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FUEL-CYCLE PROGRAMS
QUARTERLY PROGRESS REPORT

April—June 1981

by

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Chemical Engineering Division

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ABSTRACT

A program continues for the development of an interim waste form capable of being transported from facilities where waste is generated to terminal waste processing. In work on a process for converting high level liquid waste to a phosphate-immobilized solid waste and heating the mixture to dryness (400°C), the amount of phosphate required to be added to simulated waste has been found to be 233% of the theoretical amount to balance the cationic charge as PO_4^{3-} .

Rates of dissolution (*i.e.*, penetration rates) of various interim waste forms (such as synthetic waste salt with and without synthetic sludge, phosphate-immobilized specimens, and silicate-agglomerated Fe_2O_3) in stagnant water ranged from 1×10^{-5} to 1×10^{-4} cm/s.

For sintered silicate/sludge systems, compacts having the desired mechanical strength were obtained by using a maximum of 30 wt % sludge and compaction at >211 MPa. In other experiments, it was observed that pellets of adequate strength were prepared from mixtures of 75 wt % sludge, 20 wt % sodium silicate, and 5 wt % $\text{Ca}(\text{OH})_2$; these specimens showed no weight loss upon immersion in water.

Measurements of rates of leaching from simulated waste glasses are continuing. The leach rates of different elements from the same glasses sometimes differ by several orders of magnitude so that no single analytical technique appears to be optimum for all elements. Leach tests on over 90 SYNROC and irradiated glass samples have been completed.

Laboratory-scale impact tests of solid alternative waste forms are being performed (1) to assess source terms of airborne release (from particle size distributions) and (2) to assess the increases in source terms of leach rates (from increases in surface area). From this, dispersion from mechanical impacts during normal and

accidental conditions of transport can be determined. Cylindrical specimens (ceramics, frits, and glass) were impacted diametrically with a striker bar. Particle size measurements were made, and plots show that size distributions are lognormal in the range, 10 μm to 2 mm.

A review of the methodology under development for the characterization of the impact behavior of brittle materials included the following topics: evaluation of measurements of particle size distributions; the relation of energy and stress distributions to particle-size distributions; and energy partitioning in impact testing machines.

Logging techniques are being developed to measure the relative amount of residual oil in a depleted oil reservoir by injecting gamma-active solution into it. For planned laboratory-scale experiments, equipment has been collected, sandstone samples acquired, and an aqueous solution prepared having a composition similar to that of brine reservoir fluid.

The flow of groundwater through igneous rocks is of considerable interest in connection with geologic storage of high-level radioactive waste. Analyses of samples from the Notch Peak (House Range, Utah) intrusive body suggest that groundwater flow was through fractures and not through the rock matrix, indicating that no new processes of migration need be considered in the design of a nuclear waste repository.

Testing and development of equipment for the destructive analysis of full-length irradiated fuel rods from the LWBR is in progress. This work is in support of the LWBR Proof-of-Breeding Project.

SUMMARY

Development of Interim High-Level Waste Forms

Continued experimentation on phosphate immobilization (i.e., the use of phosphate as a binder to form an interim waste suitable for shipping to a terminal processing site) has indicated that to consistently prepare a high-density, glassy, structurally strong product, the amount of phosphoric acid added to the simulated NFS waste must be equal to or greater than 233% of the theoretical amount to balance the cationic charge as PO_4^{3-} . In experiments run with 233% phosphate, the addition of water during distillation is required to help remove nitric acid as a water/nitric acid azeotrope.

The rates of dissolution of various interim waste forms in stagnant water were measured. Massive pieces of synthetic Nuclear Fuel Services (NFS) waste salt with or without 8 wt % synthetic sludge yielded a penetration rate of about 4×10^{-4} cm/s. Penetration rates for phosphate-immobilized specimens from different preparations varied from 6×10^{-5} to 1×10^{-4} cm/s. Two samples of silicate-agglomerated Fe_2O_3 had penetration rates of 1×10^{-5} to 2×10^{-5} cm/s in stagnant water and were the least reactive materials in stagnant water.

Preliminary results on the hydrolysis of FePO_4 suggest that instead of FePO_4 , previously reported to be present in the NFS waste tank, ferric ion is probably present as hydrated Fe_2O_3 .

Testing of sintered silicate/sludge systems indicated that SS-65 and SS-C compacts containing ≥ 50 wt % sludge were mechanically extremely weak (strength 0-0.5 MPa). Only SS-C compacts containing 30 wt % sludge and compacted at ≥ 211 MPa exhibited the desired mechanical strength.

Studies were continued on the cementitious bonding of sodium silicate-calcium hydroxide-synthetic sludge systems. Cold-pressed samples are exposed to a controlled high-humidity air (90% relative humidity) for 24 h at 35°C . Samples thus prepared and containing 75 wt % sludge, 20 wt % sodium silicate, and 5 wt % $\text{Ca}(\text{OH})_2$ yielded pellets of sufficient strength. Such a specimen showed no detectable weight loss when immersed in stagnant water at room temperature.

Neutron Activation and Tracer Studies

Comparative MCC-1 type leach rate measurements of SRL frit 211 and SRL frit 131 simulated waste glasses are in progress. Conventional solution analytical methods (colorimetry, ICP and DCP emission spectroscopy, atomic absorption), neutron activation techniques, and radioactive tracers are all being employed to measure the leach rates of about seventeen different elements in these glasses. Leach rates of different elements from the same glasses are observed to sometimes differ by several orders of magnitude (i.e., $\text{Eu} \ll \text{Cs}$) so that no single analytical technique appears to be optimum for all elements. Many analyses are in progress.

Significant protective layers which retard leaching are observed on SRL glasses. These layers, studied using electron microprobe and scanning electron microscopy techniques, were found to be depleted in sodium and silicon and enriched in manganese, magnesium, and rare earths. These observations correlate well with solution analysis results.

Leach tests on over 90 SYNROC and irradiated glass samples have been completed and the results obtained. For SYNROC leaching in Teflon and polypropylene bottles, there seems to be a container effect whereby the leach rates of SYNROC in polypropylene are one-third those in Teflon.

Brittle Fracture Studies

Seven additional impact tests were made using a standardized test procedure, and the results are compared with similar tests of simulated alternative waste materials reported in the previous report period. In all tests, cylindrical specimens of about 2.5 cm by 2.5 cm were impacted diametrically with a 10-kg steel striker bar that fell from a height predetermined to produce a maximum energy input of 10 J/cm^3 of material. Particle size measurements made by both sieving and Coulter counter analysis in the range of $5 \mu\text{m}$ to 2 mm were used to determine the lognormal size parameters which describe the complete size distribution of all particles smaller than 2 mm; this fraction contains more than 95% of the total geometric surface area formed by fracture, as estimated from the lognormal size parameters. The respirable size fractions of PNL 76-68 glass, SYNROC ANL, LLL SYNROC B, LLL

SYNROC D, and SRL frit 131 glass were very similar; respirable fractions constituted 0.10 to 0.18 wt % of the particles. In a test made to allow comparison, a specimen of high-silica glass from Catholic University showed a respirable fraction of 0.22 wt %, which is similar to the result of 0.27 wt % obtained for a Pyrex specimen. The above results are within the range of respirable fractions previously reported for Rockwell TAILORED CERAMIC (0.05 wt %) and ORNL FUETAP concrete (0.43 wt %). Replicate tests were done for SRL 131 glass and SYNROC MSD. The results for each material agreed within the standard error of the regression analysis for the respirable fraction and the lognormal parameters.

A review of the methodology under development for the characterization of the impact behavior of brittle materials included the following topics: evaluation of measurements of particle size distributions; the relation of energy and stress distributions to particle-size distributions; and energy partitioning in impact testing machines.

Fluids in Rock

Reported are preparations to test the performance of proposed nuclear-waste repositories and to develop procedures for core-flood experiments. The core-flood experiments will be used to examine proposed methods of logging the oil in depleted oil reservoirs. The proposed logging methods use gamma-active fluid injected into the reservoir to detect the presence of oil.

Trace-Element Transport in Lithic Material by Fluid Flow

It was previously reported that NaCl-CaCl₂ brine ($[Cl^-] > 0.24M$), which has a very high F⁻ content ($>3.3mM$), was eluted from granite from Northern Illinois drill hole UPH-3. This brine is similar in composition, and is believed to be of similar origin, to brine of sedimentary origin from the Illinois Basin. The coexistence of calcium and fluoride in the water implies the presence of a complexing agent, most likely boron.

The absolute concentrations of ions in the pore water were not determined because of ambiguity in the effective pore volume. Elution of tritium-labeled water through the core shows that the effective porosity is at most 0.07%. Three improved sampling techniques, which promise to give information on absolute concentrations, are discussed.

Preservation of samples is discussed. It is estimated that granite core 4.8 cm in diameter may dry out in as little as 28 days.

Work on the Notch Peak intrusive body is also summarized. The evidence indicates that there was no perceptible migration of major elements or trace elements, except possibly for rubidium, from the Notch Peak, Utah, monzonite intrusion into surrounding limestones and siltstones, except at skarns. The evidence suggests that nearly all flow was directed through fractures, and not through the rock matrix.

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

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

Activity is reported on four main subactivities of this Project: (1) the full-scale shear (FSS), (2) the single-unit or prototype dissolver (SUD), (3) multiple dissolvers needed for the destructive analyses of full-length (about 3-m) irradiated fuel rods for the EOL campaign, and (4) scrap/waste disposal. In addition, current work by the Analytical Section 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.

I. DEVELOPMENT OF INTERIM HIGH-LEVEL WASTE FORMS
 (Seymour Vogler, G. F. Vandegrift, Jacqueline Williams,
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A. Introduction

High-level liquid radioactive wastes (HLLW) are often produced at facilities in which terminal processing of the waste is not practical because of the high cost or hazards involved in such an operation. Under these circumstances, the waste could be incorporated into an interim solid waste form for shipping to a terminal processing site. The interim form should require only simple processing methods, so that extensive additional facilities will not be required at the originating site. Additionally, the interim waste form must satisfy shipping criteria, particularly in relation to transportation accidents; should be mechanically and chemically stable in the ambient environment; and should be readily compatible with the terminal-waste-form processes. From this research, there should evolve a technology for preparing interim waste forms compatible with transportation requirements and with subsequent terminal waste form processing.

B. Experimental Studies on Interim Waste Forms

Seymour Vogler, G. F. Vandegrift, T. J. Gerding, E. T. Kucera,[†]
 and Jacqueline Williams)

Studies were continued on two possible interim waste forms (fused salt and phosphate-immobilized waste) that may be suitable for solidifying the HLLW at the Nuclear Fuel Services (NFS) Plant at West Valley. The fused salt form would be prepared by mixing the supernate and sludge constituents of NFS waste, evaporating away its water content, and melting the low-melting $\text{NaNO}_3/\text{NaNO}_2/\text{Na}_2\text{SO}_4/\text{NaOH}$ salts while suspending the nonmelting oxides in this melt. The cooled solid suspension product would be shipped and stored.

A phosphate-immobilized interim waste form would be prepared by adding H_3PO_4 to the supernate sludge mixture, followed by a distillation progressing to about 400°C . As the distillation proceeds (i.e., as the temperature rises), the distillate would change from H_2O to $\text{H}_2\text{O}/\text{HNO}_3/\text{HCl}$ and back to H_2O again as all traces of nitrate, nitrite, and chloride would be removed from the waste and replaced with phosphates, pyrophosphates, and metaphosphates. The product is not a glass (much higher temperatures, $850\text{--}1000^\circ\text{C}$, would be necessary for this) but a glasslike homogeneous solid solution of mostly sodium (plus other cationic) pyro- and metaphosphates.

1. Fused Salt

Studies are under way to measure the resistance of the fused salt (basically NaNO_3 , NaNO_2 , and Na_2SO_4) to irradiation. These studies are necessary to ensure that storage of NFS waste in this form for up to 20 y will

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not unduly pressurize its sealed containment canisters. Literature information [JOHNSON-1961, -1970] indicates that sodium nitrate is decomposed when exposed to gamma radiation:

There is no information, however, to indicate the response to gamma irradiation of (1) a 70% NaNO_3 /30% NaNO_2 salt alone or (2) a similar mixture in which the sludge components of NFS waste are suspended. Our studies will measure the effects of these additional chemical components on the irradiation of NaNO_3 .

In studies completed thus far, the ability of our equipment and techniques to duplicate the literature g value for reaction 1 has been tested and verified. These studies will be reported in more detail when they are completed.

2. Phosphate Immobilization

HLLW converted to a phosphate solid appears to be an attractive interim waste form. Phosphate, pyrophosphate, and metaphosphate ions form strong bonds with most metal ions, and their salts with multivalent metal cations have low aqueous solubilities. Phosphate and acid phosphate cements, used as dental cements, have low leachability and high compressive strengths.

a. Preparation of Phosphate-Immobilized Simulated NFS Waste

Further experiments have been performed this month in the manner described previously [STEINDLER-1981C]. The procedure for preparing a phosphate-immobilized waste form is basically one of adding phosphoric acid to the liquid waste and heating the mixture to dryness (400°C). After an amount of phosphoric acid greater than that necessary to balance the cationic charge as PO_4^{3-} is added to the waste, the resultant solution is heated. Nitrate and chloride are distilled away from the waste as azeotropic mixtures of HNO_3 , HCl , and H_2O .

Three aspects of the experiments were studied:

- The effect of the ratio of phosphoric acid to total amount of cationic charge in the simulated NFS waste on the physical properties of the product.
- The effect of additional water, added to the distillation kettle at elevated temperatures, on driving off more of the HNO_3 before the product solidifies.
- Testing our ability to duplicate experimental and product conditions.

Results have indicated that to consistently prepare a high-density, glassy, structurally strong product, the amount of phosphoric acid added to the simulated NFS waste must be equal to or greater than 233% of the theoretical amount to balance the cationic charge as PO_4^{3-} . (We have done experiments in which 117 to 400% of the theoretical amount was added.) In experiments with 233% phosphate, water must be added during distillation to help remove nitric acid as a water/nitric acid azeotrope. If there is still nitrate in the phosphate-immobilized waste after its viscosity rises too high, the final product becomes very porous because NO_2 gas is evolved during the thermal decomposition of nitrate. An experiment run with a phosphate ratio of 291% and with no water added during distillation showed slight signs of nitrate decomposition; the material appeared to be more ceramic than glassy. When the amount of phosphate was raised to 389% and no water was added during distillation, the material was glassy. A preparation containing only 117% of the theoretical amount of phosphoric acid was extremely porous and of very low structural integrity.

b. Rates of Dissolution of Possible Interim Waste Forms for NFS Wastes

Studies of dissolution/disintegration rates in stagnant water have been complete on four preparations of phosphate-immobilized simulated NFS waste. The specifics for each of these preparations are:

- 209-140. The phosphoric acid added was 233% of that needed to balance the cationic charge as PO_4^{3-} . All of the phosphoric acid was added at one time before distillation started. Water was added incrementally during distillation. The solid product remaining after distillation was complete was gray glassy, nonporous, and homogeneous-looking with a density of 2.64 g/mL.
- 209-147. The phosphoric acid added was 233% of that needed to balance the cationic charge as PO_4^{3-} . In this experiment, only 75% of the phosphoric acid was added initially; the remainder was diluted with water and added incrementally during distillation. The solid product produced in this experiment was gray, extremely porous, homogeneous, ceramic-looking, and massive and had a density of 1.68 g/mL.
- 214-03. The phosphoric acid added was 291% of that needed to balance the cationic charge as PO_4^{3-} . All of the H_3PO_4 was added before heating began, and no additional water was added during distillation. The massive product of this experiment was more ceramic than glassy. It appeared to be homogeneous and was basically nonporous.
- 214-08. The phosphoric acid added was 400% of that needed to balance the cationic charge as PO_4^{3-} . All of the H_3PO_4 was added before heating, and no additional water was added during distillation. The product was glassy and nonporous. It appeared to be homogeneous and had a light green tint to its gray color.

For the sake of comparison, the dissolution/disintegration rates in stagnant water of other materials were also measured. These materials were:

- Salt Block Samples (obtained from M. G. Seitz, Argonne National Laboratory). This material, taken from the Mississippi Chemical Corp. potash mine in southern New Mexico, contained (in order of approximate wt %) NaCl, KCl (sylvite), Fe_2O_3 , $\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, and a host of other minerals.
- Simulated NFS Waste Fused Salt containing the concentrations of NaNO_3 , NaNO_2 , NaOH, and oxides of other metals (except U), present in NFS waste.
- Fused Salt prepared to simulate the supernate only of NFS waste--63.4 g NaNO_3 /27.2 g NaNO_2 /17.5 g Na_2SO_4 /1.0 g KOH.
- Pellets of Silicate-Agglomerated Fe_2O_3 (prepared by G. Bandyopadhyay et al., Materials Science Division, ANL).
- A piece of Brach's Sparkler lemon-flavored hard candy.

Several samples of different geometries and therefore different surface areas were tested for each of several waste forms--the phosphate-immobilized simulated waste forms, the fused salt simulated waste form, and the salt block. The rates of dissolution/disintegration for these three materials could therefore be correlated with initial surface areas.

(1) Experimental

Sample preparation varied from material to material; each is therefore discussed separately:

- Brach's lemon-flavored hard candy: used as taken from the wrapper.
- Silicate-Agglomerated Fe_2O_3 : used directly in the pelletized form as received.
- Salt Block: a hacksaw and a file were used to cut rectangular samples.
- Simulated NFS Fused Salt: samples were prepared by heating the solid mixture of the salt and metal oxide mixture in a small furnace contained in a dry box. When the $\text{NaNO}_3/\text{NaNO}_2$ mixture melted, the suspension was swirled and poured into crucibles having various geometries. As the material cooled, a pipe formed down the center of these samples; additional material was then poured into these pipes to fill them or at least seal them.

- Phosphate-Immobilized Simulated NFS Waste: because this material acts like glass, simple geometric shapes are very difficult to prepare. It is too hard to cut with a hacksaw or to file. It also does not cleave very well. Consequently, only sharp corners could be removed, and surface geometries of samples needed to be defined by as many as thirteen faces.

Before rate studies were started, the samples were weighed on a top-loading balance to the nearest 0.01 g and the surface areas were estimated. To estimate a surface area, the samples's surface was defined as a series of geometric planes (rectangles and triangles), and the length of each side of these planes was measured to the nearest millimeter with a ruler.

The equipment for measuring the dissolution/disintegration rates consisted of a 4 L beaker containing 4 L of distilled/deionized water, a stainless steel mesh basket tied (with Teflon string) to a hook located on the underside of a Mettler 1200 top-loading balance, and a timer capable of measuring seconds. Experiments were begun by placing the sample in the basket and the basket in the water. The timer was then started. (The weight of the empty basket had previously been tared.) The weight of the sample and the elapsed time were periodically recorded. Figure 1 is a plot of the weight of sample in water vs. time for a typical experiment.

Fig. 1.

Typical Dissolution/Disintegration
Experiment, Exp 210-48, Simulated
NFS Fused Salt Sample

As would be expected, the shapes of these curves vary with the geometries of the dissolving/disintegrating pieces. In general, the smaller the change in surface area with weight loss, the less the curve deviates from the initial linear slope as the sample loses weight. The weight loss vs. time curve for a flat thin object, whose surface area shrinks only slightly with weight loss, is linear over a much wider range than for a cubic object.

For each experiment, a rate was measured as the negative slope at the initial linear portion of the curve. This rate, measured in g/s, was corrected for the buoyancy effect of water by the relationship:

$$\text{Rate}_{\text{corr}} = \text{Rate} \left(\frac{\text{sample weight in air}}{\text{initial sample weight in water}} \right)$$

Also, the densities of these materials were derived by measuring the sample weights in air and in water:

$$\text{density} = \frac{\text{weight in air}}{\text{weight in air} - \text{weight in water}}$$

(2) Results

The rate of dissolution/disintegration was measured as a function of surface area for seven materials--salt block procured from M. Seitz, simulated NFS fused salt wastes with and without sludge material, and four different phosphate-immobilized NFS waste forms. To give credence to the method, the salt block was tested first. The salt block was mostly soluble material but did contain a sizable amount (about 10%) of Fe_2O_3 , which has a very low solubility in water. This material has, therefore, the same type of soluble/insoluble material mix as the possible interim waste forms.

All materials tested showed a linear correlation of initial rate of dissolution/disintegration with surface area. Figures 2 and 3 are typical examples of the results.

In addition, dissolution/disintegration experiments were performed on two samples of silicate-agglomerated Fe_2O_3 that were prepared as described earlier [STEINDLER-1981B]. The first sample was SS-C/ Fe_2O_3 in a ratio of 2/1 (SS-C is a 2/1 weight ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ silicate powder). The second sample was prepared with a 6/1 SS-C/ Fe_2O_3 ratio. The weight loss vs. time dependencies of these experiments were different from those of all other materials tested; there was an induction period of 20-30 min before weight loss began. After this induction period (when the samples not only did not lose weight but gained weight), these two samples behaved like the other materials.

To give a qualitative significance to the dissolution/disintegration rates of the above-mentioned materials, the dissolution rate of a piece of Brach's Sparkler lemon-flavored hard candy was measured. The dissolution of this material proceeded in the same manner as did the other materials even though all of this sample was soluble.

Fig. 2. Salt Block: Rate of Dissolution/
Disintegration vs. Surface Area

Fig. 3. Phosphate-Immobilized Simulated NFS
Waste: Dissolution/Disintegration
Rate vs. Surface Area

The rates of dissolution/disintegration for all of these materials (Table 1) may be compared. By dividing the rate of weight loss per cm^2 by the density of the material, a penetration rate constant in units of cm/s is obtained. This rate constant appears to be the most appropriate for comparing one waste form with another. These comparisons show that silicate-agglomerated Fe_2O_3 (a stand-in for NFS sludge material) has the lowest rate of dissolution in quiescent water.

Table 1. Dissolution/Disintegration Rate Constants^a

Materials ^b	Density, g/cm^3	Rate Constant, $\text{g/cm}^2\text{-s}$	Rate Constant, cm/s
Salt Block	2.14	4.8×10^{-4}	2.2×10^{-4}
NFS Waste Salt (Supernate with Sludge)	2.24	9.7×10^{-4}	4.3×10^{-4}
(Supernate Only)	2.22	9.7×10^{-4}	4.4×10^{-4}
Brach's Sparkler (lemon)	1.53	3.1×10^{-4}	2.0×10^{-4}
Sodium Silicate SS-C/ Fe_2O_3 Pellet 6/1	2.48	1.6×10^{-5}	6.4×10^{-6}
Sodium Silicate SS-C/ Fe_2O_3 Pellet 2/1	2.48	5.3×10^{-5}	2.1×10^{-5}
Phosphate-Immobilized Exp. 209-140	2.64	2.2×10^{-4}	8.5×10^{-5}
Phosphate-Immobilized Exp. 209-147	1.68	9.4×10^{-5}	5.6×10^{-5}
Phosphate-Immobilized Exp. 214-03	2.30	2.0×10^{-4}	8.7×10^{-5}
Phosphate-Immobilized Exp. 214-08	2.50	3.3×10^{-4}	1.3×10^{-4}

^aAll measurements were made at ambient temperature (20-26°C) in 4000 mL of stagnant deionized water.

^bThe compositions of these materials are described in the text.

The dissolution/disintegration rates of phosphate-immobilized simulated NFS wastes are disappointing. The rate, fivefold lower than that obtained by merely dehydrating the $\text{NaNO}_3/\text{NaNO}_2$ salt solution, may not be worth the extra difficulty in preparing this form. It is important to note, however, that although the solid product from these distillation experiments appeared to be completely homogeneous and appeared to disintegrate homogeneously, at the end of disintegration, the product was nonhomogeneous--a colorless leachate and a very fine white powder remained in the beaker. Samples of the leachate from phosphate-immobilized samples were analyzed for metal cation content by d-c arc spectrometry. These analyses show that the only cation soluble in the leachate of these interim waste forms is sodium ion. Iron, for example, was determined to be present in the leachate at less than 0.1% of the concentration possible if the iron had all dissolved.

There were only trivial differences in dissolution/disintegration rates for the four phosphate-immobilized waste forms studied. The dissolution/disintegration rate was not significantly altered by changing the volume ratio of H_3PO_4 to simulated NFS waste in the narrow range studied.

The same penetration rate was measured for simulated NFS fused salt, whether the sludge components were present or absent. This result would be expected since the sludge material is only 8 wt % of the fused salt and there is no significant chemical reaction possible between the supernate and the sludge components in the solid state.

c. Thermal Properties of Phosphate-Immobilized Simulated NFS Waste

A preliminary differential thermal analysis (DTA) in the range 20-1000°C was run on phosphate-immobilized simulated NFS waste prepared in Exp. 209-140. There were three distinct endothermic regions. The first occurred at about 275°C; the second, a wide region with many changes occurring one after another, began at about 570°C; the third was in the region of 950-1000°C. Thermal gravimetric analyses will be performed on this same material to learn whether these changes were due to melting, a chemical reaction, or vaporization of constituents. Discussion of the significance of this DTA has been postponed until more experimental data are obtained. The same kind of experiments will also be performed for other preparations of phosphate-immobilized simulated NFS waste.

C. Stability of FePO_4

(G. F. Vandegrift and E. T. Kucera*)

Because there is a question as to whether large amounts of FePO_4 are stable in Nuclear Fuel Services (NFS) sludge [STEINDLER-1981C], the following reaction is being studied:

* Member of the Analytical Chemistry Laboratory, Chemical Engineering Division.

Experiments are being performed to determine the extent of reaction of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ solid with an aqueous solution simulating NFS supernate (6M NaNO_3 and 0.18M NaOH). The reaction is being investigated by measuring the concentrations of iron and phosphorus in the aqueous phase contacted with various amounts of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ($+90 \mu\text{m}$ - $180 \mu\text{m}$ particle size) for various times. The ratio of iron to phosphorus in the solid residues of these reactions is also being measured.

The technique used for each sample to measure iron and phosphorus simultaneously is energy-dispersive X-ray fluorescence (EDXRF). A sample is prepared for analysis by EDXRF by evaporating to dryness aqueous solutions and drying all residues overnight in an 85°C oven, combining the dried residue with cellulose binder (3 parts dried residue to 1 part cellulose), and pressing the mixture into a $3/4$ -in.-dia 1-g pellet.

At this time, only qualitative statements can be made about the hydrolysis reaction:

1. The higher the pH, the further reaction 3 proceeds and the more rapid is its approach to equilibrium.

2. The extent to which the above reaction progresses to the right is limited by the solubility of PO_4^{3-} in the NaNO_3 solution and possibly by a surface reaction of PO_4^{3-} with solid Fe_2O_3 or FePO_4 .

3. If the composition of the supernate in Tank 8D2 is as reported in the companion report [WNYNSCS], then, based on the experiments reported above, FePO_4 should be absent from the sludge; all ferric iron should be present as Fe_2O_3 .

These results are preliminary and will be discussed further when more data are available.

D. Interim Waste Form Development: Materials Studies

(G. Bandyopadhyay,* J. E. Slattery,* and T. M. Galvin*)

The work performed during the past quarter includes (1) completion of the studies of densification, fracture behavior, and stability in the presence of water of several sintered silicate simulated sludge[†] specimens and (2) continuation of the investigation of the properties of specimens containing sodium silicate/calcium hydroxide binder. The results are summarized below.

* Member of the Materials Science Division, Argonne National Laboratory.

[†] Simulating Nuclear Fuel Services sludge.

1. Sintered Silicate/Sludge System

Several silicate/sludge specimens containing SS-65 ($\text{SiO}_2:\text{Na}_2\text{O} = 3.22:1.00$) or SS-C ($\text{SiO}_2:\text{Na}_2\text{O} = 2.00:1.00$) sodium silicate* and 30, 50, or 70 wt % synthetic sludge were cold-pressed at different compacting pressures (from 28 to 351 MPa) and subsequently fired at 600°C for 4 h. Figure 4 shows the sintered density of these specimens as a function of sludge content and compacting pressure. The strength data of these specimens, as obtained by the diametral compression technique, are shown in Fig. 5. It is evident that both SS-65 and SS-C compacts containing ≥ 50 wt % sludge were mechanically extremely weak (strength 0–0.5 MPa). High compacting pressure improved the strength to some extent. However, only SS-C compacts containing 30 wt % sludge and that had been compacted at ≥ 211 MPa exhibited the desired mechanical strength.

In contrast to the data presented in Fig. 5, recent experiments with sludge/silicate specimens containing 75 wt % synthetic sludge and 25 wt % SS-65 or SS-C indicated that substantially stronger pellets (fracture strength, about 10 MPa) could be prepared by exposing the specimens to a high-humidity environment at 35°C prior to the sintering step. Additional tests are being performed to confirm this finding. The mechanisms contributing to the improvement of the mechanical properties of the pellets are also being investigated.

Fig. 4.

Sintered Density of SS-65 and SS-C Specimens as a Function of Compacting Pressure during Fabrication and Sludge Content of the Specimens

* Sodium silicates were obtained from PQ Corporation, Valley Forge, PA.

Fig. 5.

Fracture Strength, as Measured by Diametral Compression Technique, of Sintered SS-65 and SS-C Specimens as a Function of Compacting Pressure during Fabrication and Sludge Content of the Specimens

The stability in water of silicate/sludge specimens (prepared by conventional cold-pressing and sintering technique without the humidity treatment) was examined by determining the time taken for collapse of the specimens when immersed in 4000 cm³ of static water at room temperature. Both SS-C and SS-65 sintered cylindrical compacts (surface area, about 5 cm²) containing 30 wt % sludge and cold-pressed at 351-MPa pressure collapsed in about 2-3 h. The remaining specimens, containing >30 wt % sludge and/or cold-pressed at lower pressures, failed in shorter time periods. Although pure SS-65 powder is one-sixth as water-soluble as pure SS-C powder at 25°C, the silicate/sludge specimens did not show any strong effect of composition on the solubility. SS-C/sludge compacts were, in fact, somewhat more stable in water than similar SS-65/sludge specimens--probably because of the superior mechanical stability of the former compositions.

The silicate/sludge specimens were, in general, considerably more resistant to water than were fused-salt samples simulating the salt ratio in the NPS supernatant composition. A fused-salt specimen of surface area about 5 cm² and containing 20 wt % sludge dissolved in about 30-40 min. Additional water stability tests will be performed on silicate/sludge specimens prepared by the improved processing technique (which includes the humidity treatment prior to the sintering step).

2. Cement-Silicate System

We reported earlier [STEINDLER-1981C] that a potential interim waste form having attractive chemical and mechanical properties was prepared in the laboratory by a room-temperature process, using sodium silicate and calcium hydroxide as a binder. Reaction between sodium silicate and calcium hydroxide in the presence of moisture forms a cementitious bond which provides the desirable chemical and mechanical properties of the waste form. Extensive studies have been initiated during this reporting period to identify optimal compositions of the sodium silicate-calcium hydroxide mixture for achieving desirable properties at a reasonably high sludge loading. Some of the data are presented below.

A series of powder mixtures was prepared by intimately blending various proportions of synthetic sludge (simulating NFS waste) with anhydrous, amorphous sodium silicate (SS-65 and SS-C compositions) and calcium hydroxide. Cylindrical specimens were cold-pressed, and samples were then exposed to a controlled high-humidity air (90% relative humidity) for 24 h at 35°C. Determined were the weight gain of the samples due to water absorption, the mechanical strength, and the room temperature stability of the specimens in static water. Table 2 summarizes the water absorption and fracture strength data for various compositions.

Table 2. Water Absorption during the Humidity Treatment;
the Fracture Strength of Specimens Containing
Synthetic Sludge, Sodium Silicate, and $\text{Ca}(\text{OH})_2$

Composition			Water Absorption, wt %	Fracture Strength, ^a MPa
Sludge, wt %	Sodium Silicate, wt %	Ca(OH) ₂ wt %		
<u>SS-65</u>				
50.0	25.0	25.0	8.91	7.2
90.0	5.0	5.0	2.42	2.3
75.0	25.0	0	6.19	4.0
75.0	20.0	5.0	6.90	7.2
75.0	12.5	12.5	3.70	4.7
75.0	0	25.0	2.33	2.4
<u>SS-C</u>				
75.0	25.0	0	17.62	
75.0	20.0	5.0	11.63	7.3
75.0	12.5	12.5	6.5	4.2

^aStandard deviation, $\pm 20\%$.

Note that pellets of sufficient strength were obtained with compositions containing 75 wt % sludge, 20 wt % sodium silicate, and 5 wt % Ca(OH)_2 . Immersion of the specimens containing silicates and Ca(OH)_2 in static water at room temperature for 24 h indicated no detectable weight loss, whereas the specimens containing only sodium silicate collapsed in water during similar treatment. Additional experiments are continuing on the chemical and mechanical stability of the pellets during high-temperature (about 600°C) treatment (simulating hot fire condition), the impact properties, and the effect of small amounts of supernatant salt on the properties of the cement-silicate waste form.

II. NEUTRON ACTIVATION AND TRACER STUDIES

(L. J. Jardine, J. K. Bates,
and J. E. Kincinas)

A. Introduction

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

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

Major goals are: (1) completion of the development of the NAA method for leach-rate determinations, (2) definition of the accuracy, sensitivity, and limitations of NAA, and (3) establishment of the applicability of the test results to larger-scale waste forms. Goals for the development of methods utilizing radioactive tracers are similar.

B. Qualification of Radioactive Tracer Method

1. Introduction

A series of experiments have been defined to qualify the use of NAA and radioactive tracers to measure the leach rates of SRL frit 131 and SRL frit 211 waste glasses. Four classes of chemical elements, present as minor (<5 wt %) elements in SRL defense wastes and of concern to radioactive waste management, will be the focus of the measurements. Later, PNL 76-68 glass may also be used. The four classes are alkali metals (Cs), alkaline earths (Sr and Ba), rare earths (Ce and Eu), and noble metals (Ru). Samples of simulated waste glass spiked with radioactive tracers have been prepared; this glass is being leached directly; also, spiked and nonspiked glasses are submitted for neutron activation prior to leaching.

Leach rates will be measured wherever possible by four different techniques: (1) conventional chemical solution analysis (ICP,* AA,† DCP,‡ flame emission) of leachates from nonneutron-activated glass, (2) gamma-ray spectroscopic analysis of leachate solutions from neutron-activated glass

* Ion-coupled plasma emission spectroscopy.

† Atomic absorption.

‡ Direct current plasma emission spectroscopy.

specimens (A), (3) gamma-ray spectroscopic analysis of leachate solutions from glass specimens containing radioactive tracers (S), (4) gamma-ray spectroscopic analysis of leachate solutions from neutron-activated glass specimens containing radioactive tracers (S/A).*

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

2. Radioactive Glass Preparation and Source Counting

Gamma-ray analyses of the current series of samples have been done by R. Malewicki of the Analytical Chemistry Laboratory (ACL), Argonne National Laboratory; by the University of Missouri (U of M); and by the Fuel Cycle Section (FCS) of the Chemical Engineering Division (CEN). To ensure that the results from each laboratory are consistent, careful documentation and calibration of each procedure has been done. For the FCS/CEN procedure, calibration over the energy range of 100-2000 keV of the absolute photopeak efficiency of the Ge gamma-ray spectrometer has been performed during this period. Calibrations were done at 5, 10, 20, 30, and 40 cm source-to-detector distances. Standards included ^{182}Ta , ^{241}Am , ^{57}Co , ^{133}Ba , ^{22}Na , ^{137}Cs , ^{54}Mn , ^{88}Y , ^{60}Co , and ^{152}Eu . A FORTRAN computer program was written to calculate the absolute photopeak efficiencies. Preliminary results are shown in Fig. 6.

Fig. 6.

Measured Absolute Photopeak Efficiencies of Germanium Detector as a Function of Gamma Energy and Source-to-Detector Distances for Standard Given in this Text

* "S" represents spiked glass. "S/A" represents spiked and activated glass. "A" represents activated glass.

Several data points are being remeasured because of the high count rates and poor peak shapes at the closer distances with the available standards. A procedure is being developed for the analysis of high-priority samples of leachates and solids on the Ge gamma-ray spectrometer system.

No new preparations were made during the report period, but more samples of already-cast SRL 211*** (S) and SRL 131* (S) glass were sectioned and prepared for leach testing. The tests will be analyzed using the FCS/CEN detector calibrated with the above-mentioned standards.

3. Leaching Characterizations

To qualify the spike/leach method, tests are being done on five different glasses, SRL-211*, SRL 211**, SRL 211***, SRL 131, and SRL 131* (compositions, previously reported, are presented again in Table 3). For each type

Table 3. Nominal Compositions of Simulated SRL Waste Glasses Used in this Work

	Wt %					
	SRL 211 ^a	SRL 211*	SRL 211**	SRL 211***	SRL 131 ^b	SRL 131*
<u>Element</u>						
Si	20.34	20	19.65	19.60	19.9	19.4
Na	11.5	11.15	11.04	11.08	9.9	9.7
Fe	10.28	10.08	9.75	9.91	9.7	9.5
B	2.48	2.43	2.40	2.39	3.3	3.2
Ca	3.78	3.78	3.66	3.64	0.9	0.9
Mn	2.46	2.41	2.38	2.37	2.3	2.2
Al	2.01	1.96	1.94	1.94	1.8	1.7
Li	1.48	1.47	1.44	1.44	1.9	1.8
Ni	1.34	1.31	1.29	1.29	1.3	1.3
Mg	-	-	-	-	0.9	0.9
Ti	-	-	-	-	0.4	0.4
Zr	-	-	-	-	0.3	0.3
La	-	-	-	-	0.3	0.3
<u>Additive</u>						
Cs	-	0.19	0.12	0	-	0
Sr	-	0.07	0.30	0.32	-	0.3
Ba	-	0.10	0.05	0.29	-	0.3
Ce	-	0.52	0.73	0.74	-	0.7
Nd	-	0.63	0.79	0.81	-	0.8
Eu	-	0.003	0.01	0.11	-	0.1
Ru	-	-	0.51	0.41	-	0.4
Mg	-	0.11	-	0	-	0
K	-	-	-	0.05	-	0

^aAnalysis from [SRL-1980A].

^bAnalysis from [SRL-1980B].

of glass, the leach rates obtained with spiked glass will be compared to leach rates obtained by another method. The tests described below are in progress.

a. SRL 211**

Leach testing of SRL 211** glass has been done using cold, activated, spiked, and spiked/activated samples. Leachate analyses and test conditions for each glass type are given in updated Tables 4 and 5, and weight loss results through 100 days are shown in Fig. 7, a modification of an earlier published figure [STEINDLER-1981C].

Fig. 7. Summary of Weight Loss Data for Simulated Waste Glasses

Leaching of activated samples (L-134 to L-146) through 182 days has been completed, and experiments are in progress that will continue for one year. Leachate analysis was done using gamma-ray spectroscopy; for tests through 42.7 days, only ^{134}Cs could be detected. Since cesium leach rates were being obtained for cold SRL 211** glass, no such analyses were planned for activated glass. However, for leachates starting at 98.8 days, both ^{152}Eu and ^{141}Ce can also be detected. Thus, complete gamma-ray analyses of samples L-143 (98.8 days) and L-144 (182 days) are in progress.

Cold samples have been leached for 182 days, and an additional test is in progress that will terminate at 364 days. For Cs, Na, and Li, leachate analysis was done using atomic absorption or flame emission by the Analytical Chemistry Laboratory of the Chemical Engineering Division, and for 18 other elements, TEI Analytical used DC plasma spectroscopy.

Table 4. Summary of Test Conditions, Leachate Analytical Results, and Weight Loss Rates for SRL 211** Glass under Study

Sample	Sample No. L-	Test Conditions						Final Leachate Volume, mL	Δ Mass, SA g/m ²	Leachate Analysis Element Concentration, μ g/mL											
		Temp, °C	Time, days	Initial Mass, g	Δ Mass, g $\times 10^{-4}$	SA, m ² $\times 10^{-4}$	Final pH			ACL ^a	ACL	ACL	ACL	TEI ^b	TEI	TEI	TEI	TEI	TEI	TEI	
										Si	Na	Li	Cs	Si	B	Mn	Ca	Al	Fe	Ba	
SRL 211** (activated)	134	90	3.6	0.5874	30	3.69	9.8		8.1												
	135		7.0	0.5746	38	3.64	9.7	50.6	10.5	21.48											
	136		14.6	0.4573	43	3.61	9.6		11.9												
	137		14.6	0.5839	48	3.67	9.6		13.1												
	138		14.6	0.5525	40	3.67	9.8		10.9												
	139		28.0	0.6276	55	3.80	9.7		14.5												
	140		42.7	0.5273	60	3.87	9.8		15.5												
	141		42.7	0.5824	57	3.73	9.7		15.3												
	142		42.7	0.6174	62	3.74	9.8		16.6												
	143		98.8	0.5750	62	3.91	9.7		15.9												
	144		182	0.6396	60	4.10	9.5		14.6												
	145			0.6098		3.94															
146			0.7473		4.18																
SRL 211**	154	90	3	0.3655	32	4.21	9.8	spilled													
	154a		3	0.3866	31	4.22	9.7	42.2	7.4		12.1	1.40	0.12	20	2.6	0.05	2.4	1.8	0.28	<0.05	
	155		5	0.3776	33	4.19	9.6	43.0	7.9		13.5	1.60	0.12	18	2.8	<0.05	2.5	1.6	0.05	<0.05	
	156		7	0.3833	38	4.20	9.7	43.8	9.1		15.8	1.88	0.14	19	3.3	<0.05	2.4	1.8	0.09	<0.05	
	157		14	0.3735	40	4.20	9.7	41.5	9.5		19.1	2.28	0.17	21	4.0	<0.05	2.6	1.9	0.12	<0.05	
	158		14	0.3889	39	4.19	9.7	41.2	9.3		18.7	2.22	0.17	21	3.9	0.06	2.6	1.8	0.17	<0.05	
	159		14	0.3576	40	4.18	9.6	42.5	9.6		18.1	2.14	0.16	21	3.8	0.05	2.6	1.9	0.12	<0.05	
	160		28	0.3760	48	4.20	9.6	40.5	11.4		21.5	2.72	0.19	23	4.5	0.06	2.7	1.8	<0.05	<0.05	
	161		42	0.3817	51	4.20	9.5	42.5	12.1		23.6	2.93	0.21	26.2	4.76	0.05	2.48	1.87	0.09	<0.05	
	162		42	0.3634	45	4.19	9.5	41.2	10.7		22.2	2.71	0.19	25.2	4.54	0.05	2.65	1.85	0.08	<0.05	
	163		42	0.3803	48	4.20	9.5	41.5	11.4		24.7	2.82	0.20	25.5	4.59	0.06	2.61	1.88	0.13	<0.05	
	164		94.7	0.4200	50	4.24	9.7	40.5	11.8		26.1	3.44	0.26	29.8	5.46	0.05	2.33	1.45	0.08	<0.05	
	165		182	0.3775	56	4.10	9.2		13.4												
	166			0.3661		4.18															

(contd)

Table 4 (contd)

Test Conditions										Leachate Analysis										
										Element Concentration, µg/mL										
Sample	Sample No. L-	Temp, °C	Time, days	Initial Mass, g	Δ Mass, g×10 ⁻⁴	SA, m ² ×10 ⁻⁴	Final pH	Final Leachate Volume, mL	Δ Mass, SA, g/m ²	ACL ^a	ACL	ACL	ACL	TEI ^b	TEI	TEI	TEI	TEI	TEI	
										Si	Na	Li	Cs	Si	B	Mn	Ca	Al	Fe	Ba
SRL	222	90	3	0.4393	23	3.90	9.5	39.7	5.9											
211**	223		7	0.4505	35	3.93	9.7	38.0	8.9											
(spiked	224		14	0.4577	42	3.93	9.4	37.5	10.7											
and	225		14	0.4537	46	3.86	9.4	37.9	11.2											
acti-	226		14	0.4528	42	3.91	9.4	38.1	10.7											
vated)	227		28	0.4532		3.97	9.3	35.3												
	228		42	0.4542	46	3.95	9.7	32.3	11.7	35.5										
	229		42	0.4504	49	3.95	9.5	32.4	12.4	35.4										
	230		42	0.4572	47	3.97	9.7	33.0	11.8	34.4										
	231		95	0.4526	47	3.97	9.7	23.2	11.8	37.2										
SRL	257	90	3	0.4194	25		9.5	39.0												
211**	258		7	0.4549	38	3.91	9.5	38.9	9.7											
(spiked)	259		14	0.4297	44	3.74	9.4	37.5	11.8											
	260		14	0.4152	44	3.94	9.4	37.0	11.2											
	261		14	0.4493	41	3.99	9.4	37.9	10.3											
	262		28	0.5513			9.4	35.8												
	263		42	0.4597	45	3.98	9.6	32.6	11.3	36.2										
	264		42	0.4432	44	3.98	9.6	33.1	11.1	35.3										
	265		42	0.4483	47	3.92	9.4	32.8	12.0	37.2										
	266		95	0.4424	42	3.89	9.6	25.6	10.8	51.4										

(contd)

Table 4. (contd)

Sample	Sample No. L-	Element Concentration ($A_i/A_0 \times 10^3$)								
		NAA by either ACL or University of Missouri								
		^{51}Cr	^{59}Fe	^{85}Sr	^{124}Sb	^{131}Ba	^{134}Cs	^{137}Cs	^{141}Ce	^{152}Eu
SRL	222	<.5			3.32	0.31	4.86	5.57	0.025	0.026
211**	223	2.11			4.61	0.21	7.55	8.82	ND	ND
(spiked	224	1.55			5.04	0.15	7.62	8.87	0.028	ND
and	225	1.22			6.65	0.22	8.49	9.93	0.037	0.021
acti-	226	2.41			6.45	0.26	8.62	10.1	ND	ND
vated)	227	1.77			7.04	0.19	9.28	12.0	ND	0.033
	228	4.66			9.51	0.16	12.4	14.3	ND	ND
	229	3.22			8.64	0.14	11.2	13.0	ND	0.009
	230				4.41	0.16	10.6	12.4	ND	0.010
	231									
SRL	257					0.05		6.27		
211**	258					0.20		7.41		
(spiked)	259					0.19		9.69		
	260					0.22		10.50		
	261					0.23		9.93		
	262					0.14		8.82		
	263					0.15		12.60		
	264					0.15		12.90		
	265					0.14		13.40		
	266									

^aAnalyses done by the Analytical Chemistry Laboratory of the Chemical Engineering Division.

^bAnalyses done by Trace Elements, Inc.

Table 5. Summary of Normalized Leach Rates Calculated from Data in Table 4 for SRL 211** Glass. Temperature = 90°C.

Normalized Elemental Loss, (NL) _i , g/m ²													
Sample	Sample No. L-	Time, days	ACL ^a Si	ACL Na	ACL Li	ACL Cs	TEI ^b Si	TEI B	TEI Mn	TEI Ca	TEI Al	TEI Fe	TEI Ba
SRL 211** (acti- vated)	134	3.6	15.3										
	135	7.0											
	136	14.6											
	137	14.6											
	138	14.6											
	139	28.0											
	140	42.7											
	141	42.7											
	142	42.7											
	143	98.8											
	144												
	145												
	146												
SRL 211**	154	3											
	154a	3		11.1	11.2	11.4	10.3	10.7	0.2	7.0	9.9	0.3	
	155	5		12.8	13.1	11.5	9.5	11.9	<0.2	7.5	9.0	0.06	
	156	7		15.3	15.7	13.7	10.2	14.2	<0.2	7.3	10.3	0.1	
	157	14		17.4	18.0	16.0	10.7	16.3	<0.2	7.5	10.3	0.1	
	158	14		17.0	17.5	16.1	10.6	15.8	0.3	7.5	9.7	0.2	
	159	14		17.0	17.4	16.1	11.0	16.0	0.2	7.7	10.6	0.2	
	160	28		19.1	21.0	17.6	11.4	17.9	0.3	7.6	9.5	<0.06	
	161	42		21.8	23.4	20.0	13.5	19.7	0.2	7.2	10.3	0.1	
	162	42		20.2	21.3	18.1	12.7	18.4	0.2	7.6	10.0	0.1	
	163	42		22.5	22.3	18.8	12.9	18.7	0.3	7.5	10.2	0.2	
	164	94.7		22.7	26.0	23.7	14.6	21.6	0.2	6.5	7.6	0.1	
	165												
	166												

(contd)

Table 5. (contd)

Normalized Elemental Loss, (NL) _i , g/m ²													
Sample	Sample No. L-	Time, days	ACL ^a Si	ACL Na	ACL Li	ACL Cs	TEI ^b Si	TEI B	TEI Mn	TEI Ca	TEI Al	TEI Fe	TEI Ba
SRL	222	3											
211**	223	7											
(spiked	224	14											
and	225	14											
acti-	226	14											
vated)	227	28											
	228	42	14.9										
	229	42	14.9										
	230	42	14.7										
	231	95	11.2										
SRL	257	3											
211**	258	7											
(spiked)	259	14											
	260	14											
	261	14											
	262	28											
	263	42	15.2										
	264	42	15.1										
	265	42	16.0										
	266	95	17.4										
	234	182											

(contd)

Table 5. (contd)

Normalized Elemental Loss, (NL) _i , g/m ²																	
Sample	Sample No. L-	Time, days	⁵¹ Cr	⁵⁹ Fe	⁸⁵ Sr	¹⁰³ Ru	¹⁰⁶ Ru	¹³¹ Ba	¹³³ Ba	¹³⁴ Cs	¹³⁷ Cs	¹³⁹ Ce	¹⁴¹ Ce	¹⁴⁷ Nd	¹⁵² Eu	¹⁵⁴ Eu	¹²⁴ Sb
SRL	134	3.6															
211**	135	7.0															
(acti-	136	14.6															
vated)	137	14.6															
	138	14.6															
	139	28.0															
	140	42.7															
	141	42.7															
	142	42.7															
	143	98.8								10.0			0.36		0.33		
	144																
	145																
	146																
SRL	222	3	0.85						0.58	9.1	10.4		0.05		0.05		6.2
211**	223	7	3.9						0.39	14.0	16.4		ND		ND		8.6
(spiked	224	14	2.9						0.29	14.2	16.6		0.05		ND		9.4
and	225	14	2.3						0.43	16.3	19.0		0.07		0.04		12.7
acti-	226	14	4.6						0.49	16.4	19.1		ND		ND		12.2
vated)	227	28	3.1						0.33	16.0	20.7		ND		0.06		12.1
	228	42	7.2						0.25	19.2	22.3		ND		ND		14.8
	229	42	5.1						0.22	17.6	20.4		ND		0.01		13.6
	230	42	8.0						0.26	17.0	19.9		ND		0.02		7.1
	231	95															
SRL	257	3							0.92		14.0						
211**	258	7							0.50		18.2						
(spiked)	259	14							0.43		22.8						
	260	14							0.46		22.0						
	261	14							0.48		20.4						
	262	28							0.34		21.9						
	263	42							0.28		23.3						
	264	42							0.28		23.7						
	265	42							0.26		24.3						
	266	95							0.44		12.4				1.50		
	234	182															

^aAnalyses done by the Analytical Chemistry Laboratory of the Chemical Engineering Division.

^bAnalyses done by Trace Elements, Inc.

Spiked and spiked/activated leach tests were run concurrently to ensure temperature equalization. These 95-day tests have been completed. Gamma-ray analysis for the radionuclides and analysis for silicon, a matrix element, are nearly complete for the entire series of tests.

Two major issues pertain to the data presented for 211** glass: (1) does radiotracer spiking give a reliable measurement of leach rates from simulated nuclear waste glasses and, if it does, what are the optimized tracer loading parameters; (2) what inferences can be drawn about the leaching behavior of the waste glass? The first point is of the greatest concern to this program and will be developed fully, while the second point, more interesting, will be developed insofar as resources allow.

The following observations can be made for the various treatments of SRL 211** glass:

- (1) The silicon leach rates, $(NL)_{Si}$ have been determined for each glass (except activated) at 42 days (Table 4). At this time, triplicate samples were analyzed; within experimental error, no difference in $(NL)_{Si}$ was observed. $(NL)_{Si}$ was also determined at 91 days for the same glasses; the spread of data is larger, but these analyses were for single samples and have a greater uncertainty. Silicon analyses are being done for the 182-day samples, but the results are not available. The data obtained thus far indicate the same rate of leaching of the matrix for all glass treatments.
- (2) Cesium leach rates were/are being determined for each type of glass treatment. With only a few analyses remaining to be done, the leach rates, $(NL)_{Cs}$, measured for cold glass appear to be the same as those for ^{134}Cs measured in S/A glass and ^{137}Cs measured in S/A and S glass (Table 4).
- (3) Barium leach rates could be measured only in S/A and S glass. No barium could be detected in cold glass using DC plasma. In S/A and S glass, ^{133}Ba as spiked was detected for all samples and the $(NL)_{Ba}$ values agreed for the two glasses.
- (4) Leach rates for the rare earths, ^{141}Ce and ^{152}Eu , could be detected in some of the S/A samples, but the values, $(NL)_{RE}$, are near the detection limit. For the A and S samples, Ce and Eu may be detectable in the 91- and 182-day samples for which analyses are still in progress.

Overall, for SRL 211** glasses, the leach rates of Cs have been shown to be consistent for different methods of detection, but the other elements of interest, Ba, Ce, Eu, Y and Ru could not be detected for enough glass types (i.e., treatments) to allow comparison of methods of detection. (For this reason, SRL 211** was modified to SRL 211***, which contains less cesium.)

The general leaching behavior of SRL 211** glass is shown in Fig. 8--Na, Li, Cs, B, and Si have nearly the same release after three days. All of these elements continue to be leached throughout the next 29 days, but at a reduced rate. The Si rate for this period is significantly less than the rates for the other elements. There is significant release of Ca and Al for the first three days, but no release after that. Release of Mn and Fe

Fig. 8. Preliminary Leach Test Results for Cold SRL 211** Glass. MCC-1 tests. Leaching in deionized water at 90°C.

is initially low and thereafter $(NL)_i$ is constant. This leachate analysis data can be combined with surface studies, using SEM/EDAX and electron microprobe analysis. The surface studies indicate that after 91 days of leaching, a reaction layer about 7 μm thick exists on the glass. This layer is enriched with Mn and Mg at the surface and is somewhat enriched in rare earths throughout. Si and Na are depleted in the reaction layer.

Surface studies on a sequence of leached samples are in progress in order to monitor changes occurring with leaching time. The durability of these layers is confirmed by long-term weight-loss data which indicate that little additional weight loss occurs after about 20 days of leaching.

b. SRL 211***

Since SRL 211** glass contains too much cesium to allow detection of most other gamma-emitters, SRL 211*** glass was made. This glass contains nominally no added cesium. Tests were done on cold, activated, and spiked (^{137}Cs , ^{141}Ce , ^{152}Eu , and ^{106}Ru) samples of this glass. Results on

all samples are not complete, but preliminary data (Tables 6 and 7) indicate that the leach rates of all spikes plus more than 10 activated isotopes can be detected. Preliminary results for the activated glass through 28 days are shown in Fig. 9.

Fig. 9. Preliminary Leach Results for Activated SRL 211*** Glass (Leaching at 90°C in deionized distilled water; MCC-1 tests)

Cold glass has been leached, and analyses have been completed through 91 days. Experiments that will extend through 364 days are in progress. The activated samples are being run simultaneously with the cold samples; thus, experiments with these two materials have been completed through 91 days. However, sample analyses have been delayed. Experiments on activated samples are planned to continue through 364 days. Spiked experiments, complete through 91 days, will continue for 364 days.

The neutron-activated-and-spiked leachates are being analyzed by the University of Missouri, using gamma-ray counting. Several reports have been received, but since there have been problems in normalizing the solids counting procedures, these results have been delayed. Leachate counting has proceeded without any such problems. Until analyses are complete, comparisons will be deferred.

c. SRL 131 and SRL 131* Glass

The SRL 131 glass is the current SRL reference frit glass, and leach tests are in progress to determine the leaching behavior of both this frit glass and this glass containing about 3 wt % waste additives of minor

Table 6. Summary of Test Conditions, Leachate Analytical Results,
and Weight Loss Rates for SRL 211*** Glass

Test Conditions										Leachate Analysis										
Sample	Sample No. L-	Temp, °C	Time, days	Initial Mass, g	Δ Mass, g×10 ⁻⁴	SA, m ² ×10 ⁻⁴	Final pH	Final Leachate Volume, mL	Δ Mass, SA g/m ²	Element Concentration, µg/mL										
										ACL ^a				TEI ^b						
										Si	Na	Li	Cs	Si	B	Mn	Ca	Al	Fe	Ba
SRL	276	90	3	0.4056	33	4.13	9.7	44.4	5.0		11.5	1.49		15.4	2.56	0.06	2.43	1.54	0.12	0.07
211***	277		7	0.3974	36	4.22	9.7	41.7	8.5		16.4	2.03		20.2	3.45	0.06	2.47	1.86	0.11	0.06
	278		14	0.3970	43	4.24	9.7	41.9	10.1		18.0	2.23		22.0	3.91	0.05	2.73	1.76	0.13	0.06
	279		28	0.4048	47	4.28	9.8	44.7	11.0		19.2	2.53		21.4	4.50	0.06	2.76	1.82	0.16	0.05
	280		28	0.3835	49	4.17	10.0	44.1	11.8		19.8	2.60		24.3	4.49	0.05	2.66	1.76	0.09	<0.05
	281		28	0.4129	48	4.27	9.8	44.8	11.2		19.6	2.52		24.3	4.01	0.06	2.23	1.95	0.12	0.05
	282		42	0.3748	51	4.21	9.5	44.2	12.1		21.4	2.81								
	283		91	0.3621	59	4.15	9.7	42.5	14.2											
	284			0.3698		4.21														
	285			0.3917		4.21														
SRL	287	90	3	0.4541	24	4.11	9.6	39.9	5.8											
211***	288 ^c		7	0.4430	36	4.00	9.8	39.4	8.8											
(spiked)	289		14	0.4482	35	4.09	9.5	36.5	8.6											
	290		28	0.4501	39	4.09	9.5	34.9	9.5											
	291		28	0.4618	41	4.12	9.0	37.9	10.0											
	292		28	0.4607	38	4.11	9.4	34.6	9.3											
	293		42	0.4407	40	4.08	9.5	31.4												
	294		91	0.4496		4.09														
	295			0.4458		4.08														
	296			0.4946		4.15														

(contd)

Table 6 (contd)

Sample	Sample No. L-	Test Conditions					Final Leachate Volume, mL	$\frac{\Delta \text{ Mass, SA}}{\text{SA}}$, g/m ²	Leachate Analysis Element Concentration, µg/mL										
		Temp, °C	Time, days	Initial Mass, g	$\Delta \text{ Mass, g} \times 10^{-4}$	SA, m ² $\times 10^{-4}$			Final pH	Element Concentration, µg/mL									
										ACL ^a	ACL	ACL	ACL	TEI ^b	TEI	TEI	TEI	TEI	TEI
									Si	Na	Li	Cs	Si	B	Mn	Ca	Al	Fe	Ba
SRL	237 ^c	90	3	0.4194		4.30	9.4	39.5											
211***	238 ^c		7	0.3878	36	4.28	9.4	38.7											
(acti- vated)	239 ^c		14	0.3993	58	4.36	9.6	37.1											
	240 ^c		28	0.3712	53	4.26	9.6	39.5	NS										
	241 ^c		28	0.4119	49	4.30	9.6	35.0	32.5										
	242 ^c		28	0.3694	85	4.30	9.6	34.3	33.2										
	243		43.1	0.4054	112	4.34		32.5											
	244		91	0.3945	73	4.28	9.4	77.9	17.1										
	245			0.3680		4.29													
	246			0.4098		4.36													

Element Concentration ($A_1/A_0 \times 10^3$)											
NAA by either ACL or University of Missouri											
Sample	Sample No.	⁵¹ Cr	⁵⁹ Fe	⁸⁵ Sr	¹²⁴ Sb	¹³¹ Ba	¹³⁴ Cs	¹³⁷ Cs	¹⁴¹ Ce	¹⁴⁷ Md	¹⁵² Eu
SRL	288						18.9				1.21E-3
211*** (spiked)											
SRL	237	0.63	0.058	0.97	3.97	0.46	2.22		0.022	0.036	0.019
211***	238	1.14	0.056	1.02	7.27	0.29	3.12		0.024	0.032	0.018
(acti- vated)	239	1.71	0.038	1.14	7.20		3.72		0.020		0.017
	240	5.20	0.089		16.0						0.023
	241	3.60	0.140		13.0						-
	242	5.30	0.049		14.0						0.027

^aAnalyses done by the Analytical Chemistry Laboratory of the Chemical Engineering Division.

^bAnalyses done by Trace Elements, Inc.

^cElement concentrations are given at the end of this table.

Table 7. Summary of Normalized Leach Rates Calculated from Data in Table 6 for SRL 211*** Glass. Temperature = 90°C.

			Normalized Elemental Loss, (NL) _i , g/m ²										
	Sample No.	Time,	ACL ^a	ACL	ACL	ACL	TEI ^b	TEI	TEI	TEI	TEI	TEI	TEI
Sample	L-	days	Si	Na	Li	Cs	Si	B	Mn	Ca	Al	Fe	Ba
SRL	287	3											
211***	288	7											
(spiked)	289	14											
	290	28											
	291	28											
	292	28	13.3										
	293	42											
	294												
	295												
	296												
SRL	237	3											
211***	238	7											
(acti-	239	14											
vated)	240	28											
(contd	241	28	13.6										
below)	242	28	13.6										
	243	43.1											
	244	91	17.5										
	245												
	246												
SRL	276	3		11.4	12.8		8.5	11.4	0.3	7.6	9.1	0.2	2.6
211***	277	7		15.0	16.1		10.2	14.1	0.3	7.1	10.1	0.2	2.0
	278	14		16.4	17.6		11.2	16.0	0.2	7.8	9.6	0.2	2.0
	279	28		18.5	21.1		11.5	19.5	0.2	8.4	10.4	0.2	<1.7
	280	28		19.3	22.0		13.2	19.7	0.2	8.2	10.2	0.1	<1.7
	281	28		19.0	21.2		13.1	17.5	0.3	6.8	11.2	0.2	<1.7
	282	42		20.8	23.6		14.6	20.8	0.3	8.2	8.8	0.2	<1.7
	283												
	284												
	285												

(contd)

Table 7 (contd)

Sample	Sample No. L-	Time, days	Normalized Elemental Loss, (NL) _i , g/m ²														
			⁵¹ Cr	⁵⁹ Fe	⁸⁵ Sr	¹⁰³ Ru	¹⁰⁶ Ru	¹³¹ Ba	¹³³ Ba	¹³⁴ Cs	¹³⁷ Cs	¹³⁹ Ce	¹⁴¹ Ce	¹⁴⁷ Nd	¹⁵² Eu	¹⁵⁴ Eu	¹²⁴ Sb
SRL	287	3					0.09				9.3		1.7E-3		1.8E-3		
211***	288	7									20.5				4.8E-3		
(spiked)	289	14															
	290	28															
	291	28															
	292	28															
	293	42															
	294																
	295																
	296																
SRL	237	3	1.3	0.12	1.9			0.9		4.4		0.04	0.07	0.04			7.9
211***	238	7	1.6	0.09	1.9			0.5		5.3		0.04	0.05	0.03			12.4
(acti- vated)	239	14	2.9	0.06	1.9					6.2		0.03		0.03			12.0
	240	28	6.9	0.12										0.03			21.4
	241	28	5.6	0.21										--			20.0
	242	28	7.4	0.07										0.04			20.8
	243	43.1															
	244	91															
	245																
	246																

^aAnalyses done by the Analytical Chemistry Laboratory of the Chemical Engineering Division.

^bAnalyses done by Trace Elements, Inc.

elements (SRL 131*), as shown in Table 3. Tests are being done on cold glass, activated glass, and spiked (^{85}Sr , ^{137}Cs , ^{133}Ba , ^{141}Ce , ^{152}Eu) glass. The tests have been completed through 150 days (data available only through 91 days), and preliminary results (Tables 8 and 9) indicate that a complete description of the leaching behavior of this glass will be possible.

d. PNL 76-68 Glass

The 76-68 glass supplied by the Materials Characterization Center (MCC) contains no europium and too much cesium to be useful for analysis by the NAA technique. Therefore, a new batch of 76-68 glass has been made and will be submitted for activation. This should allow the determination of noble metal and rare earth elements (which cannot be measured with spectroscopic techniques).

From the previously described leach tests, the usefulness of radioisotopic tracers for measuring leach rates will be qualified. Additionally, the behavior of several types of glasses upon contact with water will be observed. This behavioral information can be used to demonstrate elemental release from the glass and to study the mechanism by which the glass is attacked. However conclusions and qualifications must await completion of all current leach tests. Data presented in Tables 4 to 9 are preliminary and should be treated as such.

4. Auxiliary Leach Studies

a. SYNROC

Analyses have been completed on 97 solid samples submitted for leach testing. The samples, leaching conditions, and results are shown in Table 10. The SYNROC composition is shown in Table 11.

The solid samples were leached according to MCC-1 static leach test procedures, and the normalized leach rates, $(\text{NL})_i$, were obtained in the following fashion:

Nonactivated Samples

$$(\text{NL})_i = \frac{M_i}{f_i - \text{SA}}$$

where M_i is the mass of element "i" in the leachate

f_i is the mass fraction of element "i" in the original solid

SA is the surface area (m^2) of the sample

Table 8. Summary of Test Conditions, Leachate Analytical Results,
and Weight Loss Rates for SRL 131 Glass under Study

Sample	Sample No. L-	Test Conditions					Final pH	Final Leachate Volume, mL	Δ Mass, SA g/m ²	Leachate Analysis Element Concentration, μ g/mL										
		Temp, °C	Time, days	Initial Mass, g	Δ Mass, g $\times 10^{-4}$	SA, m ² $\times 10^{-4}$				ACL ^a ACL ACL ACL TEI ^b TEI TEI TEI TEI TEI TEI										
										Si	Na	Li	Cs	Si	B	Mn	Ca	Al	Fe	Ba
SRL 131	298	90	3	0.4393	33	4.08	9.8	41.4	8.1		12.9	2.32		18.5	4.15	<0.05	0.09	1.55	<0.05	<0.05
	299		7	0.4854	51	4.13	9.8	42.4	12.4		19.0	3.52		25.0	6.22	<0.05	<0.05	1.99	0.05	<0.05
	300		14	0.5093	57	4.16	9.8	45.1	13.7		22.3	4.02		27.9	7.77	<0.05	<0.05	1.88	0.15	<0.05
	301		28	0.4917	75	4.17	9.8	45.0	18.0		26.2	5.09		37.0	9.44	0.16	0.05	2.50	0.54	
	302		28	0.4624	75	4.10	9.8	43.9	18.3		26.0	4.89		35.6	9.12	0.16	0.06	2.35	0.48	
	303		28	0.5066	86	4.16	9.8		20.7		25.7	4.81		34.6	8.92	0.12	0.05	2.03	0.28	
	304		42	0.3893	77	4.02	9.4	44.6	19.1		27.4	5.42								
	305		91	0.4769	103	4.13	9.8	41.8	24.9											
	306			0.4259		4.09														
	307			0.4978		4.15														
	308			0.5308		4.18														
	309			0.4925		4.15														
SRL 131*	311	90	3	0.4527	29	4.15	9.7	42.5	7.0					16.0	3.68	0.05	0.33	1.39	0.09	0.05
	312		7	0.3030	39	3.32	9.7	38.0	11.8					24.1	5.36	0.05	0.11	1.91	0.07	0.05
	313		14	0.4025	55	4.29	9.7	46.4	12.8					28.7	6.88	0.05	0.06	1.98	0.05	0.05
	314		28	0.3697	67	4.14	0.8	44.9	16.2		25.5	4.87		34.2	8.96	0.06	<0.05	4.14	<0.05	<0.05
	315		28	0.4887	69	4.43	9.8	44.9	15.6		25.2	4.91		34.6	8.96	0.06	<0.05	1.87	<0.05	<0.05
	316		28	0.3891	65	3.64	9.8	45.9	17.9		24.5	4.51		32.6	8.42	0.07	<0.05	1.77	<0.05	<0.05
	317		37	0.4556	74	4.12	9.6	45.5	18.0		27.2	5.22								
	318		91	0.4987	80	4.01	9.6	40.2	20.0											
	319			0.4699		4.27														
	320			0.4799		4.35														
	321			0.4125		4.11														
	322			0.4851		4.38														
	323			0.4919		4.29														

(contd)

Table 8 (contd)

Sample	Sample No. L-	Test Conditions						Final Leachate Volume, mL	Δ Mass, SA g/m ²	Leachate Analysis Element Concentration, μ g/mL												
		Temp, °C	Time, days	Initial			Final pH			ACL ^a	ACL	ACL	ACL	Element Concentration, μ g/mL								
				Mass, g	Δ Mass, g $\times 10^{-4}$	SA, m ² $\times 10^{-4}$								Si	Na	Li	Cs	Si	B	Mn	Ca	Al
SRL 131* (acti- vated)	327 328 329 330 331 333	90	2.25 7 14 28 28	0.3112 0.3986 0.3989 0.4595 0.4067	21 15 24 39 49	3.77 3.86 3.90 4.33 4.21	9.5 9.2 5.2	 35.4 34.0	5.6 3.9 6.2 9.0 11.6	41.2 43.2												
SRL 131 (spiked)	339 340 341 342 343 344 345 346	90	3 7 14 28 28 28 42 	0.5174 0.4869 0.4842 0.4772 0.4866 0.4965 0.4733 0.4651	17 32 54 56 50 58 51 	4.35 4.26 4.27 4.28 4.29 4.29 4.27 4.26	9.5 9.3 9.4 9.2 9.0 9.3 9.2 	39.5 39.0 37.7 34.0 34.2 34.5 31.9 	3.9 7.5 12.7 13.1 11.7 13.5 11.9 	 43.3 36.2 46.5												

^aAnalyses done by the Analytical Chemistry Laboratory of the Chemical Engineering Division.

^bAnalyses done by Trace Elements, Inc.

Table 9. Summary of Normalized Leach Rates Calculated from Data in Table 8 for SRL 131 Glass. Temperature = 90°C.

Sample	Sample No. L-	Time, days	Normalized Elemental Loss, (NL) _i , g/m ²										
			ACL ^a	ACL	ACL	ACL	TEI ^b	TEI	TEI	TEI	TEI	TEI	TEI
			Si	Na	Li	Cs	Si	B	Mn	Ca	Al	Fe	Ba
SRL 131	298	3		13.2	12.4		9.4	12.8	<0.2	1.0	8.7	<0.05	
	299	7		19.7	19.0		12.9	19.4	<0.2	<0.6	11.4	<0.05	
	300	14		24.4	22.9		15.2	25.5	<0.2	<0.6	11.3	0.2	
	301	28		27.3	27.6		19.2	29.5	0.7	0.6	14.3	0.6	
	302	28		28.1	27.6		19.2	29.6	0.7	0.7	14.0	0.5	
	303	28											
	304	42		30.6	31.6								
	305	91											
	306												
	307												
	308												
	309												
SRL 131*	311	3					8.5	11.8	<0.2	3.8	8.4	0.1	<1.7
	312	7					14.2	19.2	0.3	1.4	12.9	0.08	<1.7
	313	14					16.0	23.3	0.3	0.7	12.6	0.07	<1.7
	314	28		28.5	29.3		19.1	30.0	0.3	<0.5	26.4	<0.06	<1.7
	315	28		26.3	27.7		18.1	28.4	0.3	<0.5	11.1	<0.06	<1.7
	316	28		31.8	31.6		21.2	33.2	0.4	<0.5	13.8	<0.06	<1.7
	317	37		31.0	32.0								
	318												
	319												
	320												
	321												
	322												
	323												

^aAnalyses done by the Analytical Chemistry Laboratory of the Chemical Engineering Division.

^bAnalyses done by Trace Elements, Inc.

Table 10. Test Conditions and Leach Results^a
for SYNROC Samples

Sample	Sample No.	Time, days	Temp, °C	Initial Mass, g	Δ Mass, g×10 ⁻⁴	SA, m ² ×10 ⁻⁴	Final pH	Final Leachate Volume, mL	Δ Mass, SA, g/m ²	Leachate ^b	Method of Analysis
B9A-8	L-347	1	90	0.2942	4	2.01	5.1	19.8		DIW	DCP/AA
	L-348	4.75		0.2586	4	2.01	5.1	19.7			
	L-349	7		0.2689	3	2.01	4.6	20.0			
	L-350	14		0.3014	4	2.01	4.8	21.1			
	L-351	28		0.3044	2	2.01	4.8	22.8			
	L-352	28	40	0.3052	2	2.01	4.4	22.2			
	L-353	1	200	0.2914	6	2.01	4.9	10.0			
	L-354	28	200	0.2856	9	1.97	5.7	10.2			
B9A-9	L-355	28	90	0.3131	2	1.99	4.9	22.2			
	L-356	28		0.3263	2	2.00	9.4	21.2		SW	
	L-357	28		0.2778	1	1.98	3.6	19.9		B	
B9A-10	L-358	4.75		0.2746	3	1.94	4.7	20.1		DIW	
	L-359	7		0.2927	3	1.94	4.7	19.6			
	L-360	14		0.3145	4	1.95	4.1	24.2			
	L-361	28		0.2904	1	1.93	5.3	19.9			
	L-362			0.2618	2	1.95	4.8	20.0			
	L-363			0.3158	2	1.98	4.8	22.2			
	L-364			0.3003	1	1.94	9.3	20.1		SW	
	L-365			0.2934	3	1.92	3.7	21.4		B	
	L-366		40	0.3037	1	1.95	4.7	20.2		DIW	
	L-367		200	0.2967	3	1.94	4.8	9.9			

(contd)

Table 10 (contd)

Sample	Sample No.	Time, days	Temp, °C	Initial Mass, g	Δ Mass, g×10 ⁻⁴	SA, m ² ×10 ⁻⁴	Final pH	Final Leachate Volume, mL	Δ Mass, SA, g/m ²	Leachate ^b	Method of Analysis
B9A-7	L-368	28	90	0.3075	2	2.03	4.4	20.6		DIW	DCP/AA
	L-369			0.2904	1	2.02	4.3	20.6			
	L-370			0.2974	2	2.08	5.8	21.6			
B9A-11	L-371			0.3135	21	2.10	5.9	21.0			
	L-372			0.2875	16	2.20	6.4	21.0			
	L-373			0.2705	16	2.08	5.7	21.6			
B9A-12	L-374			0.2591	13	2.08	5.7	21.6			
	L-375			0.2650	14	2.11	6.0	20.3			
	L-376			0.2896	22	2.18	6.1	19.6			
B9-3	L-377	1		0.3072	1	1.90	ND ^e	22.4			
	L-378	3		0.2717	0	1.90	ND	19.0			
	L-379	7		0.2718	6	1.88	ND	20.0			
	L-380	28		0.2465	0	1.88	ND	19.7			
	L-381	28		0.2864	1	1.92	ND	20.2			
	L-382	28		0.2291	0	1.90	ND	20.1			
	L-383	28		0.2804	1	1.91	ND	20.8			
	L-384	95		0.2394	2	1.85	ND	14.2			
	L-385	1		0.2692	1	1.94	ND	23.0		SW	
	L-386	7.2		ND		1.91	ND	19.7		DIW ^f	
	L-387	28		0.2939	0	1.92	ND	19.8		DIW ^f	
	L-388	1		0.2913	2	1.90	ND	22.0		B	
	L-389	7.2		ND		1.93	ND	19.4		DIW ^g	
	L-390	28		0.2757	1	1.91	ND	20.1		DIW ^g	

(contd)

Table 10 (contd)

Sample	Sample No.	Time, days	Temp, °C	Initial Mass, g	Δ Mass, $g \times 10^{-4}$	SA, $m^2 \times 10^{-4}$	Final pH	Final Leachate Volume, mL	$\frac{\Delta \text{ Mass}}{\text{SA}}$, g/m^2	Leachate ^b	Method of Analysis
XB9-3	L-391	28	40	0.2859	0	1.92	ND	19.7		DIW	DCP/AA
	L-392	1	200	0.2748	5	1.89	5.1				
	L-393	7	200	0.3445	3	1.97	5.5	28.7			
	L-394 ⁱ	28	200	0.2801		1.92					
Neutron activated	L-395	30.7	200	0.2755	0	1.98	ND	10			NAA
XB93	L-396	30.7	200	0.2677	0	1.95	ND	10			NAA
T ₀ =3/10/81, 22:95	L-397 ^j		200			1.93					
XB93-1500-4	L-398	28	90	0.2808	1	2.06	4.4	18.6			DCP/AA
XB93-1500-5	L-399	28		0.2982	2	2.02	4.3	20.5			
XB93-1500-6	L-400	28		0.2817	1	1.92	4.4	19.3			
XB93-500-1	L-401	28		0.2991	2	1.94	4.4	20.6			
XB93-500-2	L-402	28		0.3026	2	1.92	4.5	19.6			
XB93-500-3 ^k	L-403	1		0.3025	ND	1.92	3.6	19.4			
IAEA	L-404	7			ND	1.92	ND	21.0			
Procedure	L-405	14			1	1.92	4.9	19.6			
Blank (no mesh)	L-406	28					3.9	24.4			
Blank ^l (mesh)	L-407	28					3.9	20.8			
XB93-1500-1	L-408	28		0.2995	1	1.92	4.3	20.3			
XB93-1500-2	L-409	28		0.3008	0	1.96	4.7	17.2			
XB93-1500-3 ^k	L-410	1		0.2576	ND	1.89	3.9	21.3			
IAEA	L-411	7			ND		ND	20.8			
Procedure	L-412	14			3		5.3	19.6			

(contd)

Table 10 (contd)

Sample	Sample No.	Time, days	Temp, °C	Initial Mass, g	Δ Mass, $g \times 10^{-4}$	SA, $m^2 \times 10^{-4}$	Final pH	Final Leachate Volume, mL	$\frac{\Delta \text{ Mass}}{\text{SA}}$, g/m^2	Leachate ^b	Method of Analysis
XB93-500-He-1	L-413	3	90	0.2631	0	1.90	4.6	24.3		DIW	DCP/AA
XB93-500-He-2	L-414	28	90	0.2928		1.90	4.5	20.6		DIW	
XB93-500-He-3	L-415	ext								DIW	
										DIW	
XB93-500-He-4	L-416	3	200	0.3109		1.90	4.9	18.5		DIW	
	L-417 ^m	Total								DIW	
		28								DIW	
XB93-1500-He-4	L-418	3	90	0.2680	+1	1.90	4.3	21.4		DIW	
XB93-1500-He-5	L-419	28	90	0.2956	1	1.90	4.5	20.2		DIW	
XB93-1500-He-6	L-420	3	200	0.3042	3	1.91	3.2	19.4		DIW	
XB93-1500-He-7a	L-421 ^m	28	200	0.1736		1.17				DIW	
XB93-1500-He-7b	L-422	3	90	0.1355	1	0.93	4.4	23.3		DIW	
XB93-1000 μCi -He-8	L-427	14.5	145	0.3158						DIW	
XB93-1000 μCi -He-9	L-428	3	90	0.2799		1.92	9.5	19.9		SW	
IAEA procedure	L-429	25	90		2	1.92	9.1	20.0		SW	
XB93 (control)	L-430	28	90	0.2814	1	1.89	4.5	19.6		DIW	
Blank	L-431										

(contd)

Table 10 (contd)

Sample		Sample No.	Time, days	Temp, °C	Initial Mass, g	Δ Mass, $g \times 10^{-4}$	SA, $m^2 \times 10^{-4}$	Final pH	Final Leachate Volume, mL	$\frac{\Delta \text{Mass}}{\text{SA}}$, g/m^2	Leachate ^b	Method of Analysis
76-68 (MCC)	I	L-445	1	90	0.2126		2.05	3.8	20.0		DIW	DCP/AA
I-500 μ Ci	A											
	E	L-446	2					3.8	~21			DCP/AA
	A	L-447 ⁱ	25									
76-68 (MCC)		L-448	1		0.4525	6	4.45	3.9	43.9	1.4		DCP/AA
76-68 (MCC)	I	L-449	1		0.4861		4.47	4.3	43.5			NA ⁿ
	A	L-450	2					4.8	~44			
	E											
SRL-211***	A	L-451 ⁱ	25									DCP/AA
		L-452	1		0.1639		1.92	4.1	26.7			NA ⁿ
		L-453	2					4.3				NA
I-500 μ Ci		L-454	4									NA
		L-455	ext									NA
		L-456	1		0.4421	20	4.35	9.2				
SRL-211***		L-457	1		0.3410		2.69	6.1				NA
I-1000 μ Ci		L-458	3/4					9.0				NA
		L-459	6									NA
		L-460	ext									NA
SRL-211***		L-461	1/4	90	0.3168		3.63	8.7	36.2		DIW	NA
		L-462	3/4					8.8				NA
		L-463	6									NA
SRL-131		L-464	1		0.2604		2.36	3.9	23.6			DCP
I-1000 μ Ci		L-465	2					7.1				NA
		L-466	4									NA
SRL 131		L-467	1		0.4420	15	4.04	8.7	40.0	3.7		DCP

(contd)

Table 10 (contd)

Sample	Sample No.	Cs		Ca		Ba		Al		Mo		Sr ^c		Ti		Si		Ni		Fe	
		mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)
B9A-8	L-347	0.02	0.5	0.26	0.3	0.28	0.34	0.09	0.13	0.58	8.7			<0.02		0.27	133	0.20	9.0	0.09	1.1
	L-348	0.11	2.5	0.40	0.5	0.85	1.02	0.54	0.80	1.54	13.6					<0.05	<24	0.09	4.0	0.13	1.6
	L-349	0.10	2.3	0.56	0.7	1.19	1.45	0.73	1.10	1.56	14.0					1.12	557	0.26	11.8	0.13	1.7
	L-350	0.16	3.9	0.47	0.6	1.46	1.88	0.95	1.50	0.99	9.4					1.32	693	0.20	9.5	0.09	1.2
	L-351	0.20	5.3	0.55	0.8	1.56	2.17	1.07	1.83	1.24	12.7	0.075	2.2			1.49	845	0.24	12.4	0.16	2.3
	L-352	<0.02	<0.5	0.22	0.3	0.37	0.50	0.24	0.40	0.84	8.4					0.32	177	0.16	8.0	0.08	1.1
	L-353	NS ^d		2.51	1.6	1.00	0.61	2.28	1.71	4.16	18.7					6.88	1711	0.05	1.1	0.08	0.5
	L-354	2.44	28.8	3.00	2.0	8.58	5.40	0.74	0.58	3.03	14.1					6.69		0.07	2.6	0.12	
B9A-9	L-355	0.21	5.5	0.37	0.5	1.65	2.26	1.26	2.12	0.74	7.4	0.075	2.2			1.48	826	0.17	8.6	0.06	0.9
	L-356	0.19	4.7	<0.05	<0.07	0.20	0.26	0.14	0.22	0.53	5.1	0.007	0.2			32.9		<0.05	<2.4	<0.05	<0.7
	L-357	ND ^e		<0.05	<0.07	0.43	0.53	1.60	2.44	0.75	6.8	0.07	2.2			0.23	456	0.24	11.3	1.10	14.6
B9A-10	L-358	0.13	3.1	0.10	0.1	1.44	1.83	0.67	1.05	0.78	7.3					0.88	445	0.15	6.9	0.32	4.1
	L-359	0.18	4.2	0.16	0.2	1.67	2.07	0.80	1.22	0.80	7.3					0.81	503	0.16	7.4	0.42	5.4
	L-360	0.21	6.1	0.16	0.25	1.01	1.54	0.94	1.76	0.71	7.9					0.98	608	0.15	8.5	0.31	4.9
	L-361	0.34	8.2	0.17	0.22	2.51	3.17	1.21	1.88	0.92	8.6					1.24	639	0.18	8.4	0.39	5.2
	L-362	0.33	7.9	0.18	0.23	2.50	3.14	1.22	1.89	0.90	8.3					1.30	667	0.17	7.9	0.37	4.9
	L-363	0.37	9.7	0.15	0.21	2.91	4.00	1.14	1.93	0.90	9.1					1.43	802	0.16	8.2	0.33	4.7
	L-364	0.18	4.3	<0.05	<0.07	0.10	0.13	0.09	0.14	0.47	4.4					31.8		<0.05	<2.4	<0.05	<0.7
	L-365			0.08	0.10	0.73	0.93	1.81	2.84	1.07	10.0					0.46		0.32		2.05	
	L-366	0.03	0.7	0.11	0.14	0.72	0.91	0.29	0.45	0.73	6.8					0.31	160	0.19	9.0	0.36	4.8
	L-367	1.0	11.8	0.53	0.67	0.17	0.11	0.07	0.05	2.81	12.9					7.78		<0.05	<2.4	0.05	

(contd)

Table 10 (contd)

Sample	Sample No.	Cs		Ca		Ba		Al		Mo		Sr ^c		Ti		Si		Ni		Fe	
		mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)
B9A-7	L-368	0.86	20.3	0.36	0.46	3.40	4.23	1.42	2.17	<0.05	<0.5			<0.02		1.66	842	0.28	12.9	<0.05	<0.7
	L-369	0.74	17.6	0.29	0.37	3.29	4.11	1.39	2.13	<0.05	<0.5					1.57	801	0.24	11.1	<0.05	<0.7
	L-370	0.14	27.5	0.33	0.43	3.76	4.15	0.26	0.41	<0.05	<0.5					1.94	1007	0.22	10.4	<0.05	<0.7
B9A-11	L-371	33.3	737	2.57	3.24	6.62	8.11	0.19	0.29	22.5	202					3.15	1575	<0.05	<2.4	<0.05	<0.7
	L-372	27.3	606	2.64	3.17	7.10	8.31	0.15	0.22	19.5	168					3.31	1580	<0.05	<2.4	<0.05	<0.7
	L-373	24.3	507	2.61	3.41	8.04	10.23	0.15	0.23	15.6	146					2.85	1480	<0.05	<2.4	<0.05	<0.7
B9A-12	L-374	16.7	409	2.89	3.83	6.95	8.97	0.15	0.24	12.1	115					2.98	1570	<0.05	<2.4	<0.05	<0.7
	L-375	19.9	445	3.16	3.83	6.58	7.76	<0.05	<0.08	12.1	105					3.67	1765	<0.05	<2.4	<0.05	<0.7
	L-376	20.8	435	7.96	9.01	9.74	10.73	0.17	0.23	13.1	106					5.69	2558	<0.05	<2.4	<0.05	<0.7
B9-3	L-377	0.09	2.5	0.13	0.19	0.15	0.22	0.08	0.14	<0.09	<0.5					0.08	47	0.10	5.4	<0.05	<0.7
	L-378	0.14	3.3	0.17	0.21	0.23	0.28	0.08	0.12	<0.05	<0.5					0.16	80	0.09	4.1	<0.05	<0.7
	L-379	0.19	4.7	0.21	0.28	0.28	0.37	0.09	0.14	<0.05	<0.5					0.21	112	0.09	4.4	<0.05	<0.7
	L-380	0.36	8.9	0.12	0.16	0.38	0.49	0.07	0.11	<0.05	<0.5					0.30	157	0.12	5.7	0.06	0.8
	L-381	0.36	8.8	0.11	0.15	0.37	0.48	<0.05	<0.08	<0.05	<0.5					0.29	153	0.08	3.8	<0.05	<0.7
	L-382	0.36	8.9	0.11	0.15	0.39	0.51	<0.05	<0.08	<0.05	<0.5	0.015	0.42			0.28	148	0.09	4.3	<0.05	<0.7
	L-383	1.13	28.6	0.35	0.48	0.98	1.31	0.70	1.15	0.09	0.88					0.86	226	0.55	27.2	0.06	0.8
	L-384	0.61	10.9																		
	L-385	0.09	2.5	<0.06	<0.07	0.08	0.12	0.07	0.13	<0.05	<0.5					32.6		<0.05		<0.05	<0.7
	L-386	0.21	5.0	0.29	0.38	0.33	0.42	<0.05	<0.08	<0.05	<0.5					0.19		0.11		<0.05	
	L-387	0.53	12.7	0.36	0.74	0.57	0.72	0.11	0.17	0.05	0.5					0.49		0.15		0.13	
	L-388	ND	ND	<0.05	<0.07	0.16	0.21	1.38		0.26						0.10		0.33		1.10	
	L-389			0.23	0.30	0.35	0.44	<0.05	<0.08	<0.05	<0.5					0.18		0.10		<0.05	
	L-390	0.37	9.1	0.17	0.23	0.40	0.52	<0.06	<0.08	<0.05	<0.5	0.044				0.30		0.10		<0.05	

(contd)

Table 10 (contd)

Sample	Sample No.	Cs		Ca		Ba		Al		Mo		Sr ^c		Ti		Si		Ni		Fe	
		mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)
XB9-3	L-391	0.33	8.0	0.16	0.21	0.32	0.41	<0.05	<0.08	<0.05	<0.5					0.28		0.08		0.08	
	L-392	ND	ND	1.87		3.61		0.59		0.15						2.41	145	0.46	21.7	0.12	1.6
	L-393	2.05	69.6	AIP ^k																	
	L-394 ⁱ																				
Neutron activated	L-395		40																		
XB93	L-396		51																		
T ₀ -3/10/81, 22:95	L-397 ^j																				
XB93-1500-4	L-398	1.23	25.8			1.43	1.57	0.81	1.11	0.07	0.57					0.85		0.57		0.14	
XB93-1500-5	L-399	1.18	27.9			1.01	1.25	0.72	1.11	0.09	0.82					0.82		0.60		0.11	
XB93-1500-6	L-400	1.22	28.5			1.00	1.23	0.70	1.07	0.07	0.63					0.86		0.57		0.13	
XB93-500-1	L-401	1.08	26.7			1.19	1.54	0.80	1.29	0.08	0.77					0.74		0.54		0.11	
XB93-500-2	L-402	1.11	26.4			1.26	1.57	0.74	1.14	0.07	0.64					0.80		0.55		0.13	
XB93-500-3 ^k	L-403	0.10	2.4			0.27	0.33	0.20	0.31	<0.05	<0.5					0.14		0.28		0.10	
IAEA	L-404	0.11				0.12	0.16	0.06	0.10	<0.05	<0.5					0.10		<0.05		<0.05	
Procedure	L-405	0.11	2.4			0.09	0.11	0.09	0.14	<0.05	<0.5					0.15		<0.05		<0.5	
Blank (no mesh)	L-406																				
Blank ^l (mesh)	L-407	1.07	26.3			1.20	1.55	0.71	1.14	0.08	0.76					0.83		0.60		0.09	
XB93-1500-1	L-408	1.32				1.53	1.64	0.94	1.25	0.08	0.63					1.08		0.71		0.18	
XB93-1500-2	L-409	0.08				0.24	0.33	0.20	0.34	<0.05	<0.5					0.13		0.25		0.07	
XB93-1500-3 ^k	L-410	0.14				0.14	0.19	0.05	<0.08	<0.05	<0.5					0.12		<0.05		<0.05	
IAEA	L-411	0.14				0.11	0.14	0.07	0.11	<0.05	<0.5					0.15		<0.05		0.06	
Procedure	L-412																				

(contd)

Table 10 (contd)

Sample	Sample No.	Cs		Ca		Ba		Al		Mo		Sr ^C		Ti		Si		Ni		Fe	
		mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)
XB93-500-He-1	L-413	0.25	7.44			0.33	0.51	0.20	0.39	<0.05	<0.5					0.21		0.23		<0.05	
XB93-500-He-2	L-414	0.95	24.0	AIP																	
XB93-500-He-3	I																				
	A																				
XB93-500-He-3	E																				
XB93-500-He-4	A																				
	I	L-416	2.62	59.3	AIP																
	E	L-417 ^m																			
XB93-1500-He-4	L-418	0.37	9.7			0.41	0.56	0.23	0.39	0.05	0.5					0.29		0.26		<0.05	
XB93-1500-He-5	L-419	1.00	24.7	AIP																	
XB93-1500-He-6	L-420	1.63	38.5	AIP																	
XB93-1500-He-7a	L-421 ^m																				
XB93-1500-He-7b	L-422	0.17	9.9			0.22	0.67	0.12	0.46	<0.05	<0.5					0.14		0.12		<0.05	
XB93-1000- μ Ci-He-8	L-427					0.12	0.15	0.06	0.15	<0.05	<0.5					3.05		<0.05		0.09	
XB93-1000- μ Ci-He-9	L-428	0.19	4.6																		
IAEA procedure	L-429	0.27	6.5	AIP																	
XB93 (control)	L-430	1.10	26.5																		
Blank	L-431																				

(contd)

Table 10 (contd)

Sample	Sample No.	Cs		Ca		Ba		Al		Mo		Sr ^C		Ti		Si		Ni		Fe	
		mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)	mg/L	(NL)		
76-68 (MCC)	I	L-445	0.31	4.9	AIP																
I-500 μ Ci	A																				
	E	L-446	0.36	5.7	AIP																
	A	L-447 ⁱ																			
76-68 (MCC)		L-448																			
76-68 (MCC)	I	L-449	0.22	3.3	AIP																
	A	L-450	0.25	3.8	AIP																
	E																				
	A	L-451 ⁱ																			
SRL-211***		L-452																			
I-500 μ Ci		L-453																			
		L-454																			
		L-455																			
SRL-211***		L-456																			
SRL-211***		L-457																			
I-1000 μ Ci		L-458																			
		L-459																			
		L-460																			
SRL-211***		L-461																			
		L-462																			
		L-463																			
SRL-131		L-464			AIP																
I-1000 μ Ci		L-465																			
		L-466																			
SRL 131		L-467			AIP																

(contd)

Table 10 (contd)

^a(NL)_i values are calculated using the composition of XB393 as reported in Table 11.

^bDIW = deionized water. SW = silicate water. B = brine.

^cCorrected for blank.

^dNS - No solution.

^eND - Not determined.

^fLeachate was supposed to be SW but was actually DIW.

^gLeachate was supposed to be B but was actually DIW.

^hAIP - Analysis in progress.

ⁱTest completed 7/2.

^jTest aborted.

^k(NL)_i values are cumulative for sequential time periods.

^lLeachate spilled in preparation.

^mTest to be completed 7/10.

ⁿNA - Not analyzed.

Table 11. Solid SYNROC Sample Analyses

Sample	Sample No.	Initial Mass, g	Residue, g	Volume of Solution, mL	Calcium			Barium			Aluminum			Titanium			Cesium	
					mg/L	wt % Oxide	wt % Element	mg/L	wt % Oxide	wt % Element	mg/L	wt % Oxide	wt % Element	mg/L	wt % Oxide	wt % Element	wt % Oxide	wt % Element
H115 (1250°C)	S-1	0.1101	0.0005	100	1.15	0.15		226	22.9		103	18.5		403	61.0		0.6	
H115 (900°C)	S-2	0.21497	0.00478	100	1.73			441	22.9		172	15.1		832	64.6		1.1	
XB93	S-3	0.2758	0.0023	100	219	11.1	7.9	225	9.1	8.2	183	12.5	6.6	918	55.6	33.3	0.45	0.43
Blank	S-4				<0.05			<0.05			0.06			0.08				

Sample	Sample No.	Initial Mass, g	Residue, g	Volume of Solution, mL	Molybdenum			Mg			Nickel			Iron		
					mg/L	wt % Oxide	wt % Element	mg/L	wt % Oxide	wt % Element	mg/L	wt % Oxide	wt % Element	mg/L	wt % Oxide	wt % Element
H115 (1250°C)	S-1	0.1101	0.0005	100	0.11			0.11						0.45		
H115 (900°C)	S-2	0.21497	0.00478	100	0.40			0.36						0.58		
XB93	S-3	0.2758	0.0023	100	30.6	1.67	1.11	1.17	0.04	6.14				21.5	0.8	
Blank	S-4				<0.05			<0.05						<0.05		

Activated Samples

$$(NL)_i = \frac{A_i}{A_o} \times \frac{\text{Vol Efflt}}{\text{SA}} \times M$$

where A_i is the activity of element "i" in the leachate at T_o

A_o is the activity of element "i" in the solid at T_o

SA is the surface area (m^2) of the sample

M is the original mass of the sample

Vol Efflt is the inverse fraction of the leachate used for analysis

No conclusions concerning leachate trends will be made until all analyses have been received; however, the following points may affect interpretation results:

(1) Leach tests (except 377-382, 384-391, 404, 405, 411, and 412, done in polypropylene bottles) were done in teflon containers by MCC-1 or IAEA procedures. There seems to be a definite effect whereby the leach results in polypropylene bottles are one-third those in teflon. This is best observed by comparing the results for tests L-380, L-381, L-382, L-387, and L-390 (which are replicates) with tests L-383 and 430 (which are replicates). Analysis of the results of two further tests should settle the issue.

(2) Tests at 200°C were done in two different types of teflon containers. Although no effect of type of teflon is expected, it cannot be ruled out.

(3) NAA of SYNROC leachates could detect only ^{134}Cs , ^{131}Ba , and ^{141}Ce . This is because the large quantity of ^{134}Cs in the leachate creates a high background, masking the other elements.

(4) NAA of SYNROC samples may cause the leach rate of ^{134}Cs to increase five to seven times while not affecting the leach rate of ^{131}Ba .

Points 3 and 4 should be considered in future work.

b. Weathering Studies

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

III. BRITTLE FRACTURE STUDIES

(L. J. Jardine, W. J. Mecham, and G. T. Reedy)

A. Introduction

A property of solid radioactive waste forms that must be known is their resistance to dispersion from mechanical impacts received during normal and accidental conditions of processing, handling, interim storage, and transportation. A brittle fracture methodology is being developed which relates the impact-stress distribution to the lognormal size distribution of the particles generated by impact fracture. The practical application of this fracture model is to predict the total fracture-surface area and the mass of particles of respirable sizes produced by impact fractures.

Development and preliminary verification of this model has been provided by laboratory-scale tests of impacts of reference glass specimens and by analyses of data available in the technical literature on (1) impacts of various brittle materials and (2) impacts of large-scale simulated waste-glass canisters.

Examination of the validity and utility of this brittle-fracture methodology is being made for a range of practical impact conditions and for various solid waste materials. It is anticipated that the experimental results will establish correlations with impact energy of (1) lognormal size-distribution parameters and (2) fracture surface areas, as well as the effects on particle size and surface area of material properties of brittle-waste packages having various sizes and configurations.

B. Comparative Impact Testing of Alternative High Level Waste Forms: Generation of Respirable Sizes

1. Introduction

Impact test data of solid alternative waste forms are needed, in conjunction with other characterization measurements, to assess the probable and/or worst-case performance of waste forms during handling, transportation, and storage conditions. The two major measurable responses useful to characterize the results of mechanical impacts of brittle waste forms are (1) the particle size distribution of the impact fracture fragments, including the quantity of particles which could become airborne or respirable and (2) the increase in surface area caused by the generation of impact fracture fragments. The particle size distribution can be used to assess source terms for airborne releases, and the surface area increase can be used to assess the increase in source terms for leach rates.

A brittle fracture study at Argonne National Laboratory (ANL) is currently developing the experimental characterization methodologies required to assess the above two major responses to impacts for large canisters of glass waste forms. The ANL study utilizes modeling in conjunction with closely coupled laboratory-scale experimental verification to establish engineering correlations, and eventually to predict these two measurable responses. As a consequence of these impact testing and characterization measurements, detailed procedures for impacting waste forms and for measuring particle size distributions of fracture particulates have been developed.

Because of a current, immediate need for comparative impact response data for the alternative waste forms under development in the High Level Waste Technology Program and the lack of standard impact test procedures (*i.e.*, MCC-10) from the Materials Characterization Center at Battelle Pacific Northwest Laboratory, standardized sets of impact test criteria and characterization procedures have been defined and used to measure the respirable sizes (arbitrarily defined as all particles sizes $\leq 10 \mu\text{m}$ in these test comparisons) for the currently available alternative waste forms.

This report summarizes the results of standardized drop-weight impact test and characterization procedures used to generate, collect, and measure the respirable sizes generated in the impact testing of alternative waste forms. The seven simulated alternative waste forms impacted were (1) SRL frit 131 borosilicate glass, (2) ORNL FUETAP concrete, (3) LLL SYNROC ceramic (4) Rockwell TAILORED CERAMIC, (5) Catholic University (Cath. U) high-silica glass, (6) PNL 76-68 glass, and (7) ANL-MSD SYNROC. Preliminary test results produced variations in the measured respirable fractions of a factor of only seven between the "best" and "worst" waste forms.

The measurement of increases in surface area produced by fracture is not addressed in this report.

2. Experimental Procedure

A standardized set of drop-weight impact test conditions and characterization procedures were defined and applied to seven generic types of alternative high-level waste forms to characterize the resulting respirable sizes of the fracture particulates. To allow additional comparison, Pyrex glass and coal were also tested. The test procedures are believed to be suitable for consideration as a standard MCC-10 dynamic impact test for brittle waste forms.

For all tests, cylindrical samples of similar size (about 2.5 cm by 2.5 cm) were impacted by dropping a steel bar of about 9.9 kg from a predetermined height to provide a maximum input kinetic energy of 10 J/cm^3 of specimen volume. The specimens were all impacted on their sides within a closed impact chamber where particles were collected. The chamber, provided with a bellows to transmit the impact force, is described in the report for the previous quarter [STEINDLER-1981C].

The complete size distributions of the particles resulting from fracture were measured in a Sonic Sifter sieving device (for particles larger than $90 \mu\text{m}$) and in a Coulter counter (for particles whose size was between about $5 \mu\text{m}$ and $90 \mu\text{m}$). Size fractions based on the total mass of the specimens were plotted on lognormal graphical coordinates, and the values of the lognormal size parameters (the mass median, D_g , and the geometric standard deviation, σ_g) were calculated by linear regression of the measured size data. The particles of respirable size were determined as the cumulative mass fraction of particles smaller than $10 \mu\text{m}$ (as a weight percent of the specimen mass).

3. Preparation of Test Specimens

Cylindrical specimens were core-drilled from available bulk material in all but three cases (SYNROC MSD, FUETAP, and PYREX, the last of which is a reference material), which were available in cylindrical form of the required diameter. The ends of the specimens were flat. All glass specimens were annealed, but the others not.

4. Description of Materials Tested

The results for materials tested in this report period are compared with results reported in [STEINDLER-1981C]. Plots of the particle-size distribution data for seven new tests are reported here. The plots of the other tests were given in the previous quarterly report [STEINDLER-1981C]. The chemical compositions of simulated waste materials are summarized in Table 12.

a. FRIT 131 Glass

This is a simulated borosilicate waste glass supplied by Savannah River Laboratory (SRL). The glass contained no uranium, but was loaded with about 28 wt % simulated SRL TDS calcine. The glass was supplied by SRL from their pilot 1/3-scale continuous melter. Specimens for impact testing were prepared by remelting the SRL frit 131 glass in stainless steel crucibles at 1100°C for about 1/2 h under a nitrogen purge, annealing the glass at 550°C for several hours, and then core-drilling specimens 25.5 mm OD by 27 mm long. The composition (presented in [STEINDLER-1981C]) is repeated in Table 12.

One test of this material was reported in [STEINDLER-1981C]. A second specimen, SRL 131 glass (2), was tested during the present report period, and the particle size distribution is plotted in Fig. 10. The principal fracture result, the respirable size fraction at $D = 10^{-5}$ m or 10 μ m, is evident from the plot, and the quantitative results for all the tests are presented and may be compared in Table 13, along with earlier reported results. The respirable fractions for the specimen frit 131 glass (2) and for the previously made test frit 131 glass (1) agree. A more complete comparison of results is given later. The straight line shown in Fig. 10 represents the best statistical size distribution of the actual fracture particulate, for the full range of particle sizes (smaller than 2 mm). The significance of the departures of data points from the straight line is discussed below in Section III.C.2.

b. PNL 76-68 Glass

This is a simulated waste glass produced by Pacific Northwest Laboratory (PNL) for the Materials Characterization Center (MCC) "round robin" tests. A supply was obtained from PNL, and a bulk piece was prepared for core drilling by remelting. Tests results are shown in Fig. 11 and Table 13. They agree closely with those for the SRL frit 131 glass specimens.

c. SYNROC MSD

Two cylindrical specimens of SYNROC, each containing 10 wt % PW-4b [MENDEL] simulated waste, were obtained from the Materials Science Division (MSD) of ANL. The specimens were made by cold-pressing and sintering

Table 12. Nominal Compositions of Alternative Waste Forms
Used in this Comparative Impact Study

Component "Matrix"	Waste Form						
	SRL 131 Glass	SYNROC		TAILORED CERAMIC	FUETAP Concrete	High-Silica Glass	Pyrex
		"B"	"D"				
Weight percent of component							
SiO ₂	41.7				27.75a	54.9	81
B ₂ O ₃	10.6					3.3	13
TiO ₂	0.7	59.4	18.7	2.0			-
Al ₂ O ₃		6.5	1.0	5.8		8.0	2
Li ₂ O ₃	4.1						-
Na ₂ O	12.7						4
Cs ₂ O			0.3			0.1	
MgO	1.4						
CaO		15.2	3.4				1
BaO		8.0	1.4				
ZrO	0.4	10.9	4.9			0.01	
La ₂ O ₃	0.4			7.2			
Flyash					11		
Cement, type 1					22		
Water					18 ^b		
Water Reducer					1.25 ^b		
"Matrix" Totals	72	100	32.8	15	80	66.3	100
SRL "Waste"							
Fe ₂ O ₃	13.9	-	24.2	12.6	9.4	14.5 ^c	
Al ₂ O ₃	3.0	-	18.9	46.2 ^d	1.8		
MnO ₂	3.7	-	7.5	10.4	2.6	4.3	
CaO	1.0	-	1.3	0.8	0.5	0.6	
NiO	1.6	-	3.1	1.8	1.2	1.9	
SiO ₂		-	0.5	1.4	0.2		
Na ₂ O	0.6	-	3.4	4.6	1.3	2.0	
Na ₂ SO ₄	0.4	-	0.6	0.4	0.2		
SrO		-	0.4		0.2	0.1	
CeO ₂		-	0.4		0.4	1.1	
Gd ₂ O ₃		-	0.4		0.4		
Nd ₂ O ₃		-	0.4			0.4	
Eu ₂ O ₃		-	0.4				
UO ₂		-	2.1	d			
Zeolite	2.7	-	-	7.3	1.6		
P ₂ O ₅	-	-	-	-	-	5.0	

^aFUETAP used Ottawa sand, which was placed in SiO₂ column.

^bFor this table, the 19.25 weight percent water was included in normalizations.

^cBased on FeO, not Fe₂O₃, as supplied by Catholic University.

^dThree weight percent UO₂ was replaced with 3 weight percent Al₂O₃.

Table 13. Respirable Particles Generated in Comparative Impact Tests^a

Material	Source Laboratory	Size of Cylindrical Specimen Impacted			Input Energy of Impact		Particle-Size Distribution: Lognormal Parameters		Fraction of Fracture Particles, of Respirable Size, wt %
		Dia., mm	Length, mm	Mass, g	Total Energy, J	Energy Density, J/cm ³	D _g , mm	σ _g	
SRL Frit 131 glass (1)	SRL	25.5	27	39.7	146	10	2.6 ± 0.4	6.4 ± 0.2	0.14 ± 0.02
SRL Frit 131 glass (2)	SRL	25.4	20.1	40.7	148	10	2.6 ± 0.2	6.6 ± 0.4	0.18 ± 0.05
PNL 76-68 glass	PNL	25.4	25.2	37.7	128	10	2.7 ± 0.3	6.9 ± 0.1	0.18 ± 0.01
SYNROC MSD (1)	ANL	20.7	20.4	29.9	69	10	6.3 ± 2.1	8.6 ± 0.6	0.14 ± 0.03
SYNROC MSD (2)	ANL	20.7	19.9	28.4	67	10	7.1 ± 3.3	8.3 ± 0.7	0.10 ± 0.03
SYNROC B	LLL	26.8	25.9	60.5	146	10	4.2 ± 0.8	7.6 ± 0.3	0.15 ± 0.02
SYNROC D	LLL	25.4	27.3	53.5	138	10	4.7 ± 0.7	8.1 ± 0.3	0.16 ± 0.02
High-silica glass	Cath U	28.1	28.9	47.2	178	10	2.7 ± 0.6	7.2 ± 0.3	0.22 ± 0.03
Pyrex glass	ANL	25.0	25.8	28.0	127	10	1.4 ± 0.2	6.0 ± 0.2	0.27 ± 0.03
Coal	ANL	25.3	26.0	16.8	131	10	2.1 ± 0.6	6.3 ± 0.3	0.19 ± 0.04
TAILORED CERAMIC	Rockwell	26.8	18.2	40.8	102	10	10 ± 2	8.3 ± 0.3	0.05 ± 0.01
FUETAP concrete	ORNL	25.4	25.5	23.0	131	10	2.3 ± 0.3	7.9 ± 0.2	0.43 ± 0.04

^aFurther description of materials and test conditions are given in the text.

Fig. 10. Lognormal Plot of Cumulative Measured Weight Percent [P%] vs. the Measured Particle Diameter or Mesh Size [D(m)] for SRL Frit 131 Glass (2) Impact Test. 10 J/cm^3 .

Fig. 11. Lognormal Plot of Cumulative Measured Weight Percent [P %] vs. the Measured Particle Diameter or Mesh Size [D(m)] for PNL 76-68 Glass Impact Test. 10 J/cm^3 .

at 1300°C for three hours in about 1 MPa (10 atm) of CO/CO₂. The density (calculated from geometry and mass) was 4.26 g/cm³. Test results are shown in Figs. 12 and 13 and in Table 13. As shown in Table 13, these results are similar to those for the previously tested SYNROC B and SYNROC D, which are described below.

Fig. 12. Lognormal Plot of Cumulative Measured Weight Percent [P] vs. the Measured Particle Diameter or Mesh Size [D(m)] for MSD SYNROC (1) Impact Test. 10 J/cm³.

d. SYNROC B and SYNROC D

These are ceramic forms received from Lawrence Livermore Laboratory (LLL). SYNROC B ceramic contained no waste and was reported by LLL to have a density of 4.2 g/cm³ (96% T.D.). SYNROC D contained 64 wt % waste, with a reported density of 3.96 g/cm³ (92% T.D.). Compositions are given in Table 12. Details of manufacture and sample preparation were given in [STEINDLER-1981C] along with graphs of the particle-size distributions. To allow comparison, previously published test results are included in Table 13.

e. High-Silica Glass

The composition of this simulated waste is given in Table 12. The specimen, received from Catholic University (CU), had been core-drilled from a larger piece which had been formed by sintering powder in a crucible for 4 h at 1250°C in a vacuum. The as-received material was tested. It appeared to be heterogeneous (unlike glass), with zones of different colors. No analysis of the microstructure was available. Test results are shown in Fig. 14 and Table 13.

Fig. 13. Lognormal Plot of Cumulative Measured Weight Percent [P%] vs. the Measured Particle Diameter or Mesh Size [D(m)] for MSD SYNROC (2) Impact Test. 10 J/cm^3 .

Fig. 14. Lognormal Plot of Cumulative Measured Weight Percent [P%] vs. the Measured Particle Diameter or Mesh Size [D(m)] for CU High-Silica Impact Test. 10 J/cm^3 .

f. Pyrex Glass

This commercial glass contained no waste and was included only as a reference material. The specimen was cut from rod stock and annealed. Results are shown in Fig. 15 and Table 13.

Fig. 15. Lognormal Plot of Cumulative Measured Weight Percent [P%] vs. the Measured Particle Diameter or Mesh Size [D(m)] for Pyrex Impact Test. 10 J/cm^3 .

g. Coal

To examine the possibility of using our test procedures for other research programs, a specimen of coal obtained from the ANL power plant stockpile was tested. Special care was necessary to obtain a sound specimen by core drilling. The particle size analysis shown in Fig. 16 and Table 13 is comparable to those of other materials tested.

h. TAILORED CERAMIC

This hot-pressed ceramic was core-drilled from a bulk piece received from Rockwell International. The available size limited the length to that shown in Table 13. The previously reported composition is again given in Table 12; the graph of particle-size distribution and the details of manufacture are given in [STEINDLER-1981C]. The result of this test is included here to allow respirable fractions to be compared. The TAILORED CERAMIC showed the smallest respirable fraction of the materials tested.

Fig. 16. Lognormal Plot of Cumulative Measured Weight Percent [P] vs. the Measured Particle Diameter or Mesh Size [D(m)] for Coal Impact Test. 10 J/cm^3 .

i. FUETAP Concrete

This is an Oak Ridge National Laboratory (ORNL) simulated waste concrete loaded with 20-25 wt % simulated SRL waste; the concrete was dewatered at 250°C . Cylindrical material was cut to size. Its composition (no uranium) is again presented in Table 12. Details of manufacture and a particle size plot are given in [STEINDLER-1981C]. Test results for one FUETAP lot shown in Table 13 are included to allow comparison.

5. Discussion of Results

The plots of empirical size data from sieving and Coulter counter analysis show lognormal size distribution in the range of $10 \text{ }\mu\text{m}$ to 2 mm . It is presumed that this establishes lognormality for particles smaller than $10 \text{ }\mu\text{m}$ (which are not measurable with the present equipment). The particulates of 2-mm particle size and smaller contain 95% or more of the total surface area of a complete lognormal distribution (*i.e.*, for diameters from zero to infinity) for particulates with the values of D_g and σ_g listed in Table 13. A comparison of particle size distributions is provided by Fig. 17, in which straight-line plots for all tests in Table 13 are shown. The plotted points are shown for each test particulate and correspond to (1) the cumulative mass fractions at diameter $10 \text{ }\mu\text{m}$, (2) the cumulative mass fraction for the particle diameters which corresponds to 50% of the cumulative surface area distribution and (3) the geometric mean diameters, D_g , defined for the mass fractions of 50%. Measured surface areas are to be reported later.

Fig. 17. Comparison of Lognormal Size Distributions for Eight Impact Tests at 10 J/cm^3 as Described in the Text

For all of the simulated waste glasses and ceramics except TAILORED CERAMIC, the values for respirable fraction agree within a factor of two. The highest respirable fraction of all is for FUETAP concrete. The lowest is that for TAILORED CERAMIC (Table 13).

In the two cases which show replication (Table 13), SRL frit 131 glass and SYNROC MSD, the results agree within the standard error of the regression analysis, for both the respirable fraction and the lognormal parameters. The LLL SYNROC B and D specimens also are in good agreement.

As the data points on the plots of the particle-size distributions show (Figs. 10-16), there are departures from lognormality in Coulter counter (CC) data at about $5 \mu\text{m}$ and $90 \mu\text{m}$. This is an artifact of the method. At the lower limit of the CC range ($5 \mu\text{m}$ for our instrument), particles are systematically undermeasured because of pulse electronics. Therefore, extrapolation to smaller sizes is the more accurate representation of the actual fracture particulate. The departure from lognormality of CC data at its upper size limit ($90 \mu\text{m}$) is also an artifact caused by the particular features of the wet sieving method used to prepare the CC sample. The particle diameter is determined differently by CC analysis and by sieving analysis, which contributes to the variations in the $80\text{-}100 \mu\text{m}$ size range. Overall, the large number of data points provide a reasonable statistical accuracy for the lognormal parameters, D_g and σ_g , which, in turn, provide the best estimate of the actual size distribution of the fracture particulate.

C. Methodology Development (W. J. Meham)

1. Background

As part of the brittle fracture study, a comprehensive methodology is being developed to characterize the impact behavior of brittle materials under conditions of practical interest such as may be encountered in accidents during manufacture, handling, and transport of solid radioactive waste forms. One aim is to characterize the impact-resistance property of waste materials in terms of the increased environmental dispersability of the material as a consequence of impact fracture--namely, (1) the increased surface area generated for possible leaching by groundwater and (2) the amount of fracture particulate which is of respirable sizes (particles smaller than about 10- μ m diameter). A second aim is to characterize impact severity (with respect to brittle fracture) in terms of body size and shape for practical collision velocities and other relevant factors.

In previous quarterly reports of this series (see title page), a review was presented of the technical literature, which showed the practical inadequacies of theoretical fracture mechanics and of experimental testing with respect to the above aims. The methods of continuum mechanics cannot deal either with discontinuities in the stress field nor with thermodynamically irreversible and time-dependent energy transformations. Reported experimental approaches relevant to the impact strength of materials have been largely confined to concerns with structural failure and brittle metals, rather than the extent of fracture of truly brittle materials such as glasses and ceramics.

The methodology discussed here is based on a combination of dimensional-analysis modeling principles, empirical energy-surface correlations for the crushing of minerals, lognormal particle statistics, and axisymmetric dynamic stress analysis. Methodology development has been described in quarterly progress reports of this series and in a topical report [MECHAM].

In this report, methodology on the following topics is updated: (a) evaluation of measurements of particle-size distributions, (b) evaluation of surface areas of fracture particulates, (c) energy and stress relations in impact compression, (d) stress distributions calculated from particle-size distributions, (e) energy partitioning in impact testing machines, and (f) modeling of impact severities in free-fall impacts of waste-form prototypes.

2. Evaluation of Measurements of Size Distributions of Impact-Fracture Particulates

Size distributions of solid particulates are measured by separating the solid particulate sample into mass (or volume) increments according to particle size, *i.e.*, the characteristic linear size, the particle diameter, D . For material of a given density, mass increments are equivalent to volume increments, ΔV_j , for a given size range, $D_j - D_{j-1} > 0$ (where D_j is the upper size limit), so that the total material in the sample, V_n , is size-characterized by the sum of the increments:

$$V_n = \sum_{D_{\min}}^{D_{\max}} \Delta V_j \quad (1)$$

The size distribution is described by the cumulative volume data $V(D_j)$:

$$V(D_j) = \sum_{D=0}^{D_j} \Delta V_j \quad (2)$$

The particle size distribution normalized to the same volume is described by the measured data for (a) the incremental volume fractions, $\Delta V_j/V_n$ and (b) the cumulative volume fraction, $V(D_j)/V_n$. The empirical size distribution is typically presented graphically by a plot of the cumulative volume (or mass) fraction vs. particle diameter D , with a continuous line drawn through the data points to represent the continuous function, $V(D)/V_n$.

In the case of Coulter counter (CC) size analysis, the volume, v , of each particle is measured and the particle diameter, D is calculated as that of a sphere of equal volume:

$$D = \left(\frac{6}{\pi} v \right)^{1/3} \quad (3)$$

The volume increments, ΔV_j , of the particulate are calculated as the sum of particle volumes over the range of sizes defined by a constant ratio:

$$\frac{D_j}{D_{j-1}} = 2^{1/3} \quad (4)$$

Such size increments are equal on a log scale of D . Thus, for CC data,

$$\begin{aligned} \Delta V_j &= \sum_{D_{j-1}}^{D_j} v_j \\ &= \frac{\pi}{6} N_j (\bar{D}_j)^3 \end{aligned} \quad (5)$$

where N_j is the total number of particles in this size range, $D_j - D_{j-1}$, and $\bar{D}_j$ is the mean size of this range, which is based on the mean particle volume, $\bar{v}_j$:

$$\begin{aligned}\bar{v}_j &= \frac{1}{2} (v_j + v_{j-1}) \\ &= \frac{\pi}{6} (\bar{D}_j)^3\end{aligned}\quad (6)$$

From Eqs. 3 through 6, the mean size $\bar{D}_j$ of the volume increment, ΔV_j , is a function of the upper-size limit, D_j , of the size range; thus,

$$\bar{D}_j = 0.909 D_j \quad (7)$$

and correspondingly,

$$\Delta V_j = 0.393 N_j (D_j)^3 \quad (8)$$

In CC analysis, the incremental volume fractions, $\Delta V_j/V_n$, are calculated for each of the CC size channels (indexed by the upper-limit size, D_j), from which the cumulative volume fractions, $V(D_j)/V_n$, are calculated and plotted. Typically, CC analysis is carried out on a sample consisting of only that part of a total fracture particulate which passes through a 90- μ m mesh. The CC size analysis based on sample size, V_n , can be renormalized to the total volume, V_o , of the fracture particulate:

$$\frac{V(D_j)}{V_o} = \frac{V(D_j)}{V_n} \frac{V_n}{V_o} \quad (9)$$

Since CC analysis actually counts individual particles, the total mass of sample required is relatively small compared to other methods, e.g., sieving. When CC analysis is done in conjunction with sieving, the -90 μ m sample submitted for CC analysis can be weighed beforehand, and the value of V_n in Eq. 9 can be obtained independently of the V_n obtained internally by Eqs. 1 and 5 by the CC instrument. The small sample requirement and the internal measurement of absolute values of sample volume V_n are advantages of CC analysis. Certain other features of CC data are discussed later in connection with plots of combined CC and sieving data in lognormal graphical coordinates.

In sieve (SV) analysis, the entire volume (or mass) V_o of the impacted specimen is used, and the absolute values of the volume increments by size, ΔV_j , are determined by weighing. The size increments, $D_j - D_{j-1}$, are defined by a constant ratio,

$$\frac{D_j}{D_{j-1}} = 2 \quad (10)$$

which as in CC analysis, are equal linear increments on a scale of $\log D$. The mean size, $\bar{D}_j$, of the volume increment, ΔV_j is given by

$$\begin{aligned}\bar{D}_j &= \frac{1}{2} (D_j + D_{j-1}) \\ &= 0.75 D_j\end{aligned}\quad (11)$$

In our measurements, we have combined CC data in the size range of 5 μm to 100 μm with sieving (SV) data for larger size particles, all normalized to specimen volume, V_0 . The combined data are used to determine the best values of the lognormal parameters, the geometric mean, D_g , and the geometric standard deviation, σ_g , as described in detail previously. The general method involved equating the cumulative normal probability function $P(u)$ with the empirical data provided by the cumulative volume fractions $V(D)/V_0$ described above. That is,

$$P(u_j) = V(D_j)/V_0 \quad (12)$$

where the standardized normal variate u is related to D_j by the lognormal parameters, D_g and σ_g :

$$u_j = \frac{\log D_j}{\log \sigma_g} - \frac{\log D_g}{\log \sigma_g} \quad (13)$$

Equation 13 shows a linear relation between u and $\log D$, and this is the basis of the straight-line plots of particle size distributions on cumulative log-normal probability coordinates described in previous quarterly reports (see title page). The continuous lognormal probability function $P(u)$ can be used both graphically and analytically to interpolate and extrapolate the measured values of the cumulative volume fractions, $V(D_j)/V_0$.

The lognormal frequency function $p(u)$ is defined in terms of the cumulative probability function, $P(u)$, as

$$\begin{aligned}p(u) &= \frac{dP(u)}{du} \\ &= \frac{1}{\sqrt{2\pi}} e^{-u^2/2}\end{aligned}\quad (14)$$

where u has the same meaning as before. In terms of the normalized finite volume increments, $\Delta V_j/V_0$,

$$\begin{aligned}\frac{\Delta V_j}{V_0} &= \Delta P_j \\ &= P(u_j) - P(u_{j-1}) \\ &= p(\bar{u}_j) \Delta u_j\end{aligned}\quad (15)$$

Thus, the empirical values $\Delta V_j/V_0$ are related to the normal probability frequency function $p(u)$ by

$$p(\bar{u}_j) = \frac{\Delta V_j}{V_0} \frac{\log \sigma_g}{\log (D_j/D_{j-1})} \quad (16)$$

where $\bar{u}_j$ is related to D_j as defined for CC data in Eq. 7 and for SV data in Eq. 11. The empirical values, $\Delta V_j/V_0$, plot as straight lines on log-normal frequency coordinates.

The lognormal analysis of measured size distribution data from both CC and SV allows characterization of the fracture particulate in terms of the parameters, D_g and σ_g . This has been demonstrated for numerous test data. The lognormal size distribution is mathematically consistent with a binary-cleavage mode of fracture in impacts. That is, if it is assumed that every particle is the result of n successive stages of three-dimensional binary cleavage in the portion of the impacted volume where the particle was formed, then the diameter, D_j , of that particle is related to n and to the lognormal parameters by

$$\begin{aligned} \frac{D_j}{D_g} &= \left(\frac{1}{2}\right)^{n-n_g} \\ &= \sigma_g^{u_j} \end{aligned} \quad (17)$$

where n_g is the number of stages to form a particle of size D_g from the original whole body of diameter, D_0 : $D_g/D_0 = \left(\frac{1}{2}\right)^{n_g}$. The lognormal characterization of the size distribution of a brittle-fracture particulate does not rest on any theoretical assumptions; it rests on empirical measurements. These implications for particle surface areas and for stress distributions will be developed in subsequent sections of this report. In the present section, the evaluation is directed to empirical particle size measurements.

One potential problem in combining Coulter counter (CC) data and sieving (SV) data is the fact that these methods determine particle diameter (D) differently. In CC analysis, D is the equivalent spherical diameter of the measured particle volume. In SV analysis, D is the square mesh opening through which particles (of whatever shape) can fall under gravity while being agitated by mechanical vibrations. It can be shown by simple geometrical models that needle-shaped particles will have a smaller D in SV analysis than in CC analysis. In the case of plate-shaped particles, the reverse is true. This state of affairs is shown graphically in Fig. 18, for plots of cumulative volume fractions vs. particle size, which are linear on lognormal graphical coordinates. Actual measurements typically do not show major displacement of the lines, as illustrated for the calculated plate-shaped and needle-shaped size distributions. Actual fracture particulate measurements appear to approximate a common straight line, as shown for a mixture of shapes,

Fig. 18.

Illustration of Shape Effect on Particle Size Distribution when Measured by Coulter Counter (CC) and Sieves (SV)

probably because shape variations tend to average out. Current presentation of empirical size distributions from combined CC and SV analysis have not been adjusted in any way; the actual data points (as in Fig. 16) indicate the extent to which this averaging effect takes place.

However, in the case of particles larger than about 2 mm, there is a fundamental departure from linearity for impact tests. This effect, associated with the surface area of the fracture particulate, is discussed in the following section, but typical empirical results are illustrated in Fig. 19. A typical size distribution is shown for (1) the cumulative mass function and (2) the cumulative surface area function of the lognormal fracture particulate, the latter of which consists of all particles smaller than size D_{98} and which includes more than 98% of the total surface area.

Also in Fig. 19, minor departures from linearity are seen at the extreme ends of the CC data, *i.e.*, the downward concavities $D < 10 \mu\text{m}$ and at $D > 70 \mu\text{m}$. The former effect is due to the insensitivity of the CC device to the measurement of particle volumes in the size range below about $5 \mu\text{m}$. Thus, the cumulative volume fraction for the CC sample is inaccurate because material less than $5 \mu\text{m}$ in size (which amounts to less than 1% of the total CC sample) is not detected. The practical result is to distort the shape of particle-size distribution curves for particles smaller than about $8 \mu\text{m}$. This error of less than 1% in V_n , as determined internally by the CC, is not practically significant. The correct V_n is known from the weight of material in the Counter counter sample, as discussed above in connection with Eq. 9.

Fig. 19. Illustration of Lognormal Size Parameters in Relation to Measured Particle Size Distributions. $D_{98s} = 1 \text{ mm}$. $D_L = 5 \text{ mm}$. Typically, D_g is approximately equal to D_{98s} . The slope of both straight lines $= 1/\log \sigma_g$.

The downward concavity of the CC data for $70 \mu\text{m} < D < 100 \mu\text{m}$ is due to an artifact of sieving. Typically, the CC sample is prepared by wet-sieving the fracture particulate to collect the $-90 \mu\text{m}$ material. On the other hand, the sieving analysis itself is done dry, and additional material (not collected in wet sieving) falls through the $90\text{-}\mu\text{m}$ sieve into the fines catcher. Although wet sieving provides efficient separation of small particles from large particles, it gives a different sieve calibration--that is, dry sieving allows larger particles to penetrate the $-90 \mu\text{m}$ sieve than does wet sieving. Very properly, these nonlinear CC points should be ignored, so long as the first point of the SV data is an accurate cumulative volume fraction. Of course, when many points are used, the error of one point does not have a significant effect on the determination of D_g and σ_g . The above discussion is a reminder that accurate results depend on good calibration of all measurement devices used in particle size analysis.

3. Correlation of Lognormal Particle Size Parameters with Input Energy Density

a. Energy Distribution in Impact Compression

Brittle fracture is not a thermodynamically reversible process, nor can it be described in terms of chemical equilibrium states nor the continuous differential equations of physical mechanics. Nevertheless, the

principle of conservation of energy applies to the transformations of the input kinetic energy and provides the basis for an overall description of the fracture process. This is described below, both for the general case of impact and for the use of testing machines.

In general, the stresses that generate fracture result from the force, F , applied to the brittle body by the deceleration of a mass, M , as it moves with decreasing velocity, v , as a function of time, t :

$$\begin{aligned} F &= M \frac{dv}{dt} \\ &= A_f \sigma \end{aligned} \quad (18)$$

where σ is the stress at the load-bearing surface area, A_f , normal to the force axis. During the initial compression stage of impact, F and σ increase monotonically with time, because the elastic compression offers continually increasing resistance to further movement. Maximum stress occurs when velocity $v = 0$.

In practice, typical brittle materials can be treated as homogeneous and isotropic in their elastic behavior. Hooke's law describes the linear relation of elastic stress, σ_x , and strain, ϵ_x , as a directional point property in a continuous medium.

$$\sigma_x = E \epsilon_x \quad (19)$$

where E is Young's modulus, a constant for a given material. In a volume element, $dx dy dz$, subject to normal stress (in the x -direction) only, the force on the element is the product of σ and the area element $dy dz$, and this force does work in producing a linear compression $\epsilon_x dx$. For the volume element, this work dW is

$$dW = 1/2 (\sigma_x \epsilon_x) dx dy dz \quad (20)$$

The "1/2" in Eq. 20 is a consequence of the integration of the work (over time) as strain goes from zero to ϵ within the volume element. From Eqs. 19 and 20, we may write the strain energy density in the volume element, $dV = dx dy dz$, as dW/dV :

$$\frac{dW}{dV} = \frac{\sigma_x^2}{2E} \quad (21)$$

Since we are concerned with application of a single unidirectional stress, the subscript x is dropped in further expressions of stress, σ .

Saint-Venant's principle describes physical results of the local distribution of stress within a body, and the principle of energy conservation accordingly describes the total strain energy, W , in the body due to the applied force on the volume element in the volume integral of dW in Eq. 21:

$$W = \int \frac{\sigma^2}{2E} dV \quad (22)$$

If the force, F , is applied uniformly normal to the flat end of a cylinder of diameter, D , and length, L , the load-bearing surface is $A_f = \pi/4 D^2$, the stress, σ , is uniform over the volume $V = A_f L$, and the work, W , is

$$W = \frac{\sigma^2}{2E} V \quad (23)$$

In Eq. 23, the stress, σ , is uniform, and so stress, σ , and energy density, W/V , are mutually defined. In Eq. 22, the overall energy density is also W/V , which defines a volume mean stress, $\bar{\sigma}$, corresponding to:

$$\frac{W}{V} = \frac{\bar{\sigma}^2}{2E} \quad (24)$$

This has significance with respect to the impact-fracture process. If the fracture results correlate with the mean stress, then the overall energy density determines the fracture results, independent of the actual stress distribution. This appears to be so, at least under some impact conditions, and it is a fortunate result because dynamic stress distributions are in practice indeterminate.

The above consideration of strain energy density shows that for any body shape or size, the overall stress state is defined by the overall energy density, W/V , where W is equal to the input energy. For impact compression alone, the loss of kinetic energy is equal to the overall strain energy, and the mean stress is the same for all configurations, as defined in terms of overall energy density, W/V . For example, diametral compression of a cylinder (between flat plates) gives the same overall energy density as for axial compression, even though the peak stress and the stress distribution are different.

If the chief practical interest were to characterize the structural strength of a brittle material in impacts, then the proper experimental test would be to determine the threshold stress for fracture under various controlled dynamic load conditions. However, if the practical interest is to characterize the way impacts of various severities result in the formation of a particulate (measured by surface area and respirable fraction), then the stress per se is not important, even though stress is the driving force for brittle fracture. In this impact-fracture process, stress varies greatly with both time and location in the compressed body, and the first crack propagation destroys the continuous stress field, so that stresses during crack propagation are actually indeterminate. In practice, even the threshold stress cannot be made uniform in the axial impact of a specimen, because of small directional misalignments and local surface-contact perturbations of the stress field in the compressed material.

As described above, impact severity is measured overall for the specimen by stress energy density, which is a direct correlate of the mean stress in the material. This mean stress is anticipated to correlate

with the mean size, D_g , and mean shape factor, α , as characterized statistically. Only experimental tests will establish adequate experimental procedures for characterizing impact results.

4. Stress Distributions Calculated from Particle-Size Distributions

The preceding sections show how impact energy is converted to strain energy density (which is equivalent to stress) and how the total fracture surface is related to the lognormally distributed fracture particulate. If impact conditions are such that there are no significant pathways for energy dissipation other than brittle fracture, then the impact kinetic energy will be "used up" by being converted into strain energy, which is then dissipated into heat by collisions of the particles ejected by the impact. The extent of fracture measured by the total fracture surface area, S_f , may then be correlated with impact energy density, W_i/V_o :

$$\epsilon \frac{W_i}{V_o} = \gamma_f \left(\frac{S_f}{V_o} \right) \quad (25)$$

where ϵ is an efficiency factor (allowing for some dissipation of input energy to the surroundings) and γ_f is an impact resistance property (reported to be 77 J/m² for Pyrex glass and for mineral quartz) [ZELENY].

The total surface area, S_n , of the lognormally distributed fracture particulate is equal to S_f , the total fracture-cleavage surface area. Mathematically, S_n is related to V_n by the lognormal parameters, D_g and σ_g :

$$\begin{aligned} \frac{\epsilon}{\gamma_f} \left(\frac{W_i}{V_n} \right) &= \frac{S_n}{V_n} \\ &= \frac{\alpha \sigma_g}{D_g} \end{aligned} \quad (26)$$

which gives the overall relation for impact energy and particle characteristics, including surface area. If we consider a volume increment of the fully compressed material about to fracture in the particulate mode, the local energy density, $\Delta W/\Delta V$, corresponds to local stress by Eq. 23:

$$\frac{\Delta W}{\Delta V} = \frac{\sigma^2}{2E} \quad (27)$$

We may also apply the overall relation between particulate surface area and energy density given in Eq. 26 to apply to this volume increment:

$$\left(\frac{\epsilon}{\gamma_f} \right) \frac{\Delta W}{\Delta V} = \frac{\Delta S}{\Delta V} \quad (28)$$

The surface and volume increments, ΔS and ΔV , are related to the lognormal distribution of particle diameter, D . In the notation introduced previously,

$$\begin{aligned}\frac{\Delta V}{V_n} &= \frac{V(D_j)}{V_n} - \frac{V(D_{j-1})}{V_n} \\ &= P(u_{v,j}) - P(u_{v,j-1})\end{aligned}\quad (29)$$

$$\begin{aligned}\frac{\Delta S}{S_n} &= \frac{S(D_j)}{S_n} - \frac{S(D_{j-1})}{S_n} \\ &= P(u_{v,j} + \ln \sigma_g) - P(u_{v,j-1} + \ln \sigma_g)\end{aligned}\quad (30)$$

For factor-of-two size increments,

$$u_{v,j-1} = u_{v,j} - \frac{\ln 2}{\ln \sigma_g} \quad (31)$$

and $\Delta S/\Delta V$ is defined for each value of u_v (a function of D).

Combining Eqs. 27 through 31,

$$\begin{aligned}\frac{\sigma^2}{2E} &= \left(\frac{\epsilon}{\gamma_f}\right) \left(\frac{\Delta W}{\Delta V}\right) \\ &= \frac{\Delta S}{\Delta V} \\ &= \frac{P(u_v + \ln \sigma_g) - P(u_v + \ln \sigma_g - \ln 2)}{P(u_v) - P(u_v - \ln 2)}\end{aligned}\quad (32)$$

so that $\sigma = f(u_v) = f(D)$. Thus, for given values of the parameters in these equations, σ is defined in terms of particle size. That is, there is a fraction of the specimen volume, given by $P(u_v) = V(D)/V_n$, which has a particle size less than D . Correspondingly, that fraction of the volume is stressed at a level of at least $\sigma = f(D)$, as given by Eq. 32.

A plot of such stress destruction calculations was made for a test of Savannah River Laboratory 131 waste glass, for which $D_g = 2.6$ mm, $\sigma_g = 6.4$, $\alpha = 30$, $\gamma_f = 77$ J/m², $\epsilon = 1.0$, and $E = 7 \times 10^{10}$ Pa. The results are plotted in Fig. 20.

It is assumed that each particle is formed by multiple stages of three-dimensional binary cleavage of the original body of diameter D_o ,

$$\frac{D}{D_o} = \left(\frac{1}{2}\right)^n \quad (33)$$

Fig. 20. Volume Distribution of Stress and Energy Density for Sample of SRL 131 Waste Glass

where n is the number of stages of binary cleavage. A similar relation of the lognormal parameters is

$$\frac{D}{D_g} = \sigma_g^u \quad (34)$$

Equations 33 and 34 define the relation between u and u_v for a given D_1 . For given values of D_g and σ_g , the values of the distribution of n as a function of volume are plotted in Fig. 21. The plot indicates that 50% of the volume has had at least two stages of binary cleavage, but only 0.2% of the specimen volume has had more than ten stages of binary cleavage. The cumulative surface area fraction as a fraction of the cumulative volume fraction (starting from the smallest size particles) is also plotted in Fig. 21.

The significance of these calculations depends on whether the results are consistent with all of the available information and whether correlations for the values of the parameters have predictive values. One possibility is that the range of particle sizes may be related to the range of stress levels in the material. This can only be established by systematic experimental tests.

One other calculation of possible significance can be made if particle diameter, D_{98s} , as shown in Fig. 20, is taken as defining the upper-limit size of the fracture particulate proper. The stress corresponding

Fig. 21. Volume Distribution of Surface Area and Number of Binary Cleavage Stages

to this value of D can be considered the threshold stress for particulate fracture. It is marked in Fig. 18, indicating a value of 4×10^8 Pa or 58,000 psi. This is a reasonable value for a threshold fracture stress in impacts.

5. Energy Partitioning in Impact Test Devices

The initial compression stage of impacts of brittle specimens has been analyzed above without consideration of the deformation of the surroundings. In this section, the principal ways in which the surroundings interact with the specimen during compression and brittle fracture are identified. Since the deceleration force causing stress and fracture in the specimen is also borne by the components of the surroundings in contact with the specimen, these components are subject to elastic compliance or plastic deformation, which reduces the severity of impact on the specimen. In impact tests, the principal components of the test device are chosen for their resistance to elastic and inelastic deformation. It is assumed here that these components have the properties of typical hardened steel and consist of an anvil upon which the specimen rests and a hammer which strikes the specimen. The general configuration is shown in Fig. 22.

Dynamic force loading in test devices can be characterized according to the degree of compliance of the steel hammer and anvil. As the force is increased, compressive stress increases in both the specimen and the steel. Typically, the steel deforms elastically but does not deform plastically. When stress in the specimen exceeds the elastic limit, the specimen fractures and the pieces are ejected in a direction normal to the force axis, which is

NOMINAL DIMENSIONS

L_1 = length (along force axis) of specimen

L_2 = length (along force axis) of each steel

LINEAR DEFORMATION UNDER COMPRESSIVE FORCE F

X_1 = approximate value for specimen

X_2 = approximate value for steel

Fig. 22. Model of Impact Test Device

the only "open" space to which they can move. This "fracture dislocation" relieves the elastic stress in the specimen and also relieves the force holding the hammer and anvil in compression at the contact surfaces between them and the specimen. The hammer and anvil immediately expand to achieve a new force balance, and the amount of such expansion depends on the compliance of the steel. In a "perfectly hard" loading, with no compliance at all in the steel components, the resistance force presented to the hammer and anvil drops to zero and no further compressive energy is "fed into" the specimen after the initial fracture event. In real tests, there is some compliance and there may be some residual force presented to the hammer and anvil, depending on the downward motion of the hammer and on the speed with which the specimen disintegrates. If there is no mechanical stop between the hammer and the anvil, the hammer will finally come to rest atop whatever brittle fragments have failed to escape the hammer's path. Clearly, impact fracture in such a case consists of several stages of impact. In drop-weight impact tests of this type, the total extent of fracture is that which results from the complete dissipation of kinetic energy, however the fracture process occurs. Motion pictures, however, indicate that the primary fracture "explosion" is the dominant event and that successive stages probably produce relatively little fracture.

If a mechanical stop limits the travel of the hammer, the secondary crushing stage is avoided. However, depending on the compliance of the steel and the fracture behavior of the brittle material, there may be some additional feed-in of energy to the specimen after fracture has commenced. The elastic compression stage is analyzed below, and an estimate is made of the minimum compliance of the steel relative to that of the specimen. Also estimated is the partitioning of compression energy between the specimen and the steel at the point of maximum developed force, when fracture is just beginning. Although the complete fracture process takes place in a fraction of a millisecond in typical test specimens, the force can be measured as a function of time with a high-speed piezoelectric force transducer with video readout. Force measurement within about 1- μ s time resolution can be achieved. The fluctuations of force during impact give information on the stagewise progress of brittle fracture in tests.

In Fig. 22(a), the general configuration is shown under the zero force conditions. In Fig. 22(b), the elastic deformation is shown under maximum force, assuming that fracture has not developed sufficiently to distort the stress fields. (The deformation, as shown, is exaggerated for illustrative purposes.)

Since compressive forces propagate at speeds up to the acoustic velocity (which for a typical glass is about 5000 m/s), a force balance is approximately maintained even under the rapid and brief decelerations involved in impact tests. This balance of force, F , in the specimen and the steel can be expressed in terms of the dimensions identified in Fig. 22 by the following equations, where E_1 is the elastic modulus of the specimen and E_2 that of steel:

$$\begin{aligned} F &= \frac{A_1 E_1 X_1}{L_1} \\ &= \frac{A_2 E_2 X_2}{L_2} \end{aligned} \quad (35)$$

The compressive work W_1 in the specimen and W_2 in the steel are given by

$$W_1 = \frac{A_1 E_1 X_1^2}{2L_1}; \quad W_2 = \frac{A_2 E_2 X_2^2}{2L_2} \quad (36)$$

The ratio of W_2/W_1 is thus

$$\begin{aligned} \frac{W_2}{W_1} &= \frac{X_2}{X_1} \\ &= \frac{A_1 E_1 L_2}{A_2 E_2 L_1} \end{aligned} \quad (37)$$

Typical specimen dimensions are of the order of 1-cm diameter and length, and specimens have an elastic modulus smaller than that of steel. The estimate of the minimum ratio of W_2/W_1 is the product of the estimated minimum values for the component ratios as follows:

$$\frac{A_1}{A_2} = 0.1; \frac{L_2}{L_1} = 4; \frac{E_1}{E_2} = 0.25 \quad (38)$$

Therefore,

$$\frac{W_2}{W_1} > 0.1 \quad (39)$$

and the fraction of the total work of elastic compression which is stored in the steel is

$$\frac{2W_2}{2W_2 + W_1} > 18\% \quad (40)$$

This shows a relatively small fraction but not a negligible amount of total energy is stored. A more typical set of dimensions would give $W_2/W_1 = 0.6$, or possibly a higher value. The partitioning of energy limits the stress in the specimen, depending on the impact-energy impact. In addition, the energy stored in the steel can "feed in" to the specimen during fracture, and thus can contribute to the fracture results.

In the technical literature relevant to force-instrument testing devices, an analysis is given which relates (1) the measured force to (2) the energy input to the test specimen. This analysis does not consider the energy partition outlined above, but is of interest in describing the test dynamics, particularly when a force transducer is used.

In general, the compression force, F , is determined by the moving mass, M (typically, the hammer), and its velocity, v , as a function of time, t , that is,

$$F = M \frac{dv}{dt} \quad (41)$$

The time integral of force, I_F , is equal to the loss of momentum (Mv) from the original velocity, v_0 , to $v(t)$:

$$\begin{aligned} I_F &= \int_0^t F dt \\ &= Mv_0 - Mv \end{aligned} \quad (42)$$

The original kinetic energy is $1/2 Mv_o^2$, and the loss of kinetic energy, W , corresponding to the loss of momentum is

$$W = 1/2 Mv_o^2 - 1/2 Mv^2 \quad (43)$$

where v can be found from Eq. 42:

$$v = v_o - \frac{I_F}{M} \quad (44)$$

Substituting v from Eq. 44 in Eq. 43,

$$\begin{aligned} W &= v_o I_F - \frac{I_F^2}{2M} \\ &= v_o I_F \left(1 - \frac{v_o I_F}{2Mv_o^2} \right) \end{aligned} \quad (45)$$

The mean velocity, $\bar{v}$, can be defined in terms of Eq. 44:

$$\begin{aligned} \bar{v} &= \frac{v_o}{2} + \frac{v}{2} \\ &= v_o - \frac{I_F}{2M} \\ &= v_o \left(1 - \frac{v_o I_F}{2Mv_o^2} \right) \end{aligned} \quad (46)$$

$\bar{v}$ of Eq. 46 can be substituted in Eq. 45:

$$\begin{aligned} \Delta W &= \bar{v} I_f \\ &= \bar{v} \int_0^t F dt \end{aligned} \quad (47)$$

If v does not change much in this time interval, $\bar{v} \doteq v_o$, and from Eq. 47,

$$\Delta W = v_o \int_0^t F dt \quad (48)$$

where the loss of kinetic energy is associated with the gain of elastic strain energy in the compressed specimen. Although Eq. 48 is sometimes said to define the energy input into the test specimen in terms of the readings of a force transducer, it is evident from the above mathematical basis that such a claim makes two assumptions: (1) the mean velocity, $\bar{v}$, in the time period is known and (2) the steel components of the test device are perfectly hard and do not share any of the elastic strain energy. In general, these conditions do not hold, although for some impact conditions they may be close enough approximations that test results so interpreted are not seriously in error with respect to the energy input to the specimen.

The direct measure of force does indicate the level of mean stress in the specimen at the time when the decrease of force indicates that fracture is extensive. The calculation of energy density from the mean stress (and vice versa) is discussed in Section III.C.4 above. Impact tests may be arranged so that stresses in the test specimens are approximately uniform. As mentioned above, it is hard to verify such uniformity. Probably, only consistent test results will show the consequences of nonuniform stress in impact. Possibly, the range of particle sizes in axial impacts of cylindrical specimens will indicate the nonuniformity of the stresses causing fracture.

In accidents, impact stresses are not uniform. A methodology for characterizing the severity of impact in terms of (1) overall impact energy density, (2) body size, and (3) the configuration of impact is being developed.

IV. FLUIDS IN ROCK
(M. G. Seitz, D. L. Bowers,*
and C. L. Herzenberg†)

Work is being conducted to test the performance of proposed nuclear-waste repositories using laboratory-analog experiments and to improve nuclear logging methods for oil-depleted oil reservoirs. Final plans were made for the seminar, Hazardous-Waste Management, to be held at Argonne July 15 and 16, 1981, for university faculty.

A. Repository-Analog Experiments

Work conducted in preparation for the repository-analog experiments to be conducted for the U.S. Nuclear Regulatory Commission included (1) the development of a data acquisition system for monitoring the experiments and (2) preparation of aqueous fluid that is representative of groundwater in the Pasco Basin, Washington state, for the experiments.

The data acquisition system is based on (1) a Digital Equipment Central Processing Unit with disc storage and (2) Crate analog-to-digital conversion systems. The acquisition system will record temperatures and pressures during the experiments. The system is currently located in the Chemical Engineering Division building for testing and preliminary use.

B. Water for the Analog Experiments

A solution was prepared to simulate groundwater found in the Grande Ronde formation of the Columbia Basin [CEPHART]. The salts listed in Table 14 were dissolved in 20 L of pure (about 18 MΩ/cm) water. Because few silica compounds are readily dissolved, sodium silicate was chosen as the source of silicate. Using this compound causes the total sodium concentration to be higher than that listed for the reference groundwater (330 mg/L vs. 250 mg/L). Analytical reagent grade chemicals were used to prepare the solution (Table 14).

The concentrations of the individual anions and cations were calculated and are reported in Table 15 along with the concentrations in the reference groundwater.

The solution was sparged with nitrogen for approximately five hours. The pHs at both the top and bottom of the solution were measured: pH (top) = 11.06 and pH (bottom) = 11.03. The pH is higher than the reference value (pH of 10.1), but this was expected because of the extensive sparging with nitrogen and because of the addition of sodium silicate.

C. Well Logging

Preparations were made during the final month of the quarter to conduct core-flood experiments. Laboratory space was obtained for work with radiochemicals, and the pumps, rock-core holder, and other apparatus for the

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Table 14. Compounds Used to Formulate Solution Similar to the Groundwater in the Grande Ronde Formation

Compound	Quantity Added to 20 L of Water
Sodium chloride, NaCl	4.8866 g
Sodium Sulfate, Na ₂ SO ₄ ·10H ₂ O	7.2493 g
Sodium borate, Na ₂ B ₄ O ₇ ·10H ₂ O	0.2458 g
Sodium fluoride, NaF	1.6361 g
Sodium carbonate, Na ₂ CO ₃	1.2013 g
Sodium bicarbonate, NaHCO ₃	1.1844 g
Sodium silicate, Na ₂ SiO ₃ ·9H ₂ O	11.4622 g
Potassium sulfate, K ₂ SO ₄	0.0853 g
Magnesium sulfate, MgSO ₄ ·7H ₂ O	3.58 mg
Calcium sulfate, CaSO ₄ ·2H ₂ O	0.112 g

Table 15. Concentrations of Constituents in Aqueous Solution and in Groundwater of the Grande Ronde Formation

Element or Compound	Aqueous Solution Calculated Values, mg/L	Reference Values for Groundwater of the Grande Ronde Structure, ^a mg/L
Na	330	250
Cl ⁻	148	148
SO ₄ ²⁻	114	108
B	1.39	1.39
F ⁻	37	37
CO ₃ ²⁻	34	34
HCO ₃ ⁻	43	43
SiO ₂	121	121
K	1.9	1.9
Mg	0.04	0.04
Ca	1.3	1.3

^aFrom analyses of groundwater reported in [Table III-45, GEPHART].

experiments were collected. The experiments are designed to test the proposed method of injecting gamma-active solution into a reservoir to measure residual oil [STEINDLER-1981C]. The objective of the experimental program is to determine if the gamma signal from rock injected with radioactive fluid depends on the oil content of the rock.

Ten samples of Berea sandstone obtained for the work appear to have a uniform appearance and uniform density. The ten samples have an average density of 2.098 g/cm^3 with a pooled variance of 0.005 g/cm^3 . In comparison, an error in density of 0.039 g/cm^3 is estimated from the error expected in weight and dimension measurements. Thus, the densities of the ten samples appear to be the same. Porosity (based on a density of 2.655 g/cm^3 for quartz) was estimated to be 21%.

The injection medium chosen for the core flood tests is an aqueous solution with a composition similar to that of a brine reservoir fluid. A long-chain hydrocarbon surfactant, Tricon X-100,* will be added to give the aqueous solution favorable surface properties to effectively displace petroleum. A surfactant concentration of $1 \times 10^{-4} \text{ mol}$ was chosen. The choice was made on the basis of the low (22 dynes/cm) oil-water interfacial surface tension displayed by the surfactant at that concentration. The surfactant is nonionic and therefore should not adsorb to a great degree onto the quartz surfaces (previous rock mechanics experiments by Dunning and others seem to confirm this). Also, the surfactant should not complex readily with the ^{22}Na radiotracer.

D. Experimental Series

Four cores will be used in the experimental series. In the planned tests, two of the cores will be saturated with the crude oil and inserted into the jacketed vessel assembly. The cores will be "produced" by injecting the aqueous solution into the cores. This will establish a condition comparable to the situation existing in a watered-out reservoir. The other two cores, containing no oil, will be saturated with the aqueous solution. Then all four cores will be injected with sodium-22 bearing aqueous fluids, and "logged" using a scintillation crystal and electronic counting equipment. The gamma signals of oil-saturated cores will be compared with signals detected on cores that do not contain oil. The difference in signals will be analyzed to determine the net effect of the oil present in two of the cores. The two cores containing oil are expected to have different residual-oil-saturation values because of the use of surfactant in one of the cores.

*The surfactant is made by Rohm and Haas.

V. TRACE-ELEMENT TRANSPORT IN LITHIC MATERIAL BY FLUID FLOW (M. G. Seitz and R. A. Couture)

A. Introduction

In the preceding report in this series [STEINDLER-1981C], we reported on the composition of pore water eluted from a core sample of Precambrian granite from Northern Illinois drill hole UPH-3. It was found that the pore water is NaCl-CaCl₂ brine ($\text{Cl}^- > 0.24 \text{ M}$), and that the water is extraordinarily high in fluoride (at least 3.3 mM). However, the absolute concentration of salt in the brine was not determined--only the ionic ratios. It was suspected that the water may have been influenced by brine in overlying sediments (although no brine was reported in sediments in this hole), or that the brine may be representative of old, granitic groundwater, which derived its unique composition by long reaction with the granite.

In this report, we discuss the origin of the brine, and we present work on some experimental refinements. We consider methods for determining the absolute concentrations of ions in the pore water and the effective pore volume, and we present calculations on the rate of drying of the samples after sampling.

We have also begun some tests to estimate the rate of leakage around the rock core; the data will be given in the next report when the work is complete.

On another subject, evidence for trace-element migration from the Notch Peak Intrusion of Western Utah is summarized briefly. This work was carried out primarily by James Papike and coworkers; permeability measurements in our laboratory and field work by M. Seitz were discussed previously [STEINDLER-1981A, 1981B].

B. Origin and Significance of the Brine

The composition of the pore water from drill hole UPH-3 more closely resembles that of sedimentary brine than that of brine from granitic rocks from the Sudbury region of the Canadian Shield (Fig. 23; [FRAPE]). It is suggested that the water was derived from the overlying Cambrian sediments, which are very briny, especially in the deeper parts [MEENTS, BOND, ILLINOIS]. The fluoride in the water may be related to the presence of up to 2% fluorite (CaF_2) present in the granite as a late-stage mineral. The presence of fluoride has been confirmed with a fluoride-specific electrode: in eluate fraction 11 [STEINDLER-1981C], $0.35 \pm 0.04 \text{ mM F}^-$ was found by ion chromatography, compared to $0.32 \pm 0.05 \text{ mM}$ by electrode (Florence Williams, analyst).

The high concentrations of F^- in the presence of Ca^{2+} imply a complexing agent for F^- . No trivalent elements were present in the solutions, and the concentration of Mg^{2+} is lower than that of F^- . A survey of complex formation constants suggests that the most likely complexing agent is boron, with silica a possibility. The detection limit for boron was too high for measurement, and fluoride is known to coexist with calcium and boron in water from the Mt. Simon aquifer [ILLINOIS]. Incidentally, tourmaline (a borosilicate) is present in the granite. This fact may be irrelevant, but it shows that there is boron in the system. We tentatively consider the composition of the

Fig. 23. Composition of Groundwater and Pore Water from Precambrian Granite, 1288 m, Drill Hole UPH-3, Stevenson Co., Ill.; from Mt. Simon Aquifer, 1225 m, Du Page Co., Ill. [ILLINOIS]; and from a Diabase Dike, 1219 m, Sudbury Area, Ontario [FRITZ]. Ca/Cl ratio in UPH-3 is much lower than in any saline water reported from the Canadian Shield [FRAPE].

brine to be consistent with the influx of sedimentary brine along fractures from the overlying Cambrian sediments at some time in the past, and subsequent modification by interaction with the granite.

C. Elution of Tritium through the Core

By pumping tritiated water through the core, we can, in principle, obtain a measure of the effective pore volume. The core described in the preceding report in this series [STEINDLER-1981C] was used. The core and equipment were disassembled and dried before the experiment, so that there was no water in the apparatus between the injection valve and the outlet from the core.

A 10- μ L spike of water labeled with 0.90 nCi (33.3 Bq) of tritium was injected into the stream of deionized water pumped into the core. The effluent was collected and analyzed for tritium.

The results are shown in Fig. 24. The flow rate could not be monitored during the experiment, but it was steady at 0.010 mL/h before the injection (confining pressure = 8.5 MPa, pressure drop across core = 3.4 MPa). There is a peak at approximately 5-10 h, which corresponds to 50-100 μ L. This corresponds approximately to an effective porosity of less than or equal to

Fig. 24. Elution of Tritium from Granite Core

0.00033 to 0.00067. This is approximately one order of magnitude lower than the measured total porosity of 0.005. Since the volume is very small and there is a possibility of a substantial volume in the gaps between the rock and the end plates, a more exact analysis would be difficult.

Only 43% of the tritium was recovered in 1.5 mL of flow. The remainder presumably diffused into the rock.

If the effective flow porosity were larger, it would be feasible to obtain an estimate of effective porosity (more correctly, we obtain a single parameter which includes effective crack width and effective diffusion coefficient) as a function of flow rate. This could be related to initial concentration in the effluent. In practice, we will have to polish the ends of the rock quite flat in order to minimize end volume.

We can do a mass balance calculation which is instructive. A total of 2.4×10^{-4} mol of Cl^- was eluted in 10.3 mL, 10% of it in the first 0.10 mL [STEINDLER-1981C]. If we have an effective pore volume of ≤ 0.1 mL, the initial Cl^- concentration was at least $\frac{0.1 (2.4 \times 10^{-4})}{10^{-4}} = 0.24\text{M}$. Guessing a total porosity of 0.005 and a core volume of 149 mL, the concentration of Cl^- was at least 0.31M. This means that a large fraction--about 10% or more--of the salt in the rock was eluted.

D. Improved Sampling Techniques

Unfortunately, the pore volume observed by tritium elution is rather small and is rather close to the unavoidable void volume formed between the rock and the core holder end plate. In this case, we find it difficult to obtain an unambiguous elution curve. There are several good ways of solving this problem.

1. Tracers

A very useful method for determining the pore water volume is to use labeled H_2O as the eluent. We will probably use tritium tracer. If the first fraction had a NaCl concentration of, say, 0.1M and an unlabeled water concentration of 10%, then the NaCl concentration could be presumed to be $0.1/0.1 = 1M$.

2. Elution by Gas or Immiscible Liquid

Inert gas may be suitable as the eluent. The advantages are that the samples would be of excellent quality and easy to obtain. The disadvantage is that it might not work.

Immiscible liquids should be very effective eluents. The disadvantage is possible slight contamination of the sample by the immiscible liquid.

3. Porosity Measurement and Leaching

The salt concentration can be determined from the amount leached and the effective porosity. The amount leached can be determined by flow through a core (which may be dry) or by leaching of crushed material. Either method is particularly useful for dried core samples. It is likely that the cores from UPH-3 had already dried out by the time they were received.

Information on porosity should be obtainable by weighing cores before and after elution and after drying in an oven. High precision in weighing is required.

E. Drying of Samples

The UPH-3 samples were not fresh as received, and so, aside from being stored in plastic bags, no measures were taken to prevent further drying.

We can estimate how fast a core will dry. A good approximation assumes isothermal diffusion of water vapor, since evaporation does not cool a large rock mass very much. We assume as an approximation that the relative humidity is 100% at the water/vapor interface and 50% at the core surface.

The equation in cylindrical coordinates for diffusive flux, F , through an infinite cylinder of rock is

$$F = \frac{-D\epsilon\delta}{\tau} \frac{\partial c}{\partial r}, \quad (1)$$

where c = concentration, ϵ = porosity, D = diffusion coefficient, and δ/τ^2 is a geometrical factor characteristic of the rock matrix. Let

r_f = position of water/vapor interface

r_o = radius of cylinder.

From the concentration of pure liquid water

$$F = -0.0555 \epsilon \, dr_f/dt; \quad (2)$$

F is given in terms of $\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$.

For steady state diffusion, the gradient $\frac{\partial c}{\partial r}$ is nearly constant and will be assumed to be so. The concentration of water vapor in saturated air at 22°C is $1.08 \times 10^{-6} \text{ mol/cm}^3$. Then

$$\frac{dc}{dr} = \frac{1.08 \times 10^{-6}}{2(r_f - r_o)}, \quad r_f \leq r \leq r_o \quad (3)$$

Combining Eqs. 1 and 2, and 3, we obtain

$$\frac{dr_f}{dt} = \frac{1.08 (10^{-6})}{0.0555} \frac{D\delta}{2\tau^2} \frac{1}{(r_f - r_o)}$$

$$r_f - r_o = 4.4 (10^{-3}) \left(\frac{D\delta}{\tau^2} t \right)^{1/2}$$

Using a reasonable value of $\delta/\tau^2 = 0.5$ [NERETNIEKS] and $D = 0.25 \text{ cm}^2/\text{s}$, $r_f - r_o = 0.00156 \sqrt{t}$, where r_f is in cm and t is in seconds.

That means that a 4.7-cm-diameter rock core may dry out in as short a time as 28 days. Thus, it is very important that rocks be protected against evaporation after sampling.

F. Migration during Intrusive Emplacement

This is a summary of the implication of the intrusive processes that have been studied in relation to nuclear repository safety assessments. The Jurassic Notch Peak Stock, House Range, Utah, is a granitic intrusion in carbonate strata. The hot magmatic emplacement of the porphyritic quartz monzonite may show processes analogous to those expected from a nuclear waste repository. In particular, migration of trace elements from the stock may be related to the possible dispersal of radionuclides from a nuclear waste repository. Skarns occur around the stock at contacts between the monzonite and strata; these are obviously formed by trace-element migration, as well as major-element migration. In this analysis, however, we are interested in migration through the volume of the rock strata which are host to the intrusion.

Evidence to data indicates no perceptible migration of trace elements from the stock. Most of the recent information has been summarized by [HOVER] and discussed by [COUTURE]. A large portion of the variance seen in the composition of samples taken at different distances from the stock resulted from mixing of the argillaceous and calcium carbonate components of the strata during deposition. Only the enrichment of rubidium relative to potassium in the higher grade samples is a possible migration-produced phenomenon. Considerably more work would be required to establish even this minor phenomenon as migration-produced.

The results suggest no new processes of migration that would need to be considered in the design of a nuclear waste repository.

A more likely structure to exhibit trace-element migration would be a kimberlite pipe of South Dakota. The pipes involve the intrusion of melts that are much more fluid (containing more water and alkalis) than the monzonite intrusion, and this would be expected to lead to migration. In studying migration from these kimberlite pipes, its applicability, if any, to the migration processes at a nuclear waste repository would have to be considered.

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

(N. M. Levitz, R. E. Brock, T. F. Cannon, G. L. Chapman, P. G. Deeken,
J. E. Fagan, Henry Lautermilch, R. J. Meyer, R. E. Nelson, John Osudar,*
J. E. Parks, L. E. Trevorrow, C. G. Wach, I. O. Winsch,
and D. G. Graczyk)

A. Full-Scale Shear (FSS)

(P. G. Deeken, J. E. Fagan, and C. G. Wach)

Installation of the full-scale shear (FSS) in shielded hot Cell M-3, scheduled for this quarter, was deferred as a result of an ongoing program review by DOE of the draft ANL Project Plan accommodating the 3-y extension of LWBR operations. Installation is expected to proceed after plans reflecting the extended project schedule are approved. During the present period, the shear remained in a mockup area adjacent to the shielded cell facility, in short-term storage. Shear and feed system components and modules were removed, boxed, and stored, and the machine base assembly was wrapped and a nitrogen purge provided to minimize corrosion of the feed system bearings, ways, and ball screw.

The shear control and instrumentation consoles were reworked during this period to incorporate the numerous changes and additional instrumentation which had been added on a trial basis to the shear and consoles during the previous out-of-cell testing (refer to [STEINDLER-1981]). The computer interface module (CAMAC) was located in a separate, third console to minimize electrical noise problems. The CAMAC was fully rewired to the shear controls. Also, feed-through cables and wire harnesses for the added instrumentation that will pass through cell penetrations to the shear were fabricated and wired into the existing cell junction boxes.

Some minor rework on the previously installed in-cell equipment was completed. The enclosure mercury vapor lamps were modified to permit remote lamp replacement in the event of lamp failure. The fuel rod entry port on the alpha-enclosure side wall was modified to ease the handling of the IN-40 (fuel rod secondary) container when used to deliver a fuel rod to Cell M-3. Also, an extended-reach manipulator was refurbished by hot-cell personnel to complete Cell M-3's complement of eight master-slave manipulators.

Modifications were also made to the IN-40 extractor device, which removes the container containing the fuel rod from the shipping cask and delivers it to Cell M-3. Following these modifications (again made to improve remote-handling capability), a dry run of the fuel rod delivery procedure was completed successfully.

Documentation of the shear's design and operation was begun, and a draft version completed. A summary of this document was sent to the American Nuclear Society for possible presentation at the Remote Technology Seminar in November, 1981.

* Science Applications, Inc., Oak Brook, IL.

B. Single Unit Dissolver (SUD)

(I. O. Winsch, T. F. Cannon, Henry Lautermilch, and R. E. Brock)

A series of water and acid boilup tests was successfully completed, using the new single unit dissolver (SUD). The new SUD, consisting of a tantalum alloy primary vessel within a stainless steel secondary vessel, incorporates an external heater design, rather than the annular heater used in the initial SUD design. The annular heaters, which were wrapped on the tantalum vessel, experienced repeated failures. This, coupled with the difficulty in remotely replacing the heater elements, led to the external heater design in which 18 cartridge heaters are mounted in wells around the secondary vessel. A helium atmosphere between the primary and secondary vessels is used to enhance heat transfer.

In the dozen boilup tests completed using the external heaters, no significant increases in the time required to reach operating temperature (195°C) and pressure (860 kPa or 125 psig) were observed. In one test, a 3-L charge of Thorex was brought to vigorous boiling conditions in approximately 40 min (indicated by an accelerometer-audio system attached to the dissolver). Wall temperatures of the stainless steel outer vessel were found to be 325-334°C. The acid was afterward cooled to 80°C (nominal temperature before transfer to the blend tank), using a 19 Ls⁻¹ (40-cfm) blower directed at the SUD. Cool-down time was approximately 1.25 h. The other boilup tests conducted, in which various amounts of acid or water charges were used, confirmed these results. During these tests, the four SUD heater temperature-controllers were calibrated. All heaters now operate within several degrees of each other.

Plans for future SUD testing have been prepared, including dissolution tests using unirradiated ThO₂ charges as a stand-in for fuel. Samples of sheared ThO₂, including Zircaloy hulls, have been prepared to simulate the dissolution of 35.5-cm (14-in.) segments of blanket rod. Additionally, cross-contamination studies using U₃O₈ as a tracer will be performed to determine the extent of contamination from run to run, and to aid in developing dissolver and blend tank decontamination procedures.

Also planned are corrosion studies using coupons made of the tantalum alloy used in fabricating the SUD primary vessel. These tests will involve placement of the coupons in the liquid and vapor regions of the dissolver during actual dissolutions. Data from these tests are to be used in determining an expected primary vessel lifetime.

Selection of the methods and materials to be used in sampling the dissolver solution is also in progress. A procedure for sampling the dissolver solution, after the second dissolution (for dissolution of residual fuel) was tested successfully. The method uses a disposable sampler connected to a vacuum source, and draws samples from the transfer line between the dissolver and the blend tank. The selection of vials to be used to store archive samples is under review (plastic vials used in the pilot-scale program failed due to radiation exposure). At present, plastic-coated glass vials [STEINDLER-1981C] appear to be satisfactory for this purpose.

The temperature-control system (TCS), installed in the SUD hot cell to maintain the electronic balance temperature within specified operating limits, performed satisfactorily in recent tests. Tests included determination of the effects of temperature changes on the balance performance and calibration. The balance, a Mettler PS-15, is used to support and weigh the blend tank assembly in the cell. Cooling of the balance is required because the blend tank assembly is heated during sampling and spiking. Results will provide input for the design of the multiple-dissolver system. These tests showed that the TCS maintained the stability of the balance output over the operating temperature range.

C. Multiple-Dissolver System (MDS)

(I.O. Winsch, T. F. Cannon, Henry Lautermilch, and R. E. Brock)

Design work continued at ANL-ENG on the multiple-dissolver system (MDS). A package with specifications for procurement of the dissolver condenser cooling system and piping was completed, as were installation drawings for the various systems such as condenser cooling, off-gas, and acid transfer; also, design of the waste tanks and off-gas tanks was completed. Design work was halted on June 15 for review of the Project, with the system design about two-thirds complete. Acceptability of the four tantalum primary dissolver vessels [STEINDLER-1981C] will be established next quarter after additional corrosion data are received.

Exploratory testing of the effects of radiation on electronic balances was carried out. The purpose of these tests, done in cooperation with the Mettler Instrument Co. of Highstown, NJ, was to identify the radiation susceptibility of the Model PK-60 balance. This balance has been proposed for use in weighing the blend tank assemblies in the MDS. (The Mettler PS-15 balance, used in the SUD prototype will no longer be used.) The balance was tested in the cobalt-60 Irradiation Facility at ANL. It was found that the balance is susceptible to radiation damage; after a dose of 8000 R, the balance stopped functioning completely.

An examination of the electronic balance revealed that three components had been damaged by the gamma radiation. The failed components were three IC (integrated circuit) chips: a ROM (read-only memory), a Z-80 microprocessor, and a MOS (metal-oxide semiconductor). Recent tests of radiation effects on electronic components done at the Jet Propulsion Laboratory in Pasadena, CA, indicate that these particular components will fail after an accumulated dose of approximately 3000 R. Thus, it appears necessary that the balance electronics be located outside the hot cell. Plans to modify our balances are being made.

D. Scrap and Waste

(L. E. Trevorow and R. E. Nelson)

Planning for the disposal of LWBR Proof-of-Breeding (POB) residues had been focused on converting the dissolver solution to solids at ANL by spray calcination followed by shipment to the Rockwell-Hanford (R-H) storage facility. Recently, however, in an effort to reduce costs, DOE-HQ has been encouraging shipment of these solutions in liquid form to another DOE contractor if shipment is feasible. Furthermore, DOE-HQ has recommended that

the procurement of calcination equipment be deferred until a review of waste form options is made. As a result, activities on the disposal of the dissolver solutions have been restricted to finishing the design of the spray calciner, studying the effectiveness of ferric oxide for calcined off-gas traps, and studying the feasibility of shipping the dissolver solutions in liquid form to another site. Progress in these activities is briefly summarized here.

Effort on preparing to calcine dissolver solutions consisted mainly of detailing design layouts from which fabrication drawings of equipment may be made. These efforts have been focused on equipment items for a portion of the system that would permit calcination tests of nonradioactive solutions. This portion of the system is being referred to as the mockup. The items include: calciner, scrubber, feed tank, ruthenium traps, mounting rack, drip pan, and associated prefabricated components of the piping and instrumentation system. For the items that can be used for calcination tests, the design phase is nearing completion. The final design review of this equipment is to consist of a series of reviews of individual items or small groups of associated items. To date, Chemical Engineering Division (CEN) and ANL-ENG personnel completed and approved the design of the scrubber and feed tank, making only relatively minor changes. Review of the remaining items is expected to be completed next quarter.

Ferric oxide is the intended active ingredient in traps for removal of ruthenium from calciner off-gas. The behavior of ferric oxide on exposure to simulated calciner off-gas was tested. Since off-gas from calcination of the LWBR analytical residues will have an unusually high nitric acid concentration and may contain HF, it is important to determine whether these components will cause any significant physical effects (e.g., caking or plugging) or chemical changes of the trap media. In tests of duration up to 16 h at 250°C, the media showed no plugging or caking. Although changes in color occurred, analyses showed that the iron content of the bed remained unchanged. It was concluded that no loss of the active ingredient by exposure to the acid-air mixture should be expected. The color change remains unexplained.

Calculations by the ANL Office of Health and Safety (W. Lipton) have verified the need to incorporate surge vessels in the calciner off-gas train to slow the velocity of the gas and to permit decay of radon-220 within the shielded area. Current plans are to provide several segments of 30-cm-dia (12-in.-dia) pipe for this purpose. The solid daughters (decay products) of radon-220, which have a controlling half-life of about 11 h and high-energy gammas (≤ 2.6 MeV) would collect in these segments of pipe (located in the cell).

The reduction of costs for disposal of the dissolver residues has been emphasized recently by DOE-HQ in their recent request for the preparation of a "position" paper summarizing conclusions on the comparison of alternative methods of disposal of LWBR dissolver residues. As reported previously [STEINDLER-1981C], it is requested that shipping the dissolver residues in the form of liquids to another DOE contractor is to be considered in this study, as the primary alternative to the original plan of calcination at ANL followed by shipment of the powdered calcine to Rockwell-Hanford. Shipment of liquids to another contractor who could store liquid or who has calcination

equipment already installed has been suggested by DOE-HQ as a possible means of reducing costs. This practice would require (a) compliance with applicable regulations, (b) a DOE contractor capable of dealing with the liquids, and (c) the availability of licensed transport equipment, compatible with the characteristics of the LWBR residues.

The DOE Manual indicates that the liquids could be shipped if they are in compliance with the Manual.

With regard to acceptance of liquid by other DOE contractors, a previous survey indicated reluctance, but recent communications between DOE-CH and other field offices indicate that the Savannah River Plant (SRP), Idaho Nuclear (ID), and Battelle Pacific Northwest Laboratory (PNL) are at least willing to consider this scheme.

DOE-CH is presently reviewing the directories of DOE-licensed equipment to determine the availability of transport equipment that is suitable for shipping the LWBR dissolver solutions. Important considerations in any scheme that involves transport of liquids are the needs and costs for equipment to transfer liquid from the transport vessels to receiver's equipment that would be used for storage or processing.

E. Computer System
(J. E. Parks and J. E. Fagan)

An integrated computer system is being developed which will provide automatic data acquisition, process monitoring capabilities, and some automatic process control. Currently, computer system hardware consists of a VAX-11/780* (shared with other Chemical Engineering Division users) and a PDP-11/23.* The latter unit is connected to the FSS and the SUD via standard CAMAC interfaces. Work on the computer system during the report period is summarized below.

1. Hardware

The interface between the PDP-11/23 and the SUD controls was completed, except for sensors associated with the dissolver heaters. Debugging of the interface between the computer and the two balances in Cell K-3 continues. The linkage between the VAX-11/780 and the PDP-11/23 was connected, and part of the software to implement data transfer was installed.

2. Software

Software developments fall into two areas--general applications software for the Project computer system, and programs for operating the SUD. General applications software completed during this quarter include the following:

EDITOR - a program to permit entering and modifying the operating procedures for the Project operating systems (presently the FSS and SUD), and

*Products of Digital Equipment Corp. (DEC), Maynard, Mass.

MONITR - a program which will continually monitor all Project sensors and controls and which will transfer pertinent data to storage.

Ongoing software efforts include programs for intercomputer data transfer and interprogram communication within the PDP-11/23.

Operating programs completed for the SUD include those programs which will replace the function of the MODICON, a programmable controller [STEINDLER-1981B] and several of the specific steps in the SUD operating procedure. These procedure steps (dissolver leak test, blend tank leak test) have been used to familiarize the SUD operators with computer operations.

Technical documentation of the Project computer system has been updated.

F. Error Analysis

(D. G. Graczyk and J. E. Parks)

A comprehensive error analysis for the LWBR-POB Project is in preparation. During this work, it was found that a contribution to the possible bias error in the uranium assays had been overlooked in a previous treatment [ANL]. This bias contribution arises from uncertainty in the ^{235}U -to- ^{238}U ratio of the NBS U-500 isotopic standard reference material (SRM). Copies of a memorandum summarizing the mathematical treatment of this error source and change pages reflecting the consequent revisions to the VR report were forwarded to BAPL for review. This revised treatment was promptly and thoroughly reviewed by BAPL personnel, who carried out a rigorous mathematical analysis of the bias contributions. The BAPL analysis gave expressions which yielded slightly different estimates of bias error than did the ANL treatment. Upon investigation, it was found that an algebraic error had been made in the ANL treatment. In the course of rectifying this error, it was noted that the relationship between bias error in the uranium assays and uncertainty in the U-500 isotopic standard is influenced by the mass dependence of the correction factors on the mass spectrometrically determined isotope ratios. This development, which did not affect earlier results, has been incorporated into ANL's error analysis; final revision and review of the Validation Rod (VR) report is under way.

G. Analytical

(R. J. Meyer)

The preshipment testing and inspection of the mass spectrometer at V. G. Isotopes, Winsford, England, were completed on June 27, 1981, and approval to ship the instrument to ANL was granted.

All components of the instrument function properly, and instrument specification parameters such as peak shape, peak top flatness, and abundance sensitivity were within ANL specifications. The precision obtained on 15 analyses of NBS U-500 uranium standard, $\pm 0.04\%$, was slightly outside ANL specifications of $\pm 0.03\%$. This deviation is not considered significant since the operator's sample loading technique was not optimized. It is anticipated that after installation at ANL, where analytical conditions can be more carefully controlled, all specifications will be met.

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