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CHEMICAL ENGINEERING DIVISION
FUEL CYCLE PROGRAMS
QUARTERLY PROGRESS REPORT
October-December 1979

by

M. J. Steindler, J. K. Bates, R. A. Couture, K. F. Flynn,
T. J. Gerding, L. J. Jardine, W. J. Mecham, R. H. Pelto,
and M. G. Seitz

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ANL-79-45 January-March 1979
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ABSTRACT

Efforts to characterize and develop metal matrix waste forms with increased resistance to dispersion were continued. Drop-weight impact tests were carried out on small lead ingots (forerunners of tests with lead-glass bead composites). The change in length of the ingots was approximately consistent with the anticipated deformation based on correlations in the literature of impact test data for spent-fuel shipping casks.

Drop-weight tests designed to verify a brittle-material impact-fracture model were also carried out using Pyrex glass specimens. The model predicts the increase in surface area and the particle-size distribution (including the respirable fraction) resulting from an impact. Particles over a wide size range were found to follow a lognormal distribution.

Leach-rate studies were continued on ANL-SYNROC samples, using the neutron activation analysis technique. A number of metals were irradiated with 14-MeV neutrons to identify their activation products for possible use in specific studies such as those of canister corrosion. A radiochemical method is being developed which will broaden leach-rate determinations to include radionuclides that decay by beta and alpha-particle emissions.

Predicted migration velocities of radio-cesium based on distribution coefficients determined in batch experiments with basalt and groundwater solutions were compared with velocities determined in column infiltration experiments. The predicted migration velocities based on distribution coefficients were significantly slower than those determined in the infiltration experiments. This difference is attributed to the difference in contact times between the cesium-containing groundwater and the basalt in the two types of tests. The sorption of $^{10}$O$_4^-$ from aqueous buffer solutions by Fe$_2$O$_3$ was determined. It was found that $^{10}$O$_4^-$ is sorbed about four times as strongly as IO$^-_3$. The transport rate of cesium ions through kaolinite was found to be lower than calculated. One of the reasons suggested for this difference is the presence of iron oxide in the kaolinite.
SUMMARY

Encapsulation of Radioactive Waste in Metal

A casting method in air using a split mold has been developed to prepare ~2-in.-OD by ~2-in.-long (5.1 cm by 5.1 cm) laboratory-scale lead ingots and lead-glass bead composites for characterization testing. Preliminary impact tests with a drop-weight device that delivered 86 J of impact energy to three 5-cm-OD by 5-cm-long lead ingots resulted in an approximately 5% change in lengths of the deformed ingots. This is approximately consistent with the anticipated deformations based on correlations in the literature on impact-test data for spent-fuel shipping casks. Experiments have been planned to examine the leaching rates of metal-matrix composites and the compatibilities of lead alloys and an SRL defense waste glass formulation.

Brittle Fracture Studies

This is the first quarterly progress report of a new program to provide experimental verification of a lognormal brittle-fracture model developed in a previous study of the impact-fracture resistance of metal-encapsulated glass waste forms. This preliminary model was developed principally from literature data published by others; the model is essentially empirical and uses a lognormal particle-size distribution function such that two parameters are sufficient to define quantitatively the particle-size distribution. With an additional shape factor, the lognormal parameters also define the total surface area of the particles. That portion of the impact energy that is dissipated in the process of brittle fracture is empirically related to the new surface area formed in fracture.

The results of two initial tests with small Pyrex glass specimens, using single impacts of a falling weight, showed a lognormal size distribution. Particle sizes in the range of 8 to 8000 μm were measured by using sieve separation for the larger size fragments and Coulter Counter measurements of the smaller sizes. The validity of the model over a range of impact conditions and specimen configurations will be systematically tested. The model is also to be qualified for use in characterizing the dispersibility of realistic waste forms.

Neutron Activation and Tracer Studies

The use of epithermal neutrons for the production of activation products based on (n,p), (n,α), and (n,2n) reactions has been shown to be a viable technique for leach studies of elements where (n,γ) reaction products are not relevant.

Studies of the leach rates of ANL-SYNROC samples, prepared by ANL-MSD, are continuing. Various fabrication techniques are being tried in order to establish one that incorporates the cesium and strontium into a solid-solution matrix, based on leach-rate measurements.
Counting procedures based on low-background alpha- and beta-counting techniques are being established. These procedures will be used to increase the sensitivity of radiochemical methods for characterization studies, as well as to broaden their use to non-gamma-emitting radionuclides.

Transport Properties of Nuclear Waste in Geologic Media

In evaluations of the safety of nuclear-waste repositories, the concept of a distribution coefficient, $K_d$, is widely used to predict the migration velocity of a radionuclide in moving groundwater through rock. In this work, velocity predictions from distribution coefficients for cesium on basalt measured in batch experiments of 15- and 28-day duration are compared with velocities of cesium in basalt measured in column infiltration experiments having groundwater solution flow rates of 0.43 and 4.6 km/y. The batch experiments of different duration resulted in similar distribution coefficients and show a dependence on cesium concentration.

The distribution coefficients give slower migration velocities than those observed in infiltration experiments. The column experiments at the lower flow rate give results closest to that predicted by the batch tests and there is an indication that migration measured at very low groundwater solution flow rates (2 to 100 m/y) would agree with distribution coefficient predictions. Groundwater flow rates greater than these are not uncommon so that kinetic effects such as seen in infiltration experiments need to be considered for repository safety evaluations.

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

Transport of Cs$^+$ through kaolinite columns by fluid flow in 0.1M NaHCO$_3$ was studied, and the results were compared with transport rates calculated from ion-exchange adsorption measurements. Sorption of IO$_4^-$ by Fe$_2$O$_3$ in buffer solutions was also studied.

The Cs$^+$ ions were transported through a kaolinite column about three times more slowly than calculated. The difference may be due to deformation of the kaolinite in the column, or to the streaming potential, or to inadequately controlled pH, or to iron oxide present in the column.

The IO$_4^-$ is sorbed by Fe$_2$O$_3$ about four times as strongly as IO$_3^-$. At pH 3.87, a distribution coefficient of 400 cm$^3$/g was determined for IO$_4^-$ on Fe$_2$O$_3$ which has a specific surface area of 10 m$^2$/g.
I. ENCAPSULATION OF RADIOACTIVE WASTE IN METAL  
(L. J. Jardine and T. J. Gerding)

A. Introduction  
Concentrated radioactive wastes* destined for deep geologic disposal must be in solid forms that are demonstrably stable. Waste forms are being sought by DOE as alternatives to borosilicate glass monoliths, in the event that glass monoliths fail to meet NRC criteria not yet issued. These alternative waste forms offer potentially superior solid-product performance or process characteristics. Many alternative crystalline waste forms (e.g., supercalcine, SYNROC) are granular materials that will require the use of other materials for consolidation to a less dispersible solid form. Less dispersible alternative waste forms can be fabricated by encapsulating solid waste forms into a corrosion-resistant metal matrix that inherently has good impact resistance. For example, waste in the form of small glass beads encapsulated in a lead-alloy matrix might serve as an alternative to large glass monoliths. This alternative waste form would greatly enhance the quality assurance and recycle process options, as well as increase the resistance to dispersion of the final waste form.

The objective of the present program is to establish the technical feasibility of encapsulating alternative waste forms in a metal matrix to produce a less dispersible waste form acceptable for geologic disposal. The advantages of encapsulating radioactive waste forms in a metal matrix will be identified, evaluated, and compared with those of other solid waste forms, primarily monolithic glasses.

The approach in FY 1980 will consist of (1) developing casting fabrication techniques for the preparation of laboratory-scale specimens, primarily metal-glass composites, and (2) developing and implementing techniques for characterizing the properties of such composites. Fabrication methods will attempt to simulate larger scale production concepts for metal encapsulation. Characterization techniques will be developed and applied to study the mechanical-impact resistance of metal composites, the leach rates and leach mechanisms of composites, and the chemical and physical compatibilities of glass and metal matrices. Relationships between the characterization measurements of the composite and the method and conditions used for its fabrication will also be sought in order to identify important design parameters of the encapsulation process.

Two activities previously reported as part of this metal-encapsulation program, viz., (1) the application of neutron activation analysis techniques for measuring leach rates of simulated waste forms and (2) the studies of the brittle fracture of waste forms during mechanical impacts, are now funded and reported as separate sections of this quarterly report.

*High-level defense and commercial wastes, TRU, fractionated cesium and strontium, and spent fuel.
B. Laboratory-scale Specimen Preparation

Lead and composites of lead and glass beads will be initially fabricated as right cylinders, approximately 2 in. OD by 2-in. long, to be used for various characterization studies. A mold for preparing this configuration is being manufactured by a commercial vendor, and shipment is anticipated during the next quarter.

While awaiting delivery of the commercial mold, a cylindrical 2-in.-OD by 3-in.-long open-top, split mold was fabricated from mild steel. Lead ingots with tolerable top surface imperfections were fabricated by casting lead (chemical grade) with this simple mold. Excellent release of the ingots from the mold was achieved by maintaining a thin deposit of soot on the mold walls.

Three lead ingots were fabricated using the mold; the top surface of each ingot was removed and the ingot machined to produce a uniformly flat surface very nearly parallel to the bottom surface plane. The final dimensions (i.e., length $L_0$ and diameter $D_0$) and the percent of theoretical density (T.D.) of each ingot are reported in Table 1. The density of these ingots was approximately 99% of T.D.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>% T.D.</th>
<th>$L_0$, cm</th>
<th>$D_0$, cm</th>
<th>$A_0$, cm$^2$</th>
<th>AL Measured, cm</th>
<th>AL Calculated, cm</th>
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<td>150-23</td>
<td>99</td>
<td>4.99</td>
<td>5.029</td>
<td>19.86</td>
<td>0.23</td>
<td>0.127</td>
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<tr>
<td>150-25</td>
<td>98.9</td>
<td>5.011</td>
<td>5.04</td>
<td>19.95</td>
<td>0.24</td>
<td>0.126</td>
</tr>
<tr>
<td>150-28</td>
<td>98.9</td>
<td>5.015</td>
<td>5.056</td>
<td>20.08</td>
<td>0.26</td>
<td>0.126</td>
</tr>
</tbody>
</table>

$^a$T.D. is theoretical density.
$^b$Assumes that a 9.935 kg weight drop from 0.88 m delivers energy $W_d$ of 85.7 J and that the dynamic flow stress $\sigma_d$ is 5000 psi or 34 J/cm$^3$.
$^c$The error in measurement of AL is believed to be approximately ± 0.01 cm.

Experiments aimed at fabricating 2-in.-OD by 2-in.-long lead-glass bead composites are being initiated.

C. Sample Characterization Testing

The lead ingots were subjected to a mechanical weight-drop impact test to study the resulting deformation (i.e., length change, $AL$) and to compare the results to that expected from our previous analysis of the ORNL Shipping Cask Studies [STEINDLER-1979A].

The impacts were conducted in the same impact chamber and with the same drop weight device that is being used for the brittle-fracture studies (see Section II of this report). In the tests, a 9.935-kg weight was dropped from a height of 0.88 m. From these drop conditions, the impact energy ($W_d$) was calculated to be 85.7 J. After impact, the lead specimens were remeasured to establish the length and diametrical changes that resulted from the impact. The changes in
length sustained in three similar tests varied from 2.3 to 2.6 mm. This suggests that the experimental reproducibility is about 20%. There may be a trend in which $\Delta L$ increases as the T.D. decreases; however, further investigation is needed to establish the cause of the variability of the measured $\Delta L$ values.

The expected length change for a drop weight impacting on lead may be calculated from the following equation, which involves the available impact energy $W_d$ for lead displacement and the dynamic flow stress $\sigma_d$:

$$W_d = \sigma_d \Delta V_d \quad (1)$$

where $\Delta V_d$ is the displaced lead volume as a result of the impact [STEINDLER-1978A]. The $\Delta V_d$ may be replaced by a term that involves the initial cross sectional area $A_o$ and the change in length $\Delta L$ of the impacted ingot,

$$\Delta V_d = A_o \Delta L \quad (2)$$

Thus, $\Delta L$ may be calculated or estimated from the following relationship, if the terms $W_d$, $\sigma_d$, and $A_o$ are known, or are measurable, or can be estimated:

$$\Delta L = \frac{W_d}{\sigma_d A_o} \quad (3)$$

The values for $A_o$ are presented in Table 1. The value of $W_d$, assuming no frictional or other energy losses, may be taken as 85.7 J, the value calculated above from the drop-weight conditions. The ORNL shipping cask work [SHAPPERT] suggests a value for $\sigma_d$ of 5000 psi (34 J/cm$^3$) for lead, although quite a range is possible (3700-19000 psi), depending on the test conditions and the particular type of lead alloy.

If the above values for $A_o$ and $W_d$ are used and a $\sigma_d$ value of 5000 psi is assumed, the corresponding calculated or predicted $\Delta L$ is 1.3 mm and is essentially the same for all three ingots. This result is ~50% lower than the actual measured values. Alternatively, a value for $\sigma_d$ of ~2600 psi would give good agreement and perhaps is the appropriate value to be used in these dynamic impact tests. The measured and calculated results are compared in Table 1. There is uncertainty regarding the proper values for $\sigma_d$ and $W_d$ (which depends on the efficiency of energy transfer at impact and which could lead to a lower value of $W_d$ than actually used) that should be used for this lead composition and these test conditions. These parameters must be examined further before any definitive conclusions can be made regarding these preliminary impact results.

Experiments have been planned to examine the reaction or compatibility of simulated SRL defense waste glass with two lead alloys. The alloys are lead ("chemical lead") and lead ("chemical lead") - 10 wt % tin. This information is needed since the SRL defense glass formulation contains significantly higher amounts of $\text{Fe}_2\text{O}_3$ and $\text{MnO}_2$ than the previously simulated commercial waste glasses examined for compatibility with lead alloys.
Experiments are being planned to define the leach resistance and leaching mechanisms of lead alloy-glass bead composites. The results of these tests will be used to define the composites that need to be fabricated and characterized.

D. Economic Comparisons of Metal-Matrix Solidification Processes

A comparative economic analysis is in progress of four alternative methods for waste solidification that are representative of those that have been proposed for high-level liquid wastes. The four waste-solidification methods under evaluation may be summarized as:

- Spray calcination of high-level liquid waste followed by melting in a continuous glass melter to form a glass monolith
- Direct feed of high-level liquid waste into a continuous glass melter to form a glass monolith
- Production of glass beads from a continuous glass melter which are then cast into a lead metal matrix
- Spray calcination of high-level liquid waste followed by agglomeration into supercalcine pellets which are then sintered and cast into a lead metal matrix.

Conceptual processing flowsheets and solidification systems have been developed for each of these methods. Conceptual designs and preliminary equipment and facility layouts were prepared in sufficient detail to allow preliminary (conceptual) engineering cost estimates of the capital and operating costs associated with a solidification facility for each process. Costs for process equipment will include the installation costs while operating costs for the solidification alternatives will include all labor, consumables, and utilities services. The total solidification facility cost is being estimated based on an AGNS (Allied-General Nuclear Services) design as modified for the various solidification alternatives of this study; facility costs have been subdivided into those for concrete, structural steel, building support services, and stainless steel liner plate. The cost evaluation is being structured to allow direct comparison of each of the waste solidification methods. Costs are not included in this study for waste transportation, geologic waste disposal, potential impact of the plant sites on the solidification facility, long-term high-level liquid waste (HLLW) storage, or HLLW recovery and transfer from tanks.

This study is approximately 80% complete and is being conducted with the aid of a subcontract with TERA Corporation. Completion of a final subcontractors report is anticipated during the next quarter.
II. BRITTLE FRACTURE STUDIES  
(W. J. Mecham, R. H. Pelto, L. J. Jardine)

A. Introduction

The resistance of solid radioactive waste forms to dispersion from mechanical impacts received during normal and accident conditions of processing, handling, interim storage, and transportation is a property that must be known. The objective of this program is to formulate and experimentally test analytical impact models that describe the brittle-fracture characteristics of brittle waste-form materials subjected to a mechanical impact. The emphasis is on predicting, for given impact scenarios for brittle waste forms, the increase in surface area (for leaching) and the quantity (weight fraction) of fragments within the respirable particle-size (i.e., <10 μm). Initially, the brittle materials for the impact tests will be limited to small sizes similar to those of brittle waste forms destined for metal encapsulation. The data from these laboratory-scale tests may be directly applicable to metal-encapsulated waste forms. Tests will also be designed to develop the scaling laws required to predict the impact-behavior characteristics of much larger brittle waste forms and perhaps thereby reduce the R&D efforts and costs associated with impact tests of these larger forms.

This is a new program, starting this quarter. The progress made previously and the background material already developed for this program were reported in a sequence of quarterly reports in this series (ANL-79-6, ANL-79-29, ANL-79-45, ANL-79-99, ANL-79-109), as part of the metal-encapsulation program.

B. Brittle Fracture Modeling Studies

1. Results

A preliminary model for the brittle fracture process associated with mechanical impacts has been developed, based on our repeated observations that particle-size distributions of laboratory-scale, mechanically impacted brittle materials can be fitted to a lognormal distribution. The lognormal particle-size distribution has two parameters, a geometric mean diameter $D_g$ and a geometric standard deviation $\sigma$. This distribution has received much attention in the literature of applied statistics [HERDAN], and appears to be well suited for describing the fracture process for brittle materials [MECHAM-1979A]. In developing this fracture model, these particle-distribution parameters are related to the ratio of the impact energy ($W_i$) to the total volume ($V_o$) of the specimen; this ratio is referred to as the energy density $W_i/V_o$ [MECHAM-1979B].

Two typical distributions from impact experiments with Pyrex glass beads (6 mm) at two different energy densities are shown in Fig. 1. Examination of these data and those for other glasses from several other sources (Savannah River Laboratory, Pacific Northwest Laboratory, and Mound Laboratory) can be correlated in this linear fashion; all data seem to show that the slope of the
line is relatively independent of the impact energy density, but is probably a weak function of the type of glass or other brittle material [MECHAM-1979B].

![Graph showing lognormal plot of (6-mm-dia) Pyrex Glass Beads impacted at Energy Densities of (1) 3 x 10^6 and (2) 7 x 10^6 J/m^3.]

Since the particle-size data form a straight line when plotted on lognormal graph paper, each line can be characterized by a single point and the slope of the line through that point. The mean, D_g, is the diameter at the 50% cumulative mass fraction, and the slope is a function only of the standard deviation $\sigma$. The $\sigma$ is obtained graphically as the ratio of the diameters at 50% and the 16% mass fractions. For the data of Fig. 1 at the energy density of 3 x 10^6 J/m^3, $D_g$ is 2100 $\mu$m and $\sigma$ is 4.4. As might be expected, the mean diameters are observed to shift to smaller sizes as the energy density is increased.

These linear relationships are obviously quite amenable to extrapolation in order to obtain the fraction of respirable size, and experiments are under way to confirm this. However, an additional relationship of the lognormal distributions may be used to determine the total surface area, $S_f$, of the particle-size distribution that resulted from an impact. The relationship involves the volume $V_o$, of the original waste form and a numerical constant, $\alpha$ (shape factor), used in the equations for surface area-to-volume ratio of solids (i.e., $\alpha$ = 6 for cubes and spheres, and is ~10-20 for fractured brittle particles) in addition to $D_g$ and $\sigma$. The relationship is

$$S_f = V_o \alpha \sigma^{0.5} \ln \sigma \frac{D_g}{v}$$

(1)
Thus, once the values of $D_g$ and $\sigma$ have been determined, estimates of the total surface area can be obtained from Eq. 1, and the respirable fraction formed in impact tests can be calculated or obtained graphically.

Further, the new surface area formed by impact fracture appears to be proportional to the energy dissipated. Laboratory-scale experiments at the University of Minnesota [ZELENY] with Pyrex and quartz specimens of a few cm$^3$ volume show that the increase in surface area, $\Delta S_f$, of an impacted specimen is directly proportional to the fracture energy, $W_f$, absorbed in the specimen during impact. Values of $\Delta S_f$ were determined by gas-adsorption measurements. Typically, the absorbed energy $W_f$ was only $\sim$50% of the total available impact energy, $W_i$, as revealed in calorimeter measurements done within a special impact apparatus that used hardened steel surfaces to minimize metal deformations and heat losses. The energy losses that do not contribute to increasing the surface area in impacting of brittle materials can be represented by introducing an impact efficiency, $\varepsilon$, which is arbitrarily defined by the relationship $W_f = \varepsilon W_i$. Laboratory tests that establish the values of $\varepsilon$ essentially amount to defining the partition of the impact energy among the brittle and ductile components in the test system. Since $\varepsilon$ is not unity, it must be explicitly considered in all impact tests. In actual practice, $\varepsilon$ would be much less for a real waste form (by engineering design) than for these bare laboratory-scale specimens and would be directly related to the packaged waste form design system, which obviously would be constructed to minimize $\varepsilon$. The experiments by Piret et al. determined the relationship between the surface area increase, $\Delta S_f$, and the absorbed impact energy $W_f$ by showing that the fracture surface energy, $\gamma_f$, was relatively constant at about 80 J/m$^2$ for quartz and Pyrex throughout a 100-fold variation in the impact energy density ($W_i/V_0$). This may be expressed as:

$$\Delta S_f = \frac{W_f}{\gamma_f} = \frac{\varepsilon W_i}{\gamma_f}$$  (2)

If further investigation shows that this relation remains valid, the increase in surface area can be predicted for impacted waste forms from the available impact energy and estimates of the impact efficiency.

Equations 1 and 2, which incorporate the above approaches to laboratory-scale impact tests, can be combined to obtain:

$$\varepsilon \frac{W_i}{V_0} = \gamma_f \frac{0.5 \ln \sigma}{D_g}$$  (3)

since $S_f = \Delta S_f$. The left-hand side of Eq. 3 represents the specific impact energy density ($W_i/V_0$), a function of kinetic energy and material volume, and the impact efficiency $\varepsilon$, which depends upon packaging-design details. The terms on the right involving $\gamma_f$, $\alpha$, and $\sigma$ are statistical properties of the waste-form specimen that can be evaluated in laboratory-scale tests as outlined above. If the above relationships continue to hold true in our tests, it may then become
possible to predict $D_g$ by means of Eq. 3 for larger scale test conditions. Consequently, the lognormal distribution for such a $D_g$ can determine the respirable size fraction, while Eq. 2 can be used to estimate the increase in surface area (relevant to leaching source terms) for various impact scenarios.

2. Conclusions of Preliminary Modeling

More analysis and experiments are needed to broaden the above approach to impact characterizations. Of immediate concern are the mechanics and the scaling laws of fracture. The reason for this is that, in impact tests of small specimens, the entire specimen is fractured, whereas full-scale cylindrical canisters of glass that have been dropped by Battelle Pacific Northwest Laboratory fracture in a highly localized area near the dropped corner or end. Thus, it is necessary to consider stress distributions and concentrations for large impacted specimens rather than to assume that the strain energy from the impact is distributed uniformly, producing a stress insufficient to cause any brittle fracture (threshold effect). Such tests also need to be applied to ceramic or crystalline materials that are being proposed for waste forms.

C. Experimental Impact Tests

1. Introduction

A systematic program of impact testing of laboratory-scale glass has been initiated. The general objective is to verify the applicability of the lognormal fracture model as described above, particularly with respect to its capability to predict the surface area and particle size. Later, other glass compositions (in particular, realistic simulated waste glass) will be examined. Preliminary tests are being made of small, bare glass specimens under impacts of varying energy, but sufficient to fragment the whole body. Later tests will examine particle fragmentation (of a sharp corner edge), stress threshold for fracture, and the effect of the canister.

In its present form, the fracture model predicts the same surface area and particle-size distribution for a given energy density ($W_i/V_o$) regardless of the impact velocity or the size of the specimen. This means that multiple impacts on multiple bodies will produce the same fragmentation as a single impact on a single body for the same overall energy and volume of material. Two impact tests are reported below: one for a number of small Pyrex spheres in contact with one another and the other for a single Pyrex glass cylinder.

2. Test of Pyrex Spheres

A 16.6-J impact test was made on nineteen 6-mm Pyrex beads, with a total sample mass of 5.29 g. The energy was delivered to the sample by a 0.88-kg weight that was dropped from a height of 192 cm. With the assumption that friction losses were insignificant, the energy density was calculated to be $7.0 \times 10^6$ J/m$^3$. 
After impact, the impact chamber containing the particles was rinsed with distilled water (filtered to 0.45 µm absolute). The rinse water was then passed through a 90-µm sieve. The material passing through the sieve was analyzed with a Coulter Counter Model TA-II, fitted with a 280-µm aperture tube, which is capable of analysis in the size range from 5 to 110 µm. The material remaining on the sieve was dried in a desiccator.

The Coulter Counter measurement seemed to include the entire distribution of particles less than 90 µm in size, with the lowest size channel containing less than 1% of the total sample volume. The data from the Coulter Counter analysis which are shown in Fig. 2, give the linear plot expected of a lognormal distribution plotted on lognormal graph paper. The data points at the extremes of the measured range fall short of the line. This may be the result of the small number of particles at these extremes or of losses in this initial test. From the plotted straight line, the lognormal parameters were $\sigma = 5.9$ and $D_g = 1200$ µm.

![Lognormal Plot of Data for ANL Impacted Glass Beads](image)

The ATM sonic sifter was fitted with three stacks of sieves. Each stack was used independently starting with the finest sieve stack and working toward the coarsest sieve stack. The material left on the top sieve, after the sieving was complete, was transferred to the next larger sieve stack. The weight of particles retained on each sieve was measured on a Metler balance (model H31 AR) by subtracting the tare weight of each sieve. The tare weights varied from 34 g for the 75-µm sieve to 54 g for the 100-µm sieve. The sieves were placed in a desiccator before weighing to minimize the effect of moisture. The mass of material passing through the 75-µm sieve was 0.70% of the sample mass and 0.11% of the sieve tare weight.

The complete ATM sieve series (16 screens) was used in this experiment. This is probably unnecessary and future tests will use fewer screens. This should reduce the losses and the time required for data analysis. It will also increase the mass of sample on each sieve.
The data analyzed by sieving are also plotted in Fig. 2. The plot is linear on this lognormal graph paper. The deviation observed could be the result of weighing errors or of incomplete sieving cycles. Each sieve stack was sieved for 12 min using an amplitude high enough to move the largest particle on the top sieve (7-8 on the ATM amplitude setting). The lognormal parameters for this plotted straight line were $\sigma = 5.9$ and $D_g = 880 \mu m$.

Sieve and Coulter Counter data are in agreement in that they yield the same standard deviation, namely, $\sigma = 5.9$, for the particle population. However, the $D_g$ from the Coulter Counter is larger than the $D_g$ of the sieve data by a factor of 1.33. This difference is due to the different methods of measuring linear size. The Coulter Counter electronically measures the particle's volume and then reports it as the diameter of a sphere that has the same volume as that measured for the particle. The mesh size of a sieve is a square opening through which an elongated particle could pass endwise because sieving is done with a vibratory motion of the particles. Of course, an elongated particle could have an equivalent spherical diameter larger than the mesh size.

Consider an elongated glass particle of square cross section of area $W^2$ and length $L = aW$, where $a > 1$. For a particle of this shape to be retained on a mesh of size $D$, $W > D$. The equivalent spherical diameter $D_e$ of a particle of size $W = D$ is $D_e = (6a/\pi)^{1/3}W = 1.241a^{1/3}D$. For the plotted ratio of $D_e/D = 1.33$, $a = (1.33/1.24)^3 = 1.23$. Thus, a needle shape with a length about 1.2 times the diameter could account for the difference observed in size measurements. It is possible, however, that the Coulter Counter measurement of volume is also sensitive to particle shapes that depart widely from equiaxed symmetry. Subsequent tests will examine this effect.

The geometric shape factor $\alpha$ is defined as the relation of particle surface area $S$, volume $V$, and maximum linear dimension $L$. For spheres and cubes, $\alpha = 6.0$. For a lognormal population of spherical particles, the total surface $S_f$ and total volume $V_f$ are given by:

$$\frac{S_f}{V_f} = \frac{6\sigma^{0.5 \ln \sigma}}{D_g}$$

where $D_g$ is for the equivalent spherical diameter $D_e$.

For a particle having a needle shape with $L = aW$, $S/V = (\sigma + 2/a)/W = (4a + 2)/L$. For $a = 1.23$, $S/V = 6.92/L = 5.63/W$. Thus, the lognormal particle population has a different shape factor depending on where the mean diameter $D_g$ is taken for the $L$ or the $W$ dimension:

$$\frac{S_f}{V_f} = \frac{6.9\sigma^{0.5 \ln \sigma}}{D_g(L)} \neq \frac{5.6\sigma^{0.5 \ln \sigma}}{D_g(W)}$$
In summary, preliminary support for the model and the methods employed is provided by the following facts: (1) the Coulter Counter and the sieve analysis yield size data of the same slope (i.e., same $a$) and (2) the small difference in $D_g$ may be explained by considering slight differences in shape as they relate to the two measurement techniques. In the present tests, surface areas were not measured. In later tests, a direct measurement of surface area by a gas-adsorption technique will be used to establish the shape factor $a$ and to compare these results with present observations.

3. Test of a Pyrex Glass Cylinder

An initial impact test has been completed on a cylindrical solid Pyrex sample that was 6.43 cm long and 3.81 cm in diameter. The sample was annealed through two heating and cooling cycles. In the first cycle, the sample was heated to 1000°F over a 30-min period, soaked at 1000°F for 2 h and then cooled to room temperature over 18.5 h. Examination with an optical polarimeter showed that little if any strain had been removed. In the second annealing cycle, the sample was heated to 950°F over a 30-min period, soaked at 950°F for 3 h, and then cooled to room temperature over 18.5 h. None of the strain was visible with the polarimeter.

The impact was made inside a hermetically sealed chamber by dropping a 9.9350-kg weight from a height of 0.32 m onto the sample. The sample was oriented between two hardened tool-steel plates (Rockwell hardness, 58) so that the energy of impact was delivered across the diameter of the sample. Filtered distilled water was introduced into the chamber to reduce the loss of fine particles during the sample collection and transfer. The sample was rinsed from the chamber onto a 90-μm sieve. (In future tests, the material passing through this sieve will be analyzed with a Coulter Counter.) The material remaining on the sieve was divided into eight sieve fractions with a Sonic sifter.

Examination of the fractured glass determined that the seven largest particles accounted for more than 2/3 of the entire sample mass. These particles were assembled back together, and it was found that the two halves of the original cylindrical sample were relatively intact. Evidently, most of the finer particles came from the center portion between the two halves. This would correspond to the material between the two points of initial contact and corresponds to the region with the most intense stress concentrations at impact.

These data are plotted in Fig. 3 as cumulative mass percent through each sieve. It is remarkable that these sieving data show a straight line for particles sized less than 8000 μm for this test in which the energy density was low. (This energy density corresponds to that which would be transmitted to the sample in a free fall of ~60 ft.) It appears that, at least, particles less than 8 mm follow a lognormal distribution, even when the impact energy is so low that most of the mass remains in large pieces.
Future impact tests will extend the particle-size distribution characterizations to smaller sizes (i.e., 1 to 10 μm) with the Coulter Counter and examine the effects of sample impact orientations and specimen impact energy densities upon the particle-size distributions of the fractured specimens.

A. Introduction

Dispersion of wastes into the biosphere is the most commonly accepted principal hazard of nuclear waste disposal. Characterization of waste forms requires sensitive methods in order to establish sound extrapolatable dispersion data for low-rate phenomena. Neutron activation analysis (NAA) has been shown [FLYNN-1979] to be applicable to waste-form characterizations, particularly for the determination of leach rates. Data obtained by NAA and also by use of tracers are needed to describe the performance of waste forms.

The general objective of this program is to develop techniques and qualify methods utilizing NAA and radioactive tracers to characterize simulated waste forms. Comparison of characterization test results obtained using these two methods and of other existing characterization data will be used to specify conditions for which data derived from such tests may be considered extrapolatable to fully radioactive specimens. The current focus is on leach-rate characterizations of simulated waste glasses and alternative ceramic waste forms.

The NAA method for measuring leach rates was developed during 1977-1979 and has been previously reported as part of the metal-matrix program. Completing the development of the NAA method for leach-rate determinations and defining the method's accuracy and limitations, and the applicability of the test results to larger scale waste forms will be a major goal in FY 1980. Addition of radioactive tracers to simulated glass waste will be performed since some elements cannot be studied conveniently with NAA. The simultaneous use of selected tracers and NAA for the same sample will be applied to directly compare the behavior of elements from different origins; study of selected polyvalent elements will be of most interest and importance. Radiochemical techniques and beta counting will be used to enhance the sensitivity of characterization methods.

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

1. Results

One of the most likely methods by which hazardous waste materials can be transported to the biosphere is by aqueous leaching from an inert solid phase to a mobile aqueous phase. To study this phenomenon, nondestructive radiochemical techniques of high sensitivity have been developed [FLYNN]. Studies completed thus far have been based primarily on thermal-neutron activation.

The use of a 14-MeV neutron generator for the production of activation products by reactions other than the (n,γ) reaction [i.e., by (n,p) (n,α), and (n,2n) reactions] is being investigated. The desirability of using the
activation products of these reactions in specific cases such as canister integrity studies has been discussed in a previous report [STEINDLER-1979A]. Samples of copper, iron, lead, titanium, nickel, and aluminum have been irradiated in the Argonne National Laboratory (ANL) Applied Physics Division Dynamitron. The results are given in Table 2.

TABLE 2. Activation Products from 14-MeV Neutron Activation of Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Reaction</th>
<th>Product Species</th>
<th>Half Life</th>
<th>Radiation</th>
<th>Specify Activity, a dpm/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (Al)</td>
<td>(n,a)</td>
<td>$^{24}$Na</td>
<td>15 h</td>
<td>$\beta,\gamma$</td>
<td>4 E+7</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>(n,a)</td>
<td>$^{60}$Co</td>
<td>5.3 y</td>
<td>$\beta,\gamma$</td>
<td>2 E+4</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>(n,p)</td>
<td>$^{54}$Mn</td>
<td>312 d</td>
<td>$\gamma$</td>
<td>2 E+4</td>
</tr>
<tr>
<td></td>
<td>(n,y)</td>
<td>$^{59}$Fe</td>
<td>45 d</td>
<td>$\beta,\gamma$</td>
<td>b</td>
</tr>
<tr>
<td>Stainless Steel (Co)</td>
<td>(n,y)</td>
<td>$^{60}$Co</td>
<td>5.3 y</td>
<td>$\beta,\gamma$</td>
<td>1</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>(n,p)</td>
<td>$^{204}$Tl</td>
<td>3.8 y</td>
<td>$\beta$</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>(n,a)</td>
<td>$^{203}$Hg</td>
<td>47 d</td>
<td>$\beta,\gamma$</td>
<td>1 E+4</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>(n,p)</td>
<td>$^{60}$Co</td>
<td>5.3 y</td>
<td>$\beta,\gamma$</td>
<td>1 E+4</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>(n,p)</td>
<td>$^{46}$Sc</td>
<td>84 d</td>
<td>$\beta,\gamma$</td>
<td>5 E+4</td>
</tr>
</tbody>
</table>

aData based on a 10-h irradiation with 300-μA deuteron beam; dpm (corrected to time at end of irradiation) per gram of matrix material irradiated.

b$(n,Y)$ products listed as potential alternatives.

c$^{204}$Tl is a beta emitter and hence it was not analyzed in these experiments.

The specific activities obtained from the reactions listed in Table 2 were somewhat less than anticipated. Similar samples will be irradiated in the University of Illinois TRIGA reactor to see whether the relatively high-energy fast flux in this reactor will result in significantly higher specific activities for the reaction products than those obtained with the 14-MeV neutron generator.

The 15-h $^{24}$Na activity from the $(n,a)$ aluminum reaction is too short lived for studies of this type (Table 2), and furthermore, the sodium would not be representative of an aluminum matrix. Therefore, aluminum remains a problem for the neutron activation technique. Copper, lead, nickel, and titanium are possible candidates for additional studies using the NAA method. Lead represents a rather interesting case. Thallium-204 is a beta emitter and hence requires chemical separation, whereas $^{203}$Hg may not require separation since it has a characteristic gamma ray that is easily identified. Comparative leach rate measurements of these two isotopes might provide information regarding mobility, or the lack thereof, in the solid lead phase. Iron and stainless steel are best studied via the $(n,y)$ activation products.

Studies are continuing on ANL-SYNROC samples prepared by Argonne's Materials Science Division (MSD). Accumulated leach-rate data are presented in Table 3. Some interpretation of these numbers is in order. Comparisons of the
cesium leach rates are the most striking. All three SYNROC samples show significantly higher cesium leach rates (by a couple of orders of magnitude) than that for PNL borosilicate glass at comparable temperatures. Also, the SYNROC samples show an increase in leach rate with temperature as does also the PNL-glass sample. In all cases, the cesium seems to leach faster from the SYNROC than the bulk matrix material. These results suggest that the cesium has not been successfully incorporated into a solid-solution matrix. Sequential leach tests on these samples corroborate these findings.

TABLE 3. Initial Leach Rates for ANL-SYNROC Samples, Using Distilled Water Leachant

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Incremental Leach Rate, g/cm²·d</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYNROC-1c</td>
<td>SYNROC-2d</td>
</tr>
<tr>
<td>Temp, °C</td>
<td>Timeg</td>
</tr>
<tr>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>95Zr</td>
<td>1.7 E-7</td>
</tr>
<tr>
<td>131Ba</td>
<td>1.6 E-6</td>
</tr>
<tr>
<td>134Cs</td>
<td>1.3 E-3</td>
</tr>
<tr>
<td>152Eu</td>
<td>1.6 E-6</td>
</tr>
<tr>
<td>181Hf</td>
<td>1.0 E-7</td>
</tr>
<tr>
<td>192Ir</td>
<td>h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>i</td>
</tr>
</tbody>
</table>

aSYNROC samples prepared by ANL-MSD according to a formulation developed by A. E. Ringwood. Samples were 1-cm dia by 2-mm discs, weighing about 1 g each.
bThis unit (g/cm²·d) represents the equivalent grams that would have been leached if the entire matrix had leached at the same rate as the specific isotope measured.
cFirst sample received; contained no added cesium.
dSecond sample received; contained added cesium.
eThird sample received; contained added cesium; sample identified as SRB-R4.
fStandard borosilicate glass; PNL formulation 76-68.
gLength of time in days for leach test.
hThese data have not yet been resolved from the counting data.
iThese numbers could not be determined because they were below the detection threshold.

Radiochemical studies of the leach rates of hazardous radionuclides from solid radioactive waste forms are being broadened to include radioisotopes that decay by beta radiation and alpha-particle emission. For these studies, a Tennelec LB5100 low-background alpha/beta counting system has been procured [STEINDLER-1979A]. Operating parameters appropriate to the optimal use of this instrument have been determined. This instrument is an end-window proportional counter, which operates with commercial P10 gas and is equipped with anticoincidence shielding, automatic dead-time correction capability, and a fifty-sample automatic sample changer. Alpha and beta events are counted simultaneously and sorted out by pulse-shape discrimination. The "crosstalk" between the alpha and beta channels has been optimized at less than 0.5%. The solid angle subtended between the source and the counter approaches 2π (i.e., 50%), which is the maximum possible for an end-window counter. The window for this counter is 5.7 cm in diameter and 0.5 mg/cm² thick. This geometry serves to minimize scattering problems, as well as errors associated with geometry correction.
Efficiency determinations based on procedures outlined in a previous report [FLYNN-1975] have been made for this counting system. Weightless samples of $^{22}$Na (0.55 MeV $\beta^+$) were deposited on tantalum discs. Tantalum was chosen as the backing material because it is a metal with a high atomic number (Z=73), and hence saturates the back-scattering effect of the beta radiation. Sodium-22 has a sufficiently high beta energy (0.55 MeV) so that external absorption effects are negligible. The absolute disintegration rate of the sample was determined using $^{21}$m beta counting techniques [FLYNN-1975]. The beta-counting efficiency for a weightless source on tantalum was determined to be 57%. The counting efficiency for weightless alpha sources ($^{239}$Pu) on aluminum (the Z of the backing is unimportant for alpha counting since the back-scattered radiation is negligible) was determined to be 35%. The window for this counting arrangement (0.5 mg/cm$^2$) is sufficiently thick to cause some problems for very low energy beta radiation (e.g., less than 0.2 MeV) and to a lesser extent for alpha radiation. Windows of 0.08 mg/cm$^2$ thickness are available for situations requiring additional sensitivity.

Counting efficiencies for thick samples are more complex because they take into account not only backscattering, external absorption, and solid angle, as is the case for weightless samples, but also self-absorption and self-scattering phenomena related to the sample itself. Hence, for maximum accuracy, counting efficiencies for each radioisotope being investigated should be determined under the specific counting conditions being used (e.g., sample thickness, sample material, backing material, cover material, etc.). Counting-efficiency data for a limited number of isotopes are recorded in Table 4. Counting efficiencies for different radioisotopes show considerable variation, depending on both the energy of the emitted radiation and the physical characteristics of the sample. Nevertheless, for any particular radioisotope and sample conditions, the counting efficiency can be determined very accurately (i.e., to within 1%).

### Table 4. Beta Counting Efficiencies: Thick Samples

<table>
<thead>
<tr>
<th>Isotope (Chemical Form)</th>
<th>Sample Weight, mg</th>
<th>Count Rate, cpm</th>
<th>Efficiency, %</th>
<th>Beta Energy, MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{137}$Cs-1$^{37m}$Ba(CsClO$_4$)</td>
<td>19.2</td>
<td>5180</td>
<td>31.8</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>36.8</td>
<td>4440</td>
<td>27.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>55.7</td>
<td>3930</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>$^{87}$Rb(RbClO$_4$)</td>
<td>11.1</td>
<td>27.4</td>
<td>9.8</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>22.9</td>
<td>42.0</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>44.8</td>
<td>54.3</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>66.7</td>
<td>57.0</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>$^{90}$Sr-90$^{m}$Y(SrCO$_3$)</td>
<td>32.5</td>
<td>2120</td>
<td>37.0</td>
<td>0.55(2.27)</td>
</tr>
<tr>
<td></td>
<td>48.2</td>
<td>2070</td>
<td>36.2</td>
<td></td>
</tr>
<tr>
<td>$^{147}$Pm(La$_2$O$_3$)</td>
<td>18.1</td>
<td>191</td>
<td>11.1</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>51.2</td>
<td>104</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>$^{125}$Sb-125$^{m}$Te(Sb)</td>
<td>10.5</td>
<td>240</td>
<td>17.6</td>
<td>Complex</td>
</tr>
<tr>
<td></td>
<td>22.6</td>
<td>228</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.7</td>
<td>204</td>
<td>13.5</td>
<td></td>
</tr>
</tbody>
</table>

*aThese samples are 1.75-cm-dia discs (2.4 cm$^2$) mounted on stainless steel planchets with 0.5 mg/cm$^2$ Mylar covers.

bMaximum beta energy of the emitted radiation.
Thick-sample counting efficiencies for reasonably energetic beta radiation (e.g., $^{90}$Sr/$^{90}$Y--0.55 MeV $\beta^-$/2.27 MeV $\gamma$) under the counting conditions extant in these determinations are about 37% for 10 mg/cm$^2$ surficial density and are only a slowly varying function of sample weight (see Table 4). Conversely, counting efficiencies for low-energy beta radiation (e.g., $^{87}$Rb--0.27 MeV $\beta^-$) are significantly lower (i.e., about 7% for 10 mg/cm$^2$ surficial density) and are a strong function of sample weight (see Table 4). Hence lower energy beta emitters require more careful calibration to attain optimum accuracy. Counting-efficiency data for three other radioisotopes of concern in hazardous waste disposal ($^{137}$Cs, $^{147}$Pm, and $^{125}$Sb) are given in Table 4.

The counter background has been established as 0.6 cpm beta and 0.03 cpm alpha [STEINDLER-1979A]; hence samples with count rates as low as 1 cpm beta and 0.1 cpm alpha can be readily analyzed. These low backgrounds, coupled with the high efficiency indicated above, greatly increase the sensitivity of the radiochemical technique for leach-rate determinations.

2. Conclusions

The use of epithermal neutrons for the production of activation products other than $(n,\gamma)$ [i.e., $(n,p)$, $(n,\alpha)$, and $(n,2n)$] has been concluded to be a viable technique for the study of specific cases where the $(n,\gamma)$ reaction products are not relevant.

Studies of the leach-rates for ANL-SYNROC samples prepared by the ANL Materials Science Division (MSD) show that the cesium has not been successfully incorporated into a solid solution matrix. New samples using alternative fabrication techniques are being prepared by ANL-MSD and will be characterized in the future.

Leach-rate determinations using radiochemical methods are being broadened to include low background beta and alpha counting procedures. Counting techniques based on high counting efficiencies (~40%) coupled with low backgrounds (~0.6 c/m beta and 0.03 c/m alpha) have been established. These techniques will be used to increase the sensitivity of the radiochemical methods and expand their use to nongamma-emitting radionuclides (e.g., $^{90}$Sr, $^{99}$Tc, $^{239}$Pu).

C. Review of Leach-rate Models and Leach-rate Data (J. K. Bates)

Neutron activation analysis (NAA) is the analytical method being used by ANL [FLYNN] to determine the release rates of elements trapped in various waste forms when the waste forms are contacted with an aqueous environment. Particular emphasis has been placed on studying glass waste forms. Because this application of NAA is new, demonstration of its validity for these measurements is necessary. This will be accomplished by probing the NAA technique in two ways. (1) A general mechanism describing the effect that an aqueous medium has on glass will be established. This will be based on a review of recent
experiments and will address the effects that both extensive (temperature, pH, etc.) and intensive factors (glass composition, inhomogeneities) have on glass attack. This review will serve as one basis for interpreting NAA results and will define the test conditions that should be met if the experimental results are to be meaningful. (2) The results obtained from NAA experiments will be reviewed and compared with experimental results from other release-rate investigations.

From this study, the utility of NAA will be documented and additional experiments, if any, necessary to validate the technique will be suggested.
IV. TRANSPORT PROPERTIES OF NUCLEAR WASTE IN GEOLOGIC MEDIA

(M. G. Seitz, J. Williams, S. Fried, A. M. Friedman, P. Rickert, and M. J. Steindler)

A. Introduction

A method considered for permanent disposal of radioactive waste from nuclear power generation is to place the waste in geologic formations deep beneath the earth's surface. The safety of such disposal can depend on the capability of the rock surrounding the repository to immobilize radionuclides that are carried from the repository by flowing groundwater. In safety evaluation, the concept of a distribution coefficient, \( K_d \), is widely used to predict the migration velocity of a radionuclide through rock [INOUE and KAUFMAN, BURKHOLDER, DEMARSLILY]. The distribution coefficient expresses the amount of a radionuclide partitioned onto a solid phase per mass of solid and per amount of the radionuclide in solution. Among the many possible reasons that a prediction of migration velocity from a distribution coefficient might fail are (a) the radionuclide may not be locally in equilibrium with the rock and solution [RICKERT], (b) the fraction of radionuclide sorbed by the rock may depend on nuclide concentration [SEITZ], and (c) the sorption reaction invoked experimentally to measure a distribution coefficient (such as sorption on the surfaces of crushed rock) may not represent the sorption reactions required in the prediction (such as sorption on pores or fissures of rock).

In spite of these limitations, interest in distribution coefficients to predict nuclide velocity continues because of the ease with which a coefficient for any nuclide-rock pair is measured and because of the mathematical simplification that such an approach affords. Because there is a wealth of distribution-coefficient data available and the amount of such data continues to grow, we have conducted experiments to establish the relationship between migration observed experimentally in columns of rock material and migration predicted by distribution coefficients measured in the same material. This work is considered as the first of several steps required to be able to successfully predict nuclide migration in geologic formation from distribution coefficients measured in the laboratory.

Results of two infiltration experiments using basalt and aqueous cesium-containing solutions are reported here and compared with results of batch and infiltration experiments that were reported previously [WILLIAMS]. The results of the experiments allow a comparison of cesium migration obtained at different flow rates.

*Member of the analytical chemistry group of the Chemical Engineering Division.
**Member of the Chemistry Division.
B. Experiments

Column-infiltration experiments and batch partitioning experiments were performed using portions of the same batch of 20-50 mesh Sentinel Gap basalt particles described by Ames [AMLS]. An aqueous solution was prepared to simulate the composition of groundwater in basalt. Stable and radio-cesium ($^{137}\text{Cs}$) were added to this groundwater to form the solutions needed in the experiments. The velocities of cesium relative to flowing water in a column of the granulated basalt were measured in infiltration experiments by sampling and analyzing the effluent from a column. In the batch experiments distribution coefficients for cesium were determined by gamma counting of the solutions after two-week contact times. Series of batch and column experiments were performed, and the results reported previously. The earlier infiltration experiments were performed with a solution flowing at a rate of $\sim 4.4$ km/y.

In this quarter, two additional infiltration experiments were completed (Expt. No. 164-39 and 164-67); they differed from the earlier experiments in that the solution flow was considerably slower (0.43 km/y). The experiments each used individual columns of granulated basalt, 1 cm in diameter, 9.9 cm long, and having a density of 1.41 g/cm$^3$. The solution used in one experiment had a nominal cesium concentration of $1 \times 10^{-4}$M; the solution used in the other experiments had only background cesium from traces in chemicals, etc. ($< 4 \times 10^{-5}$M). Details of the experiments and results are listed in Table 5. The table also lists data from two experiments (164-2 and 164-17) that were performed at a higher flow rate.

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>CsCl, M</th>
<th>Flow Rate, mL/min</th>
<th>Col. No.</th>
<th>Porosity, %</th>
<th>Cs-137(^a) Elution, %</th>
<th>Peak, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>164-2</td>
<td>background</td>
<td>0.32</td>
<td>1</td>
<td>43.6</td>
<td>60</td>
<td>550</td>
</tr>
<tr>
<td>164-39</td>
<td>background</td>
<td>0.03(^b)</td>
<td>4</td>
<td>51.8</td>
<td>81</td>
<td>2300</td>
</tr>
<tr>
<td>164-17</td>
<td>$1 \times 10^{-4}$</td>
<td>0.33</td>
<td>1</td>
<td>43.6</td>
<td>229</td>
<td>100</td>
</tr>
<tr>
<td>164-67</td>
<td>$1 \times 10^{-4}$</td>
<td>0.027</td>
<td>5</td>
<td>57.4</td>
<td>146</td>
<td>390</td>
</tr>
</tbody>
</table>

\(^a\)Percent elution at termination of experiment.
\(^b\)Flow rate varied from 0.05 to 0.006 mL/min.

Elution curves obtained from the two experiments using $1 \times 10^{-4}$M cesium solution listed in Table 5 are given in Fig. 4.

C. Discussion of Results

The results given in Table 5 and illustrated in Fig. 4 for two experiments indicate that at a lower flow rate, but at the same cesium concentration, the cesium retention time is longer. This indicates that within the
range of flow rates used in the experiments, kinetic factors are important to cesium migration through the granulated basalt.

![Graph showing elution activity vs. eluate volume](image)

**Fig. 4**
Elution of Cesium-137 from Columns of Granulated Basalt at Different Flow Rates Using a Groundwater Solution Containing $1 \times 10^{-4}$ M Cs. The elution rate is lower at the lower flow rate.

The results of the infiltration tests reported here were compared with results of previously performed batch tests at various cesium concentration levels by converting distribution coefficients to relative cesium velocities, $V_{Cs}/V_w$ (velocity of the cesium relative to the velocity of the water front), by the equation:

$$V_{Cs}/V_w = \frac{1}{1 + K_d \rho / \varepsilon}$$

where $\rho$ is the density of the rock column and $\varepsilon$ is the porosity of the rock column. The principle used to derive this equation is that the relative velocity of cesium is equal to the fraction of cesium in solution.

The relative velocities of cesium were determined from the elution volume of tritium (which gives the flow volume of the column) and the peak volumes of cesium as measured in the different infiltration experiments. [The velocities of cesium and of the water are equal to the length of the column (~9.9 cm) times the water flow rate (in mL/s) divided by the elution volume for cesium and tritium, respectively. Therefore, the relative velocity of cesium is equal to the elution volume of tritium divided by the elution volume for the cesium.] The relative velocities obtained from the different experiments at specific cesium concentrations are given in Table 6.

Alternatively, we could have converted results of infiltration experiments to distribution coefficients and made the comparisons. However, because the goal of this program is to understand nuclide migration and not, necessarily, distribution coefficients, we have selected to compare relative velocities. The data in Table 6 can be converted to distribution coefficients using the porosities given in Table 5 and the column density of 1.41 g/cm$^3$ that is characteristic of the columns.
TABLE 6. Relative Velocities of Cesium in Basalt from Column-infiltration Experiments and Batch-partitioning Experiments

| Cesium Concentration in Solution | Column Infiltration | Batch Partitioning
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fast Flow</td>
<td>Slow Flow</td>
</tr>
<tr>
<td>1.0 x 10^{-4}</td>
<td>0.04-0.03</td>
<td>0.012</td>
</tr>
<tr>
<td>1.8 x 10^{-5}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0 x 10^{-5}</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>1.0 x 10^{-6}</td>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>7.8 x 10^{-7}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0 x 10^{-7}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.4 x 10^{-8}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0 x 10^{-8}</td>
<td>0.006</td>
<td>-</td>
</tr>
<tr>
<td>3.4 x 10^{-9}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.8 x 10^{-10}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.0 x 10^{-11}</td>
<td>0.005</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Concentrations are for solutions "equilibrated" with the column in infiltration experiments or for solutions at the termination of batch experiments.

A column density of 1.41 g/cm³ and a porosity of 0.436 were used to calculate the relative velocities from results of batch-partitioning experiments. Cesium concentrations were calculated from the amount of 137Cs remaining in solution.

The flow rate averaged ~0.30 mL/min for the experiments, corresponding to a linear-flow rate of 4.6 km/y.

The flow rate averaged ~0.028 mL/min for the experiments, corresponding to a linear flow rate of 430 m/y.

A broken line indicates that a measurement was not made at the corresponding experimental conditions.

The data in Table 6 indicate that (1) the relative velocity is dependent on concentration and (2) at lower flow rates, the relative velocity measured in infiltration experiments is closer to the relative velocity predicted by results of batch experiments.

These relationships can be seen in Fig. 5, in which the relative velocities are plotted against the logarithms of the cesium concentration. Also given in the figure are the times during which the solutions from which cesium was sorbed or desorbed and the basal particles were in contact (for both infiltration and batch experiments). The data for the batch tests indicated in the figure were reproduced in duplicate experiments.
For the infiltration experiments (indicated by circles and diamonds) the relative migration rate decreases when the contact time is increased from \( \sim 700 \) to \( 7000 \) s, but the relative velocity is higher than that indicated from batch experiments with a contact time greater than \( 10^6 \) s.

To compare contact times in both types of experiments we can assume (1) that sorption or desorption is limited by the surface area between the rock and solution or (2) that sorption is limited by diffusion within pores, cracks, or other defects in the rock and is independent of the surface contact area. The surface area contacted by a volume of solution is \( \sim 40 \) times larger in the column experiments than in the batch experiments. Therefore, if item 1 above is true, then sorption is \( 40 \) times faster in columns than in batch tests. If item 2 is true, then sorption proceeds at the same rate in both experiments because the diffusion geometry is the same in both types of experiments. (The factor may be between 1 and 40 if the real case lies between items 1 and 2.)

Even if the factor of 40 applies, the extent of sorption in a column may be significantly less than that obtained in batch experiments. Therefore, the higher relative velocities measured in column experiments may be due to the limited time the solution can react under flow conditions.

The results from batch tests do not appear to be time dependent since the extent of sorption obtained in \( 1.3 \times 10^6 \) s (15 d) is about the same as that obtained in \( 2.4 \times 10^6 \) s (28 d). To achieve a similar extent of sorption in column experiments would require flow rates from 96 m/y to as low as 2.4 m/y. To elute the cesium peak at the low cesium concentration would require \( \sim 1.5 \) to 59 y. Because groundwater flow rates higher than 96 m/y are not uncommon, kinetic effects such as those exhibited in the results of the infiltration experiments need to be considered for repository safety evaluations.
V. TRACE-ELEMENT TRANSPORT IN LITHIC MATERIAL BY FLUID FLOW AT HIGH TEMPERATURE (M. G. Seitz and R. A. Couture)

A. Introduction

This report covers two subjects: (1) ion-exchange sorption of Cs+ ions from aqueous solutions and the transport of Cs+ ions through kaolinite columns, and (2) sorption of anions of iodine by Fe$_2$O$_3$.

Ion exchange on clay minerals at high temperatures is of interest because of the possible use of clay minerals as backfill in a repository for high-level radioactive waste. The temperature dependence of ion-exchange sorption of Cs$^+$ by kaolinite was previously reported by us at temperatures up to 225°C [STEINDLER-1978B]. This was determined in column experiments from the rate of transport due to fluid flow. Since Cs$^+$ is transported much more slowly at room temperature than at higher temperatures, the experiments are very long at room temperature. A point determined for a 25°C temperature was extrapolated from 0.5M NaHCO$_3$ solution to a 0.1M solution, but did not seem to fit well on the temperature-dependence curve. Therefore, this point was determined again, without extrapolation. Moreover, the value so derived was compared with data from static experiments. The results of the static experiments and the new column experiment are reported here.

It was reported in a previous quarterly report [STEINDLER-1978A] that oxidized species of iodine are strongly retarded by kaolinite columns. Retardation of iodine species is of interest in the disposal of radioactive $^{129}$I. The evidence suggested that traces of iron oxide in the columns were responsible for the retardation. Subsequently, isotherms for sorption of IO$_3^-$ by Fe$_2$O$_3$ over a range of 10 orders of magnitude in dissolved IO$_3^-$ concentration were presented [STEINDLER-1979A]. The column experiments showed that at least two oxidized species of iodine, namely, IO$_3^-$ and IO$_4^-$, were retarded by the columns. We now present data on the sorption of IO$_4^-$ by Fe$_2$O$_3$.

B. Sorption of IO$_4^-$ by Fe$_2$O$_3$

The amount of IO$_4^-$ sorbed by reagent-grade Fe$_2$O$_3$ was determined by reacting solid with liquid in rotating test tubes. The procedures were identical to those reported previously for IO$_3^-$ [STEINDLER-1979B]. Measured quantities of NaIO$_4$ were added to test tubes containing aqueous buffer solutions, and the amounts remaining in solution after reaction and centrifugation were determined by reduction with I$^-$ and titration of I$_2$ with Na$_2$S$_2$O$_3$.

The Fe$_2$O$_3$ is reagent-grade material which has the crystal structure of natural, moderately well crystallized hematite. The particles are rounded equant crystals with diameters of 0.20 to 0.25 µm. The specific surface area was estimated to be 10 m$^2$/g by N$_2$ sorption (B.E.T. isotherm) and 5 m$^2$/g from the observed particle size.
The results of the sorption tests are shown in Table 7. The compositions of the buffer solutions are shown in Table 8. A blank run was made to check for sorption by the test tubes. The blank had an initial $\text{IO}_4^-$ concentration of $2.38 \times 10^{-4} \text{M}$; three titrations gave final concentrations of $2.41 \times 10^{-4}$, $2.37 \times 10^{-4}$, and $2.4 \times 10^{-4} \text{M}$. The data are compared with the isotherms for $\text{IO}_3^-$ sorption in Fig. 6. The $\text{IO}_4^-$ is sorbed about four times as strongly as the $\text{IO}_3^-$ and is as strongly sorbed at pH 8.7 as $\text{IO}_3^-$ is sorbed at pH 3.9.

<table>
<thead>
<tr>
<th>pH</th>
<th>$[\text{IO}_4^-]$, M</th>
<th>$\Gamma$, mol/g</th>
<th>$K_d$, cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.87</td>
<td>$1 \times 10^{-6}$</td>
<td>$3.0 \times 10^{-7}$</td>
<td>2100</td>
</tr>
<tr>
<td>2.87</td>
<td>$2 \times 10^{-6}$</td>
<td>$1.24 \times 10^{-6}$</td>
<td>600</td>
</tr>
<tr>
<td>2.87</td>
<td>$3 \times 10^{-6}$</td>
<td>$3.2 \times 10^{-6}$</td>
<td>1100</td>
</tr>
<tr>
<td>2.87</td>
<td>$6 \times 10^{-6}$</td>
<td>$6.4 \times 10^{-6}$</td>
<td>1100</td>
</tr>
<tr>
<td>3.87</td>
<td>$7.8 \times 10^{-6}$</td>
<td>$3.1 \times 10^{-6}$</td>
<td>397</td>
</tr>
<tr>
<td>5.73</td>
<td>$1.79 \times 10^{-4}$</td>
<td>$3.0 \times 10^{-6}$</td>
<td>168</td>
</tr>
<tr>
<td>8.7</td>
<td>$5.4 \times 10^{-5}$</td>
<td>$2.5 \times 10^{-6}$</td>
<td>46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.93</td>
<td>50 mL 0.1M CH$_3$COOH</td>
</tr>
<tr>
<td></td>
<td>8.9 mL 0.1M CH$_3$COONa</td>
</tr>
<tr>
<td>2.87</td>
<td>50 mL 1M CH$_3$COOH</td>
</tr>
<tr>
<td></td>
<td>8.9 mL 0.1M CH$_3$COONa</td>
</tr>
<tr>
<td>5.77</td>
<td>2.8 mL 0.1M CH$_3$COOH</td>
</tr>
<tr>
<td></td>
<td>50 mL 0.1M CH$_3$COONa</td>
</tr>
<tr>
<td>8.67</td>
<td>0.1M NaHCO$_3$</td>
</tr>
</tbody>
</table>

**Fig. 6**

Sorption of $\text{IO}_4^-$ by Fe$_2$O$_3$ as a Function of pH and Dissolved Concentration, Compared with Sorption of $\text{IO}_3^-$. $\Gamma$ = amount sorbed, mol/g. Numbers indicate pH. Data points are for $\text{IO}_3^-$. Lines are for $\text{IO}_4^-$.  

**C. Cs$^+$ Sorption by Kaolinite**

1. **The Column Experiment**

   A 50-μL volume of 0.100M NaHCO$_3$ with a trace of $^{134}\text{Cs}$ was injected into a stream of 0.100M NaHCO$_3$, of which 730 mL was pumped through kaolinite column 7 at a flow rate of 0.025 mL/min. Pressure and temperature were monitored. The temperature varied by 1 to 2°C during the experiment; the
The average temperature was about 20°C. The column was prepared by pumping a slurry of kaolinite into an empty tube 1 cm in diameter by 5 cm long. The clay was supported by Type 316 stainless steel sintered filter frits at the top and bottom. The apparatus was constructed of Type 316 stainless steel. The kaolinite used was Hydrite R (Georgia Kaolin Co.), which had been sized and treated by the manufacturer to remove free iron and manganese oxides. It contained 0.27% Fe$_2$O$_3$. Mössbauer spectroscopy (by Gopal Shenoy, ANL Solid State Science Division) showed that less than 5% of the iron was present as free oxide.

After the conclusion of the experiment, the pH of the solution that had not passed through the system was 9.80 at 20°C. The pH of the effluent was 9.76; thus, the pH was not greatly affected by flow of the solution through the kaolinite. At the end of the experiment, after 730 mL of flow, the column was opened, dissected, and analyzed. The results are plotted in Fig. 7. Since the free column volume was 1.76 cm$^3$ and the peak migrated through 0.6 of the column volume, the peak velocity $R_f$, relative to the velocity of water,

can be calculated from

$$\frac{1}{R_f} = \frac{730}{1.76 \times 0.60} = 691.$$  

Then the distribution coefficient

$$K_d = \left( \frac{1}{R_f} - 1 \right) \frac{\text{porosity}}{(1 - \text{porosity})p_{\text{solid}}}$$

$$= 690 \frac{0.45}{0.55 \times 2.67} = 211 \text{ cm}^3/\text{g}.$$  

The selectivity coefficient

$$K' = \frac{X_{Na}}{X_{Cs}} \frac{[Cs^+]}{[Na^+]} = \frac{10^{-3}Q}{K_d[Na^+]}. $$  

$$K' = 4.3 \times 10^{-3},$$

where $Q$ = ion exchange capacity = $9.1 \times 10^{-5}$ mol/g and $X_{Cs}$ and $X_{Na}$ = the respective mole fractions of the found Cs and Na.

The value of $K'$ is compared with the previously obtained values in Fig. 8, with the solid line drawn to fit the previous data. The dashed line through the new point suggests that the temperature dependence is less than had been previously thought.
2. The Static Experiments

Kaolinite Hydrite R samples were reacted in glass test tubes with 0.100M NaHCO₃ solutions containing ¹³⁴Cs tracer. After centrifugation, the solutions were analyzed by gamma counting, and the amount in solution and the amount sorbed were calculated. The results are shown in Table 9. No sorption by the test tubes was detected. The best value of Kₐ appears to be 50 cm³/g.

<table>
<thead>
<tr>
<th>Solid/Solution Ratio, g/cm³</th>
<th>Solution Concentration, counts·s⁻¹·cm⁻³</th>
<th>Amount Sorbed, counts·s⁻¹·g⁻¹</th>
<th>Kₐ, cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.018</td>
<td>128</td>
<td>9200</td>
<td>72</td>
</tr>
<tr>
<td>0.129</td>
<td>37</td>
<td>1960</td>
<td>53</td>
</tr>
<tr>
<td>0.233</td>
<td>24</td>
<td>430</td>
<td>48</td>
</tr>
</tbody>
</table>

However, the experiment was repeated because one sample gave substantially different results from the others. In the repeat experiment, the concentration dependence was checked. The same NaHCO₃ was used as in the column experiment (Section C.1 above). The final pH was 9.76 at 25°C. The results are shown in Table 10. In a blank test with no kaolinite, a test tube sorbed 8% ± 3%* of the ¹³⁴Cs. Thus the reported Kₐ values may be up to 8% too high. There is no question that the isotherm is linear over 2.6 orders of magnitude. The concentration range includes the concentration observed at the end of the column.

*Errors in Section V are standard errors due to counting of samples and background.
experiment. This agrees with the observation in previous column experiments that peaks were very nearly symmetrical. The best value of $K_d$ is $75 \text{ cm}^3/\text{g}$. This is a factor of 3 smaller than the value obtained from the column experiments, and it is not clear why.

| Table 10. Cesium-134 Sorption by Kaolinite in 0.1M $\text{NaHCO}_3$—Second Test |
|---|---|---|---|
| Solid/Solution Ratio, g/cm$^3$ | Solution Concentration, counts*s$^{-1}$*cm$^{-3}$ | Amount Sorbed, counts*s$^{-1}$*g$^{-1}$ | $K_d$, cm$^3$/g |
| 0.037 | 0.049 ± 0.008 | 4.07 ± .25 | 83 ± 15 |
| 0.037 | 0.223 ± 0.022 | 15.65 ± .70 | 70.2 ± 7.6 |
| 0.037 | 1.134 ± 0.037 | 79.6 ± 2.2 | 70.1 ± 3.0 |
| 0.038 | 5.25 ± 0.07 | 413 ± 10 | 78.7 ± 2.2 |
| 0.038 | 10.88 ± 0.11 | 816 ± 20 | 75.0 ± 2.0 |
| 0.038 | 21.78 ± 0.33 | 1631 ± 41 | 74.9 ± 2.2 |

The difference may be attributed partly to retardation by the streaming potential, although this effect is believed to be small. The difference may be related to deformation of the kaolinite in the column, or to the iron oxide present in the column. Unfortunately, the stainless steel frit at the top of the column was quite corroded. Corrosion with subsequent chemical alteration of the solution may be a problem in these long experiments.

A second problem is the pH. Unfortunately, the pH of the solution was not measured until long after the experiment, at which time the solution had lost considerable $\text{CO}_2$. It will be necessary to determine what effect the $\text{CO}_2$ loss had on the experimental results reported here.
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Steindler-1979A

Steindler-1979B

Williams

Zeleny