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FUEL-CYCLE PROGRAMS
QUARTERLY PROGRESS REPORT

January—March 1981

by

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Chemical Engineering Division

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CHEMICAL ENGINEERING DIVISION

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ABSTRACT

A program continues for the development of an interim waste form that can be transported from facilities where waste is generated to terminal waste processing. Waste forms being studied include phosphate-immobilized waste, fused salt, sodium silicate/sludge, cement-silicates, sodium silicate/ Fe_2O_3 compacts, and fused salt/sludge. A sodium silicate/calcium hydroxide binder for interim waste forms is being developed; metals are being evaluated for their resistance to corrosion by molten salt.

Measurements of rates of leaching from simulated nuclear waste forms are continuing. The leaching of ^{85}Sr , ^{106}Ru , ^{133}Ba , ^{137}Cs , ^{139}Ce , and ^{152}Eu (added to simulated waste glasses as radiotracers) has been monitored, together with the leaching of several matrix elements. The data, combined with surface analytical studies, suggest that leaching from SRL glasses is inhibited by the formation of a Si/Ca/Fe/Al-rich surface layer.

Impact tests of solid alternative waste forms are being performed to assess source terms of airborne release (from particle size distributions) and to assess the increases in source terms of leach rates (from increases in surface area). Tests were made with simulated waste glasses and several ceramics. For particles formed by the impact fracture of brittle specimens, it has been found that particle size distributions are described in terms of the two parameters* of the lognormal probability function using computer-assisted linear regression analysis.

Logging techniques are being developed to measure the relative amount of residual oil in a depleted oil reservoir. An experimental plan has been developed for reducing the proposed log-inject-log method to a tangible set of reservoir materials--i.e., rock, aqueous fluid, and petroleum. Also, a computer program was developed to

*The standard deviation and the geometric mass mean diameter.

identify characteristic elements or ratios of elements in aqueous fluids that correlate with rock type in oil reservoirs.

The composition of groundwater from igneous rocks is of considerable interest in connection with geologic storage of high-level radioactive waste. A simple technique for the elution of pore fluid (groundwater) from igneous rocks is described, using a special coreholder, as is the elution of brine (in the same apparatus) from a core of Precambrian granite.

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

SUMMARY

Development of Interim High Level Waste Forms

Two experiments have been completed in which phosphate was used to immobilize simulated waste, the first with a typical neutralized waste solution and the second with a low-sodium, low-pH solution (unneutralized). For the first experiment, the product was a hard, green, plastic-looking material. The product from the second experiment was a pea-green, powdery, low-density material similar in appearance to elemental sulfur. Additional tests will be performed to determine the optimum conditions for preparing a waste form that has low leachability and high compressive strength.

Examination of the literature has indicated that FePO_4 may hydrolyze in aqueous solutions, which means that the estimate of the FePO_4 content of the sludge in Nuclear Fuel Services Waste (Tank 8D2) may be greatly in error. A further study of the literature should indicate whether an experimental effort is warranted.

Preparations are in progress to measure the radiation stability of the sodium nitrate salt composition found in the waste tank at the Nuclear Fuel Services plant at West Valley, New York.

Laboratory experiments were continued on several simulated interim nuclear waste forms, such as fused salt, sodium silicate/sludge, and cement-silicates. Experiments on fused salt mixtures containing 0 to 20% simulated West Valley sludge indicated that the presence of sludge reduced the rate of solubility of the salt in water and increased the fracture strength. Fused salt/sludge systems were found to be highly hygroscopic, necessitating that they be stored in a reasonably dry environment ($\lesssim 50\%$ humidity at 35°C).

Instrumented impact test were performed on several sintered sodium silicate/ Fe_2O_3 compacts and fused salt/sludge specimens. Data are reported on impact conditions and fines ($\lesssim 10\ \mu\text{m}$) generation. The results indicate several modifications that are necessary to exploit the unique advantages of the instrumented impact system; these modifications are being made.

Microstructural examination of the Fe_2O_3 -silicate compositions by optical and scanning electron microscopy indicated that the distribution of silicates in pelletized samples was much more uniform than in the sintered compacts. The particle size distribution in the sludge could play a major role in affecting which fabrication procedure is selected. Microstructural examination of the sintered compacts further indicated that a chemical reaction between sodium silicate and Fe_2O_3 probably occurred during the processing steps.

All components of the laboratory disk pelletizer system have been received and assembled. Preliminary experiments have been initiated using Fe_2O_3 and water as the binder.

An effort to develop sodium silicate/calcium hydroxide binder for application as an interim waste form was initiated. A room temperature processing technique at high humidity has been developed to fabricate an interim waste form from simulated West Valley sludge. The waste form prepared by this technique was highly dense and was 10-15 times stronger than similar sintered silicate/sludge specimens. The advantages of high strength and room temperature processing make further development of the silicate- $\text{Ca}(\text{OH})_2$ binder system very attractive.

A preliminary literature search has been conducted to identify the corrosion behavior of commonly available metals and metallic alloys in salt solutions or fused-salt compositions similar to the composition of West Valley supernate. The presence of NO_2^- and OH^- in the West Valley supernatant solution is highly beneficial in reducing corrosion. Mild steel should perform reasonably well in the presence of the West Valley supernatant solution; a stainless steel might be a good choice as the material for the melter and canisters, both of which may come in contact with molten salt.

Neutron Activation and Tracer Studies

The spike/leach program is designed to demonstrate and qualify the use of radiotracers for the measurement of leaching from simulated nuclear waste forms. Samples of SRL 211 and SRL 131 glass frits with radionuclide waste additions have been leached for up to 150 days. From the experimental results, the leaching behavior of spiked, neutron-activated, and "cold" glass samples can be compared and the leaching behaviors of waste elements identified. The leaching of ^{85}Sr , ^{106}Ru , ^{133}Ba , ^{137}Cs , ^{139}Ce , and ^{152}Eu , which were added to the glass as radiotracers, had been monitored, together with the leaching of several matrix elements.

These data, combined with surface analytical studies, suggest that leaching from SRL glasses is inhibited by the formation of an adhering Si/Ca/Fe/Al-rich protective layer.

Leaching experiments have also been completed on Westinghouse alkoxide glass and SYNROC B samples. Westinghouse glass appears to be two to three times more durable than typical SRL glasses. A protective layer forms on this glass also.

Brittle Fracture Studies

Impact tests of solid alternative waste forms are being performed to assess source terms of airborne releases (from particle size distributions) and to assess the increases in source terms of leach rates (from increases in surface area). A set of comparative impact tests at the same impact energy per specimen volume showed that SRL frit 131 glass, SYNROC B ceramic, and SYNROC D ceramic each generated the same mass of particles of respirable sizes. A TAILORED CERAMIC waste form generated four-tenths as much mass of respirable sizes and a FUETAP waste form generated 2 1/2 times the mass of respirable sizes generated by either glass or SYNROC. The amount of waste loading in a waste form was identified as a parameter that also must be considered when assessing the quantity of respirable sizes. Additional impact tests are still needed to determine the experimental reproducibility and the effects of variations of specimen size and specimen energy density.

Computer assistance has been developed for size analysis of particles formed by the impact fracture of brittle test specimens. Particle size distributions have been found to be described in terms of the two parameters of the lognormal probability function. Linear regression is used to find the best-straight-line fit of the data, and computer graphics are used to plot the size data on lognormal graphical coordinates. This method appears promising. A report is being written showing the application of this methodology to experimental data.

Stress is the driving force for the propagation of cracks upon impact. Models of stress distributions are being developed which will correlate the dynamic stress distributions with body size and shape and impact energy. An outline of the general approach in developing these stress models is based on the scaling laws for impact stresses and on the time-dependence of stress-induced crack propagation.

A topical report describing the impact characterization of brittle waste forms was drafted and is being reviewed internally.

Fluids in Rock

The project technical activities, continued this month, covered the following two topics:

1. Development of a proposed experimental plan to reduce the proposed log-inject-log method for determining residual oil saturation of depleted oil wells to a tangible set of reservoir materials, i.e., rock, aqueous fluid, and petroleum.

2. The development of a computer program to identify characteristic elements or ratios of elements in aqueous fluids that correlate with rock type in oil reservoirs.

The proposed experimental plan uses core flood experiments to determine the net gamma ray signal caused by residual oil (SOR) in the cores. To adjust for displacement efficiencies of the reservoir aqueous fluid smaller than 100% in these experiments, an efficiency term, E_m , is incorporated in the equation for SOR. The efficiency term is related to the capillary number,

N_{ca} , which in turn is related to the injection fluid viscosity, the injection velocity, the reservoir porosity, and the oil-water surface tension. These properties are considered parameters in the proposed experimental plan.

A computer program was designed and developed to identify groupings of characteristic elements or ratios of elements in aqueous fluids that correlate with rock type in oil reservoirs. This work is a continuation of the manual effort, discussed in the preceding report in this series, to identify fluid composition characteristics that reflect reservoir rock type. If the fluids are chemically distinguishable, the fluids may be identified and differentiated on the basis of their log response.

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

The composition of groundwater in deep-seated rocks is of great interest, both geochemically and in connection with the disposal of radioactive waste. However, sampling of deep-seated groundwater is expensive and often difficult.

We describe here a simple technique for the elution of pore fluid (groundwater) from igneous rocks, and we describe brine eluted from a core of Precambrian granite from Northern Illinois drill hole UPH-3. The brine is similar to brine in the Illinois Basin, and it may have been derived from the overlying sedimentary rocks, or it may be genetically related to previously described deep-seated CaCl_2 - NaCl brine from granitic rocks of the Canadian Shield.

Transport of solutes through rocks is an important consideration in the siting of radioactive waste repositories. The elution technique is applicable to the study of transport, and experiments are in progress. We discuss the theory of transport by advection and diffusion. If fluid flows through cracks and if solutes diffuse perpendicular to the cracks into the rock matrix for sufficiently long times and distances, the time required for a solute concentration front to move a given distance is approximately proportional to the square of the distance divided by the square of the flow velocity.

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

This project includes responsibility for the destructive analysis of full-length irradiated fuel rods from the light water breeder reactor (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. Other work in support of this project is being done by the Analytical Section in the areas of planning and procurement. An integrated computer/data acquisition system for the entire project is also being developed.

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 the 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 (1) must satisfy shipping criteria, particularly in relation to integrity in the event of transportation accidents, (2) should be mechanically and chemically stable in the ambient environment, and (3) should be readily compatible with the terminal-waste-form processes. From this research, a technology should evolve 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, and Jacqueline Williams, and
 T. J. Gerding)

In a previous report, the strengths and weaknesses of five possible waste forms were evaluated based on product and process criteria [STEINDLER-1981B, VOGLER]. The interim waste forms are

Fused salt
 Calcine
 Silicate-agglomerated calcine
 Borate glasses
 Phosphate-immobilized waste

Experimental studies are in progress for the fused salt, the silicate-agglomerated calcine, and the phosphate-immobilized interim waste forms.

1. Fused Salt

Currently, preparations are being made to measure the resistance of the fused salt (basically NaNO_3 , NaNO_2 , and Na_2SO_4) to irradiation. Literature information had indicated that sodium nitrate is decomposed to sodium

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nitrite and oxygen when exposed to gamma radiation [JOHNSON]. Based on these measurements, calculations had indicated that sealed canisters might become unduly pressurized when stored for long periods. However, there were indications that the decomposition rate decreased with total dose, due perhaps to back-reaction of the reaction products, sodium nitrite and oxygen.

There is no information that indicates the initial response to gamma irradiation of a salt composed of approximately 70% NaNO_3 -30% NaNO_2 . Since this is the composition of the salt in the West Valley Nuclear Fuel Services (NFS) high-level-waste tanks, the response of such a salt to gamma irradiation is important. The effect of gamma radiation upon such a salt will be one of the primary objectives of irradiation studies.

2. Silicate-Agglomerated Calcine

Calcined waste agglomerated by the use of soluble silicates such as sodium silicates is thought to be a viable interim waste form [VOGLER]. Agglomeration of the calcine would lower its potential dispersibility and leachability and would increase its thermal conductivity. The contents of Tank 8D2 (2.2×10^6 L) is the neutralized waste from the first cycle Purex extraction and consists of (1) a supernatant liquid that is basically $\text{NaNO}_3/\text{NO}_2$ and (2) sludge (28,000 L) that is primarily $\text{Fe}(\text{OH})_3$ and FePO_4 . Tank 8D4 (45,000 L) contains $\text{Th}(\text{NO}_3)_4$ and $\text{Al}(\text{NO}_3)_3$ in nitric acid.

Since the original examination of the literature, additional information has been found through personal communication with experts from PQ Corporation:

a. The amount of soluble silicates needed as a binder is thought to be in a range of 4 to 6 wt % of the material to be bound.

b. An important characteristic of gelled silicates is that they contain large amounts of water after they set. As these gels age, they may shrink considerably; water weeps out as this shrinking occurs. If soluble silicates are considered for use as a binder or as a matrix to hold the calcined sludge, this shrinking and subsequent weeping characteristic should be studied very carefully and a composition of the binder and process conditions chosen that minimize this property.

c. To lower the potential solubility and leachability of pelletized silicate-agglomerated calcine, the use of CaCl_2 , CaO , ZnO , or sodium fluosilicates is suggested. One of these compounds could be used as a coating for the pellets after agglomeration and calcination. These compounds react with silicate polymers to form a hard, water-insoluble product; thus, a small amount of this additive would serve as a tough, water-impermeable coating for each pellet.

d. Lithium silicates could be used instead of sodium silicates as another means of reducing aqueous solubility. This would be an expensive alternative.

3. Phosphate-Immobilized Waste

An interim waste form using phosphate as a binder appears to be attractive. The phosphate ion forms strong bonds with most metal ions, and its salts (for the most part) have low aqueous solubilities. Phosphate and acid phosphate cements, used as dental cements, have low leachability and high compressive strength.

Two experiments have been performed thus far to prepare phosphate-immobilized waste. In the first experiment, phosphoric acid was used to immobilize simulated NFS high-pH, high-sodium waste (the composition can be found in the previous quarterly report [STEINDLER-1981B]). In the second experiment, a low-sodium, low-pH solution was immobilized (its composition is given in Table 1).

Both experiments were performed in the apparatus shown in Fig. 1.

Table 1. Acid Solution Simulating West Valley Tank 8D2 Waste^a

Ion	Conc, <u>M</u> ^b	Ion	Conc, <u>M</u> ^b
K ⁺	0.009	BF ₄ ⁻	0.0182
Fe ³⁺	0.866	NO ₃ ⁻	2.1
Cr ³⁺	0.050	Cl ⁻	0.079
Ni ²⁺	0.025	SO ₄ ²⁻	0.94
Mn ²⁺	0.034		
Nd ³⁺	0.0054		
UO ₂ ²⁺	0.0134		
Sr ²⁺	0.0048		
Ru ³⁺	0.0036		
Zr ⁴⁺	0.0120		
H ⁺	1.0		

^aWaste to be diluted to 1 L after NaNO₃, NaNO₂, H₃PO₄, and NaOH are added.

^bTotal volume after acid waste preparation is approximately 44% of the final volume.

Fig. 1. Apparatus for Studying Phosphate Immobilization of NFS Waste

- ^a0-800 rpm variable-speed motor.
- ^bFlexible shaft connected to 10-mm glass stirring shaft and stirrer; glass stirring shaft enters the reaction kettle by a water-cooled bearing with a 24/40 ground glass joint.
- ^cA pressure-equalizing, graduated addition funnel.
- ^dA -10 to 400°C thermometer with an automatic heating mantle shutoff device.
- ^eVariable-voltage power supply for heating mantle.
- ^f500-mL or 1000-mL reaction kettle with heating mantle.
- ^gVariable-height lab jack permitting quick removal of heating mantle.
- ^hPyrometer and thermocouple for measuring internal temperature of heating mantle.
- ⁱDistillation head with a thermometer for reading the temperature of the vapor.
- ^jWater-cooled condenser and graduated distilling receiver.

The experimental procedure was basically that of a batch distillation. Simulated HLLW was transferred to the reaction kettle and, while the waste solution/suspension was stirred, phosphoric acid was slowly added. After the addition of phosphoric acid, the mixture was heated to boiling. During distillation, the pot temperature, vapor temperature, and volume of distillate were monitored. Experiments were ended when the pot temperature reached 400°C.

Heating the phosphoric acid/simulated HLLW is important for two reasons--(1) nitric acid, hydrochloric acid, and possibly sulfuric acid are driven off, and (2) water from acid phosphates is driven off, leading to the formation of pyro- and metaphosphates and thus better neutralizing the charge and decreasing the aqueous solubility of the product. The removal of HCl, HNO₃, and H₂SO₄ is important to the integrity of the interim waste form product. Salts of nitrate, nitrite, and chloride are for the most part extremely soluble in water; sulfates, in general, also have moderate aqueous solubilities. All three of these acids have high-boiling azeotropes: 20.22% HCl/boiling at 109°C, 68.8% HNO₃/boiling at 122°C, and 98% H₂SO₄/boiling at 330°C. It seems fairly certain from the results of these two experiments that HCl and HNO₃ can be removed by this method; because of the higher boiling point of H₂SO₄, its removal is far less certain.

Increasing the pot temperature is also critical for balancing the cation and anion charges of the product and thereby lowering its acid content. As the pot temperature is raised, phosphoric acid is converted to pyrophosphoric acid:

thereby changing the acid equivalent of each phosphorus from 3 to 2. As the temperature is raised higher, additional water is lost and metaphosphates are formed:

and the acid equivalent per phosphate is lowered further. This feature of phosphoric acid makes the formation of solid salt product much simpler; two or three times more phosphoric acid than is needed can be handled at a pot temperature of 400°C.

a. Experimental Results

(1) Experiment with Simulated NFS Waste (First Experiment)

In the preparation of simulated NFS waste, 6.38 mL of 2.9M H₃PO₄ was added to 75 mL of acidic metal ion stock solution (the composition in Table 1). The solution was made basic with 48 mL of 13M NaOH solution; 45.6 g of NaNO₃ and 26.5 g of NaNO₂ were also added to the suspension. The suspension was transferred to the reaction kettle with washing to yield a total volume of about 350 mL.

When 20 mL of concentrated phosphoric acid was added to the suspension in the reaction kettle, the temperature of the suspension rose from 26.5°C to 36.0°C. Brown fumes began to evolve from the solution,

continuing until the total volume (100 mL) of H_3PO_4 had been added to the suspension; the last 80 mL was added incrementally over a period of 20 min. As the brown fumes subsided, the color of the suspension changed from dark brown to light yellow with black flakes. An additional 50 mL of phosphoric acid was added during the next five minutes, and the suspension became bright green.

Distillation began when the pot temperature reached $110^\circ C$ and proceeded as shown in Fig. 2 until the heating mantle was turned off at a pot temperature of $402^\circ C$. The vapor temperature and the density of nine distillate fractions as a function of pot temperature are also shown in Fig. 2. Brown fumes evolved from the pot residue at a pot temperature of $280^\circ C$ and continued until $340^\circ C$.

At the completion of distillation, the cooled residue consisted of a hard green plastic-looking material with black flakes. A week after the experiment, this material showed no signs of being hygroscopic and

Fig. 2. Distillation of Phosphate Solution Mixed with NFS Synthetic Waste

seemed to be as hard or harder than it was right after cooling. After two months of sitting in an open beaker, the material had begun to sweat, having the oily look of a viscous liquid, with black insoluble flakes on its surface.

This sweaty appearance is probably due to the presence of excess pyrophosphoric acid in the product. More phosphoric acid had been added to the simulated NFS waste than could possibly be converted to salts--even by raising the temperature to 400°C. The simulated waste had contained 1780 meq of cations, to which was added 6720 meq of phosphate, an excess of almost 300%. Later experiments will be done at much lower phosphoric acid/metal cation ratios.

(2) Immobilization of Acidic Solution with Phosphoric Acid (Second Experiment)

This experiment differed from the first in that the simulated waste was not alkaline, nor did it have a high sodium content. Instead, only acidic metal stock solution (Table 1) and concentrated phosphoric acid were added to the reaction kettle.

Approximately 700 mL (827.5 g) of acidic metal stock solution was added to the reaction vessel. As the vessel was stirred, 100 mL of concentrated phosphoric acid was added, and heating was begun. Distillation began when the pot temperature reached 105°C. The pot was heated until the pot temperature reached 400°C; a total of 693 mL of distillate was collected during distillation. The experiment proceeded as indicated in Fig. 3.

The appearance of the still pot residues from this experiment was vastly different from that in the first experiment, *i.e.*, the product from the caustic waste produced earlier was a smooth, dense, glassy residue, while this acid waste residue was a pea-green, powdery, low-density, crystalline material. Except for its green color, the acid waste phosphate product is similar in appearance to elemental sulfur.

In this experiment, the ratio of meq (PO_4^{3-})/meq (cations) was $4400/2200 = 2$, which is adequate for a low-acid solid. However, 1300 meq of sulfate was also present. Because sulfate probably remains in this product the product acidity is probably still high.

(3) Distillate Characterization

The distillates for both experiments were collected in fractions, and the volume and density for each of these fractions were measured. Qualitative SO_4^{2-} and Cl^- tests were also done on each fraction, using standard $\text{Ba}(\text{NO}_3)_2$ and AgNO_3 tests. The densities of all distillate fractions were greater than 1. The data listed in Table 2 indicate strongly that most of the nitric and hydrochloric acids and little of the sulfuric acid were removed from the phosphate residue during distillation. The vapor temperatures and densities noted in these experiments are basically what would be observed when distilling a solution of nitric acid. In future experiments, the nitrate and nitrite contents of distillate fractions will be determined with specific ion electrodes.

Fig. 3. Distillation of Phosphate Solutions Containing Acidic Metal Solution

(4) Product Phosphate Solid Characterization

No characterization of the solid products has yet been undertaken. We do, however, plan to study the aqueous leachability and solubility of these products. Because water stabilities as high as those expected for final forms such as borosilicate glasses will not be realized, the standard leach tests will be modified.

b. Stability of FePO_4

The compositions of the sludge and the supernate present in the 8D2 tank at West Valley have been estimated and reported previously [WNYNSCS]. The literature we have examined in connection with the phosphate immobilization experiments gives reason to believe that the estimate of the FePO_4 content of the sludge may be greatly in error. The estimate of the contents of NFS Tank 8D2 projects that the bulk of the phosphate is precipitated as FePO_4 and that the supernate contains little phosphate; 29% of the iron in the sludge is said to be present as FePO_4 .

Table 2. Results of Qualitative and Quantitative Testing on Distillates Originating from Phosphate-Immobilization Experiments

Expt. and Distillate No.	Total Vol, mL	Density at 20°C, g/mL	Vapor Temp, ^a °C	Cl ⁻ Reaction with Ag ⁺	SO ₄ ²⁻ Reaction with Ba ²⁺
1-1	97.0	1.00	95	neg	neg
1-2	102.5	1.03	95	neg	neg
1-3	51.1	1.04	98	sp ^b	neg
1-4	50.2	1.05	108	vp ^c	neg
1-5	26.0	1.20	112	vp	neg
1-6	16.5	1.35	114	vp	neg
1-7	26.5	1.37	111	neg	neg
1-8	13.0	1.33	104	Brn ppt	neg
1-9	5.0	1.15	97	sp	neg
2-1	100.0	1.01	95	neg	neg
2-2	100.0	1.00	96	sp	neg
2-3	99.0	1.01	98	vp	neg
2-4	102.5	1.03	102	vp	neg
2-5	49.0	1.08	104	vp	neg
2-6	54.5	1.12	109	vp	neg
2-7	29.0	1.21	112	vp	neg
2-8	39.1	1.27	114	vp	neg
2-9	49.5	1.28	113	vp	neg
2-10	33.1	1.14	101	vp	neg
2-11	12.2	1.08	98	vp	sp
2-12	10.2	1.07	96	vp	sp

^aThermometer was not calibrated.

^bsp - Slightly positive, turbid.

^cvp - Very positive, agglomeration.

Many researchers reporting the preparation of various ferric phosphates and acid phosphates have warned against washing the products with water [MELLOR]. There are reports that repeated washing of the precipitate tends to transform it into a hydrated oxide:

According to one source referenced in [MELLOR], "the precipitated phosphate is only very sparingly soluble in water; but is rapidly decomposed by contact with that liquid. The quantity hydrolyzed

at any particular temperature depends on the amount of water present, and the decomposition does not proceed beyond a fixed limit, unless the phosphoric acid which has entered into solution is removed from the sphere of action. In the presence of a large excess of water, the whole of the phosphoric acid is eventually drawn from the iron phosphate."

Several researchers have substantiated this result and have gone on to learn that hydrolysis can be promoted or retarded by various saline solutions. Ferric phosphate hydrolyzes more rapidly in alkaline solutions than in water alone. According to [MELLOR], one source observed "... ferric phosphate is immediately colored reddish-brown by a solution of potassium hydroxide, and the greater part of phosphoric acid is extracted, but no ferric oxide is dissolved."

A search of Chemical Abstracts from 1930 to 1980 yielded 40 references in addition to those found in [MELLOR]. These references have shed some additional light, and shade, on the problem. For example, according to one study [LAKOMKIN], FePO_4 , AlPO_4 , and CrPO_4 hydrolyze in dilute NH_4OH solutions and lower the pH to 3-4. As the concentration of NH_4OH is increased, these phosphates hydrolyze further; "... the PO_4^{3-} ions pass into solution, peptize the hydroxides, and transform them into colloidal solution. For this reason it is impossible to ppt. these hydroxides with NH_4OH in the presence of PO_4^{3-} ions." Other references also mention phosphate-hydroxide colloidal solutions. Also, a large number of studies point to the conclusion that reaction 1 does not go to completion, but rather stops at some ratio of $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}/\text{FePO}_4$; the ratio at which reaction stops is determined by the pH and by the other salts present in the aqueous phase. It is a surface reaction controlled by the affinity of phosphate ion or other ions for ferric hydroxide.

Because of the importance of the hydrolysis reaction of FePO_4 for estimating the supernate and sludge compositions of West Valley waste, we will study this reaction at conditions approximating those of NFS Tank 8D2-- i.e., high sodium nitrate and high pH. We are presently evaluating the use of energy-dispersive X-ray fluorescence (EDXRF) for determining both iron and phosphate concentrations in the aqueous phase.

C. Interim Waste Form Development: Materials Studies

(G. Bandyopadhyay,* S. M. Gehl,* H. Yamada,* T. M. Galvin,* J. E. Slattery,* and W. J. Grajek*)

The work performed during the last quarter of our study includes (1) the investigation of several properties of the fused salt/sludge system, (2) instrumented impact tests on several pressed and sintered Fe_2O_3 -sodium silicate compacts and fused salt/sludge compacts, and modification of the impact test system and the test procedure, (3) microstructural characterization of Fe_2O_3 -sodium silicate compositions, (4) assembly and scoping experiments with the disk pelletizer system, (5) development of sodium silicate/calcium hydroxide binder for interim waste form, and (6) a literature search for materials of construction for the salt/sludge process. The results are summarized below.

1. Fused Salt/Sludge System

Several fused salt specimens with compositions simulating West Valley supernate and containing 5, 10, and 20 wt % simulated sludge were prepared by the procedure described earlier [STEINDLER-1981B]. The sludge was

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prepared by intimately mixing suitable amounts of dry Fe_2O_3 , FePO_4 , Cr_2O_3 , NiO , Nd_2O_3 , MnO_2 , UO_2 , SrO , RuO_2 , and ZrO_2 in a plastic jar. Fused salt specimens containing >20 wt % sludge could not be fabricated because of the low flowability of the fused salt/sludge mixture in the molten condition.

The fused salt/sludge samples were tested for their solubility in water, their chemical stability by differential scanning calorimetry (DSC) and thermogravimetry (TG), their fracture strength, and their hygroscopic character in a controlled-humidity environment. Data were obtained on the dissolution behavior of fused salt samples containing 0-20 wt % of simulated sludge in 4000 cm^3 of stagnant water at room temperature. Samples of different surface areas were placed in the water, and the time for complete dissolution noted. The presence of sludge in the composition increased the time required for complete dissolution by a factor of about two. A sample with no sludge and a surface area of 10 cm^2 dissolved in approximately 10 min.

Since the rate of solubility of the salt mixture was reduced significantly in the presence of sludge, one can speculate that chemical reactions of sludge constituents with the salt mixture occurred during the preparation of the fused cakes. This hypothesis appears to be reasonable when we note that the fused salt/sludge systems show considerable differences in melting and weight loss behavior on the basis of DSC and TG in comparison to the salt mixtures containing no sludge. Figure 4 shows the DSC and the TG data as a function of temperature for three compositions. Melting of the salt mixture (Fig. 4a) appeared to have initiated at the start of the large DSC peak (about 220°C). The weight loss at $\leq 600^\circ\text{C}$ due to decomposition of

Fig. 4

Differential Scanning Calorimetric and Thermogravimetric Measurements of Simulated West Valley Supernatant Salt Mixture Containing 0, 5, and 20 wt % Simulated Sludge

the salt was negligible. The temperature at which melting in the fused salt/sludge systems began was somewhat obscured due to overlapping of minor peaks* with the major peak due to melting. However, the major peaks in the fused salt/sludge samples were at slightly lower temperatures than the salt mixture containing no sludge, indicating that the presence of sludge may have brought the melting temperature down to some extent. Such a depression of the melting point would have been likely if some of the sludge components had dissolved or reacted with the salt mixture. Note further that the weight loss in the fused salt/sludge systems was substantially higher than that observed for salt alone. A two-stage weight loss (one at about 375-450°C and the second at >600°C) was detected (Fig. 4c) in the fused salt/sludge samples containing 20 wt % sludge, indicating the possibility that two reactions occurred during the heating process.

Fracture strength data, determined by the diametral compression technique for fused salt samples containing 0 to 20 wt % sludge, are shown in Fig. 5. A slight increase in fracture strength upon the addition of sludge was detected whereas we noted earlier that the addition of Fe_2O_3 resulted in a small reduction of fracture strength [STEINDLER-1981B].

The weight gains of fused salt samples containing 5 to 20 wt % sludge in a controlled-humidity environment are shown in Fig. 6. At $\geq 70\%$ humidity at 35°C, substantial weight gains due to moisture absorption were detected. The samples were often partly or completely dissolved in the

Fig. 5. Strength of Fused Salt Specimens as a Function of Weight Percent Sludge in the Composition

* The causes of these minor peaks are not known at this time.

Fig. 6. Hygroscopicity of Fused Salt Samples Containing Sludge

absorbed moisture. These data indicate that to avoid moisture absorption, the fused salt waste form must be stored in a reasonably dry (≤ 50 -60% humidity at 35°C) environment.

2. Instrumented Impact Tests

Instrumented impact tests have been completed on the fused salt/sludge systems containing up to 20 wt % sludge. The results of these tests are discussed below along with the results for silicate compacts.

a. Impact Tests on Silicate Specimens

The impact fracture behavior of sintered SS-C ($\text{SiO}_2:\text{Na}_2\text{O} = 2.00:1$) and SS-65 ($\text{SiO}_2:\text{Na}_2\text{O} = 3.22:1$) compacts containing up to 33% Fe_2O_3 by weight were discussed in earlier reports [STEINDLER-1981A and 1981B]. During the present report period, several instrumented impact tests have been performed on SS-C and SS-65 compacts containing more than 50 wt % Fe_2O_3 .

The results are summarized in Table 3. During all impact tests reported in Table 3, the initial velocity of the impacting tup was maintained at 120 cm/s with a corresponding maximum available energy of 58.4 J. Since it has been observed [STEINDLER-1981A] that experimental parameters, such as sample size and the travel of the impact tup after the initial contact, can strongly influence the impact fracture and compacting of the specimens and can thereby influence the generation of inhalable particulates during impact tests, an attempt was made to keep these two parameters as constant as possible.

The size distributions of fracture particles generated by the instrumented impact tests was determined by sieving the fracture fragments collected after the impact tests. The results are summarized in Table 4. As reported previously [STEINDLER-1981B], several size distributions seem to follow a "log-normal" relationship between cumulative weight percent of particles and particle diameter. In order to estimate the quantity of particles with diameters smaller than 10 μm , the data were extrapolated to a diameter of 10 μm on a log-normal graph paper (e.g., see Fig. 7). Estimated amounts of particles with diameters smaller than 10 μm are listed in the last column of Table 3 except that no attempt has been made to extrapolate the data to a 10- μm diameter for the particle size distributions (Tests 77 and 79) which show deviations from the lognormal straight-line relationship.

Fig. 7. Size Distribution of Fracture Particles Generated by the Instrumented Impact Test on Sodium Silicate/ Fe_2O_3 Compact (Test 76)

Table 3. Estimated Fractions of Inhalable Particulates Generated by Instrumented Impact Tests of Sodium Silicate and Salt/Sludge Compacts

Test No.	Composition, wt %	Specimen Size		Specimen Weight, g	Tup Travel after Initial Contact		Energy Absorbed by Specimens, J	Estimated Fraction of Fines (<10 μm)
		Dia., cm	Height, cm		cm	% of Sample Height		
<u>As-received SS-C:Fe₂O₃</u>								
74	10:90	3.25	1.12	23.844	0.80	71.4	13.9	1.0 × 10 ⁻³
76	30:70	3.25	1.20	23.908	0.88	73.3	42.9	5.3 × 10 ⁻³
78	50:50	3.24	1.30	23.888	0.98	75.4	56.8	6.1 × 10 ⁻³
<u>As-received SS-65:Fe₂O₃</u>								
75	10:90	3.25	1.11	23.888	0.79	71.2	19.9	1.8 × 10 ⁻³
77	30:70	3.25	1.21	23.933	0.89	73.6	21.2	a
79	50:50	3.25	1.32	23.906	1.00	75.8	6.1	a
<u>As-received Salt:Sludge</u>								
80	95:5	2.52	1.35	14.356	1.03	76.3	3.9	a
81	90:10	2.52	1.33	13.763	1.01	75.9	3.9	a
82	80:20	2.52	1.32	12.939	1.00	75.8	9.8	1.1 × 10 ⁻³

^aNot available due to deviation from the lognormal distribution.

Table 4. Size Distributions of Fractured Particulates Generated by the Instrumented Impact Tests on Sodium Silicate/Fe₂O₃ and Salt/Sludge Compacts

		Test No.								
		74	75	76	77	78	79	80	81	82
Specimen Weight, g		23.844	23.888	23.908	23.933	23.888	23.906	14.356	13.763	12.939
Total Weight of Fracture Particulates Collected, g		23.290	23.430	23.700	23.694	23.772	23.783	14.307	13.673	12.822
Mass Fraction Smaller than Particle Diameter Indicated, %	Particle Diameter, μm									
	1400	21.07	25.48	18.20	17.43	12.95	19.86	10.03	12.42	16.76
	600	9.67	12.99	9.92	10.59	7.46	13.58	5.01	5.79	9.80
	180	3.99	5.98	5.74	6.73	4.80	10.45	2.29	2.21	3.94
	150	3.44	5.19	5.15	6.26	4.36	9.96	1.93	1.85	3.22
	75	1.71	2.66	3.20	4.34	2.91	7.17	0.97	0.86	1.51
	45	0.55	0.88	1.66	0.22	1.46	1.38	0.16	0.21	0.61

The impact energies absorbed by SS-C and SS-65 compacts are plotted in Fig. 8 as a function of Fe_2O_3 content. Although the SS-C compacts show a wide variation in the impact energies absorbed, they are usually stronger upon dynamic impact than are SS-65 compacts. This is consistent with the static fracture strength measurements by a diametral compression technique reported previously [STEINDLER-1981A]. The SS-65 compacts show good impact strengths both in high- Fe_2O_3 (>70%) and low- Fe_2O_3 (<12%) contents, but are weaker at intermediate Fe_2O_3 contents (12-70%). Additional impact tests are planned to confirm these observations.

Fig. 8. Impact Energies Absorbed by SS-C and SS-65 Compacts Containing Fe_2O_3

b. Impact Tests on Salt/Sludge Systems

Instrumented impact tests have been conducted on salt/sludge compacts containing up to 20 wt % sludge (see Section I.C.1). The results are summarized in Table 3. In order to estimate the amount of fines generated by the impact tests, all of the fracture particulates were sieved; the results are listed in Table 4. Only the particle size distribution for Test 82 seems to follow a lognormal relationship. The particle size distributions for both Tests 80 and 81 show a significant deviation from lognormal distribution.

Load-time traces and the high-speed movies taken during the impact test indicate that the impact fracture behavior of the salt/sludge compacts resemble very closely those of the SS-C and SS-65 silicate compacts--namely, the first impact was followed by compaction of the specimens. Although the impact energies absorbed seem to increase with increasing sludge content, further impact experiments should be conducted to verify this effect.

c. Modification of the Dynatup Impact System and Test Procedure

The results of the instrumented impact experiments performed to date in the Materials Science Division (ANL) clearly indicate that significant additional effort will be required in order to exploit the unique capabilities of the system. The Dynatup instrumentation provides load-time traces and allows us to measure impacting velocity, total available energy, the energy absorbed by the sample, the impact duration, the peak load at fracture, and the dynamic strength of the material. Most of these parameters (except for impacting velocity and total available energy) can only be obtained by the instrumented impact method. In addition to these parameters, high-speed photography (up to 5000 frames/s) of the impact event provides a direct visual observation of the macroscopic fracture behavior. An airborne-particle analyzer, which we plan to incorporate in our experimental setup, will yield direct information on respirable fines generated during impact. The data obtained from these experiments and the microstructural parameters of the waste forms (such as porosity, grain size, and phase distributions) may be correlated to provide a quantitative relationship of the impact and materials parameters and the respirable fines. Some efforts have been made to collect and analyze the impact-generated particle-size distributions for various waste forms. However, very little has been done to correlate the generation of respirable fines with the intrinsic materials properties and the actual energy absorbed by the specimens during the impact experiments.

An extensive development of the instrumented testing method and its application to waste forms is beyond the scope of our current program. However, we made some major modifications in our testing machine during this reporting period. The modifications are (1) reduce the weight of the crosshead so that a more prototypic impact velocity can be obtained without increasing the impact energy, (2) adapt a hemispherical tup head made of tungsten carbide instead of the Charpy impact block so that experimental results can be analyzed thoroughly by use of a simple elasticity theory, and (3) fit an airtight enclosure around impact specimens so that any airborne particles generated by impact testing can be sampled and analyzed by a particle analyzer. Since the second modification described above assures a point contact between the specimen and the tup head, it eliminates an alignment difficulty associated with impact testing using the Charpy impact block.

3. Microstructural Characterization of Fe₂O₃-Silicate Compositions

Selected specimens of Fe₂O₃-anhydrous silicate and pelletized Fe₂O₃-silicate waste form were examined by optical microscopy (OM) and scanning electron microscopy (SEM). This characterization is being performed to determine the degree to which sodium silicate bonds the structure together and encapsulates the Fe₂O₃.

The anhydrous silicate waste forms were prepared by mechanically mixing various proportions of Fe₂O₃ and sodium silicate powders (SS-65 and SS-C), cold-pressing cylindrical specimens, and sintering. The Fe₂O₃ content of the specimens ranged from 0 to 90 wt %.

Examination by optical microscopy of polished sections of sintered SS-C compacts containing Fe_2O_3 indicated that at <50 wt % Fe_2O_3 , sodium silicate formed a continuous phase whereas Fe_2O_3 is the continuous phase at >50 wt % Fe_2O_3 . Some chemical interaction between the Fe_2O_3 and sodium silicate was observed. Figure 9 shows a high-magnification view of a section through a 70% Fe_2O_3 -30% SS-C specimen. The silicate phase is composed of isolated, blocky particles. (The apparent porosity of many of the silicate particles is an artifact of the specimen preparation procedure.) Note that a light-colored reaction product has formed on the surface of almost every silicate particle. SEM examination showed that this layer contains approximately equal amounts of iron and silicon. The phase is probably an iron-sodium silicate compound.

The SEM examination also revealed that the Fe_2O_3 particles are much smaller ($<1 \mu\text{m}$) than the silicate particles ($50\text{--}200 \mu\text{m}$) in the sintered compacts. This disparity in size may be responsible for nonuniform mixing of the phases. Thus, the silicate phase may not have effectively bonded the structure of the currently available Fe_2O_3 -anhydrous silicate compacts. Selection of suitable size fractions of the phases could lead to significantly improved strength of the sintered compacts.

Microstructural examination of the pelletized Fe_2O_3 -sodium silicate samples prepared by methods that were described earlier [STEINDLER-1981B] indicated that the distribution of silicate in the pellets was much more homogeneous than that observed in sintered samples. Therefore, at the

Fig. 9. Polished Section of 70% Fe_2O_3 -30% Anhydrous Silicate Specimen. A white reaction layer may be seen on the surface of the silicate particles. Magnification, 200X

present stage of development, the pelletized waste form appears to have a greater potential for effectively encapsulating, in a silicate matrix, sludge particles of the sizes (<325 mesh) used in these experiments. However, substantial improvement in the encapsulation performance can probably be obtained merely by using anhydrous silicate powders that are the same size or smaller than the sludge particles. The pelletization process, on the other hand, may not be able to effectively encapsulate any large (>20 mesh) particles present in the sludge. It is thus apparent that any decision about using silicates as a waste form binder should be based on knowledge of the particle-size distribution of the sludge to be encapsulated.

4. Assembly of Disk Pelletizer System

In an earlier report [STEINDLER-1981B], we indicated that controlled experiments will be required to determine the suitability of pelletization as an option for the preparation of interim waste forms. During the present quarter, we received a Mars Model DP-14 pelletizer, a Vibra-Screw Line Bin powder feeder, and a Pulsafeeder Model 1720 solution pump for pumping silicate solution to the powder. The pelletizer was placed in a fume hood to minimize the spread of dust. The powder feeder and solution pump were mounted on wheeled platforms. These items can be positioned in front of the fume hood during a pelletization run and rolled out of the way when access to the pelletizer is needed.

Process optimization studies were initiated with the pelletization equipment. Several scoping experiments have been completed, using Fe_2O_3 powder and water as the binder. The disk angle and rotating speed, powder and solution feed rates, and the position of the water spray were optimized for the production of uniform pelletized samples of sufficient strength. Currently, experiments are being performed using sodium silicate solutions.

5. Development of Sodium Silicate/Calcium Hydroxide Binder

The addition of $\text{Ca}(\text{OH})_2$ to sodium silicate can increase the strength of a waste form by cementitious bonding, *i.e.*, the formation of hydrated calcium silicates. Since these reactions occur at room temperature, a calcium hydroxide-modified sodium silicate binder has the potential advantage of providing adequate mechanical strength without the need for sintering at elevated temperatures.

Preliminary studies of binders incorporating sodium silicate and calcium hydroxide were performed. In the initial tests, dry powders of the desired compositions were blended, cold-pressed into cylindrical specimens, and exposed to a controlled high-humidity (90% relative humidity) air environment at 35°C for 24 h. The humid air provided the required water of hydration without the need for adding liquid water. The weight gain (water uptake) and the mechanical strength (measured by either axial or diametral compression) were determined for each specimen immediately after it was removed from the high-humidity environment. Selected specimens were then transferred to a nitrogen-atmosphere dry box and were subsequently examined by scanning electron microscopy (SEM). The SEM examination was performed to determine the existence, morphology, and approximate chemical composition of the interparticle bonds that formed as a result of the humidity treatment.

In the first experiment, various compositions of SS-65 anhydrous sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O} = 3.22:1$) and $\text{Ca}(\text{OH})_2$ powders were pressed into 21-mm dia slugs and exposed to 90% relative humidity air as described above. The results of weight gain crushing strength measurements on these specimens are summarized in Table 5. (Crushing strengths were measured by compressing the specimens axially between flat-ended, parallel platens.) Note that water pickup increased monotonically with increasing silicate content and that crushing strength reached a maximum at an intermediate composition. The calcium hydroxide-rich specimens had a considerably lower strength than the silicate-rich specimens.

Table 5. Weight Gain and Crushing Strength of $\text{Ca}(\text{OH})_2$:SS-65 Compacts

Sample Composition $\text{Ca}(\text{OH})_2$:SS-65	Weight Gain, %	Crushing Strength, MPa
0:5.09	5.57	62.3
1.00:4.00	3.98	62.0
2.14:3.06	2.41	67.9
2.87:1.98	1.94	52.5
5.05:0	1.01	50.2

The SEM examination of fracture surfaces from this series confirmed that interparticle bonding did occur. Most of the bonds were between $\text{Ca}(\text{OH})_2$ particles, although interpenetration of Ca and Si also occurred, indicating that bonds also formed between silicate and $\text{Ca}(\text{OH})_2$ particles. The SEM examination also revealed that size disparity between the large silicate particles and much smaller $\text{Ca}(\text{OH})_2$ particles prevented the formation of a large number of $\text{Ca}(\text{OH})_2$ -silicate bonds.

Accordingly, for the next series of experiments, the particle size of the silicate powder was reduced by ball-milling and sieving to pass a 200-mesh screen. In these tests, equal amounts of $\text{Ca}(\text{OH})_2$ and SS-65 powders were blended with various amounts of simulated NFS sludge. Pellets containing 50, 75, or 90 wt % sludge were cold-pressed in a 6.6-dia die at pressures of 130 and 195 MPa. The as-pressed densities of these specimens are shown in Fig. 10. The weight gains and fracture strengths after exposure to high relative humidity are presented in Figs. 11 and 12, respectively. Each data point in these figures is an average of readings taken on two to six pellets. The strength values in Fig. 12 were obtained by loading the specimens in diametral compression and are thus not directly comparable with the crushing strength values in Table 5.

Specimen density increased with increasing sludge content. As expected, the higher cold compaction pressure produced substantially higher specimen densities. The weight gain data in Fig. 11 exhibit a monotonic

Fig. 10. As-pressed Density as a Function of Sludge Content for the Silicate- Ca(OH)_2 Specimens at Two Compaction Pressures

Fig. 11. Weight Gain at Two Compaction Pressures after High-Humidity Exposure as a Function of Sludge Content for the Silicate- Ca(OH)_2 Specimens

Fig. 12. Fracture Strength (diametral compression) as a Function of Sludge Content for the Silicate- Ca(OH)_2 Specimens

decrease with increasing sludge content. Cold compaction pressure had a negligible effect on the amount of water pickup. The fracture strength data in Fig. 12 appear to show an effect of cold compaction pressure. However, the difference between the two curves is smaller than the statistical variations in strength for specimens pressed at 195 or 130 MPa.

The fracture strength for these specimens is larger by a factor of 10-15 than the fracture strength of sintered sludge-silicate specimens.* This strength advantage, coupled with the advantage of room temperature processing, makes further development of the silicate- Ca(OH)_2 binder system very attractive.

SEM examination of the sludge-silicate- Ca(OH)_2 specimens showed that considerable bonding of the particulate structure occurred during exposure to high humidity. The bonding was apparently aided by the smaller silicate particles. In addition, the iron phosphate in the sludge was involved in the bonding process. A typical fracture surface from this series of specimens is shown in Fig. 13. The structure is virtually pore-free, suggesting that the Ca(OH)_2 -silicate- FePO_4 - H_2O reaction product expanded to fill the available pore space. At higher magnification (Fig. 14), individual particles in a matrix of finer grained material are visible.

*The strength data on sintered sludge-silicate specimens have recently been obtained. These data show that specimens containing sludge instead of Fe_2O_3 were significantly weaker than were Fe_2O_3 -silicates.

Fig. 13. Fracture Surface of a 75% Sludge,
12.5% SS-65, 12.5% $\text{Ca}(\text{OH})_2$
Specimen. Magnification, 500X

Fig. 14. Higher Magnification View of
Specimen Shown in Fig. 13.
Magnification, 2000X

Compositions of small areas within the field of view varied widely. Observed ratios of Ca:Si in the bonding-forming regions ranged from 25:1 to 1:4. The phosphorus content varied from negligible to about four times the silicon content. Similar variations were observed in the iron and chromium levels. Although a complete morphological and chemical characterization of this complex system is beyond the scope of this investigation, SEM characterization of selected specimens will be continued as a part of the optimization of this waste processing procedure.

Because of the promising initial results, further studies in the $\text{Ca}(\text{OH})_2$ -silicate system are planned. Future tests will include studies of the effect of varying the $\text{Ca}(\text{OH})_2$:silicate ratio in sludge-containing system, as well as the effect of curing time on the strength of these composites.

6. Materials of Construction for Salt/Sludge Process

Fabrication and transportation of fused salt interim waste forms after processing of neutralized high-level radioactive liquid wastes similar to that stored in West Valley, N.Y., will require that chemically and mechanically stable, cost-effective materials of construction be selected for the processing equipment and for the waste canisters to be transported. Conceptually, the processing steps involve (a) removal of the bulk of the water from the salt-sludge slurry by evaporation, (b) melting of the salt to remove the final traces of water and to form a castable product, and (c) filling of the canisters with fused salt/sludge mixtures for transportation. In normal operation, the evaporator will be in contact with the supernatant solution at about 100°C , whereas the melter and the canisters will be in contact with the fused salt mixture at about $300\text{--}400^\circ\text{C}$.

Which materials of construction are selected depends on (1) life expectancy and (2) the type of processing operation (such as one-time operation or routine processing of interim waste). For cost effectiveness, readily available materials at acceptable prices should be selected. The technical requirements, moreover, will dictate the selection of materials with (1) good corrosion resistance at elevated temperatures and pressures to the supernatant salt solution, to fused salt mixtures, or to both so that the materials will be safe in normal and off-normal conditions, (2) good mechanical properties in the corrosion environment at elevated temperatures and pressures, (3) good weldability by usual welding techniques, and (4) good stability in a radiation field.

A preliminary literature search has been conducted to identify the corrosion behavior of commonly available metals and metallic alloys in salt solutions or fused salt compositions similar to the composition of West Valley supernate. A limited amount of data is available on the general corrosion and stress corrosion cracking (SCC) of iron and mild steel in NaNO_3 solution containing NO_2^- and OH^- (NaNO_3 and NaNO_2 are the primary constituents of the West Valley supernatant solution) and on the corrosion of iron alloys in molten $\text{NaNO}_3\text{--KNO}_3\text{--NaNO}_2$ salt. The significant results which are of interest in our present study are summarized below.

a. Corrosion in Salt Solution

General corrosion and SCC of mild steel in nitrate solutions have been studied by several investigators. Cracking, which is initiated independently of the stresses present, is intergranular in nature. Stresses facilitate crack propagation. The presence of NO_2^- and OH^- in the nitrate solution appears to inhibit SCC. The effectiveness of NO_2^- and OH^- as inhibitors depends strongly on their concentrations in the solution. [DONVAN] performed a series of experiments to determine the factors that control stress corrosion cracking of a mild steel (composition: C, 0.12; Mn, 0.49; P, 0.01; and S, 0.015 wt %) in NaNO_3 solution. He also determined the concentrations of NO_2^- and OH^- required to inhibit SCC in NaNO_3 solution. Figure 15 maps the concentration zones in which the cracks in a precracked and loaded sample (apparent stress intensity, $49.5 \text{ MPa } \sqrt{\text{m}}$) either grow or do not grow within 1000 h in a 5M NaNO_3 solution at 368 K. Sufficient concentration of either ion ($1.8\text{M } \text{NO}_2^-$ and $1.25\text{M } \text{OH}^-$) can prevent crack growth. If both ions are present, SCC can be prevented by a solution containing less than $1.8\text{M } \text{NO}_2^-$ and less than $1.25\text{M } \text{OH}^-$.

Table 6 summarizes the times to crack initiation in Donvan's work for various bulk solution compositions. The limited data suggest a correlation of initiation time with composition; generally, the greater the concentration of the inhibitor, the longer time to initiation of cracks.

Fig. 15. Influence of Sodium Nitrite and Sodium Hydroxide on Propagation of Stress Corrosion Cracking of a 285 B Steel in 5M NaNO_3 at 368 K

Table 6. Time to Crack Initiation for Various Amounts of NO_2^- and OH^- in 5M NaNO_3 Solutions at 368 K

NO_2^- , M	OH^- , M	Crack Initiation Time, h
-	-	75-200
0.5	-	200
0.75	-	400
1.5	-	600
3.0	-	∞
-	0.3	75
-	0.5	400
-	1.0	350
-	1.2	∞
0.2	0.5	615
0.2	0.2	525
0.3	0.3	1100
0.5	0.1	150

A threshold stress intensity (K_{ISCC} , the stress intensity below which cracks do not propagate) and crack velocity were measured. These parameters were independent of the bulk solution composition and had values of 31 MPa $\sqrt{\text{m}}$ and 8.4×10^{-6} m/s, respectively.

As discussed above, very limited data are available for the selection of materials of construction for the treatment of neutralized high-level radioactive waste. For an understanding of corrosion behavior, experiments must be performed in which iron-based alloys (mild steel and stainless steel) are contacted with prototypic solution compositions, temperatures, and pressures.

The literature data indicate that the presence of NO_2^- and OH^- in the West Valley supernatant solution is highly beneficial from a corrosion standpoint. We need to determine whether the concentrations of NO_2^- and OH^- in the solution are high enough to completely inhibit SCC in mild steel compositions. The literature data further indicate that corrosion of mild steel in nitrate solutions at about 100°C should be negligible unless stresses above a certain threshold value are present. Since crack propagation velocity above the threshold stresses is rather high, one must carefully evaluate off-normal situations which might lead to elevated pressures and temperatures in the operating vessels.

b. Corrosion in Fused Salt

[KRAMER] discussed in a recent paper the corrosion at 823 K (550°C) of six iron alloys in molten $\text{NaNO}_3\text{-KNO}_3\text{-NaNO}_2^*$ (7 wt % NaNO_3 , 53 wt % KNO_3 , and 40 wt % NaNO_2 , having a melting point of 415 K). The alloy compositions are listed in Table 7. The results show that all alloys formed oxide

* Hitec[®] composition, E. I. duPont de Nemours Company.

Table 7. Nominal Chemical Compositions of Alloys Immersion-Tested
in Molten $\text{NaNO}_3\text{-KNO}_3\text{-NaNO}_2$

Alloy	Cr, wt %	C, wt %	Ni, wt %	Mn, wt %	Mo, wt %	Si, wt %	Fe
1018 Steel	0.0	0.15-0.2	-	0.6-0.9	-	<0.5	balance
2.25 Cr-1 Mo	1.9-2.6	<0.15	-	0.3-0.6	0.5	<0.5	balance
5 Cr-0.50 Mo	5.13	<0.12	-	0.44	0.5	0.37	balance
9 Cr-1 Mo	8.0-10.0	<0.15	-	0.3-0.6	0.9-1.1	<1.0	balance
316 Stainless	16.0-18.0	<0.08	10.0-14.0	<2.0	2.0-3.0	<1.0	balance
310 Stainless	24.0-26.0	<0.25	19.0-22.0	<2.0	-	<1.5	balance

layers within one month. The amount of oxidation spanned two orders of magnitude and was strongly dependent on the chromium content. Stainless steels were particularly resistant to corrosion. Carbon steel, 5 Cr-0.50 Mo, and 9 Cr-1 Mo are suitable for lower temperatures than temperatures at which stainless steel must be used. The 2.25 Cr-1 Mo alloy tends to spall and may not be a useful alloy at 823 K.

The salt composition in Kramer's investigation is not prototypic of the West Valley supernatant composition. However, the results indicate that stainless steels might be good choices as melter and canister materials. Final selections should be made after tests have been performed with prototypic salt compositions. The effects of stress and temperatures typical of fire conditions should also be examined.

II. NEUTRON ACTIVATION AND TRACER STUDIES (L. J. Jardine, J. K. Bates, 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 dispersion at a low rate. Neutron activation analysis (NAA) has been shown to be one applicable method for measuring leach rates. Radioactive tracers 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. Comparison of (1) characterization test results obtained using these two methods and (2) other existing characterization data will be used to specify conditions under which such tests and the resulting data may be extrapolated to fully radioactive specimens. The current focus is on leach-rate characterizations of simulated waste glasses and, to a lesser extent, advanced alternative waste forms.

Major goals are completion of the development of the NAA method for leach-rate determinations, definition of the accuracy, sensitivity, and limitations of NAA; and establishment of the applicability of the test results to large-scale waste forms. Goals for the development of methods for radioactive tracers are similar.

B. Radioactive Tracer Method Qualification

1. Introduction

A series of experiments have been defined to qualify the use of NAA and radioactive tracers to measure the leach rates of Savannah River Laboratory (SRL) frit 131, SRL frit 211, and Pacific Northwest Laboratory (PNL) 76-68 simulated 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 will also be used. The four classes are alkali metals (Cs), alkaline earths (Sr and Ba), rare earths (Ce and Eu), and noble metals (Ru). Simulated waste glass containing radioactive tracers (spiked glasses) has 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 analyses (ICP* and DCP† emission spectroscopy, AA,‡ flame emission, colorimetry) of leachates from non-neutron activated glass, (2) gamma-ray spectroscopic analyses of leachate solutions from neutron-activated glass specimen, (3) gamma-ray spectroscopic

* Ion-coupled plasma emission spectroscopy.

† Direct current plasma emission spectroscopy.

‡ Atomic absorption.

analyses of leachate solutions from glass specimens containing radioactive tracers, and (4) gamma-ray spectroscopic analyses of leachate solutions from neutron-activated glass specimens that also contained radioactive tracers.

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. In addition, these experiments will provide data for assessing the long-term leaching behavior of waste elements from glass waste forms.

2. Radioactive Glass Preparations

A batch of modified SRL frit 211*** glass containing about 2600 μCi of radioisotopes was prepared. The nominal composition of this frit 211*** SRL glass is shown in Table 8 where it is compared with other SRL frit 211 glasses being used in these studies [STEINDLER-1981B]. SRL frit 211*** glass contains no cesium additive but larger amounts of strontium (about 6X), barium (about 3X), europium (about 30X), and ruthenium than previous SRL frit 211 glasses.

In the preparation of tracer, 7010 λ of four radioactive tracers was placed in a 31.9-g platinum crucible. The tracer radioactivity totaled about 2621 μCi and consisted of ^{141}Ce (820 μCi in 1000 λ), ^{152}Eu (1000 μCi in 5000 λ), ^{106}Ru (800 μCi in 1000 λ), and ^{137}Cs (1.3 μCi in 10 λ). A 5 λ aliquot of the above tracer solution was taken from the platinum crucible and prepared for γ -ray analysis to verify the levels of tracers.

About forty grams (41.6 g) of the 211*** SRL glass frit, powdered and pulverized, was placed in the platinum crucible, mixed with the tracer solution with a glass stirring rod, and left to dry in a Blickman hood overnight.

The amount of activity (per gram of glass) was about 40 times that in the SRL frit 211** glass. The increase in activity was selected on the basis of previous leach rate measurements of neutron-activated frit 211** glass containing detectable amounts of ^{141}Ce , ^{152}Eu , and ^{106}Ru .

The glass was melted at 1050°C for four hours. The melt was then poured into a Pt-5 wt % Au mold to cast a glass ingot for subsequent sectioning with the Isomet saw. The glass ingot was annealed at about 500°C for about 2 h. Then, the furnace power was turned off, and the furnace was allowed to cool off naturally overnight with the glass ingot inside.

The 30 g ingot was then sectioned into about 1-mm-thick by about 7-mm by 21-mm pieces for leaching studies described below.

A batch of modified SRL frit 131* glass containing about 3800 μCi of radioisotopes was also prepared. The nominal composition of this SRL frit 131* glass is shown in Table 8 where it may be compared with frit 131 and frit 211 SRL glasses previously used in these studies. Frit 131* glass contains no bulk cesium additive, and its additives are otherwise similar to the SRL frit 211*** additives; frit 131 glass contains Mg, Ti, Zr, and La, none of which are in the frit 211 basic glass.

Table 8. Nominal Compositions of Simulated SRL Waste Glasses Used in this Work

	wt %					
	SRL 211 ^a	SRL 211*	SRL 211**	SRL 211***	SRL131	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

^a[DP-80].

About forty grams (40.1 g) of the SRL 131* glass, powdered and pulverized, was placed in a (27.4-g) platinum crucible, after which 12,005 λ of five radioactive tracers was added. The tracers totaled about 3786 μ Ci and consisted of ¹⁴¹Ce (1640 μ Ci in 2000 λ), ¹⁵²Eu (2000 μ Ci in 4000 λ), ⁸⁵Sr (100 μ Ci in 4000 λ), ¹³³Ba (45 μ Ci in 2000 λ), and ¹³⁷Cs (0.65 μ Ci in 5 λ). The amount of activity (per gram of glass) for these experiments was about 40 times that in the first experiments in this series with SRL frit 211**.

The increase in activity was selected on the basis of previous leach rate measurements of neutron-activated frit 211** glass containing detectable amounts of ^{141}Ce , ^{152}Eu , ^{133}Ba , and ^{137}Cs . No leach rate data have been obtained yet for ^{85}Sr .

A 5 λ aliquot of the tracer solution was taken from the platinum crucible and was prepared for γ -ray analysis to verify the composition of the tracers and the levels of tracers added to the glass.

The powdered frit 131* glass was mixed with tracer solution with a glass stirring rod and left to dry in a Blickman hood overnight. The glass was melted at 1050°C for four hours. The melt was then poured into a Pt-5 wt% Au mold to cast a glass ingot for subsequent sectioning with the Isomet saw. The glass ingot was annealed at about 500°C for about 2 h. Then, the furnace power was turned off, and the furnace was allowed to cool off naturally overnight with the glass ingot inside.

The 40-g ingot was then sectioned into about 1-mm-thick by about 7-mm by 21-mm pieces for leaching studies at 90°C in deionized water, using a MCC-1 type procedure [STRACHAN].

3. Leaching Characterizations

To qualify the spike/leach method, tests are being done on four different glasses, SRL 211**, SRL 211***, SRL 131*, and PNL 76-68.[†] For each type of glass, the leach rates obtained with spiked glass will be compared with leach rates obtained by another method.

Leach testing for up to 100 days of activated and nonactivated samples has been completed. Eighty days of testing are completed on spiked and spiked/activated samples. Leachate analyses and test conditions for each glass type are given in Tables 9 and 10. Weight loss results through 100 days of leaching are shown in Fig. 16.

a. SRL 211**

Analysis of the nonactivated samples using DC plasma spectroscopy (by Trace Elements, Inc.) and atomic absorption (by Analytical Chemistry Laboratory, Chemical Engineering Division) indicates the constituent elements leach at three different rates (Table 10). Na, Li, Cs, B, and Si had nearly the same release after three days. All of these elements continued to leach throughout the next 29 days, but at a reduced rate. The Si leach rate for this period is significantly less than for the other elements. There is significant release of Ca and Al in the first three days, but no release after that. Mn and Fe have initially low release and constant release behavior thereafter. This leachate analysis data, combined with preliminary surface studies, suggests that Ca, Fe, Al, and Si form a protective outer covering on the glass surface. Under this protective layer is a diffusion or hydration layer which is rich in Fe, Mn, and other rare earth and transition metal elements. The durability of these layers is confirmed by long-term weight loss data which indicate there was no additional weight loss after about 20 days of leaching.

[†]Results to be reported later.

Table 9. Summary of Current Leachate Analyses and Weight Loss Leach Rates for SRL 211**, SRL 211***, and SRL 131 Glass Under Study
Note: SA is "surface area."

Sample	Test Conditions										Leachate Analysis										
	Sample No.	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, ug/mL											
										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** (activated)	134	90	3.6	0.5874	30	3.69	9.8		8.1	21.48											
	135		7.0	0.5746	38	3.64	9.7	50.6	10.5												
	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			0.6396		4.10															
	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		11.8												
	165			0.3775		4.10															
	166			0.3661		4.18															

(contd)

Table 9 (contd)

Sample	Test Conditions									Leachate Analysis											
	Sample No.	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 Si	ACL Na	ACL Li	ACL Cs	TEI ^b Si	TEI B	TEI Mn	TEI Ca	TEI Al	TEI Fe	TEI 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			0.4526		3.97															
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		28	0.4152	44	3.94	9.4	37.9	11.2												
	261		28	0.4493	41	3.99	9.4	35.8	10.3												
	262		28	0.5513			9.4	32.6													
	263		42	0.4597	45	3.98	9.6	33.1	11.3	36.2											
	264		42	0.4432	44	3.98	9.6	32.8	11.1	35.3											
	265		42	0.4483	47	3.92	9.4		12.0	37.2											
	266			0.4424		2.89															
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-	239 ^c		14	0.3993	58	4.36	9.6	37.1													
vated)	240		28	0.3712	53	4.26	9.6	39.5		NS ^d											
	241		28	0.4119	49	4.30	9.6	35.0		32.5											
	242		28	0.3694	85	4.30	9.6	34.3		33.2											
	243		43.1	0.4054	112	4.34		32.5													
	244			0.3945		4.28															
	245			0.3680		4.29															
	246			0.4098		4.36															

(contd)

Table 9 (contd)

Test Conditions										Leachate Analysis										
Sample	Sample No.	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 Si	ACL Na	ACL Li	ACL Cs	TEI ^b Si	TEI B	TEI Mn	TEI Ca	TEI Al	TEI Fe	TEI Ba
SRL	276	90	3	0.4056	33	4.13	9.7	44.4	8.0		11.5	1.49		15.4	2.65	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								
	280		28	0.3835	49	4.17	10.0	44.1	11.8		19.8	2.60								
	281		28	0.4129	48	4.27	9.8	44.8	11.2		19.6	2.52								
	282		42	0.3748	51	4.21	9.5	44.2	12.1											
	283			0.3621		4.15														
	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		7	0.4430	36	4.08	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		34.9	9.5											
	291		28	0.4618	41	4.12		37.9	10.0											
	292		28	0.4607	38	4.11		34.6	9.3											
	293		42	0.4407		4.08														
	294			0.4496		4.09														
	295			0.4458		4.08														
	296			0.4946		4.15														

(contd)

Table 9 (contd)

Sample	Sample No.	Temp, °C	Time, days	Test Conditions						Leachate Analysis										
				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 Si	ACL Na	ACL Li	ACL Cs	TEI ^b Si	TEI B	TEI Mn	TEI Ca	TEI Al	TEI Fe	TEI 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	43.0	18.0		26.2	5.09								
	302		28	0.4624	75	4.10	9.8	43.9	18.3		26.0	4.89								
	303		28	0.5066	86	4.16	9.8		20.7		25.7	4.81								
	304		42	0.3893	77	4.02	9.4	44.6	19.1											
	305			0.4769																
	306			0.4259																
	307			0.4978																
	308			0.5308																
309		0.4925																		
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								
	315		28	0.4887	69	4.43	9.8	44.9	15.6		25.2	4.91								
	316		28	0.3891	65	3.64	9.8	45.9	17.9		24.5	4.51								
	317		37	0.4556	74	4.12	9.6	45.5	18.0											
	318			0.4987			4.01													
	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 9 (contd)

Sample	Sample No.	Test Conditions							Leachate Analysis												
		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 Si	ACL Na	ACL Li	ACL Cs	TEI ^b Si	TEI B	TEI Mn	TEI Ca	TEI Al	TEI Fe	TEI Ba	
SRL	327	90	2.25	0.3112	21	3.77	9.5		5.6												
131*	328		7	0.3989	18	3.90			4.6												
(acti- vated)	329		14	0.3986	21	3.86			5.4												
	330		28																		
	331		28																		
	333																				
SRL	339	90	3	0.5174	17	4.36	9.5		3.9												
131	340		7	0.4869	32	4.26			7.5												
(spiked)	341		14	0.4842		4.27															
	342		28	0.4772		4.28															
	343		28	0.4866		4.29															
	344		28	0.4965		4.29															
	345		42	0.4733		4.27															
	346			0.4651		4.26															

Sample	Sample No.	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	^{147}Md	^{152}Eu
SRL	237	0.63	0.058	0.97	3.97	0.46	2.22		0.022	0.036	0.01
211***	238	1.14	0.056	1.02	7.27	0.29	3.72		0.024	0.032	0.01
(acti- vated)	239	1.71	0.038	1.14	7.20				0.020		0.01

^aAnalyses done by the Analytical Chemistry Laboratory of the CEN Division.

^bAnalyses done by Trace Elements, Inc.

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

^dNo solution.

Table 10. Summary of Normalized Leach Rates Calculated from Data in Table 9 for SRL 211**, SRL 211***, and SRL 131 Glasses. Temp = 90°C

Sample	Sample No.	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 211** (activated)	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											
	165												
	166												

(contd)

Table 10 (contd)

Sample	Sample No.	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	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												
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												
SRL	237 ^c	3											
211***	238 ^d	7											
(acti-	239 ^e	14											
vated)	240	28	13.6										
	241	28	13.6										
	242	28											
	243	43.1											
	244												
	245												
	246												

(contd)

Table 10 (contd)

Sample	Sample No.	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	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								
	280	28		19.3	22.0								
	281	28		19.0	21.2								
	282	42											
	283												
	284												
	285												
SRL	287	3											
211***	288	7											
(spiked)	289	14											
	290	28											
	291	28											
	292	28											
	293	42											
	294												
	295												
	296												

(contd)

Table 10 (contd)

Sample	Sample No.	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	298	3		13.2	12.4		9.4	12.8	<0.2	1.0	8.7	<0.05	
131	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								
	302	28		28.1	27.6								
	303	28											
	304	42											
	305												
	306												
	307												
	308												
	309												
SRL	311	3					8.5	11.8	<0.2	3.8	8.4	0.1	<1.7
131*	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								
	315	28		26.3	27.7								
	316	28		31.8	31.6								
	317	37											
	318												
	319												
	320												
	321												
	322												
	323												

(contd)

Table 10 (contd)

^aAnalytical Chemistry Laboratory, Chemical Engineering Division.

^bTrace Elements, Inc.

^cNormalized elemental losses were 1.3 g/m² ⁵¹Cr, 0.12 g/m² ⁵⁹Fe, 1.9 g/m² ⁸⁵Sr, 0.9 g/m² ¹³¹Ba, 4.4 g/m² ¹³⁴Cs, 0.04 g/m² ¹⁴¹Ce, 0.07 g/m² ¹⁴⁷Nd, 0.04 g/m² ¹⁵²Eu, and 7.9 g/m² ¹²⁴Sb.

^dNormalized elemental losses were 1.6 g/m² ⁵¹Cr, 0.09 g/m² ⁵⁹Fe, 1.9 g/m² ⁸⁵Sr, 0.5 g/m² ¹³¹Ba, 5.3 g/m² ¹³⁴Cs, 0.04 g/m² ¹⁴¹Ce, 0.05 g/m² ¹⁴⁷Nd, 0.03 g/m² ¹⁵²Eu, and 12.4 g/m² ¹²⁴Sb.

^eNormalized elemental losses were 2.9 g/m² ⁵¹Cr, 0.06 g/m² ⁵⁹Fe, 1.9 g/m² ⁸⁵Sr, 6.2 g/m² ¹³⁴Cs, 0.03 g/m² ¹⁴¹Ce, 0.03 g/m² ¹⁵²Eu, and 12.0 g/m² ¹²⁴Sb.

Fig. 16. Normalized Weight Losses from Simulated Waste Glasses (leaching at 90°C in deionized distilled water with MCC-1 type tests [STRACHAN])

The neutron-activated and spiked leachates have also been analyzed by λ -ray counting techniques. These results indicate that only ^{134}Cs can be detected in the leachate from the activated samples; ^{134}Cs , ^{137}Cs , ^{133}Ba , and ^{152}Eu can be detected in the leachate from the spiked and spiked/neutron-activated samples; however, the analyses are not complete.

b. SRL 211***

Since neutron-activated SRL 211** glass contains too much cesium to detect most other α -emitters, glass SRL 211*** was made. This glass nominally contains 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 9 and 10) indicate that the leach rates of all spikes can be detected plus over 10 activated isotopes.

c. SRL 131 and 131* Glass

The SRL 131 glass is the current SRL reference frit glass. Leach tests are in progress to determine the leaching behavior of both the SRL frit 131 glass and SRL 131* glass; the latter contains about 3 wt % waste additives of minor elements, as shown in Table 8. Tests are being done on

cold glass, neutron-activated glass, and spiked glass (^{85}Sr , ^{137}Cs , ^{133}Ba , ^{141}Ce , ^{152}Eu). The tests have been completed through 42 days, and preliminary results 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 the NAA technique. Therefore a new batch of 76-68 glass has been made and will be activated. This should allow the determination of the noble metal and rare earth elements, which cannot be measured by 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 when contacted with water will be determined. 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 the completion of all of the current leach tests. Data presented in Table 9 and 10 are preliminary and should be so treated.

C. 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. Examination of the weathered samples will allow description of the hydration process. The durability of hydrated glass will be demonstrated by subjecting these samples to leaching conditions.

D. Auxiliary Leach Studies

1. SYNROC

A series of leach tests on SYNROC samples have been completed. These tests included over 50 experiments done at 40, 90, and 200°C. The leachates have been submitted for analysis, and the tests will be described when the data become available. These tests are designed (1) to provide insight as to how changes in process conditions change the leaching behavior and (2) to obtain leach data that will be acceptable for the MCC handbook.

2. Westinghouse Alkoxide Glass

A series of leach tests have also been done on three different Westinghouse glasses. These glasses, supplied by Westinghouse, vary basically in their alumina and silica contents, as shown in Table 11. To each glass frit, a simulated waste composition (1.0% Cs_2O , 1.2% CeO_2 , 1.8% ZrO_2 , 0.05% Eu_2O_3 , 0.4% SrO , and 0.6% BaO) has been added to facilitate leachate analysis by NAA. A series of leach tests following the MCC-1 procedure were done on each type of glass. The matrix of test conditions together with some auxiliary results are given in Table 12.

Table 11. Calculated Nominal Compositions (wt %) of
Waste Glasses Provided by Westinghouse

Glass	Designation	SiO ₂	Al ₂ O ₃	Na ₂ O	B ₂ O ₃	Fe ₂ O ₃	MnO ₂	CaO	NiO	Na ₂ SO ₄	Ion Siv	Cs ₂ O	CeO ₂	ZrO ₂	Eu ₂ O ₃	SrO	BaO
1	Low-alumina	44.9	6.1	11.8	10.1	12.9	3.6	0.9	1.6	0.4	2.7	1.0	1.2	1.8	0.05	0.4	0.6
2	Medium- alumina	38.2	12.8	11.8	10.1	12.9	3.6	0.9	1.6	0.4	2.7	1.0	1.2	1.8	0.05	0.4	0.6
3	High- alumina ("nepheline syenite")	35.3	16.2	10.4	10.5	13.2	3.7	0.9	1.6	0.4	2.7	1.0	1.2	1.8	0.05	0.4	0.6
	SRL 211 ^a	42.5	2.7	16.4	7.9	13.6	3.8	5.0	1.7	0.4	2.8	-	-	-	-	-	-

^aAlso 3.2 wt % Li₂O.

Table 12. Test Conditions and Auxiliary Results for Westinghouse Alkoxide Glass Leach Tests. Test procedure given in [STRACHAN]

	Sample No.	Time, days	Initial Mass, g	Δ Mass, $\text{g} \times 10^{-4}$	SA, cm^2	$\frac{\Delta \text{ Mass}}{\text{SA}}$, g/m^2	Final pH
Westinghouse Glass 1	170	3	0.2816	6	3.98	1.5	7.4
	171	7	0.2886	21	3.97	5.3	7.8
	172	14	0.2734	11	3.96	2.8	8.3
	173	28	0.2730	17	3.94	4.3	8.1
	174	28	0.3905	70	4.10		
	175	28	0.2318	16	3.94	4.1	
	176	42	0.2817	17	4.04	4.2	
	177	98	0.2706	21	3.99	5.3	
Nonactivated	183a	28	0.2421	19	4.00	4.7	7.9
Westinghouse Glass 2	184	3	0.2455	9	3.58	2.5	7.9
	185	7	0.2576	10	3.58	2.8	8.1
	186	14	0.2464	18	3.56	5.1	8.3
	187	28	0.2680	20	3.58	5.6	8.4
	188	28	0.2288	20	3.54	5.7	8.2
	189	28	0.3650	18	3.71	4.9	8.1
	190	42	0.2501	18	3.54	5.1	8.1
	191	98	0.3911	21	3.80	5.5	
Nonactivated	197a	28			3.82		8.2
Westinghouse Glass 3	198	3	0.4514	17	4.17	4.8	7.8
	199	7	0.4545	9	4.18	2.2	8.0
	200	14	0.4588	15	4.14	3.6	8.2
	201	28	0.5422	16	4.30	3.7	8.1
	202	28	0.4499	76	4.16		8.1
	203	28	0.4558	20	4.10	4.9	8.0
	204	42	0.3759	13	4.11	3.2	
	205	98	0.3939	9	4.05	2.2	
Nonactivated	211a	28			4.04		

Solution analyses were done on leachates from samples 203, 211a, and 198. NAA analyses were done on 198 and 203, and a DC plasma analysis was done on 211a (which was not activated). Gamma-ray counting indicated that in 203 leachate, ^{141}Ce , ^{152}Eu , and ^{134}Cs could be detected and in 198 leachate, ^{152}Eu and ^{134}Co could be detected. Results are given in Table 13.

Table 13. Solution Analyses of Alkoxide Glass

Sample No.	Time, days	$\frac{\Delta \text{Mass}}{\text{SA}}$, g/cm ²	Normalized Elemental Loss, (NL) _i , g/m ²									
			Cs	Eu	Ce	B	Si	Mn	Ca	Al	Fe	Ba
198 ^a	3	4.8	2.6	0.020								
203 ^a	28	4.9	3.0	0.032	0.026		5 ^b					
211a ^c	28	-				5	5	0.5	3	5	0.1	4

^aNAA analysis.

^bACL/CEN analysis.

^cDCP analysis.

Weight loss data for each type of glass are similar. Some inconsistencies exist because during or after irradiation some of the samples were broken or chipped; in a few cases, some chips were lost before leaching. The leaching behavior for these Westinghouse glasses is similar to that observed for SRL 211* glass. There is an initial weight loss which occurs in 7 days of leaching; however, thereafter, little or no additional weight loss is detected. After 28 days, the normalized weight loss, $\frac{\Delta M}{\text{SA}}$, for Westinghouse glass is 4 g/m²; the analogous values for SRL 211* and PNL 76-68 glasses are 7 and 12 g/m², respectively.

The results indicate that Westinghouse glass leaches about one-third to one-half as much as SRL 211 type glasses. Westinghouse was informed that complete leach tests analyses would be possible if they provided financial support and new samples that have a modified waste mixture.

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

A. Introduction

A requirement for licensing of solid radioactive waste forms is characterization of the fracture caused by mechanical impacts received during normal and accidental conditions of processing, handling, interim storage, and transportation. It is important to understand the resistance of brittle waste forms to dispersion of fracture fragments caused by such impacts, which could bring the fragments into contact with humans. A brittle fracture methodology is being developed which relates the impact-stress distribution to the lognormal size distribution of the particles resulting from impact fracture. The practical application of this fracture model is to predict the total fracture-surface area available for leaching or dispersal and the mass of respirable-size particles produced in impact fractures.

Development and preliminary verification of this model has been provided by laboratory-scale tests of impacts of reference glass specimens and also 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 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 Particles

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 as a result of the generation of fracture fragments from an impact. The particle size distribution can be used to assess source terms of airborne releases, and the surface area increase can be used to assess the increase in source terms of leach rates.

A brittle fracture study at Argonne National Laboratory (ANL) is currently developing the necessary models, engineering correlations, scaling laws, and experimental characterization methodologies required to assess these two major responses for large canisters of glass waste forms. The ANL study utilizes modeling in conjunction with closely coupled laboratory-scale experimental verification to establish, 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 (to be developed as MCC-10) by 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 particle sizes $\leq 10 \mu\text{m}$ for these test comparisons) for the currently available alternative waste forms.

This report summarizes a standardized drop-weight impact test and the characterization procedures used to generate, to collect, and to measure the respirable sizes produced by the impact testing of four alternative waste forms. The four simulated alternative waste forms impacted were (1) SRL frit 131 borosilicate glass, (2) Oak Ridge National Laboratory (ORNL) FUETAP concrete, (3) LLL SYNROC ceramic and (4) Rockwell TAILORED CERAMIC. In preliminary tests, the measured respirable fractions were observed to vary by only a factor of seven between the "best" and "worst" forms. The measurement of increases in surface area is not addressed in this preliminary report.

2. Experimental

A standardized set of drop-weight impact test conditions and characterization procedures were defined and applied to four generic types of alternative high-level-waste forms to characterize the respirable particulates generated upon fracture. The test procedures are believed to be suitable for consideration as a MCC-10 type dynamic impact test for brittle waste forms.

a. Simulated Alternative Waste Form Test Materials

Four types of waste forms supplied by the appropriate waste form developers were tested during March 1981. No high-silica-glass waste forms were received for testing. The current test methods are not directly applicable to coated waste forms or to metal matrix waste forms, which thus were not tested.

(1) SRL Frit 131 Borosilicate Glass

A SRL frit 131 simulated waste glass with the composition shown in Table 14 was tested. 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.

Table 14. Nominal Compositions of Alternative SRL Waste Forms Used in this Comparative Impact Study

Component "Matrix"	Wt % of Component				
	SRL 131 Glass	SYNROC		TAILORED CERAMIC	FUETAP Concrete
		"B"	"D"		
SiO ₂	41.7				27.75 ^a
B ₂ O ₃	10.6				
TiO ₂	0.7	59.4	18.7	2.0	
Al ₂ O ₃		6.5	1.0	5.8	
Li ₂ O ₃	4.1				
Na ₂ O	12.7				
Cs ₂ O			0.3		
MgO	1.4				
CaO		15.2	3.4		
BaO		8.0	1.4		
ZrO	0.4	10.9	4.9		
La ₂ O ₃	0.4		3.1	7.2	
Flyash					11
Cement, type 1					22
Water					18 ^b
Water Reducer (D65)					1.25 ^b
"Matrix" Totals:	72	100	32.8	15	80
"Waste"	SRL 131 Glass	SYNROC		TAILORED CERAMIC	FUETAP Concrete
		"B"	"D"		
Fe ₂ O ₃	13.9	-	24.2	12.6	9.4
Al ₂ O ₃	3.0	-	18.9	46.2 ^c	1.8
MnO ₂	3.7	-	7.5	10.4	2.6
CaO	1.0	-	1.3	0.8	0.5
NiO	1.6	-	3.1	1.8	1.2
SiO ₂		-	0.5	1.4	0.2
Na ₂ O		-	3.4	4.6	1.3
Na ₂ SO ₄	0.4	-	0.6	0.4	0.2
SrO		-	0.4		0.2
CeO ₂		-	0.4		0.4
Gd ₂ O ₃		-	0.4		0.4
Nd ₂ O ₃		-	0.4		
Eu ₂ O ₃		-	0.4		
UO ₂		-	2.1	c	
Zeolite	2.7	-	-	7.3	1.6
Waste Totals:	26.3	0	63.6	85.5	19.8

^aOttawa sand.

^bFor this table, 19.25 wt % water was included in normalizations.

^cThree wt % UO₂ was replaced with 3 wt % Al₂O₃.

(2) ORNL FUETAP "Concrete"

Two types of FUETAP concrete specimens were supplied by ORNL, both of which had the composition summarized in Table 14. The FUETAP contained no uranium but was loaded with about 20-25 wt % modified/simulated SRL waste. The two types of FUETAP specimens differed slightly in diameter and each had different processing conditions. Lot 1 had a 25.4-mm diameter; processing consisted of curing at 100°C at 0.1 MPa (about 15 psi) and dewatering at 250°C, each step lasting 24 h. Lot 2 had a diameter of 26.5 mm; processing consisted of curing at 250°C at 4.1 MPa (about 600 psi) and dewatering at 250°C, each step lasting 24 h. The ORNL-supplied specimens were prepared for impact testing by cutting the specimens into 25.5-mm lengths, using a low-speed Isomet saw equipped with a diamond blade and saturated lime water coolant. The cut specimens were then again dewatered for 24 h at 120°C in a vacuum oven.

(3) LLL SYNROC CERAMIC

SYNROC B (containing no waste) and SYNROC D (loaded with about 64 wt % simulated SRL waste including about 2.1 wt % UO_2) were two ceramic waste forms supplied by Lawrence Livermore Laboratory (LLL). Their compositions are shown in Table 14. The SYNROC B material was prepared by hot pressing at 1200°C and 14 MPa (2000 psi) for five minutes in a graphite die; then specimens for impact testing were prepared from a 566.8-g stock sample by core-drilling cylindrical specimens 26.8-mm OD by 25.85 mm. The SYNROC D was prepared by hot pressing at 1100°C and 28 MPa (4000 psi) for five minutes in a graphite die; specimens for impact testing 25.4 mm OD by 27.3-mm length were prepared at LLL by core drilling.

(4). Rockwell TAILORED CERAMIC

A hot-pressed ceramic material was supplied by Rockwell for testing. The simulated waste form contained no uranium but was loaded with about 85 wt % SRL "high aluminum-without aluminum removal" waste. The nominal composition is given in Table 14. The material was prepared by hot-pressing in graphite at 1300°C and 28 MPa (4000 psi) for one hour. Specimens for impact testing were prepared by core-drilling (e.g., 26.8-mm OD by 18.15 mm long). The materials supplied were too thin for a core-drilled specimen to be produced having a length-to-diameter ratio of approximately unity as do the other waste forms.

b. Impact Test and Characterization Procedures

The standard impact test consisted of placing a single specimen on its side between two hardened tool steel plates (Rockwell 58) inside a sealed chamber. A sketch of the impact chamber is given in Fig. 17. Each specimen received a dynamic impact when a 9.9 kg weight was dropped from a preselected height onto the upper hardened plate. A Plexiglas tube was used to guide the delivery of the dropped weight. Initial heights of the dropped weight were selected to hold constant at 10 J/cm³ the available impact energy per specimen volume (calculated from potential energy and ignoring any losses). Some variations in height of the weight drop were required in

Fig. 17. Chamber Used to Conduct Dynamic Impact Tests of Brittle Waste Form Specimens

these initial tests because not all specimens of the available materials had the identical geometric volumes. The nominal desired specimen volume for testing was 25.4-mm OD by 25.4-mm long. To achieve the required 10 J/cm^3 , the drop height must be 1.34 m, which potentially produces 131 J of available impact energy.

During and immediately following the impact, the chamber remains sealed by use of a metal bellows which is welded to both the removable flange at the top of the chamber and the upper hardened steel plate (see Fig. 17). A brittle specimen absorbs impact energy during the loading until fracture occurs (about 100 μs). The fracture fragments are contained within the chamber for subsequent size and/or surface area characterizations.

After several hours, the fracture fragments are collected by introducing water into the impact chamber through a valve assembly (not illustrated in Fig. 17) in the upper flange. After the upper chamber flange is removed, the slurry of fracture fragments is transferred directly to a 90- μm sieve. The bellows are then washed over the 90- μm sieve. Additional washings of the material collected on the 90- μm sieve are used to separate and collect two size fractions: $\leq 90 \text{ } \mu\text{m}$ and $> 90 \text{ } \mu\text{m}$.

3. Results

The cumulative size distributions (obtained as described above) were analyzed with a computer program that fit the data to a lognormal distribution, using a regression analysis. The results are shown graphically in Fig. 18 for each type of material and are tabulated in Table 15. All specimens tested were found to have fracture particulates that obey the lognormal size distribution function over the measured size range of 4 to 4000 μm . The two lognormal parameters (the standard deviation, σ_f , and the geometric mass mean diameter, D_g) are shown in Table 15 for all waste forms tested. The quantity (wt %) of respirable sizes,* together with the standard fitting (1σ) determined from a computer fit of the data, are shown in column nine of Table 15. A composite lognormal plot allowing comparison of all the materials tested is shown in Fig. 19. These preliminary results showed that the Rockwell TAILORED CERAMIC waste forms generated the smallest amount of respirable particles, 0.06 wt %. The SRL frit 131 glass and both types of SYNROC materials generated essentially the same amounts of respirable sizes, about 0.15 wt %. Thus, on a weight percent basis, the amounts of respirable glass and SYNROC materials generated were only two and one-half times that generated by the TAILORED CERAMIC. The two FUETAP materials registered the largest amounts of respirable particles, about 0.4 wt %, which is six times as much as the TAILORED CERAMIC.

4. Discussion

Tabulated in Table 15 are the corresponding masses of respirable particles, based on the initial specimen masses. In assessing potential hazards, the actual waste loadings of the waste forms also need to be considered. Thus, using the waste loadings given by the waste form developers, the masses of respirable sizes of actual waste components are also given in Table 15. Observe that the waste forms with the higher waste loadings (e.g., TAILORED CERAMIC) may pose more of a hazard than those with lower waste loadings (e.g., SRL glass and FUETAP). Hence, waste loading is another parameter which must be assessed along with mass of respirable particles.

This initial test series did not allow the reproducibility of the impact characterizations to be examined. This is in progress for waste forms for which sufficient supplies are available--namely SRL frit 131 glass.

The effects of modest specimen size variations at a constant available impact energy per specimen volume are not known. A lack of materials and resources has precluded examining this to date. The impact test done with the TAILORED CERAMIC (Table 15) highlights this uncertainty. In this test, only about 80% as much total energy was delivered as to the other typical test specimens. (The 27-mm-OD by 18-mm specimen size was the largest obtainable from the available TAILORED CERAMIC materials.) The smaller mass of measured respirable particles may have been due solely to the smaller amount of available impact energy, or to the properties of the TAILORED CERAMIC, or a combination thereof.

* Respirable sizes are defined for purposes of this report as all sizes <10 μm diameter, as measured with a Coulter counter. Further studies are required to correlate the term, respirable sizes, with Coulter counter diameters.

Fig. 18. Lognormal Plot of Cumulative Measured Weight Percent vs. Measured Diameter or Mesh Size. Sizes $>90 \mu\text{m}$ are based on sieve analyses, and sizes $<90 \mu\text{m}$ on Coulter counter analyses. (a) SRL Frit 131 glass, (b) LLL SYNROC ceramics, (c) Rockwell TAILORED CERAMIC, and (d) ORNL FUETAP concrete.

Table 15. Respirable Particles Generated in Comparative Dynamic Impact Tests of Four Alternative Simulated-Waste Forms--Diametral Impacts

Material	Size, mm		Impact ^a Mass, g	Energy, J	Energy ^b Density, J/cm ³	Lognormal Parameters ^c		Respirable ^d Sizes (<10 µm)		
	OD	Length				D _g , mm	σ _g	wt % ^e	mg ^f	mg ^g
SRL frit 131 ^h glass	25.5	27	39.7	146	10	2.6±0.4	6.4±0.2	0.14±0.02	56	16
SYNROC B ⁱ	26.8	25.9	60.5	146	10	4.2±0.8	7.6±0.3	0.15±0.02	91	0
SYNROC D ^j	25.4	27.3	53.5	138	10	4.7±0.7	8.1±0.3	0.16±0.02	86	55
TAILORED ^k CERAMIC	26.8	18.2	40.8	102	10	13.7±0.2	9.3±0.3	0.06±0.006	25	21
FUETAP ^l Lot 1	25.4	25.5	23.0	131	10	2.3±0.3	7.9±0.2	0.43±0.04	99	25
FUETAP ^l Lot 2	26.45	25.5	26.0	131	9.3 ^m	3.5±0.3	8.6±0.2	0.32±0.02	83	21

^aImpact energy is maximum available as delivered by dropping a ~9.9 kg weight onto the sealed chamber from a 1.3-m height.

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

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

^dRespirable size is arbitrarily defined for this study as all cumulative sizes smaller than 10 µm in diameter, as measured with Coulter counter and mechanical sieving procedures.

^eValue is obtained from computer analysis of data from one impacted specimen and is illustrated by data in Figs. 18 and 19. The wt % is based on the total initial specimen mass.

^fThe absolute mass of ≤10 µm particle sizes is shown.

^gThe absolute masses of actual simulated waste with particle sizes ≤10 µm were calculated by assuming: glass, 28 wt % waste; SYNROC B, no waste; SYNROC D, 64 wt % waste; TAILORED CERAMIC, 85 wt % waste; and FUETAP concrete, 25 wt % waste.

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

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

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

^kTAILORED CERAMIC specimens (85 wt % waste) were core-drilled from a bulk piece supplied. Density was reported to be 3.95 g/cm³.

^lFUETAP specimens (about 20 to 25 wt % waste) were cut to length with a diamond blade saw. Lot 1 was cured for 24 h at 250°C and Lot 2 at 100°C.

^mThe planned test energy density was 10 J/cm³, but a calculational error in specimen volume resulted in an actual test energy density of 9.3 J/cm³ for this single specimen.

Fig. 19. Composite Lognormal Plot of Cumulative Measured Weight Percent vs. the Measured Diameter or Mesh Size for Four Types of Alternative Waste Forms. Sizes $>90 \mu\text{m}$ are based on sieve analyses, and sizes $<90 \mu\text{m}$ on Coulter counter analyses.

These impact tests were done at one preselected fixed test parameter of 10 J per initial cubic centimeter of an impacted specimen. To achieve the constant test parameter of 10 J/cm^3 , not only was specimen size allowed to vary modestly (because of size limitations of the available materials), but also the total available energy was varied. The rather small ranges of these variations are illustrated in columns 2, 3, and 4 of Table 15. Except, possibly, for the TAILORED CERAMIC, the variations are probably not significant. Experiments are needed to establish the effect of varying the available energy per specimen volume. Studies to determine the threshold energy required to cause fracture are also important to understanding the brittle fracture process sufficiently to develop models.

5. Conclusions

In comparative impact tests at the same impact energy per specimen volume, SRL frit 131 glass, SYNROC B ceramic, and SYNROC D ceramic generated the same mass of respirable particles. In comparison, the TAILORED CERAMIC waste form generated 0.4 as much mass of respirable particles and the FUETAP

waste form generated 2 1/2 times as much mass of respirable particles as either glass or SYNROC. The amount of waste loading in a waste form was identified as a parameter that must be considered when assessing the quantity of respirable sizes.

Further impact tests are needed to examine the experimental reproducibility and the effects of variations of specimen size and specimen energy density. The rather narrow range of the initial impact test results for all four waste forms in comparison with rather disparate results of leaching tests for these same waste forms implies that it may be possible to characterize one waste form (as planned in ANL's brittle fracture study of SRL glass) by measuring and modeling its response to impact fracture, thereby establishing the methodology and data base needed to estimate the response of other brittle waste forms to impacts.

C. Preliminary Analysis of Dynamic Stresses in Impacts of Brittle Materials

When brittle bodies are impacted, force is generated by the deceleration of the mass of the body. This force produces elastic stress and strain in the body. When the stress exceeds the elastic limit, cracks propagate in the body, and the body fragments violently into particles that are propelled outward from the center of impact by elastic force. Essentially, the kinetic energy of impact is converted to elastic strain energy in the body, and this elastic energy is dissipated into heat by the collisions of the ejected particles. The energy conversion from thermal units to mechanical units is $1 \text{ cal} = 4.186 \text{ J/cm}^3$. For typical glass, a temperature rise of 1°C results from the dissipation of strain energy density of 1.9 J/cm^3 . When the body is impacted by hardened steel components at impact energies in the range of practical interest, the metal components are not deformed inelastically, and essentially all the impact kinetic energy is converted into stress and elastic energy in the brittle body and in the metal components. It is the stress in the brittle body which is the driving force for the brittle fracture process. Because the kinetic energy is converted into elastic strain energy, the extent of fracture (measured by the surface area of the particles formed) correlate with impact energy input (kinetic energy) and not with impact velocity. Because of the important role of stresses in impact fracture, stress analysis is basic to characterization of the severity of impact conditions causing fracture.

Although fracture results tend to be independent of impact velocity for a given impact energy, the process of crack propagation under applied stress is known to be time-dependent; that is, cracks form initially in the regions of the highest stress levels and small cracks propagate slowly at first and then accelerate as the crack grows larger. When bodies are impacted by free fall from a given height to an unyielding surface, bodies of the same shape have the same stress distributions, independent of body size. This is the scaling law for stress distributions, and it is well established in the technical literature. However, the time required to reach peak stresses differs for different sizes of bodies. Therefore, the scaling laws for time are different from those for stress. Since crack propagation is time-dependent, scaling laws must be known if impact results for different body sizes of the same material are to be interpreted and the results of full-scale tests are

to be predicted from small-scale experimental tests. Of course, the stress distributions differ for different impact configurations (e.g., axial impacts of cylinders, side impacts, and corner impacts). This is an additional reason for stress analysis.

Mathematical models of stress distributions for a range of body sizes and shapes have been developed in a preliminary way. Details will be reported after further study.

D. Topical Report

A topical report [MECHAM] was drafted and is being reviewed. The contents of that report are summarized below.

Characterization of the fracture of vitrified or crystalline waste forms resulting from mechanical impacts is likely to be a licensing requirement for nuclear waste forms which was not previously imposed on glass or ceramic technologies. The respirable fraction and the total surface area of the particles generated are the major criteria in this characterization. From a review of the technical literature on fracture mechanics, it appears that brittle-fracture theories and data have been applied only to quasistatic loading, as used for tests of structural strength. However, important features of impact fracture are dealt with by physical mechanics, elastic stress analyses, dimensional analyses, small-particle statistics, and engineering studies related to the crushing of minerals. After review and combination of these topics, a comprehensive brittle-fracture model was developed. The major elements are: (a) a lognormal particle-size distribution, (b) a direct linear relationship between the surface area of the fracture particulate and the elastic energy dissipated in the brittle-fracture process, and (c) an approximate axisymmetric stress-distribution model for the solid body experiencing the application of deceleration force.

This methodology was applied to others' data (obtained for both small-scale laboratory tests and large-scale waste impact tests). Further application was made to particle-size data obtained in ANL laboratory-scale tests with a range of different materials--vitreous, crystalline, and conglomerate. In all cases, the lognormal particle-size distribution provided a good approximation of the experimental measurements of the fracture particulates for all particle sizes below about 4000 μm . This size range includes, of course, the respirable size ($\leq 10 \mu\text{m}$) and typically more than 90% of the total fracture surface area. For conglomerates and for crystalline material with large grains and well-defined grain boundaries, grain size influences the size distribution of the fracture particulate, and two lognormal distributions are observed, one for intergranular fracture and one for transgranular fracture.

Lognormal size analysis has been facilitated by computer assistance in determining the error estimates of the value of the lognormal size parameters (the mean, D_g , and the standard deviation, σ_g); linear regression analyses of the lognormal straight-line plots have been made by computer graphics. Typical deviations are: D_g , 30%; σ_g , 6%; and respirable fraction, 50%. Similar computer assistance is planned in future tests to verify the effects of body size, tup velocity, and time dependence on the dynamic stress distributions.

Such tests are required to establish the scaling laws for impacts under realistic accident conditions.

From our small-scale tests made thus far, the methodology described can characterize the relative resistance to fracture for various waste compositions under development. Reproducible fracture behavior is observed in impacts, but not in quasistatic tests, because the formation of large numbers of particles show statistical averaging for the multiple stages of the binary cleavage mode of fracture in brittle materials. The effects of impact velocity and deceleration time are minor over a wide range of impact conditions of practical interest--principally because kinetic energy is almost completely converted into elastic strain energy that is stored in the material until extensive fracture has taken place. The methodology appears to be promising as a basis of experimental design for standardized impact tests of materials and for scale-model tests of canistered waste forms.

E. Computer-Assisted Analysis of Particle Size Distributions

The size distributions of particles formed by impact fracture of brittle materials plot as approximately straight lines on lognormal graphical coordinates. This straight line is determined by the two parameters of the lognormal probability function--the geometric mean, D_g , and the geometric standard deviation, σ_g . In relation to the empirical data, D_g is the mass median diameter obtained in size analysis by sieving, while σ_g is the parameter describing the slope of the plotted straight line. Specifically, the slope is $1/\log \sigma_g$. It is desirable to use statistical analysis of the original data to determine the "best" values of D_g and σ_g by linear regression and then to use computer graphics to represent the particle size distribution as the "best straight line," together with the empirical data points as a plot on lognormal coordinates. Linear regression also gives a measure of the "goodness of fit" in terms of the standard errors in the calculated values of D_g and σ_g .

The mathematical basis of lognormal graphical coordinates is in the definition of the cumulative normal probability function $P(u)$ where u is the standardized normal variate, corresponding to a normal probability distribution with mean zero and variance unity. Numerical values of the normal probability functions are tabulated in terms of u , for the cumulative probability $P(u)$ and the density function $p(u)$. The relation of these two functions to any normally distributed variate X , with mean μ and variance σ^2 is given by the following three equations.

$$P(u) = \int_{-\infty}^u p(u) du \quad (1)$$

$$p(u) = \frac{1}{\sqrt{2\pi}} e^{-u^2/2} \quad (2)$$

$$u = \frac{X - \mu}{\sigma} \quad (3)$$

In the application to particle-size distributions, the particle diameter, D , is considered to be a variate distributed lognormally, i.e.,

$$u = \frac{\log D - \log D_g}{\log \sigma_g} \quad (4)$$

where D_g and σ_g are the parameters of the lognormal distribution of D , as described above.

From Eq. 4, it is apparent that u is a linear function of $\log D$, with a slope $1/\log \sigma_g$ and with an intercept defined by $u = 0$, corresponding to $D = D_g$. The linearization of the lognormal function is achieved by plotting u vs. $\log D$ on linear coordinates. For convenience, nonlinear scales corresponding to explicit values of $P(u)$ and D are marked on the graph in Fig. 20, which is an example of computer graphics for the particle size distribution of annealed, unannealed, and tempered Pyrex cylinders impacted at 2.4 J/cm^3 , showing the lognormal coordinates.

Fig. 20. Size Distributions of Fracture Particulates from Annealed, Unannealed, and Tempered Pyrex Cylinders from 2.4 J/cm^3 Impacts as Determined from Computer Fits of the Data

The straight-line fit of the data by linear regression determines the two parameters of the straight line defined by

$$u = A \log D + B \quad (5)$$

where A is the slope and B is the intercept at $u = 0$. From the analysis of the data by linear regression, the standard error in each of these two parameters A and B is determined as the variances: VAR A and VAR B. The straight-line parameters A and B are related to the lognormal parameters, D_g and σ_g , by these relations:

$$A = 1/\log \sigma_g = 2.3/\ln \sigma_g \quad (6)$$

$$B = -\frac{\log D_g}{\log \sigma_g} = -\frac{\ln D_g}{\ln \sigma_g} \quad (7)$$

The relation of the variances of D_g and σ_g to those of A and B are determined by the basic equation for the propagation of errors:

$$\text{VAR } \sigma_g = \left(\frac{\partial \sigma_g}{\partial A} \right)^2 \text{VAR A} \quad (8)$$

$$\text{VAR } D_g = \left(\frac{\partial D_g}{\partial A} \right)^2 \text{VAR A} + \left(\frac{\partial D_g}{\partial B} \right)^2 \text{VAR B} \quad (9)$$

The partial derivatives are found from Eqs. 6 and 7, which directly relate σ_g to A and which relate D_g and σ_g to B. Of course, the standard deviation (DEV) for each variable is related to the variance (VAR) as, for example, by

$$\text{DEV } D_g = (\text{VAR } D_g)^{1/2} \quad (10)$$

Also, the relative (%) standard error is given, for example, by

$$\% \text{ STANDARD ERROR} = \frac{\text{DEV } D_g}{D_g} \cdot 100 \quad (11)$$

These calculations and the computer graphics were programmed by Robert H. Land of the Chemical Engineering Division. The calculations, as indicated above, are not extensive, but they provide a powerful tool for the analysis of particle size data. To our knowledge, computer graphics have not been used previously to present lognormal coordinates of the convenient kind described above.

This lognormal particle-size analysis is being used to analyze our experimental particle size measurements. Preliminary results are presented in the above-mentioned topical report in preparation [MECHAM].

This lognormal analysis is not an arbitrary linearization technique. Rather, it is a consequence of the binary cleavage mode of brittle fracture exhibited in the two standard static-load brittle-strength tests: the 3-point bend test and the diametral compression test.

In the hypothetical subdivision of a single large cube (edge length = D_0) by n successive stages of binary cleavage along each of the three axes, the result would be a large number of small cubes, all of length D_n where

$$\frac{D_n}{D_0} = \left(\frac{1}{2}\right)^n \quad (12)$$

If n is a random variate distributed by the normal probability law, with n_g the mean number of stages of binary cleavage, the variability of D_n is related to the geometric mean size D_g by the relation

$$\frac{\log (D_n/D_g)}{\log 2} = n - n_g \quad (13)$$

Since n is distributed normally, D_n is distributed lognormally. Of course, the lognormal distribution of D_n is an observed fact, whereas the binary cleavage model and the normally distributed n are only implied and cannot actually be seen in impact tests because all fracture takes place in less than one millisecond.

Sieving is used to measure particle-size distributions. The measurement is of mass--i.e., the cumulative wt % of a sample with particle sizes less than a given size, D . For a given density of material, cumulative vol % and wt % are the same. The empirical cumulative vol %, $P_v(D)$, is defined in terms of (1) a cumulative volume $V(D)$ smaller than size D and (2) the normalization volume V_n , which is the volume of the whole sample being measured. The empirical cumulative volume fraction, $P_v(D)$, is equated to the cumulative lognormal probability function, $P(U_v)$, where U_v is the standardized normal variate defined for the lognormal parameters, σ_g and D_{gv} as in Eq. 4 above. These relations are

$$P_v(D) = \frac{V(D)}{V_n} = P(U_v); U_v = \frac{\log D}{\log \sigma_g} - \frac{\log D_{gv}}{\log \sigma_g} \quad (14)$$

Note that U_v is independent of whether natural logarithms or base 10 logarithms are used. It should also be noted that brittle-fracture particulates form a one-sided, or truncated probability distribution. That is, in typical tests, the particle sizes are lognormally distributed only for particle sizes smaller than about 4 mm.

Particle-size distributions are also measured by microscopic methods and by the Coulter counter technique, both of which determine the number of particles according to size, from which is determined the cumulative number percent smaller than size D . This empirical size distribution by number is represented by $P_n(D)$. In principle, the size distribution could also be measured for the cumulative surface area percent, $P_s(D)$. By analogy to Eq. 14, we have

$$P_n(D) = \frac{N(D)}{N_n} = P(U_n) \quad (15)$$

$$P_s(D) = \frac{S(D)}{S_n} = P(U_s) \quad (16)$$

The standardized normal variates, U_v , U_n , and U_s , have the same geometric standard deviation, σ_g ; this is a basic mathematical property of a lognormal distribution. The geometric means, D_{gv} , D_{gn} , and D_{gs} , are different but related:

$$D_{gv} = D_{gs} \sigma_g^{\ln \sigma_g} = D_{gn} \sigma_g^{3 \ln \sigma_g} \quad (17)$$

Note that $\ln \sigma_g$ is the natural logarithm, not the base 10 logarithm. The importance of Eq. 17 is that once the lognormal parameters are determined for one distribution, say, the volume distribution $P_v(D)$, then the distributions of particle surface area and particle number can be derived. These size distributions plot on graphical coordinates as straight lines having the same slope.

The normalization quantities, V_n , N_n , and S_n , of Eqs. 14, 15, and 16 are also mathematically related (as the moments of a normal probability function). This relation is

$$N_n = \frac{a_v \sigma_g^{4.5 \ln \sigma_g}}{D_{gv}} = \frac{a_s \sigma_g^{4.0 \ln \sigma_g}}{D_{gs}} \quad (18)$$

where a_v and a_s are the mean shape factors for volume and surface area, respectively. These shape factors are independent of particle size, but may depend on the material and the method of particle size measurement. They are determined empirically. Of particular importance is the ratio of surface area to volume (or mass) for fracture particulates. In the above nomenclature, this ratio $S(D)/V(D)$ is

$$\frac{S(D)}{V(D)} = \frac{P_s(D) S_n}{P_v(D) V_n} = \frac{P(U_s) S_n}{P(U_v) V_n} = \frac{a_s \sigma_g^{0.5 \ln \sigma_g}}{a_v D_g} \quad (19)$$

As the above relationships show, lognormal size analysis can give a complete geometrical characterization of the fracture particulate in terms of the two geometric parameters, D_g and σ_g , and the two shape factors, a_v and a_s . Further discussion of these is given in [MECHAM].

IV. FLUIDS IN ROCK (M. G. Seitz and J. Dunning*)

A. Introduction

The objective of this work is to investigate the application of nuclear logging methods for determining residual oil saturation (SOR) of depleted oil wells, to assess their limitations, to evaluate their accuracy, and to propose improvements. The effort includes a literature search, detailed studies, and a laboratory investigation to verify whether or not such techniques are feasible; if they are feasible, recommendations are to be made on field testing and additional developmental work needed for commercial applications. This effort is part of the Oil Well Logging Program sponsored by the Bartlesville Energy Technology Center.

The project technical activities completed this quarter covered the following two topics:

1. Development of a proposed experimental plan to translate the suggested log-inject-log method[†] to a tangible set of reservoir materials, i.e., rock, aqueous fluid, and petroleum.
2. The development of a computer program to identify characteristic elements or ratios of elements in aqueous fluids that correlate with rock type in oil reservoirs.

B. Proposed Experimental Series

The purpose of the experimental series described here is to translate the log-(gamma inject)-log method of SOR determination to a tangible set of reservoir materials. Uncertainties associated with the determination of detection factor, displacement efficiency, and statistical error can be quantified experimentally. The effect of oil-water stratification and interaction of the radionuclide with the rock can be assessed. Based on the results of the experimental series, a realistic estimate of the practicality of the proposed logging method can be made. The proposed test plan considers a reservoir factor (counting efficiency) for each radionuclide and accounts for reservoir fluid displacement efficiencies of less than 100%.

To account for the displacement efficiency, the efficiency term, E_m , is included in calculating SOR. The displacement efficiency is related to the capillary number, N_{ca} , which in turn is related to the injection fluid viscosity, the injection velocity, the reservoir porosity, and the oil-water surface tension. This implies that the fluid viscosity, fluid injection rate, and oil-water surface tension must be controlled in the experimental series.

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[†]The log-inject-log method consists of (1) injecting a solution containing a noninteracting radiochemical into a reservoir, (2) logging the bore hole with a gamma detector, (3) injecting a solution containing another radiochemical into the reservoir, and (4) logging the bore hole again.

The core flood tests proposed in this experimental series consist of establishing in one set of four cores a known residual oil saturation, and establishing zero residual oil saturation in another set of four cores. The cores are injected with a solution containing a radiochemical, and the gamma-ray signals (detected outside the holders) are compared to determine the net signal resulting from the residual oil in the four cores with a known residual oil saturation. Calculation of the residual oil saturation in the cores from the net signal will be attempted. Both low and high injection rates will be used. The experiments will be run in duplicate to minimize the effect of variations in the rock cores. The proposed experimental series is shown in Table 16.

Table 16. Experiments Using a Low-Viscosity, Low Oil-Water Surface Tension Fluid

Core Number	Oil Saturation ^a	Fluid Injection Rate
1	residual	high
2	residual	low
3	residual	high
4	residual	low
5	none	high
6	none	low
7	none	high
8	none	low

^a"Residual" indicates the oil remaining after the cores are flooded with water. "None" indicates that no oil was introduced into the core.

1. Injection Fluid

One injection fluid with high viscosity and high fluid-oil interfacial surface tension will be chosen. The medium will be injected into a total of sixteen cores of Berea sandstone at two significantly different injection rates. This procedure replaced the originally considered use of two fluids having different properties. (Using two injection media with large differences in viscosity and surface tension would allow the relation of displacement efficiency to viscosity and surface tension to be tested. However, the use of two fluids was precluded by a need to limit the size of the test program.) Even though only one fluid was used, modification of the log-(gamma inject)-log method allowed post-test evaluations of actual displacement efficiency to be incorporated into the evaluation of SOR.

2. Injection Rates

Two significantly different fluid injection rates will be employed in the tests. Which flow rates are chosen is dependent on the injection medium chosen. In Fig. 21, the effect of capillary number, N_{ca} , on displacement efficiency is shown. Below $N_{ca} = 10^{-4}$, displacement efficiency is 50%; above $N_{ca} = 10^{-4}$, displacement efficiency rises sharply. For (1) a given injection medium having a specified viscosity and interfacial surface tension (2) and a rock with a given porosity, the injection rates must be chosen such that for the low flow rate, the capillary number is below the inflection point at N_{ca} equal to 10^{-4} , and for the high flow rate, the capillary number is above this inflection point.

Fig. 21. Correlation of Displacement Efficiency with Capillary Number for Typical Injection Fluids (after [MELROSE]). Upper curve is for a narrow range of pore sizes; the lower curve is for a wide range of pore sizes.

C. Geochemical Characterization Relevant to Nuclear Logging

A computer program was designed and developed this quarter to identify characteristic elements or ratios of elements in aqueous fluids that correlate with rock type in oil reservoirs. The program produces seven matrices containing the elemental analyses of up to 200 reservoir fluids (for each of the seven rock types), and calculates the element ratios for elements selected by the user. The user may select up to 20 pairs of elements, which are then plotted by the program, with each rock type represented by a specific symbol. The user-interactive nature of the program improves its cost effectiveness.

compared with a noninteractive program which would plot all possible element and elemental ratio combinations (a total of greater than 11 factorial). The element concentrations or element ratios are plotted on paper having 3×3 to 7×7 log cycle scales, depending on the ranges of the element concentrations and the element ratios.

The program uses the chemical symbols for the elements, aluminum, bromine, calcium, chlorine, lithium, and strontium. The program uses the two-letter designations PT, FL, ST, SD, and OH for the solution species potassium, fluorine, sulfate, sulfide, and hydroxide, respectively. A redrawn version of the computer output is illustrated in Fig. 22.

Fig. 22. Plot of Element Ratios to Determine Grouping of Reservoir Fluid Compositions According to Reservoir Rock Type

The best grouping relating reservoir rock type to fluid composition is the iodine-bromine plot [STEINDLER-1981B].

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

A. Introduction

There is considerable interest in the composition of groundwater from igneous rocks in connection with geologic storage of high-level radioactive waste. This subject is also of considerable geochemical interest. For example, recent work [FRITZ-1979, 1980] has shown the existence of old CaCl_2 brine as groundwater in Precambrian granitic rocks of the Canadian Shield. This groundwater has been studied extensively and is thought to be the reaction product of normal groundwater and granitic rocks during a very long contact period [FRITZ-1979, 1980].

Groundwater samples are difficult and expensive to obtain from deep-seated igneous rocks. Samples can generally be obtained from wells or tunnels which cut fracture zones, although there is always the danger of contamination. Careful sampling is required, and long pumping times may be necessary.

Many studies of interstitial water in sediments, e.g., [COUTURE], suggest that it may be possible to extract uncontaminated pore fluid from cores of igneous rock. In favorable cases, a small amount of water may actually be squeezed out. More commonly, it should be possible to elute the pore fluid with distilled water. The technique is potentially very valuable; in many cases, it may be possible to determine groundwater composition from rock samples, whereas sampling of well water is difficult and expensive. Moreover, the technique is likely to work best in nearly impermeable rocks from which sampling of groundwater by conventional techniques is nearly impossible.

Elution may be a useful technique for studying the transport of dissolved materials through rocks. Transport of dissolved materials is also of great interest in relation to radioactive waste disposal. The problem has been the subject of several theoretical studies [e.g., GRISAK-1980A, 1980B, 1980C, 1981; NERETNIEKS-1979, 1980] and field studies [LANDSTROM, CATHLES]. The theoretical work has suggested that diffusion from cracks into the rock matrix may be an important factor in the mechanism retarding transport, but there has been very little laboratory work on solute transport through igneous rocks.

Cores of Precambrian granite from Northern Illinois drill hole UPH-3 were obtained in order to test these ideas. A fairly impermeable rock core (from 1288 m below the surface) was selected and prepared, and a special core holder was built for elution. We report here the composition of the pore fluid and discuss its origin, and we briefly consider the theory of transport through rocks by flow and diffusion.

B. Experimental Methods

The rock core is 4.70 cm in diameter by 8.61 cm long. The side was sanded to remove a shattered surface layer and to make possible a good seal. Distilled water was the only cutting lubricant used in preparation of the core.

The core holder consists of two cylindrical end plates with zero-dead-volume fittings. Teflon tape is wrapped around the cylinder of rock, and a tight butyl rubber sleeve (bicycle tire inner tube) is placed over the rock and the end plates. The sleeve is cemented to the end plates, capillary tubing is fitted to the end plates, and the assembly is placed in a pressure vessel. The result is a totally enclosed rock cylinder with capillary tubes leading to the ends.

The end plates are constructed of stainless steel (type 316); the inlet tubing is stainless steel and has an inner diameter of 0.25 mm; and the exit tubing is glass-lined steel with an inner diameter of 0.3 mm. The corrosion resistance of stainless steel has proved to be adequate so far.

Deionized water was pumped through the core under 3.4-MPa pressure. Confining pressure was 6.9 MPa. The temperature was controlled at 25.0°C.

The index of refraction of the eluate was determined at ambient temperature with an Abbe refractometer. Chloride in the eluate was determined by Mohr titration on 5-50 μL aliquants. Samples of eluate were submitted for analysis by emission spectroscopy, atomic emission spectroscopy, and ion chromatography (for anions); fraction 10 was analyzed with a fluoride-specific electrode.

C. Results

The results are quite surprising. The analyses in Tables 17 and 18 demonstrate that the pore water is NaCl-CaCl_2 brine. The anion/cation balance of the analyses is good. The presence of large concentrations of fluoride was confirmed by analysis of fraction 10 with an electrode.

The actual salinity of the pore water can be presumed to be higher, possibly much higher, than that of the first fraction. Additional evidence (not yet available) is required to deduce the actual composition of the pore water.

Flow was interrupted three times. Flow was interrupted overnight after fraction 4. At that point the salinity of the eluate increased because of diffusion of salt in the rock pores (Table 17). After fraction 11, flow was interrupted for three days, another 90 μL of deionized water was pumped, flow was interrupted for another 37 days, and finally pumping was resumed briefly. However, the results for pumping after fraction 11 are not given in Table 17. Then the column was dismantled, and fluid on the top of the core was sampled. Its index of refraction was 1.3347, indicating that $[\text{Cl}^-] \approx 0.14\text{M}$. The conclusion is that salt continuously diffused out of the pores, and that diffusion-accessible pores constitute a significant reservoir.

The permeability decreased markedly after overnight exposure to fresh water. Figure 23 suggests that flow rate parallels Cl^- concentration, although Cl^- concentration is not the only important factor. The permeability of the granite dropped by another order of magnitude following the interruption after fraction 11 (not shown). An attempt was made to restore the original high permeability by pumping first 0.5M NaCl solution through the rock, and then a solution containing 1M NaCl + 0.1M CaCl_2 . However, the permeability remained low. A likely interpretation is that the main channels through the

Table 17. Analyses of Solutions Eluted from Precambrian Granite with Deionized Water. Core from 1288 m below the surface, Northern Illinois drill hole UPH-3; in-situ temperature = 36°C.

Fraction No.	Mass, g	Ca, mM	Mg, mM	Na, M	Cl, M	F, mM	Br, mM	NO ₃ , mM	SO ₄ , mM	Refractive Index	Anions Cations
1	0.098	10.9	1.4	0.204	0.245					1.3360	
2	0.125	15.6	2.0	0.139	0.162	3.3	0.23	0.19	3.01	1.3350	0.99
3	0.102	10.5 ^a	1.0 ^a	0.109 ^a	0.136	2.2 ^a	0.16 ^a	0.15 ^a	2.22 ^a	1.3348	1.03 ^a
4	0.090				0.122					1.3342	
5	0.321	11.7	1.4	0.109	0.137	3.5	0.19	0.15	2.46	1.3347	1.07
6	0.619	4.0	0.7	0.052	0.0552	0.5	0.08	0.05	1.28	1.3336	0.95
7	1.809	0.95	0.8	0.021	0.0212	0.4	0.06	0.05	0.65	1.3330	1.00
8	0.271				0.0140					1.3330	
9	0.544				0.0101					1.3330	
10	2.511				0.0077	0.32 ± 0.05				1.3330	
11	3.786				0.0055					1.3330	
H ₂ O										1.3329- 1.3330	

^aEqual volumes of fractions 3 and 4.

Table 18. Spectrochemical Analyses of Eluate from Rock Core.
Units are mg/L. Accuracy = factor of 2.

Element	Fraction No.					Blank
	2	3 and 4 ^a	5	6	11	
Ag	<5	<5	<2	<1	<0.2	
Al	<10	<10	<5	<1	(0.5)	<0.2
B	<50	<50	<20	<10	<2	
Ba	<10	<10	<5	<2	<0.5	
Be	<0.1	<0.1	<0.05	<0.02	<0.005	
Bi	<50	<50	<20	<10	<2	
Ca	1000	1000	800	300	15	<0.2
Co	<10	<10	<5	<2	<0.5	
Cr	<2	<2	<1	<0.5	<0.1	
Fe	<20	1000	<10	<5	<1	<0.5
K	100	80	30	10	1	<0.2
Li	<0.5	<0.5	<0.2	<0.1	<0.02	
Rb	<10	<10	<5	<2	<0.5	
Cs	<100	<100	<50	<20	<5	
Ga	<10	<10	<5	<2	<0.5	
Mg	100	80	60	15	1	<0.1
Mn	<10	<10	<5	<2	<0.5	
Mo	<10	<10	<5	<2	<0.5	
Na	5000	5000	4000	400	200	<0.5
Ni	<5	<5	<2	<0.5	<0.2	
Pb	<50	<50	<20	<10	<2	
Sn	<50	<50	<20	<10	<2	
Sr	15	15	10	2	0.1	<0.01
Ti	<2	<2	<1	<0.5	<0.1	
V	<10	<10	<5	<2	<0.5	
Zn	<100	<100	<50	<20	<5	
Zr	<2	<2	<1	<0.5	<0.1	
Y	<1	<1	<0.5	<0.2	<0.05	
Sc	<1	<1	<0.5	<0.2	<0.05	
La	<5	<5	<2	<0.1	<0.2	

^aMixed in equal proportions.

Fig. 23. Flow Rate vs. Cl^- Concentration during Elution of Pore Water from Granite. Core from 1288 m below surface, hole UPH-3.

rock were permanently blocked by the swelling of clays in fresh water. An alternative explanation is that the channels closed slowly in response to confining pressure or that leakage around the rock core decreased with time, but this does not explain the increase in flow rate after fraction 4.

D. On the Possibility of Contamination during Drilling

We regard it as very unlikely that the granite could have been contaminated during drilling. We have conducted analyses of the drilling fluid and of water sampled in the well after completion of the hole.

Contamination is discussed here because other scientists have expressed a concern that our water samples might be contaminated.

According to Tom Baldwin, the driller, the drilling fluid consisted of 1.9 L (two quarts) each of FD-1 and FD-2 (Fluid-Drill Corporation) to 1130 L (300 gal) of Lena, Illinois, municipal water. FD-1 is degradable polyacrylamide plus KCl (according to Clarence Zink, Fluid-Drill Corp.). FD-2 is polyacrylamide in mineral oil. A chloride analysis shows that FD-1 is about 83% sylvite (KCl). FD-1 has a bulk density of about 1.06 g/mL. The sylvite contains an appreciable quantity of hematite (Fe_2O_3), which is clearly visible. X-ray fluorescence shows the presence of K, Cl, Fe, Br, Mn, and S in FD-1. FD-2 has a Cl^- content of 0.06 mol/kg. An analysis of Lena municipal water is shown in Table 19.

Table 19. Analysis of Lena, Illinois Municipal Water, Used for Drilling Fluid for Hole UPH-3. Source: town of Lena.

Na	0.28 <u>mM</u>
K	0.046 <u>mM</u>
Ca	2.4 (3.7) ^a <u>mM</u>
Mg	0.19 <u>mM</u>
Fe	0.012 <u>mM</u>
Cl	0.27 <u>mM</u>
SO ₄	0.34 <u>mM</u>
F	0.054 <u>mM</u>
Alkalinity	7.65 meq/L
pH	7.4
Total anions	8.7 meq/L
Total cations	5.4 meq/L

^aValue in parentheses calculated from hardness and Mg concentration. Indicates a calculation error, with 3.7 the preferred figure.

Thus, the drilling fluid was about 0.02M in KCl. Since we know that the chloride concentration was at least 0.24M and the K/Cl mole ratio was about 0.01 in the pore water, the high salt content of the pore water could not be due to contamination during drilling.

After completion of the hole (and possibly after flushing with water), a water sample was taken by James Scott of the U.S. Geological Survey. The resistivity was reportedly 10.5 $\Omega \cdot m$, compared with 15 $\Omega \cdot m$ for Lena municipal water. The chloride concentration was 0.0031M (our titration), compared with 0.00027M for Lena water. Thus, we have no evidence of another source of contamination.

We also present here another argument against contamination. The drilling fluid pressure was 200-300 psi (1.4 to 2.1 MPa, or 14 to 21 bars) at the surface; this equals approximately the pressure drop across the drill bit. The pore pressure in the granite is not known. However, assume a maximum depth of 300 m for the water table. The depth from which the core was taken

was 1288 m, and so the head was a minimum of $1288 - 300 = 988$ m, giving a pore pressure of ≥ 9.7 MPa. The drilling fluid pressure at the drill bit was 14.3 MPa. Thus the difference between drilling fluid pressure and pore pressure is estimated to be ≤ 4.6 MPa.

The amount of flow of drilling fluid into the granite during coring is, of course, difficult to calculate exactly, but a qualitative idea is given by elution experiment results. At a pressure drop of 3.4 MPa across an 8.6-cm-long core, about 5 h was required for the concentration of the eluate to decrease by half (Fig. 23). In contrast, the granite formation is so thick that the only flow should be transient flow allowed by the compressibility of water. The transient solution to the flow equation, shown in Appendix A, indicates that the boundary between injected water and pore water is expected to move much more slowly than the drilling rate.

E. Discussion

The composition of the pore fluid has been altered somewhat by extraction from the core. In Table 20, the concentrations of the ions are normalized against Cl^- . Dilution causes the Ca/Cl ratio to fall and the SO_4/Cl and Na/Cl ratios to rise. This suggests that the fluid might be influenced by dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and by ion exchange on clays (dissolved Ca^{2+} exchanging for bound Na^+ ion in response to dilution). The behavior of other ions may be obscured by analytical scatter.

Table 20. Normalized Compositions of Eluate Solutions.
Data from Table 19.

Fraction	Cl	Na/Cl	Ca/Cl	Mg/Cl	SO_4/Cl	F/Cl
1	0.245	0.83	0.053	0.006		
2	0.162	0.86	0.096	0.012	0.019	0.020
3 and 4 ^a	0.129	0.84	0.081	0.007	0.017	0.017
5	0.137	0.80	0.085	0.013	0.018	0.026
6	0.055	0.94	0.072	0.013	0.023	0.009
7	0.021	0.99	0.045	0.038	0.031	0.019
10	0.008					0.042

^aIn equal proportions.

The possible dissolution of insoluble salts during elution is suggested by saturation calculations for fraction 2. Using the Debye-Hückel law, ion activity coefficients were estimated, and solubility products were calculated. These were compared with values from the literature. The results, shown below, suggest that salts might have dissolved. The numbers suggest that

$$[\text{Ca}^{2+}] [\text{F}^{-}]^2 = 678 K_{\text{sp}}$$

$$[\text{Mg}^{2+}] [\text{F}^{-}]^2 = 0.07 K_{\text{sp}}$$

$$[\text{Ca}^{2+}] [\text{SO}_4^{\equiv}] = 0.18 K_{\text{sp}}$$

the leachate is roughly at or slightly below saturation with respect to fluorite (CaF_2), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and possibly sellaite (MgF_2). The presence of one of these minerals would result in undersaturation in the eluate because the rock was being flushed with deionized water. The pore water may actually be saturated with respect to one or more of these minerals.

The presence of high concentrations of fluoride and calcium is surprising, since fluorite (CaF_2) is very insoluble. This suggests that fluoride is complexed. However, boron is undetectable at concentrations of up to 50 ppm, and we consider it to be the most likely complexing agent.

The water is extraordinarily high in fluoride (Table 17). Concentrations were as high as $3.3 \times 10^{-3}\text{M}$ (62 ppm). Such high concentrations are rarely observed in nature. Concentrations of $3.5 \times 10^{-3}\text{M}$ and $42 \times 10^{-3}\text{M}$ were reported in highly acidic lakes in andesitic volcanos [WHITE]. Concentrations of $0.6 \times 10^{-3}\text{M}$ to $1.3 \times 10^{-3}\text{M}$ are occasionally observed in hot springs [WHITE], of which some are associated with granitic magmatism. We might have sampled pore water locked in the granite since its formation! There is also the chance that we sampled liquid inclusions which were released during formation of the fractures (at an undetermined time in the past).

The origin of the water is not yet clear. The water may be analogous to CaCl_2 -NaCl brine in granitic rocks of the Canadian Shield, or it may have been derived from overlying sediments. Concentrated brine, predominantly NaCl solutions, underlies fresh water in most of central, southern, and northern Illinois [ILLINOIS, MEENTS]. Resistivity logs taken in hole UPH-3 suggest that brine is absent from the sediments at that location, but the bottom 11 m of the sedimentary section was not logged [COATES]. In north central Illinois, the brine is probably very deep, if present at all. However, there is a report [BROWER] of a well in Winnebago Co. (Sect. 24, T. 44N, R2E, CO well #1), to the east of UPH-3, in which a salinity of 62,000 ppm was recorded at 809 m (about 1.5 m above the contact with granite).

F. Condensed Theory of Mass Transport through Porous Media; the Role of Diffusion

Transport through rocks by advection and diffusion has been considered in detail by Neretnieks [NERETNIEKS-1980] and by Grisak and Pickens [GRISAK-1980A, 1981]. Neretnieks [NERETNIEKS-1980] and Grisak and Pickens [GRISAK-1981] presented an analytical solution to the equation of transport, which assumes flow through parallel, widely spaced fissures and diffusion into the rock matrix perpendicular to the direction of flow. Grisak and Pickens [GRISAK-1980A] have presented a more general numerical model, which (1)

allows flow also through the matrix (not just the fissures), (2) takes into account diffusion in the direction of flow, and (3) does not require widely spaced fissures. If fissures are closely spaced, it is assumed that solute will eventually diffuse from adjacent cracks in both directions, allowing the solute to become uniformly distributed throughout the rock pores. Neither model allows diffusion into dead-end spaces, and this may be a significant limitation.

[NERETNIEKS-1980] has expended considerable effort to make realistic calculations for granitic rocks, based on various parameters in the literature. Grisak and Pickens [GRISAK-1980B] have used their model to evaluate their experimental results on transport through fractured till.

In spite of its limitations, the analytical solution offers considerable insight, and in some cases the limitations may not be significant. Diffusion in the direction of flow may not be important, and fractures may not be very closely spaced. We derive here some useful corollaries of the analytical solution and consider data from the rock core we have tested. For brevity, we omit much of the derivations.

For flow through fissures with velocity u in the x direction for an initial pulse of solute at concentration c_0 for time Δt , the solute concentration c in the fissures is given by

$$\frac{c}{c_0} = \operatorname{erfc} \frac{G}{\left(t - \frac{x}{u}\right)^{1/2}} - \operatorname{erfc} \frac{G}{\left(t - \frac{x}{u} - \Delta t\right)^{1/2}}, \quad (1)$$

$$\text{where } \operatorname{erfc} z = \frac{2}{\sqrt{\pi}} \int_z^{\infty} e^{-n^2} dn$$

t = time

x = distance

u = velocity in fissures

$$G = \frac{x}{2ub} (D_e)^{1/2} [\epsilon + (1 - \epsilon) K_d \rho]^{1/2}$$

K_d = distribution coefficient

$2b$ = fissure width

ϵ = porosity

ρ = bulk density of unfissured rock

D_e = effective diffusion coefficient

The value of D_e can be found from

$D_e = D \frac{\epsilon \delta}{\tau}$, where D = diffusion coefficient and $\frac{\epsilon \delta}{\tau}$ = the formation factor.

For sustained injection of solutes, Δt is large, and the second term of the solution approaches 0.

For short Δt (spike injection), we have expanded the solution as a Maclaurin series in Δt , and we get

$$\frac{c}{c_0} \approx \frac{\Delta t}{\sqrt{\pi}} \frac{G}{\left(t - \frac{x}{u}\right)^{3/2}} \exp \frac{-G^2}{\left(t - \frac{x}{u}\right)}. \quad (2)$$

From Eq. 1, we can find the migration distance of a front as a function of time, for a given concentration. For $\frac{c}{c_0} = \text{constant}$, $\frac{G}{t - \frac{x}{u}}^{1/2}$ is constant,

and $t - \frac{x}{u} = AG^2$, where A is a constant. For $\frac{c}{c_0} = 1/2$,

$$t - \frac{x}{u} = 2.20 G^2. \quad (3)$$

For impermeable rocks with small cracks, c is significant only at $t \gg x/u$, and $G = x/u$, so

$$t = x^2/u^2. \quad (4)$$

This is a very surprising result, which states that the distance traveled is proportional to the square root of time and inversely proportional to the square of the flow rate.

We find a similar result for a spike concentration. If $\left(\frac{\partial c}{\partial t}\right)_x = 0$, it can also be shown that the position of the peak is given by

$$t - \frac{x}{u} = 2/3 G^2. \quad (5)$$

This is very similar to Eq. 3 and shows that the peak position is proportional to the square root of time.

For $t \gg \frac{x}{u}$ the peak velocity is given by

$$\frac{dx}{dt} \approx \frac{3b^2 u^2}{D_e [\epsilon + (1 - \epsilon) K_d \rho]}. \quad (6)$$

This is equally surprising, since it shows that the peak velocity is proportional to the square of the flow velocity. The physical significance is that the solute can migrate in the direction of flow only when it is in the fissure, and the faster the flow velocity, the less important is diffusion into the matrix.

Incidentally, for constant concentration, c , with large Δt , the front velocity can also be calculated from

$$\frac{dx}{dt} = \frac{x}{2\left(t - \frac{x}{u}\right)}. \quad (7)$$

Of course, these equations are not valid if diffusion profiles in the pore fluid overlap between adjacent fissures or if diffusion is stopped by the walls of dead-end pores. The first of these conditions is expected at very slow flow rates or at great time and distance from the origin. If the accessible pores are completely permeated, then of course the solute behaves as if there were flow through the entire accessible matrix. Diffusion then plays no discernable role, and peaks migrate at constant speed.

If the peak velocity is indeed not constant, there is a practical significance from the experimental point of view. It means that transport is faster on a laboratory scale than on a field scale and is likely to be amenable to study.

Equations 3, 5, or 6 might be quite useable for testing the assumptions. It is of considerable importance to verify these equations with rock samples. Work in progress with granite cores will, hopefully, allow us to test Eq. 6.

It should be pointed out here that variable path length is not explicitly taken into consideration with either of the models mentioned. We have not determined the effect of a spectrum of path lengths on the solution. The effect does not appear to be analytically simple. It is known that dispersion in the path length produces asymmetrical elution curves [WEBSTER, NERETNIEKS-1979], as does diffusion.

G. Comparison of Equation 1 with Experimental Results from Granite

Equation 1 can be tested by estimating parameters for the granite, using procedures and data compiled by [NERETNIEKS-1980] from measurements of porosity and electrical conductivity. Assume typical values of $\frac{\epsilon \delta}{\tau^2} = 10^{-3}$, and $\epsilon = 5 \times 10^{-3}$. Permeability was initially 3.7×10^{-12} m/s. If a fracture spacing of 1 cm is assumed, we calculate a fracture width of 0.33 μm and a fracture velocity, u , of 4.3×10^{-6} m/s (from Neretnieks' Equations 18 and 19 [NERETNIEKS-1980]) for the applied pressure difference of 3.4 MPa (34 bars). For diffusion of NaCl, $D = 1.5 \times 10^{-5}$ cm²/s.

We calculate that elution (to 50% concentration) should take 6×10^7 s, or about 2 y, compared to the observed 5 h. Clearly, there is something we

don't understand about the experiment or about the internal pore spaces of the rock! This result does not appear to be very sensitive to the parameters assumed.

We know that diffusion from the pores is important, since the concentration of salt builds up in the fissure after flow is stopped, as described above. Possibly, there is rapid diffusion from small pores and slower diffusion from much larger pores. Alternatively, the water may flow through a large fraction of the accessible rock matrix, thereby quickly flushing out the salt.

VI. LIGHT WATER BREEDER REACTOR PROOF-OF-BREEDING ANALYTICAL SUPPORT PROJECT
(N. M. Levitz, T. F. Cannon, G. L. Chapman, P. G. Deeken, R. E. Nelson,
John Osudar,* J. E. Parks, L. E. Trevorow, C. G. Wach, I. O. Winsch,
J. F. Fagan, Henry Lautermilch, R. E. Brock, and R. J. Meyer)

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

Assembly and testing of the full-scale shear (FSS) were completed successfully in an out-of-cell mockup area during the report period. Completed in the mockup area were final fitup, assembly, and testing of shear components, as well as a series of shearing tests, using fully automated operations. Work in the mockup area constituted the necessary thorough checkout of the shear's mechanical, electrical, pneumatic, and hydraulic systems prior to installation of the assembly in the shielded cell.

A redesigned fuel rod weighing system was fabricated and installed on the shear feed system base. The system incorporates two high-capacity electronic balances to weigh the 3-m-long rods prior to shearing. The combined capacity of the balances (each reading to 0.01 g) is 15 kg. Initial testing of the system showed it to have a reproducibility of ± 0.016 g, well within the 0.050-g precision requirement established for fuel rod weight determinations.

Test shearing of three full-length dummy fuel rods was completed. Two power-flattening blanket rods (1.34-cm or 0.526-in. dia) and one seed rod (0.778-cm or 0.306-in. dia) were sheared using new individual sets of shear tooling (each rod size has its own tooling); the flat-bottom blade was used in each case as was a slow shear speed, about 5 cm/s or about 2 ips. Each rod, consisting of Zircaloy-4 cladding loaded with magnesia pellets, was sheared using short cut lengths, approximately equal to one-half the rod diameter; this L/D ratio results in good fuel breakout from the hulls (cladding) and good pulverization, needed for rapid dissolution in the actual fuel case. All shear components worked properly, including an automated O-ring seal (where the fuel rod enters the shear die) that prevents fuel "blowout" losses.

Some modifications were made to the shear to improve remote handling and repair capabilities. These changes included modified fasteners for improved remote access, and jacking bolts, added to various components to ease disassembly. During this period, all spare shear components were tested for proper fit and operation.

Automation of the shear was significantly advanced. All shear controls were fully interfaced with the computer system via a computer automated measurement and control (CAMAC) module. Software development was advanced to the point where automated segment shearing was instituted. In this mode, the computer (1) controls feeding of the fuel rod into the shear, (2) monitors the rod position, (3) controls shearing, and (4) collects pertinent data such as cut location, shear blade position, and force. The program actually displays blade speed and a plot of shear blade position vs. time on the cathode ray tube (CRT) terminal (see Fig. 24). This plot is expected to be a valuable diagnostic tool for shear performance.

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

Fig. 24. Shear Blade Position vs. Time for a Single Cut on a Seed Rod. (Cut length = 0.38 cm or 0.150 in.) Total Time = 1.615 s. Average Speed = 2.3 cm/s or 0.906 in./s

With out-of-cell testing of the FSS now considered complete, preparations are being made for its installation in the shielded cell and final qualification testing.

B. Single Unit Dissolver (SUD)

(I. O. Winsch, T. F. Cannon, C. G. Wach, Henry Lautermilch, J. E. Parks, and R. E. Brock)

Testing of the single unit dissolver (SUD) with its associated components continued during this period with three additional exploratory ThO_2 dissolution tests (DD-4, -5, and -6). Testing and procedure development continued on sampling from the dissolver and blend tank, off-gas collection and sampling, blend tank and dissolver decontamination, and dissolver operations. Selected details of this and earlier work are reported.

Analytical results for three earlier ThO_2 dissolution tests, DD-1, -2, and -3, showed thorium recoveries of 95, 99.4, and 106%. The scatter in the data indicates that some improvements in sampling procedures may be needed; however, dissolutions are considered to have been complete since the analysis for thorium has a precision of about 3%.

In the two more recent exploratory dissolution tests, DD-4 and -5, a sheared full-length segment of either a seed or a reflector rod, which are 36 cm $\times$ 0.78-cm dia (14 in. $\times$ 0.306-in. dia) and 13.5 cm $\times$ 2.1-cm dia

(5.25 in. $\times$ 0.832-in. dia), respectively, was used as the charge to the dissolver; the dissolvant is Thorex solution, 13.6M HNO_3 -0.06M HF. The feasibility of sampling the dissolver off-gas system for gaseous fission products was also explored in these two runs. At the start of the 4-h primary dissolution, known quantities of nonradioactive krypton were charged to the dissolver along with air for pressurization.

Thorium recoveries for tests DD-4 and -5 were 99.3 and 97.9%, respectively, indicative of complete dissolution in each case. Preliminary krypton material balances gave values of about 90 and 110%, indicating that a satisfactory sampling and analytical method can be developed for ^{85}Kr and possibly other gaseous fission products in end-of-life (EOL) dissolver off-gas.

In the next test, DD-6, a stack of five whole reflector-size thorium pellets (1.9-cm $\times$ 1.9-cm or 3/4-in. $\times$ 3/4-in. right cylinders) was charged to get some baseline data on penetration rates during the 4-h primary dissolution period. It was intended to use the results to gain insight into the problem of dissolving the extremely coarse particles produced in shearing, particularly in the shearing of reflector-size rods. Penetration after 4 h, based on crude dimensional measurement, ranged from about 0.32-cm (0.125 in.) for the upper two pellets in the stack to >0.635-cm (>0.25 in.) for the bottom pellet (which was in the most favorable position from a dissolution standpoint). Corresponding values for fraction dissolved (from weight differences) were 63% and 99%; the latter value suggests that dissolution time might be reduced significantly. Analysis of (1) the solution and (2) the difference in weights of the original charge and pellets residue gave a material balance of 102% of the amount of thorium charged. Further investigation to determine time requirements for the primary and secondary (cleanup) dissolution periods is likely.

Decontamination procedures for the stainless blend tanks (BTs), involving simple refluxing of nitric acid, were tested to show that BTs could be reused without suffering significant cross-contamination. Results appear promising, with decontamination factors of about 1×10^3 achieved by a procedure involving two sequential reflux periods and a final cold acid rinse.

The SUD has been redesigned to provide a close fitup at the lower portion of the stainless steel secondary vessel around the tantalum alloy dissolver vessel in order to permit the use of external heaters. The new system has been installed and will be tested with a series of acid boilup tests and thorium dissolution tests to evaluate the external heater system.

1. Blend Tanks (BTs)/Sampling

The status of blend tank development was reviewed, and items requiring redesign were identified--notably, O-ring seals, the sampling system, and the stirring system. Laboratory efforts have also been initiated toward testing mockups for an alternative sampling system; other work on blend tank redesign is being postponed. Highlights of current work in these areas are reported.

A weld sample of CPVC plastic material proposed for disposable blend tank liners was exposed to hot Thorex solution (13.6M HNO_3 , 0.06M HF). The CPVC plastic was unchanged by exposure to acid; the weld joint, however, failed within eight hours. As a result, work on the disposable blend tank liner concept has been stopped.

Work on the stirrer port seal was initiated when attack on the rubber O-ring in the stirrer port was observed after decontamination tests on the BT. A "bell-jar" seal, fabricated from a stainless steel beaker and rubber gasketing, has been tested as a replacement. In this concept, a gasketed metal can is fitted over the port during blend tank evacuation. Three types of gaskets were tested. An adequate seal could not be made from hard rubber channel gasketing or from a gasket formed by slitting soft rubber tubing. A satisfactory seal (38 kPa absolute pressure maintained overnight) was provided by a gasket formed on the rim of the metal can by applying three coats of plastic (PDS Air-Dry Plastic Coating, Formula #99, Plastic Dip International, St. Paul, Minn.). The "bell-jar" can be installed and removed easily with M/S manipulators. Refinement of this device is planned.

Because interaction between the magnetic stirring bar in the blend tank and the coil in the combination magnetic mixer/hot plate (which is a part of the total weighing system) gave erratic blend tank weight data, a decision was made to change the mixing device in the blend tank from a magnetic stirrer to a direct motor-driven mixer. It is also planned to add a baffle assembly to the blend tank prior to the next series of BT tests.

Two concepts for remotely sampling the blend tank were mocked up and tested during March. In one concept, liquid was withdrawn into a pipet (fashioned from a 60-mL disposable syringe body) and then dispensed into three sample vials. In the second concept, the liquid was transferred directly into the sample vial. Addition and removal of liquid were finely controlled. A Gilson peristaltic pump (Minipuls II, Gilson Medical Electronics, Inc., Middleton, Wisc.) provided a remotely controllable vacuum source for each sampling concept. The second sampling concept was found to be superior from the standpoints of ease of operation, ease of fabrication, and cost of disposable components and will be pursued.

The polyethylene sample vials used in the pilot-scale work leaked after standing filled with radioactive dissolver solution for about one year, whereupon a search was initiated for suitable vials for blend tank solution samples. Heavy-wall glass vials were suggested by the laboratory staff at ANL-W. In order to mitigate against contamination in the event of broken vials, a safety coating of plastic has been proposed. A commercial coating material (PDS Air-Dry Plastic Coating, Formula #99, Plastic Dip International, St. Paul, Minn.) has been procured, and evaluation tests have been planned. A vendor (Wheaton Glass Co., Des Plaines, Ill.) has been identified who can apply the coating to the large number (3000-4000) of vials required.

Preliminary determination of the temperature sensitivity of the blend tank balance (Model #PS-30, with remote readout, 30-kg capacity, Mettler Instrument Co., Hightstown, NJ) indicated a weight-temperature relationship of about $-0.5 \text{ g/}^{\circ}\text{C}$. Conditions for the tests were as follows: the Rotron blower (Model #021571, Rotron, Inc., Woodstock, NY) on the balance temperature control system was modified to permit continuous operation at reduced air flow rates, and thermocouples were installed in the forward and aft internal balance compartments. These thermocouples, as well as the two in the balance well, were connected to a multipoint recorder and provided accurate monitoring of the balance response to temperature fluctuations. During actual operations, it is intended that each weighing operation be carried out under near-steady temperature conditions.

C. Multiple-Dissolver System (MDS)

(I. O. Winsch, T. F. Cannon, C. G. Wach, Henry Lautermilch, and J. E. Parks)

For the EOL campaign, four dissolvers similar to that developed as the SUD will be operated in a shielded cell. This equipment will be used for the dissolution of some 300 segments from 33 LWBR fuel rods. Major activity of this subtask (centered in the ANL Engineering Division) is in the design of components other than the four primary tantalum vessels, which are on hand. Completion of major design work on remaining components during the next quarter is scheduled.

Chemical Engineering Division LWBR Project personnel made changes in the designs of the MDS off-gas system, acid transfer system, and dissolver condenser cooling system to effect cost savings.

Ultrasonic examination of the welds on the four tantalum-alloy dissolver vessels for the MDS was completed by ANL Quality Assurance Division (QAD). Out-of-specification undercutting, up to 15.5 mils, was found on many of the welds on three of the four vessels. Service life calculations were performed using the measured weld thickness and worst-case corrosion data. Although these calculations indicate that the undercut welds provide adequate material thickness to complete the presently projected number of dissolution runs, the possibility of weld repair on these vessels is being discussed with the vendor. The best of the four vessels is being used in further tests of the SUD setup.

D. Scrap and Waste

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

Current emphasis is being given to the development of a method to dispose of the highly radioactive analytical liquid residues from the dissolution of the EOL fuel rod segments. To facilitate shipment to a repository, it is planned to convert dissolver solution to solids by spray calcination. Recent activities associated with the calcination process and disposal of the product are reported.

Transport of dissolver solution from Cell M-1, which houses the MDS, to Cell M-4, which will house the calciner, by pumping it directly through tubing between the two cells, requires that the tubing in the corridor be shielded. Calculations indicated that the exposure dose rate at the surface of the shield could be restricted to about 100 mR/h by a 5-cm (2-in.) thickness of lead.

One option in the processing of the EOL dissolver solutions is denitration with formic acid prior to calcination, in order to enhance the retention of ruthenium in the calcine and to reduce corrosion in the calciner; the heat of this reaction is about -40 kcal/mol HNO_3 , necessitating the dissipation of heat. For the present, this step remains a secondary option.

Irradiated LWBR fuel emits radon-220 ($t_{1/2} = 60$ s), and it is important that a maximum of the decay of radon (released in the calcination cell) occur within the shielded area so that its solid daughters (which emit gammas of very high energy) are retained there. Data on the expected amounts of radon have been provided to the ANL Occupational Health and Safety Division (OHS) for an evaluation of two aspects of this problem: (1) whether it is necessary

to incorporate a surge tank to decrease the linear velocity of the calciner off-gas stream, and (2) the upper limit of fuel spillage (a source of radon) which can be allowed to accumulate on cell surfaces without exceeding the concentration guideline for emission of radon to the environment.

Disposal of the waste solution (a volume of about 20 L) produced in the pilot plant dissolution of the experimental GRIP-II (LWBR-type) rod was explored. Meetings of representatives of DOE-Chicago Operations and Regional Office (CORO) and Idaho Operations Office (DOE-ID) established that the waste is eligible for acceptance by the Radioactive Waste Management Complex (RWMC) on the Idaho site. Initial estimates of the expected gas-formation rate of this waste, however, indicate that water removal would be necessary to meet acceptance criteria.

It is important that the schedule for fuel receipt, shearing, dissolution, and analysis not be interrupted by temporary inability to process and ship dissolver wastes. Therefore, a survey of needs for interim liquid storage was begun, taking into account such factors as volume requirements, characteristics of equipment needed for containment and transfer, shielding, availability of appropriate storage areas, and criticality restrictions.

A reassessment of the option of shipping the dissolver wastes as liquid to a subcontractor who is capable of either solidifying them or storing them as liquids has been requested by DOE-Headquarters and is in progress. General Atomic (GA) is relicensing the Ft. St. Vrain spent fuel shipping cask to permit its use as an overpack in shipping small samples of high-level liquid waste. A GA representative suggested that the Ft. St. Vrain cask might be used as an overpack for a container with a volume of 100 L of liquid. Further assessment of this option will require authoritative interpretation of 10CFR (Code of Federal Regulations) and also the "Memoranda of Understanding" (documents filled by DOE on observance of NRC regulations in DOE activities) to determine whether ANL is constrained to solidify the dissolver wastes before shipping. The scheme would also require locating a subcontractor willing and able to receive and process or store the liquids.

Cleanout operations in Cell M-4 at the Shielded Cell Facility in the Chemistry Division, which is the intended location of the waste-treatment system, has resulted in the removal and packaging of all material and equipment that could be handled by manipulators. The next stage of cleanout will require manned entry for decontamination, cutting, and dismantling of larger items; this work is being deferred until FY 1982 because of budget considerations.

Investigation of the problem of disposal of the calcine continued. Communications continued with Rockwell-Hanford (R-H), the intended acceptor of the LWBR-POB calcined dissolver solution. Rockwell-Hanford is encouraging the use of a 380-kg (840-lb) total weight per package which allows additional shielding and in turn permits an increased payload per drum and a reduction in the total number of packages to be shipped. The most recent version of criteria for acceptance of waste by R-H, [MCCALL], has been received and is to be reviewed for impacts on plans for handling the LWBR-POB wastes.

An analysis of the waste characteristics, the licenses for existing transport hardware, DOT regulations, and Rockwell-Hanford acceptance criteria has resulted in a concept for packaging and transporting the calcined

dissolver solutions in a minimum number of packages. The calcine would be contained in a nest that includes a stainless primary vessel, a metal secondary vessel that qualifies as a Special Form Capsule, shielding, centering media, and a 55-gal drum. The drums would be transported within an Argonne M-3 bin, contained, in turn, within a "Polypanther" overpack. In this scheme, each drum could have a total weight up to 380 kg (840 lb), the Rockwell-Hanford acceptance limit, and contain up to 5000 Ci of mixed fission products. The primary and secondary vessels would be sealed by metal gaskets to avoid the high capital cost of a remote welding station.

An analysis of the manipulators needed to operate the waste-treatment equipment in the M-4 cell was made by the ANL Engineering Division (ANL-ENG). The number, location, and characteristics were specified for a desired set of manipulators and also for a set that would meet minimum requirements.

A simple tube furnace was set up to test the behavior of the packing media (Fe_2O_3) of the traps that are to be used to remove ruthenium from the calciner off-gas stream. These tests are intended to indicate whether major changes occur in the chemical and physical nature of the media when exposed to gaseous mixtures of HNO_3 -HF-water-air at 250°C.

To accommodate the postponed discharge of fuel from the LWBR, a new time and cost schedule was assembled for the design, fabrication, testing, installation, and decommissioning of the calcination system.

The design of major components of the calciner and off-gas system by ANL-ENG was brought to final form, at the layout stage, in discussions and agreements between Project and design personnel. These major components (calciner, scrubber, ruthenium traps, prototype canister, and primary heat exchanger) are to be tested in a mockup in Chemical Engineering Division (Bldg. 205). The designs are presently being detailed to produce fabrication drawings. Plans call for completing the procurement and fabrication of these components by the end of FY 1981. The layout of the piping and instrumentation (P&I) system is also considered to be in final form.

E. Computer System and Data Management (J. E. Parks)

An integrated computer system with essentially automatic data-acquisition and process-monitoring capabilities and some automatic process control functions is under development. The system is also intended to "manage" the data, including providing error analysis and summary analytical reports on individual segments. Activities in these areas, including work related to the FSS and SUD, are reported here. The bulk of the work, to date, has been done by members of the Chemical Engineering Division Computer Section under S. Gabelnick.

1. Full-Scale Shear (FSS) Support Work

a. Software

A demonstration and test program for operating the FSS was completed and used to demonstrate the system during a recent project review meeting. Although this program is not part of the EOL software, major portions

of the program, involving the shear feed/cut cycle and the can change-and-brush sequence, will be transferred to the FSS software for EOL operations. These two functions can now be executed via the computer. As described above, a CAMAC module was built (at ANL) and tested to provide timing signals used in measuring shear stroke speeds.

b. Error Analysis

In order to assure ANL's ability to meet Project requirements pertaining to errors in measurements, an approach has been taken which includes the following steps: (1) design, fabrication, and assembly of equipment, (2) development of operating procedures, (3) error analysis of Project subsystems (this process involves propagation of errors through the various equations which relate procedures and data to results; this error analysis permits identification of critical error sources), (4) experimental design for testing equipment and procedures, (5) execution and evaluation of tests, (6) modification of equipment and/or procedures to improve performance, followed by repeated testing and evaluation until requirements are met, (7) experimental design, execution and evaluation of system qualification tests, and (8) planning for quality control testing during operations and/or evaluation of data to ensure continued compliance with requirements. Pursuant to this concept, an error analysis on the operations related to the FSS was completed during March. Results of this error analysis were presented at a review meeting with BAPL and DOE-HQ personnel on March 10, 1981. This analysis identified (1) correlation of fuel rod temperatures between ANL and BAPL and (2) shear plane error [STEINDLER-1981B] as the two critical error sources in this operation. A plan for further work in these areas will be developed.

2. Single Unit Dissolver Support Work

The hardware interface devices between the Cell K-3 balances, the HP-67 calculator (product of Hewlett-Packard, Rolling Meadows, IL), and the PDP-11/23 computer (product of Digital Equipment Corp., Nashua, NH) were completed and installed in late March; minor malfunctions due to wiring and cable defects have been found and will be corrected in early April.

3. Miscellaneous

The basic systems software for the PDP-11/23 has been installed and tested except for two Digital Equipment Corp. (DEC) programs for records management and for supporting the CRT color terminals. Development of the applications software is continuing. The process signal monitoring program (MONITR) has been completed and adapted to the PDP-11/23. The Executive Operating Program is essentially complete, and incorporation of the operating procedures for the FSS and SUD is in progress.

The central shared processing unit, a VAX-11/780 computer (a DEC product), was received and made operational this quarter; it is located in Bldg. 205 (Chemical Engineering Division). Tie-in to the dedicated PDP-11/23 computer located near the shielded cell facility in Bldg. 200 will be delayed until next quarter.

Cross-connect tables (CCTs) documenting the as-built connections between the CAMAC systems and the in-cell equipment have been completed for

the FSS and have been partially completed for the SUD. The SUD CCT is stored on a PDP-11/23 computer, and tentative plans are being made to use this system for generation of all CCTs in the future. An analog signal table showing all analog signal sources from the SUD, together with precision estimates, has been prepared.

A terminal has been installed in Room M-021, Bldg. 200, and connected to the PDP-11/23. Further software development work can now be done directly on the Project computer.

F. Miscellaneous

Project status was reviewed by members of DOE-Nuclear Fuel Cycle Division (NFCD), DOE-Naval Reactors (NR), DOE-CORO, and BAPL at a meeting at ANL, March 10, 1981. At this meeting, DOE announced a 3-y (or possibly a 4-y) extension of the operating period for the LWBR, which in turn delays the EOL campaign at ANL for an approximately equivalent period of time, i.e., the first fuel will be received at ANL in early CY 1986. DOE requested that a draft plan to meet this new schedule be furnished by April 28, 1981, as well as estimates of cost impacts.

REFERENCES

BROWER

R. Brower, Illinois Geological Survey, oral communication.

CATHLES

L. M. Cathles, H. R. Spedden, and E. E. Malouf, A Tracer Technique to Measure the Diffusional Accessibility of Matrix Block Mineralization, Solution Mixing Symposium, AIME, F. F. Aplan, W. A. McKinney, and A. D. Pernichele, Eds., pp. 129-147 (1974).

COATS

M. S. Coats, Harza Engineering Co., oral communication.

COUTURE

R. A. Couture, R. S. Miller, and J. M. Gieskes, Interstitial Water and Mineralogical Studies, Log 41, Initial Reports of the Deep Sea Drilling Project, Vol. 41, Y. Lancelot and E. Seibold, Eds., U. S. Government Printing Office, Washington (1977).

CRANK

J. Crank, The Mathematics of Diffusion, Second Edition, Oxford University Press, London (1975).

DONVAN

J. A. Donovan, Factors Controlling Nitrate Cracking of Mild Steel, Proc. Conf. on Environmental Degradation of Engineering Materials, College of Engr., Virginia Tech., Blacksburg, VA, Oct. 10-12, 1977, pp. 185-188.

DP-80

Waste Management Program Technical Progress Report, January-March 1980 Savannah River Laboratory DP-80-125-1, p. 39 (September 1980); Waste Management Program Technical Progress Report, April-June 1980, Savannah River Laboratory, DP-80-152-2 (December 1980).

FRITZ-1979

P. Fritz and E. J. Reardon, Isotopic and Chemical Characteristics of Mine Waters in the Sudbury Area, Atomic Energy of Canada Limited, AECL-TR-35 (1979).

FRITZ-1980

P. Fritz and S. Frappe, Environmental Isotopes in Saline Ground Waters on the Canadian Shield, Abstract, American Geophys. Union 6th Ann. Midwest Meeting, Sept. 1980, p. 9.

GRISAK-1980A

G. E. Grisak and J. F. Pickens, Solute Transport Through Fractured Media. 1. The Effect of Matrix Diffusion, Water Resour. Res. 16, 719-730 (1980).

GRISAK-1980B

G. E. Grisak and J. F. Pickens, Solute Transport Through Fractured Media. 2. Column Study of Fractured Till, Water Resour. Res. 16, 731-739 (1980).

GRISAK-1980C

G. E. Grisak, Solute Tracer Tests in Fractured Media, Proc. Third International Well Testing Symp., pp. 1-4 (1980).

GRISAK-1981

G. E. Grisak and J. F. Pickens, An Analytical Solution for Solute Transport Through Fractured Media with Matrix Diffusion, J. Hydrol. in press.

ILLINOIS

Illinois State Water Survey and Hittman Associates, Feasibility Study on Desalting Brackish Water from the Mt. Simon Aquifer in Northeastern Illinois, Contract Publ. 153, Illinois State Water Survey, Urbana, IL (1973), 120 pp.

JOHNSON

E. R. Johnson and J. Forten, Radiation Induced Decomposition of Inorganic Nitrates, Discuss. Faraday Soc. 31, 238 (1961).

KRAMER

C. M. Kramer, W. H. Smyrl, and W. B. Estill, Corrosion of Fe Alloys in $\text{NaNO}_3\text{-KNO}_3\text{-NaNO}_2$ at 823 K, J. Mater. Energy Syst. 1, 59-65 (1980).

LAKOMKIN

I. G. Lakomkin, Tr. Leningr. Tekhnol. Inst. im Levsoveta 1956, No. 35, 34-71; C.A. 52, 9859a.

LANDSTRÖM

O. Landström, K. E. Holmberg, S. Westerberg, and C. E. Klockars, In-Situ Experiments on Nuclide Migration in Fractured Crystalline Rocks, Kaernbraenslesackerket Technical Report (1978).

MCCALL

D. H. McCall, Hanford Radioactive Solid Waste Packaging, Storage and Disposal Requirements, RHO-MA-222.

MECHAM

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

MEENTS

W. F. Meents, A. H. Bell, O. W. Rees, and W. G. Tilbury, Illinois Oil-Field Brines: Their Occurrence and Chemical Composition, IL Petroleum No. 66, Illinois State Geological Survey, Urbana, IL (1952), 38 pp.

MELLOR

J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 14, John Wiley and Sons, Inc., New York (1935).

MELROSE

J. C. Melrose and C. R. Brandner, Role of Capillary Forces in Determining Microscopic Displacement Efficiency for Oil Recovery by Water Flooding, J. Can. Pet. Technol., 1-4 (October-December 1974).

NERETNIEKS-1979

I. Neretnieks, Analysis of Some Tracer Runs in Granite Rock Using A Fissure Model, Scientific Basis for Nuclear Waste Management, Vol. 1, G. McCarthy, Ed., pp. 411-415, Plenum, New York (1979).

NERETNIEKS-1980

I. Neretnieks, Diffusion in the Rock Matrix - An Important Factor in Radionuclide Retardation, J. Geophys. Res. 85B, 4379-4397 (1980).

STEINDLER-1981A

M. J. Steindler et al., Chemical Engineering Division Fuel Cycle Programs Progress Report, July-September 1980, Argonne National Laboratory Report ANL-80-114 (July 1981).

STEINDLER-1981B

M. J. Steindler et al., Chemical Engineering Division Fuel Cycle Programs Quarterly Progress Report, October-December 1980, Argonne National Laboratory Report ANL-81-13 (July 1981).

STRACHAN

D. M. Strachan, R. P. Turcotte, B. O. Barnes, L. A. Bray, and J. H. Westside, Standard Leach Tests for Nuclear Waste Materials, Materials Research Society, Symposium D, Scientific Basis for Nuclear Waste Management, Boston, Massachusetts, Nov. 16-21, 1980.

VOGLER

S. Vogler et al., Alternatives for Conversion to Solid Interim Waste Forms of the Radioactive Liquid High-Level Wastes Stored at the Western New York Nuclear Service Center, Argonne National Laboratory Report ANL-81-46.

WEBSTER

D. Webster, Two-Well Tracer Test in Fractured Crystalline Rock, U.S. Geological Survey Water-Supply Paper 1544-I.

WHITE

Donald E. White, John D. Hem, and G. A. Waring, Chemical Composition of Subsurface Waters, U.S. Geol. Survey, Prof. Paper 440-F (1963).

WNYNSCS

Western New York Nuclear Service Center Study, Vol. 2, Companion Report TID-28905-3.

APPENDIX A.

TRANSIENT FLOW OF DRILLING FLUID
IN THE AXIAL DIRECTION INTO A WELL

Assume isotropic porosity and permeability of the rock.

Darcy's Law:

$$q = - \frac{k}{\mu} \nabla P \quad (A-1)$$

where q = flux, volume/area·time

k = permeability

μ = viscosity

P = pressure

Into a volume element, $dx dy dz$, the net rate of flow is

$$-dx dy dz \nabla \cdot q = \epsilon \frac{\partial \rho}{\partial t} dx dy dz$$

where ϵ = porosity and ρ = density of fluid. It follows that

$$\nabla \cdot q = - \frac{k}{\mu} \nabla^2 P = -\epsilon \frac{\partial \rho}{\partial t}$$

If compressibility $\kappa = \frac{-1}{V} \frac{\partial V}{\partial P}$ is constant,

then

$$\frac{\partial P}{\partial t} = \frac{k}{\mu \epsilon \kappa \rho} \nabla^2 P \quad (A-2)$$

and

$$\frac{\partial \rho}{\partial t} = \frac{k}{\mu \epsilon \kappa \rho} \nabla^2 \rho \quad (A-3)$$

These equations are identical in form to Fick's second law of diffusion, for which many solutions have been derived.

The geometry of the bottom of a well during coring is complex. Complete knowledge of fluid motion during coring operations in a well would involve, at the least, solving Eq. A-2 or A-3 for the case of a hollow cylindrical annulus moving through inhomogeneous, anisotropic rock. Fortunately, a far simpler approximation will suffice for downward flow. The greatest flow occurs at the beginning of coring or after a section of core has broken off. At this time, the bottom of the well is approximately flat, and the pressure is uniform

across the bottom surface. For sufficiently small distances from the bottom, the solution can be obtained approximately by assuming that the bottom is an infinite plane at constant pressure. We then have

$$q = - \frac{k}{\mu} \frac{\partial P}{\partial z} \quad (\text{A-4})$$

and

$$\frac{\partial P}{\partial t} = \frac{k}{\mu \epsilon \kappa \rho} \frac{\partial^2 P}{\partial z^2} \quad (\text{A-5})$$

At greater distances from the drill bit, the fluid pressure is approximately hemispherical. In spherical polar coordinates

$$\frac{\partial P}{\partial t} = \frac{k}{\mu \epsilon \kappa \rho} \left(\frac{2}{r} \frac{\partial P}{\partial r} + \frac{\partial^2 P}{\partial r^2} \right). \quad (\text{A-6})$$

Substituting $u = Pr$, then

$$\frac{\partial u}{\partial t} = \frac{k}{\mu \epsilon \kappa \rho} \frac{\partial^2 u}{\partial r^2} \quad (\text{A-7})$$

For Eq. A-5, the boundary condition and initial conditions are

$$\begin{array}{lll} P = P_0 & z = 0 & t > 0 \\ P = 0 & z > 0 & t = 0 \end{array}$$

The solution is

$$P = P_0 \operatorname{erfc} \frac{z}{2 \sqrt{Dt}}, \quad (\text{A-8})$$

where

$$D = \frac{k}{\mu \epsilon \kappa \rho} \quad [\text{CRANK, p. 21}]$$

From Eq. A-4 and differentiation of Eq. A-8, it is found that

$$q = P_0 \sqrt{\frac{k \epsilon \kappa \rho}{\mu \pi}} \frac{1}{\sqrt{t}} \exp \left(\frac{-z^2}{4Dt} \right)$$

The flow velocity at z is $q(z,t)/\epsilon$. If $\xi(t)$ = hypothetical position of the boundary between injected water and pore water,

$$\xi(t) = \frac{1}{\epsilon} \int_0^t q[\xi(t), t] dt \quad (A-9)$$

A solution was found by trial:

$$\xi(t) = A \sqrt{t}$$

where

$$D = \frac{A^2/4}{\ln B/2 - \ln A} \text{ and } B = \frac{k P_o}{\mu \sqrt{\pi D}}$$

Since $A^2/4 \ll D \ln A$, then $A \approx B/2$, and

$$\xi(t) = \frac{P_o}{2\sqrt{\pi}} \sqrt{\frac{k\kappa\rho}{\epsilon\mu}} \sqrt{t} \quad (A-10)$$

For the sample from drill hole UPH-3,

$$k = 3.8 \times 10^{-15} \text{ cm}^2$$

$$P_o \leq 3.8 \text{ MPa}$$

$$\kappa\rho \text{ for water} = 6.8 \times 10^{-10} \text{ g}\cdot\text{cm}^{-3}\cdot\text{Pa}^{-1}.$$

Assume that $\epsilon = 0.001$ to 0.0001 .

Then the position of the boundary between injected water and pore water is estimated as

$$\xi \leq 0.5 \text{ to } 2 \text{ cm in } 28 \text{ h.}$$

This is much slower than the drilling rate, which suggests that permeation of drilling fluid is not likely to contaminate cores of granite.