ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

FUEL CYCLE PROGRAMS
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by

M. J. Steindler, J. K. Bates, R. E. Brock, T. F. Cannon,
R. A. Couture, P. G. Deeken, J. E. Fagan, K. F. Flynn,
T. J. Gerding, L. J. Jardine, V. M. Kolba, Henry Lautermilch,
N. M. Levitz, W. J. Mecham, R. J. Meyer, R. E. Nelson,
J. E. Parks, M. G. Seitz, L. E. Trevorrow, Seymour Vogler,
I. O. Winsch, and A. A. Ziegler

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ABSTRACT

Development of data on various properties of radioactive waste forms is continuing in an effort to characterize the compatibility, impact resistance, and leach-resistance of solid waste forms. A series of impact tests of lead ingots and lead-glass bead composites was complete. No significant differences in deformations of the ingots or composites were measured for free-fall and drop-weight impact tests. However, the type of fracture of encapsulated beads differed for the two types of impact tests. Leach rates of glass beads and composite specimens in water were measured.

In work characterizing the impact resistance of brittle waste forms in terms of total fracture surface area and total amount of particles of respirable size, tests were made of corner impacts of Pyrex cones and cylinders. Preliminary results for Pyrex specimens show a correlation of surface area with energy input. Also, a series of tests was made of a variety of vitreous, crystalline, and conglomerate materials under comparable impacts. The overall results show promise for a general method of comparing the fracture strengths of a variety of manufactured and natural mineral materials.

Leach rate measurements were continued. A method of making radioactive glass samples on a laboratory scale has been developed. Study of the leach resistance of SYNROC-type waste forms is continuing. Studies that are to serve as a basis for comparing the leaching of weathered and unweathered waste glasses and also to serve as validation for neutron activation analytical techniques are reported.

An approach to the study of radionuclide migration by groundwater flow from a breached-waste repository in geological formations is to use stream-simulation experiments that combine engineered barriers, canisters, waste, and rock cores. Apparatus has been constructed for the experiments, which are in progress. Experiments were performed to study the flow of brine through solid and split cores of rock salt.
Testing and development of equipment for the destructive analysis of full-length irradiated fuel rods from the LWBR is in progress. This analysis will be in support of the LWBR Proof-of-Breeding Project.

A program has started to develop an interim waste form that can be transported from facilities where waste is generated to terminal waste processing. Four waste forms being studied are fused salt, calcined sludge mixed with anhydrous silicates or boron oxides, sludge mixed with aqueous silicate solutions and subsequently pelletized, and cement-silicate forms using sodium silicate and calcium salts.

SUMMARY

Encapsulation of Radioactive Waste in Metal

This program was terminated at the end of FY 1980.

A series of impact tests of lead ingots and lead-glass bead composites with and without lead envelopes was completed. The specimens tested were about 5 cm OD x 5 cm long (2 in. x 2 in.). No significant differences in deformations of lead ingots or lead-glass bead composites were measured for free-fall and drop-weight impact tests. The impacts were equivalent to 7.6- to 13.7-m (25- to 45-ft) free-fall impacts. However, the type of fracture of the encapsulated beads differed for the two types of impact tests.

Composites without protective envelopes were estimated to consume about 20% of the impact energy in the lead phase; there was further reduction (by a factor of two) of the impact energy delivered to encapsulated beads by placing the composites in protective envelopes. Envelopes of about 1/2-in. thickness consumed about 60% of the impact energy in the metal phase. Sieve analyses of glass fragments recovered from impacted composites having no protective envelopes showed that the cumulative mass fractions of particles smaller than 125 μm were reduced by a factor of 2-4, compared with sieve analyses of similarly impacted unencapsulated glass beads. Protective envelopes reduced further the fracture of encapsulated glass beads, but the magnitude by which fragmentation was reduced could not be measured due to the small absolute amounts of glass beads fractured and the difficulty of recovering glass fragments from impacted composites.

A series of leach tests for unencapsulated glass beads and for composites with specimens 5-cm OD x 5 cm long (2 in. OD x 2 in. long) was completed. All tests were for 14 days at 90°C in deionized water. Leach rates of nonactivated unencapsulated 6-mm Pyrex beads were measured to be about 2-3 x 10^{-6} g/cm^{2}.day by conventional solution analyses of Si, B, Al, and Na. Leach rates of neutron-activated Pyrex beads were measured to be 1 x 10^{-6} g/cm^{2}.day, both by measuring neutron-activated elements and by measuring silicon by conventional solution analysis techniques. These values are consistent with literature values. The corrosion rate of lead was measured to be 7 x 10^{-5} g/cm^{2}.day (0.02 mm/y). Corrosion products of red and yellow PbO and Pb3O4 were identified. Analyses of leachates from tests of composites are only partially complete.
Preliminary results for impacted and nonimpacted composites that had no protective envelopes showed that leach rates did not differ significantly. The leach rates for composites were lower than for an equivalent volume of unencapsulated beads; additional solution analyses are required to quantify the results.

Brittle Fracture Studies

Work has continued on experimental impact tests designed to establish a brittle fracture methodology for characterizing the impact resistance of brittle waste form in terms of total fracture surface area and total amount of particles of respirable size. Measurements of particles as small as 1 μm by sieving and Coulter counter analysis have shown that particles smaller than about 5 mm have size distributions that follow the lognormal probability law for the various sizes, shapes, materials, and impact conditions tested thus far.

Surface area measurements made by gas adsorption are being used to determine the specific surface area and shape factors of the particles. Preliminary results show a correlation of surface area with the energy input, which ratio defines a fracture strength property, \( Y_f \), known to be about 77 J/m\(^2\) for Pyrex and crystalline quartz. Shape factors appear to be independent of particle size. Correlations are being developed to relate particle size parameters to material properties for a range of practical impact conditions.

Tests in the current period have included end, side, and corner impacts of Pyrex cylinders in both drop-weight and free-fall impact tests.

Tests were made to determine the applicability of brittle fracture impact methodology to Pyrex, vitreous and crystalline quartz, reactor-grade uranium dioxide ceramic, a machinable glass ceramic, a coarse crystalline rock (nepheline syenite), and sandstone. Results of these tests verify the versatility of the brittle-fracture impact methodology described. This methodology also is consistent when used to analyze fracture data reported for a drop test, at PNL, of a full-sized waste-glass canister.

Neutron Activation and Tracer Studies

Studies of leaching characteristics of borosilicate glass and alternative waste forms (e.g., SYNROC produced by ANL-MSD) are continuing. Preliminary results from these studies indicate that the matrix materials and more leach-resistant type waste elements (e.g., strontium and rare earths) for this waste form have leaching characteristics somewhat better than for borosilicate glass. However, results based on cesium are significantly poorer for this waste form, showing the difficulty of incorporating cesium into the mineral phases present in this type (SYNROC) of waste form.

Samples of (1) PNL-76-68 glass, (2) SRL frit 211, and (3) SRL frit 211 containing additives representative of minor elements in SRL wastes (i.e., SRL frit 211*) have been leach-tested as part of a program to qualify the neutron-activation method of solution analysis. Tests on neutron-activated
and nonactivated samples allowed the comparison of experiments that are identical except for neutron activation. The leachates from each test are being analyzed by different methods of solution analysis, including NAA, atomic absorption (ACL), and ion-coupled plasma (ICP) spectroscopy. A comparison of preliminary data from these experiments indicates that the activation process has a minimal effort on the measured element releases. Additionally, the method is applicable to a wide range of elements at a level of sensitivity that exceeds standard methods of solution analysis of trace elements.

The leach rate results also serve as a basis for the comparison of leaching of weathered glass specimens. Efforts to accelerate the weathering (hydration) process without altering the mechanism have included elevated-temperature tests. Profiles of $\text{H}_2\text{O}^+$ in highly weathered samples indicate that water concentration decreases at greater penetrations in the glass; however, a conclusive method of measuring water penetration has not been established.

Transport Properties of Nuclear Waste in Geologic Media

The potential for radionuclide migration by groundwater flow from a breached-waste repository depends on the leaching process and on chemical changes that might occur as the 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. An alternative to synthesizing each species and studying it individually is to integrate all species and interactions, using stream-simulation experiments. Interactions identified in these studies can then be investigated in detail in simpler experiments.

Preparations for conducting stream-simulation experiments for the Waste Isolation Pilot Plant include (1) construction of apparatus that is noncorrosive in brine, (2) studies of the penetration of rock salt by brine, and (3) development of analytical methods for neptunium-237, plutonium-239, and tritium in brine.

Trace-Element Transport in Lithic Material by Fluid Flow at Elevated Temperature

This report covers new activities on the geology of the Notch Peak, Utah, area and of the Northern Illinois drill hole.

In the Notch Peak area, quartz monzonite has intruded into limestone interbedded in places with silt layers. The permeability of one sample was found to be $2 \times 10^{-6}$ darcy. Preliminary calculations suggest that considerable fluid could have been forced through the limestone during the intrusive event, but other geological evidence is necessary to determine whether this in fact happened.

Plans to determine the permeability, trace-element transport properties, and possibly interstitial water composition of precambrian granite from Northern Illinois drill hole UPH-3 are briefly described.
Light Water Breeder Reactor Proof-of-Breeding Analytical Support Project

The LWBR Proof-of-Breeding (POB) Analytical Support Project is responsible for the destructive analysis of full-length (about 3 m) 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.

Present work is aimed at developing the equipment and procedures for four main subactivities of this project: (1) the full-scale shear, (2) the single-unit or prototype dissolver (SUID), (3) multiple dissolvers needed for the destructive analyses of full-length (about 3-m) irradiated fuel rods for the EOL campaign, and (4) scrap/waste disposal. In addition, current work by the Analytical Chemistry Laboratory at ANL in support of this project is being done in the areas of planning and procurement. Development of an integrated computer/data acquisition system for the entire project is also in progress.

Development of Interim High-Level-Waste Forms

An Environmental Impact Statement (EIS) is being prepared as is necessary before the high-level liquid waste at the Nuclear Fuel Services Plant (NFS) at West Valley, N.Y., can be processed. A summary has been prepared describing selected processes that would yield an interim waste form product. One option involves removal of water and trapping the activity in molten salt, which then solidifies in a solid block. Another option calls for calcining the sludge, then stabilizing the calcine with sodium silicate binder.

A fused salt mixture representative of material in the NFS waste tanks was prepared. The melting point was determined to be 220°C, and the decomposition temperature was about 600°C. Impact tests on the fused salt showed that no more than 0.01% fines (<10 μm) formed upon impact.

Compacts made from sodium silicate powders were sintered to greater than 92% of theoretical density at 600°C. Several of the parameters for sintering were briefly examined. Preliminary microstructural examination of the fracture surfaces of pellets sintered for 55 h indicated that there was reasonable bonding of the Fe2O3 and the sodium silicate matrix. The fracture strength of these sodium silicate pellets was approximately one order of magnitude greater than that of fused salt pellets. In general, the addition of Fe2O3 resulted in weaker compacts.

Impact experiments indicated that as with fused-salt specimens, fracture in sodium silicate specimens occurred in two stages—the initial impact was followed by crushing of the samples by compaction. In contrast, Pyrex specimens exhibited brittle fracture by a single impact event. Fracture of sodium silicate yielded less than 10⁻⁶ fraction of fines (<10 μm). A greater fraction of Fe2O3 in the compacts increased the fraction of fines.
ENCAPSULATION OF RADIOACTIVE WASTE IN METAL
(L. J. Jardine and T. J. Gerding)

A. Introduction

Concentrated radioactive wastes (high-level defense wastes, commercial wastes, TRU, fractionated cesium and strontium, etc.) destined for deep geologic disposal must be in solid forms that are demonstrably stable. Waste forms that would be alternatives to borosilicate glass monoliths are currently being developed and evaluated by DOE. These waste forms offer potentially superior solid product performance or process characteristics.

Many alternative crystalline waste forms (e.g., supercalcine and SYNROC) are granular materials that must be consolidated to a less dispersible solid form by the use of other materials.

Less dispersible alternative waste forms can be fabricated by encapsulating the granular materials in a corrosion-resistant metal matrix that also has good impact resistance. For example, waste in the form of small glass beads encapsulated in a lead-alloy matrix could serve as an alternative to glass monoliths. This alternative waste form would greatly enhance the quality assurance and recycle process options and increase the resistance to dispersion of the final waste form although at the expense of introducing extra process complexities.

The objective of this program was to establish the technical feasibility of encapsulating alternative waste forms in a metal matrix in order to produce a less dispersible product that is likely to be acceptable for geologic disposal. The advantages of encapsulating radioactive waste forms in a metal matrix were identified, evaluated, and, where possible, compared with other solid waste forms, primarily monolithic glasses. This program was terminated at the end of FY 1980. A final report on this work is being prepared. Progress during this quarter is reported below.

The experimental approach consisted of (1) developing casting fabrication techniques for the preparation of laboratory-scale specimens (primarily metal-glass composites) and (2) developing and implementing techniques for characterizing the properties of such composites. Fabrication methods were selected to simulate larger scale production concepts for metal encapsulation. Characterization techniques were partially developed and applied to study the mechanical impact resistance of metal composites, the leach rates and leach mechanisms of composites, and the chemical and physical compatibilities of glass and metal matrices. Relationships between the characterization measurements and the composite fabrication method and fabrication conditions were also sought in order to identify important encapsulation process design parameters.

B. Experimental Characterization Results

1. Impact Resistance of Composites

The preceding quarterly report [STEINDLER-1980] presented a series of impact tests performed with lead ingots and with lead-glass bead (6-mm) composites. The average values of measurements from the duplicate impact
experiments have been calculated and are summarized in Table 1. The "errors" are the variations from the averages.

The mean linear compressions (i.e., axial deformation) for the lead ingots were used to calculate mean plastic flow stresses, \( \sigma_d \), of \( 1.66 \times 10^7 \) Pa \((2400 \pm 30 \) psi\) for the drop weight tests and \( 1.86 \times 10^7 \) Pa \((2700 \pm 50 \) psi\) for the free-fall tests. The plastic flow stresses, \( \sigma_d \), were calculated from the relationship \( W_i = \sigma_d A \Delta L \) where \( W_i \) is the impact energy \((86 \) J\), \( A \) is the initial impacted specimen cross-sectional area, and \( \Delta L \) is the measured axial deformation or compression. The variations of the above \( \sigma_d \) values for a given type of impact test suggests there may be different values of \( \sigma_d \) for the two types of tests. The different values of \( \sigma_d \) could be due to unaccountable energy losses during free-fall tests and/or to impact velocities in the free-fall tests being about four times those of the drop weight tests. From the above work, a value of \( \sigma_d \) equal to 2600 psi for the lead used in these tests \((99.97 \) wt \%) Pb; Ag, 5 ppm; Cd, 3 ppm; Bi, 1 ppm; and with As, Sb, Sn, Cu, Fe, Ni, and Zn all \(<1 \) ppm\) is recommended for analyses of either type of impact test. For example, this value of \( \sigma_d \) could be used to estimate deformation of lead in future drop weight and free-fall impact tests within the range of test conditions used in these impact tests.

Impact tests of composites of lead and glass beads require estimation of the fraction of total impact energy which deforms the lead; the balance of the impact energy is assumed to cause fracture of the brittle glass beads [MECHAN]. The amount of impact energy that deforms lead can be estimated from the relationship \( W_i(Pb) = \sigma_d A \Delta L \) and the value of \( \sigma_d \) determined above. The calculated energy, expressed as a percentage of initial impact energy based on averages of replicate tests assumed to be available for brittle fracture, is shown in Table 1 for the composites.

For a composite with a given envelope thickness, these experimental results show no difference in estimated energy fracturing the glass for either the drop weight or the free-fall tests. This was observed for composites having no protective envelopes and for composites having 1.3-cm \((1/2\)-in.\) axial envelopes. The composites having no protective envelopes were estimated to have transferred about 80\% of the impact energy to the glass beads; the composites with 1.3-cm protective envelopes were estimated to transfer about 40\%, or half as much, of the impact energy to the glass. This illustrates the effect of protective envelopes. The results of visual examination of beads recovered from the impacted composites and tabulated in Table 1 are also consistent with the latter statement, i.e., there were more fractured beads for the no-envelope composite. Thus, the absence of a protective envelope causes major fracture of the encapsulated glass beads due to (1) the direct point contacts of the beads which provide energy transfer paths between beads and (2) the lack of an unyielding surface (i.e., no protective-lead envelopes) on the impacting ends. The composites having protective envelopes all encountered less damage to the glass beads, as shown in Table 1. Although the free-fall impact tests of the composites with 1.3-cm protective envelopes may have resulted in more fracture of glass beads than in similar drop weight tests (Table 1), this cannot be quantified from current data.

The glass beads on which localized fractures were observed were recovered from impacted composites by a destructive type procedure.
Table 1. Summary of Characterization Results of Fourteen 2-in.-OD × 2-in.-long Specimen (all replicate tests) after 86-J Impacts

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Impact Type</th>
<th>Mean Linear Compression, ΔL, mm</th>
<th>Damage to Glass Beads</th>
<th>Calculated Fracture Energy to Glass, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fractured, %</td>
<td>Localized, %</td>
</tr>
<tr>
<td>Lead only</td>
<td>DW</td>
<td>2.56 ± 0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>FF</td>
<td>2.28 ± 0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Composite (+0 in.)</td>
<td>DW</td>
<td>0.36 ± 0.09</td>
<td>74 ± 7h</td>
<td>23 ± 5</td>
</tr>
<tr>
<td></td>
<td>FF</td>
<td>0.50 ± 0.16</td>
<td>72 ± 3h</td>
<td>21 ± 1</td>
</tr>
<tr>
<td>Composite (+1/4 in.)</td>
<td>DW</td>
<td>1.82 ± 0.18</td>
<td>3 ± 1</td>
<td>86 ± 1</td>
</tr>
<tr>
<td>Composite (+1/2 in.)</td>
<td>DW</td>
<td>1.32 ± 0.03</td>
<td>3 ± 1</td>
<td>80 ± 3</td>
</tr>
<tr>
<td></td>
<td>FF</td>
<td>1.42 ± 0.08</td>
<td>32 ± 5</td>
<td>61 ± 3</td>
</tr>
</tbody>
</table>

Specimens were all about 5 cm (2-in.) OD × ~5 cm (2-in.) long cylindrical shapes. The numbers inside parentheses for composites denote the thickness (in in.) of the axial protective metal envelopes, with (+0 in.) signifying no envelope.

Impact type is either drop weight (DW) or free fall (FF).

These values are averages of two replicate tests.

See text.

"Fractured" means all beads not in "Localized" or "None" categories.

"Localized" means that beads were observed to be damaged or fractured by localized surface contacts where beads were initially touching prior/during impacts, but were essentially the original (6-mm) bead size.

"None" means beads which were observed to contain no "Localized" fracture damage or any other type of fracture.

Sieve analyses of the recovered fragments were performed for these four specimens.
The type of localized glass bead damage was different for the higher-velocity (about 4 times) free-fall tests than for the drop weight tests. Apparently, highly localized stresses develop during the impact loading as the beads are elastically compressed at the contact points beyond the fracture threshold point, causing fracture to take place. Drop-weight tests cause localized fracture but little or no spalling of glass, i.e., glass does not leave the initial bead surface and the beads have many internally cracked damaged areas. The drop-weight tests generated localized fractures of a conoidal shape (apex truncated at point of initial glass bead contacts and its base within the glass sphere), with glass fracture occurring within the glass bead. The free-fall tests generated spalled-type fragments which produced shallow surface cavities with smooth bottoms and contours nearly matching the spherical glass bead surface of recovered glass beads. That is, the free-fall tests caused fractures, resulting in spalling. These two types of fractures are shown in Fig. 1.

![Fig. 1. Typical Fracture Observed in Pyrex Beads Recovered from Impacted Lead Matrix Composites. Left shows fractures in drop-weight tests; right shows fractures in free-fall tests. The scale units are 1 mm, and the beads are 6 mm in diameter.](image)

The difference in the types of localized damage may be in part due to the higher impact velocities (about 4 times) in the free-fall test. For all tests, the glass beads in the composites with 1.3-cm protective envelopes encountered less damage than the composites with no protective envelopes. However, in neither type of impact were any fragments released from within the metal matrix.

The two drop-weight tests done with the composites having 0.6-cm (1/4-in.) pads showed the least amount of energy transferred to the fracture of glass and damage to the glass beads. No reason is obvious to us for a 0.6-cm protective envelope resulting in less glass damage than 1.3-cm protective envelope at the same impact conditions. No free-fall tests were done with composites having 0.6-cm protective envelopes. More tests would be needed to resolve this apparent discrepancy.
Sieve analyses from impacted composites are reported below for two free-fall and two drop-weight tests in which protective envelopes were not used. No sieve analyses were performed for composites with either 0.6-cm or 1.3-cm envelopes because the quantity of glass fragments (about <500 μm) was insufficient for mass determinations required for the sieve analyses.

The sieve data (six size fractions) for the fragments recovered from the two drop-weight impacted composites (C-1-0:DW and C-2-0:DW) and the two free-fall impacted composites (C-3-0:FF and C-4-0:FF) are shown in Table 2. The masses of the particles smaller than 125 μm were too small to allow sieving. The data do not plot linearly on lognormal graph paper. This may be due to lost fragments. Such losses occur during the recovery of glass fragments from the lead matrix. The amounts of loss during recovery and losses due to subsequent sieving and handling are given in Table 2. The recovery losses varied from 0.04 to 1 wt % for the four specimens. Losses were essentially unavoidable due to the difficult recovery operation (i.e., melting of lead and acid dissolution of residual lead from the fragments) necessary to collect and prepare fragments for sieving analyses. The particle size distribution of the fragments lost during recovery is not known and so conclusions regarding any size fraction of the glass fragments include this uncertainty. The losses during sieving and subsequent transfer varied from 0.04 wt % to 0.2 wt % and must also be considered in making conclusions from these data.

From the sieve data in Table 2, which neglect any losses, the drop-weight specimens appear to give the same measured cumulative mass fractions of particles smaller than 125 μm. The mean value is 0.004 ± 0.001 wt % smaller than 125 μm. Similarly, the two free-fall impact specimens had approximately the same measured cumulative mass fractions of particles smaller than 125 μm; the mean value is 0.14 ± 0.6 wt % smaller than 125 μm. The fact that the particle size distributions of the relatively large losses reported in Table 2 are not known does not permit conclusions or comparisons to be made of the free-fall and drop weight tests. The analyses in Table 1 suggest that particle size distributions of the drop weight or free-fall impacted specimens should not differ significantly since both types of tests delivered the same fraction of the impact energy to the glass beads (about 80%) and the beads had virtually the same visually characterized damage.

One type of impact test was attempted for comparison of composites with glass beads. The same mass of 6-mm glass beads as in the tests with composites (128 g) was placed inside a solid steel pipe of the same diameter as the metal matrix composites. These beads (no lead was present) were impacted with 86 J of energy by a drop-weight impact. The fragments were recovered and sieved. The data from duplicate tests (B-1-DW, B-2-DW) are given in Table 2. These data formed linear plots on lognormal graph paper. The data suggest that the weight percent of the <125 μm fraction was greater than that of any of the impacted composites by a factor of about four (if losses are ignored).

Also shown in Table 2 for comparison is the particle size distribution of a Pyrex cylinder (38-mm OD x 64 mm long) impacted with a drop-weight device with the approximate same energy density. These data essentially agree with the bare-glass-bead data at the small size fractions, which all
<table>
<thead>
<tr>
<th>Sieve Size, μm</th>
<th>C-1-O:DW&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C-2-O:DW&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C-3-O:FF&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C-4-O:FF&lt;sup&gt;a&lt;/sup&gt;</th>
<th>B-1-DW&lt;sup&gt;a&lt;/sup&gt;</th>
<th>B-2-DW&lt;sup&gt;a&lt;/sup&gt;</th>
<th>DW-Rod&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;4000</td>
<td>18</td>
<td>4.6</td>
<td>20</td>
<td>25</td>
<td>14</td>
<td>15</td>
<td>28</td>
</tr>
<tr>
<td>&lt;2000</td>
<td>5.1</td>
<td>2.4</td>
<td>7.8</td>
<td>9.8</td>
<td>9.4</td>
<td>9.5</td>
<td>19</td>
</tr>
<tr>
<td>&lt;1000</td>
<td>1.3</td>
<td>0.6</td>
<td>2.6</td>
<td>3.0</td>
<td>5.3</td>
<td>5.3</td>
<td>10</td>
</tr>
<tr>
<td>&lt;500</td>
<td>0.4</td>
<td>0.2</td>
<td>0.9</td>
<td>1.0</td>
<td>2.8</td>
<td>2.8</td>
<td>4</td>
</tr>
<tr>
<td>&lt;250</td>
<td>0.09</td>
<td>0.04</td>
<td>0.3</td>
<td>0.4</td>
<td>1.5</td>
<td>1.4</td>
<td>2</td>
</tr>
<tr>
<td>&lt;125</td>
<td>0.005</td>
<td>0.003</td>
<td>0.08</td>
<td>0.2</td>
<td>0.72</td>
<td>0.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**Mass Loss, wt %**

- **During Recovery Only**
  - 1.0<sup>b</sup>
  - 0.1
  - 0.4
  - 0.04
  - 0.15
  - 0.16
  - 0.05

- **During Sieving Only**
  - 0.05
  - 0.2
  - 0.04
  - 0.05

<sup>a</sup>Impact test was either a drop-weight (DW) or a free-fall (FF) test.

<sup>b</sup>After sieving, 60% of the 1% of glass fragments lost were located but were not included in this analysis.
have larger fractions of their masses as <125 μm particles than do the composites. Note that (about 20%) less energy was estimated to be delivered to the glass beads when lead is present (lead absorbs some impact energy).

It is concluded that the mass fractions of fragments smaller than <125 μm generated in the impact of metal composites (5-cm OD × ~5 cm-long) no protective envelopes are reduced by a factor of about two to four, compared to the absence of metal encapsulation (i.e., glass beads only). Additional reduction in fracture is achieved with protective envelopes; however, the small mass of fragments produced from these configurations and the difficulty of recovering the fragments preclude measurements that would allow direct quantification of results.

2. Leach Resistance of Composites
   a. Introduction

   A preliminary series of leach tests designed to study the leaching characteristics of metal matrix composites was performed. Approximately spherical Pyrex glass beads (Corning Code 7740: nominal composition of 68 wt % SiO₂, 13 wt % B₂O₃, 4 wt % Na₂O, 2 wt % Al₂O₃) were used as simulated waste forms. Both nonactivated and neutron-activated (2 × 10¹⁸ neutrons/cm²) beads 6 mm in diameter were used. Metallic lead (99.97 wt % Pb; Ag, 5 ppm; Cs, 3 ppm; Bi, 1 ppm; and As, Sb, Sn, Cu, Fe, Ni, and Zn each <1 ppm) was used as the matrix alloy. All composites and lead ingots were fabricated by casting in air at about 400°C using a 304 L stainless steel split mold which yielded cylindrical specimens 5-cm OD × 5 cm long. Three types of static leach tests were performed in order to generate comparative leach rate data. All leach tests at 90°C for fourteen days used deionized distilled water and were performed in duplicate.

   One test set was designed to measure and compare the leach rates of a quantity of glass beads encapsulated in a lead composite with the leach rates of the same quantity not encapsulated. A second test set was designed to measure the leach rates of glass bead-lead composites which had been subjected to the equivalent mechanical impact resulting from a ~13.7-m free-fall drop for comparison with the leach rates for identical composites not impacted. A third set was designed to measure the corrosion rate of the metallic lead while also verifying that "zero release" was obtainable for a glass bead-lead composite having a protective envelope. Details of the experiments are given below.

   b. Leach Rates of Glass Bead-Lead Composites
      (1) Glass Beads

      About 200 glass beads were used in each of four tests to measure the leach rates of the Pyrex beads used in the composites. Two tests used neutron-activated beads. The two leachates, containing trace levels of radioactivity, were each divided for two separate analyses. One-half was submitted to Chemical Engineering Division Analytical Chemistry Laboratory (CEN-ACL) for analyses of silicon and antimony; the other half was evaporated and prepared for γ-ray analyses by the CEN-ACL. In two other tests,
nonactivated Pyrex beads were used that had been prepared in a similar way to the neutron-activated beads except for irradiation. The leachates were again split into two equal fractions. One fraction was submitted to the CEN-ACL for analyses of silicon and antimony, and the second fraction was submitted to Ames for inductively coupled plasma (ICP) analyses.

The results, all averages of duplicate runs, were converted to normalized leach rates using the geometric surface area for 200 beads (6 mm) of 226 cm$^2$, fourteen-day test duration, and the nominal Pyrex composition (Table 3). For the wet chemical analyses of CEN-ACL and Ames, the values were reported as grams of element detected in a solution, normalized from the typical Pyrex composition given above.

The results of Table 3 can be discussed in terms of the known concentrations and distributions of very minor or trace elements in the Pyrex. No matrix elements (i.e., Si, B, Al, Na) had isotopes for which activation products could be measured; trace elements (i.e., for which the initial element concentration was unknown) were measurable only by neutron activation products. Thus no direct comparisons of the neutron activation measurement method with the wet chemistry methods were possible in these experiments with Pyrex. All gamma ray counting was done by R. Malewicki of CEN-ACL.

The leach rates in Table 3 of the seven trace elements detected from the activated Pyrex beads span about two orders of magnitude. The rates suggest that $^{60}$Co and $^{65}$Zn were the most leachable, that $^{46}$Sc and $^{124}$Sb were the least leachable isotopes, and that $^{51}$Cr, $^{54}$Mn, and $^{134}$Cs had intermediate values.

The normalized leach rate of silicon in the activated beads was most consistent with the leach rates of the least leachable elements, $^{46}$Sc and $^{124}$Sb, and perhaps $^{134}$Cs. The averaged measured leach rates of silicon from nonactivated Pyrex beads appear to be about three times higher (e.g., $2.7 \times 10^{-6}$ vs. $0.8 \times 10^{-6}$) than those of the activated beads. The normalized Ames results for boron, aluminum, and sodium agree among themselves and with the CEN-ACL silicon results.

It is concluded from these data that the leach rate of the Pyrex matrix elements is about $3 \times 10^{-6}$ g/cm$^2$-day and that the trace activated elements, $^{46}$Sc, $^{51}$Cr, $^{54}$Mn, $^{124}$Sb, and $^{134}$Cs, have leach rates within a factor of about three of these matrix rates. The leach rates of the trace elements, $^{60}$Co and $^{65}$Zn, seem to be more than an order of magnitude higher that those of the matrix elements or the other trace elements in Pyrex.

Comparisons of the results in Table 3 with other measurements of the Pyrex leach rates in the literature are not meaningful because of the high variability of (and at times unknown) experimental conditions for the reported work. It is, however, informative to summarize some literature data found for Pyrex. Three leach rates based on weight loss measurements were identified. [CORNING] reports a penetration rate of $125 \times 10^{-7}$ mm/day for Pyrex in boiling distilled water; this can be converted to a matrix leach rate of $2.8 \times 10^{-6}$ g/cm$^2$-day. Savannah River Laboratory [DP-1382] reports a leach rate of $3.8 \times 10^{-6}$ g/cm$^2$-day for crushed Pyrex (8 to 12 g of 0.08-0.25 in. with a BET surface area of 41 cm$^2$/g) for a 24-h Soxhlet test.
Table 3. Leach Rates of 200 Pyrex Glass Beads (6-mm), both Neutron-Activated Beads to a Neutron Fluence of $2 \times 10^{18}$ n/cm$^2$-s and Nonactivated Beads. Tests were for 14 days at 90°C in deionized water with a geometric surface area/leachant volume ratio of 0.45 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Leached Isotope or Element</th>
<th>Primary γ-ray used, keV</th>
<th>Neutron-Activated Samples, ACL, a g/cm$^2$·day</th>
<th>Nonactivated Samples, g/cm$^2$·day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ACL a</td>
<td>Ames a</td>
</tr>
<tr>
<td>$^{46}$Sc</td>
<td>1120</td>
<td>$b(0.7 \pm 0.3)10^{-6}$</td>
<td>--</td>
</tr>
<tr>
<td>$^{51}$Cr</td>
<td>320</td>
<td>$b(15 \pm 7)10^{-6}$</td>
<td>--</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>834</td>
<td>$b(13 \pm 6)10^{-6}$</td>
<td>--</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>1332</td>
<td>$b(55 \pm 28)10^{-6}$</td>
<td>--</td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>1115</td>
<td>$b(94 \pm 23)10^{-6}$</td>
<td>n.d. c</td>
</tr>
<tr>
<td>$^{124}$Sb</td>
<td>1691</td>
<td>$b(0.8 \pm 0.1)10^{-6}$</td>
<td>n.d. c</td>
</tr>
<tr>
<td>$^{134}$Cs</td>
<td>795</td>
<td>$b(4.2 \pm 1.4)10^{-6}$</td>
<td>n.d. c</td>
</tr>
<tr>
<td>Si</td>
<td>--</td>
<td>$d(0.8 \pm 0.3)10^{-6}$</td>
<td>$d(2.4 \pm 0.4)10^{-6}$</td>
</tr>
<tr>
<td>B</td>
<td>--</td>
<td>--</td>
<td>$e(3.1 \pm 0.5)10^{-6}$</td>
</tr>
<tr>
<td>Al</td>
<td>--</td>
<td>--</td>
<td>$f(1.7 \pm 0.3)10^{-6}$</td>
</tr>
<tr>
<td>Na</td>
<td>--</td>
<td>--</td>
<td>$g(4.6 \pm 1.5)10^{-6}$</td>
</tr>
</tbody>
</table>

a Analytical results from either the CEN-ACL or Ames Laboratory.

b Rates are averages of duplicate samples calculated from relationship $[(A_{i}M_{i})/(A_{i,o}M_{o})] \times [(M_{i}/S \cdot t)]$ where $A_{i}$ is measured activity in leachate; $A_{i,o}$ is activity measured in initial beads; $M_{i}$ is mass of (200) beads leached; $M_{o}$ is mass of unleached beads used to measure $A_{i,o}$; $S$ is the total geometric surface area of all beads leached; and $t$ is the leaching period. Both $A_{i}$ and $A_{i,o}$ were corrected to the same time after irradiation.

c n.d. means not detected in solution analyses above background.

d Rate is g of silicon per cm$^2$·day and has been normalized assuming silicon is 0.38 weight fraction of Pyrex.

e Rate is g of boron per cm$^2$·day and has been normalized assuming boron is 0.04 weight fraction of Pyrex.

f Rate is g of aluminum per cm$^2$·day and has been normalized, assuming aluminum is 0.01 weight fraction of Pyrex.

g Rate is g of sodium per cm$^2$·day and has been normalized, assuming sodium is 0.03 weight fraction of Pyrex.
at 90°C. Eurochemic [ETR-296] reports a leach rate of $0.95 \times 10^{-6}$ g/cm$^2$.day for Pyrex at 200°C in a 1000-h test in a brine solution. All of these data are consistent with the leach rate for the Pyrex matrix of about $3 \times 10^{-6}$ g/cm$^2$.day observed for our test conditions (Table 3).

An earlier test at ANL [STEINDLER-1979A] using neutron activation of 4-mm Pyrex beads in 25°C distilled water indicated a leach rate of $0.3 \times 10^{-6}$ g/cm$^2$.day for $^{124}$Sb and $21 \times 10^{-6}$ g/cm$^2$.day for $^{134}$Cs. No analyses for the matrix elements Si, B, Al or Na were made. Since the sources of Pyrex beads, the leaching temperatures (25°C vs. 90°C), and the leaching periods differed from those for the experiments of Table 3, no meaningful comparisons can be made.

(2) Lead

Two ingots of 99.97 wt % lead (Samples C and D, 50-mm OD x ~52 mm long) were fabricated in the same mold as was used for composites. These ingots were subjected to a 14-day leach test at 90°C in deionized water. The leachates were each divided into two equal fractions and submitted for analysis of lead and other elements to both the CEN-ACL and Ames.

At the conclusion of the experiment, the two ingots each had an obvious corrosion layer deposit. It was not established what fractions, if any, of the corrosion products had deposited on the ingots during cooling from 90°C. The deposit was identified to contain both yellow and lesser amounts of red PbO by X-ray diffraction analyses.* Because of the deposit layers, weight loss measurements cannot be used to deduced meaningful corrosion rates. Similarly, some uncertainty of the solution analyses interpretations has to be recognized. In addition to the two pure lead ingots, two composites (Samples A and B, 50-mm OD x ~52 mm long) with 0.6-cm protective envelopes completely surrounding and isolating about 63 g of activated Pyrex beads were fabricated and subjected to the same 14-day leaching conditions at 90°C. These two composites provided two additional measurements of leach or corrosion rates of lead since no glass was exposed to the water. These two composites also had yellow PbO deposits on their surfaces at the conclusion of the experiment.

Only the CEN-ACL analyses of leachates are available at this time. Results are given in Table 4 for these four samples. The average corrosion rate is $(67 \pm 23) \times 10^{-6}$ g/cm$^2$.day or $0.022 \pm 0.007$ mm/y. This can be compared with literature values of $40 \times 10^{-6}$ g/cm$^2$.day (0.013 mm/y) for a 10-day test in distilled water at 100°C of 99.9% lead [ETR-296], and an average rate of about 0.058 mm/y for a 21-day test in deionized water at room temperature of 99.9% lead [LEAD]. Similar values have been observed for longer term tests up to 14 years in sea water [DMIC-245].

*Analyses by B. Tani of CEN-ACL.
Table 4. Leach or Corrosion Rates of 99.97 wt % Lead Ingots (50-mm OD × 52 mm long) for 14-Day Test in Deionized Water at 90°C as Analyzed by CEN-ACL for Lead. The geometric surface area to leachant volume ratio was 0.48 cm⁻¹.

<table>
<thead>
<tr>
<th>Sample</th>
<th>µg Pb/mL</th>
<th>g/cm²·dayᵃ</th>
<th>mm/yᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>145 ± 15</td>
<td>(43 ± 5)×10⁻⁶</td>
<td>0.014</td>
</tr>
<tr>
<td>B</td>
<td>203 ± 21</td>
<td>(60 ± 6)×10⁻⁶</td>
<td>0.019</td>
</tr>
<tr>
<td>C</td>
<td>328 ± 33</td>
<td>(97 ± 10)×10⁻⁶</td>
<td>0.031</td>
</tr>
<tr>
<td>D</td>
<td>234 ± 24</td>
<td>(69 ± 7)×10⁻⁶</td>
<td>0.022</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>(67 ± 23)×10⁻⁶</td>
<td>0.022 ± 0.007</td>
</tr>
</tbody>
</table>

ᵃRates calculated from solution analyses for a geometric surface area (121 cm²) and a fourteen-day test duration. Lead corrosion products which had deposited on the lead ingots were ignored in these analyses.

ᵇA uniform corrosion or penetration rate is assumed.

(3) Glass Bead-Lead Composite

Four composites (50-mm OD × 52 mm long) having two different histories were leached for 14 days at 90°C in deionized water. Each composite leached contained about 460 beads and had no protective envelope. These measurements simulated leach rates that would be obtained if the protective envelope had been removed. Two composites containing neutron-activated beads were leached; prior to leaching, the other two neutron-irradiated composites were subjected to a drop-weight impact (86 J) equivalent to a 13.7-m (45-ft) free fall. The results for the two as-fabricated composites were to be used to compare the leach rates of encapsulated and unencapsulated beads; the results for the two drop-weight impacted composites were to be compared with the two as-fabricated composites to measure the consequences of impacts on leach rates of composites.

The leachates from the four leach tests were each divided into two equal fractions, with one submitted to CEN-ACL for a silicon analysis and the other evaporated and prepared for gamma-ray analyses by CEN-ACL. No ⁴⁶Sc, ⁵¹Cr, ⁵⁴Mn, ⁵¹Mn, ⁶⁰Co, ⁶⁵Zn, or ¹²⁴Sn were detected in the leachants above background. There was some evidence that small amounts of ¹³⁴Cs were detectable above background. However, the amount of ¹³⁴Cs was not enough above room background variations to provide quantifiable results, and the amount of ¹³⁴Cs is concluded to be at least an order of magnitude less than if the 463 beads had not been encapsulated. Hence, metal encapsulation of these Pyrex beads containing trace amount of radioactivity reduced the leach rate of ¹³⁴Cs by an order of magnitude, or greater, and reduced the leach rate even more for the ¹²⁴Sb and ⁶⁵Zn. It may be that the ¹²⁴Sb and
$^{65}$Zn interacted with and deposited with the corrosion products and were not detected in the leachates. The two unimpacted composites with the glass beads exposed to the leachate had corrosion deposits that were identified by X-ray diffraction as yellow PbO, with red PbO and Pb$_3$O$_4$ also possibly present. The two impacted composites had yellow PbO in the corrosion deposits, with Pb$_3$O$_4$ possibly present. The final pH of all four leachates was 10 ± 0.3, and that of two blanks was 7.3 ± 0.2.

Leach rates are expected to increase with greater surface area of the test material. Impacted specimens have significantly greater surface areas (see Table 2) of glass fragments than do the nonimpacted composites. This greater surface area of the impacted composites would be expected to produce higher leach rates than the nonimpacted composites if the leachate were penetrating the lead-glass bead composite. Since experimental data indicate insignificant differences in the leach rates of the two types of samples, penetration of the glass bead-lead composites by the leachates may be less a factor in the leach mechanism of the composite than was previously reported [STEINDEL-1979A].
II. BRITTLE FRACTURE STUDIES

(W. J. Mecham, R. H. Pelto, G. T. Reedy,* and L. J. Jardine)

A. Introduction

The aim of this study is to characterize the resistance to dispersion of solid radioactive waste forms that receive mechanical impacts during normal and accidental conditions of processing, interim storage, and transportation. A methodology is being developed for characterizing the results of impact fracture of brittle materials in terms of the total fracture-surface area and the mass of particles of respirable size, which are the characteristics most relevant to dispersion. This methodology has the goal of combining models of impact-stress distribution and of lognormal particle-size distribution to relate fracture surface area to impact energies and to the mechanical properties of materials.

Preliminary development and verification of this methodology is being achieved by laboratory-scale tests of impacts of reference glass specimens and by analyses of impact-fracture data from the technical literature for various brittle materials, including large-scale simulated waste-glass canisters. This brittle-fracture methodology is being examined for a range of practical impact conditions and solid-waste materials. It is anticipated that the experimental results will establish correlations of impact energy and material properties with lognormal particle size and fracture surface-area parameters for brittle-waste packages of various sizes and configurations. Such correlations will be derived from the basic physical principles of the brittle-fracture process and are expected to define an efficient experimental program to provide data useful for evaluating material properties and for estimating the effects of accidents.

B. Overview of Results in this Period

Work in this period has included further tests of reference Pyrex specimens in order to verify the methods used. Several preliminary drop-weight tests were made of corner impacts of both conical and cylindrical shapes. The fracture data are being evaluated and compared with data for side and end drop-weight impacts of cylinders, which have very different stress distributions. The particle size distributions, measured by sieving and Coulter counter analysis of particles 1 μm or larger, are consistent with the lognormal fracture model.

The specific surface areas and shape factors of fracture particulates are being investigated by both gas-adsorption (BET) surface-area measurements and by stereometric measurements of individual particles by scanning electron microscopic and statistical analyses. The latter work has been subcontracted to the Ceramics Engineering Department of the North Carolina State University. Preliminary data obtained by both techniques indicate that fracture particulate distributions show shape factors that are independent of particle size. The stereometric method yields both volume and surface-area shape factors as a function of size, while the BET method determines only the surface-area-to-volume shape factor.

*Analytical Chemistry Laboratory, Chemical Engineering Division.
The current impact fracture methodology (see Overview of the Brittle-Fracture Methodology below) was also applied to the data reported [CHAPMAN, ROSS] by Battelle Pacific Northwest Laboratory (PNL) for a 2.6-m drop of a full-scale (0.61-m-dia.) canister containing simulated waste glass. Sieving of ≥44 μm particles gave a lognormal size distribution of the impact-fracture particulate that is consistent with our fracture methodology. In addition, the particle size distribution of the preimpact fracture particles (i.e., the fracture due to thermal stress) was found to be lognormal. A later report [ROSS] gives the result of a sedimentation size analysis of the fracture particulate for the respirable fraction, i.e., the mass fraction of particles smaller than 10 μm. This direct measurement of the respirable fraction agrees with the extrapolated lognormal plot based on the sieving data and supports the application of lognormal methodology to canistered full-scale glass waste forms.

A series of tests was made of a variety of vitreous, crystalline, and conglomerate materials under comparable impacts, in order to explore the range of applicability of the fracture methodology for characterizing waste forms other than glass. Included were crystalline and vitreous quartz; reactor-grade UO₂; sandstone; a coarsely crystalline mineral (nepheline syenite); a high-strength, "machinable" glass-ceramic (MACOR); and Pyrex glass. When the size distributions obtained by sieving and Coulter counter analysis were plotted on lognormal graphical coordinates, all of the materials plotted as straight lines which had approximately the same slope; this indicates lognormal distributions of about the same standard deviation. The geometric mean sizes were similar for all specimens except sandstone (a lower value) and the glass-ceramic (a higher value). This result is consistent with an analysis of relative impact strength based on energy consumed per unit of fracture surface area formed. The glass ceramic was estimated to be 40% stronger than Pyrex, and the sandstone 60% weaker. Crystalline quartz showed the same strength as Pyrex, while the UO₂, vitreous quartz, and nepheline syenite were slightly (30-50%) weaker than Pyrex.

For all materials, the smaller particles were lognormally distributed up to an upper limit size. The limiting size of the lognormally distributed portion of the fracture particulate was abnormally low for sandstone and nepheline syenite; in these two materials, the deviations corresponded to the approximate crystallite sizes. This was not observed for the crystalline forms of quartz and UO₂. The overall results show promise for a general method of comparing the fracture strengths of a variety of manufactured and natural mineral materials.

C. Overview of the Brittle-Fracture Methodology

From a literature review, it was found that three general methods developed prior to 1965 in other contexts could be applied to the characterization of impact fracture of brittle materials. These methods concern the energy consumed in the pulverization of minerals, elastic stress analysis, and small-particle statistics. Kinetic energy is related to stress through the deceleration force, which force during impact is balanced by an elastic compressive stress in the impacted body. Portions of the brittle body stressed above the threshold for fracture then deform inelastically without plastic flow, fracturing according to a binary-cleavage fracture mode which forms particles with
a size distribution described by the lognormal probability function. The size and surface area of the fracture particulate is then completely described by the two parameters of the lognormal distribution, $D_g$ and $\sigma_g$, together with appropriate mean values of surface and volume shape factors. Input kinetic energy for this process is converted to stored elastic work and then to heat.

A typical lognormal graphical analysis of a fracture particulate is shown in Fig. 2. Straight lines show lognormal distributions. The solid line is the cumulative volume (or mass) fraction, $P_v(D)$, of the particles smaller than the size $D$ indicated by the log scale of the abscissa. The ordinate is the cumulative lognormal probability function, in percent (based on the total particle volume of a complete lognormal distribution for all possible values of size $D$). The size $D_g$ corresponding to $P_v(D_g) = 50\%$ is the geometric mean of particle size, distributed by volume, as determined by sieving. The upper-limit size for the lognormally distributed portion of the fracture particulate is $D_L$. The mass median size of the empirical distribution, shown as $\bar{D}$, generally differs from the lognormal mean $D_g$. Generally, $D_g > D_L$, and so the mean $D_g$ has a mathematical but not a physical existence. The largest observed particle size is $D_M$. For reference, the equivalent cubical size of the original body (of volume $V_0$) is shown as $V_0^{1/3}$. The volume fraction of respirable particles is $P_v(D_r)$, where $D_r = 10 \mu m$.

---

* $D_g$ is the geometric mean of the lognormal particle size. $\sigma_g$ is the geometric standard deviation of the lognormal distribution.
Diameters marked $D_{84_s}$, $D_8$, $D_{16}$, $D_{2.3}$, and $D_{0.135}$ correspond to the cumulative 84%, 50%, 16%, 2.3%, and 0.135% volume (mass) fractions along the extended lognormal straight line. The ratios of these diameters define the geometric standard deviation, $\sigma_g$, of the lognormal distribution:

$$\sigma_g = \frac{D_{84_s}}{D_8} = \frac{D_8}{D_{16}} = \frac{D_{16}}{D_{2.3}} = \frac{D_{2.3}}{D_{0.135}}$$

(1)

For a lognormal distribution, the cumulative surface fraction $P_s(D)$ has the same $\sigma_g$ and the same slope as $P_v(D)$. The geometric mean of $P_s(D)$ is $D_{84_s}$ and it is determined by $D_8$ and $\sigma_g$:

$$D_{84_s} = D_8 \sigma_g^{-\ln \sigma_g}$$

(2)

The surface fraction $P_s(D)$ is plotted as a dotted line. The sizes corresponding to 84% and 98% of the cumulative surface fraction are shown as $D_{84_s}$ and $D_{98_s}$. These are also related to $D_8$ and $\sigma_g$ mathematically:

$$D_{84_s} = D_8 \sigma_g^{-\ln \sigma_g}; D_{98_s} = D_8 \sigma_g^{-2\ln \sigma_g}$$

(3)

Typically, the upper-limit lognormal size, $D_L$, lies between particle sizes $D_{84_s}$ and $D_{98_s}$ so that about 90% of the total fracture surface is made up of the lognormally distributed portion of the fracture particulate.

In sieving, the primary measurements are cumulative volumes $V(D_i)$ (actually weights), not volume fractions. These volumes are converted into volume fractions for lognormal analysis by being divided by the total volume of material. Two "total" volumes have been used. One is the total volume of the original impacted body, $V_o$, and the other is the volume of the fracture particulate, $V_p$. So defined, $V_p$ excludes the few very large fragments, which survive impact because they are in low-stress regions. Somewhat arbitrarily, $V_p$ is defined as twice the volume of all particles passing through an 8-mm mesh screen. That is, the two cumulative volume fractions calculated are:

$$P'_v = \frac{V(D)}{V_o}$$

$$P_v = \frac{V(D)}{V_p} = \frac{V(D)}{2V(8 \text{ mm})}$$

(4)

(5)

Both $P_v$ and $P'_v$ have the same points lying on a straight line on the graph. Both show the features indicated in Fig. 2. $P_v$ is, of course, larger than $P'_v$ by a constant factor:

$$P_v = P'_v \left[ \frac{V_o}{2V(8 \text{ mm})} \right]$$

(6)

$P'_v(D)$ is the preferred normalization for use in characterizing impact fragments.
The advantage, if any, of a \( P_v(D) \) plot may be that it is a more generalized characterization of the fracture particulate for specialized impacts of very uneven stress distribution, such as when a cylinder is impacted on a corner and only a local portion of the volume is fragmented. A discussion of the \( P_v(D) \) normalization is given below.

Once the parameters \( D_g \) and \( \sigma_g \) have been determined, the cumulative volume and surface functions, \( V(D) \) and \( S(D) \) can be used:

\[
V(D) = P_v(D)V(\infty),
\]

\[
S(D) = P_S(D)S(\infty).
\]

From Eq. 5, \( V(\infty) = V_p = 2V(8 \text{ mm}) \).

\( V(\infty) \) and \( S(\infty) \) are the mathematically defined (but not physically existing) volume and surface area, respectively, of a complete lognormal distribution with a given \( D_g \) and \( \sigma_g \). A complete distribution is for \( 0 < D < \infty \). \( V(\infty) \) and \( S(\infty) \) are useful as mathematical factors. For example, there is the relation

\[
\frac{S(\infty)}{V(\infty)} = \frac{0.5 \ln \sigma_g}{D_g}
\]

which defines the geometric mean surface/volume shape factor \( a_g \) for the complete distribution. Another useful relation applies to actual (truncated) lognormal distributions as a function of upper-limit size \( D \):

\[
\frac{a(D)}{a_g} = \frac{D S(D)}{a_g V(D)} = f\left(\frac{D}{D_g}, \frac{\sigma}{\sigma_g}\right)
\]

Equation 10 defines shape factors for all lognormal particulates in terms of \( D_g \) and \( \sigma_g \). Plots are given of \( \frac{a(D)}{a_g} \) and of the cumulative surface area fraction \( P_S(D) \) in Fig. 3. The relationships shown define the total surface \( S(D) \) and the total volume \( V(D) \) of any lognormal particulate as a function of size \( D \) in terms of the parameters, \( D_g \), \( \sigma_g \), and \( a_g \). They are used in correlating size data and surface area data obtained experimentally.

The surface/volume shape factors, \( a(D) \) and \( a_g \), were described above. The individual surface and volume shape factors \( a_s \) and \( a_v \) are defined for a single particle of surface area \( S_1 \), volume \( V_1 \), and linear size \( D_1 \):

\[
S_1 = a_s D_1^2; \quad V_1 = a_v D_1^3.
\]

Of course,

\[
\frac{S_1}{V_1} = \frac{a_s}{a_v D_1} = \frac{a_1}{D_1}
\]
Fig. 3. Lognormal Parameters for Fractional Surface Area $P_s(D)$ and Shape Factor $a(D)$ as a Function of Particle Size Parameter, $U_v = (\ln D - \ln D_g) \div \ln \sigma_g$

The mean shape factors are

$$S(\infty) = \bar{a}_s \sum D_i^2$$

(13)

$$V(\infty) = \bar{a}_v \sum D_i^3$$

(14)

Of course,

$$\bar{a}_i = \frac{\bar{a}_s}{\bar{a}_v} = \sigma_g$$

(15)

In summary, fracture particulates can be completely described statistically by the lognormal parameters, $D_g$, $\sigma_g$, and $a_g$. Once the correlations of these parameters are experimentally established in terms of input energy density $\frac{W_i}{V_0}$ (where $W_i$ is the impact energy) and the ratio of maximum stress to threshold stress (determined by the impact configuration), these parameters can be used to predict fracture results for different materials. The relevant
material properties other than the elastic properties are the fracture strength $\gamma_f (J/m^2)$ and the threshold stress for fracture. Other parameters of value in the analysis of particular cases are $D_{98s}/D_g$, $D_{98s}/D_l$, and $V_{(8 \text{ mm})}/V_o$. The fracture surface results are given as $S(D_L)$ and $V_{(10 \mu m)}$, which are, respectively, the cumulative surface area of the lognormal fracture particulate and the cumulative volume of the particulate up to the respirable size, 10 $\mu m$. The fracture strength property $\gamma_f$ is defined by

$$
\frac{S(D_L)}{V_o} = \frac{\epsilon W_i}{V_o \gamma_f}
$$

(16)

where $\epsilon$ is the efficiency of utilization of this energy for fracture and $V_o$ is the volume of the body impacted.

D. Reanalysis of PNL Data of Full-Scale Canister Impact Test

A PNL report [CHAPMAN, p. 39] discussed the drop test of a 0.61-m-dia waste-glass canister from a height of 7.6 m. Only glass in the immediate area of the impact was fractured and characterized, and only a limited amount of particle size data were presented for the tests. It was reported that 1.32 wt % of the glass particles in the impacted zone was smaller than 44 $\mu m$ and that the mass median (screen) size was 3.72 mm. No other data were presented.

A subsequent report [ROSS, p. 63] presented further data on this 7.6-m drop test. The carbon steel canister had a 0.6-cm-thick wall and a hemispherical bottom. Sedimentation analysis of the smaller than 44 $\mu m$ fraction collected from the fragments (i.e., from the 1.32 wt % described above) gave a value for fragments smaller than 10 $\mu m$ in size of 0.13 wt % of the glass in the impacted zone. The sieved particle size data for six cumulative weight fractions of the impact-fractured glass were also given. These data were plotted on graph paper with logarithmic coordinates, as shown in the upper curve of Fig. 4. The lower curve in the figure represents data reported for typical preimpact fracture of the glass due to thermal stresses during cooling. These curves show quantitatively the higher fraction of material of a given particle size as a result of the impact fracture of the waste-glass canister. It is notable that extrapolation of the log-log sieving data of the upper curve down to a 10-$\mu m$ size would not appear to agree with the sedimentation measurement.

All data points from Fig. 4 were replotted on a lognormal probability graph in Fig 5. Evidently, lognormal analysis is applicable throughout the size range, and shows that the extrapolated sieving data closely agrees with the sedimentation measurement of the 10-$\mu m$ fraction, namely, 0.13%. From the lognormal relationships presented in the previous section, the surface area distribution $P_S(D)$ described in Fig. 2 was calculated and plotted in Fig. 5. About 97% of the total surface area is in the lognormally distributed particle sizes—that is, the particles smaller than about 4 mm.
For this full-scale PNL test, the lognormal parameters, impact conditions, and material properties are summarized in Table 5. Properties reported for PNL glass are also given and are compared with those for Pyrex glass. Yet to be obtained is information on the total amount of material analyzed for fragment sizes. If it were available, direct comparison with our small-scale tests with Pyrex would be possible.

E. Applicability of Impact Tests to Glass and Several Crystalline Materials

To examine the versatility of the brittle fracture in methodology, seven materials of quite different compositions have been impact-tested under similar conditions. Drop-weight impacts of 1.2 J/cm$^3$ were applied to the sides of cylindrical specimens 1.4 cm to 3.8 cm in diameter. Descriptions of materials are given in Table 6. The Pyrex, quartz, and UO$_2$ specimens are essentially fully consolidated materials without grain separations. Such materials tend to fracture across grain boundaries, so that the differences between crystaline and vitreous structures are not important. MACOR is a glass-ceramic—that is, it is recrystallized from the vitreous state. It contains a mica-like second phase which acts to stop crack propagation, making it machinable. Sandstone is a conglomerate of fairly uniform separate grains of silica sand which are rather weakly cemented together by a second phase. Nepheline syenite is an alkali aluminosilicate mineral of a common type in plutonic...
Fig. 5. Lognormal Analysis of Particle-Size Data Reported by PNL for 0.61-m-dia Canister of Glass (before and after being dropped from 7.6 m onto an unyielding surface). The symbols are defined as follows: $D_g$ is the geometric mean particle size; $D_{gs}$ is the geometric mean of the surface distribution; $D_L$ is the value of $D$ at which the points begin to deviate from log-normal; $P_V(D)$ is the cumulative fraction of material volume as a function of $D$; $P_S(D)$ is the cumulative fraction of total surface area as a function of $D$; and $D_{97S}$ is the value of $D$ for which the cumulative surface is 97% of the total surface area.
Table 5. Parameters of Full-Scale Canister Test

Canister of carbon steel pipe: 0.161-m OD; length, 2.4 m; wall thickness, 0.64 cm; internal volume, 0.767 m³; hemispherical bottom.

Impact test: 7.62-m free-fall to steel target; impact energy, $1.32 \times 10^5$ J; energy density, $2.1 \times 10^5$ J/m³; Waste glass: 1520 kg, 0.626 m³.

<table>
<thead>
<tr>
<th>Glass Properties</th>
<th>PNL Glass</th>
<th>Pyrex (for comparison)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2.43 g/cm³</td>
<td>2.24 g/cm³</td>
</tr>
<tr>
<td>Young's modulus, $E$</td>
<td>$7.7 \times 10^{10}$ Pa</td>
<td>$7.0 \times 10^{10}$ Pa</td>
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<tr>
<td>Fracture stress, $\sigma_t$</td>
<td>$3.8 \times 10^8$ Pa</td>
<td>$3.0 \times 10^8$ Pa</td>
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Lognormal Parameters

<table>
<thead>
<tr>
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<th>Preimpact</th>
<th>Postimpact</th>
</tr>
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<tbody>
<tr>
<td>Original size, $V_o$ (m³)</td>
<td>0.626</td>
<td>0.626</td>
</tr>
<tr>
<td>$(V_o)^{1/3}$</td>
<td>0.86</td>
<td>0.86</td>
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<tr>
<td>Maximum particle size, $D_M$ (m)</td>
<td>$7.0 \times 10^{-2}$</td>
<td>$2.0 \times 10^{-2}$</td>
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<tr>
<td>Upper-limit size of lognormal particles, $D_L$ (m)</td>
<td>$7.0 \times 10^{-3}$</td>
<td>$4.0 \times 10^{-3}$</td>
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<tr>
<td>Geometric mean size, $D_g$ (m)</td>
<td>1.6</td>
<td>$3.4 \times 10^{-3}$</td>
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<tr>
<td>Geometric standard deviation, $\sigma_g$</td>
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<td>6.54</td>
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<tr>
<td>Size for 97% of total particle surface area, $D_{97s}$</td>
<td>-</td>
<td>$3.4 \times 10^{-3}$</td>
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<tr>
<td>Energy density, J/m³</td>
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<td>$2.1 \times 10^5$</td>
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Table 6. Materials in Tests

<table>
<thead>
<tr>
<th>Material</th>
<th>Type of Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pyrex glass</td>
<td>vitreous borosilicate</td>
</tr>
<tr>
<td>2. Fused quartz</td>
<td>vitreous silica</td>
</tr>
<tr>
<td>3. Crystalline quartz</td>
<td>single crystal (silica)</td>
</tr>
<tr>
<td>4. UO₂</td>
<td>microcrystalline; 97% theor. density</td>
</tr>
<tr>
<td>5. MACOR</td>
<td>machinable glass-ceramic</td>
</tr>
<tr>
<td>6. Nepheline syenite</td>
<td>coarse-grained alkalic feldspar</td>
</tr>
<tr>
<td>7. Sandstone</td>
<td>cemented silica grains</td>
</tr>
</tbody>
</table>

rocks, i.e., rocks formed deep underground at high temperature and high pressure but later metamorphosed to some degree. This mineral has coarse crystal grains with well-defined grain boundaries. It is found that the material is mechanically weak at the grain boundaries, and fracture can occur there.

A summary of the lognormal parameters derived from graphical analysis of the particle-size distributions is given in Table 7. These parameters were based on the complete specimen volume, $V_o$; i.e., $P_{V_0}(D) = V(D)/V_o$. The combined plot of the lognormal portion of these distributions is shown in Fig. 6. In each case, these straight-line lognormal size distributions are terminated at the upper-limit size $D_L$, as indicated by the sieving analysis. In Table 7 and especially in Fig. 6, the similarities and differences in fracture behavior are quite clear. Conclusions are summarized as follows:

1. The similar slopes indicate similar values of $\sigma_g$, the geometric standard deviation of particle size, from the mean size, $D_g$. Similar values of $\sigma_g$ are consistent with similar stress distributions and similar mechanical properties of the material, as expected for the similar impact configurations in these tests.

2. The line that is uppermost in the plot (sandstone S-1) indicates a (relative) lower resistance to fracture, and implies a lower value of $\gamma_f$ ($J/m^2$), the energy-surface strength property of the specimen. The line lowermost (for MACOR) indicates a (relative) higher resistance to fracture and a higher value of $\gamma_f$.

3. Pyrex, quartz (vitreous and crystalline), UO₂, and nepheline syenite all show similar resistance to fracture. However, nepheline syenite has a markedly lower size limit, $D_L$. This is expected, since the well-defined crystal grains are in the size range of 0.3 to 2 mm and considerable fracture occurs along the grain boundaries (transgranular).
<table>
<thead>
<tr>
<th>Material</th>
<th>Vo, m$^3$</th>
<th>Wi, J</th>
<th>DM, m</th>
<th>DL, m</th>
<th>DG, m</th>
<th>σg</th>
<th>DBG, m</th>
<th>Dg8S, m</th>
<th>PV(10 µm)</th>
<th>PS(Dg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrex-1</td>
<td>P-1</td>
<td>7.3 x10^{-5}</td>
<td>88</td>
<td>1.8 x10^{-2}</td>
<td>7.0 x10^{-3}</td>
<td>1.1 x10^{-2}</td>
<td>6.5</td>
<td>4.2 x10^{-4}</td>
<td>1.1 x10^{-2}</td>
<td>6 x10^{-5}</td>
</tr>
<tr>
<td>Pyrex-2</td>
<td>P-2</td>
<td>3.2 x10^{-5}</td>
<td>38</td>
<td>8 x10^{-3}</td>
<td>3.0 x10^{-3}</td>
<td>1.4 x10^{-2}</td>
<td>7.8</td>
<td>2.1 x10^{-4}</td>
<td>1.3 x10^{-2}</td>
<td>2.0 x10^{-4}</td>
</tr>
<tr>
<td>Fused quartz-1</td>
<td>F-1</td>
<td>3.86 x10^{-5}</td>
<td>46</td>
<td>1.4 x10^{-2}</td>
<td>1.9 x10^{-3}</td>
<td>2.7 x10^{-2}</td>
<td>9.6</td>
<td>1.6 x10^{-4}</td>
<td>1.5 x10^{-2}</td>
<td>2.2 x10^{-4}</td>
</tr>
<tr>
<td>Fused quartz-2</td>
<td>F-2</td>
<td>3.9 x10^{-5}</td>
<td>47</td>
<td>1.9 x10^{-3}</td>
<td>1.5 x10^{-3}</td>
<td>2.1 x10^{-2}</td>
<td>8.75</td>
<td>1.9 x10^{-4}</td>
<td>1.46 x10^{-2}</td>
<td>2.3 x10^{-4}</td>
</tr>
<tr>
<td>Crystalline quartz</td>
<td>C-1</td>
<td>5.78 x10^{-5}</td>
<td>70</td>
<td>8.0 x10^{-3}</td>
<td>2.4 x10^{-3}</td>
<td>2.9 x10^{-2}</td>
<td>8.5</td>
<td>2.9 x10^{-4}</td>
<td>2.1 x10^{-2}</td>
<td>1.7 x10^{-4}</td>
</tr>
<tr>
<td>UO$_2$-1</td>
<td>U-1</td>
<td>2.0 x10^{-6}$^a$</td>
<td>7.2</td>
<td>1.1 x10^{-2}</td>
<td>1.0 x10^{-2}</td>
<td>1.8 x10^{-2}</td>
<td>8.18</td>
<td>2.1 x10^{-4}</td>
<td>1.1 x10^{-2}</td>
<td>2 x10^{-4}</td>
</tr>
<tr>
<td>UO$_2$-2</td>
<td>U-2</td>
<td>2.0 x10^{-6}$^a$</td>
<td>7.2</td>
<td>1.1 x10^{-2}</td>
<td>1.7 x10^{-3}</td>
<td>3.2 x10^{-2}</td>
<td>9.4</td>
<td>2.1 x10^{-4}</td>
<td>1.9 x10^{-2}</td>
<td>2 x10^{-4}</td>
</tr>
<tr>
<td>MACOR-1</td>
<td>M-1</td>
<td>3.5 x10^{-5}</td>
<td>42</td>
<td>8.0 x10^{-3}</td>
<td>3.4 x10^{-3}</td>
<td>1.1 x10^{-1}</td>
<td>10.0</td>
<td>5.5 x10^{-4}</td>
<td>5.5 x10^{-2}</td>
<td>4 x10^{-5}</td>
</tr>
<tr>
<td>MACOR-2</td>
<td>M-2</td>
<td>8.4 x10^{-6}</td>
<td>11</td>
<td>1.6 x10^{-2}</td>
<td>6.0 x10^{-3}</td>
<td>2.0 x10^{-1}</td>
<td>14.2</td>
<td>1.8 x10^{-4}</td>
<td>3.5 x10^{-2}</td>
<td>9 x10^{-5}</td>
</tr>
<tr>
<td>Nepheline syenite-1</td>
<td>N-1</td>
<td>3.1 x10^{-5}</td>
<td>37</td>
<td>2.2 x10^{-2}</td>
<td>3.4 x10^{-4}</td>
<td>1.5 x10^{-2}</td>
<td>8.9</td>
<td>1.3 x10^{-4}</td>
<td>1.1 x10^{-2}</td>
<td>1.5 x10^{-4}</td>
</tr>
<tr>
<td>Nepheline syenite-2</td>
<td>N-2</td>
<td>3.1 x10^{-5}</td>
<td>37</td>
<td>2.6 x10^{-2}</td>
<td>3.0 x10^{-4}</td>
<td>1.7 x10^{-2}</td>
<td>8.10</td>
<td>2.1 x10^{-4}</td>
<td>1.4 x10^{-2}</td>
<td>1.3 x10^{-4}</td>
</tr>
<tr>
<td>Sandstone</td>
<td>S-1</td>
<td>1.72 x10^{-5}</td>
<td>21</td>
<td>8.0 x10^{-3}</td>
<td>1.5 x10^{-4}</td>
<td>7.0 x10^{-3}</td>
<td>7.8</td>
<td>1.0 x10^{-4}</td>
<td>6.3 x10^{-3}</td>
<td>6.0 x10^{-4}</td>
</tr>
</tbody>
</table>

$^a$Total Vo consisted of three pellets, each of the stated volume.
However, most of the surface area (about 90%) of the fracture particulate for nepheline syenite is provided by the lognormal particulate, since the relatively large size of the grains contributes a lower surface/volume ratio to the total fracture particulate.

4. The volume fraction of respirable fines (those smaller than 10 μm) varies inversely with the resistance to fracture. Common glasses and ceramics differ little; only the unusually strong or weak composite or conglomerate materials (MACOR or sandstone) show significant differences, less than one order of magnitude, in respirable fractions.

5. Total surface areas represented by $P_s(D_L)$ in Table 7 may be compared; this parameter is the cumulative fraction of surface area of the physical lognormal particulate (for all particle sizes up to $D_L$), relative to the total surface area of a (hypothetical) complete lognormal distribution for the given $D_g$ and $\sigma_g$. The size $D_{98_s}$ in the table indicates the particle size $D$ below which 98% of the surface area of a complete distribution is accounted for. For all materials except sandstone and nepheline syenite, the lognormal particulate makes up more than about 80% of the total physical particulate surface area. Even for the two exceptions, the lognormal particulate makes up more than 60% of the total surface area.
The fracture particulates of sandstone and nepheline syenite show an unusually low upper-limit size, $D_L$, for the lognormal distributed portion of the total particulate. The actual departures from lognormality for these two specimens are shown in Fig. 7, where the cumulative volume fractions are plotted as $P_V = \frac{V(D)}{2V(8\,\text{mm})}$ and where the sizes from sieve analysis are shown above $D_L$ up to 3 mm. The departures occur in the size ranges associated with grain sizes; this will be examined further. The lognormal size limit $D_L$ is marked, and the sizes corresponding to 50%, 84%, and 98% of the total particulate surface area are marked as $D_{50}$, $D_{84}$, and $D_{98}$, respectively.

![Fig. 7. Particle Size Distributions for Nepheline Syenite and Sandstone up to 8-mm Diameter](image)

From Fig. 7 it is estimated that for nepheline syenite and sandstone, respectively, the non-lognormal particulate contributes surface area of about 10% and 35% of the lognormal particulate. When this correction is made, a relative fracture strength $\gamma_f$ can be calculated for the specimens from the lognormal surface-area properties, if it is assumed that the shape factor $\alpha_g$ and the efficiency of impact energy utilization is the same for all specimens. These relative strengths are shown in Table 8. Since for Pyrex and crystalline quartz, $\gamma_f$ has been found to be 80 J/m$^2$, the $\gamma_f$ for other materials can be estimated from Table 8.

It was observed that the fraction of respirable fines $P_V(10\,\mu\text{m})$ correlates with energy density, $\gamma_f$, $\alpha_g$, and $\sigma_g$ to within a factor of two for all materials. These preliminary correlations are to be established in further tests.
Table 8. Estimated Relative Impact Strengths for Various Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative Fracture Strength, $Y_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MACOR (glass-ceramic)</td>
<td>1.4</td>
</tr>
<tr>
<td>Pyrex</td>
<td>1.0</td>
</tr>
<tr>
<td>Crystalline quartz</td>
<td>1.0</td>
</tr>
<tr>
<td>Uranium dioxide (reactor grade)</td>
<td>0.6</td>
</tr>
<tr>
<td>Fused quartz</td>
<td>0.7</td>
</tr>
<tr>
<td>Nepheline syenite (typical)</td>
<td>0.7</td>
</tr>
<tr>
<td>Sandstone (typical)</td>
<td>0.4</td>
</tr>
</tbody>
</table>

F. Preliminary Results of Corner Impacts

In most impact tests, a cylinder is impacted diametrically by the hardened steel plane surfaces of the drop-weight device. The maximum stresses for this configuration are higher than for an impact (axially) squarely on the flat end of a cylinder. However, the maximum stresses for a corner impact of a cylinder are much higher than for either of the others. Although the input energy density is relatable to a measure of the average stress in the body volume, the maximum stress and the distribution of stress levels vary at these different impact configurations.

In order to examine the differences of particle-size distributions for corner-impact configurations, two special Pyrex specimens were made: (1) a 38-mm-dia cylinder with one end formed into a 90° cone; (2) a 45° slice of a standard 38-mm-dia cylinder. These specimens were impacted squarely in the drop-weight device on the apex of the cone and the corner of the cylinder slice. The results at an input energy density of 0.42 J/cm$^3$ were that 1.4 wt % of the 68 cm$^3$ conical cylinder and 2.2 wt % of the 21 cm$^3$ corner slice were fragmented into particles smaller than 8 mm. In comparison, side impacting of a 73-cm$^3$ cylinder at the same impact energy density resulted in 28% fragmentation into particles of this size. The particle size distributions were compared after sieving and by calculating the cumulative volume fractions as a function of size in two ways: (1) as a fraction of the total initial specimen volume, $V_0$, and (2) as a fraction of the total particulate (assumed to be twice the volume of all particles that passed through an 8-mm mesh opening). The plots made by the second method are shown in Fig. 8 for the three different impact configurations at the same impact energy density--0.42 J/cm$^3$. The straight lines for particles smaller than 4 mm indicate lognormal particle-size distributions. The convergence of the plotted data points at 50% volume is a result of the method of data normalization; this point is related to the specimen volume by the fraction $2V(8\text{ mm})/V_0$ indicated in the key of Fig. 8. The ratio $2V(8\text{ mm})/V_0$ is a parameter characterizing the impact fracture and related size fraction $P(D)$ to the total volume, $V_0$, of the impacted body.
Fig. 8. Comparison of Fracture Particulates for Pyrex Specimens of Three Different Configurations Impacted at 0.42 J/cm³

The cone end and cylinder corner impacts show similar slopes and, therefore, similar geometric standard deviations of particle size. The greater slope of the diametrial (side) impact indicates the more uniform stress distribution and the more uniform degree of fragmentation over the specimen volume. Additional tests and evaluations are in progress to compare fracture results for different configurations.
A. Introduction

Dispersion of wastes into the biosphere by the transfer of radionuclides from a solid phase to a mobile aqueous phase (i.e., by leaching) is most commonly accepted to be the principal potential hazard of nuclear waste disposal. Characterization of waste forms requires the use of sensitive methods to obtain dispersion data of low-rate phenomena. Neutron activation analysis (NAA) has been shown to be applicable for the determination of leach rates [STEINDLER-1979B]. Correlations of data obtained by use of radioactive tracers are needed for applications in which NAA is not practical. In addition, NAA is likely to be useful in characterization studies (other than studies of leach rates) needed to describe the performance of waste forms.

The general objective of this program is to develop techniques and qualify methods that utilize neutron activation analysis and radioactive tracers for characterizing simulated waste forms. Comparison of characterization test results obtained using these two methods and with other existing characterization data will be used to specify conditions 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 advanced waste forms.

Major goals are completion of the development of the NAA method for leach-rate determinations, definition of the accuracy and limitations of the method, and establishment of the applicability of the test results to larger-scale waste forms. Radioactive tracers will be added to simulated glass waste because some elements cannot be studied with NAA. The simultaneous use of selected tracers and NAA for the same sample will permit the direct comparison of the behavior of elements from different origins; the study of selected polyvalent elements will be of most interest and importance. Radiochemical techniques and beta-counting will be used to enhance the sensitivity of characterization methods.

B. Experimental Radiochemical Techniques
(K. F. Flynn)

1. Studies of Borosilicate Glass

Comparisons of leach rates of borosilicate glass based on neutron activation* with those based on radioactive spiking techniques require that a satisfactory method for manufacturing suitable glass samples on a laboratory scale be developed. Pursuant to this goal, a study has been made using crucibles of various materials. High-purity Al₂O₃ crucibles may be satisfactory, but some Al₂O₃ dissolves in the glass melt. Platinum crucibles are acceptably inert, but since the glass wets the surface, it is difficult to remove on cooling. Platinum 60%-rhodium 40% alloy is advertised to be a nonwetting crucible material.

*Neutron activation of a sample precedes leaching.
Radioactive tracers for the spiking experiments and the necessary chemical reagents for incorporation into the glass melt have been obtained from various suppliers. The high-temperature furnace to be used for the production of radioactive samples has been received.

Initial tracerglass studies will be made using glass based on frit compositions used by the SRL for defense waste glass. A quantity of SRL frit 211 is being obtained for this purpose. Some preliminary measurements of the leaching characteristics of SRL frit 211, using the neutron activation technique (FLYNN), have been made. The results are given in Table 9. Since cesium, zinc, and cobalt were not deliberately incorporated into this glass and hence are only present as trace contaminants, the high leach rate observed for cesium cannot be judged unambiguously. The cesium leach rate will be remeasured using SRL frit 211 glass containing added cesium to unambiguously establish the leaching characteristics.

Table 9. Leach Rates\(^a\) for Neutron-Irradiated SRL Frit 211\(^b\) Glass Containing Trace Unknown Amounts of Cesium, Zinc, and Cobalt

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Leach Rate, g/cm(^2)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{54})Mn</td>
<td>4.7 E-6</td>
</tr>
<tr>
<td>(^{60})Co</td>
<td>5.6 E-6</td>
</tr>
<tr>
<td>(^{65})Zn</td>
<td>7.3 E-6</td>
</tr>
<tr>
<td>(^{134})Cs</td>
<td>1.2 E-3</td>
</tr>
</tbody>
</table>

\(^a\)Static fourteen-day test at 70°C and 40 mL leachant.

\(^b\)0.55-g sample with 2.7-cm\(^2\) geometric surface area; composition is given in Table 16.

Pursuant to the continued studies of leach rates of proposed waste forms, the Materials Characterization Center (MCC) at Battelle Pacific Northwest Laboratories (PNL) is issuing standard test methods to allow better comparison of leach results from various laboratories. Among the variables that must be identified are leachant purity and leachant hydrogen ion concentration (pH).

A dual ion-exchange column to make deionized water has been installed in series with the tap distilled water as a source of our leachant. A Cole-Parmer Universal/Research deionizing system was used. The product water from this system was analyzed by the Argonne National Laboratory (ANL) Analytical Chemistry Laboratory (ACL) and was found to have less than 0.55 \(\mu\)mho conductivity. This value represents the limit of their analytical detection. A conductivity meter has been installed in series with the ion-exchange column effluent for continuous monitoring of water purity.
The pH's of a variety of leaching media used in these studies have been measured. These data are reported in Table 10. The pH of leaching media at room temperature varied between three and nine. The effect of air equilibration is to increase the CO₂ concentration and hence decrease the pH. For example, the pH of deionized water shifts from 6.0 to 5.3 when the water is equilibrated with air. Saturating the water with CO₂ at room temperature can reduce the pH to the range of about 3 (Table 10). The presence of borosilicate glass tends to increase the pH.

<table>
<thead>
<tr>
<th>Aqueous Medium</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard buffer (pH 10)</td>
<td>10.0</td>
</tr>
<tr>
<td>Standard buffer (pH 4)</td>
<td>4.0</td>
</tr>
<tr>
<td>Deionized water (fresh)</td>
<td>6.0</td>
</tr>
<tr>
<td>Deionized water (air-equilibrated)</td>
<td>5.3</td>
</tr>
<tr>
<td>Lab distilled water</td>
<td>5.3</td>
</tr>
<tr>
<td>Deionized water (CO₂ saturated)</td>
<td>3.2</td>
</tr>
<tr>
<td>Lab tap water</td>
<td>9.0</td>
</tr>
<tr>
<td>Climax granite equilibrated water</td>
<td>7.7</td>
</tr>
<tr>
<td>Deionized water in 304 L stainless</td>
<td>7.1</td>
</tr>
<tr>
<td>Deionized water/Wipp salt saturated</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Samples in polypropylene containers.

The data in Table 10 indicate that most of leaching media used in laboratory studies (e.g., deionized water) have pH values below neutral (i.e., 5 to 7); however, most groundwater systems have pH values above neutral (i.e., 7 to 9).

2. SYNROC

Investigations are continuing of the leaching characteristics of waste form alternatives to borosilicate glass. Among the alternative waste forms under consideration, SYNROC [RINGWOOD] is a prime candidate. Leach testing of SYNROC-type materials prepared by the Materials Science Division (MSD) of Argonne National Laboratory (ANL) is progressing. Time sequential tests of a variety of these materials are being conducted at 25°C, 75°C, and 200°C. These materials represent both single phases and composites and have been prepared using both sintering and hot pressing procedures. The leach rates determined in these studies are based on neutron activation techniques [FLYNN].
Samples of individual mineral phases—namely, hollandite (HSN-2), zirconolite-uranium doped (ZU19-HR-1-R), perovskite (CT3HP-1), and calcium/strontium titanate (CT 3-1-6 and CT 10-1-6)—were neutron-activated and leach tested. The compositions and methods of fabrication of these samples are as follows:

**HSN-2**

(0.97 BaO, 0.03 Cs2O)·1.14 Al2O3·6.82 TiO2 powder calcined at 925°C in air for 16 h, fired at 1250°C in air for 1 h. Note—only 60% dense, and two phases were present (TiO2 and hollandite).

**ZU19-HR-1-R**

(Ca0.97U0.03)ZrTiO7·03 powder, calcined at 900°C for 64 h in CO2/CO = 7. Pellets hot-pressed in a graphite die at 1300°C for 1 h under 82700 kPa (1200 psi), then refired at 1425°C for 24 h in CO2/CO = 7.

**CT3HP-1**

(Ca0.97Sr0.03)TiO3 powder, calcined at 950°C for 40 h in air. Pellets then fired at 1300°C for 24 h in air, crushed, then hot-pressed in a graphite die at 1300°C for 3 h under 11,000 kPa (1600 psi).

**CT 3-1-6**

(Ca0.97Sr0.03)TiO3 powder, calcined at 950°C for 40 h in air. Pellets then fired at 1450°C for 24 h in air.

**CT 10-1-6**

(Ca0.90Sr0.10)TiO3 powder, calcined at 950°C for 40 h in air. Pellets then fired at 1450°C for 24 h in air.

The significant activated species in the CT 3-1-6 and CT 10-1-6 solid samples, together with the specific activity for each radioisotope (in disintegrations per minute per gram of sample, dpm/g, are added to previously reported data [STEINDLER-1980] in Table 11. Sequential leach rate data for single-phase samples in addition to those presented earlier [STEINDLER-1980] are tabulated in Table 12 and 13.

Samples of composite (i.e., multiple-phase) SYNROC material identified as NCMOD-10 and SRB-R5 have also been neutron-activated and leach-tested. The composition and method of fabrication of these samples is as follows:

**NCMOD-10**

Doped SYNROC B [RINGWOOD], fabricated at North Carolina State University. Powder calcined at 800°C in air. Pellet then fired at 1220°C for 8 h in Ar-4% H2.

**SRB-R5**

TiO2(60)-Al2O3(13)-ZrO2(9)-CaO(11)-BaO(3.6)-Ni(0.4)-Cs2O(4) as Cs2NO3. Powder was ball-milled and hot pressed at 1400°C for 6 h under 10300 kPa (1500 psi) in graphite die. Note—X-ray analysis shows perovskite, zirconolite, and a Cs-Ba-Ti phase that is not hollandite.

The significant activated species in these composites, together with the specific activity (dpm/g) for each radioisotope, are given in Table 14. The sequential leach rate data for these composites are tabulated in Table 15.
Table 11. Activated Species\textsuperscript{a} in SYNROC Mineral Phases

<table>
<thead>
<tr>
<th>Activation Product</th>
<th>Specific Activity, dpm/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HSN-2</td>
</tr>
<tr>
<td>(^{46}\text{Sc})</td>
<td>6.8E+6</td>
</tr>
<tr>
<td>(^{75}\text{Se})</td>
<td>--</td>
</tr>
<tr>
<td>(^{85}\text{Sr})</td>
<td>--</td>
</tr>
<tr>
<td>(^{95}\text{Zr})</td>
<td>--</td>
</tr>
<tr>
<td>(^{124}\text{Sb})</td>
<td>--</td>
</tr>
<tr>
<td>(^{131}\text{Ba})</td>
<td>4.9E+8</td>
</tr>
<tr>
<td>(^{134}\text{Cs})</td>
<td>3.4E+8</td>
</tr>
<tr>
<td>(^{141}\text{Ce})</td>
<td>--</td>
</tr>
<tr>
<td>(^{181}\text{Hf})</td>
<td>--</td>
</tr>
<tr>
<td>(^{182}\text{Ta})</td>
<td>--</td>
</tr>
<tr>
<td>(^{237}\text{U})</td>
<td>--</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Based on a 4-h irradiation at \(3 \times 10^{13}\) n/cm\(^2\) s (neutron fluence, \(4 \times 10^{17}\) n/cm\(^2\)); dpm is based on time at end of irradiation.

For the purpose of preliminary leach rate evaluations of SYNROC type materials, radioisotopes such as \(^{46}\text{Sc}\) [produced by the (\(n, p\)) reaction of Ti], \(^{95}\text{Zr}\) [from (\(n, \gamma\)) on Zr] and \(^{181}\text{Hf}\) [from (\(n, \gamma\)) on Hf] may be somewhat representative of the matrix material. The elements, strontium (\(^{85}\text{Sr}\)), cesium (\(^{134}\text{Cs}\)), and europium (\(^{152}\text{Eu}\)), are representative of the nuclear waste materials. The leach rates for the alkaline metal element, cesium, are of primary concern in establishing the integrity of the waste form since this element is the most leachable of the hazardous radionuclides present in the high-level waste (HLW). Weight loss data from these tests are each based on a small difference between large numbers and at best can be considered an upper limit for the leach rate of the matrix material.

Leach rate evaluations as determined in these studies are based on the assumption that the solid material can be considered semiinfinite with respect to the leaching medium [LERCH]. This assumption is valid as long as the fraction leached is relatively small (e.g., fraction leached \(< 0.10\)). This leach fraction (0.10) would correspond to a leach rate of about \(10^{-3}\) g/cm\(^2\) d for a 0.3-g sample of 3 cm\(^2\) surface area leached for 10 days. Conversely, any time the cumulative fraction leached exceeds 0.10, the material would be considered soluble (dissolved) for all practical purposes; hence, the concept of leach rate would lose its meaning in a practical sense. A primary goal of these studies is to measure relatively low leach rates with confidence and precision in order that informed conclusions regarding long-term release behavior can be drawn.
Table 12. Leach Rates for SYNROC (Single Mineral Phases), Using Distilled Water at the Indicated Temperatures—Samples CT 3-1-6, CT 10-1-6, and CT3HP-1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Leach No.</th>
<th>Time, d</th>
<th>Temp, °C</th>
<th>Leach Rate, b g/cm²d</th>
<th>⁴⁶Sc</th>
<th>⁸⁵Sr</th>
<th>Wt Loss</th>
<th>⁹⁵Zr</th>
<th>¹⁸¹Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT 3-1-6</td>
<td>1</td>
<td>7</td>
<td>25</td>
<td>4.3E-7</td>
<td>1.2E-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>36</td>
<td>25</td>
<td>1.0E-7</td>
<td>1.7E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>57</td>
<td>25</td>
<td>&lt;1.0E-7</td>
<td>1.2E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cum.</td>
<td>100</td>
<td></td>
<td>1.2E-7</td>
<td>2.1E-6</td>
<td>&lt;1E-6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CT 10-1-6</td>
<td>1</td>
<td>7</td>
<td>75</td>
<td>1.0E-7</td>
<td>2.0E-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>36</td>
<td>75</td>
<td>1.5E-7</td>
<td>2.6E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>57</td>
<td>75</td>
<td>4.2E-7</td>
<td>1.6E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cum.</td>
<td>100</td>
<td></td>
<td>3.0E-7</td>
<td>3.2E-6</td>
<td>&lt;1E-6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CT3HP-1</td>
<td>1</td>
<td>13.8</td>
<td>25</td>
<td>&lt;1.0E-7</td>
<td>6.6E-7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>57</td>
<td>25</td>
<td>4.7E-8</td>
<td>&lt;1E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>13.8</td>
<td>75</td>
<td>6.4E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>57</td>
<td>75</td>
<td>8.0E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>54.1</td>
<td>75</td>
<td>2.4E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cum.</td>
<td>125</td>
<td></td>
<td>5.4E-6</td>
<td>&lt;1E-6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>14.4</td>
<td>200</td>
<td>7.5E-4</td>
<td>6.4E-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 13. Leach Rates for SYNROC (Single Mineral Phases), Using Distilled Water at the Indicated Temperatures—Samples HSN-2 and ZU19-HR-1-R

<table>
<thead>
<tr>
<th>Sample</th>
<th>Leach No.</th>
<th>Time, d</th>
<th>Temp, °C</th>
<th>Leach Rate, $g/cm^2d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^{95}$Zr</td>
</tr>
<tr>
<td>HSN-2</td>
<td>1</td>
<td>13.8</td>
<td>25</td>
<td>$4.0E-4$</td>
</tr>
<tr>
<td>(3.3cm$^2$/0.3g)</td>
<td>2</td>
<td>57</td>
<td>25</td>
<td>$5.9E-5$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>54</td>
<td>25</td>
<td>$2.3E-5$</td>
</tr>
<tr>
<td></td>
<td>Cum.</td>
<td>125</td>
<td></td>
<td>$8.1E-5$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>13.9</td>
<td>75</td>
<td>$1.3E-3$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>57</td>
<td>75</td>
<td>$1.8E-5$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>54.9</td>
<td>75</td>
<td>$1.5E-6$</td>
</tr>
<tr>
<td></td>
<td>Cum.</td>
<td>126</td>
<td></td>
<td>$1.5E-4$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>14.4</td>
<td>200</td>
<td>$4.9E-4$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13.8</td>
<td>200</td>
<td>$&gt;0.9$</td>
</tr>
<tr>
<td>ZU19-HR-1-R</td>
<td>1</td>
<td>13.8</td>
<td>25</td>
<td>$8.8E-8$</td>
</tr>
<tr>
<td>(2cm$^2$/0.5g)</td>
<td>2</td>
<td>57</td>
<td>25</td>
<td>$0.8E-8$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>54.1</td>
<td>25</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Cum.</td>
<td>125</td>
<td></td>
<td>$1.3E-8$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>13.9</td>
<td>75</td>
<td>$1.2E-7$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>57</td>
<td>75</td>
<td>$1.5E-8$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>54.9</td>
<td>75</td>
<td>$4.1E-8$</td>
</tr>
<tr>
<td></td>
<td>Cum.</td>
<td>126</td>
<td></td>
<td>$3.8E-8$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>14.4</td>
<td>200</td>
<td>$2.1E-6$</td>
</tr>
</tbody>
</table>

The data presented in Table 12 indicate that the matrix material for these single mineral phases (as exemplified by the leach rates for $^{46}$Sc) are indeed low. The leach rates for strontium (the only waste material included in these samples) are somewhat higher (i.e., about one order of magnitude) but are still competitive with the leach rate of borosilicate glass. The sequential leach rates for the matrix element (i.e., $^{46}$Sc) are constant with time.

After a somewhat higher initial leach rate (i.e., during the initial 7-day test), the $^{85}$Sr leach rates become constant with time, indicating that this waste element was successfully incorporated into the mineral phase. However, it should be reiterated that the $^{85}$Sr leaches about one order of magnitude faster than the matrix material, indicating some mechanistic difference. The hot-pressed material (CT3HP-1) has a somewhat lower leach rate (by about a factor of two) than the sintered materials (CT 3-1-6 and CT 10-1-6).
Table 14. Activated Species\textsuperscript{a} in SYNROC Composites

<table>
<thead>
<tr>
<th>Activation Product</th>
<th>Specific Activity, dpm/g</th>
<th>NCMOD-10</th>
<th>SRB-R5</th>
</tr>
</thead>
<tbody>
<tr>
<td>4\textsuperscript{6}Sc</td>
<td>4.8E+6</td>
<td>4.9E+6</td>
<td></td>
</tr>
<tr>
<td>5\textsuperscript{4}Mn</td>
<td>8.4E+4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5\textsuperscript{9}Fe</td>
<td>4.3E+5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8\textsuperscript{5}Sr</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9\textsuperscript{5}Zr</td>
<td>1.3E+7</td>
<td>4.2E+6</td>
<td></td>
</tr>
<tr>
<td>12\textsuperscript{4}Sb</td>
<td>3.3E+6</td>
<td>5.0E+6</td>
<td></td>
</tr>
<tr>
<td>13\textsuperscript{1}Ba</td>
<td>2.6E+8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13\textsuperscript{4}Cs</td>
<td>1.7E+8</td>
<td>7.1E+7</td>
<td></td>
</tr>
<tr>
<td>14\textsuperscript{1}Ce</td>
<td>1.3E+8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18\textsuperscript{1}Hf</td>
<td>5.6E+7</td>
<td>2.3E+7</td>
<td></td>
</tr>
<tr>
<td>18\textsuperscript{2}Ta</td>
<td>7.3E+5</td>
<td>1.2E+6</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Based on a 4-h irradiation at 3 \times 10^{13} \text{n/cm}^2 (neutron fluence, 4 \times 10^{17} \text{n/cm}^2). The specific activity is corrected to the time at the end of neutron irradiation.

The data presented in Table 13 are for a cesium-spiked hollandite sample (HSN-2) and a uranium-spiked zirconolite sample (ZU19-HR-1-R). Note that the hollandite sample was only sintered and contained a second phase of TiO\textsubscript{2}. Also this material was only 60\% dense and hence the use of geometric surface area can be misleading. The zirconolite sample was sintered and hot pressed and represented a single phase.

The leach rates for cesium from the hollandite sample were so high that the gamma ray spectra were swamped by this activity and hence no other radioisotopes could be determined. This would seem to indicate that the cesium had not been incorporated into the hollandite phase. However, the very porous nature of the sample (i.e., 40\% porosity) would lead to a very large surface area available to the leaching medium. Hence, no conclusions can be drawn until samples of high density have been prepared and tested.

The leach rates for cesium from the zirconolite material are competitive with the leach rates for borosilicate glass, and the leach rates for the matrix materials (i.e., zirconium and hafnium) are somewhat lower than is generally observed for borosilicate glass. At higher temperatures, however, (e.g., 200\textdegree C) the cesium leaches from this material very rapidly.

The data presented in Table 15 are for SYNROC composites. The results for the NCMOD-10 look particularly good. The leach rates for cesium and barium are essentially the same as the leach rate for the matrix material.
Table 15. Sequential Leach Rates for SYNROC Composites, Using Distilled Water at the Indicated Temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Leach No.</th>
<th>Time, d</th>
<th>Temp, °C</th>
<th>Incremental Leach Rate, g/cm²d</th>
<th>95Zr</th>
<th>124Sb</th>
<th>134Cs</th>
<th>131Ba</th>
<th>Wt Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCMOD-10</td>
<td>1</td>
<td>7</td>
<td>25</td>
<td>7.4E-6</td>
<td>1.3E-4</td>
<td>1.2E-5</td>
<td>4.2E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0.8cm²/0.14g)</td>
<td>2</td>
<td>36</td>
<td>25</td>
<td>--</td>
<td>6.6E-6</td>
<td>1.9E-7</td>
<td></td>
<td></td>
<td>&lt;1E-5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>43</td>
<td>25</td>
<td>--</td>
<td>--</td>
<td>2.2E-7</td>
<td></td>
<td></td>
<td>&lt;1E-5</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>7</td>
<td>75</td>
<td>5.8E-6</td>
<td>1.0E-4</td>
<td>7.8E-6</td>
<td>2.9E-6</td>
<td></td>
<td>&lt;1E-5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>36</td>
<td>75</td>
<td>--</td>
<td>2.3E-6</td>
<td>4.2E-7</td>
<td></td>
<td></td>
<td>&lt;3E-6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>43</td>
<td>75</td>
<td>--</td>
<td>--</td>
<td>2.4E-7</td>
<td></td>
<td></td>
<td>&lt;3E-6</td>
</tr>
<tr>
<td>SRB-R5</td>
<td>1</td>
<td>6.8</td>
<td>25</td>
<td>2.4E-5</td>
<td>9.0E-4</td>
<td></td>
<td></td>
<td></td>
<td>&lt;3E-6</td>
</tr>
<tr>
<td>(2.2 cm²/0.9g)</td>
<td>2</td>
<td>73.2</td>
<td>25</td>
<td>6.7E-6</td>
<td>4.8E-5</td>
<td></td>
<td></td>
<td></td>
<td>&lt;1E-6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>56.8</td>
<td>25</td>
<td>--</td>
<td>4.3E-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

zirconium. Also, there seems to be little if any increase in leach rate with temperature at 75°C. This effect will be studied further by leach-testing this material at 200°C.

3. Conclusions

Studies of the leaching characteristics of SYNROC-type waste forms produced by ANL-MSD are continuing. Results to date indicate that the matrix materials and the more leach-resistant waste elements (e.g., strontium and rare earths) have somewhat better leaching characteristics (i.e., lower leach rates) in this waste form than in borosilicate glass.

C. Mechanistic Studies
   (J. K. Bates)

Leaching experiments using nonactivated samples of PNL-76-68 glass, SRL-frit-211* glass and SRL-frit-211 glass, and activated PNL-76-68 glass have been concluded. Glass compositions are given in Table 16. SRL-frit-211* is made by adding known amounts of seven minor constituents to SRL-frit-211 glass to make it better match the composition of actual defense waste glass. These tests, in part, serve as validation of the NAA method and also form the basis of comparison for the leaching of weathered and unweathered glass. The matrix of leaching conditions is given in Table 17. As an overview, the leach tests with non-activated material follow the procedure described in the Standard NAA-ANL Static Leach Test, with the leachates being analyzed by the Analytical Chemistry Laboratory (ACL) for silicon (colorimetry) and cesium (flame emission) and by Ames Laboratory (by inductively coupled plasma or ICP and by flame emission) for other glass constituents. The solid samples were analyzed for weight loss and surface profile changes; the original solid samples were analyzed for composition and uniformity.
Table 16. Compositions of Glasses Used in Leach Testing

<table>
<thead>
<tr>
<th>Oxide in Glass, wt %</th>
<th>Glass Type</th>
<th>PNL-76-68&lt;sup&gt;a&lt;/sup&gt;</th>
<th>SRL-frit-211&lt;sup&gt;b&lt;/sup&gt;</th>
<th>SRL-frit-211&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td></td>
<td>38.2</td>
<td>38.3</td>
<td>43.8</td>
</tr>
<tr>
<td>Na</td>
<td></td>
<td>12.40</td>
<td>15.1</td>
<td>15.2</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>9.89</td>
<td>11.9</td>
<td>12.4</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>9.37</td>
<td>7.8</td>
<td>8.0</td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td>2.0</td>
<td>4.9</td>
<td>5.1</td>
</tr>
<tr>
<td>Mn</td>
<td>--</td>
<td>3.5</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>--</td>
<td>6.5</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>--</td>
<td>2.8</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.28</td>
<td>0.9</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.52</td>
<td>0.2</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0.38</td>
<td>0.07</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.40</td>
<td>0.2</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Ce</td>
<td>1.11</td>
<td>0.7</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>4.21</td>
<td>0.6</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>0.08</td>
<td>0.003</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>1.7</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>4.5</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>8.7</td>
<td>0.2</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Analysis reported by PNL using KOH fission/ICP solution analysis [STRACHAN].

<sup>b</sup>Analysis by acid dissolution/ICP solution analysis.

To validate the NAA method, a similar series of tests is being conducted with neutron-activated samples. These tests follow the standard leach test modified for NAA, with ACL analyzing the leachates by the NAA method. Thus, comparison of activated samples with nonactivated samples will be possible.

a. Results—Solid Sample Analysis before Leaching

The solid samples of SRL-frit-211 and -211* glass used in these leach tests have been analyzed for composition, using energy dispersive X-ray analysis (EDAX), emission spectroscopy, and ICP spectroscopy. These studies were done to determine which method is best suited for the analysis of glass samples. Results for all methods are shown in Table 18.

From the results, it is observed that making the glass in alumina crucibles (the standard procedure in this work) increases the aluminum content of the final glass and that the original nickel content in the SRL-211 frit is lower than the reported nominal composition. Solid sample analysis by ICP was the method selected.

b. Results—Solid Sample Analysis after Leaching

A complete description of the solid sample after leaching requires mass loss, general appearance, and surface analytical (SEM, EDAX,
Table 17. Experimental Plan for Leaching Experiments

<table>
<thead>
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<sup>a</sup>Geometric surface area.
<sup>b</sup>PH of original solution is 5.5.
<sup>c</sup>Where no value is given, samples were air-dried.
<sup>d</sup>Glass composition given in Table 16.

ESCA) studies. Here, the mass loss data are reported while the work on general appearance and surface characterization is still in progress.

The mass loss data are presented in Table 17 and Fig. 9. Mass loss is presented as mass lost per unit area (g/m<sup>2</sup>) and obviously is not specific to any one element. Not all samples were oven-dried at 120°C (as called for by the procedure) for fear of damage to the surface and subsequent surface analysis. Oven-dried and air-dried samples did not have the same mass loss. The data are most complete for PNL-76-68 glass and show a general increase in weight loss with time (Fig. 9), as expected.

![Fig. 9. Weight Loss of PNL-76-68 Glass (leaching at 90°C)](image-url)
Table 18. Solid Composition—Results of Analysis

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Concentration, wt %

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<sup>a</sup>Inductively coupled plasma.

<sup>b</sup>Energy dispersive X-ray analysis.

<sup>c</sup>Lost in dissolution.
c. Results--Leachate Analysis (Nonactivated Samples)

Solutions L-1 to L-44 were each divided into two parts, and analyses were done by the Analytical Chemistry Laboratory (ACL) and by Ames Laboratory. ACL analyzed the samples for cesium silicon, using standard chemical techniques; Ames used ICP to analyze for silver, aluminum, boron, barium, calcium, cadmium, iron, magnesium, molybdenum, nickel, antimony, silicon, strontium, tellurium, titanium, yttrium, and zinc and used flame emission to analyze for cesium, lithium, sodium, and rubidium. The results are presented as normalized elemental mass loss, \( (NL)_i \), which is defined as

\[
(NL)_i = \frac{m_i}{f_i \cdot SA}
\]

where \( m_i \) is the mass (in g) of element "i" in solution at the end of the experiment, \( f_i \) is the mass fraction of element "i" in the initial specimen, and SA is the geometric surface area (m\(^2\)) of the sample when the experiment started. This term, \( (NL)_i \), can be converted to the common units of g/cm\(^2\)·day by dividing by the duration of the experiment.

The ACL data for nonactivated samples are presented in Table 18 and Figs. 10 through 12. The data for PNL-76-68 glass leached at 90°C (Fig. 10) indicate that cesium leaches at a faster rate than silicon and that

![Graph showing normalized mass loss of Cs and Si over time](image-url)
the solution reaches a constant pH of about 10 within two days. The data for PNL glass leached at 40°C and SRL-frit-211* glass leached at 90°C (Figs. 11 and 12) is not as complete or as reliable as that for PNL glass at 90°C due to the lower temperature (Fig. 11) or the smaller number of replicates analyzed (Fig. 12). However, these data do indicate a substantial decrease in leach rate with temperature and an apparently lower leach rate for the SRL-frit-211* glass composition than for the PNL-76-68 glass.

The above results can be directly compared with the Ames results, which are presented in Table 19. Silicon and cesium were analyzed by both laboratories for the same samples. The (NL)Si values obtained from the Ames results are consistently 10% higher than those obtained from the ACL results. Comparison of the cesium results is complicated by inconsistencies in the Ames results. For example, for Sample L-11, which is a blank, Ames reports 1.1 µg of Cs/mL, while for Samples L-25 to L-31, which have cesium concentrations >1 µg/mL, no cesium was detected. The method of cesium analysis used by Ames is not considered reliable for the cesium concentrations present in the current samples.

The data obtained from Ames can further be compared with some leach rate data on PNL-76-68 glass, as reported by the Material Characterization Center (MCC). The solid samples and leaching conditions were the same.
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<td>L-42</td>
<td>0.2</td>
<td>1.8</td>
<td>--</td>
<td>0.04</td>
<td>--</td>
<td>0.05</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>L-43</td>
<td>0.2</td>
<td>0.7</td>
<td>--</td>
<td>0.04</td>
<td>--</td>
<td>0.08</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>L-44</td>
<td>0.2</td>
<td>0.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.05</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
in both experiments. The comparison is made in Table 20. The ratio of the values, $(NL)_i^{Ames}/(NL)_i^{MCC}$, for the highly leachable species, boron, molybdenum, and sodium averages 0.64 for the 14- and 28-day tests; the ratio, $(NL)_i^{ACL}/(NL)_i^{MCC}$ for silicon and cesium is 0.68. This indicates that some factor in the ANL experiments (i.e., differences in composition of two glasses, slight differences in temperature) decreased the element loss by an absolute value of about 35% in the ANL experiments. However, it does indicate a consistency between the ANL and MCC results in that the ratios for the different elements are nearly the same.

Another important point that must be determined from these experiments is at what point in time steady-state leaching conditions are reached. Such conditions are necessary to allow a valid comparison of different waste forms. Steady-state conditions exist when the leach rate has reached a constant level and thus can be extrapolated with time. One indication that steady state has been reached is the plot of $NL_i$ vs. time becoming linear. At 90°C, PNL-76-68 glass does not clearly give a linear plot. Further evidence must be obtained to draw a firm conclusion.

Fig. 12. SRL-Frit-211* Glass Leached at 90°C
Table 20. Comparison of Leach Analytical Results for PNL-76-68 Glass--Three Sites

<table>
<thead>
<tr>
<th>Analytical Laboratory</th>
<th>Si</th>
<th>Cs</th>
<th>B</th>
<th>Ca</th>
<th>Mo</th>
<th>Na</th>
<th>Sr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°C Samples L-6, 7, 8--14 days&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCC</td>
<td>21.6</td>
<td>38.0</td>
<td>32.8</td>
<td>0.77</td>
<td>33.6</td>
<td>26.7</td>
<td>0.75</td>
<td>--</td>
</tr>
<tr>
<td>ACL</td>
<td>14.4</td>
<td>25.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AMES</td>
<td>16.2</td>
<td>--</td>
<td>18.1</td>
<td>1.05</td>
<td>22.3</td>
<td>18.0</td>
<td>--</td>
<td>0.15</td>
</tr>
<tr>
<td>AMES/MCC</td>
<td>0.75</td>
<td>--</td>
<td>0.55</td>
<td>1.36</td>
<td>0.66</td>
<td>0.67</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ACL/MCC</td>
<td>0.67</td>
<td>0.68</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Based on Data from 90°C Samples L-1 to L-10 and L-45 to L-53--28 days

| MCC | 36.1 | 64.0 | 65.2 | 0.32 | 66.4 | 54.6 | 0.28 | 0.11 |
| ACL | 25.0 | 45.1 | --   | --   | --   | --   | --   | --   |
| ACL | -- | 40.5 | -- | -- | -- | -- | -- | -- |
| NAA | -- | 34.5 | -- | -- | -- | -- | -- | -- |
| AMES | 26.1 | 43.0 | 37.2 | -- | 45.8 | 37.0 | -- | -- |
| AMES/MCC | 0.72 | 0.67 | 0.57 | -- | 0.69 | 0.68 | -- | -- |
| ACL/MCC | 0.69 | 0.71 | -- | -- | -- | -- | -- | -- |
| NAA/MCC | -- | 0.63 | -- | -- | -- | -- | -- | -- |

<sup>a</sup>Each value is the average for the three runs.

### d. Leachate Analyses of Activated Samples

Leach tests of neutron-activated PNL-76-68 glass have been completed (L-45 to L-60). The test conditions, outlined in Table 19, are the same as those used for the nonactivated samples (L-1 to L-22). Thus, the results for the two sets of tests should be directly comparable. The leachates from the activated samples were divided into two parts and analyzed by NAA and the ACL. Table 21 makes several comparisons possible.

1. The values (NL)Cs determined by using NAA are 20% lower than those obtained from the ACL results in the 90°C experiment, but the two are the same in the 40°C experiment (see Tables 17 and 21).

2. Samples L-45 through L-58 were leached under the same conditions as Samples L-1 through L-22, and all of these leachates were analyzed for silicon and cesium by the ACL. A comparison of these two sets of results (activated vs. nonactivated) indicate that silicon and cesium release from the activated samples is 10% greater than from the nonactivated samples after 40 days.
Table 21. Normalized Leach Results for Neutron-Activated PNL-76-68 Glass Based on Analyses by NAA and by the ACL

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Sample No.</th>
<th>NAA, g/m$^2$</th>
<th>ACL, g/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$^{134}$Cs</td>
<td>$^{65}$Zn</td>
</tr>
<tr>
<td>L-45</td>
<td>41.6</td>
<td>0.63</td>
<td>0.13</td>
</tr>
<tr>
<td>L-46</td>
<td>37.4</td>
<td>0.39</td>
<td>--</td>
</tr>
<tr>
<td>L-47</td>
<td>44.1</td>
<td>0.71</td>
<td>0.14</td>
</tr>
<tr>
<td>L-49</td>
<td>20.3</td>
<td>--</td>
<td>0.08</td>
</tr>
<tr>
<td>L-50</td>
<td>21.0</td>
<td>--</td>
<td>0.06</td>
</tr>
<tr>
<td>L-51</td>
<td>19.4</td>
<td>--</td>
<td>0.10</td>
</tr>
<tr>
<td>L-52</td>
<td>12.0</td>
<td>--</td>
<td>0.03</td>
</tr>
<tr>
<td>L-53</td>
<td>7.2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>L-54</td>
<td>0.9</td>
<td>0.39</td>
<td>--</td>
</tr>
<tr>
<td>L-55</td>
<td>1.1</td>
<td>0.33</td>
<td>--</td>
</tr>
<tr>
<td>L-56</td>
<td>0.4</td>
<td>0.23</td>
<td>--</td>
</tr>
<tr>
<td>L-57</td>
<td>0.7</td>
<td>0.24</td>
<td>--</td>
</tr>
<tr>
<td>L-58</td>
<td>0.2</td>
<td>0.23</td>
<td>0.05</td>
</tr>
</tbody>
</table>

On the basis of elemental loss comparisons for both activated and nonactivated samples, it may be preliminarily concluded that all methods of analysis give results that are consistent to within about 20%. A complete analysis of the data, including leaching trends, surface analysis, and interpretation of results, will be presented once all the analyses are complete.

e. NAA Sensitivity

The sensitivity and applicability of the NAA method to a typical waste glass (PNL-76-68 + 33 wt % PW-8a-3 calcine) have been quantified for specific irradiation and counting conditions. The sensitivity depends on the abundance of strong gamma-emitters in the sample. For example, if substantial amounts of $^{134}$Cs and $^{152,154}$Eu are present, weaker gamma-emitters may not be detected above their background. The limit of detectability of each element has been set at the concentration below which the error in the standard computer program used in the analysis is 20%. The applicability of NAA to PNL-76-68 glass is shown in Table 22. The elements listed are those which could be consistently detected in the leachates after 42 days of leaching at 25°C. The elements that can be monitored with NAA do not include any network-forming elements, i.e., silicon, boron, or sodium, but the elements are representative of elements having a wide range of chemical behavior.
Table 22. Applicability of NAA to PNL-76-68 Glass

<table>
<thead>
<tr>
<th>Element</th>
<th>Number of Atoms Activated at Zero Time, $A_0$</th>
<th>Number of Atoms at Lower Limit of Detectability, $A_l$</th>
<th>Sensitivity, mg/L</th>
<th>$(NL)_1$, Minimum Detectable Normalized Elemental Loss, g/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{65}$Zn</td>
<td>$2 \times 10^{13}$</td>
<td>$5 \times 10^7$</td>
<td>$2.5 \times 10^{-3}$</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{95}$Zr</td>
<td>$1 \times 10^{12}$</td>
<td>$1 \times 10^7$</td>
<td>$2 \times 10^{-3}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>$^{134}$Cs</td>
<td>$4 \times 10^{14}$</td>
<td>$1 \times 10^8$</td>
<td>$2 \times 10^{-5}$</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^{141}$Ce</td>
<td>$3 \times 10^{12}$</td>
<td>$1 \times 10^7$</td>
<td>$4 \times 10^{-4}$</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>$6 \times 10^{14}$</td>
<td>$4 \times 10^8$</td>
<td>$5 \times 10^{-6}$</td>
<td>$8 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

f. Weathering Studies

Studies are in progress [STEINDLER-1980] to evaluate the effect of weathering (i.e., hydration) on the leach resistance of glass. These experiments are designed to measure and compare the leach rate of weathered glass with the leach rate of freshly cut or as-cast glass. To simulate the weathering that would occur over long time periods, a method of accelerating the weathering rate (hydration rate) without altering the mechanism must be established. There are two parts to these experiments, weathering (described below) and leaching.

Weathering tests done at $85^\circ$ and $130^\circ$C were terminated during this quarter. The matrix of test conditions is given in Table 23. As indicated in Table 23, penetration of the hydration layer (a measure of weathering) at these conditions is expected to be less than 1 μm (10,000 Å), and the hydration profile should be amenable to study by the use of secondary ion mass spectroscopy (SIMS). In this technique, an area of the sample surface is rastered with a beam of ions, sputtering a crater in the surface; the sputtered ions (secondary ions) are detected with a mass spectrometer. SIMS is especially sensitive for profiling a sample having a thickness of less than 1 μm.

The weathered samples have been analyzed by the use of two different SIMS instruments. One (in the Chemical Engineering Division) uses a beam of oxygen ($O^-$) ions as the primary beam and detects hydrogen ($H^+$) ions as the secondary ions. Analyses of four samples were done ($W$-5, $W$-5a, $W$-1, and $W$-2)* (Table 23), and the data are presented in Table 24 and Fig. 13.

* $W$-5 sample was PNL-76-68; $W$-5a sample was SRL-frit-211*; $W$-1 sample was PNL-76-68; and $W$-2 sample was SRL-frit-211*. 
Table 23. Experimental Plan for Weathering Experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample No.</th>
<th>Temp, °C</th>
<th>H₂O Condition</th>
<th>Atmosphere</th>
<th>Expt. Duration</th>
<th>Est. Penetration, Å</th>
<th>Method of Analysis Completed</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNL-76-68</td>
<td>W-1</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>X</td>
</tr>
<tr>
<td>SRL-frit-211*</td>
<td>W-2</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>SRL-frit-211</td>
<td>W-3</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-4</td>
<td>80</td>
<td>90%</td>
<td>Air</td>
<td>1 week</td>
<td>1650</td>
<td>X</td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-5</td>
<td>80</td>
<td>90%</td>
<td>Air</td>
<td>2 weeks</td>
<td>2300</td>
<td>X</td>
</tr>
<tr>
<td>SRL-frit-211*</td>
<td>W-5a</td>
<td>80</td>
<td>90%</td>
<td>Air</td>
<td>2 weeks</td>
<td>2300</td>
<td>X</td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-6</td>
<td>80</td>
<td>90%</td>
<td>Air</td>
<td>4 weeks</td>
<td>3300</td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-7</td>
<td>80</td>
<td>90%</td>
<td>Air</td>
<td>10 weeks</td>
<td>5000</td>
<td>X</td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-8</td>
<td>80</td>
<td>90%</td>
<td>Air</td>
<td>10 weeks</td>
<td>5000</td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-9</td>
<td>80</td>
<td>90%</td>
<td>Air</td>
<td>10 weeks</td>
<td>5000</td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-10</td>
<td>130</td>
<td>Satur.</td>
<td>Air</td>
<td>6 h</td>
<td>1926</td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-11</td>
<td>130</td>
<td>Satur.</td>
<td>Air</td>
<td>1 day</td>
<td>3845</td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-12</td>
<td>130</td>
<td>N. Satur.</td>
<td>Air</td>
<td>3.5 days</td>
<td>7206</td>
<td>X</td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-13</td>
<td>130</td>
<td>N. Satur.</td>
<td>Air</td>
<td>3.5 days</td>
<td>7206</td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-14</td>
<td>130</td>
<td>Satur.</td>
<td>Air</td>
<td>3.5 days</td>
<td>7206</td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-15</td>
<td>130</td>
<td>Satur.</td>
<td>Air</td>
<td>2 weeks</td>
<td>14,400</td>
<td></td>
</tr>
<tr>
<td>PNL-76-68</td>
<td>W-16</td>
<td>130</td>
<td>Satur.</td>
<td>Air</td>
<td>8 weeks</td>
<td>29,000</td>
<td></td>
</tr>
<tr>
<td>SRL-frit-211*</td>
<td>W-17</td>
<td>130</td>
<td>Satur.</td>
<td>Air</td>
<td>2 weeks</td>
<td>14,400</td>
<td></td>
</tr>
<tr>
<td>SRL-frit-211</td>
<td>W-18</td>
<td>130</td>
<td>Satur.</td>
<td>Air</td>
<td>2 weeks</td>
<td>14,400</td>
<td></td>
</tr>
</tbody>
</table>

*1 μm = 10000 Å
Table 24. Results of SIMS Analysis of Hydrated Glass at Chemical Engineering Division

<table>
<thead>
<tr>
<th>Time, s</th>
<th>Depth, Å</th>
<th>W-5 (PNL-76-68)</th>
<th>W-5a (SRL-frit-211*)</th>
<th>W-1 (PNL-76-68)</th>
<th>W-2 (SRL-frit-211*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H⁺, counts/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>92</td>
<td>236</td>
<td>276</td>
<td>601</td>
</tr>
<tr>
<td>50</td>
<td>11</td>
<td>20</td>
<td>34</td>
<td>17</td>
<td>31</td>
</tr>
<tr>
<td>100</td>
<td>22</td>
<td>40</td>
<td>38</td>
<td>17</td>
<td>30</td>
</tr>
<tr>
<td>200</td>
<td>43</td>
<td>162</td>
<td>73</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>250</td>
<td>54</td>
<td>492</td>
<td>150</td>
<td>137</td>
<td>25</td>
</tr>
<tr>
<td>300</td>
<td>65</td>
<td>505</td>
<td>262</td>
<td>317</td>
<td>92</td>
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<tr>
<td>350</td>
<td>76</td>
<td>539</td>
<td>290</td>
<td>342</td>
<td>159</td>
</tr>
<tr>
<td>400</td>
<td>86</td>
<td>490</td>
<td>374</td>
<td>328</td>
<td>239</td>
</tr>
<tr>
<td>450</td>
<td>97</td>
<td>387</td>
<td>378</td>
<td>239</td>
<td>198</td>
</tr>
<tr>
<td>500</td>
<td>108</td>
<td>361</td>
<td>366</td>
<td>168</td>
<td>176</td>
</tr>
<tr>
<td>750</td>
<td>162</td>
<td>252</td>
<td>317</td>
<td>140</td>
<td>151</td>
</tr>
<tr>
<td>1000</td>
<td>216</td>
<td>172</td>
<td>280</td>
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<td>113</td>
</tr>
<tr>
<td>1500</td>
<td>324</td>
<td>117</td>
<td>183</td>
<td>72</td>
<td>87</td>
</tr>
<tr>
<td>2000</td>
<td>432</td>
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<td>147</td>
<td>68</td>
<td>66</td>
</tr>
<tr>
<td>2500</td>
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<td>90</td>
<td>128</td>
<td>66</td>
<td>59</td>
</tr>
<tr>
<td>3000</td>
<td>648</td>
<td>92</td>
<td>93</td>
<td>58</td>
<td>57</td>
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<tr>
<td>3500</td>
<td>757</td>
<td>70</td>
<td>75</td>
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<td>--</td>
</tr>
<tr>
<td>4000</td>
<td>846</td>
<td>71</td>
<td>--</td>
<td>--</td>
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</tr>
<tr>
<td>5000</td>
<td>1081</td>
<td>70</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6000</td>
<td>1297</td>
<td>67</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>7000</td>
<td>1513</td>
<td>66</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>8000</td>
<td>1729</td>
<td>81</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

The samples had been coated with gold, the initial sputtering removed this gold layer (about 75 Å), and little hydrogen was detected. Upon penetration of the glass by the primary beam, sputtering of H⁺ ions sharply increased, then more gradually decreased. The differences observed for both the PNL-76-68 and the SRL-frit-211* glass (hydrated vs. blank) in the depth at which H⁺ ions are sputtered and the absolute numbers of ions are believed to be real. Thus, it appears that the penetration of water into the hydrated samples (W-5 and W-5a) is greater than that found in the blanks (W-1 and W-2). For PNL-76-68 glass, the penetration depth for W-1 is about 200 Å, and for W-5 it is about 625 Å; for SRL-frit-211* glass, the value for W-2 is about 280 Å and for W-5a it is about 660 Å. These depths are less than those predicted from currently available data for other glasses.

SIMS analysis of leached glass samples was also done using the facilities of Perkin Elmer/Physical Electronics. This instrument uses Ar⁺ (4 keV and 100 nA) as the primary beam and profiles up to ten secondary ions simultaneously. The surface is neutralized with an electron beam to offset the buildup of positive charge due to the Ar⁺ ions.
The secondary ions monitored in this SIMS analysis were H, H2, B, O, H3O+, Na, Si, Ca, Cs, and Nd. In Fig. 14, the results from a typical sample are given. The depth of sputtering is related to the sputtering time, but no exact correspondence of the two is available. The rate is about 30-50 Å/min. As is evident, the profiles for H+, H2+, and H3O+ are constant throughout. This observation is true in all samples that were weathered at 80°C and 130°C. For boron and calcium, an increase of concentration to a depth of about 400 Å was found in all weathered samples but did not correlate with the duration of weathering. Similar behavior was not observed in the blank. The depletion of boron and calcium near the surface (curves 11 and 40) might be due to polishing of the original surface.

An additional profile obtained by Physical Electronics is shown in Fig. 15. This profile was done on a sample weathered at 250°C for 14 days, for which the predicted water penetration is about 30 µm. The depth of the scan is about 2500 Å. Hydrogen (mass 1) was not monitored, suggesting a possible problem in H+ detection. There is a noticeable decrease in the H3O+ (mass 19) concentration at greater sputtering times. Whether this H3O+ profile is indicative of the weathering process will have to be confirmed in separate experiments.
Fig. 14. SIMS Analysis of Weathered PNL-76-68 Glass, Sample W-4 Profile

Fig. 15. SIMS Profile of Extremely Weathered Glass
A comparison of the SIMS results reveals a contradiction in the hydrogen profiles. Both groups performing the analysis are confident that they are able to profile hydrogen. Yet, on the same sample (W-5), opposite results were achieved. Hydrogen detection is extremely sensitive to background water. The partial pressure of water $P$ in the vacuum system at the time of measurement must be $<10^{-10}$ torr for the results to be meaningful. The work by Physical Electronics was done right after the system had accidently shut down and the partial pressure of water was very high. Therefore, the hydrogen profiles obtained by Physical Electronics are suspect.
IV. TRANSPORT PROPERTIES OF NUCLEAR WASTE IN GEOLOGIC MEDIA
(M. G. Seitz, Jacqueline Williams,* N. J. Meldgin,†
Mojmir Seliga,‡ D. L. Bowers,* P. G. Rickert,**
S. M. Fried,* A. M. Friedman,** and M. J. Steindler)

A. Introduction

Disposal of radioactive waste in geologic formations offers a practical method of permanently isolating the waste from the biosphere. Even if groundwater infiltrates a repository, leaches radionuclides from the solid waste, and transports them into fissures and pores of the surrounding geologic structure, the radionuclides can react with the rock and again become immobile. Both the solid waste form and the geologic structure (together with any engineered barriers or canisters) prevent the dispersal of radioactivity into the biosphere.

A comprehensive technical treatment of potential radionuclide dispersal from a repository is not simple. In a generalized approach to an understanding of nuclide migration by groundwater flow, there are enormous numbers of solution and sorbed species that would have to be considered over a large range of element concentrations, temperature, radiation field, groundwater flow velocity, and other conditions. Migration is complicated compared to that which occurs in a natural, undisturbed formation by materials extraneous to a geologic structure that will be introduced as part of a nuclear waste repository.

In most experimental work to evaluate the potential for dispersal of radioactivity, either the leach resistance of solid wastes has been examined or the adsorption of nuclides by rock has been investigated. Both approaches investigate potentially very complex processes. Details of the chemical species at the solid-solution interface are sought in particular to establish mechanisms of leaching. In certain cases [INOUE], results of adsorption experiments can be related to nuclide migration by flowing groundwater. However, the results of these experiments give little guidance for predicting leaching or migration under general conditions. In fact, the species and concentrations of nuclides formed during leaching can affect migration so that the migration is not independent of leaching [SEITZ-1979B].

Migration also depends on the chemical changes that might occur as a radionuclide moves away from the repository. Thus, 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.

* Member of the Analytical Group of the Chemical Engineering Division.
† Consultant from Mayfield Engineering Co., Chicago Ridge, IL.
‡ CEN temporary staff participating in on-the-job training through an International Atomic Energy Agency fellowship.
** Member of the Chemistry Division.
Some of these interactions would occur in the radiation and thermal gradients centered on the solidified waste. There is little hope that studies of individual repository components will allow all important interactions in a breached repository to be identified.

B. An Approach to the Study of Radionuclide Migration

Instead of working with a part of a repository in the hope that the findings of each part can be integrated by a computer model, our approach in the Waste Rock Interactions Technology (WRIT) Program has been to integrate repository components in laboratory experiments under the conditions expected for a breached repository. Earlier work has combined leaching and migration in a single groundwater stream [SEITZ-1978, -1980]. The waste solids used contained actinide elements, fission products, and activation nuclides. Cores of both porous rock and impermeable rock containing fresh or old fissures have been used as the geologic media. The experiments identified relations between leaching and migration that were then studied in simpler adsorption tests [SEITZ-1979A]. Leach–migration experiments are being planned by others [COLES].

Experiments termed stream-simulation experiments are now in progress that combine engineered barriers, canisters, and rock cores in a single flowing groundwater stream. The stream-simulation experiments are an elaboration of the leach-migration experiments conducted for the WRIT program in which solid waste at elevated temperature and geologic media were combined into one groundwater stream. By use of the stream-simulation experiments, we are attempting to consider all potential interactions that occur when repository components are combined. The interactions, once identified, can then be studied in detail by simpler experiments.

C. Stream-Simulation Experiments

The objective of the stream-simulation experiments is to reproduce the essential processes that occur in a breached repository. In a breached repository, groundwater may flow through the disrupted engineered barrier and canister and contact the solid waste. The groundwater may leach radionuclides and stable elements from the waste, and the altered groundwater may flow from the breached canister and engineered barrier into the geologic structure surrounding the repository. The radiation and thermal fields are centered on the solid waste but are also influenced by heat and radiation from surrounding waste packages.

D. Apparatus

Apparatus for a stream-simulation experiment that reproduces the essential processes along the groundwater stream is shown in Fig. 16. In the apparatus, groundwater is pumped through an engineered barrier, contacts the solid waste, and then exits through more of the engineered barrier. This part of the groundwater stream is maintained at elevated temperature in a radiation field. The groundwater then passes through rock cores held at the temperatures that would exist at increasing distances from the repository. By monitoring the groundwater exiting from the apparatus for chemical
changes (of both stable and radioactive species) and by analyzing the rock and engineered barrier after an experiment, the behavior of the radionuclides can be established. The rock cores currently being used have a 6.8-cm dia and are 17 cm long; about 0.5 g of solid waste is used in an experiment.

The entire apparatus defining the groundwater stream is made of Hastelloy C-276 or Teflon. The Hastelloy alloy shows excellent corrosion resistance in groundwater and brines and has been tested as a candidate metal for waste canisters [BRAITHWAITE]. The Teflon (enclosing the rock cores) is used to prevent water from bypassing the rock cores (9.5-cm dia by 23 cm long) and as seals in the solution-metering pump.

The apparatus is assembled with tube fittings and valves that allow groundwater to be sampled at several points along the groundwater stream. The stream is monitored with pressure transducers and thermocouples. The radiation field is provided by waste solid sometimes augmented by a cobalt-60 gamma source.

For slow flow rates (below 0.2 mL/h) the syringe pump shown in Fig. 16 is replaced with a proportioning pump which, in turn, is driven by the syringe pump. A proportioning pump designed to isolate the corrosive brine from the
primary driving fluid and to produce a flow rate of the brine equal to 0.1 that of the primary fluid is illustrated in Fig. 17. The parts wet by brine are made of Hastelloy-C276 with Teflon ring seals.

Fig. 17. Flow-Proportioning Pump to Produce a Flow of Corrosive Brine that is One Tenth the Flow of the Primary Driving Fluid

E. Flow Through Rock Salt

The flow of brine through solid and split cores of rock salt was examined to determine a suitable method of performing stream-simulation experiments that give results relevant to evaluating the safety of the Waste Isolation Pilot Plant. This work was funded by the U.S. Department of Energy through Sandia National Laboratories.

1. Permeability of Solid Rock Salt—Experiment 1

To examine the ability to create a flow of groundwater through rock salt, we applied water at a pressure of 4.5 MPa (650 psi) to the end of a right circular cylinder of McNutt Halite (6.38-cm dia by 15.2 cm long) in a Hastelloy rock core holder. The outside confining pressure was maintained in excess of 12.4 MPa (1800 psi) to prevent water from bypassing the core. No water was observed to have been transmitted through the core after 8 days (a quantity of water smaller than 2 mL might not have been detected). On the basis of this observation, the permeability was calculated to be less than 29 µdarcy.

Because of the absence of flow, the end pressure was raised until it exceeded the confining pressure, and flow commenced around the rock core. The confining pressure was maintained at the desired level by periodically using the manual pump. After 6 days, 197 mL of water passed around the core, with a resultant weight loss to the core of 79.6 g. The Teflon sleeve was severely distorted and conformed to a flat side (of the core) that had been formed by dissolution.
2. Fissured Rock Salt Permeability—Experiment 2

Because of the low permeability of the McNutt salt, a second infiltration experiment was performed using halves of two right circular cylinders of the salt. In the experiment, water that had passed through a 1.0-m-long column of crushed McNutt salt (contacting the salt for ten days) was applied to the bottom of the two core halves confined in a rock-core holder, as depicted in Fig. 18. The confining pressures on the salt core for the first week were between 26.4 MPa (3.83 \times 10^3 \text{ psi}) and 30.5 MPa (4.43 \times 10^3 \text{ psi}), which corresponds to a lithostatic pressure at 1150 m for rock of density 2.70 g/cm$^3$.

The pressures for the second and third week ranged from 14.8 MPa (2.15 \times 10^3 \text{ psi}) to 18.9 MPa (2.75 \times 10^3 \text{ psi}). The brine was pumped using a Varian Model 8500 syringe pump at 1.0 mL/h until the pressure reached the preset limiting value of 5.2 MPa (751 psi), corresponding to a hydrostatic head of 520 m and ranged between 4.96 MPa (719 psi) and 6.71 MPa (974 psi) during the three weeks.

Upon disassembly of the column from the three-week-long experiment, the core was found to be in one piece, the two halves having recemented together. The Teflon sleeve was closely examined and was found to have held the rock core very well, as indicated by the impressions of the core and end plugs on the sleeve. No brine was present in the distilled water that confined the Teflon sleeve around the core. From this data (and assuming the viscosity of salt water to be 1.05 cP), we have calculated the permeability of the split rock salt core to be below 10 \mu\text{darcy}.
3. Rock Salt Infiltration by Water—Experiment 3

An experiment was set up to measure the penetration of water into rock salt. Because of the low permeability exhibited by the salt in previous experiments, we used tritiated water that could be monitored radiochemically to provide us with a sensitive measure of the penetration of water into the salt.

The experiment consists of placing four McNutt rock salt cores (8.89 cm long and 2.20-cm dia.) in core holders of a design similar to those used in the previous experiments (but smaller to accommodate the smaller cores). Four of these cores and holders were assembled, and pressure (14 MPa, about 2000 psi) was applied to the Teflon core sleeves with a Haskel MS 188 pump. This pressure was used to confine the Teflon sleeve around the sides of the core, making a nearly perfect seal. A 2-mL solution (consisting of about 80% saturated McNutt salt solution, 20% distilled water, and 20 μCi tritium as water per mL solution) was added to the top of each core. The atmosphere above the solution was purged with argon, and argon was applied at a pressure of 760 kPa (110 psi). The experimental setup is depicted in Fig. 19. One core was to be analyzed after each 30-day interval.

![Fig. 19. Schematic of the Experimental Setup to Study Water Penetration into McNutt Salt Cores](image)

After one month, the argon gas pressure to the top of one of the four core holders was released and the solution on the core was removed. The volume of the solution was measured to be ≤2 mL. The pressure to the sides of the Teflon sleeve was released, and the core was removed. The top of the core showed little or no evidence of dissolution or pitting. A small amount of liquid observed on the bottom plate of the holder was probably residual liquid from the top of the core that had traveled down the side of the core after the Teflon sleeve pressure was released. This liquid was rinsed off the plate and saved for analysis. The outlet tube from the bottom plate was also rinsed and the rinsings saved for analysis. The core was then placed on
a Buehler diamond saw and, with Freon used as a lubricant, was cut axially from the top of the core through part of its length. The cut portion was chiseled off from the remainder of the core, and was cut into four segments (see Fig. 20). Each of the segments was dissolved in water, and the solution was diluted to 50 mL. The tritiated water that had been added to the original brine solution provided a means of detecting the penetration of water. A test using brine directly for liquid scintillation counting is described in Section F.2 below. The results of the analyses for tritium are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Original Solution</th>
<th>Solution Remaining</th>
<th>Segment 1</th>
<th>Segment 2</th>
<th>Segment 3</th>
<th>Segment 4</th>
<th>Bottom Plate Rinse</th>
<th>Outlet Tube Rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.27 x 10^7 d/min·mL</td>
<td>2.19 x 10^7 d/min·mL</td>
<td>1.72 x 10^4 d/min</td>
<td>4.66 x 10^3 d/min</td>
<td>Background</td>
<td>Background</td>
<td>2.48 x 10^3 d/min</td>
<td>Background</td>
</tr>
</tbody>
</table>

Fig. 20. Sectioning of the Rock Salt Core
a. Mass Balance Calculations

A mass balance was calculated for the tritium and the weight of core before and after cutting. The concentration of the original solution differed from the concentration of that collected at the end of the experiment by 3.5%. This difference could be caused by the increase in volume if there had been even a slight dissolution of salt from the core. Also, the analytical error was 1-2%, and the real difference is small, perhaps nonexistent. The contribution from the tritium content of the segments and rinses is insignificant. The weights and lengths of the core, section, and segments are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Weight, g</th>
<th>Length, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>73.6</td>
<td>8.89</td>
</tr>
<tr>
<td>Section (axial)</td>
<td>12.31</td>
<td>2.98</td>
</tr>
<tr>
<td>Segment 1</td>
<td>1.24</td>
<td>0.32</td>
</tr>
<tr>
<td>Segment 2</td>
<td>2.33</td>
<td>0.64</td>
</tr>
<tr>
<td>Segment 3</td>
<td>4.10</td>
<td>0.95</td>
</tr>
<tr>
<td>Segment 4</td>
<td>3.97</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The sum of the weights of the individual four segments is 11.74 g, a difference of 4.6% from the calculated weight of the original section. The cutting losses were calculated to be about 4% and are sufficient to explain the discrepancy. The kerf (cutting width) was measured (microscopically) in order to calculate the half-cylinder volume. By use of the density (2.18 g/cm³), and the three half-cylinder volumes, the total cutting loss is calculated to be 0.50 g. The losses from cutting reduce the difference between the section weight and total segment weight to <0.5%. A comparison of measured segments width and weight was performed: i.e., the measured width (volume) times the density should equal the weight of a segment.

<table>
<thead>
<tr>
<th></th>
<th>Weight of Segment, g</th>
<th>Calculated Weight, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Segment 1</td>
<td>1.24</td>
<td>1.32</td>
</tr>
<tr>
<td>Segment 2</td>
<td>2.33</td>
<td>2.61</td>
</tr>
<tr>
<td>Segment 3</td>
<td>4.10</td>
<td>3.91</td>
</tr>
<tr>
<td>Segment 4</td>
<td>3.97</td>
<td>3.91</td>
</tr>
</tbody>
</table>
b. Water Penetration Depth

The penetration depth appears to be greater than 0.3 cm and less than 0.9 cm (see tritium analyses above). The amount of water penetration is low (about 0.4% of the mass of the rock). The water penetration to the first millimeter of the top of the core, which would have had higher concentrations of tritium from the tritiated brine, was probably lost in the cutting lubricant (Freon), but the water penetration depth into the core is of greater importance and is not affected by the lubricant. The analysis of the second rock core (to be examined after two-month exposure) will be of interest. This data will show whether the water has penetrated deeper with prolonged contact time.

An autoradiograph was taken of the segment (axial side), using fast X-ray film (LKB Ultrafilm $^3$H). The film was developed after a two-day exposure with no visible darkening. The procedure was repeated with the top of the segment exposed for eight-days; again, there was no darkening of the film. These negative results are not surprising. The tritium in the surface had been washed off by the Freon lubricant, and tritium beta has a low energy (18 keV max). The low-energy beta cannot escape from the core media unless it is within about 10 μm of the surface.

Variations in the Teflon sleeve pressure (10,300 to 15,200 kPa) were observed during the one-month experiment. There was no apparent trend in the variation, nor were there any visible leaks in the system to cause this phenomenon. Also, there was no correlation of the ambient temperature with the pressure. Although the causes are not known and no appropriate corrective action is foreseeable at this time, there seems to be no danger of the variation harming the validity of the ongoing experiment.

F. Analytical Development

To monitor the behavior of actinide elements in stream-simulation experiments for the WIPP program, the capability of analyzing for actinide elements in the brine is needed. For sensitive and accurate analyses of the radio nuclides, neptunium-237 and plutonium-239, they must be separated from the brine.

1. Radiochemical Separation of Neptunium and Plutonium from Brine

A literature search for suitable radioanalytical techniques and procedures produced what appeared to be an ideal candidate for the analysis [REGO]. In the technique, neptunium and plutonium were coprecipitated with La(OH)$_3$, and soluble ions were washed from the precipitate. Plutonium and neptunium were separated by reducing Pu to Pu$^{3+}$ and extracting the Np$^{4+}$ into thenoyltrifluoroacetone (TTA).

The procedure was set up and run using neptunium and plutonium tracers ($^{239}$Np and $^{242}$Pu) with a solution of McNutt rock salt (consisting of 200 mg salt per mL water). The method followed was as described [REGO] and no visible problems were observed with La(OH)$_3$ precipitation, dissolution of La(OH)$_3$, reduction of neptunium and plutonium, and subsequent
neptunium extraction into thenyltrifluoroacetone (TTA). Because of the relatively short life of $^{239}$Np (2.35 days), back-extraction of the TTA fraction and electrodeposition were carried out first. The electroplated planchet was then counted on a Ge(Li) detector to determine the quantity of gamma-emitting $^{239}$Np.

The plutonium fraction undergoes additional purification by LaF$_3$-PuF$_3$ precipitation. Because of the large amounts of reductant chemicals present in this solution, the procedure was difficult. The LaF$_3$-PuF$_3$ precipitate tended to contain chemicals that made the precipitate insoluble in HCl. The addition of concentrated HNO$_3$, followed by heating to dryness prior to precipitation, removed I$^-$ and destroyed the hydroxylamine, but the precipitate still did not completely dissolve in the HCl. Repeated additions of HNO$_3$ and evaporation helped, but total dissolution of the residue in HCl could not be obtained. The cloudy solution was placed on a 9M HCl preconditioned AGI X8 ion-exchange column, rinsed with 9M HCl, and converted to a NO$_3^-$ column with 8M HNO$_3$. The plutonium was eluted with 0.5M HNO$_3$, with subsequent electrodeposition.

After several attempts and failures caused by the above problems, a standard was processed through the procedure. The neptunium planchet was counted on a Ge(Li) detector, with $^{239}$Np recovery calculated to be about 25%. The plutonium planchet was analyzed on a surface barrier silicon detector for the quantity of $^{242}$Pu, which was calculated to be about 10% yield. The alpha spectra of plutonium and neptunium planchets showed little or no cross-contamination, i.e., no $^{242}$Pu was present on the neptunium planchet.

The yields were far from ideal, but the important separation of neptunium from plutonium was achieved. This separation is necessary because $^{237}$Np and $^{242}$Pu have essentially the same alpha-decay energies (about 4.8 MeV), causing the two isotopes to be indistinguishable when analyzed by alpha spectrometry. Even with the poor yield, the method is sensitive and will be adequate at the concentration levels expected in the experiments. Improvements will be sought in percent yield—as by attempting to reduce the amount of reductant chemicals in the method while still achieving the separation of neptunium and plutonium needed for meaningful results.

2. Investigation of the Quenching Effect of Salt in the Determination of Tritium by the Liquid Scintillation Counting Technique

Counting tritium directly in solutions of natural salts would be considerably easier than having to separate the tritium into distilled water before counting. To determine the effect of salt on tritium counting, twenty grams of natural rock salt (McNutt) was dissolved in 100 mL of water (a small amount of insoluble material settled to the bottom of the flask). Aliquots of this salt solution were used for a study of the quenching of tritium scintillation by various concentrations of salt. The vials (Table 25) each contained 0.01 mL tritiated water standard (total activity of each 0.1 mL was 1845 d/min) and 15 mL of Insta-Gel scintillation medium.
Table 25. Vials Prepared to Study the Quenching of Tritium Scintillation by Salt

<table>
<thead>
<tr>
<th>Vial</th>
<th>Salt Solution, mL</th>
<th>H₂O, mL</th>
<th>Salt, mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>0.25</td>
<td>150</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0</td>
<td>200</td>
</tr>
</tbody>
</table>

Vials 3 and 4 were cloudy after mixing, and vial 4 had a precipitate after standing, but repeated shaking of the vials turned the solutions clear. The vials were then placed in a liquid scintillation counter (Packard Model 2660) and were each counted several times. Counting efficiency results are listed in Table 26.

Since there was no real difference in the efficiency factors, we conclude that rock salt can be dissolved in water and the tritium content of the water still be readily analyzed. The detection limit for a 1 g solution is about 4 d/min⋅g; therefore, the detection limit for salt would be about 20 d/min⋅g if the salt is dissolved at 20 mg/mL.

Table 26. Counting Efficiencies of Vials Having Solutions of Various Salt Concentration

<table>
<thead>
<tr>
<th>Vial Number</th>
<th>Avg. Eff. Factor, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.1</td>
</tr>
<tr>
<td>2</td>
<td>42.3</td>
</tr>
<tr>
<td>3</td>
<td>42.3</td>
</tr>
<tr>
<td>4</td>
<td>42.6</td>
</tr>
</tbody>
</table>
V. TRACE-ELEMENT TRANSPORT IN LITHIC MATERIAL BY FLUID FLOW AT ELEVATED TEMPERATURE
(M. G. Seitz and R. A. Couture)

A. Introduction

This report covers new activities on the geology of the Notch Peak, Utah, area and of the Northern Illinois drill hole.

B. Notch Peak Intrusion

An intrusion of quartz monzonite into limestone interbedded with thin silt layers near Notch Peak, Utah, allows observation of the alteration of limestone by magmatic intrusions, with attendant skarn formation and infiltration metasomatism.

The initial sequences of limestone and the subsequent intrusion and block faulting of these beds are illustrated in Figs. 21, 22, and 23. The potential exists that elements migrate due to the flow of fluids originating from the drying of the sediments (as part of the metamorphic process) or originating from the quartz monzonite magma itself.

Fig. 21. Stratigraphy of Compacted and Recrystallized Sediments at Notch Peak, Utah. Each member consists of a series of limestone and siltstone beds.

The laboratory studies planned in this work will be conducted as part of a larger study of the Notch Peak Intrusion. Workers at the State University of New York, Stoney Brook (James J. Papke is the principal investigator) are conducting petrologic and major chemistry studies of rocks from this area. J. C. Laul of Battelle Northwest Laboratory is measuring the distribution of trace elements in the rocks of the Notch Peak region.
Fig. 22. Intrusion of Quartz Monzonite into Sediments. Main body of the intrusion has dikes and sills. Broken lines indicate limits of metamorphic grade. Arrows indicate possible fluid flow with subsequent major and trace element migration.

Fig. 23. Block Faulting and Subsequent Erosion Reveal the Intrusion for Scientific Examination of the Extent of Migration. Rock samples were collected from the Orr to the Marjum formations (Fig. 21).
From our studies, we hope to be able to explain in quantitative terms the petrologic and chemical features observed in the rocks. It has been suggested on the basis of chemical evidence that fluids have migrated several kilometers through the limestone. Rocks from the Notch Peak area were sampled for use in laboratory experiments to determine the quantity of fluid that may have passed through the rock and the quantities of trace elements deposited at various distances from the formation. Rocks collected for this study were mainly of low metamorphic grade found 2 km (or further) from the intrusion. Rocks of various metamorphic grades and of the intrusion itself were selected for a sampling of the area.

The unmetamorphosed limestone is quite compact, and appears to be of very low permeability. There are, however, a few interconnecting joints which appear to follow grain boundaries. The scale of jointing is such that the joints can be sampled in a core 2.2 cm in diameter, which we have used for permeability measurements. Measurements on one core of limestone from the Big Horse member of the Orr Formation indicate permeabilities of only \(1.8 \times 10^{-6}\) to \(2.1 \times 10^{-6}\) darcy at 25°C and pressure differences of 500-2000 psi (3.4-13.8 MPa), respectively. Details of the experimental method will be published in the next report. The permeability was determined from the formula

\[
k = \frac{\mu q}{Vp}
\]

where
- \(k\) = permeability, darcys
- \(\mu\) = viscosity, cP
- \(q\) = flux, \(\text{cm}^3\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\)
- \(Vp\) = pressure gradient, atm/cm.

A simple calculation suggests that \(2 \times 10^{-6}\) darcy may be, in fact, a substantial permeability. Assume, for example, burial to 4.4-km depth, which would imply an upper limit for fluid pressure of about 1.2 kbar (about 1.2 atm or 120 MPa). Assume also a fluid path flow length of 4.4 km horizontally. Assume a viscosity of 150 \(\mu\)Pa·s (0.15 cP), which is the value for water at 200°C; this implies a flux of up to 1 \(\text{cm}^3/\text{cm}^2\) per year, or 10 L through a square centimeter in 10,000 y. Assuming an effective porosity of 1%, this means flow over a distance of 10 km in 10,000 y, seeming to indicate that substantial amounts of fluid could be forced through small cracks on a small scale, although this conclusion is based on tentative assumptions and only one sample. It would not be surprising if thermal and mechanical stress open many of these joints further during intrusion, increasing the permeability.

However, permeability measurements are only adequate to decide the question of whether fluid could have migrated through the limestone, not whether it actually did migrate. Additional field evidence and chemical evidence will have to be obtained. For example, skarns have formed near the contact, and scheelite is being mined. It may be helpful to ask whether the same phenomenon that occurred on a large scale also occurred on the microscale of the small cracks.
C. Northern Illinois Drill Hole

Plans are being made to measure permeability and trace-element transport properties of granite from the Northern American Shield, obtained from Northern Illinois drill hole UPH-3. (Data cited here are from various persons who have logged the hole.) The granite (it appears to be true granite in hand specimen) is fresh except for a few meters of weathered zone near the upper contact. There are two zones of relatively fractured material, but the fractures are small and few indeed. An average of 0.6 fracture/m of core were found; many of them are barely visible. Permeability measurements made inside the hole indicate values of $10^{-4}$ to $10^{-9}$ darcy, generally decreasing downward, compared with $2 \times 10^{-6}$ darcy obtained for the limestone from the Notch Peak area (described in this report).

An interesting experiment we plan to perform in the course of our other studies on the granite is to sample the interstitial water. *In situ* neutron backscatter measurements indicate that bulk porosities are about 0.5-2%, although these numbers are near the background for the instrument and may not be reliable. We have attempted to sample the cracks, and so some of our samples may have higher porosities than are obtained by *in situ* measurements. If an effective porosity of 0.5% is assumed, 2.5 mL of fluid can be sampled in a 500-mL volume rock core. It seems reasonable that in pumping water through a core, we would sample an appreciable amount of groundwater and obtain some information on its composition. It may not matter greatly if water has been lost by evaporation since most of the soluble constituents would be expected to be redissolved in the pumped water.

It was recently discovered that much of the deep groundwater in the Canadian Shield consists of CaCl$_2$ brine. The question arises whether Northern Illinois also has brine in the deep part of the formation. However, because of the very low permeability of the rock, it would be very difficult to sample the brine by ordinary methods. We wonder if perhaps we can sample it by pumping water through the core.

In order to confine the granite cores, special core holders have been designed. The principle is that Teflon sleeves, squeezed by external fluid pressure, are used to seal around the edges of the cores and to confine the cores. However, the core holders were designed for another size. Extra Teflon inserts will be necessary, tripling the Teflon thickness (from 0.45 cm to 1.50 cm). It is hoped that the apparatus so modified will still function as planned.
VI. LIGHT WATER BREEDER REACTOR PROOF-OF-BREEDING ANALYTICAL SUPPORT PROJECT
(N. M. Levitz)

The LWBR Proof-of-Breeding (POB) Analytical Support Project is responsible for the destructive analysis of full-length (about 3-m) 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.

A. Full-Scale Shear (FSS)
(P. G. Deeken, J. E. Fagan, and R. E. Brock)

Testing and development work with the full-scale shear (FSS) continued during the current report period with work in two areas: (1) test shearing with the shear head-end assembly in one mockup area and (2) testing of the feed system and controls in a second out-of-cell mockup area. Shearing tests were carried out (a) to further characterize shear performance with respect to fuel breakout and fuel recovery and (b) to prepare samples for shear plane characterization. The latter is pertinent to two aspects of the work, i.e., to establish the uncertainty in the location of a given boundary cut (which is important to both boundary location and segment length determination) and secondly, to assess cross-contamination at segment boundaries.

1. Shear Head-End Assembly Testing
   a. Shear Performance Tests

   Two breeder mockup (BMU) rod sections (35.5-cm-long by 0.75-cm-dia Zircaloy tubes filled with high-density thoria pellets) were sheared for the shear performance tests; a total of three separate tests were performed by using two half-rod sections and one intact piece. These rods are smaller in diameter (0.77 cm) than any of the four regular LWBR fuel rod sizes, and it is necessary that a modest amount of work be done with them in order to develop a method for processing a similar-diameter, full-length irradiated Validation Rod (VR) scheduled for destructive analysis in late CY 1982, prior to start of the end-of-life (EOL) campaign. Present plans call for adaptation of the shear head for the seed-size (0.77-cm-dia) rod to accommodate this size, rather than fabrication of special tooling, since only one VR will be processed.

   The BMU were sheared at a slow (about 5 cm/s) cutting speed to a cut length of 0.38 cm, equivalent to an 0.6 L/D (length of cut piece/rod diameter). Complete dislodgement of the fuel from the hull sections and good pulverization were achieved. Fuel and overall rod recovery were >99.9% for the three separate tests; this recovery is similar to the shearing results with the other rod sizes.

   The present results with slow-speed shearing of BMU rods and an L/D of 0.6 are better in three areas than those obtained earlier with high-speed shearing in the pilot plant [LEVITZ]: (a) "fuel" breakout was complete (i.e., all hulls were free of thoria) in this work, while on the order of 20%
of the hulls remained partly or completely filled in the earlier case; (b) somewhat better pulverization was achieved--average particle size being about 0.4 mm compared with 0.5 mm after pilot plant shearing; and (c) rod and fuel recovery was >99.9%, compared with earlier values of about 99.5%. Improvements (a) and (b) may be due to the greater force (11 tons) available with the FSS, compared with 6 tons for the pilot unit.

b. Shear Plane Characterization Tests

Shear plane characterization tests are being carried out on specially prepared sections of thoria-filled Zircaloy tubing, representative of all four EOL rod sizes (diameters). In earlier work, cuts made at pellet-pellet interfaces showed that "clean separation" is achieved, with minimum cross-contamination. However, in actual EOL work, segment boundary locations may not coincide with such interfaces, and so "worst case" conditions were chosen for this work. The test method involves making a cut through a pellet midplane (as opposed to cutting at a pellet-pellet interface) and then making a careful material balance and a determination of the void volume in the face of the remaining (uncut) portion of the fuel pellet (thoria). The initial studies are intended to characterize the shear plane and establish a data base for the uncertainty in the location of the cut under high-speed (about 0.9 m/s) cutting conditions. A comparison with slow-speed cutting is planned also.

Preliminary results of a single experiment for each rod size are available. Results on three additional rod sections for each rod size are pending. The void volume at the face of the remaining (uncut) fuel section, expressed as grams of thoria, was relatively small--ranging from 0.009 to 0.056 g--for the three smaller rod sizes [seed (0.77-cm dia), power-flattening blanket (1.34-cm dia), and standard blanket (1.46-cm dia)]. However, the voidage at the face of the reflector rod section (2.11-cm dia) corresponded to a value of 1.947 g. These voidages may also be expressed in terms of length (of fuel rod) for the four rod sizes; the corresponding lengths are 0.0031, 0.0033, 0.0045, and 0.073 cm; these values represent one of several contributions to the uncertainty in the level of cross-contamination and in the determination of segment length. An additional uncertainty in the cut location is associated with the clearances between the shear blade (ram) and housing--in this case, a maximum of 0.0063 cm. The ratio of the uncertainty-to-segment length is a measure of cross-contamination.

Since there are two boundary cuts per segment, the total observed uncertainty in the segment length measurement appears to approach the 0.0013-cm uncertainty limit established for the standard blanket rod by DOE - Division of Naval Reactors (DOE-NR) for this parameter, but the uncertainty observed far exceeds the limit in the case of the reflector rod.

It is important to note that this is the first time such data have become available for this project. It is premature to draw firm conclusions regarding the potential for cross-contamination and the impact of these results on the existing error limits, but there are indications that some of these limits may need to be reviewed. A mitigating factor exists in regard to error limits for reflector rods alone, in that there are no binary fuel sections in these rods and thus no step changes in axial fuel loading which require special attention in the course of segmenting. A distinct (larger) error limit for reflector rods may be tolerable.
2. Shear Feed System and Controls Testing

A laser calibration of the FSS Fuel Measurement System was performed jointly with Argonne's Engineering Division (ANL-ENG) in a mockup area adjacent to the shielded cells. A total of 46 traverses of the carriage along a 230-cm-long span were made in both directions; also, each major spare component used in positioning the carriage and in measuring carriage travel was tested during the calibration. The data is presently being reduced. Preliminary results indicate there is near zero backlash in positioning the carriage and that the two independent position indicators agree within 0.0025 cm.

Several design changes and rework of FSS systems and controls were requested of ANL-ENG; this Division provides direct support for design and procurement activities. The changes included a more accurate temperature-monitoring system (for rod measurement corrections), manifolding of valve-bank connections, a more accurate rod end locator, rework of the carriage overload protection device, and a rework of the shear control console layout for computer integration. Most of these changes are being made and are nearly completed.

The redesign of a fuel rod weighing system was initiated as a result of requirements issued by Bettis Atomic Power Laboratory (BAPL) in August 1980. Efforts were made to locate more sensitive balances to replace the load cell weigh system previously designed. A two-balance approach to weighing each fuel rod is under investigation. Using two remoted balances, it may be possible to determine fuel rod weight with a resolution to 0.01 g. A mockup of a two-balance weigh system is in progress; preliminary results are encouraging.

B. Single-Unit Dissolver (SUD)

(I. O. Winsch, T. F. Cannon, and H. Lautermilch)

Installation of the equipment for the single-unit dissolver (SUD) system in the shielded cell (Cell K-3) was 95% complete as of September 30, 1980. The remaining work consists of installation of the two Mettler balances and the blend tank; however, these two systems are still under development (see Subsection 5 below).

Miscellaneous functional tests and calibration of components of the dissolver system were completed. Components tested were the pressure relief valves, transducers, system valves, thermocouples, peristaltic pumps, dissolver heaters, pneumatic wrench, and dissolver basket-lifting mechanism. One dissolver heater was found to be damaged and will be inoperable in future tests. Major problems were found in the control panel and refrigeration cooling system; these have been corrected with considerable effort.

The performance characteristics of the SUD and SUD system are being determined by performing boiling water and boiling nitric acid tests. A major purpose of these tests is to establish the appropriate operating conditions (mainly, heater controller settings) for actual dissolutions. Since it is not practical to use internal thermocouples for control (the corrosion rate would be too high), external thermocouples are provided for this purpose. These tests, then, serve to calibrate the external thermocouples by use of a special
set of internal thermocouples that are used solely for this boilup work. Data obtained in these tests include external thermocouple traces (thermocouple response) as a function of heater controller settings and condenser water flowmeter settings. In time, most of the operating data will be monitored by the computer system.

Six boiling water tests were completed during the present report period while the dissolver was pressurized to $8.6 \times 10^5$ Pa (125 psig) with CO$_2$; the temperature was 178°C. Water charges of 500, 1500, and 3000 cm$^3$ were used in these tests and heater power inputs were 3000, 4500, and 6000 W, respectively. Results showed that heatup time to reach boiling ranged from 12 to 15 min, which was considerably more rapid than the 1-h periods experienced in past work with pilot-scale equipment. By the use of the rapid cooldown system, dissolver solutions were cooled from boiling to 80°C in periods of 25 to 35 min, which is considered reasonable.

C. Multiple Dissolver System
(I. O. Winsch)

Cell M-1 is to be used for the installation of four dissolvers similar to the SUD. This equipment will be used for the dissolution of 33 LWBR-POB fuel rods during the end-of-life (EOL) campaign. The cell has been cleaned out and decontaminated in preparation for installation of the equipment. Major activity in this subtask is being done by ANL-ENG. Most of the equipment for the multiple unit dissolver system is in a design stage. A contract for the four tantalum vessels has been let, and fabrication is about 20% complete.

1. Blend Tanks (BTs)
(J. E. Parks)

The blend tank is a key part of the dissolver systems for the EOL campaign. The vessel provides for combining and mixing the several solutions obtained from the dissolution of each segment. Samples for the critical isotopic analyses are subsequently taken from the vessel, both before and after an isotopic spike (a reference $^{238}$U$_3$O$_8$ material) has been added. Therefore, requirements for blending are strict, i.e., mixing must be thorough, samples must be truly representative of the weighed contents of the vessel, and cross-contamination must be negligible. A recent review of its function indicates that design and management of the blend tank(s) require further development. Work in three areas was advanced: (1) BT design, (2) management system for BTs (considerations of decontamination and reuse versus disposal, one size or several sizes, etc.), and (3) evaluation of mixing and sampling error.

Two prototype BTs have been procured. Their design was reviewed for ease of remote operation and for analytical suitability. A preliminary cost analysis has been prepared, addressing possible strategies for BT usage, including (1) the number of BT sizes to be used and (2) the alternatives of decontamination/reuse and single use/disposal. This analysis indicates a wide range of costs for BT procurement and use, depending upon the decisions in these areas. Further work on a management system awaits the results of BT decontamination tests (see below).
Decontamination and reuse of BTs require that ANL's limits of allowable error in analyses not be violated. Requirements for a BT decontamination procedure have been established. Decontamination procedures are under development and await testing, which is planned for next quarter.

ANL has been required by BAPL to demonstrate negligible sampling error in the mixing and sampling of solutions from the BT. A draft test plan for this purpose has been prepared and submitted to the New Brunswick Laboratory (NBL) for review and comment. This test plan is expected to be implemented as a part of the qualification of the SUD system for EOL operation.

D. Scrap and Waste
   (L. E. Trevorrow and R. E. Nelson)

Spray calcination has been selected as the reference method for converting the dissolver solution to a dry powder to facilitate disposal at a repository. Process and instrumentation layout drawings for the waste calciner system have been reviewed by Project personnel and returned to ANL-ENG for incorporation in the concept review work package.

A preliminary draft of a concept criteria document for the waste calciner system was completed by ANL-ENG and reviewed by Project personnel. Comments are being incorporated in the draft revision. Calculations by ANL-ENG included: (a) determination of off-gas line size, (b) estimation of the required size of traps packed with stainless steel mesh and iron oxide to remove ruthenium from the off-gas, (c) estimation of the holdup system (line size and length) for radon decay, and (d) cell heat balances. Requisitions have been placed for fabrication of a minor portion of the calciner and also for some components of the off-gas system.

An initial draft of a Safety Analysis Report on the packaging and shipping of the calciner product to a repository was completed. Input was provided by a transport-theory (DOT-IV) code which has been adapted for calculation of gamma dose rates from packages of calcined waste. The computer program provides detailed graphics of the radiation level in two dimensions (radially and axially) for a multi-layered, concentric configuration. Radiation levels have been determined for canisters of about 10.2-cm dia, containing calcine in a 0.21 m³ (55-gal) drum, at various distances from the center of the drum. The program may be applicable for the calculation of dose rates from other sources of radiation in this project.

E. Computer System
   (J. E. Parks)

A computer system is being developed for the EOL campaign. This system is intended to serve the following functions: (1) automatic collection and storage of all data generated during processing of the fuel rods during EOL operations, such data to include both analytical and process monitoring and control information; (2) process control of selected systems, through operator interaction, including the shear hydraulic system, balance cooling systems, dissolvers, and off-gas systems; (3) full automation of the highly repetitive shear cut/feed cycle; (4) real-time statistical evaluation of data quality;
(5) error analysis of analytical results; and (6) computer production of interim reports, including equipment and process performance reports, to be forwarded to BAPl. Operator control for the shear and dissolver systems will be provided through computer-store detailed operating procedures made available to operators through CRT-computer terminals at work stations.

This system will employ two computers. A Central Processing Unit (CPU), a VAX-11/780,* is being procured by Chemical Engineering Division to be installed in the Chemical Engineering Building. This computer will provide the functions of data storage, calculation of results, error analysis, and report generation; this computer will be shared with other Chemical Engineering Division users. An intermediate computer, a PDP-11/23, dedicated to the LWBR-POB Project, will be located in the Chemistry Division building near the shielded cell facility and will be interfaced with the shear, dissolvers, balances, and waste calciner. Both of the major analytical machines, the mass spectrometer and automatic gamma counting system, will be interfaced with the local dedicated computer and will provide data directly to the VAX-11/780 as well. This computer will provide the remaining functions listed above.

During this report period, an overall plan for the direction of work for the computer system was firmed, and overall hardware requirements were identified. A decision was made to maximize computer usage at the earliest possible date to provide early operator experience. An initial hardware configuration for the computer system was selected. High priority was given to interfacing the computer system with the SUD system, to provide a model for the proposed multiple dissolver system. All major subsystems, including the waste calciner system, will be connected to the computer system.

Ordering and receipt of the LWBR-POB dedicated intermediate computer (PDP-11/23) plus the CAMAC system for interfacing the PDP-11/23 to the FSS and SUD were essentially completed during the report period. A limited amount of installation and testing of these components has been initiated. Diagrams for interconnecting the SUD and its CAMAC system are being developed; these are about 50% completed. The projected date for receipt of CEN's main computer (VAX-11/780) remains December, 1980.

Overall organization of the software for both the VAX-11/780 and the PDP-11/23 was completed, with all major subprograms identified as well as the interrelationships between them. Coding was completed on the monitoring program, which continuously reads all project sensors (temperature, pressure, flow), compares sensed values with set points, and transmits data to storage display, and/or activates alarms as appropriate. Functional flow diagrams for operation of the FSS and SUD are 90-95% completed in both cases. Corresponding operating procedures are about 25% and 70% complete, respectively. Further work in this area will proceed in conjunction with operational testing of the systems.

* Digital Equipment Corporation.
F. Analytical
   (R. J. Meyers)

An order has been placed for a new mass spectrometer, to be dedicated to the LWBR-POB program; delivery is scheduled for June, 1981. A key feature of the new unit is a turret arrangement which permits automation of the analysis. After the samples have been loaded and the housing evacuated, round-the-clock, unattended operation is possible. Up to 16 samples can be analyzed in 24 h, depending on the type of analysis performed. All functions of the instrument are controlled by a desk-top computer. Direct transfer of the data to the VAX-11/780 computer is planned.

G. Miscellaneous

Cleanout was started in Cell A-5, which had been used for the earlier pilot-scale work; the cell is to be used for EOL analytical work. Transfer of sample solutions to a shielded waste solution pot was carried out, for eventual transfer to the ANL Reclamation Section. This was followed by a general wipe-down of the cell and equipment. Transfer of excess equipment from the cell to the Reclamation Section for disposal was also initiated. The main equipment items (shear and dissolver) will remain in place until need for other work is evaluated.

Cell M-4 is to be used for the waste calciner system, which will convert the dissolver solution to a dry powder, facilitating shipment to a repository. Cleanout of this cell by Reclamation Section technicians has started.

This report period was highlighted by Project review meetings at ANL in August with BAPL and in September with DOE-NFCD and DOE-CORO personnel. BAPL provided a list of Project requirements for the actual measurements and analyses to be performed by ANL. On the basis of present knowledge, these are considered acceptable by ANL, it being understood that all qualification work is being done with unirradiated materials. Since the work continues to be developmental, a need for renegotiation of some of the requirements remains a possibility.
VII. DEVELOPMENT OF INTERIM HIGH-LEVEL-WASTE FORMS
(Seymour Vogler, L. E. Trevorrow, A. A. Ziegler,
V. M. Kolba, G. Bandyopadhyay,* J. E. Slattery,†
T. M. Galvin,* W. J. Grajek,* J. T. Dusek,*
R. M. Arons,* and R. B. Poeppel*)

A. Introduction

This new program has the purpose of yielding an interim waste form for the high-level waste that is generated or located at facilities unsuitable for final processing. From this research, a technology should evolve for preparing interim waste forms that are compatible with transportation requirements and with subsequent terminal waste form processing.

Before the start of generic work, effort has been directed toward providing assistance (described in Section B below) in the preparation of an Environmental Impact Statement for the long-term management of the high-level waste at the Nuclear Fuel Services (NFS) Plant at West Valley, N.Y. This is the only commercial nuclear fuel reprocessing plant in the United States. The facility processed 640 metric tons of spent fuel from 1966 to 1972. The plant was shut down in 1972 to expand its capabilities and to reduce the radioactive effluents and radiation exposure levels of plant personnel. In 1972, NFS estimated that this would require two years and $15 million. However, changing standards and licensing requirements resulted in an estimated escalation of costs to $600 million. NFS decided to withdraw from fuel processing and indicated their intention to surrender responsibility for the wastes to New York State when the lease came up for renewal in late 1980. Current legislation before Congress proposes that the federal government take responsibility for the high-level waste.

A major option under consideration for handling the West Valley waste is the processing of all liquid waste at West Valley to yield a solid that is suitable for transport, with terminal processing being performed elsewhere. The interim processing methods should be simple enough to avoid the requirement for extensive additional facilities at West Valley. The interim waste form (1) must satisfy shipping criteria, particularly in relation to transportation accidents, (2) should be mechanically and chemically stable in the ambient environment, and (3) should be readily compatible with processing methods for preparing a terminal waste form.

B. Interim Waste Forms for West Valley Wastes

Currently, plans are being made to process the West Valley waste. Before action can be taken, an Environmental Impact Statement (EIS) must be prepared that reviews the candidate processes for handling of waste. In support of the EIS, CEN has prepared and delivered a summary of descriptions of selected processes that would yield an interim waste form product.

The waste to be processed is from the West Valley Nuclear Fuel Services Plant and consists of material from two tanks, 8D2 and 8D4. The contents of Tank 8D2 (2.2 x 10^6 L) is the neutralized waste from first cycle Purex

* Material Science Division, Argonne National Laboratory.
extraction and consists of (1) a supernatant liquid that basically contains NaNO₃/NO₂ and (2) a sludge (28,000 L) that is primarily Fe(OH)₃ and FePO₄. The contents of Tank 8D4 (45,000 L) consists of Th(NO₃)₄ and Al(NO₃)₃ in nitric acid.

Examination of the alternatives suggests several options—processing each of the component phases (sludge and supernate from Tank 8D2 and solution from Tank 8D4) either separately or in various combinations. These options may be graphically represented in Fig. 24.

1. Process Tanks 2 + 4 → into monolithic salt block
2. Process Tanks 2 + 4 → calcine → stabilize calcine
3. Process Tanks 2 + 4 → separate → sludge → calcine → stabilize

Salt (supernate)

Decontaminate

Dispose as low level waste on-site

Fig. 24. Processing Options for Preparing Interim Waste Forms

The interim forms considered are (1) calcined waste and (2) fission activity immobilized in molten salt. For each of these two interim waste forms, there are several variations.

In one calcine option, the total waste, (supernate, sludge, and the contents of tank 8D4) may be calcined, followed by shipping of either the calcined powder or pellets prepared from the powder and a sodium silicate binder. A second calcination option involves separating the supernate from the sludge (Tank 8D2) and processing the supernate by ion-exchange techniques to remove the cesium-137 activity. This would lower the fission product activity of the salt sufficiently so that the salt could be cast into concrete blocks and buried on site. The contents of Tank 8D4, the sludge from Tank 8D2 and the ion-exchange resins (containing the cesium activity) from the salt purification would then be calcined. The calcine from this step could then be treated in either of the two ways (see above) considered for the total calcine. This procedure for preparing calcine should yield a smaller volume of calcine than would be obtained by calcining all waste.
Immobilization of fission products in salt involves combining the sludge, the supernate, and the contents of Tank 8D4 and forming a uniform slurry. This slurry is then fed to evaporators where the water is removed until a molten salt solution and suspension remain. Storage canisters are then filled with this molten salt (containing all of the fission product activity). On cooling, a monolithic salt block is formed.

These two techniques for immobilizing the NFS wastes were considered, and basic flowsheets were developed.

For the molten salt immobilization technique, cost estimates have been made for the major equipment items. The proposed arrangement of these items in a 92 by 22 by 43 ft processing cell is shown in Fig. 25.

The scoping design of major components for the fused salt process was based on the use of Type 304 stainless steel at a maximum pressure of \(6.89 \times 10^2\) kPa (100 psig). ASME Boiler and Pressure Vessel Code, Section III, Class II, was used as a guide in the design of the vessels. Sizing of the components was based on data in "Alternatives for Conversion of NFS Wastes to Interim Forms," a report in preparation.
Estimated costs for "standard" wiped film evaporators and chillers were obtained from vendors by telephone (based on previous contacts). Costs of the vessels were based on "as-fabricated costs in dollars/pound," obtained from personnel in the Argonne Procurement Division on the basis of costs for comparable vessels fabricated of stainless steel.

The cost for the major equipment items--two feed mixing tanks, three wiped film evaporators, two intermediate heat exchangers, two chillers, two melters, and the condensate hold-up tank--was estimated to total $381,000. These costs do not include the cost of modification of commercial evaporators or mixers for remote operation. In addition to these equipment costs, the costs of pumps, piping, valves, remote connectors, structure, motors, instrumentation, control consoles, installation of equipment, plant modifications, and miscellaneous items must be included in the ultimate cost estimate for this process.

C. Interim Waste Forms for West Valley: Materials Studies

(G. Bandyopadhyay,* J. E. Slattery,* T. M. Galvin,* W. J. Grajek,* J. T. Dusek,* R. M. Arons,* and R. B. Poepepl*)

Several interim waste forms are being studied that could be suitable for West Valley wastes. The current emphasis is on the study of basic material properties (such as physical and chemical stability, strength, impact behavior, solubility, etc.) of the waste forms; simulated materials are being used in laboratory-scale experiments. The waste forms being considered are (1) fused salt, (2) calcined sludge mixed with anhydrous silicates or boron oxides, (3) sludge that is first mixed with aqueous silicate solutions and subsequently pelletized, and (4) cement-silicate forms containing sodium silicates. Laboratory experiments on the first three options have been initiated.

1. Fused Salt

The largest portion of material in the main waste tank (containing about 560,000 gal) at the West Valley site consists of solutions of sodium nitrate and nitrite salts produced by the sodium hydroxide neutralization of the vast quantities of nitric acid used in Purex reprocessing and a sludge of hydrous oxides. The suggested procedure for using fused salt as an interim waste form consists of the following basic steps: (1) evaporate water from the supernate, (2) melt the precipitated salts, (3) slurry the oxide and hydroxide sludge components into the fused salt, and (4) freeze cakes of this salt. These cakes might then be shipped and later redissolved or remelted during terminal processing.

Although this process appears to be very simple, acceptance of this interim form requires the determination of certain properties of the fused-salt waste form, such as (a) the chemical and physical stability of the salt in the ambient environment, (b) the rate of solubility of the salt in water, (c) the dispersibility of the waste form if subjected to an impact (e.g., in the event of a transportation accident), and (d) the effects of hot fires on

*Materials Science Division, Argonne National Laboratory.
the salt during its transport. Several experiments have been initiated to study these properties for a salt mixture containing NaNO₃, NaNO₂, Na₂SO₄, and KOH (with a NO₃/NO₂ ratio of 7/3 and a Na/K ratio of 99/1). This mixture simulates the salt composition of the West Valley supernate.

The salts (in proper proportions) were dissolved in distilled water. The water was evaporated on a hot plate and, as the temperature increased, the salt mixture melted at 220°C. The molten salt was poured into a cylindrical mold, cooled to room temperature, and subsequently cut to proper sizes for experiments. In some cases (identified later), the salt mixture was heated to 350°C for 15 min before being poured into the mold. The salt mixture was sometimes mixed with Fe₂O₃ (simulating sludge) before the fused cakes were prepared.

Differential scanning calorimetry and thermogravimetric analyses were performed in air on the salts to determine their melting and decomposition temperatures. The simulated salt mixture melted at 220°C, and decomposition started at about 600°C.

Various sizes of cylindrical samples of the fused-salt mixture were individually placed in static water at room temperature, and the time for complete dissolution was noted. From the time for dissolution, the weight, and the surface area, the rate of dissolution (in g/min) as a function of surface area was calculated (Fig. 26).

![Fig. 26. Average Rate of Water Dissolution of Cylindrical Fused-Salt Samples Simulating West Valley Supernate Composition](image)
The samples prepared from salt mixtures were deliquescent, indicating that the salt cake waste form must be stored in a dry leak-tight environment. The samples absorbed as much as 7.8 wt% moisture at 70% relative humidity and 79°F (20°C).

Fracture strength of fused-salt pellets was determined via the diametral compression technique. The strength, \( \sigma \), was determined by using the relation \( \sigma = \frac{2P}{\pi ld} \) [RUDVIK], where \( P \) is the load at failure, \( l \) is the length of the cylindrical pellet, and \( d \) is the pellet diameter. The strength of the fused salt mixture specimens was 4400 ± 1000 kPa. We note below that the strength of these specimens (prepared from salt mixtures) is about one order of magnitude less than the strength of sintered anhydrous sodium silicate compacts. However, the salt mixture specimens are considerably stronger than the specimens prepared from NaNO\(_3\) (strength 190.8 × 50.0 kPa) or NaNO\(_2\) (strength <50 kPa) alone.

Several impact experiments have been performed on specimens (about 2.54-cm dia., 1.24 cm high) prepared from simulated salt mixtures alone, as well as mixtures containing simulated sludge (Fe\(_2\)O\(_3\)). The objective of these tests is to provide information about the generation of respirable-size fines (about 10 \( \mu \)m) upon impact. The tests were performed on the Dynatup instrumented impact test machine* having a modified test block that was specifically designed for crushing-type impact tests on solid cylindrical specimens. Two different velocities (150 and 300 cm/s) of the impacting tup were used during these tests, corresponding to maximum available impacting energies of about 92 and 375 joules, respectively. The impacting tup was allowed to travel 0.32 cm from the impact block (on which the sample was placed), at which point the brake was automatically applied to stop the motion of the tup. A high-speed movie was taken during each experiment to determine the fracture initiation and compaction process. The crushed specimens were collected, and sieve analyses were performed. Since the impact experiments were performed in an unsealed chamber, some loss of material may have occurred during sample collection.

Before discussion of the impact-induced size fraction data, it is important to point out several features of the impact fracture behavior, as identified by the Dynatup system and the high-speed motion pictures taken during these experiments. Such information, not available previously on the nuclear waste forms, is directly relevant to the generation of fines and should be considered when applying the size fraction data from the Dynatup system to more realistic impact events such as transportation accidents.

The Dynatup machine with its instrumentation and data collection systems generated quantitative data on load-time deflection during the impacting event (as exemplified in Fig. 27). These data clearly indicated that the fracture in fused-salt specimens occurred in two stages: the initial impact, which fractured the samples into a few large pieces, was followed by crushing of the samples by compaction. Here, we present only the particle-size analysis data from the impact of the fused-salt specimens. Discussion of the fracture behavior in instrumented impact tests and the

Fig. 27. Load-Time Trace for Test 30 with Fused-Salt Mixture Sample during the Impact Experiment in the Dynatup System

The significance of the load-time traces is presented below in relation to the discussion of the impact fracture of other interim waste forms (e.g., anhydrous sodium silicate compacts).

Figures 28 and 29 show particle-size distribution data, as determined by sieve analysis, for fused-salt specimens after impacting at two different velocities of the tup. Each figure includes data from two similar tests. The reproducibility of the tests is evident. Particle sizes smaller than 44 μm (325 mesh) could not be determined by the sieve analyses. Note that the data in Figs. 28 and 29 can each be represented by two straight lines. Extrapolation of the curves to 10-μm size provided an estimate of the fraction of fines generated during these tests. Although a significant uncertainty could be introduced in such extrapolation since only limited data are available (particularly in the lower size range), the results provide a relative comparison of different compositions and waste forms. Table 27 summarizes the fines-generation data obtained by impacting fused-salt specimens containing no or 10 wt % Fe₂O₃ (to simulate sludge).

The above-discussed properties of fused-salt cakes prepared from simulated West Valley supernate compositions are summarized in Table 28.
Impact Velocity: 314 cm/s  
Total Energy Available: 375 joules

**Fused Salt Cake**
- Test No. 29
- Test No. 30

**Fig. 28.** Impact-Induced Particle Size Distribution in Fused-Salt Cake Samples. Impact velocity was 314 cm/s.

Impact Velocity: 151.2 cm/s  
Total Energy Available: 92.5 joules

**Fused Salt Cake**
- Test No. 31
- Test No. 32

**Fig. 29.** Impact-Induced Particle Size Distribution in Fused-Salt Cake Samples. Impact velocity was 151.2 cm/s.
Table 27. Fraction of Fines Generated during Impact of Fused-Salt Compacts Containing No Fe₂O₃ or 10 wt % Fe₂O₃

<table>
<thead>
<tr>
<th>Composition</th>
<th>Impact Velocity, cm/s</th>
<th>Total Energy Available, joules</th>
<th>Estimated Fraction of Fines (&lt;10 µm), wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused salt prepared by melting at 220°C</td>
<td>314</td>
<td>375</td>
<td>0.001</td>
</tr>
<tr>
<td>Fused salt prepared by melting at 220°C</td>
<td>151</td>
<td>93</td>
<td>0.0008</td>
</tr>
<tr>
<td>Fused salt prepared by melting at 350°C</td>
<td>304</td>
<td>374</td>
<td>0.007</td>
</tr>
<tr>
<td>Fused salt prepared by melting at 350°C</td>
<td>150</td>
<td>91</td>
<td>0.0035</td>
</tr>
<tr>
<td>Fused salt containing 10 wt % Fe₂O₃; melted at 220°C</td>
<td>304</td>
<td>375</td>
<td>0.011</td>
</tr>
<tr>
<td>Fused salt containing 10 wt % Fe₂O₃; melted at 220°C</td>
<td>152</td>
<td>94</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Table 28. Properties of Simulated Fused-Salt Mixtures

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>220°C</td>
</tr>
<tr>
<td>Decomposition Temperature</td>
<td>600°C</td>
</tr>
<tr>
<td>Average Rate of Dissolution</td>
<td>~0.03 g/min·cm²</td>
</tr>
<tr>
<td>Strength</td>
<td>4430 ± 1000 kPa</td>
</tr>
<tr>
<td>Deliquescence</td>
<td>7.8 wt % moisture absorbed at 70% humidity and 20°C</td>
</tr>
<tr>
<td>Fines (&lt;10 µm) Generation on Impact</td>
<td>0.001-0.007 wt %</td>
</tr>
</tbody>
</table>
2. Simulated Sludge Mixed with Anhydrous Silicates

The proposed approach in this option is to mix calcined sludge with anhydrous sodium silicate (or boron oxide), to cold-press to a certain size, and then to sinter at a relatively low temperature (about 600°C). The primary efforts were devoted to (1) identifying the optimum sintering conditions for commercially available sodium silicate compositions with and without simulated sludge (Fe₂O₃) additions and (2) studying the strength and impact properties of the sintered compacts and their microstructural characteristics.

Table 29 lists the four powder compositions used in this investigation. The "G" and the "GD" powders were crystalline sodium silicate containing about 18.5% water; the SS-65 and SS-C powders were amorphous and contained no water. Most of the sintering studies were conducted in air on specimens (about 1.2-cm dia and about 1.9 cm high) cold-pressed to about 60% of theoretical density.

<table>
<thead>
<tr>
<th>Powder Type</th>
<th>Composition (SiO₂:Na₂O weight ratio)</th>
<th>Water Conc., wt %</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>3.22:1</td>
<td>18.5</td>
<td>Crystalline</td>
</tr>
<tr>
<td>GD</td>
<td>2.00:1</td>
<td>18.5</td>
<td>Crystalline</td>
</tr>
<tr>
<td>SS-65</td>
<td>3.22:1</td>
<td>0</td>
<td>Amorphous</td>
</tr>
<tr>
<td>SS-C</td>
<td>2.00:1</td>
<td>0</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>

*Powders were supplied by the PQ Corporation, Valley Forge, PA.*

Representative sintering data for specimens prepared from G and GD powders are shown in Table 30. Note that for both powders, sintering without prior calcination resulted in extensive swelling of the compacts—probably because of the water retained in these samples. Calcination (at 200°C) of the compacts prepared from G powder, followed by sintering at 625°C, produced about 78% dense samples. Higher sintering temperatures (>625°C) resulted in desintering of the samples (Table 30). The specimens prepared from GD powder always exhibited desintering upon calcination and sintering. Since the crystalline hydrated sodium silicate powder could not be sintered to a dense body, the remainder of the effort was concentrated on the amorphous SS-65 and SS-C powders, both of which exhibit good sinterability.
Table 30. Sintering Experiments with "G" and "GD" Sodium Silicate Powders. The green density of all samples was 60% of theoretical.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Calcination in Vacuum</th>
<th>Sintering</th>
<th>Fired Density</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp, °C</td>
<td>Time, h</td>
<td>Temp, °C</td>
<td>Time, h</td>
</tr>
<tr>
<td>G</td>
<td></td>
<td></td>
<td>600</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td>1.75</td>
</tr>
<tr>
<td>200</td>
<td>16</td>
<td></td>
<td>625</td>
<td>4.0</td>
</tr>
<tr>
<td>200</td>
<td>14</td>
<td></td>
<td>700</td>
<td>2.0</td>
</tr>
<tr>
<td>200</td>
<td>2</td>
<td></td>
<td>825</td>
<td>1.5</td>
</tr>
<tr>
<td>150</td>
<td>16</td>
<td></td>
<td>825</td>
<td>2.0</td>
</tr>
<tr>
<td>GD</td>
<td></td>
<td></td>
<td>600</td>
<td>1.9</td>
</tr>
<tr>
<td>100</td>
<td>16</td>
<td></td>
<td>600</td>
<td>1.9</td>
</tr>
<tr>
<td>200</td>
<td>16</td>
<td></td>
<td>700</td>
<td>1.8</td>
</tr>
<tr>
<td>200</td>
<td>2</td>
<td></td>
<td>825</td>
<td>1.8</td>
</tr>
<tr>
<td>150</td>
<td>16</td>
<td></td>
<td>825</td>
<td>1.8</td>
</tr>
<tr>
<td>200</td>
<td>16</td>
<td></td>
<td>890</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 31 summarizes typical sintering data for SS-65 and SS-C compacts. Note that SS-65 powder could be sintered to about 92% density at 600°C, while SS-C powder could easily be densified to about 94% of theoretical. For both powders, calcination was not necessary to achieve the final densities. In general, SS-65 compacts sintered to glassy, translucent bodies; SS-C, on the other hand, densified to opaque white compacts, indicating greater crystallinity of these samples. To study the effect of green density on fired density, several SS-65 compacts of various green densities were sintered at 600°C for 4 h. Figure 30 shows that the green density did not influence the final density at all. It is interesting to note that even loose SS-65 powder which had not been packed could be sintered to >90% density samples.

Several SS-65 and SS-C compacts (60% green density) were prepared from powders mixed with various fractions (up to 33.3 wt %) of simulated sludge (Fe₂O₃). Figure 31 shows that the sintered density of both types of compacts decreased with increasing amounts of Fe₂O₃ in the composition. Preliminary microstructural examination of the fracture surfaces of SS-65 and SS-C compacts indicated that there was reasonable bonding of Fe₂O₃ and the sodium silicate matrix after 55 h of sintering (Fig. 32). There was no evidence of the presence of loose Fe₂O₃ in these compacts. The greater crystallinity of the SS-C compacts than of the SS-65 samples was also evident from the microstructural examination.
Table 31. Sintering Data for SS-65 and SS-C Sodium Silicate Compacts

<table>
<thead>
<tr>
<th>Composition</th>
<th>Green Density, % of Theor.</th>
<th>Calcination in Vacuum</th>
<th>Sintering</th>
<th>Fired Density</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-65</td>
<td>67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 19</td>
<td>615 3.5</td>
<td>2.36 92.1</td>
<td>Translucent - glassy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 16</td>
<td>600 16.0</td>
<td>2.36 92.1</td>
<td>Some opaque (white) area, indicating crystallinity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200 16</td>
<td>500 5.0</td>
<td>1.76 68.7</td>
<td>Opaque - white</td>
<td></td>
</tr>
<tr>
<td>SS-C</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>600 4.0</td>
<td>2.35 91.7</td>
<td>Translucent - glassy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700 4.0</td>
<td>2.43 99.4</td>
<td>Opaque - white</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>700 4.5</td>
<td>2.315 94.9</td>
<td>Opaque - white</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>700 4.75</td>
<td>2.314 94.6</td>
<td>Opaque - white</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>500 4.0</td>
<td>-</td>
<td>Did not sinter</td>
<td></td>
</tr>
</tbody>
</table>
Sintered Loose Powder

SS-65 Powder
Sintered at 600°C for 4h

Fig. 30. Effect of Green Density on the Fired Density of SS-65 Compacts Sintered at 600°C for 4h

SS-5

SS-65

SS-C

Fig. 31. Effect of Fe₂O₃ Addition on the Sintered Densities of SS-65 and SS-C Compacts
The fracture strength of the sintered SS-65 and SS-C compacts containing Fe₂O₃ was determined via the diametral compression technique. These specimens were prepared by cold pressing (1) as-received powders (no particular size fractions) and (2) powders screened through -200 +325 mesh, followed by sintering of the compacts of air at 600°C for 4 h. Figure 33 shows fracture strength data for sintered SS-65 and SS-C compacts prepared from as-received powders, as a function of wt % Fe₂O₃ in the compacts. Note that the SS-C compacts, which were more crystalline due to their lower SiO₂ content, were stronger than SS-65 compacts. In general, Fe₂O₃ addition resulted in a weaker compact. Both SS-65 and SS-C compacts were considerably stronger than the fused-salt samples.

Additional SS-65 specimens were prepared using controlled size fractions (-200 +325 mesh) of sodium silicate and Fe₂O₃. Figure 34 shows the strength data for these samples as a function of wt % Fe₂O₃ in the composition. Upon comparison of the data in Fig. 34 with the SS-65 data in Fig. 33, it becomes evident that controlled particle sizes of the starting powder resulted in stronger compacts. The significance of these results is that the particle size and size distribution of the calcined sludge directly affect the mechanical stability of the waste form.
Fig. 33. Strength as a Function of $\text{Fe}_2\text{O}_3$ Content of Sintered SS-65 and SS-C Compacts Prepared from As-Received Powders. All samples were sintered at $600^\circ\text{C}$ for 4 h.

Fig. 34. Strength as a Function of $\text{Fe}_2\text{O}_3$ Content of SS-65 Compacts Prepared from -200 +325 Mesh Powders by Sintering at $600^\circ\text{C}$ for 4 h.
Several impact experiments have been completed on SS-65 and SS-C compacts (about 2.9-cm dia, 1.6 cm high) containing various amounts of Fe₂O₃. The tests were performed on the Dynatup instrumented impact-testing machine described above. The maximum available impacting energy during these tests was 56 joules and the velocity of the impacting tup was 120 cm/s.

The load-time deflection data (Fig. 35) and photographs from the high-speed movie (Fig. 36) of these impacts tests clearly indicated that as with fused-salt specimens, fracture in SS-65 and SS-C compacts occurred in two stages; the initial impact was followed by crushing of the samples by compaction. In contrast, Pyrex samples, tested as a model system, exhibited brittle fracture by a single impact event (Figs. 37 and 38).

![Fig. 35. Load-Time Trace for Sintered SS-65 Compact Containing 11% Fe₂O₃ during Impact Experiments in the Dynatup System](image)

The load-time deflection curves, shown in Figs. 27, 36, and 38, provide a means of calculating the actual impact energies absorbed by the specimens, a parameter which is directly related to the new surfaces created during impact, and therefore is considered to be a much more relevant parameter to the modelers than the maximum available energy. Analysis of the load-time curves for tests performed on SS-65 and SS-C compacts is continuing in order to determine the duration of and the actual energy absorbed during each stage of impacting.

Results of the particle-size analyses for two impacted SS-C samples are shown in Fig. 39. The reproducibility of the tests is evident from these data. Similar reproducibility was also observed in earlier tests with fused-salt samples. The data in Fig. 39 can be represented by two straight lines, similarly to the case of impact-tested fused-salt samples (Figs. 28, 29).
Fig. 36. Series of Photographs from the High-Speed Movie Taken during the Impact Experiment of a SS-C Compact Containing 14 wt % Fe₂O₃ (Test 52). Time elapsed between the frames is shown on the left-hand corner of the photographs. ANL Neg. No. 306-80-278

Fig. 37. Typical Load-Time Trace for Pyrex in Impact Experiments in the Dynatup System
Fig. 38. Series of Photographs from a High-Speed Movie Taken during the Impact Experiment with a Pyrex Sample. Time elapsed is shown in the left-hand corner of each photograph. ANL Neg. No. 306-80-277

Fig. 39. Impact-Induced Particle-Size Distributions of Two SS-C Compacts
Since it has been established from the load-time curves and the high-speed movies that crushing by compaction is an important mode of fracture for the SS-65 compacts, SS-C compacts, and fused-salt cakes, the particle-size distributions of the impacted specimens (and thus the fraction of fines generated) are expected to be strongly dependent on the travel of the impacting tup after the first impact. The data presented in Fig. 39 were obtained from tests in which the experimental arrangement allowed the tup to travel to 0.32 cm from the impact block (on which the sample was placed), at which point the brake was automatically applied to stop the motion of the tup. The data from a similar experiment (test 42) on SS-65 compact are shown in Fig. 40. Also shown in this figure are the data from another experiment (test 43) in which the tup traveled to 0.62 cm from the impact block before it stopped. In both cases, the graphs were used to obtain an estimate of the fraction of fines generated during these tests. The estimated fraction of fines generated during test 42 (in which the tup traveled to 0.32 cm from the impact block as opposed to 0.62 cm for test 43) appears to be significantly greater than that estimated for test 43. This is in agreement with the load-time data (Fig. 41), which indicate significantly less compaction in test 43 than was observed in test 42.

Several other impact experiments have been performed on SS-65 and SS-C compacts containing various amounts of Fe₂O₃. In all of these tests, the tup traveled to 0.62 cm from the impact block. The results show that a starting powder with a controlled particle size distribution generated less fines upon impact. The data for fines generated from SS-C compacts (prepared from -200 +325 size powder) as a function of Fe₂O₃ are shown in Table 32. An increased fraction of Fe₂O₃ in the compacts increased the fraction of fines.

<table>
<thead>
<tr>
<th>Fe₂O₃ in SS-C Compacts, wt %</th>
<th>Fraction of Fines (&lt;10 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \times 10^{-8} )</td>
</tr>
<tr>
<td>11.1</td>
<td>( 5 \times 10^{-6} )</td>
</tr>
<tr>
<td>14.3</td>
<td>( 6 \times 10^{-3} )</td>
</tr>
<tr>
<td>33.3</td>
<td>( 4 \times 10^{-2} )</td>
</tr>
</tbody>
</table>
Fig. 40. Impact-Induced Particle-Size Distribution in SS-65 Compacts. The travel of the tup was to distances 0.32 and 0.62 cm from the impact block in tests 42 and 43, respectively.

Fig. 41. Load-Time Trace for (a) Test 42 and (b) Test 43 during Impact Experiments in the Dynatup System.
3. Sludge Pelletization with Aqueous Sodium Silicate

The proposed approach in this option involves agglomeration of calcined sludge into small (≤2.54-cm) spherical pellets in a disk or drum-type pelletizer (pressureless pelletizing), using sodium silicate solution as the binder. Firing of the agglomerated spheres at temperatures up to 550°C is expected to remove the water and form hard pellets. Since the process of pelletization is strongly dependent on the particle size and size distribution of the calcined sludge, initial characterization of the sludge compositions is extremely critical. If the majority of the sludge particles are in the larger than 200 mesh size range, pelletizing may not be practical; instead, briquetting of the compositions should be considered.

Since no information is currently available on sludge particle size and size distributions, we attempted to pelletize simulated sludge (Fe₂O₃) with sodium silicate solution in preliminary experiments in our laboratory. In these experiments, weighed amounts of as-received Fe₂O₃ powder (-325 mesh) were placed in a rotating glass jar. Sodium silicate solution was fed into the jar through a long copper tube drilled with small holes. Fe₂O₃ agglomerates formed as sodium silicate was mixed with the powder. The agglomerate sizes varied widely, as is expected in drum pelletizing operation. It is known that disk pelletizers can generate uniform-sized pellets. However, some variation in pellet sizes is desirable for better packing efficiency during storage. Several experimental parameters such as the amount, concentration, composition, and the rate of addition of sodium silicate solution, the amount of Fe₂O₃ powder, and the speed of the rotating jar are being investigated to identify their effects on the agglomeration process and the quality of the agglomerates.
BRAITHWAITE

CHAPMAN

COLES

CORNING

DMIC-245

DP-1382

ETR-296

FLYNN

INOUE

LEAD
Lead for Corrosion Resistant Applications, Lead Industries Association Inc., N.Y., N.Y.

LERCH
LEVIIZ


MECHAM


REGO


RINGWOOD


ROSS


RUDVIK


SEITZ-1978


SEITZ-1979A


SEITZ-1979B


SEITZ-1980

STEINDLER-1979A

STEINDLER-1979B

STEINDLER-1980

STRACHAN