to define the reproducibility, sensitivity, limitations, and precision of leach rate measurements by the various methods.

2. Leaching Characterizations of Defense Glass

To qualify the spike/leach method, tests were done on four different glasses: SRL 211**, SRL 211***, SRL 131, and SRL 131* (typical of glasses made from defense wastes). For each type of glass, the leach rates obtained with spiked glass will be compared with those obtained by another method. All the leach tests except those of 362-day duration have been completed. Surface analytical studies of the leached glasses are being performed and will be correlated with the solution analysis results. The data are being compiled and will be presented as a topical report.

3. Leaching Characterizations of Commercial Glass

PNL 76-68 glass [STEINDLER-1980] is the most studied of commercial waste glasses and currently is being used in the Laboratory Analog Program (by the Fuel Cycle Section of Chemical Engineering Division, FCS/CEN) as the main glass to be tested. A batch of PNL 76-68 glass containing uranium, actinides, and radiotracer spikes was made (see Section IV of this report). Leach tests are being performed on this glass to establish a base leaching behavior under static MCC-1 test conditions [MENDEL] and to compare rare earth and actinide leach rates to see if rare earths can act as a stand-in for actinides.

The conditions for the tests and some results for tests through 14 days are given in Table 1. The radiotracers added to the glass are ^{85}Sr , ^{133}Ba , ^{137}Cs , ^{141}Ce and ^{152}Eu and leachates are being analyzed for these elements using gamma-ray spectroscopy (FCS/CEN). Actinides added to the glass are ^{239}Pu , ^{237}Np , and ^{241}Am ; these are being analyzed using alpha-counting (FCS/CEN).

The gamma-counting procedure is that used in previous radiotracer studies [STEINDLER-1981B]. In the leachates from leaching periods up to 14 days, ^{85}Sr , ^{133}Ba , and ^{137}Cs can be detected. However, ^{137}Cs is present in the original glass at too low a level to be detected in the solid, and so cesium leach rates will have to be back-calculated using atomic absorption values for cesium in the 28-day samples. If leach rates for matrix elements and uranium are needed, analyses will be done later.

a. Preliminary Alpha Spectrum Analysis of Glass Leachates

A portion of the leachate from a MCC-1 leach test (seven days in deionized water at 90°C) of PNL 76-68 glass containing radioactive tracers and actinides was prepared as an alpha source. The purpose was to examine analytical detection and resolution capabilities for the alpha-emitting actinides with our existing equipment and initial alpha source preparations. The procedure used heat-lamp evaporation onto a 1 1/8-in. stainless planchet, followed by flaming in a meeker burner to fix the actinides to the planchet.

Table 1. Leaching Conditions^a for PNL 76-68 Glass (containing U, actinides, radiotracer spikes)

Sample No.	Leaching Period, days	Mass of Sample, g	Initial SA, cm ²	Δ Mass, ^b g $\times 10^{-4}$	Final pH	Final Leachate Vol, mL	Normalized Elemental Loss, (NL) _i , ^c g/m ²		
							¹³³ Ba		⁸⁵ Sr
							303 keV	356 keV	514 keV
501	3	0.4322	2.889	13	4	27.76	2.0	1.5	5.1
502 ^d	7	0.4391	2.742	18	4	26.85	0.4	0.4	1.9
503	14.9	0.5320	3.139	24	4.5	29.50	0.7	0.7	4.9
504	28	0.3863	2.570						
505	28	0.5021	3.044						
506	28	0.5227	2.931						
507	56	0.4270	3.075						
508	91	0.4360	2.667						
509	91	0.3647	2.596						
510	91	0.4171	2.978						
511 blank	28								
512 blank	91								
513 blank	28								

^aMCC-1 test conditions were used, including deionized water (DIW) and 90°C, in these tests.

^bLoss of mass.

^cNormalized leach rates for each element are presented as a function of the gamma-ray energy used in the analysis.

^dThe solid sample did not stay suspended in the center of the liquid, but fell to the bottom of the container at some time during the test period.

The high-resolution alpha spectrum from this test is shown in Fig. 1A. Three alpha groups were clearly resolved and identified as ^{237}Np , ^{239}Pu , and ^{241}Am . The ratios of the alpha intensities relative to that of ^{241}Am were 83.7 ± 0.2 , 3.3 ± 0.2 , and 1.0. For comparison, Fig. 1B gives an alpha spectrum for an aliquot of the initial starting mixture of the ^{237}Np , ^{239}Pu , and ^{241}Am before its addition to the PNL 76-68 glass; the intensities of the alpha groups relative to ^{241}Am were 0.10 ± 0.1 , 3.0 ± 0.1 , and 1.0. The data analysis of both of these spectra are summarized in Table 2.

From comparison of the alpha spectra data in Figs. 1A and 1B, it is obvious that ^{237}Np leaches from the glass at a much faster rate than either ^{239}Pu or ^{241}Am . These data suggest that the rate is about 10^3 times faster. The ^{239}Pu and ^{241}Am leach at virtually the same rates, and these two actinides are easily measurable in this initial seven-day test. Leach tests for periods longer than seven days will also allow measurements of the leach rates of ^{237}Np , ^{239}Pu , and ^{241}Am .

Fig. 1.

Alpha Spectra. A. Leachate from Seven-Day, 90°C Test of PNL 76-68 Glass. B. Aliquot of Starting Mixture of Actinides before Addition to PNL 76-68 Glass

Table 2. Summary of Alpha Spectrum Analysis of Data Given in Figure 1

Sample ID	Isotope	Integrated Counts	Count Time, s
Leachate: 7 days	^{237}Np	35000 ± 200	163470
	^{239}Pu	1400 ± 40	163470
	^{241}Am	418 ± 20	163470
Starting Glass Composition	^{237}Np	3415 ± 60	2732
	^{239}Pu	98400 ± 300	2732
	^{241}Am	33060 ± 200	2732

From this preliminary analysis, it is concluded that measurement of alpha leach rates of ^{237}Np , ^{239}Pu , and ^{241}Am is possible for PNL 76-68 glass. Techniques of source preparation for counting will need to be refined so that reproducible and standardized analyses may be performed. Techniques for dissolving portions of actinide-containing glass of known masses and of preparing alpha sources must also be defined to establish the fractions leached. The same source-preparation techniques and data, if coupled with statistical sampling, can be used (1) to verify sample homogeneity required for the Nuclear Regulatory Commission program (see Section IV of this report) and (2) to provide additional sensitivity and resolution not available with the autoradiograph techniques.

4. Auxiliary Leach Studies

a. Neutron-Activated SYNROC

One subject to be addressed in the current program for Savannah River Laboratory is the use of NAA in measuring leaching from crystalline waste forms. This problem was addressed by doing a set of MCC-1 leach tests on SYNROC (MSD-XB93) [STEINDLER-1981A]. This SYNROC contains 10% waste additives (PW-4b) and provides a spectrum of activation products suitable for gamma-ray analysis.

It was planned that the test procedure would involve a MCC-1 test on activated SYNROC and the same type of test set on nonactivated SYNROC. The activated SYNROC leachates would be analyzed with gamma-ray counting and ICP/AA spectroscopy, and the nonactivated SYNROC leachates would be analyzed with ICP/AA spectroscopy. From these analyses, it would be possible to compare the leach rates of waste and matrix elements in both activated and nonactivated samples and thereby determine whether neutron activation of the solid affects the leaching process.

The leaching conditions used in this test are given in Table 3 and the results for activated SYNROC in Table 4.

All tests except L-488 and L-497 have been completed and all activated leachates have been analyzed by gamma-ray counting. To complete this project, as designed, it will be necessary to do ICP and cesium (AA) analyses on 19 samples (10 radioactive, 9 cold). Two problems prevent completion of this work:

- (1) There is no money for the analyses, and
- (2) there is no ICP available to do the analyses.

The unanalyzed leachates have been acidified and are being stored.

The aforescribed work provides SRL with independent documentation on whether NAA can be used for measuring leach rates from SYNROC. Apparently they have been using this technique in past work and their conclusions may be open to question.

Table 3. Leaching Conditions and Results for NAA SYNROC. Deionized Water

Sample	Sample No.	Temp, °C	Leaching Time, days	Mass of Sample, g	Initial SA, cm ²	Δ Mass, ^a g $\times 10^{-4}$	Final pH	Final Leachate Volume, mL
SYNROC XB93 activated. Start of leaching, T _O = 9/25/81	L-482	90	3	0.2051	1.914	1	5.9	18.44
	L-483	90	7	0.2295	1.861	1	6.7	17.88
	L-484	90	14	0.2298	1.895	0	6.8	18.36
	L-485	90	28	0.2763	1.916	1	7.5	17.68
	L-486	90	28	0.2881	1.936	2	7.2	18.05
	L-487	90	28	0.2648	1.890	0	7.7	17.74
	L-488	90	91	0.2825	1.923			
	L-489	200	28	0.2639	1.896	2	7.4	15.31
	L-490	40	28	0.1316	1.758	0	6.2	17.01
	L-491	40	28	0.2746	1.913	3	6.5	18.75
SYNROC XB93 nonactivated	L-492	90	3	0.2527	1.896	0	6.0	18.64
	L-493	90	7	0.2271	1.847	+1		17.59
	L-494	90	14	0.2596	1.911	1	7.2	18.45
	L-495	90	28	0.3211	1.976	+1	7.2	18.74
	L-496	90	28	0.2295	1.858	0	7.8	17.35
	L-497	90	91	0.2566	1.900			
	L-498	200	28	0.2591	1.893	0	7.2	15.18
	L-499	40	28	0.2617	1.907	1	6.4	18.61
	L-500	40	28	0.2443	1.884	0	5.8	18.64

^aLoss of mass, except plus values represent gains of mass.

Table 4. Leaching Results for NAA SYNROC

Sample No.	Temp, C°	Time, days	Normalized Elemental Loss, (NL) _i , ^a g/m ²				
			131Ba		134Cs		124Sb
			123 keV	497 keV	795 keV	1037 keV	1691 keV
L-482	90	3	3.3	2.2	5.3	4.8	13.0
L-483	90	7	5.8	3.5	8.3	8.2	13.6
L-484	90	14	2.6	2.1	9.9	8.8	
L-485	90	28	2.9	1.7	14.4		12.6
L-486	90	28	4.4	2.9	12.9	12.2	12.2
L-487	90	28	4.7	3.3	13.7	12.4	10.8
L-489	200	28	12.2	6.6	79.4	73.1	
L-490	40	28	2.5	1.9	0.7	0.6	9.4
L-491	40	28	3.0	1.9	0.8	0.7	10.6

^a Normalized leach rates for each element are presented as a function of the gamma-ray energy used in analysis.

b. Weathering Studies

Weathering studies designed to produce weathered (hydrated) glass samples are continuing. Samples of PNL 76-68 glass, SRL frit 211, and SRL frit 211* are being weathered at 80°C and 90% relative humidity. The weathered samples will be studied to obtain a description of the hydration process; when subjected to leaching conditions, they will be used to determine the durability of hydrated glass.

In addition, an experimental plan has been drafted for performing glass hydration experiments at other conditions. The hydrated glasses obtained by weathering will then be characterized by leaching.

II. BRITTLE FRACTURE STUDIES (L. J. Jardine, W. J. Mecham, and G. T. Reedy*)

A. Introduction

Knowledge is needed of the resistance of solid brittle radioactive waste forms to dispersion from mechanical impacts received during normal and accidental handling conditions of processing, interim storage, and transportation. A brittle fracture methodology has been partially developed which relates the impact-stress distribution to the lognormal size distribution of the particles resulting from impact fracture [STEINDLER-1981B]. The practical application of such a fracture model is for predicting both the total fracture-surface area and the mass of particles of respirable sizes produced in impact fractures.

Development and preliminary verification of this model has been provided by (1) laboratory-scale tests of impacts of reference glass and ceramic specimens and (2) analyses of data available in the technical literature on impacts of various brittle materials and impacts of large-scale simulated waste-glass canisters. The validity and utility of this brittle-fracture methodology have been examined for a range of laboratory-scale impact conditions and for various solid waste materials. The experimental results have been used to establish preliminary correlations of lognormal size-distribution parameters, fracture surface areas, and material strength properties of brittle-waste forms of various sizes and configurations.

The preceding quarterly report [STEINDLER-1981B] summarized the experimental impact test results. Efforts during this quarter were focused on further documentation of both the brittle fracture characterization methodology and the experimental results. This is the final progress report for these brittle fracture studies. Other documents will be published during FY 1982 as this program is closed out.

B. Axial Impact of a Pyrex Cylinder Incorporating a Mechanical Stop (G. T. Reedy and W. J. Mecham)

In the preceding quarterly report [STEINDLER-1981B], the particle-size distribution formed in an axial impact was compared with diametral impacts for Pyrex cylinders (2.5 cm by 2.5 cm) impacted at an energy density of 10 J/cm^3 by our standard impact procedure. No significant difference was found in the fracture results of these two different impact configurations. In the present period, a similar axial impact test was made with a Pyrex cylinder incorporating a mechanical stop that prevented the dropped weight from coming to rest on the fracture particulate.

The use of such a mechanical stop is one of the preliminary recommendations of the Materials Characterization Center (MCC) at the Pacific Northwest Laboratory (PNL). The MCC is charged with developing a standard test for characterizing the impact resistance of solid waste forms. (Further details of the proposed MCC test procedure are reviewed in section II.E. below.)

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In the proposed MCC test, a mechanical stop is specified that allows the axially impacted cylindrical specimen to be compressed no more than 40% of the cylinder height [MERZ]. The maximum fractional amount of linear compression (i.e., the maximum strain) permitted by the stop is selected in a somewhat arbitrary manner. Clearly, if the allowed strain is too small, the characteristic particulate fracture cannot take place because the impact force will mostly be taken up by the mechanical stop. The general intent of using the stop is to allow impact fracture to take place as a result of elastic compression, but to prevent any secondary crushing effect that might be incurred by the falling weight coming to rest on the fragments. In our experimental test, a maximum linear compression strain of 26% was allowed. The stop consisted of a type 304 stainless steel ring (7.6-cm ID and 1.90 cm high) made of 3-in. standard (schedule 40) pipe. The axially impacted Pyrex specimen (2.5 cm by 2.5 cm) was centrally located within this ring, and the impact with the 10-kg falling weight was carried out under standard conditions in the bellows impact chamber.

A typical particle-size distribution of the axial impact test of a specimen of Pyrex glass, incorporating this mechanical stop, is shown in Fig. 2, along with the results of a comparable test made without the stop. No difference is seen for the smaller-sized particles, including the respirable fraction, which consists of all particles with a diameter smaller than 10 μm

Fig. 2. Particle Size Distributions for 10 J/cm³ Axial Impacts of Pyrex with and without a Mechanical Stop

(10^{-5} m). In the test with the stop, the cumulative volume (mass) fractions for particle sizes of about 0.1 mm and larger are slightly less than without a stop. The general shapes of the particle size distributions are the same.

The lognormal parameters determined for the particle-size data are shown in Table 5. The respirable fractions for the two types of impact are the same, and the particle diameter corresponding to 98% of the total surface area is the same. The test with the stop showed a somewhat larger standard deviation (σ_g) and a somewhat larger mean diameter (D_g) than the impact without a stop.

Table 5. Lognormal Parameters for Axial Impact of Pyrex with and without a Mechanical Stop

Parameter, Units	Without Stop	With Stop
Respirable fraction, $P(10 \mu\text{m})$, %	0.30 ± 0.10	0.29 ± 0.09
Standard deviation, σ_g , dimensionless	5.6 ± 0.3	6.7 ± 0.5
Geometric mean diameter, D_g (mass distribution), mm	1.1 ± 0.4	1.9 ± 0.8
Geometric mean diameter, D_{gs} (surface area distribution), mm	0.06	0.05
Diameter, upper-limit for 98% of surface area, D_{98s} , mm	2	2

The fact that the respirable fraction and the surface-area distribution of the particulates were essentially the same with and without the stop indicates that the presence of the stop did not change the fracture process and did not alter the results of practical concern--namely, the amounts of surface area and respirable particles. These results are consistent with the conclusions from our previous analysis of impact fracture of brittle materials, namely, that fracture results depend only on the input energy density of compression and are not sensitive to the velocity of impact per se nor are they sensitive to the actual (and varying) stress distribution during the compression stage of impact. In other words, the kinetic energy of impact is essentially completely converted into elastic strain energy before fracture begins, and the impact-fracture process is a very rapid disintegration consisting (in effect) of multiple stages of binary cleavage. A discussion of the possible role of stress waves is given in section II.D. below.

1. Discussion of Implications for Impact Test Procedures

In the test results described above, the energy available for compression and fracture, 10 J/cm^3 , is equivalent to $1.2 \times 10^9 \text{ Pa}$ (172,000 psi) if an ideal (uniform-stress) axial compression is assumed for the elastic

properties of Pyrex (Young's modulus, 7×10^{10} Pa). The strain or linear compression corresponding to this stress is 1.7%, which is quite a bit lower than the 26% compression allowed by the mechanical stop. However, when the mechanical stop is used, it should not prevent the full force of impact being received by the specimen. For this reason, the strain allowed by the stop should be as large as is consistent with the reasons for its use: a strain of 40% or even 50% would seem preferable. This would be especially true for diametral impacts.

The force associated with the stress calculated above is 6.1×10^5 N (1.4×10^5 lb). The force of gravity for the 10-kg falling mass is just 98 N. Clearly, the mere weight of the falling mass adds practically nothing to the force of impact, and no significant additional crushing would occur if the mass were allowed to come to rest on top of the particles (as would be the case if no stop were present). Therefore, the concern that secondary crushing might occur does not constitute a valid reason for using the stop.

Another possible reason for using a mechanical stop is to allow impact compression to take place at a nearly constant velocity, equivalent to a nearly constant loading rate of the applied force. In order for this to be carried out, a very massive falling weight with a very large kinetic energy must be used, so that the weight will not be appreciably slowed while the specimen is being compressed to the desired energy density. Most of the input kinetic energy (about 90% or more in this case) will be absorbed by the mechanical stop, since the stop checks the motion of the falling mass. In such a procedure, the gross energy input must be ten times (or more) the energy input to the specimen, necessitating a very massive (and more expensive) impact apparatus. In general, the more nearly constant a loading rate is desired, the more massive is the required impact device.

Nearly constant loading rates are commonly used in dynamic tests of the structural strength of metals. However, the impact resistance of brittle glasses and ceramics is measured in terms of the fracture particulate--not primarily in terms of structural strength or threshold conditions for fracture. Since it has been shown that the fracture particulate is not sensitive to loading rate (or impact velocity), a requirement for a nearly constant loading rate is questionable. Certainly a constant loading rate is not consistent with impacts that realistically could occur in accidents. Since the above experimental data indicate that the presence of a stop makes no significant difference in the fracture particulate, the use of the stop seems questionable with respect to its affecting fracture results.

The use of a stop has the disadvantage that energy input to the specimen cannot be measured from a simple energy balance. That is, in the absence of a stop, the input kinetic energy is converted directly to elastic strain energy in the specimen. But with a stop, most of the input energy is picked up by the stop and there is no direct measure of the energy input (or stress) to the specimen. To remedy this, a force transducer (load cell) with high-speed (cathode ray tube) readout is required. That is, of course, an expensive method of measuring energy input to the specimen. (An analysis of this method is given in section II.E. below.)

The fact that the fracture particulate is essentially the same in the presence and absence of a stop tends to confirm that the impact fracture mechanism includes an elastic compression stage of energy conversion. Although comparative impact tests can be made without a stop, a supplementary test with a stop may be useful in confirming that the fracture mechanism is also common to various conglomerate materials, such as cements, sandstones, and salt cakes.

C. Particle Size Distributions in Full-Scale Impact Tests Reported for Waste-Glass Canisters (W. J. Mecham)

A recent Pacific Northwest Laboratory (PNL) report [PETERS] describes the results obtained in a study of the fracturing of simulated high-level waste glass in canisters. In two cases, the fracturing resulted from free-fall impacts from 9.0 and 30 m; in five other cases, fracturing resulted from thermal stresses induced by cooling the glass from the molten state. Particle sizes were measured by sieving in three cases, after which empirical log-log plots were made; these are reproduced in Figs. 3A, B, and C. The empirical particle size data for the most highly fractured zones (bottom zone; 25-mm layer adjacent to the wall) in the two impact cases are replotted on lognormal coordinates in Fig. 4; the data points follow a straight-line lognormal distribution for all particles smaller than about 2 mm. The straight lines show approximately the same slope and the same geometric standard deviation: $\sigma_g = 8.7$. The geometric mean diameters are: for a 30-m drop, $D_g = 1.5$ mm; for a 9-m drop, $D_g = 2.6$ mm.

For particulates with a lognormal distribution, the distribution of the surface area can be calculated from the measured cumulative mass fraction. That is, 98% of the total surface area is contained in the particles with sizes smaller than D_{98s} , and the ratio D_{98s}/D_g is calculated from σ_g :

$$\begin{aligned}\frac{D_{98s}}{D_g} &= \sigma_g^{2 - \ln \sigma_g} \\ &= 0.70\end{aligned}$$

Thus, the lognormally distributed particulate ($D < 2$ mm) contains almost 98% of the total surface area, just as in small-scale drop-weight tests (Table 5).

The report cited [PETERS] explicitly stated that the size distributions were not lognormal. This statement may have been made because of the departures from lognormality for particles larger than 2 mm (as shown in Figs. 3A, 3B, and 3C) or because the fractured material as a whole had more than one mode of fracture due to the particular stress distribution. This reflects the observation that, generally, the fracture particulate proper, which contains nearly all of the fracture-surface area, is lognormally distributed, while some portions of the impacted glass body do not show this particulate mode of fracture--probably because of uneven stress distribution during the impact-fracture process. The empirical cumulative mass fraction for particles larger than D_{98s} (defined above) is dominated by this residual amount of material, which has a size distribution different from the lognormal fracture particulate proper. Thus, the complete size analysis showed two lognormal distributions: (1) the distribution for the fracture particulate proper,

Fig. 3A. Particle Size Distribution of Simulated High-Level Waste Glass (melted in can) for Various Axial Positions in 30-cm-dia (not drop-tested) Canister. Fractures occurred as a result of thermal stresses [PETERS]

Fig. 3B. Particle Size Distribution of Simulated High-Level Waste Glass (melted in can) for Various Axial Positions in 40-cm-dia Canister Dropped from 30-m Height [PETERS]

Fig. 3C. Particle Size Distribution of Simulated High-Level Waste Glass (melted in can) for Various Axial Positions in 30-cm-dia Canister Dropped from 9-m Height [PETERS]

Fig. 4. Particle Size Distributions for 9-Meter and 30-Meter Canister Drop. Bottom zone, first 25 mm from wall

which contains most of the surface area and all of the respirable particles, and (2) a residual distribution of large fragments.

The lognormal parameters of the fracture particulate proper correlate with the impact energy density; the lognormal parameters of the residual distribution correlate with: (a) the original linear size of the original body and (b) the upper-limit size, D_{98S} , as defined above for the fracture particulate proper, on the basis of the fracture surface area. From conditions (a) and (b), lognormal parameters can be empirically defined for this second (residual) particle population; however, there is usually no practical incentive to do so, since this fractured material contains relatively little surface area and no respirable fines.

In comparison to small-scale drop-weight tests of uncanistered glass specimens, the reported total surface areas for these full-scale impacts are low, relative to the gross input energy. This is not surprising, since bending of the canister wall absorbs some of the impact energy. Moreover, these canistered waste forms were thermally fractured before impact. In this condition, the energy absorbed by the canister wall would be expected to be greater than in an impact in which the canistered glass was originally unfractured. If means are devised to reduce the amount of thermal fracture, impact fracture of the waste glass might be more extensive than in the cases reported here.

The thermal fracture data of one zone (bottom zone, first 25 cm from the wall) in Fig. 3A (for the not-dropped waste canister) is replotted on lognormal coordinates in Fig. 5. Note that fractures in the four zones

Fig. 5. Particle Size Distribution for Thermal Fracture of 0.3-m-dia Waste-Glass Canister (not dropped)

differed little (Fig. 3A). The solid line shows the empirical data. Analysis of the data into two lognormal particle populations was done as follows:

1. A best straight line (solid, with a dashed extrapolation) was drawn through the four points representing the smaller-size particles; this defines the small-particle-size population.

2. "Corrected" points were drawn for the three data points representing the largest particles by subtracting the ordinates of the small-particle population from the measured data points; a straight line (dotted) was drawn through the corrected points. This defines the lognormal parameters for the large-particle-size population ($D_g = 27 \text{ mm}$; $\sigma_g = 3.0$).

3. The small slope of the line defined by the four smallest particle data points indicates that these particles come from a small local zone of greater than average stress. It was assumed that this local zone was 5% of the total glass volume. The given ordinates for the four smallest particle data points were multiplied by 20 to give "corrected" points. A straight line (dotted) drawn through these points gives the lognormal parameters for the small particle population ($D_g = 30 \text{ mm}$; $\sigma_g = 15$).

4. The empirical particle-size data can be expressed in terms of the two lognormal populations defined above and shown graphically in Fig. 5. The empirical data is represented by $P(D) = 0.05 P_1(D) + 0.95 P_2(D)$, where P_1 and

P_2 are the lognormal cumulative volume fractions for the small and large populations, respectively. From the above analysis, it appears that lognormal analysis can be made of these large-scale fracture results, for the cases of canistered waste glass in both free-fall impacts and thermal fractures.

The incentive for using lognormal analysis is that it yields parameters describing the particle size distribution, and that these parameters can be correlated with impact-severity parameters. These generalized correlations provide more understanding of the actual physical process involved than do uncorrelated data. These correlations also offer a basis for predicting accident effects. From a research point of view, these correlations using lognormal parameters are a more efficient use of experimental data; full-scale impact tests of canistered waste glass are especially costly.

D. Analysis of Impact Fracture as Solid-State Turbulence
(W. J. Meham)

1. Introduction: Impact Fracture, Continuum Mechanics, and Fluid Dynamics

a. Impact Fracture of Brittle Materials

All solids exhibit elastic behavior describable by the well-known Hooke's law, which relates stress to strain from the range of zero stress up to some limiting value which depends on the material. Truly brittle materials, exemplified by common glasses and ceramics, experience fracture cleavage without any plastic flow when the elastic limit is exceeded. Typically, this is not true for metals; metals fracture only after some plastic flow. When the degree of plastic flow is small, metals are termed "brittle" in a comparative sense, but the fracture behavior in impacts of truly brittle materials is quite different from that of metals due to the difference in solid-state structure.

In practice, the study of brittle fracture of metals addresses the question of structural failure, which occurs with a single cleavage crack. This is also a possible concern for brittle materials such as glass or ceramic. However, the distinctive particulate mode of fracture of brittle materials raises other concerns related to the increased dispersibility of the fractured material--namely the large surface area formed and the small particle size. Characterization of the impact fracture of brittle materials, therefore, aims at relating impact severity to the properties of the solid particulate formed by fracture, with threshold conditions being of minor concern.

A brittle body may be impacted in two ways: (1) free-fall (FF) impact, in which the kinetic energy of impact is generated by the free-fall (under gravity) of the body itself; and (2) drop-weight (DW) impact, in which a separate moving mass strikes the brittle body. Of course, realistic impacts can be quite complex, but basic analysis can be made using the assumption that the brittle body is impacted by a flat unyielding surface in either FF or DF impact.

b. The Inability of Continuum Mechanics to Describe the Brittle-Fracture Process

Elastic compression of a body by mechanical impact can be described by well-established methods of stress analysis, which is based on the physical mechanics of continuous media. However, when a crack propagates in a compressed body, the continuous stress field no longer exists and the stresses are redistributed. Essentially random subdivisions of the stress field take place, with random and time-dependent stress fluctuations. As a result, practical characterization of the results of impact fracture can be made only on an overall basis that employs statistical averaging of effects.

The application of energy balances and force balances to impact fracture requires the recognition of (a) stress waves that propagate through the material and (b) motions of the material. The propagation of stress (by stress waves) proceeds at a different (usually much higher) velocity than the rate of linear deformation of the body by an impact. On this basis, stresses can be described as functions of time in the compression stage of impact, until the first fracture cleavage.

The principal measure of impact severity is the elastic strain energy per unit volume of material; this strain energy density applies to the body as a whole, as well as to the local energy density of compression. This local energy density is equal to the square of the local stress, divided by twice the modulus of elasticity of the material. The distribution of strain energy density follows Hooke's law and Saint-Venant's principle and provides a basis for energy balances over both the compression and the fracture stages of impact.

Crack propagation under compression proceeds with a linear velocity that increases with the length of the crack. For a representative glass, the velocity of 1-mm crack length may be as low as 100 m/s, but a 1-cm crack may have a velocity of 1400 m/s. These may be compared with the maximum velocity of stress waves, which for typical glass is the acoustic velocity (about 5000 m/s) [DOREMUS]. The propagation of a crack involves motion of the material, *i.e.*, a velocity that gives rise to a stress wave as described in the paragraph above. The quantitative descriptions are given in section II.D.2 below. The point here is that the fracture process itself cannot be treated by conventional stress analysis, but is amenable to more generalized methods. The fluctuations of stresses during the fracture process can be compared to the turbulence of fluid motion, as treated in fluid dynamics.

c. Turbulence and Energy Conversions in Brittle Fracture Compared to Fluid Flow

For fluids, "the fluctuations in the instantaneous values of continuum properties at a fixed point of space is called turbulence" [PA0]. The principal feature of turbulence is the changing magnitude and direction of the local fluid velocities. Basic to fluid dynamics is the concept of fixed spatial coordinates defined by a "control volume." The local fluid velocity (v) is associated with material of a given density (ρ), so that a local kinetic energy density is defined ($\rho v^2/2$). Energy density is a scalar

(nondirectional) property, while others, notably velocity, momentum, and shear stress, are vectors. The principal material property for resistance to flow is viscosity, which is defined as the ratio: (shear stress)/(velocity gradient). The shear stress has the dimensions: force/area. The velocity gradient is defined as normal to the shear plane and has the dimensions: (length/time)/(length). The net dimensions of this dynamic viscosity are thus:

$$\frac{FT}{L^2}$$

where F is force, L is length, and T is time.

The shear stress in fluid flow, when integrated over the length of travel, gives the energy consumption (per unit time) to maintain the flow velocity in the viscous flow regime. In the turbulent flow regime, the flow energy cannot be calculated by continuum mechanics, but empirical correlations based on dimensional modeling [LANGHAAR] are used to define the energy loss for flow in terms of the system dimensions and the fluid properties (density and viscosity). Dimensional modeling applies to the principles of geometrical similitude and continuum mechanics to the randomly varying velocities of turbulent flow, essentially providing statistical mean values for the macro flow system. This approach is well-established in engineering practice [PERRY], but formal use of mathematical statistics has not been developed to the point of engineering utility [PAO, p. 317].

The methods used in fluid dynamics are at least in part applicable to brittle fracture, when the following analogical concepts are considered:

- (a) energy, momentum, and force balances,
- (b) constant material (control) volume, even when the body is fractured into particles,
- (c) geometrical similitude and dimensional analysis for force and energy transformations in elastic compression and in fracture,
- (d) statistical variation of continuum properties--stress, energy, etc.,
- (e) resistance to fracture, a property of the material.

d. Energy Conversions in Fluid Flow and in Brittle Fracture

The energy conversions in the flow of liquid from one tank to another tank (at a lower elevation) is well understood [PERRY]. The energy conversions involved in the free-fall of a brittle body to an unyielding surface are analogous to those of fluid flow, but are less well understood. The stages of impact fracture are the following:

- (1) The potential energy of impact is determined by the body mass and the fall distance (under gravity).

(2) The potential energy is completely converted into kinetic energy by the moment of impact.

(3) The falling body decelerates during collision, and the kinetic energy is converted into elastic strain energy of compression.

(4) When the elastic stress of compression exceeds the threshold for fracture, cracks propagate and the body divides into particles which are energetically ejected, acquiring kinetic energy at the expense of the elastic energy stored in the compressed material.

(5) The motions of the particles are arrested by their environment, and their kinetic energy is dissipated as heat.

The local strain energy density referred to in step (3) above is defined in terms of local compressive stress and Young's modulus, E , an elastic property of the material; the local strain energy density (energy per unit volume) is given by $\sigma^2/2E$ where σ is stress. This is analogous to the kinetic energy density $\rho v^2/2$ of turbulent fluid motion. In both cases, continuum mechanics can be applied only statistically over the space occupied by the material; the actual local movements of the material in brittle fracture and in fluid flow are random and indeterminate.

The lognormal size distribution of the fracture particulate (produced by impact on brittle materials) implies that impact fracture proceeds by multiple stages of binary cleavage (in three dimensions) of the brittle solid. The lognormal distribution of particle size in such a process is mathematically equivalent to the normal distribution of the number of such binary-cleavage stages. (This normal frequency distribution is the familiar Gaussian curve, and its prevalence in physical phenomena also is established by the Central Limit Theorem of Statistics.) The quantitative measure of the extent of fracture is the total geometric surface area of the particles formed, that is, the sum of the cleavage surfaces. Statistical analysis of brittle fracture is made possible by the fact that the surface area and the size of solid particles provide a permanent record of the turbulent stress conditions that caused fracture; no such record is provided for liquid turbulence in fluid flow. However, in fluid flow, geometric modelling has been used to define overall mean effects in terms of dimensionless numbers. This is described below.

e. Characterization Methods in Fluid Dynamics

In fluid dynamics, force (F) is derived from the equation of motion as the time rate of change of momentum (Mv)

$$F = \frac{d(Mv)}{dt} = M \frac{dv}{dt} + v \frac{dM}{dt} \quad (1)$$

For the case of constant velocity, $dv/dt = 0$, with dM/dt the mass acted on per unit of time for the defined system and with A the cross-sectional area of the flow channel:

$$\frac{dM}{dt} = \rho Av \quad (2)$$

By combining Eqs. 1 and 2 for these conditions, the force F is

$$F = f \rho A v^2 \quad (3)$$

where f is a constant defined for geometrically similar systems. The physical meaning of F in Eq. 1 is the time rate of change of momentum of material entering and leaving the fixed control volume. The meaning of F/A , as defined by Eq. 3, is pressure, while $\rho v^2/2$ is the kinetic energy density of the material. The dimensionless Reynold's number (R_e) defines similitude for fluid flow in terms of (1) two fluid properties (density ρ and viscosity μ), (2) the flow velocity v , and (3) a characteristic linear dimension of the flow channel, L . In consistent units, R_e has the same value for different dimensions and properties when the flow behavior is the same:

$$R_e = \frac{L_1 \rho_1 v_1}{\mu_1} = \frac{L_2 \rho_2 v_2}{\mu_2} \quad (4)$$

Equation 4 is used to calculate R_e for the system. Empirical measurements of the resistance to fluid flow for standard geometries have been correlated with R_e , so that flow resistance can be calculated for a particular system once the Reynold's number is known [PERRY].

Dimensionless numbers for characterizing the results of impact fracture of brittle materials are presented below in section II.D.3.c.

2. Dynamics of Impact Compression

a. Basic Dynamics

From the well-established theory of elasticity, the basic dynamics of impact compression can be demonstrated very simply for the case in which a constant force, F , is suddenly applied to the end of a stationary bar of elastic material of uniform cross-sectional area, A . At the moment of application of the force (time $t = 0$), an infinitesimal layer of material at the force-contact surface is accelerated to velocity, v , and a compression-stress wave of velocity C starts to propagate along the bar. The stress intensity of the wave is also the stress σ to which the bar is compressed. The velocity v is the movement of the end of the bar as the bar is compressed to $\sigma = F/A$ by the stress wave. Since the force F and the bar cross section A are assumed to be constant during the time of compression, σ is constant as the bar is linearly compressed by the stress wave. By elapsed time t , the length of the bar that has been compressed is the same as the distance travelled by the stress wave, which is Ct , where C is the stress wave velocity. Note that the assumption is made that the bar itself is longer than the distance travelled by the stress wave; this is necessary so that the primary stress wave can be examined without the superposition of stresses that would be reflected if the wave should reach the far end of the bar.

By the application of Hooke's law and the conservation of momentum, the following general relations are demonstrated [TIMOSHENKO]:

$$\text{stress wave velocity} = C = \sqrt{E/\rho} \quad (5)$$

$$\text{material motion of impact} = v = \frac{\sigma C}{E} = \frac{\sigma}{\sqrt{E\rho}}, \quad (6)$$

where ρ is the density of the material and E is Young's modulus. Note that these equations do not contain a time factor. Equation 5 shows that the compression wave velocity, C , is independent of the stress level, σ , and also is independent of the impact velocity v . Equation 6 shows that the stress σ is directly proportional to the impact velocity, v , for a given material. These relations are generally valid, even when the force of compression is not constant, provided that $v < C$, which is the practical range of interest. The only assumptions made are Hooke's law and the conservation of momentum, which are valid in cases of practical interest. Stress wave velocity, Eq. 5, is always independent of time, but of course σ in Eq. 6 may vary with time, as it does in practical cases during the compression stage of impact of a body. However, the significance of Eq. 6 is that the initial collision velocity of impact v gives rise to a compression wave (of velocity C) which has a stress of intensity σ . Also, when a cleavage crack occurs, material is set in motion by elastic recoil, and this motion, v , will also give rise to compression wave with stress, σ , as in Eq. 6. For example, a collision impact velocity of 5 m/s (23 mph) will give rise in Pyrex glass ($\rho = 2300 \text{ kg/m}^3$; $E = 7 \times 10^{10} \text{ Pa}$) to a compression wave of $C = 5500 \text{ m/s}$ with a stress level, σ , of $6.3 \times 10^7 \text{ Pa}$ (7,200 psi). This level of stress is not sufficient to cause fracture, and therefore the primary compression wave will not fracture the glass. It should be noted that Pyrex shows a considerably higher stress threshold in impacts than in quasistatic load tests; tests show that in impacts Pyrex can be compressed to about five times the above stress level without fracture.

When a cleavage crack does appear, the compression force in the material will accelerate material at the crack surface to some velocity, v . This movement will generate a stress wave of intensity, σ , by Eq. 6, which may be much higher than the stress calculated above for the collision velocity of 5 m/s. If the stress, σ , of the impact compression is above the stress threshold for prompt fracture, then the stress waves generated by the first cleavage crack will fracture all material through which the stress wave travels at 5500 m/s. This mode of stress-wave fracture probably accounts for the catastrophic fracture of glass into particles in less than one millisecond, as observed in impact tests. The general relation between compression stress and the material velocity that results from fracture at that stress level can be shown by an energy balance for a unit volume of material:

$$\left. \begin{aligned} \text{elastic strain energy density} &= \frac{\sigma^2}{2E} \\ \text{kinetic energy density} &= \frac{\rho v^2}{2} \\ \text{thermal energy density} &= C_v \Delta T(^{\circ}\text{C}) \end{aligned} \right\} \quad (7)$$

where C_v is the heat capacity. In the brittle-fracture process, there is the following energy conversion: strain energy + kinetic energy + heat. If the energy densities of Eq. 7 are equated, it will be found that the relation between velocity v and stress σ is the same as that defined previously by Eq. 6. This is to be expected, since both momentum and energy are conserved.

Also, when heat capacity, C_v , for the material is known, the local temperature rise may be calculated, neglecting heat loss. There is evidence of substantial temperature rises when impacts are severe enough to form small particles (smaller than about 4 μm).

It should be noted that stress waves themselves bear equal amounts of potential and kinetic energy [TIMOSHENKO]. This kinetic energy can also be degraded into heat by interparticle friction.

In previous quarterly reports [STEINDLER-1981A, 1981B], the modeling of impact compression has been described. In a straightforward way, balances of force, momentum, and energy can be used to find the strain energy and stress as a function of time for the input conditions in either free-fall or drop-weight impacts. The impact severity is measured by the energy density input to the brittle material. In a drop-weight test in which the motion of the falling weight comes to rest on the brittle body (rather than on the mechanical stop of the test device), the input energy density is calculated from the kinetic energy of the impact.

The modelling of impact results is given in the following section, II.D.3., and impact test machines are discussed in section II.E.

3. Modeling of Fracture Results

a. Binary Cleavage as a Fracture Mode

As described above, an impact results in elastic compression of a brittle body. When sufficient stress is generated, a cleavage crack forms along the plane of maximum tensile strain--that is, parallel to the force axis. (This is true for both diametral and axial impacts of cylinders.) The cleavage crack propagates stress waves which generate catastrophic fragmentation into particles. The impact fracture process has the effect of subjecting the brittle body to multiple stages of binary cleavage in all three dimensions.

b. Particle Size and Surface Areas

The particles formed have a size distribution that can be described statistically as if (1) the number of successive stages of binary cleavages (in various portions of the body) were distributed randomly by the normal probability law and (2) the resulting linear size of particles was distributed by the corresponding lognormal probability function [HERDAN].

The extent of fracture is measured by the total surface area of the fracture cleavages, which is the same as the total surface area of the solid particulate formed by the impact. An empirical correlation between the energy dissipated in the brittle material and the total surface area formed has been found:

$$\epsilon W_i = \gamma_f S_n \quad (8)$$

where W_i is the kinetic energy input to impact fracture and S_n is the surface area formed. S_n has been measured by BET gas adsorption [ZELENY]. ϵ is a dimensionless efficiency factor to account for dissipation of different amounts

of input energy in system components other than the brittle material; ϵ has been measured in tests using an impact calorimeter [ZELENY]. γ_f is an empirical property of the material, calculated by Eq. 8 when the other quantities are known; for small Pyrex and natural quartz specimens, $\gamma_f = 77 \text{ J/m}^2$ [ZELENY]. The basis of the above equation is the energy conversion in the impact fracture process: kinetic energy + elastic strain energy + kinetic energy in the fragments of the fractured body + heat. A more general relation of energy conversion is obtained by combining Eq. 8 with Eq. 7:

$$\epsilon \left(\frac{W_i}{V_n} \right) = \frac{\sigma^2}{2E} = \gamma_f \frac{S_n}{V_n} = \left(\frac{\rho v^2}{2} \right) = C_v \Delta T \quad (9)$$

where the terms (from left to right) follow the course of the impact-fracture process.

The overall surface/volume ratio resulting from impact fracture is also related by geometry to the lognormal particle parameters: the geometric mean diameter, D_g , and the geometric standard deviation, σ_g :

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

where α is the overall mean surface/volume shape factor for the lognormally distributed fracture particulates [HERDAN]. α is dimensionless; it appears to be independent of particle size, and in tests with small Pyrex specimens, $\alpha \approx 20$. (In comparison, α is at a minimum of 6 for spherical or cubical particles.) D_g and σ_g are determined by particle size analysis, i.e., sieving, Coulter counter, and microscopy (optical or electron microscope). The value of α is calculated from Eq. 10 from known values of the other quantities.

In controlled-impact tests, the input energy density, W_i/V_n , is known and all the other variables can be measured or calculated. From such tests, correlations are made between W_i/V_n and the other variables: ϵ , γ_f , D_g , σ_g , S_n , and α . Equations 9 and 10 provide the basis for complete characterization of the results of impact fracture of brittle materials.

c. Dimensionless Numbers and Scaling Laws

In order to provide scaling laws for the impact-fracture process, it is desirable to have dimensionless relations, as in fluid mechanics. From Eq. 9,

$$\epsilon = \left(\frac{W_i}{V_n} \right) / \gamma_f \left(\frac{S_n}{V_n} \right) \quad (11)$$

The dimensionless number, ϵ , characterizes the external conditions of impact--in particular, how input kinetic energy is partitioned between the brittle body and other components. For a given ϵ , the surface/volume ratio is proportional to input energy density, independent of body size. This must be qualified by considering the duration of impact: if the applied stress is removed (for example, by elastic rebound) before cracks have time to develop (about 100 μs), the characteristic particulate fracture may not develop.

Another dimensionless number is derived from Eq. 10.

$$\alpha = \frac{S_n}{V_n} D_g \sigma_g^{-0.5} \ln \sigma_g \quad (12)$$

The dimensionless number, α , characterizes the internal conditions of impact--in particular, how the stress distributes as a result of impact configuration and the elastic properties of the material.

It is expected that D_g , σ_g , and S_n/V_n all correlate with energy density, independently of body size, but thus far, tests have been made only on small specimens, smaller than 200 cm³. It is known, of course, that compressive stress correlates with energy density in free-fall impacts, so that maximum stress is a function of fall height only and is independent of body size for a given material (that is, for given density and elastic properties) [LANGHAAR].

4. Conclusion: Impact Fracture as Solid-State Turbulence

In this section, random fluctuations of local energy density during the impact-fracture process were related to (1) overall energy conversions in the various stages of dissipating input kinetic energy in the brittle material and (2) the statistical averaging inherent in the binary-cleavage mode of fracture of brittle materials in impacts. Stress-severity parameters (principally strain energy density) were related to lognormal particle parameters (D_g , σ_g , α), to material properties (E , ρ , γ_f), and to impact conditions (W_i , V_n , ϵ). The effects of impact configuration and time are implicit in energy density; these effects were treated in detail when modeling impact severity for various configurations in the elastic compression stage of impact.

The principles of dimensional similitude have been used, as in fluid turbulence, to define overall relationships of practical interest in dimensionless form, as a basis for the correlation of experimental measurements and prediction of the effects of changed conditions. In this sense, impact fracture of brittle bodies, while not amenable to the classical methods of continuum mechanics, can be treated as a sort of solid-state turbulence.

As described above, the compression stage of impact does not itself fracture the glass but rather steadily raises the level of compressive stress throughout the impacted body. If the body is essentially flaw-free, microcracks propagate slowly relative to the rate of increase of compressive stress, so that when the first cleavage crack has developed (about 100 μ s), this crack sends out a stress wave powerful enough to shatter the glass in its path. Of course, the succeeding cracks do the same, until the strain energy density is used up. These energy conversions are indeed turbulent, but the effects can be correlated statistically with parameters for the fracture particulate as a whole.

E. Analysis of a Proposed Standard Impact Test Procedure for Waste Materials
(W. J. Meham)

1. An Analysis of the Proposed MCC-10 Test for Characterization of the Impact Resistance of Brittle Waste Materials

1. Objectives and Scope of MCC-10

A summary report has been issued [MERZ] containing the preliminary recommendations of the Materials Characterization Center (MCC) for a standard test procedure (MCC-10) for measuring the impact resistance of glass and ceramic solid-waste materials for high-level radioactive waste disposal. The recommendations have the following objectives:

1. The tests are to provide comparative data on the amount of respirable fines and surface area produced in impacts, relevant to (a) the selection of a waste form and (b) risk assessment.
2. Realistic testing of canistered wastes is not included in MCC-10 scope; energy input to the specimen and stress levels are not considered relevant to either the selection of waste forms or risk assessment; loading rate (force per unit time) is the specified impact condition.
3. The standard test is to be a drop-weight impact of cylindrical specimens of simulated waste glass; a specified mass is to be dropped a specified distance on the specimen; a standard device and procedure is to be used to obtain comparative results under conditions severe enough so that the "strongest" materials will be extensively fractured. A diagram of the preliminary test device is shown in Fig. 6.

Fig. 6.

Impact Test Device for MCC-10

4. Final recommendations on the detailed specifications of the standard tests will depend on reproducibility, and review of data is to be done by the Materials Review Board (MRB).

5. Preliminary specifications of the standard test device and procedure are presented [MERZ], which embody the following features:

- a. Axial impact is preferred over diametral impact on the basis of uniformity of stress;
- b. The recommended specimen size is 1.3-cm diameter and 3.2-cm length;
- c. Following recovery of the fracture particulate from a sealed impact chamber, respirable fines are to be measured aerodynamically after they are rendered airborne by elutriation in a separate step. This is done to obtain the respirable fracture on the basis of the aerodynamic diameters of particles;
- d. Sieving analysis is considered adequate for obtaining the total surface area generated by fracture;
- e. In the proposed impact test, a relatively massive dropped weight (230 kg to 795 kg) and a mechanical stop are used; selection of this weight is consistent with providing a constant loading rate as the condition for comparable impact severity in standard impact tests of different materials.
- f. A load cell (force transducer with high-speed CRT readout) can be used to establish that reproducible loading rates are being obtained by the impact device; the load cell is not anticipated to be necessary equipment for routinely performing tests by MCC-10; tests are under way to evaluate the need for a load cell.

b. Review of Initial Test Results

Initial test results were reported [MERZ] as showing that loading rates are reproducible within 5% and that peak loads are reproducible within 7%. Typical load curves were reported and are reproduced in Figs. 7 and 8. Note that these are linear plots of force (measured by the load cell) as a function of time (in ms). The ordinate scale units for the alumina specimen have twice the magnitude of those for the Pyrex specimen; units are 10^5 pounds (force).

The approach recommended by MCC is an extension of a standard method for testing the structural strength of metals under dynamic loads. Since the fracture process for even the most brittle of structural metals is fundamentally different from that of truly brittle materials (glasses and ceramics), it remains to be seen whether this approach gives useful results.

Fig. 7. Force-Time Plot for Axial Impact of a Pyrex B Cylinder [MERZ]. See Table 5 for conditions.

The dynamic loading rate (the fundamental MCC criterion for impact severity in standard comparative tests) has not been established as a useful parameter for correlating the measurements of impact results, which are (1) surface area and (2) fractions of particles of respirable size. Of course, dynamic loading rates do correlate with threshold conditions for first fracture, which determines structural strength. This correlation is basic to characterizing structural strength, but it may not be so useful for the stated criteria of impact results. The latter are relevant, not to the structural strength of the waste forms, but to the increase in their potential dispersibility in case of accidents. Aerodynamic methods of characterizing particle sizes (cyclones and cascade impacters) are well developed for particles of nearly spherical shape, but have not been evaluated for sharp-edged particles of widely varying shape and size, such as particles produced in impact fracture of brittle materials. There is a certain "realism" in using aerodynamic methods of particle-size characterization with respect to respirable particles, but a realistic condition for the impact itself was explicitly excluded by the scope (see item 2 of the preceding subsection).

Sieving is well established for characterizing particle size distributions (by mass), for particles larger than about 60 μm (above the respirable size fraction). Sieving by itself cannot characterize the surface

Fig. 8. Force-Time Plot for Axial Impact of an Alumina B Cylinder [MERZ]. See Table 5 for conditions.

area of the irregular particles--especially the surface area of particles smaller than 60 μm , which are the particles that contain most of the surface area.

The overall approach recommended does not take advantage of any of the theoretical or empirical generalizations that relate surface area or particle size and shape to impact conditions--principally, the energy dissipated in the brittle material. The approach taken is (1) development of

dynamic testing machines for brittle materials, (2) development of cascade impactors for measuring the size distributions of irregular particles, and (3) development of sieving for surface-area measurement. These developments may be costly for the stated objectives. The use of established measurement methods for characterization of a material property (impact resistance) would seem to be a more efficient way to proceed, especially since impact resistance is a rather low-priority item among those on the waste management agenda for materials characterization. The approach proposed may not be the most efficient for the stated objectives, since there are significant alternatives.

The approach recommended aims at comparing surface areas and respirable fractions of different materials; a standard test would be used, and a given loading rate. This can give a ranking order of material behavior for the specific impact tests, and can give a quality-control standard for material manufacture. It may well be, however, that the range of materials of interest will vary to the extent that the ranking order may be an artifact of the particular test machine and specimen size. Since neither (a) the design basis of the recommended test device nor (b) acceptance criteria for surface area and particle size measurements have been fully reported, the present recommendations or the stated objectives may require modification after evaluation tests are made. Certain assumptions stated as a basis for the recommendations are examined in more detail below.

A simplified force-time plot for an impact test with a constant loading rate is shown in Fig. 9. In Fig. 9, the loading rate is dF/dt , the slope of the force-time curve, and it is constant up to a peak observed load force, at which point it falls to zero. This curve shows (1) the monotonic increase of force (as a function of time) applied to the specimen during elastic compression and (2) the fall to zero force as a result of catastrophic

Fig. 9. Simplified Force-Time Plot of an Impact Test with Constant Loading Rate

fracture of the specimen and the ejection of fragments from the path of the descending striker rod. Actually, there is a finite time during which microcracks can develop prior to those whole-body cleavages, which give the solid particulates typically observed. Thus, some cracks may be developing during the constant-rate loading period before the abrupt loss of resistance to the force applied by the descending rod. Available empirical evidence indicates that it takes more than about 60 μ s for extensive cracks to develop from microcracks in typical specimens. When the impact loading is applied for a longer time than this, developing cracks might prevent the loading curve from being as linear as shown in Fig. 9.

The observed loading rates in Figs. 7 and 8 are not quite constant; peaks and irregularities are shown, and the overall trend of the loading rate, dF/dt , is concave downward. The fact that the first peak and the highest peak occur at the same time for materials of different elastic properties and strengths and the fact that the loading rates are different for different materials suggest that the similarity of the times to catastrophic fracture may not reflect similar impact resistance, but either coincidence or the way the specimens interact with the test machine.

The stresses calculated for the first peaks, at about 0.2 ms, are about 0.64×10^9 Pa (92×10^3 psi) and 1.1×10^9 Pa (156×10^3 psi), respectively, for Pyrex and alumina. These stresses are greater than the static-load threshold stress for fracture, so that it is possible that some cracking is taking place at 0.2 ms and later times and that the observed irregularities in the measured force are a result of these developing cracks. The point here is that, if cracks are actually developing in the time between 0.2 ms (the first peak) and 0.72 ms (the highest and last peak), the compression stress cannot be uniform during the period described by the curve. This is mentioned because axial impact is recommended on the basis of uniform stresses during impact compression (objective 5.a. above).

The assumption of a uniform stress may be misleading in some respects. A basic source of nonuniformity of stress, even in the initial stages of elastic compression before the first crack occurs, is misalignment of components along the force axis combined with departure of the surface of the specimen from an exact perpendicularity to the force axis. Even for the specified tolerances of ± 0.050 mm for specimen dimensions, such misalignments could cause factor-of-two stress differentials across the specimen surface. In view of the near impossibility of attaining truly uniform stresses, the cost of very precise alignment is probably unjustified for a standard test method.* The proposed method calls for matching end pieces to the specimen in order to reduce end effects that produce stress variation in the specimen. A material of fabrication for these end pieces has not yet been selected.

A stress analysis of the data in Figs. 7 and 8 on the basis of available information is given in the following section.

*The insensitivity to alignment for diametral impacts is a major reason for diametral impacts being used in standard quasistatic tests of the strength of brittle materials.

c. Stress Analysis of Proposed Impact Test

From available information on the materials, dimensions, and impact conditions under which the tests described by Figs. 7 and 8 were conducted, a stress analysis was made. It is assumed that the axially impacted specimens were 19.0 mm in diameter and that the specimen length was 2.5 times the diameter. Values of Young's modulus were assumed, namely, 7.0×10^{10} Pa for Pyrex and 37×10^{10} Pa for alumina. The falling mass was taken to be 775 kg and the fall distance 0.50 m. The striker bar was assumed to have a diameter of 57 mm and a length of 450 mm; its Young's modulus was assumed to be that of steel, 21×10^{10} Pa. This analysis makes use of energy, momentum, and force balances and assumes ideal elastic behavior and ideal uniform stress in the axial impact.

Although it is customary to speak of compressive stress causing fracture, in actuality, compression cannot cause fracture; only tension (more accurately, tensile strain) can cause a crack to form and propagate. (Compression can seal cracks.) What actually happens is that unidirectional compressive strain causes tensile strain normal to the force axis; for Pyrex, the ratio of tensile strain to compressive strain is about 0.20. This is Poisson's ratio, a constant elastic property of the material.

In the impact device shown in Fig. 6, there is a balance of two forces: (1) force is generated by the deceleration of the falling mass as it hits the upper end of the striker bar, which transmits this force through the specimen to the load cell and the baseplate, and (2) the motion of the falling mass compresses both the striker and the specimen, giving rise to strain, compressive force, and elastic compression energy in both the striker and the specimen. By an energy balance, this elastic strain represents a loss of kinetic energy of the moving mass, M . The mass ($M = 775$ kg) for the tests represented by Figs. 7 and 8 has an original velocity, u_0 , of 3.1 m/s. Since the mass of the steel striker bar is only about 10 kg, the striker bar is immediately accelerated to a velocity nearly equal to u_0 as determined by a momentum balance.

Quantitative analysis of force and energy relationships in the proposed impact test has not been presented in the MCC report, but it is quite simple and will be summarized below for convenience in interpreting the data presented in Figs. 7 and 8.

The force $F(N)$ is generated by deceleration of mass M (kg) from its initial velocity, u_0 (m/s), to a lower velocity, u , a function of time t (s); the deceleration force is balanced by the compressive force

$$F = -M \frac{du}{dt} = A\sigma \quad (1)$$

where σ is the stress (Pa) and A is the cross-sectional area (m^2) of the specimen. The loss in kinetic energy is the total energy, W_t , available for compression:

$$W_t(J) = 0.5 M u_0^2 - 0.5 M u^2 \quad (2)$$

There is a corresponding change of momentum, which is related to the impulse, I . The value of I is given by the force-time integral, which is the area under the force-time curve in Figs. 7 and 8:

$$I(N-s) = - \int_0^t F dt = Mu_0 - Mu \quad (3)$$

where the small mass of the striker bar is neglected. From Eqs. 2 and 3, the loss of kinetic energy can be found in terms of the impulse, I :

$$W_t = u_0 I - \frac{I^2}{2M} \quad (4)$$

Since the force, F , is transmitted from the deceleration mass M to the specimen and to the base plate, F can be related to the mean stress, σ , of the specimen over its load-bearing surface area, A . The same relation holds for the mean stress, σ_s , in the striker bar and its cross-sectional area, A_s :

$$F = A\sigma = A_s\sigma_s \quad (5)$$

Since A and A_s do not change appreciably,

$$\sigma_s = \left(\frac{A}{A_s} \right) \sigma = 0.11\sigma \quad (6)$$

when evaluated for the dimensions of Fig. 6. Equation 6 is valid for all values of σ and F .

The overall strain energy, W , in the specimen and in the striker rod, W_s , can be calculated in terms of the mean stresses defined above. That is, for volume V of the specimen and volume V_s of the rod,

$$W_t = W + W_s = \frac{V\sigma^2}{2E} + \frac{V_s\sigma_s^2}{2E_s} \quad (7)$$

where E is Young's modulus for the specimen and E_s is Young's modulus for the rod (7×10^{10} Pa for Pyrex and 21×10^{10} Pa for steel). For the respective values of V and V_s (13 cm^3 and 1180 cm^3),

$$W_s = 0.34 W \quad (8)$$

This relation is valid for all values of F and σ . Equation 8 represents the partition of the total energy W_t , defined by Eq. 4 in terms of F measured by the load cell, between the specimen and the striker rod for given impact conditions. For these particular conditions, the following relations hold:

$$\text{Pyrex and alumina: } \sigma(\text{Pa}) = 3.6 \times 10^3 F(\text{N}) \quad (9)$$

$$\text{Pyrex: } W(\text{J}) = 2.4 \times 10^{-10} F^2(\text{N}) \quad (10)$$

in which the units are shown.

In Table 6 are presented values calculated from the data of Figs. 7 and 8 for the peaks observed in the force-time plots for Pyrex and alumina. Young's modulus for well-sintered alumina is 5.3 times that of Pyrex and gives a different relation for W_s/W and W :

$$\text{alumina: } W_s = 1.80 W; W(J) = 2.4 \times 10^{10} F^2(N) \quad (11)$$

Table 6 shows the kinds of information that can be extracted from the data presented in Figs. 7 and 8. The methods of calculation are given in the footnotes to the table.

In Table 6, the time is shown for each peak on the force-time plots for Pyrex and alumina in Figs. 7 and 8. For each time, the loading rate (dF/dt), the impulse, and the mean stress in the specimen are calculated from the measured force. The absorbed energy is calculated for the specimen alone, the striker alone, and the specimen and the striker combined, and calculated

Table 6. Stresses and Absorbed Energies Calculated from Force Data in Axial Impacts of Pyrex and Alumina Cylinders

Reference Conditions					
a. Falling mass, 775 kg; distance, 0.50 m; velocity, 3.1 m/s; energy, 3.7×10^3 J.					
b. Dimensions of cylindrical specimen: dia, 0.019 m; length, 0.048 m.					
c. Steel striker bar; dia, 0.057 m; length, 0.45 m.					
d. A mechanical stop limits the linear displacement to about 0.012 m.					
Measured or Calculated Value	Pyrex		Alumina		
	First Peak	Final Peak	First Peak	Second Peak	Final Peak
Time, μs	200	720	160	450	720
Force, 10^6 N	0.18	0.33	0.30	0.50	0.66
Mean slope, ^a dF/dt , 10^9 N/s	0.90	0.46	1.8	1.1	0.92
Impulse, ^b N-s	18	122	48	112	260
Mean stress, ^c 10^9 Pa	0.65	1.2	1.1	1.8	2.4
Mean stress, ^c 10^3 psi	94	172	156	261	344
Absorbed energy ^d					
in specimen, J	39	131	22	60	104
in striker, J	13	44	39	108	188
in both, J	52	175	61	168	292
Specimen energy density ^d					
specimen only, J/cm ³	3.0	10	1.7	4.6	8.0
specimen + striker, J/cm ³	4.0	13	4.7	13	22
Loss of kinetic energy, ^e J	56	370	148	340	762
Loss of K.E., J/cm ³	4.3	28	11	26	59

^aSlope of force-time = time plot from load cell.

^bImpulse, $I = \int_0^t F dt$ (or area under force-time curve).

^cStress = measured force/cross-sectional area of specimen.

^dEnergy density = $(\text{stress})^2/2 \times \text{Young's modulus}$; energy = volume $\times$ energy density.

^eLoss of kinetic energy calculated from impulse I , falling mass M , and maximum velocity u_0 ; $\Delta(K.E.) = u_0 I - I^2/2M$. When divided by specimen volume, it is expressed as energy density.

from the impulse, assuming that the energy absorbed is equal to the kinetic energy lost, as given by Eq. 4.

The above absorbed energies, when divided by the specimen volume, yield the energy densities (also given in Table 6).

The mean slope of the force-time curve, dF/dt , is the loading rate: it is 1×10^9 N/s for all cases, within a factor of two.

The stress at the first peak was 0.65×10^9 Pa (94,000 psi) for Pyrex and 1.1×10^9 Pa (156,000 psi) for alumina. The stress at the final peak was 1.2×10^9 Pa (172,000 psi) for Pyrex and 2.4×10^9 Pa (344,000 psi) for alumina. Possibly, some crack propagation occurs between the first and final peaks, as discussed above.

The impulses in Table 6 are equivalent to momentum transfers. The input momentum was 1.2×10^3 N-s and the maximum impulses measured were 122 N-s for Pyrex and 260 N-s for alumina. The differences between input and measured impulses were absorbed by the mechanical stop, according to the momentum balance, Eq. 3.

The energy absorbed in the Pyrex specimen was 39 J at the first peak and 131 J at the final peak. The energy absorbed in the alumina specimen was 22 J at the first peak and 104 J at the final peak. Possibly, some energy absorbed in the striker fed into the specimen when the specimen began to crack. The energies available in the striker are shown in the table; the different values are due to Pyrex and alumina having different elastic properties.

The maximum energy densities absorbed were calculated to be 10 J/cm^3 for the Pyrex specimen and 8.0 J/cm^3 for the alumina specimen.

The difference between the kinetic energy input (3.7×10^3 J) and the loss of kinetic energy at the final peak (calculated from the impulse) is the amount of energy absorbed by the mechanical stop; this difference was 90% for Pyrex and 79% for alumina. These fractional amounts are identical with those for momentum, as expected. There is some question, however, as to how the energy absorbed by the striker fits into the energy balance. Does it contribute to fracture, or not? Possibly, this could be determined by a detailed analysis of the test as a function of time.

In summary, the above analysis indicates the kinds of information that can be obtained from the force-time plots. Additional test data, together with measurements of surface area and particle sizes of the fracture particulate, are required to evaluate the procedure. The question of whether the Pyrex and the alumina received impacts of comparable severity is not completely clear, although the loading rates agreed within a factor of two and the absorbed energy densities in the specimens at the final peak also agreed within a factor of two. The question of whether crack formation was occurring in the specimen before the final peak was recorded could be answered with high-speed motion pictures.

F. Documentation and Reports of this Brittle Fracture Study

A topical report on the progress made in our brittle fracture study prior to October 1980 was published early in December 1981:

W. J. Mecham, L. J. Jardine, R. H. Pelto, G. T. Reedy, and M. J. Steindler, Interim Report of Brittle-Fracture Impact Studies: Development of Methodology, Argonne National Laboratory Report ANL-81-27 (October 1981).

Two papers were presented November 19, 1981, at the Materials Research Society International Symposium in Boston:

Respirable Fines Produced by Impacts of Simulated Alternative High-Level Waste Materials,
A Methodology for Characterizing Brittle Fracture of Solid Waste Forms in Accidental Impacts.

These are to be published in Scientific Basis of Nuclear Waste Management, Vol. IV (1982), S. V. Topp, Editor, Materials Research Society.

Four short papers have been drafted for submission to appropriate refereed journals:

- (1) Evidence and Analysis of Fusion of Glass Particles Formed by Mechanical Impact,
- (2) An Illustration of a Method of Measuring Size Distributions of Glass Particles Adhering to Container Walls,
- (3) General Description of Impact-Fracture Particulates Formed by Brittle Materials in Impact Tests,
- (4) Scale-Modelling of Impact Severity for Brittle Fracture.

A summary topical report is being drafted as an Argonne National Laboratory report: Final Report of Experimental Laboratory-Scale Brittle Fracture Studies of Glasses or Ceramics.

III. NUCLEAR LOGGING OF OIL RESERVOIRS (M. G. Seitz and G. Vandegrift)

A. Logging Method

Work performed this quarter centered on performing core-flood experiments to test the possibility of logging oil in rock using gamma-active fluid. In the proposed method of logging the oil, the radioactivity of the rock (plus fluid) is first measured using a gamma-sensitive probe. The rock is then injected with water containing a gamma-emitting radionuclide, and the radioactivity of the rock is logged again with the probe. Differences in the measured radioactivities can be related to the residual oil saturation of the reservoir.

B. Experimental Approach

An experimental program conducted to test this concept consisted of a series of experiments using two sets of cores—one set with a known residual oil saturation and the other set with zero residual oil saturation. The cores, of Berea sandstone, were cylinders 6.83-cm diameter by 14.60-cm long. A schematic of the experimental setup is shown in Fig. 10. The scintillation detector is a 5.1-cm-dia by 5.1-cm-long crystal of NaI with thallium dopant and having a well 2.0 cm in diameter and 3.5 cm deep. The crystal was placed 8.2 cm from the 2.2-cm-thick end plate of Hastelloy-C276 alloy that was in contact with the core.

Fig. 10. Schematic of the Apparatus Used in the Core-Flood Experiments

C. Experimental

The composition of the simulated groundwater used in the experiments is again given in Table 7. The water has a density of 1.02 g/cm^3 , based on the assumption that its volume did not change upon the addition of salts. The water is similar in ionic content to brines from sandstone oil reservoirs.

Table 7. Constituents of the Simulated "Groundwater" (Brine) Used in the Core-Flood Experiments

	Concentration, ^a mg/L
Na^+	7788
Mg^{2+}	240.8
Sr^{2+}	7.30
Fe^{3+}	22.5
Cl^-	11005
CO_3^{2-}	60.6
SO_4^{2-}	1599
HCO_3^-	615.4
Total	21340 ^b

^aChemicals were dissolved in distilled water.

^bThis compares with 30220 mg/L total solids in the "average" sandstone reservoir fluid, calculated using about 10 analyses from Dowell, U.S. Geological Survey, Gulf Oil Corp., and the Indiana Geological Survey.

The cores were first injected with nonradioactive water to prepare them for the experiments. This injection was continued for about 18 h and forced a substantial amount of oil out of the oil-saturated cores. The cores were then each injected with water containing the gamma-emitting radionuclide, sodium-22. The fluid was injected at a constant rate of 0.90 mL/min or 4.5 mL/min into the cores (6.9-cm-dia cross section and 21% porosity). During injection, the gamma-ray signals detected outside the core holders were measured at 400-s intervals.

The experiments were done in two series. The first series consisted of two experiments, one on an oil-bearing core (170-118) and one on an oil-free core (170-113). The results of these experiments are described first.

The second series of experiments was done on oil-bearing and oil-free cores, with surfactant and oil-stripping solvents. Only a preliminary analysis of the comprehensive second series of experiments was completed in the quarter.

1. First Series

The gamma signals from the oil-bearing and oil-free cores are shown in Fig. 11. The zero injection time on the graph indicates the start of pumping radioactive water.

Fig. 11. Gamma Signals from Oil-Free and Oil-Bearing Cores Measured in Core-Flood Experiments

The signal from the core without oil rose to a higher level than did the signal from the core containing oil. The signals stabilized after about 140 mL (9000 s), and 95 mL (6000 s) of solution was injected into the oil-free and oil-bearing cores, respectively. These stable signals during continued injection suggest that radioactive sodium was not adsorbed from the solution by the rock. After stabilization, the gamma signal from the oil-free core was 63% higher than the signal from the oil-bearing core. This difference is substantial and suggests that the oil in a reservoir might be accurately logged by injecting gamma-active water into the reservoir.

Plots of the radioactivity of solutions leaving the cores are given in Fig. 12, as measured by a 7.6-cm-dia by 7.6-cm-long NaI detector. As injection of radioactive water continued, the solutions exiting from both cores rose from the background level to a level of 37.5 counts/s·mL. This activity is slightly below the values of 39.0 counts/s·mL measured for the radioactive solution and suggests some mixing with nonradioactive fluid. The solution

Fig. 12. Activity in Fluids Leaving the Cores

from the oil-free cores rose in activity more slowly than did the solution from the oil-bearing core. The difference in injection times at half-maximum values of the curves is 4080 s, which corresponds to 64 mL of pumped solution. This can be considered the difference in flowing water in the two cores. This volume, 64 mL, is very nearly equal to the 60 mL of oil known to have been in the oil-bearing core.

To investigate the reproducibility of the results reported here, the oil-bearing core was injected with gamma-active water a second time. The activities measured from the core after each injection were the same, to within experimental uncertainty ($\sigma \approx 3\%$). This was expected since residual oil saturation in the core was nearly the same for the two injections.

2. Second Series

A second series of experiments was done to examine the reproducibility of the results discussed above (using different cores), to examine the potential benefit of using surfactant in the injected water, and to determine the effect of stripping oil from the cores by use of a mixture of toluene and methanol.

The following experiments were performed in the second series.

a. Exp 170-128

An oil-saturated core was placed in the rock core holder, and approximately 300 mL of nonradioactive brine solution was pumped through the rock core at 0.92 mL/min. (This flow rate was used for this and for all

following experiments.) This treatment removed 48% of the oil. The core was then pumped with ^{22}Na -containing brine. (The brine is the same as the simulated "groundwater" described in Table 7.) During this experiment and Exp 170-131 that followed, the eluate contained approximately 2 vol % oil. When the rock core activity appeared to reach a plateau, nonradioactive brine solution was again pumped through the rock core to clear the core of radioactivity.

b. Exp 170-131

After 300 mL of nonradioactive brine solution had been pumped through the core, experiment 170-131 was begun by again switching to the ^{22}Na -containing brine. After 71 mL of the radioactive solution was pumped through, brine containing ^{22}Na and 60 μL of a surfactant (Triton X-100) per liter was pumped into the core. The activity of the core was again allowed to plateau, and nonradioactive solution was then pumped through the core again.

c. Exp 170-132

Following Exp 170-131, approximately 600 mL of a 1/4 volume ratio of methanol/toluene was pumped through the same core. This treatment removed essentially all of the remaining oil in this core. Six hundred milliliters of nonradioactive brine was passed through the core before radioactive brine was once again pumped into the core. The core was then pumped with radioactive brine, and the gamma signal recorded as described previously for the first series of experiments.

d. Exp 210-106

This experiment was performed using the same core as in Exp 170-132. The radioactive brine solution in this case, however, contained the surfactant, Triton X-100.

e. Exp 210-113

This experiment was performed on a core which had been saturated, not only by oil, but by brine solution before it was placed in the rock core holder. The radioactive brine solution contained Triton X-100.

f. Results

Table 8 numerically shows the results of the experiments described above. The parameters listed in Table 8 were all measured from data of the same type depicted in Figs. 11 and 12 of this report. The second column of Table 8, the maximum core activity minus background, was determined by averaging the count rate at the plateau of the core activity curve and subtracting the count rate when no radioactive brine solution was in the core. The third column, the percent of eluate count rate greater (or less) than that of the input solution, was measured by subtracting the count rate of an equal volume of input solution from the maximum count rate of the eluate, dividing by the count rate of the input solution, and multiplying by 100.

Table 8. Parameters Measured in Oil-Logging Experiments as Radioactive ^{22}Na Salt Solutions Were Pumped Through Sandstone Cores

Exp No.	Max. Core Activity Less Background, counts per 400 s	Count Rate of Eluate Compared to Count Rate of Input Water, %	Time to Reach 1/2 Maximum Activity, 10^3 s		(Tangential Slope at Point of 1/2 Maximum Activity)/(Max Activity), 10^{-4} s	
			Core	Eluate ^a	Core	Eluate ^a
170-128	309	-2.1	1.4	3.3	3.0	3.8
170-131	332	+0.7	1.4	3.2	3.3	3.6
170-132	386	-1.9	1.4	4.7	3.1	2.5
210-106	423	+1.9	1.7	5.2	2.4	1.2
				5.3		-1.1
210-113	477	+0.6	2.1	8.0	1.7	2.4
				7.9		-2.2

^aTwo values in the same column are measurements of both the ascending curve, when switching from nonradioactive to radioactive water, and the descending curve, when switching from radioactive to nonradioactive water.

In the fourth and fifth columns are the time intervals after switching to radioactive solution at which the count rates in the core and in the eluate reached one-half the maximum value above background. In the last two columns of Table 8 are the tangential slopes of the count rate change for the core and the eluate vs. time, measured at the point of 1/2 maximum. These parameters are a function of both the void volume and the nonuniformity of pathways through the core.

g. Discussion of Results of the First and Second Series of Experiments

Data from the first series of experiments and that presented in Table 8 show that the amount of oil in these sandstone cores does affect the maximum measured ^{22}Na gamma activity at the face of the rock. The time necessary to reach that maximum and the slope of count rate vs. time at 1/2 maximum are also correlatable to the amount of oil present. Future work will deal with these correlations and with the testing of mathematical models to interpret them.

The higher measured count rate at the face of the rock when Triton X-100 was present in the brine is striking and suggests that a surfactant may have an important role in this technique. The probable explanation

for this phenomenon is that with the surface tension of water lowered substantially, the radioactive brine solution is able to move more easily through smaller channels and thus can more quickly displace nonradioactive solution in these channels; it can also better mix with brine solution caught in dead-end pores.

Further evidence for this effect was found in the eluates of experiments 210-106 (with surfactant) and 170-132 (without surfactant). After the methanol/toluene wash had removed most of the oil from the rock core (in Exp 170-132), no oil was detected in either the eluate of that experiment, or the eluate of the following experiment, 210-106, until the surfactant-containing solution began to elute from the rock core in both experiments. This eluate had small amounts of oil associated with it. This is evidence that the surfactant-containing water was entering pores impenetrable by water alone.

3. Future Work

Future work on this program will include a complete analysis of the experimental data summarized here. The results of the laboratory tests will be transformed to results expected under field conditions. An important question to answer is this--is the gamma signal capable of measuring the oil, even with the uncertainties that can be expected during field operation?

Several new investigations are suggested by the results of the experimental program. Surfactants at various concentrations in the water could be tested for their ability to improve logging sensitivity. Gamma signals from oil-bearing cores could be measured for many different oil contents. Finally, a radionuclide in chemical form that partitions between the water and oil could be tested to see if it would give a calibration of pore volume and be applied to the gamma-inject logging method.

IV. LABORATORY-ANALOG PROGRAM

(D. Bowers,* S. Fried,† T. Gerding, G. Vandegrift, and M. Seitz)

An experiment was begun this quarter in the laboratory-analog program funded by the Nuclear Regulatory Commission. The experimental operations described in this report include automatic recording of experimental parameters by digital equipment. In addition, the rock cores and the experimental apparatus are described. A waste glass composition was selected for use in the experiments; details of its composition, preparation, and characterization are described. Finally, the stability (resistance to plugging) of a rock fissure while water flowed through it in the initial experimental work is discussed.

A. Introduction

The potential for radionuclide migration by groundwater flow from a breached nuclear-waste repository depends on the leaching process and on chemical changes that might occur as a radionuclide moves away from the repository. Therefore, migration involves the interactions of leached species with (1) the waste and canister, (2) the engineered barrier, and (3) the geologic materials surrounding the repository. Some of these interactions would occur in the radiation and thermal fields centered on the solidified waste. Rather than trying to predict what the important interactions are and then to study them individually, we plan to consider all potential interactions, using experiments that combine repository components analogous to their combination in a repository breached by flow water.

The analog experiments are an elaboration of the leach migration experiments in which solid waste at elevated temperature and geologic media were combined into one groundwater stream [SEITZ-1979A, 1979B, 1979C, 1980A, 1980B].

B. Preparation

Preparations made for performing the laboratory-analog experiments included (1) the programming of digital equipment to record the experimental variables over the six-month duration of the experiments, (2) the development of methods to split basalt cores for use in the experiments, (3) assembly of the laboratory apparatus, and (4) examination of the effects of ionizing radiation on components of laboratory apparatus. The preparation of ionic water and the testing of SW-1 bentonite clay were described in the preceding quarterly report [STEINDLER-1981B].

1. Digital Equipment

The equipment used for data acquisition in the laboratory-analog program consists of a Digital Equipment (DEC) PDP 11-23 processor with two RL02 discs for storage of digital information. Operator's consoles are a DEC printer (DEC writer) and DEC videoterminal (DEC VT-105). Analog signals

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are converted for digital use by means of Kinetic Systems Crate Controllers for thermocouples (T-type, Kinetic Co. Model 3525-Alt, 16 channel) and pressure transducers (0-5V, Kinetic Co. Model 3512, 16 channel).

In use, temperature and pressure signals are scanned at 10-min intervals. If there is a change of 1% in any pressure (compared to the preceding recorded pressure), the system records the data and the time on disc storage and prints the results for operator monitoring. For each experiment, two temperatures (ambient and oven temperature) and three pressures (pump pressure, water steam pressure, and core sleeve pressure) are recorded.

2. Method of Splitting Basalt Cores

About eight cores were drilled from blocks of Pomona-flow basalt from the Pasco Basin. A photograph of the finished core and the coring bit is shown in Fig. 13. The cores were ground to size (6.83-cm dia by 14.60 cm long), using a lathe, with distilled water coolant. The unsplit cores could not be permeated by water (6.9-MPa water pressure across the length of the core for one week did not transmit a measurable quantity, 0.1 mL, of water). Therefore, the cores were split, using the splitter shown in Fig. 14. The edge of the splitter was made of Brown & Sharpe gauge stock (tool steel) which had been oil-quenched to about 60 Rockwell hardness and ground.

Fig. 13. Cores Drilled from Blocks of Basalt
Using the Cylindrical Coring Bit

Fig. 14. Core Splitter Used to Provide Water Passages through the Basalt Cores. ANL Neg. No. 308-81-261

To split a core, the sharp wedge edge was pressed along the length of the core, using a hydraulic press. When the force exerted on the splitter by the press was increased to about 28.5×10^3 kg, the core fractured. The newly split core halves were constrained by sandbags to prevent them from falling from the press.

3. Assembly of Laboratory Apparatus

The equipment assembled for the laboratory-analog program is depicted in Fig. 15. The apparatus consists of a pump, two vessels for retaining basalt, the engineered barrier and the waste form, and a rock core holder. A disassembled rock core holder is shown in Fig. 16. The first vessel holds the components shown in Fig. 17.

4. Effect of Ionizing Radiation on Teflon Component

One of the components of the rock core holder is a flanged Teflon sleeve (9.52 cm OD $\times$ 17.8 cm high, see Fig. 16) used to confine the split rock core under high pressure.

Fig. 15. Apparatus Used in the Laboratory-Analog Experiments

Fig. 16. Components of the Rock Core Holder.
ANL Neg. No. 308-81-262

Fig. 17. The First Vessel in the Experiments, which Holds the Granulated Basalt, Engineered Barrier, and Waste Glass

Under ordinary conditions, Teflon is very inert and cannot be expected to have any chemical influence on the experiment. However, ionizing radiation (to be used in one experiment) may make the Teflon reactive. Hence, an experiment was done to test the stability of Teflon towards radiation in an aqueous milieu. In the experiment, approximately 1 g of Teflon shavings was put in a Teflon test tube and covered with about 8 mL of distilled water that had been degassed in a vacuum system. The system of water-Teflon was maintained in a vacuum and exposed in a radiation field to a total of 1×10^7 rads.

The irradiated sample and water were submitted to the Analytical Group of Chemical Engineering Division, and the water was analyzed for fluoride ion and acidity. Found were $18 \mu\text{g}$ of F^- ion/mL and a pH of 3.2. This means that the aqueous-liquid was approximately 10^{-3} M hydrofluoric acid.

It is obvious, then, that Teflon will introduce fluoride ion into a solution contacting it during irradiation. Whether the effect will be significant depends on the amount of fluoride released from Teflon exposed to water, in comparison to the original concentration of fluoride in the water ($2 \times 10^{-6} \text{ M}$). The HF-containing water, in passing through a fissure, would leach radionuclides differently from what would be expected for water in an actual repository. For this experiment, it may be necessary to employ a material that has suitable mechanical characteristics and is more inert to radiation than Teflon--possibly polyethylene.

C. Waste-Glass Characterization

1. Introduction

A series of analog experiments are being run to measure the migration through repository components of radionuclides leached from a nuclear-waste-containing glass. The glass to be used in the experiments is composed of radioelements and stable elements that are expected in an actual waste glass. The elements include alkali metals, alkaline earths, rare earths, and actinides. To provide test samples for the experiments, the glass was prepared in the following steps: (a) mixing of glass frit and radioactive components, (b) melting of the mixture, (c) annealing and partially devitrifying of the glass ingot, (d) cutting or sectioning of the radioactive glass into wafers, and (e) cleaning of the sectioned radioactive wafers.

The analog experiments can be of most benefit to the technical community if the waste glass is properly characterized. Summarized in this section are the method of preparing the glass and plans for characterizing the glass.

2. Glass Preparation

Uranium was added to nonradioactive glass having the average composition shown in Table 9. To form a glass containing 3.4 wt % U_2O_3 , 36.3 g of uranium nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was mixed with 500 g of nonradioactive glass. The mixture was heated for about six hours at 1050°C in air, then poured into water to make glass frit (frit is a highly fractured form of the glass). The frit was remelted and poured into water a second time to increase its homogeneity. Five samples of the frit (Lot 2) were prepared for X-ray diffraction analyses. Upon normal exposure to X-rays, no crystallinity was seen in any of the samples. Overnight exposure of three samples to X-rays revealed diffraction lines of the spinel group attributed to Fe_2O_3 (maghemite) or FeCr_2O_4 (chromite). The mineral in the glass is estimated to have been present at less than the 5 wt % level. The 500-g batch of frit was used as the source of glass for the preparation of radioactive glass.

Radioactive tracer-bearing glass was prepared by melting the uranium-bearing glass frit with radioactive tracers. For the radioactive glass, 40 g of glass frit was the base to which was added a liquid tracer mixture containing ^{137}Cs (about 1 μCi), ^{85}Sr (100 μCi), ^{141}Ce (1640 μCi), and ^{152}Eu (2000 μCi), along with liquids containing ^{241}Am (500 μCi), ^{239}Pu (1400 μCi), ^{237}Np (80 μCi), and ^{133}Ba (45 μCi). The quantities of radionuclides, their original chemical forms, and their radiodecay characteristics are given in Table 10. The total volume of liquids which contained the radionuclides was less than 10 mL.

The solutions were added to glass frit contained in a 95% platinum, 5% gold crucible, and the contents were thoroughly mixed. Prior to heating of the mixture, the liquids were allowed to evaporate at room temperature overnight. The mixture was put into a graphite secondary crucible and then into the Brew furnace, where it was heated in an atmosphere of 7.9×10^4 Pa (600 mm) argon at 1050°C for six hours. The power to the furnace was then shut off, and the furnace was cooled to less than 100°C in 30 min. After

Table 9. Compositions of 76-68 Frit from Analyses of Three Bars of Lot 2 Glass^a

Constituent	Analyses, wt %			
	Bar 104E	Bar 160	Bar 22E	Avg.
Al ₂ O ₃	0.65	0.65	0.59	0.63
B ₂ O ₃	9.12	9.03	8.82	9.32
BaO	0.55	0.54	0.52	0.54
CaO	2.17	2.14	2.34	2.22
CdO	0.04	0.05	0.05	0.05
CeO ₂	0.73	0.71	0.90	0.78
Cr ₂ O ₃	0.47	0.47	0.46	0.47
Cs ₂ O	1.15	1.13	1.13	1.14
Dy ₂ O ₃	0.007	0.006	0.007	0.007
Eu ₂ O ₃	0.006	0.005	0.005	0.005
Fe ₂ O ₃	9.71	9.47	9.39	9.52
Gd ₂ O ₃	0.02	0.02	0.02	0.02
K ₂ O	0.3	0.3	0.2	0.3
La ₂ O ₃	4.52	4.41	4.06	4.33
MgO	0.14	0.13	0.14	0.14
MnO ₂	0.07	0.06	0.06	0.06
MoO ₃	2.01	1.96	1.92	1.96
Na ₂ O	11.3	11.1	11.5	11.3
Nd ₂ O ₃	1.52	1.50	1.38	1.47
NiO	0.22	0.24	0.21	0.23
P ₂ O ₅	0.54	0.71	0.74	0.66
SiO ₂	41.1	40.5	40.6	40.7
SrO	0.43	0.43	0.41	0.42
TiO ₂	3.08	3.02	3.02	3.04
ZnO	4.80	4.78	4.71	4.76
ZrO	1.78	1.73	1.87	1.79

^aAnalyses of Lot 2 Glass by J. Mendel, Battelle Pacific Northwest Laboratories, Richland, WA.

Table 10. Radioactive Isotopes Added to the Waste Glass and their Radiation Properties

Radioactive Isotope	Half-Life	Decay Mode	Primary γ or α Radiation, keV (photons or alphas/100 decays)	Quantity per 40-g Batch	Original Chemical Form of the Isotope
<u>Alkali</u>					
^{137}Cs	30.2y	β^-	γ : 661.7(8.50)	0.65 μCi	CsCl
<u>Alkaline Earths</u>					
^{85}Sr	64.7d	EC	γ : 514.0(99.3)	100 μCi	SrCl_2
^{133}Ba	10.7y	EC	γ : 356.0(62), 81.0(31.7), 302.8(18.1), 383.8(8.0), 276.4(7.0)	45 μCi	BaCl_2
<u>Rare Earths</u>					
^{141}Ce	32.5d	β^-	γ : 145.4(48.4)	1640 μCi	CeCl_4
^{152}Eu	14y	73% EC (β^+) 27% β^-	γ : 1408.0(21.3), 121.8(29.1), 344.3(27.2), 964(14.8), 1112.1(13.8), 778.9(13.2)	2000 μCi	EuCl_3
<u>Actinides</u>					
^{241}Am	432y	α α	α : 5486(85.2), 5443(12.8) γ : 60(36)	500 μCi	$\text{Am}(\text{NO}_3)_3$
$^{239}\text{PuO}_2$	24131y	α	α : 5155(73), 5143(15.1), 5105(11.5)	23 mg (0.06 wt %), 1400 μCi	$\text{Pu}(\text{NO}_3)_6$
$^{237}\text{NpO}_2$	$2.14 \times 10^6\text{y}$		α : 4817(1.5), 4803(1.6), 4788(51), 4770(19), 4765(12), 4664(1.6), and 4639(4.6) γ : 86(12.6)	115 mg (0.3 wt %), 80 μCi	$\text{Np}(\text{NO}_3)_4$

^aQuantity on November 19, 1981.

cooling, the sample was removed from the Brew furnace and the 40-g glass ingot was separated from the primary crucible.

The glass ingot was transferred to another platinum crucible (inside an Al_2O_3 secondary crucible) for annealing. The glass was heated to 500°C , held for 1 h, then cooled slowly for 5 h until the temperature was below 150°C , at which point power to the furnace was turned off.

After the heat treatment, the annealed glass was sectioned into 24 pieces* (about 1/2-g slabs, each about $11\text{ mm} \times 9.3\text{ mm} \times 1.2\text{ mm}$). All but one of the samples were cut from the interior of the glass ingot. Distilled water was used as the cutting lubricant for a low-speed Isomet saw (Model 11-1180). The cuts were made at a linear speed of about 13000 cm/min, using a 10-cm-dia circular blade with low-concentration diamond abrasive and a blade thickness of 0.3 mm. The cutting scheme is depicted in Fig. 18. The cut pieces were washed in ethanol in small beakers in an ultrasonic bath, then put into clean labeled polypropylene bottles for storage until use. Five samples will be used in the program; the other pieces will be used for characterization.

Fig. 18. Cutting Scheme Used to Obtain 23 Waste-Glass Wafers (one discarded) for the Laboratory-Analog Experiments

*One piece of glass was discarded that had on its surface a part of a gas bubble that existed on the surface of the ingot.

3. Characterization

Characterization of the waste glass is undertaken for two reasons. First, a technical description of the waste glass will make the results of the laboratory-analog program useful to more workers. By knowing how the waste glass compares to formulations used in other programs, these workers can relate the results of different programs.

Secondly, the characterization should establish the degree of homogeneity of the glass samples used in the programs. If the extent of inhomogeneity is known, differences in the results of the analog program can be attributed to causes other than variation in waste glass properties.

Characterization of the borosilicate glass to be used in the laboratory-analog experiments will be by destructive and nondestructive analyses of the glass wafers. Methods planned to be used in the analyses are (i) leach tests, (ii) gamma activity versus mass of the wafers, (iii) alpha and gamma radiography of the wafers, (iv) electron beam, X-ray fluorescence analyses, and (v) optical microscopic methods. In addition, the laboratory-analog program incorporates duplicate tests to establish reproducibility of the results. The extent to which results are produced will provide added information on the heterogeneity of the glass samples.

a. Leach Tests

The leach properties of the glass are of primary importance in the laboratory-analog program. Knowledge of the leach properties relative to those of other waste-glass formulations is of direct use in interpreting results from the laboratory-analog program.

Eleven of the slabs cut from the glass ingot will be used in a test of the leach properties of the glass. The MCC-1 Static Leach Test of the Materials Characterization Center [MENDEL] was chosen as the leach test, with the long-term, 90°C schedule selected specifically. This schedule, referred to as matrix-D, is used to measure the kinetics of the approach to the steady-state, saturated condition in a closed leaching system. The temperature of 90°C is identical to the temperature of the initial laboratory-analog experiments. The leaching will be continued for 182 days and encompasses the 90-day leaching time envisioned in the laboratory-analog program. The matrix-D schedule used in the tests is listed in Table 11.

Table 11. Matrix-D Schedule for the MCC-1 Test

	Number of Samples Used for Each Time Period						
	3d	7d	14d	28d	56d	91d	182d
No. of Wafers	1	1	1	3	1	3	1

The tests of triplicate samples for time periods of 28 and 91 days will give results of direct relevance to the homogeneity of the glass samples with regards to bulk leaching, provided that the results of the MCC-1 test are reproducible.

This is essentially a destructive test since the samples cannot be used for other tests after being leached. However, if the leached surface layer can be completely removed--by polishing, for example--the samples can be used as unaffected samples.

b. Gamma Activity

The intensities of gamma rays emitted by the radionuclides in each glass sample reserved for the laboratory-analog program will be measured using a lithium-drifted silicon crystal detector. The detector can resolve the energy of gamma rays sufficiently to allow the activities of all radionuclides except plutonium-239 to be measured. A plot of the activity of each radionuclide versus the mass of the glass samples will indicate whether any inhomogeneity (between samples) of the gamma-emitting radioelements exists. It is possible to examine the homogeneity of cesium, strontium, barium, cerium, europium, americium, and neptunium in the glass samples. Since these elements have significantly different chemical and physical properties (such as valence state and vapor pressure), any significant compositional inhomogeneity in the samples is likely to be detected in the gamma intensity plots.

This examination is nondestructive; following these analyses, the samples can be used directly in analog experiments.

c. Alpha and Gamma Radiography

Each glass sample used in the laboratory-analog program will be radiographed, using alpha-sensitive and beta-gamma sensitive detectors.

Radiographs, using plastic detectors, can be made to be specifically sensitive to alpha particles. Because of the short range of alpha particles in plastic (about 20 μm), the alpha radiographs give detailed information on the microscopic distribution of actinide elements near the cut surfaces of the glass. The alpha radiographs have a resolution of about 5 to 10 μm ; they can detect submicron size particles having concentrations of actinides that contrast with the concentrations in the surrounding medium.

The alpha-emitting nuclides in the glass are ^{241}Am , ^{239}Pu , and ^{237}Np . The specific activity of these nuclides are in the proportion, 0.35:1.00:0.05. Therefore, the alpha radiographs will primarily record plutonium, with about 25% of the radiographic image due to americium and about 3% due to neptunium.

By comparing alpha radiographs for the different surfaces of each glass sample and comparing radiographs for different samples, we can get an idea of any large-scale inhomogeneity of the actinide elements.

Beta-gamma radiographs will be made using Polaroid film. The film is primarily sensitive to beta particles but also records an image from

gamma rays alone. The film is also sensitive to alpha particles. The contribution from alpha particles can be removed by placing a thin sheet (about 20 μm thickness) between the film and glass during exposure; the sheet will adsorb the alpha particles but will allow the beta and gamma rays to pass through. The light-sensitive package of the Polaroid film provides a convenient absorber for alpha particles, and the samples can be radiographed without a dark room being needed.

The beta-gamma radiographs give another view of the microscopic distribution of radioelements in a glass sample. These radiographs have less resolution than do the alpha radiographs, but similarly can reveal the presence of tiny particles having higher concentrations of radioelements than the surrounding (about 50- μm radius) medium.

A comparison of beta radiographs would give an indication of whether there is large-scale homogeneity of the beta-gamma emitting radio-nuclides. However, much more detailed information of this kind is expected from the gamma intensity measurements.

These radiographic methods are nondestructive and are not expected to alter the properties of the glass. All samples used in the analog program will be analyzed by this method.

d. Electron Beam Fluorescence

Portions of the glass removed by cutting from the ingot will be characterized using electron beam methods. A sample extending from the surface to about 1 cm into the interior of the ingot will be investigated explicitly. The chemical inhomogeneity of this sample would therefore be expected to be greater than for the interior slabs alone of the other samples.

The sample will be examined in an electron beam microprobe. X-rays characteristic of individual elements will be examined to identify any spatial inhomogeneity of the sample. Easily detected elements are calcium, titanium, and silicon. Detectable, but with less sensitivity, are sodium (10.9% Na_2O), zinc (4.60% ZnO), and lanthanum (4.18% La_2O_3). Minor constituents such as chromium (0.47% Cr_2O_3), neodymium (1.42% Nd_2O_3), and uranium (3.4%) may be readily detected and can provide detailed information about the homogeneity of the glass. Microprobe techniques have about 5- μm size resolution. Inhomogeneities of submicron size, as may be expected due to phase separation in the borosilicate glass, will not be revealed by the microprobe.

Electron-beam scans of the sample will be made and the results displayed as images of element concentration. Alternatively, traces will be made of the element concentrations extending from the edge to the interior of the ingot. Compositions of the exterior and interior portions of the original glass ingot may differ. The element traces can be used to examine this point.

Because for a microprobe analysis the sample will be coated with a conductive layer then subjected to vacuum, electron radiation, and heating, microprobe analyses are considered to be destructive. Consequently, none of the samples designated for the analog program will be subjected to this analysis.

e. Optical-Microscope Methods

The glass samples prepared for the laboratory-analog program will be examined by optical microscopy to determine the extent of crystallinity in the samples. Glass and crystals will be contrasted by using polarized light.

Phases within the transparent glass samples may become visible because of their different refractive indices. The reflectivity of the glass surface will be examined to identify mineral phases on the surface of the glass.

If crystalline phases are identified, modal analyses will be made to estimate the concentrations of the different phases. Optical methods are nondestructive and much more accurate in determining percent crystallinity than are diffraction analyses.

4. Summary

A borosilicate glass, containing radionuclides of eight elements, was formulated to represent solidified high-level waste for the laboratory-analog program supported by the Nuclear Regulatory Commission. The glass will be characterized by a number of analytical methods to provide a description of the glass for workers in nuclear waste management and to examine the homogeneity of the various samples that will be used in the analog program.

D. Rock Fissure Stability

The first experiment in the laboratory-analog program was begun this quarter. The groundwater solution was pumped over the engineered barrier and through a fissured core of Pomona basalt. No waste form was introduced into the experiment at this time.

The experiment used bentonite clay, SWy-1, from the Clay Minerals' Society's Source Clay Collection. The bentonite was packed into tubes of Hastelloy-C-276 alloy that were crimped at one end. The tubes were submerged in the groundwater solution for 48 h, during which time the bentonite near the water surface swelled and flowed out of the tube. The bentonite was trimmed flush with the tubes, and two tubes were placed in the laboratory-analog apparatus (the two vessels on the left in Fig. 15).

The rock core used in the initial part of the experiment was a split core of basalt. The two halves of the core were butted together and loaded into the holder. Initially, the water flowed steadily, with a pressure of about 1.6 MPa (230 psi) required to pump 1 mL/h of water through the split core. However, the flow of water slowed and finally ceased when a portion of the bentonite in the engineered barrier moved to the rock core and clogged the fissure. The core was removed from the holder and remounted after shims of 0.025-cm-thick gold foil were placed along the edges of the core halves to keep them separated. The metal tubes were reloaded with bentonite, and flow was initiated once again. The system was fitted with a back-pressure regulator near the exit to the pump. This assembly (shown in Fig. 15) appears to work satisfactorily and is expected to be the configuration used in all of the analog experiments.

V. TRACE-ELEMENT TRANSPORT BY FLUID FLOW (M. Seitz and R. Couture)

A. Introduction

The two preceding quarterly progress reports have described the composition of oil and pore water extracted from granite from Northern Illinois drill hole UPH-3. A profile of the chloride concentration was presented which showed that the chloride concentration generally increases with depth to about 2.4M, 624 m below the contact with the overlying sandstone.

Fluids were extracted from rock cores because of recent interest in the geochemistry of deep groundwater, because of the possibility of siting a nuclear waste repository in deep geological formations, and because of the difficulty in sampling deep groundwater by other methods.

Two different methods of extraction gave somewhat similar results, except that washing of crushed rock gave high potassium analyses, while elution from an intact rock core gave very low potassium levels.

This report presents emission spectrographic analyses of the salts leached from crushed material. These analyses, not available previously, reveal an analytical error and clarify the cause of the high potassium contents in the leachates.

We also present a novel method for very accurate determination of endpoints in chloride titrations.

Additional work in progress, not reported further, includes the observation of oil as a natural marker for viewing connected rock pores, the design of a simple pressure vessel for use up to about 68 MPa and up to 100°C, and the beginning of work on sampling of pore fluids in rocks from the Canadian Shield.

B. Soluble Salts in Crushed Rock

Rock samples from drill hole UPH-3 were crushed and washed with water. Previous analyses of the solutions are presented in Table 12. New data (Edmund Huff, analyst) are presented in Table 13. The potassium analyses in Table 12 are by ion chromatography; the value for 1288 m disagrees with the results from emission spectroscopy (see Table 13) and is assumed to be in error.

The high potassium concentrations probably are due to leaching of potassium feldspar, which is one of the most reactive of the silicate minerals. However, at present, we cannot be entirely sure that the potassium was not derived from contamination by drilling fluid.

C. Potentiometric End-Point Determination in Chloride Titrations

For the determination of chloride in pore fluids from granitic rocks, a sensitive, accurate microtechnique is required. Titration with potentiometric

Table 12. Analyses of Leachates from Crushed Rock, Drill Hole UPH-3. Alkalinity is given in milliequivalents/l; other concentrations are given in mM.

Depth, m	Porosity, %	Cl ^a	Alkali- nity	SO ₄ ^a	P ^a	Pb	Na ^a	NH ₄ ^a	Ca ^c	Mg ^c	K ^a
553	17	0.26	0.074	0.027	-	0.014	0.087	0.026	0.022	0.020	0.50
666	3.0	0.33	0.40	0.110	0.149	0.151	0.257	<0.006	0.147	0.136	0.80
670	0.49	0.18	0.105	0.024	<0.003		0.255	0.017	0.045	0.033	0.31
840	0.14	0.32	0.037	0.025	0.151	0.22	0.457	<0.006	0.018	0.004	0.30
1180	0.23	1.26	0.041	0.82	<0.003		1.13	<0.006	0.79	0.003	0.34
1288	0.49	2.72	0.152	<0.021	<0.003		0.72	<0.006	0.41	0.074	<0.003

^aBy ion chromatography.

^bBy ion-specific electrode.

^cBy atomic absorption.

Table 13. Spectrochemical Analyses (Emission Spectroscopy) of Leachates from Crushed Rock, Drill Hole UPH-3. Only those elements which have detectable concentrations are shown. Units are mM.

Depth, m	Al	Ca	K	Li	Mg	Na	Sr
553	<0.007	0.04	0.4	<0.0007	0.04	0.07	0.002
666	0.04	0.1	0.5	0.001	0.08	0.1	0.006
670	0.04	0.07	0.5	0.001	0.06	0.2	0.003
840	0.01	0.02	0.3	<0.0007	0.008	0.3	0.0006
1180	<0.007	0.8	0.3	0.0007	0.04	0.4	0.002
1288	0.04	0.8	0.3	<0.0007	0.12	(0.9)	0.003
Blank	<0.007	<0.005	<0.005	<0.0007	<0.0008	<0.009	<6 × 10 ⁻⁵

end-point determination was selected as the best method because of its simplicity, sensitivity, and accuracy. A new method was found for determining end points. The method is a simple mathematical refinement of the Gran plot and appears to give improved results. The method is novel enough that the results are reported here.

Chloride was titrated with AgNO_3 . The excess Ag^+ was determined with a silver wire electrode. A calomel/saturated KCl reference electrode was used with an external salt bridge consisting of 0.1M KNO_3 with a Beckman fiber junction. The electrode response is nearly instantaneous, and with allowance for the activity coefficient of Ag^+ , the response is within 1/2% or less of the theoretical slope.

The electrode is used to determine the Ag^+ concentration by means of the Nernst equation.

If c = concentration

mV = voltage, in mV

S = slope of electrode response ($=59.2$ $mV/10$ -fold change in concentration)

c_0 and mV_0 = c and mV for a known solution,

according to the Nernst equation

$$\frac{c}{c_0} = 10^{(mV - mV_0)/S} \quad (1)$$

Rearranging, we get

$$10^{mV/S} = c \frac{10^{mV_0/S}}{c_0} = Ac, \text{ where } A \text{ is a constant.} \quad (2)$$

The number of moles of Ag^+ in solution, $c(v + v_0)$, is given by

$$Ac(v + v_0) = (v + v_0)10^{mV/S} = F_1, \quad (3)$$

where $v + v_0$ is the titre volume plus the original solution volume. This function is defined as F_1 . In the Gran method, F_1 is plotted against the volume of titrant added. F_1 can be extrapolated asymptotically to zero, and the end point determined. This procedure will be demonstrated in a later paragraph.

A linear plot would be preferable. If the solubility product of AgCl is K , the excess concentration, x , of Ag^+ is given by

$$x = [\text{Ag}^+] - [\text{Cl}^-] = [\text{Ag}^+] - K/[\text{Ag}^+] \quad (4)$$

From Eq. 2 above, it follows that

$$Ax = 10^{mV/S} - A^2K10^{-mV/S}.$$

We define $Ax(v + v_0)$ as F_2 . A plot of F_2 against titre volume is made linear by adjusting the value of A^2K . This is easily done by fitting data on both sides of the end point. A^2K should depend only on temperature, the electrode system, and the presence of complexing agents, if any.

Results of a titration are shown in Fig. 19. Apparently, great accuracy is possible with this method.

Fig. 19.

Titration of 1 mL of $1.23 \times 10^{-4} \text{ M}$ NaCl with 0.0100 M AgNO₃

VI. LIGHT WATER BREEDER REACTOR (LWBR) PROOF-OF-BREEDING ANALYTICAL SUPPORT PROJECT

(N. M. Levitz, E. L. Callis,* T. F. Cannon, G. L. Chapman, P. G. Deeken,
J. F. Fagan, D. G. Graczyk,* R. R. Heinrich,* J. C. Hoh, R. W. Kessie,
J. E. Kincinas, H. Lautermilch, R. J. Meyer, R. E. Nelson, J. Osudar,[†]
J. E. Parks, L. E. Trevorow, and C. G. Wach)

The Department of Energy-Division of Naval Reactors (DOE-NR) announced in November a foreshortening of the extended LWBR operating schedule. The LWBR is now scheduled for shutdown in October 1982. Accordingly, the schedule for performing the Proof-of-Breeding Project, including the destructive fuel rod assay performed at ANL, has been rescheduled. Initial fuel shipment to ANL is now scheduled for January 1984 instead of January 1986.

The processing of the fuel rods at ANL will involve precision shearing of the rods, individual dissolution of a total of some 120 segments, sampling, and preanalysis workup of liquid samples in the M-wing shielded-cell complex, which is part of the Chemistry Division facility (Building 200). Four manipulator-equipped cells (of the 12-cell complex) will be in use for the LWBR-POB program--i.e., two megacurie cells (M-1 and M-3) and two kilocurie cells (K-1 and K-3). Mass spectrometric and radiometric analyses will be performed in nearby laboratories.

To aid in reducing overall program costs, the scope of the destructive fuel analysis has been reduced. It is now planned to analyze 16 rods, rather than the initial 33, from which 120 segments (instead of the original 350) will be dissolved for analysis. Project plans to reflect the reduced scope of work have been developed. The main points of the plan are:

1. Install two dissolvers in Cell M-1, rather than the four originally planned.
2. Remove the prototype dissolver installed in Cell K-3 for use as one of the two units in Cell M-1.
3. Install a waste storage tank in Cell M-1 to hold the entire about 600 L volume of liquid waste to be generated in the revised destructive assay program.
4. Modify Cell K-3 for use by the Analytical Chemistry Laboratory, rather than fabricating and installing an alpha containment in Cell A-5, as originally planned.

Overall, this revised plan is expected to significantly reduce the cost and effort required to prepare for and execute the end-of-life (EOL) destructive fuel rod analysis.

*Analytical Chemistry Laboratory, ANL.

[†]Science Applications, Incorporated, Oak Brook, IL.

A. Full-Scale Shear (FSS)

(J. Fagan, J. Kincinas, R. Nelson, and C. Wach)

Considerable progress toward in-cell installation and operation of the full-scale shear (FSS) was made during this reporting period. The unit was removed from its temporary storage location and installed in Cell M-3. All of the shear's modular components were reassembled on the machine base and tested after all services (hydraulic, pneumatic, electric power and instrumentation) were connected. Testing of most lines and circuits was completed satisfactorily, including connections made to the computer interface.

Installation of the remaining portions of the in-cell alpha containment structure was begun. Some modifications to the design were made to improve access to bagout and sample transfer ports in the containment wall, and to enlarge the worktable area within the structure for equipment repair or storage. All installation efforts associated with the FSS and in-cell components are expected to be completed by the end of January 1982. A period of shear testing, consisting of shearing dummy fuel rods in-cell, will then begin. This final testing phase will be done under fully remote conditions, completely simulating rod handling, measurement, and shearing during the end-of-life (EOL) campaign. Qualification of the FSS is now scheduled for the first quarter of FY 1983.

Design of the two remaining shear dies was completed [for the 0.572-in. (1.45-cm) dia standard blanket rod and for the 0.832-in. (2.11-cm) dia reflector rod]. Acquisition of these dies may be deferred to FY 1983.

The paper, Precision Measurement and Shearing of Fuel Rods for Destructive Analysis, by J. Fagan et al., was presented at the winter American Nuclear Society meeting (November 29-December 2, 1981).

B. Single-Unit Dissolver (SUD)

(T. Cannon, P. Deeken, D. Graczyk, J. Hoh, H. Lautermilch, and J. E. Parks)

Work continued related to evaluating the overall performance of the SUD and associated systems, particularly the new external heater system. A number of diverse objectives were addressed. Those pertaining to the electro-mechanical performance of the various subsystems were discussed in the preceding quarterly report [STEINDLER-1981]; areas where chemical analysis was required before the experimental results could be evaluated are discussed below. The objectives addressed using the analytical results include: (1) to demonstrate complete dissolution and recovery of thorium, (2) to demonstrate quantitative recovery of uranium, (3) to evaluate fission-gas sampling procedures, (4) to evaluate cross-examination for successive dissolutions, using uranium, cesium, and zirconium as monitors, and (5) to evaluate the solution mixing and sampling systems.

The test criteria by which each objective was evaluated made use of statistical data analysis, using a significance level of 0.10 for the critical parameters against which the test results were compared. For qualification of the dissolver system, Bettis Atomic Power Laboratory (BAPL) has recommended

a significance level of 0.05. For the purpose at hand, however, a level of 0.10 was advisable, both because the amount of data was limited and because the stricter tolerances imposed increase the confidence with which conclusions can be drawn from marginally successful tests.

Thorium recoveries for the two segment-dissolution tests (Runs DD-8 and -10) averaged 100.45%. This value is sufficient to demonstrate that both complete dissolution and quantitative recovery of the segment thorium charge were achieved, within experimental error. Recovery of the uranium added in these runs was also quantitative, as indicated by a mean uranium recovery of 99.96%.

The procedures used for collection and analysis of krypton, which had been added (as nonradioactive krypton) to the dissolver cover gas, provided a recovery of krypton in Run DD-10 of 103%. (A leaking line in the gas sampling system during Run DD-8 precluded reliable analysis for krypton in that experiment.) Statistical analysis of the experimental data suggests that fission gas in the dissolver can be accounted for quantitatively with a relative standard deviation of about 5%.

Analysis of the blend-tank solutions from blank runs (Runs DD-9 and -11) gave uranium concentrations on the order of those in the dissolution reagents, indicating that there was a carry-over between consecutive dissolutions of less than $10^{-3}\%$ of the uranium dissolved in the previous run. Similarly, less than $3 \times 10^{-3}\%$ of the cesium added during a given segment dissolution was found in the succeeding blank run. These results demonstrate that cross-contamination between runs for these elements is sufficiently small to be negligible in most of the situations expected in the end-of-life (EOL) campaign, and is easily controllable in exceptional cases where dissolution of a very low-load segment might follow dissolution of a high-load segment.

Cross-contamination between consecutive dissolver runs by zirconium (introduced as Zircaloy cladding) for the same blank runs proved to be larger than that for the other elements tested. About 0.07% of the zirconium in a segment dissolution run was found in the following blank run. This higher level of carry-over for zirconium probably occurred because cladding is dissolved to a significant extent during the second dissolution cycle. Thus, the second dissolution does not serve as a first wash of the dissolver for cladding zirconium, as it does for the other elements. It is anticipated that better decontamination would be obtained for actual fission-product zirconium in EOL runs, since it would be essentially all dissolved with the fuel during the primary dissolution cycle. Because fission product zirconium is of primary analytical interest, further testing will be necessary to verify the present conclusion.

To evaluate the adequacy of mixing during blending of primary and secondary dissolver solutions, variations in results obtained from independent samples drawn from the blend tank solution were statistically compared with variations observed when duplicate aliquots of each separate sample were analyzed. Samples from both runs, DD-8 and -10, were used in making this comparison, using the F-test. This test did not provide any evidence for the existence of a significant variance among the samples other than that associated with the measurement technique. In light of the observation that

the analytical measurements exhibited a relative standard deviation (RSD) of only 0.03%, this demonstration of negligible sampling error in the blend tank operations stands out as a notable achievement.

Material losses during sampling of the dissolver systems were measured by determining the quantity of uranium remaining on the tubing and in tissue wipes used with the samplers. For the blend tank sampling procedure, loss corresponded to $5 \times 10^{-4}\%$ of the uranium charged; and for sampling the dissolver after the second dissolution, the loss corresponded to $2 \times 10^{-5}\%$ of the uranium charged. Such losses are negligible in comparison to errors from other sources in the segment analysis.

In summary, the analytical performance of the SUD was demonstrated to be satisfactory in a series of tests for all aspects investigated except cross-contamination from zirconium (in this case, contributed by cladding). This single failure might not be important since fission product zirconium can be expected to behave more like the other elements studied in the cross-contamination studies. Cross-contamination by fission product zirconium needs further study to be quantified.

1. Heater Evaluation

An evaluation of the external heater system was completed, using data from the recent thoria-dissolution runs. The data revealed two important characteristics of the system: first, the efficiency of heat transfer from the external heaters to the tantalum primary vessel of the dissolver is very good. During steady-state operation, the integral dissolver reflux condenser removes 80 to 90% of the heat applied by the 18 external cartridge heaters. Secondly, the heat required to effect agitation and boiling is lower than calculated; design calculations determined that a heat input requirement of 5900 W (20,200 Btu/h) from the heaters would be required to agitate the thoria particles in the fashion of fluidized-bed-type behavior to enhance dissolution; however, the dissolution tests demonstrated that complete dissolution of the thoria charge is obtained within the 4-h boilup by use of a heat input of only 1450-1750 W (6000 to 7000 Btu/h). The lower heat rate is desirable from the standpoints of extending both heater and vessel life (less severe thermal stresses) and minimizing severe boiling action which could lead to the deposition of salt on the inner dissolver wall above the acid level.

Following the dissolver tests, the external heaters were removed and inspected. Two models of cartridge heaters had been used in the tests. Heaters of the type used in the lower heater assembly were removed from their holders without difficulty. However, most of those used in the upper heater assembly had swelled in their holders; this would prevent remote removal, in the event replacement of a failed heater was necessary. Also, these heaters suffered an extreme loss of resistance, reducing their performance. For these reasons, the type of heater tested in the lower assembly will be used for the upper assembly also. The system is overdesigned and so individual heater failure will not require shutdown of the dissolver.

2. Blend Tank

Drawings of a modified blend tank assembly were prepared, reviewed, and approved, and fabrication of a prototype tank is in progress. This blend

tank design differs from the original in that the troublesome lid gasket seal is eliminated by welding the tank and lid together. Other revisions are also being incorporated to improve the performance of the mechanical stirrer. The new tank is also being provided with a highly polished internal finish, to aid in tank decontamination between uses.

3. Sample Storage

ANL is required to store highly radioactive archive samples of the dissolver solution for periods up to one year after the EOL campaign. Glass vials for storage of these samples have been tentatively selected, each coated with plastic to resist breakage. Polypropylene caps for the vials were received and subjected to nitric acid exposure and a drop test. The acid had no observable effect on the caps during a one-month exposure, but the caps shattered in 5-ft drop tests. A search for more resilient caps continues.

C. Multiple Dissolver System (MDS)

(P. Deeken, J. E. Parks, L. Trevorror, M. Slaweki, and G. Chapman)

Design layouts of equipment installation in Cell M-1 were changed to reflect the new plan for a two-dissolver installation, to replace the previously selected four-unit multiple dissolver system (MDS). Changes to the piping and instrumentation drawings were also made, to reflect the new layout.

Plans include the use of the single-unit dissolver (SUD) as one of the two units in Cell M-1 and the salvaging of components from the SUD cell (Cell K-3). The reuse of components is expected to significantly reduce the costs for procurement of the new system and to allow installation efforts to begin in early CY 1982. Cell K-3 will now be converted to an analytical preparation cell.

Procurement of the second stainless steel dissolver secondary vessel and external heating system was initiated at ANL Central Shops. Receipt of the second vessel assembly by April 1982 is expected.

Finalized listings of the instrumentation needed to complete the two dissolver system were made, and purchase orders for these items initiated. A blend tank balance* with remote electronics was included in the package to allow early performance testing of such balances, which are new to the project.

D. Scrap and Waste

(L. Trevorror and R. Nelson)

As a result of the analysis of waste disposal options for disposal of the liquid analytical residues (dissolver solution) carried out in the July-September quarter [STEINDLER-1981B], it has been concluded that for several reasons, most importantly the costs, neither calcination at ANL nor shipment in liquid form to the custody of another contractor is likely to be acceptable. Accordingly, all design work on calcination equipment has been

*Mettler, PK-60/SE, product of Mettler Instrument Co., Hightstown, NJ.

stopped. In the past quarter, options other than calcination and liquid shipment were briefly reviewed with the aim of selecting the most inexpensive and technologically simple option that would produce acceptable waste forms and packaging.

Three immobilization techniques have been briefly examined: (1) incorporation of the solutions into a mineral matrix such as kaolinite, bentonite, or artificial monazite (orthophosphates), (2) dehydration of the solutions to a salt, and (3) incorporation of the solutions into cement. A brief consideration of the characteristics of these options indicates that in this particular situation, cement is likely to offer the best combination of cost, safety, and convenience. Moreover, incorporation of dissolver solution into cement has the advantages of simple (existing) technology and the potential for minimizing contamination of the cell where waste immobilization is performed, making eventual cleanout simpler and less costly.

Informal communications with the potential waste storage contractor, Rockwell-Hanford, indicate that the cement waste form may be acceptable if the radiolytic gas-generation rate and resulting pressurization of the closed container are not excessive. Although Rockwell has not written a specification for gas generation rate in a sealed waste container, the limit suggested in this communication was $10 \text{ mol gas m}^{-3} \text{ y}^{-1}$. Approximate gas-formation rates, estimated from BAPL's calculations of radioisotopic concentrations in LWBR fuel and G-values from literature reports of gas formation in irradiated cement [BIBLER] are about two to three times this suggested limit. Nevertheless, literature reports suggest that the rate can be reduced by the addition of nitrite and also that it can be reduced by factors of 3 to 30 by partial dehydration of the cement after it has set. Furthermore, even if the gas generation rate is unacceptable for a closed container, a vented container might be accepted by Rockwell.

Elementary design work was carried out on a package (to contain a cement waste form) consisting of a cement cylinder cast into a 5-gal steel vessel that is surrounded by a 2-in.-thick cylindrical lead shield and centered in a 55-gal drum. It is estimated that the entire quantity of dissolver solution (about 600 L) could be disposed of in 60 to 100 of such packages. For this immobilization and packaging concept, preliminary costs and schedules were assembled; a brief description has been drafted and forwarded to DOE-CH with a request for review and approval-in-principle.

E. Computer System and Data Management
(J. Parks, G. Chapman, J. Osudar, and R. Kessie)

An integrated computer system is being developed which will provide automatic data acquisition and calculation of results, process monitoring, and some automatic process control. Computer system hardware currently consists of a VAX-11/780* (shared with other CEN users) and a PDP-11/23.* The latter unit has been completely connected to the FSS and the SUD via standard CAMAC modules. Work on the computer system during the report period is summarized below. Plans for shifting the system to the new two-dissolver system in Cell M-1 are being made.

*Products of Digital Equipment Corp., Maynard, Mass.

1. Hardware

Following installation of the FSS into Cell M-3, all associated controls and sensors were reconnected to the PDP-11/23 computer and the circuits were tested as satisfactory, using the CAMAC test program and the automation demonstration program. Following completion of testing of the SUD, the latter was disassembled and disconnected from the PDP-11/23. Further testing involving dissolver hardware will be deferred until Cell M-1 is operational.

2. Software

Work has continued on POBSYS, the set of programs for the PDP-11/23 computer. These programs will serve the functions of automatic data collection, operator instruction, and process monitoring and control for the FSS and dissolver systems. Developments during the report period include progress on the programs, MASTER, DATMAN, SYSDAT, and EXCHAN.

MASTER is the general executive program which receives instructions from the computer-stored operating procedures and sends instructions to various slave programs for execution of functional steps. DATMAN is the Project data manager program, directing the automatic acquisition of data and funneling it into proper memory locations. SYSDAT is the Project's data file set up individually for each fuel rod analyzed. EXCHAN (Exception Handler) is the program which responds to out-of-spec process conditions and takes a variety of actions such as automatic shutdown, operator alerts [bells, video station (CRT) messages], and recording of out-of-spec conditions.

Procedures for carrying out leak tests of the blend tank and dissolver have been programmed and used to test full-system development. Such a test was successfully carried out in December when, for the first time, the programs OPRSUD,* MONITR,[†] and EXCHAN worked together [STEINDLER-1981B]. A new clarified format video display was developed and met with the approval of the operators.

Additional work during the report period involved the programming of procedures for weighing operations and balance calibrations, updating the technical documentation of POBSYS, and some progress toward CRT graphic displays of piping diagrams. Further work on the latter subject is presently being deferred.

F. Error Analysis (D. Graczyk and J. Parks)

A comprehensive error analysis of all project measurement operations is in progress. During the report period, a question was raised concerning ANL's ability to meet the bias and precision requirement for the uranium isotopic

* OPSUD--overall software for the operation of the SUD.

[†] MONITR--the monitoring program, which continuously reads approximately 130 process sensors. In addition, the program stores data, compares sensed values with set points, actuates alarms, etc.

and assay analyses on the segments containing the smallest amounts of uranium. A test plan for experimentally evaluating this issue was proposed, planned, and executed. Preliminary examination of the test results indicate that the uranium isotopic determination is more sensitive to contamination by natural uranium sources (e.g., reagents), whereas the uranium assay determination is more sensitive to contamination by uranium-233 from the fuel rod.

Work was also performed this quarter to identify equipment and procedures suitable for carrying out EOL weighing operations. Procedures were recommended for regular QA checks on balance performance, and were submitted for implementation by the computer programming personnel. These procedures are designed both to verify adequate balance performance and to accumulate statistical data needed for valid assessment of errors associated with EOL analytical results. Dummy data sets to be used in evaluating the computational and decision-making abilities of the programs were also assembled.

G. Analytical

(D. Graczyk, E. Callis, and R. Heinrich)

The isolation transformer used to control a problem with voltage "spikes" on the dedicated mass spectrometer was received and installed. The instrument is now ready to resume acceptance testing as soon as a return visit by the vendor's engineer can be scheduled.

Component procurement activities and some assembly work associated with the gamma/alpha spectrometer system were started this quarter. Bid packages for the high-purity-germanium detector (HPGe) were reviewed, and the low bidder was accepted. The unit was received during the last week of December 1981.

Wiring of the automatic sample changer for the gamma system has been completed, and the microprocessor, which regulates relays and busy signals to the computer, has been programmed.

Specifications for the associated multichannel analyzer/computer system were prepared and reviewed by the Quality Assurance Division (QAD). Revisions to include QAD recommendations were started.

H. Miscellaneous

The cleanout of Cell A-5, begun in late September, was completed this quarter. The cell housed the pilot-scale shear and dissolver, which were successfully used in demonstrating the LWBR-POB analytical process scheme, using irradiated test rod sections. The cleanout consisted of the remote disassembly of in-cell components, followed by manned suited entry for removal and disposal of the worktable and alpha barrier assembly. The manned entry stage was completed quite successfully, without incident. Total exposure to all personnel involved was only 0.00207 Sv (207 mrem), indicative of the fairly complete remote decontamination of in-cell items before entry was made. The cell surfaces were subsequently decontaminated and repainted, and the cell was released to the Chemistry Division for other use. At present, due to the modified plan for the EOL campaign, this cell will not be further used by the POB Project.

Two patent applications and assignments were made for material transfer devices developed by Chemical Engineering Division and ANL-ENG personnel. The first device comprises a preassembled cartridge and accordian bag which simplifies remote bagout operations. The second item is a specially designed transfer box, which facilitates intercell transfers of radioactive samples. Both items are presently incorporated into the design of hot cells used by the POB project.

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