Nuclear Waste Management Quarterly Progress Report July through September 1977

A. M. Platt

January 1978

**Prepared for the
U.S. Department of Energy
under Contract EY-76-C-06-1830**

Battelle

Pacific Northwest Laboratories

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

The views, opinions and conclusions contained in this report are those of the contractor and do not necessarily represent those of the United States Government or the United States Department of Energy.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.50
026-050	\$5.00
051-075	\$5.50
076-100	\$6.00
101-125	\$6.50
126-150	\$7.00
151-175	\$7.25
176-200	\$8.50
201-225	\$8.75
226-250	\$9.00
251-275	\$10.00
276-300	\$10.25

3 3679 00051 8227

PNL-2377-3
UC-70

NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
JULY THROUGH SEPTEMBER 1977

Compiled by
A. M. Platt
Nuclear Waste Technology Program

January 1978

BATTELLE
Pacific Northwest Laboratories
Richland, Washington 99352

FOREWORD

This document is one of a series of technical progress reports designed to report on commercial radioactive waste management programs at Battelle, Pacific Northwest Laboratories. These programs were funded by the Waste Management, Production and Reprocessing Division of ERDA. The Commercial Radioactive Waste Fixation Program is reported elsewhere. These reports are issued on a quarterly basis.

The prior report in this series is Nuclear Waste Management Quarterly Progress Report April Through June 1977, BNWL-2377-2. As of October 1, 1977, Pacific Northwest Laboratories changed the designation for reports from BNWL to PNL. Thus the next report to be issued in this series will be PNL-2377-4.

1.0 DECONTAMINATION AND DENSIFICATION OF CHOP-LEACH CLADDING RESIDUES

R. L. Dillon and R. S. Kemper - Project Managers

Fuel element cladding residues from the chop-leach head end process constitute a low-density, high-surface-area metallic waste with a substantial actinide element contamination. The objective of this study is to determine the feasibility of and to develop methods for removal of long half-life transuranics from the cladding residues and for consolidation of the zirconium and stainless steel residues. The study involves:

1. *selection and laboratory testing of methods for transuranic removal by*
 - a) *aqueous reagents*
 - b) *molten salt reagents*
 - c) *fluxing during melting*
2. *consolidation of the fuel element hulls by melting and casting Zircaloy, stainless steel, Inconel or alloys of the three*
3. *testing and evaluating the consolidated fuel hulls for long-term waste management*
4. *absorption and fixation of tritium into waste ingots*
5. *consolidation of transuranics removed.*

SUMMARY

The removal of surface oxide and contamination from BWR Zircaloy fuel cladding by an HF-Ar decontamination process produced results similar to those of previous PWR hull treatments.

Pilot-scale equipment for chemical decontamination of cladding hulls is being designed and fabricated. This equipment will be installed in the prototype decontamination/densification facility in the 306W Building. There the equipment will undergo nonradioactive demonstration and testing before being removed for actual

processing of radioactive cladding hulls in the 324 D Hot Cell.

The decontamination process parameters were reviewed to locate potential problems before scale-up identified several secondary waste stream treatment methods. Treatment method evaluations to select the best paths to follow are indicated.

Installation of the Inductoslag ingot melting furnace in the prototype decontamination and densification facility is nearly complete. After nonradioactive testing, the furnace will be used in hot cell densification of chop-leach fuel hulls. Melting

experiments to demonstrate that the Inductoslag melting process can be scaled up were performed with other Inductoslag equipment. Experiments evaluating methods and materials for the recasting of Zircaloy are described here.

DECONTAMINATION PROCESS

The removal of surface oxides and contamination from BWR fuel cladding by the HF-Ar modified aqueous process was checked by treating 21.5 cm of 1.13-cm-dia leached fuel cladding in a 25% Ar-75% HF mixture at 1 atm and 600°C for 1 hr. This was followed by treatment in 0.4 M ammonium oxalate-0.16 M ammonium citrate-0.1 M ammonium fluoride-0.3 M hydrogen peroxide solution at 95°C for two separate half-hour rinses. The process was carried out in the previously described⁽¹⁾ K-Area cave facility, chopping the nitric acid-leached BWR cladding into about 3-cm-long pieces and combining the pieces with an equivalent number of unirradiated specimens.

The result of the treatment was the removal of all visible surface oxide and the weight loss indicated below:

irradiated tubing = 3.8 g/dm^2
(2.3 mils)

unirradiated tubing = 3.3 g/dm^2
(2.0 mils)

unirradiated tubing (oxidized) = 2.9 g/dm^2 (1.7 mils).

These results compared with 3.1 g/dm^2 and 2.8 g/dm^2 for irradiated and unirradiated specimens in the previous treatment run⁽²⁾ and are in general

agreement with all previous tests of irradiated and oxidized tubing. Decontamination and secondary waste stream treatment are being evaluated.

The scale-up of the decontamination process to pilot scale (2 kg/hr) was described in two previous reports.^(2,3) Contracts were awarded for the HF reactor-aqueous washer system. The design of auxiliary process solution tanks is in progress, and special equipment for remote operation is being procured.

The proposed chemical decontamination process was reviewed by the Materials Resources and Process Metallurgy Section of Battelle Columbus Laboratories. Briefly, their review indicated that several bench-scale studies of potential secondary waste stream treatment processes should be started to define potential recycle stream parameters. Specifically the review indicated that:

1. A room-temperature granular bed of sodium fluoride might be used to absorb hydrogen fluoride from the AR-HF-H₂-H₂O (trace) effluent gas. The absorbed HF and the NaF bed might then be recycled by heating the bed and driving off the HF.
2. The same stream might be treated by condensation at -80°C followed by a double distillation to free the HF from water vapor so that it may be recycled.
3. Off-gas streams from the HF reactor and calciner should be analyzed in order to optimize temperature and treatment processes.

DENSIFICATION PROCESS

Installation of the Inductoslag ingot melting furnace described last quarter is nearly complete, with melting scheduled to start in January 1978.⁽¹⁾ Tests to demonstrate that the Inductoslag melting process can be scaled up have been performed at a different Inductoslag furnace in contract work supervised by the U.S. Bureau of Mines. A 36-kg ingot of mild steel was melted in an Inductoslag crucible 20.3 cm dia by 21.6 cm deep using CaF_2 slag. Total melt time was 23 min using 240 kW of power at a frequency of ~ 2 kHz. Based on the result of these tests and previous Zircaloy Inductoslag melting experience, it is estimated that 260 kW would melt a 20.3-cm-dia ingot and that 19 kg could be poured for casting. Inductoslag melting performed prior to these tests had been limited to a 10-kHz, 100-kW power source; that source could melt Zircaloy ingots up to 10 cm in diameter, producing 2 kg of Zircaloy for poured casting.

Previous Zircaloy casting work for producing reusable shapes has been described.⁽¹⁾ Choice of a casting system depends on the selection and design of the part to be cast and the selection of the mold materials to be used. In the decision to reduce overall waste storage costs by casting radioactive Zircaloy for reuse these points must be considered:

- The casting should have a large volume requiring a minimum volume of mold materials, i.e., thick sections with little or no coring material.

- Mold-metal reactions should be minimal and not deleteriously affect metal or casting quality.
- If the mold material is recycled, then the mold-making process must be simple and easily adaptable to remote operation.
- If the mold material is to be disposed of as a once-through material, then the disposal process must reduce the volume of used mold materials and be remotely operable.

Zircaloy castings will be made from clean decontaminated hulls with or possibly without an intermediate melting step. The decontamination process followed by melting will reduce the TRU content of the castings, hopefully below 10 nCi/g. In this case it should be possible to treat the molding materials as being radioactive but nontransuranic.

The previous work mentioned above concluded that Zircaloy is potentially castable, but that thin section castings may not be achievable. This work used rammed and baked zircon sand molds with a sodium silicate binder. Although this demonstration showed potential for casting Zircaloy, the molding system used is not practical for casting radioactive materials. The volume of sand used is greater than the volume of castings produced. This would require a remote recycle molding system involving crushing, screening, sodium silicate blending, ramming, and baking. In addition, the recycle sand has a finite life because of sodium and silicon contamination. Volume reduction of the sand for disposal would be difficult.

A second molding process⁽²⁾ involved use of a polystyrene pattern with several inches of dry zircon sand vibrated around the polystyrene pattern. Five castings were made in which molten titanium was poured into the polystyrene, which evaporated and formed the mold cavity. The resulting castings were not usable because of innumerable gas voids caused by vaporization of the polystyrene. Although titanium rather than Zircaloy was used in these tests, there is no reason to assume that Zircaloy would behave much differently.

Casting work during this reporting period was aimed at evaluating a patented investment molding technique currently used for making titanium castings--"Monograf Mold." This process uses a mold built up in layers (0.25 to 0.5 cm thick) of a carbonaceous shell. Two 1.8-kg Zircaloy-4 castings were made using this molding technique. Melting was performed in the Inductoslag casting furnace operated by the U.S. Bureau of Mines. The first heat was melted in 1/3 atm of helium with CaF_2 flux and poured with the mold temperature at $\sim 50^\circ\text{C}$. There was no metal-mold reaction, and the mold filled completely. After the mold was broken away from the casting, several cold shuts and scabs could be seen on the casting surface. This was attributed to inadequate superheat in the mold and to improper gating, which allowed too much turbulence as the metal entered the mold.

A second heat was melted in 1/3 atm of argon with an approximate 100 g of additional CaF_2 flux. Mold temperature

was $\sim 150^\circ\text{C}$, with an approximate increase of 50°C superheat in the melt. The pour was made faster than the first. The mold filled but upon examination showed cold shuts and some evidence of gassing as well as some metal-mold reaction. The gassing and metal-mold reaction could have been caused by the faster pouring plus the additional superheat of the metal and the higher mold temperature.

Very little is known about the fluidity of Zircaloy. Zircaloy fluidity tests are being planned to give some information as to the casting design limitations of Zircaloy.

Initial burning tests on a 50-g sample of crushed Monograf Mold material showed a residue of less than 5 g after heating the sample under static air and charge conditions for ~ 18 hr at 950°C . Burning tests will continue until standard test conditions are developed and reproducible results are achieved. This will allow assessment of the qualifications of this and other candidate mold materials for use in radioactive waste disposal.

REFERENCES

1. A. M. Platt, compiler, Nuclear Waste Management and Transportation Quarterly Progress Report July Through September. BNWL-2179, Battelle, Pacific Northwest Laboratories, Richland, WA, January 1977.
2. A. M. Platt, compiler, Nuclear Waste Management Quarterly Progress Report April Through June 1977. BNWL-2377-2, Battelle Pacific Northwest Laboratories, Richland, WA, November 1977.

3. A. M. Platt, compiler, Nuclear Waste Management Quarterly Progress Report January Through March 1977. BNWL-2290, Battelle, Pacific Northwest Laboratories, Richland, WA, July 1977.

2.0 MONITORING METHODS FOR PARTICULATE AND GASEOUS EFFLUENTS FROM WASTE SOLIDIFICATION PROCESSES

R. L. Gordon - Project Manager

The objective of this program is to develop reliable and accurate techniques for process monitoring and stack emission monitoring for future waste solidification facilities.

SUMMARY

During this reporting period, experiments to determine the operating characteristics of the particle generator were performed. The generator can produce particles in the size range below $1\ \mu$. A survey was conducted to determine the elements amenable to detection by direct inlet mass spectrometry. The technique appears sufficiently promising to warrant experimental investigation of situations appropriate to effluent streams from waste solidification processes.

PARTICLE GENERATOR PERFORMANCE - D. C. Hamilton and H. G. Rieck, Jr.

The particle generator, designed and assembled for filter efficiency measurements, was described in the previous quarterly report.⁽¹⁾ During the current reporting period the performance of the apparatus was characterized by determining the particle size distribution produced for various generator operating conditions. To provide results pertinent to the required sampling of the vitrification off-gas treatment system, filter

trapping efficiencies must be measured with particles below $1\ \mu$ in size. Results of the tests indicate that the generator is capable of producing particles in this size range.

The particle generator employs a jet mill driven by dry nitrogen gas. In our experiments, ball-milled calcine from WSEP run PW7a-2 is introduced into the grinding chamber. The grinding chamber consists of a cylindrical section with 6 tangentially mounted 27-gauge hypodermic needles on its periphery. Three or four short bursts of N_2 at a flow rate of 2 to 3 liters/min are used to prime the system; after this the desired flow rate is set and allowed to remain constant for 5 min to establish steady-state conditions. The finer powder, through centrifugal action, migrates toward the center of the grinding chamber and passes up a settling tube about 1 m long. Particles with mass less than a critical value, determined by a balance of buoyant, drag and gravitational forces, drift up the tube with a velocity determined by flow rate and geometry. The maximum particle diameter can be shown to be given by⁽²⁾

$$D_p = \frac{5.19 U_t^{0.877} \rho^{0.254} \mu^{0.377}}{[g(\rho_p - \rho)]^{0.623}} \quad (1)$$

Parameters in Equation 1 have the following definitions and values:

ρ_p = 237.2 lb/ft³, particle density (estimated)

ρ = 0.0725 lb/ft³, nitrogen gas density

μ = 1.24×10^{-5} lb/ft sec, nitrogen viscosity

g = 32.0 ft/sec², gravitational acceleration

and U_t , the terminal velocity in the settling tube, is related to the flow rate s and tube diameter D by

$$U_t = 8s/\pi D^2.$$

At a flow rate of 0.7 l/min and a tube diameter of 7 cm, the terminal velocity is 0.61 cm/sec. Equation 1 then predicts a maximum particle diameter of 1.4 μ .

Samples for particle size distribution measurements were collected on a Nuclepore filter positioned at the top of the settling tube about 1 m above the grinding chamber. Inlet airflow across the filter was provided by a vacuum pump and measured with a rotameter. The pump was placed 4.6 m (15 ft) from the collection point to avoid contamination by oil vapor. To achieve an unbiased sample, isokinetic conditions were approximated by matching the flow velocity in the tube with the velocity at the filter orifice. The nitrogen flow rate was sufficiently small to prevent significant departure from laminar flow at the filter position.

A 4-hr collection time was found to be sufficient to obtain a sample suitable for required measurements. At the end of the collection period the filters exhibited a light gold color from calcine deposition.

Particle size distribution measurements were performed by analyzing scanning electron microscope (SEM) photographs of the filter. Six regions on the filter were chosen at random, and photographs were taken at magnifications of 1000X, 2000X and 5000X. The 2000X magnification was found to be optimum for measurements of particle size distribution. At 2000X, a workable trade-off between resolution and particle number density was achieved. Particle size distribution was determined with a Millipore IIMC Particle Measurement System, which yields a cumulative distribution by counting all particles over a certain set size, the "oversize set" on the instrument. The procedure amounts to adjusting the parameters of the IIMC instrument and pressing a "count/measure" button. After proper calibration of the instrument, 10 cumulative readings were performed at each value of oversize set to obtain a representative average. Particle diameters were determined by their maximum horizontal chord length.

Results

Figure 2.1 shows a plot of the frequency of counts versus particle diameter, and Figure 2.2 shows the cumulative distribution plotted on log-normal probability paper. These data were produced by scanning a

FIGURE 2.1. Particle Size Frequency Distribution. PW7a-2 cold synthetic calcine.

FIGURE 2.2. Fit of Particle Size Distribution to Log-normal Distribution, $\bar{1}\mu = 116 \pi$ MC Units. Total number of particles: 1815

total area of $9512 \mu^2$ of the filter surface. The total number of particles counted was 1815. The particle size distribution behaves log-normally, especially in the region of intermediate particle diameters where statistics are most favorable. Analysis of the plots indicates that 87% of the particles are less than 1μ in diameter, while 97% are less than 2μ in diameter. The geometric mean diameter of the particle size distribution is 0.37μ . The observed distribution indicates typical results which can be expected in similar flow and geometric conditions.

After the particle size distribution produced was established, the apparatus was installed in a hood in a radiation zone in 325 Building. Measurements of filter efficiencies using irradiated calcine are currently being conducted.

DIRECT INLET MASS SPECTROMETRY - R. L. Gordon

Direct inlet mass spectrometry (DIMS) is a promising candidate for continuous real-time monitoring of the particulate component of vitrification off-gas streams. In this recent application of mass spectrometry^(3,4) an air-inlet system is used to permit a stream of air and any entrained particulates to strike a hot rhenium filament. Atmospheric oxygen which enters the source region of the mass spectrometer forms a layer of rhenium oxide on the surface of the filament, increasing the work function of the filament to about

7.2 eV. Constituent atoms are then ionized at a rate determined by the surface work function W and the ionization potential IP of the atoms or molecules resulting from evaporation. This behavior is given expression by the well known Langmuir-Saha equation:

$$\frac{n^+}{n^0} = \frac{w^+}{w^0} \exp[(W-IP)/kT].$$

Here, n^+ and n^0 are number densities of ionized and neutral atoms leaving the filament, respectively, and w^+ and w^0 are the statistical weights of the ion and neutral ground states, respectively. Experiments have shown that materials with ionization potentials as high as 8.0 eV can be ionized with sufficient efficiency on a rhenium oxide surface to permit detection of mass-analyzed components at the nanogram per cubic meter level.^(3,4)

Of the elements expected to be in the effluent as particulates or adsorbed on particles in the effluent, only tellurium, selenium, antimony, and mercury possess ionization potentials above 8.0 eV, and hence would fall outside the range of applicability of the DIMS technique with oxidized rhenium as the surface ionization filament. Applicability of the DIMS technique therefore covers strontium, cesium, cerium, all rare earths, ruthenium, sodium, and zirconium. A comparison of pertinent ionization potentials for atomic species of interest is shown in Table 2.1.

Achievable detection limits for the DIMS technique depend on a wide range of variables. In addition to the atomic

TABLE 2.1. Ionization Potentials of Expected Particulate Constituents in Solidifier Off-gas

Element	Ionization Potentials, Electron Volts
Na	5.14
Se	9.75
Sr	5.70
Zr	6.84
Ru	7.37
Sb	8.64
Te	9.01
Cs	3.89
Ce	6.65
Hg	10.44
Rare earths	$5.42 < IP < 6.25$

ionization potential, important parameters include the chemical form containing the species and the atmospheric environment in which the particles are entrained. The chemical form determines the details of the evaporation and dissociation of the compound containing the atom of interest when it strikes the surface ionization filament. The ambient atmosphere may contain gases and vapors which reduce the work function of the filament. Or it may be a source of impurities which could cause competing chemical reactions, conceivably presenting a path other than ionization and resulting in sample loss. As an indicator of the ultimate sensitivity of the technique, Davis reports in Reference 3 that a particle of LiCO_3 containing as few as 800 Li atoms ($IP = 5.4 \text{ eV}$) can be detected, while for CuO the minimum detectable particle contains 7000 Cu atoms ($IP = 7.7 \text{ eV}$).

In effluent streams of the solidification process, the elements of interest are expected to be present predominantly as oxides, with some sulfates and phosphates. Since the DIMS technique is new, no data are available to indicate ultimate sensitivities available for these forms of elements of interest. Further, the effects of the gaseous components of the effluent, which is expected to be largely NO_x and water vapor, on the surface ionization are not known. For these reasons an experimental system designed to permit answers to these questions will be assembled and measurements pertinent to the application of DIMS to waste solidification effluent performed.

As an example of the sensitivity to be gained by using the DIMS technique, consider the analysis of ^{137}Cs ($IP = 3.9 \text{ eV}$) at the release limit level of $5 \times 10^{-10} \mu\text{Ci cm}^{-3}$. The most effective gamma spectrometer employs a lithium-drifted-germanium well-type detector. The minimum detectable activity in the absence of an anti-coincidence annulus for background reduction is near 0.23 pCi for a 1440-min counting time.⁽⁵⁾ In contrast, the DIMS approach would permit detection of single particles containing perhaps as few as 1000 ^{137}Cs atoms and would do so on a real-time basis. The release limit corresponds to approximately 2.5×10^{10} atoms per cubic meter of air. The detailed physical distribution is of course not known at this time, but this would correspond to about 10^7 particles containing 1000 atoms each in a cubic

meter of effluent off-gas. State-of-the-art sampling techniques for DIMS is near $3 \times 10^{-4} \text{ m}^3/\text{min}$,⁽⁶⁾ which, at an off-gas flow rate of 50 CFM ($1.4 \text{ m}^3/\text{min}$), corresponds to a sampling efficiency of about 0.02%. At the release limit the DIMS technique should produce approximately 2000 ion bursts per minute of sampling time if the ^{137}Cs were present at the above concentration of 10^7 particles/ m^3 in the stream. Admittedly, these assumptions may be optimistic, but in the absence of further data, these estimates certainly indicate the need for a more detailed examination of the DIMS technique for the present application.

The system to be assembled for testing the DIMS technique in this

application will use a quadrupole mass filter as the main element. The particle generator will be essentially the same as the one developed for filter efficiency measurements using irradiated sample materials, and described in previous reports. The tube used to mock up the flow in the system will include provisions for changing the atmosphere of the flowing gas used to carry particles to the inlet system to the mass spectrometer. With this experimental design it will be possible to control the particle size distribution in the flow as well as the gaseous constituents introduced into the DIMS source region. Early estimates of the DIMS technique's applicability to the present problem should be possible.

REFERENCES

1. A. M. Platt, compiler, Nuclear Waste Management Quarterly Progress Report April Through June 1977. BNWL-2377-2, Battelle, Pacific Northwest Laboratories, Richland, WA, November 1977, pp. 2.1-2.2.
2. Warren L. McCabe and Julian C. Smith, Unit Operations of Chemical Engineering, McGraw-Hill, New York, 1956, p. 168.
3. W. D. Davis, "Continuous Mass Spectrometric Analyses of Particulates by Use of Surface Ionization." Environmental Sci. Technol. **11**: 587, 1977.
4. W. D. Davis, "Continuous Mass Spectrometric Determination of Concentration of Particulates in Air by Use of Surface Ionization." Environmental Sci. Technol. **11**: 593, 1977.
5. F. P. Brauer and W. A. Mitzlaff, "Evaluation of Well-Type Ge(Li) Detectors for Low-Level Radiochemical Analysis." To be published in IEEE Trans. on Nucl. Sci. Meeting held in October 1977.
6. J. J. Stoffels and C. R. Lagergren, "A Direct-Inlet Mass Spectrometer for Real-Time Analysis of Particulate Contaminants in Air." BNWL-SA-5645, Battelle, Pacific Northwest Laboratories, Richland, WA, June 1976.

3.0 TRU WASTE FIXATION STUDIES

J. H. Jarrett - Program Manager

The objectives of this program are to: 1) develop candidate criteria for the immobilization of TRU wastes; 2) provide technological bases needed to support the adoption of those criteria; 3) evaluate waste forms from current commercial and ERDA TRU-waste programs relative to the recommended criteria; and 4) develop improved waste management systems and final waste forms if necessary.

SUMMARY

The scope of the TRU waste management criteria task was reduced to a fact-finding effort to determine the status of TRU-related waste programs throughout the U.S. An overview of the situation was developed and discussed briefly with LASL staff. This

overview, along with recommendations for future efforts, was forwarded to ERDA Richland Operations.

The FY-1977 concrete waste form characterization work at Brookhaven Labs has been completed. Their results will appear in the next quarterly report of this series.

4.0 KRYPTON SOLIDIFICATION

G. L. Tingey - Project Manager

The objective of this program is to determine the feasibility of alternative techniques for storing krypton in a solid matrix. Two techniques are currently being investigated: dissolution in a glass matrix and entrapment in solids during high-rate sputtering.

SUMMARY

Krypton contents in excess of 10 at.% may be achievable in low-density glasses. Therefore tests are planned to evaluate this potential using low-density glass rods and further evaluation of sputter-deposited glasses.

The sputter-deposited amorphous metal matrix alloy of 87 at.% Fe and 13% Y with up to 11 at.% Kr was examined by heating under vacuum to 1100°C. The samples showed excellent gas retention properties, with release occurring between 700 and 950°C. This treatment, however, caused disintegration of the sample to a fine powder apparently associated with release of the large quantity of krypton.

DISSOLUTION OF KRYPTON IN GLASS - G. L. Tingey

Data presented in the last quarterly report⁽¹⁾ showed that krypton solubilities in the dense glasses studied were too low to be of interest for storage of radioactive krypton as a solid waste form. However, Doremus⁽²⁾ has shown that the solubility of inert gases in glasses is

a function of the free volume in the glass matrix. To test this phenomenon, we have obtained low-density glass rods with a surface area of 200 to 300 m²/g. Krypton will be loaded into these rods at pressures up to 30 atm to measure the volume of gas that can be dissolved. The glasses will then be densified to reduce the rate of gas release from the samples.

An indication of the volume of gas that can be dissolved or trapped in a glass matrix is given by an experiment where SiO₂ was sputter-deposited using Kr⁺ ions, and the deposit apparently trapped a large amount of Kr. Preliminary x-ray fluorescence measurements indicate that the SiO₂ contains in excess of 10 at.% Kr. Gas release measurements were then conducted to obtain a quantitative measure of the krypton content and gas release properties. The samples were heated to 1100°C under vacuum, and very little krypton release was observed. Subsequent x-ray fluorescence measurements of the heat-treated samples showed essentially the same krypton content. We interpret these data to mean that high krypton loadings can be achieved in glasses and that the release rates in SiO₂ would be almost negligible at temperatures below 1000°C.

Confirmatory tests will be required and are scheduled to be conducted in the next quarter.

KRYPTON ENTRAPMENT DURING SPUTTERING -
E. D. McClanahan and M. A. Bayne

In the last quarterly report⁽¹⁾ we presented data showing krypton loadings of about 11 at.% trapped in an amorphous metal matrix of 87 at.% Fe-13 at.% Y. Krypton release measurements have now been completed on these samples. Gas retention in this material was excellent, with release occurring between 700 and 950°C. Since this sample was deposited by sputtering with a mixture of krypton and xenon, both gases were trapped simultaneously in the deposit. The xenon and krypton were released simultaneously, with no evidence of selective release of either gas.

During the trapping, xenon was selectively ionized, as indicated by both measurements of gas composition and analysis of the gas released. This effect is apparently due to the lower ionization potential of xenon (12.1 eV) compared to that of krypton (14.0 eV). Thus xenon is ionized by a larger fraction of the available electrons.

Upon removing the sample, which had been heated to 1100°C, from the furnace, it was discovered that the 0.05-mm-thick sample had disintegrated to a dark granular powder. Apparently stresses induced during heat treatment had caused this effect. Consistent with the gas release data, no residual xenon or krypton was observable by x-ray fluorescence analysis.

Using $\text{CuK}\alpha$ radiation, x-ray diffraction of the powder produced four lines which may have resulted from crystalline Fe_4Y . These lines had not been present in the diffraction pattern of the sample prior to the heat treatment. The material was further analyzed using differential scanning calorimetry. With a heating rate of 20°C/min, two transitions were observed: an exothermic reaction occurring at about 700°C and an endothermic process beginning at about 670°C and continuing to the maximum temperature of the test (725°C). The exotherm may be attributable to the onset of crystallization of the amorphous metal and the endotherm appears to be a result of krypton release which we have observed at about this temperature by gas analysis of heat-treated samples. All metal samples loaded with krypton disintegrated to powder in a manner similar to that observed with the previous samples. However, another sample not containing significant krypton did not disintegrate upon heating. This may be an indication that the stresses involved during gas release exceed the strength of the krypton-loaded sample.

The high yields achieved by this amorphous metal are very encouraging, and several other systems will be tested which are predicted to yield an amorphous alloy. Two such systems are planned for the coming quarter. The first, and most obvious, is another FeY alloy with a composition of about $\text{Fe}_{0.97}\text{Y}_{0.03}$. The second candidate is a commercial noncorrosive iron-silicon alloy called "Duriron."

REFERENCES

1. A. M. Platt, Compiler, Nuclear Waste Management Technology Quarterly Progress Report. BNWL-2377-2, Battelle, Pacific Northwest Laboratories, Richland, WA, October, 1977.
2. R. H. Doremus, "Physical Solubility of Gases in Fused Silica." J. Amer. Cer. Soc., 49(9):461, 1966.

5.0 CARBON-14 AND IODINE-129 FIXATION

L. L. Burger - Project Manager

The objectives of this program are to evaluate the various options for solidification or fixation of iodine-129 and carbon-14 collected from reprocessing plant streams.

SUMMARY

Stability studies of iodates and iodides have resulted in a list of potential metal compounds suitable for iodine fixation. A brief examination was also made of carbonates for the fixation of carbon-14.

Data showing the oxidation of mercuric iodide to the iodate are presented.

Preliminary consideration is being given to criteria for both the shipping and storage of iodine-129 and carbon-14.

The application of the fixation studies to the SURF program was terminated during this period. However, before this work was eliminated, a number of R&D problems were identified, and a plan was developed to determine the necessary data on fission gas releases and, if necessary, gettering agents.

FIXATION COMPOUNDS - R. D. Scheele and L. L. Burger

Studies of thermal stability of candidate iodine-129 and carbon-14 chemical fixation forms were continued. The compounds which appear most suitable from a thermal standpoint for iodine are the iodates of

barium, strontium, lanthanum, copper, silver, mercury, and lead, and the iodides of silver and lead. The first three iodates and silver iodide demonstrate excellent thermal stability to 500°C. Silver and mercury iodates decompose first to the iodide before decomposing further. The remainder decompose directly to the oxide between 400 and 500°C. The carbonates of barium, strontium, and calcium did not decompose over the temperatures studied. Calcium carbonate has a measurable decomposition pressure at temperatures above 500°C. Barium carbonate is stable to temperatures in excess of 1400°C, while the strontium compound is intermediate.

Before a choice for fixation form is made, the environmental conditions that will exist during shipping and storage, and during a credible accident for each, must be determined. The Code of Federal Regulations 10-71 (1977) describes the standards for shipping conditions of radioactive material which might be exposed to normal and credible accidents. Storage conditions are less well defined.

For normal conditions of transport the shipping package must be designed and constructed so that no release of radioactive material will occur at temperatures varying from -40°C to

54°C in still air, at an atmospheric pressure of 0.5 atm, and if the package is wetted continuously by a spray of water over its entire surface except the bottom.

Under credible accident conditions, a temperature of 802°C for 30 min, the package must allow no release of radioactive material except gas or coolant containing a total radioactivity exceeding either 0.1% of total or 10 Ci of iodine-129 or carbon-14. The package is exempt from the regulation if the content does not exceed a concentration of 0.3 mCi/g. The specific activities of iodine-129 and carbon-14, undiluted with other isotopes or matrix materials, are 0.16 mCi/g and 4.5 Ci/g, respectively. The specific activity of carbon-14 will be much lower due to large amounts of carbon-12 also trapped.

The conditions, both normal and credible accident, which could exist during interim or long-term storage are less well defined. Repository temperatures are expected to be low compared to the temperatures investigated above.

SURF PROGRAM - L. L. Burger

Effort directed toward management of unprocessed irradiated fuels, after a short period of activity, has been eliminated from the program. However, considerable effort was expended during the first part of the report period. The survey of available information was completed, and experiments were designed to obtain volatile fission product release

data as a function of temperature. Facilities were located for the experiments which were to consist of heating of both complete fuel pins, punctured under vacuum, and chopped segments and pellets that have been exposed to the air. Both mass spectrometry and radiochemical analysis were planned for noble gases and for trace amounts of T, ^{129}I , and ^{14}C .

Another part of the program was to analyze the various chemical equilibria that may exist after a long period of time at the storage temperature and to determine which reactions may be kinetically significant. This includes the lower temperature (ambient to ~300°C) oxidation reactions.

Based on the above data, getters were then to be devised and tested for use in fuel storage canisters.

All work on this problem was terminated during the quarter.

REMOVAL OF IODINE FROM MERCURIC NITRATE SCRUB SOLUTIONS -

R. D. Scheele

By carefully controlling temperature and anode current density, we can successfully separate dissolved iodine as mercuric iodate from mercuric nitrate-nitric acid solutions. Current efficiencies for the iodide to iodate conversion are up to 50% at 60% conversion.

The results of the parametric study are presented in Table 5.1. To insure conversion to the iodate at low acidity, the current density must be small, ~0.1 amp/cm²; otherwise iodine will volatilize. At high acid

TABLE 5.1. Electrolytic Separation of Dissolved Iodine from Mercuric Nitrate-Nitric Acid Solutions as Mercuric Iodate

Anode Current Density, amp/cm ²	HNO ₃ Conc., <u>M</u>	Temperature, °C	Current Efficiency ^(a) %
0.10	0.92	10	46.9
0.10	0.85	10	48.4
1.0	0.85	10	0.0 ^(b)
1.0	0.85	10	0.0 ^(b)
0.10	10.71	10	44.1
0.10	10.71	10	39.5
1.0	11.02	10	27.9
1.0	10.71	10	30.8
0.1	0.92	50	52.6
0.1	0.85	50	44.1
1.0	0.85	50	0.0 ^(b)
1.0	0.85	50	0.0 ^(b)
0.1	11.02	50	42.9
0.1	10.71	50	40.5
1.0	11.02	50	26.1
1.0	11.02	50	24.0
1.0	11.02	50	29.3
0.6	6.24	30	33.5
0.6	6.24	30	39.0
0.6	6.24	30	37.7
0.6	6.24	30	40.0

a. At 60% conversion

b. Iodine volatilized or precipitated as mercuric iodide.

concentrations, the current density effect is less critical as no loss of iodine will occur; however, a higher efficiency is attained at the low current density. Temperature has

little or no effect except at low acidity and low current density. The maximum current efficiency was obtained at 0.1 amp/cm², 0.9M HNO₃, and 50°C.

6.0 INTERNATIONAL PROGRAM COORDINATION

K. M. Harmon - Project Manager

Promote waste management technology exchange between the United States and other nations through establishment of an international technology coordination center at PNL.

SUMMARY

Collection and review of significant documents continued. Waste management program summaries were prepared for Canada, India, Mexico, and the international organizations

with major involvement in nuclear waste management research and development: International Atomic Energy Agency (IAEA), International Energy Agency (IEA), Nuclear Energy Agency (NEA), and Commission of European Communities (CEC).

7.0 WASTE MANAGEMENT SYSTEM STUDIES

J. W. Bartlett - Project Manager

The objective of this program is to develop and apply methods for assessment of alternative waste management systems and technologies.

SUMMARY

End-of-fiscal-year reports were written for all activities concerned with nuclide transport and data base development. Operability of the GETOUT code on the PDP-11/45 was tested; a program to model nuclide transport in unsaturated groundwater systems was designed; output and graphics display programs for the waste management data base were written and tested; and additional output programs for the seismic data base were prepared.

In the public attitudes work, analyses of issues and media content neared completion. Some of the responses to the knowledge/interest questionnaire were received and coded for data analysis. Development of the risk evaluation and risk perception questionnaires was completed.

INTERFACE OF THE GETOUT MODEL WITH THE PDP-11/45 SYSTEM - J. F. Washburn

The GETOUT Model was tested on a radionuclide transport case for a hypothetical accident in a subsurface nuclear power reactor. The "no dispersion" equations were added to the model codes. Output comparisons were made between the BASIC language program and the PDP-11/45 version of the program.

Review of the final report indicated need for a number of changes and modifications. These changes are now being made, and the final report will be issued in October.

RADIONUCLIDE TRANSPORT IN UNSATURATED GROUNDWATER SYSTEMS - C. R. Cole

Work continued on review of models and codes for use with assessment of radionuclide transport in unsaturated groundwater systems, and this task was completed during the reporting period. A recommended program to implement transport modeling in unsaturated groundwater systems was designed. A draft of the final report was completed.

INTERACTION OF EVALUATION CRITERIA FOR RADIOACTIVE WASTE MANAGEMENT ALTERNATIVES - M. L. Warner

Work was discontinued on this project due to the inability to assemble a task force to participate in judgment analysis sessions. A final status report was issued.

DATA BASE DEVELOPMENT FOR NUCLEAR WASTE MANAGEMENT - G. B. Lane, T. N. Bishop and H. P. Foote

During this reporting period, the setup program was updated to include more pertinent information for the user

and for the related data base programs. A data input program was developed that will place data into the correct positions of the data base depending on the data type and the number of words needed for that type.

A data output and graphics display program were written and tried on selected data. The data input and editing programs have functioned properly when put to repeated use on different trial bases. The data base system has evolved such that any size and type of data base can be initiated. The base may consist of any number of distinct layers as required by the user, and each layer may contain any number of words to describe that layer's data. The user has the options of selecting real, integer, or byte words for layer description with the constraint that each layer must be homogeneous (i.e., no mixing of word types in a layer). The input and display programs are limited to selected types of data at this time, but these programs can be upgraded to include any type of data to be stored in the base.

The data base "setup" program (CORAS3) gathers the parameters needed to create a data base file on magnetic disk; opens the file on disk; and reports to the user the pertinent information required to operate the data base within its assigned scope.

The input program (INPUT) reads selected binary files from the system disk and loads the information into the base in the proper positions (referenced by latitude and longitude in decimal degrees).

The editing program (CORED) allows the user to access any word of the base and to change the value of that word. All editing can be performed by stating the degree coordinates and layer number of the word in question and then inserting the proper value for that word. Any word of any layer is accessible, and all editing can be done in one program run.

The output program (COROUT) yields a lineprinter listing of all layers and layer values for each latitude and longitude node within the scope of the base.

The graphics display program (LPMAP) can produce a lineprinter map in matrix form with emplaced nodal values (for single byte words and small file size at this time, mainly due to lineprinter paper space limitations); a scope display with boundaries drawn between unlike nodal values; a CalComp plotter output which yields a hardcopy of the scope display; any combination of the above depending on user requests.

A small data set was input to the system. This set defines (in a general manner) the distribution of natural forest and vegetation types in the State of Washington. The data were digitized in nodal format from a small-scale land cover map.

All programs have been written in FLECS for easier logic comprehension, and all use File-Q for efficient data transfer. All programs can be used by the noncomputer-oriented individual with only a very minor knowledge of the computer (e.g., which disk unit(s) are being used, how to begin program operations, etc.), and no knowledge of computer languages. A "User's Guide" was prepared.

The final report draft was completed for this project, and the report will be issued in October.

SEISMIC DATA BASE DEVELOPMENT -

T. N. Bishop, G. B. Lane and
H. P. Foote

Methods were developed to display selected earthquakes with the mapping programs. Additional faults were digitized, and revised locations for the eastern Washington array have been entered. Programs were developed which plot histograms of selected files and which plot a cross section of the earth, projecting hypocenter depths on a vertical plane.

Programs were written to update and sort the seismic data base.

An additional program was developed which generates maps of the earth as viewed from any point in space. The program is extremely flexible and shows great promise for viewing subsurface tectonic events.

A volcano data base of the 512 active volcanoes of the world (from MacDonald's Volcanoes) was compiled.

Writing of the final report was started. It is expected to be completed and issued in October.

NUCLEAR WASTE COMMUNICATIONS -

S. M. Nealey, HARC

Three tasks are to be carried out within the Waste Communication Task:

- (a) analysis of public issues pertaining to disposal of nuclear waste;
- (b) media analysis of newspapers and magazines that involves two subtasks--content analysis and journalistic

analysis; and (c) administration of a nuclear waste knowledge-interest questionnaire.

Official Source Issues Analysis

The issues analysis task is nearing a major milestone, with the expected issuance about December 1 of a draft report exploring an extensive set of public issues in nuclear waste management. Issues have been divided into four substantive clusters: 1) temporal equity issues (the problem of benefits in the present and potential risks in the future from waste disposal), 2) geographic equity (the benefits of nuclear power are widely distributed, but waste management facilities will be in only a few locations), 3) public involvement in nuclear waste management planning, and 4) issues attendant to implementing waste management plans (regulatory issues, needed organizations, financing and waste monitoring activities).

This report will form the basis for follow-on research activities in FY-1978, particularly documentation of the relative emphasis given these issues by agencies responsible for waste management planning and attempts to define the interrelations between sets of public issues in waste management planning.

Media Analysis

The content analysis subtask of the media analysis of nuclear waste coverage is nearly complete. A first draft report has been through internal review, and a second draft is now nearly ready to issue.

The journalistic analysis is also nearing completion. Nuclear and coal coverage by four newspapers have been read and analyzed for the target period (second calendar quarter of 1977). A first draft of the report on this aspect of the media analysis has been written and is now undergoing internal review. We expect to issue this report in November or December. During FY-1978 we expect to extend the media analysis task to include an analysis of nuclear power and nuclear waste coverage by the national television networks.

Knowledge-Interest Questionnaire

During the last quarter, sponsor approval of the questionnaire was received, and the questionnaire was sent to a random sample of 1350 adults in the State of Washington and to a random sample of 150 adults in the Tri-Cities area (nuclear neighbors). Subsequently, permission was also granted by an environmentalist group to survey 100 of their members. Surveys were sent to these individuals just before the end of the quarter. About half the number of completed questionnaires we expect to receive had been returned by the end of the quarter. To facilitate speedy analysis and reporting, data are being coded and keypunched as they are returned. We expect to complete analysis and reporting on this task during the first quarter of FY-1978.

In addition to undertaking the analysis of television nuclear coverage in FY-1978, we expect to analyze the nuclear waste information

dissemination process of the Department of Energy. With this task complete, we expect to be in a position to conduct an integrated analysis of the role of communication in public knowledge, attitudes, and acceptance of nuclear power and nuclear waste management programs. Work recently completed and currently under way should enable us to gain perspective on the way nuclear waste management issues are treated by Federal agencies, by committed opponents of nuclear power, and by the print and electronic media. Our data on nuclear waste management related public values, attitudes, and knowledge should both reflect the outcomes of media treatment and form a basis for predicting public response to issues in management of nuclear waste.

PUBLIC PERCEPTION AND EVALUATION OF RISK - John A. Hébert, HARC

FY-1977 Survey

During this quarter, work was completed on the development of the risk evaluation and risk perception questionnaires. In the interim between completion of questionnaire development and receipt of sponsor approval to initiate data collection, the primary work emphasis has been on developing software support. An improved program for the cluster analysis of questionnaire data has been acquired and adapted for use on the Battelle-Columbus computing facilities. Preliminary runs on test data indicate that the ICLUST program provides a very efficient and flexible approach to the analysis of questionnaire data.

New Issues

Development of the current questionnaire has raised a number of issues in risk perception and risk evaluation that need to be addressed. Specifically, despite the fact that many studies have shown that the public perceives nuclear power to be a very hazardous source of energy, little is understood about more specific aspects of the public perception of how nuclear materials put them at hazard. One exploratory study has been designed to assess the perceptions of the public with regard to the level of risk of living at specific distances (16, 32 or 160 km, for example,) from a number of different hazardous technological facilities, such as electric power plants, chemical plants, and storage areas for hazardous materials. A second exploratory study is designed to supplement current work on risk

evaluation. This study will seek to integrate the work of others on the relative acceptability of public versus occupational risk within our own research framework. Public preferences for different distributions of occupational and public risk over time also need to be measured.

Related Work

During this quarter, two concept papers have been produced on topics related to the scope of work encompassed in this project. Both relate to problems involved in facility siting. The first outlines some important considerations in studying the role of social groups in supporting or resisting the siting of controversial facilities. The second identifies research needed to develop a promising technique for managing local resistance to facility siting.

8.0 WASTE MANAGEMENT SAFETY ASSESSMENT

W. K. Winegardner and P. J. Pelto - Project Managers

Evaluate the safety of alternative waste management schemes for viable nuclear fuel cycles up to the final disposal step; develop the methodology necessary to permit the safety assessment; identify portions of waste management systems which could benefit by safety design emphasis.

SUMMARY

The three-report set was completed that presents user instructions for PNL-developed computer programs for drawing fault trees and for assessing these trees in terms of risk. The reports were undergoing review/approval for publication at the end of the quarter.

TECHNICAL PROGRESS

The three reports out for review are:

- J. L. Carter, ACORN: A Computer Program for Plotting Fault Trees, BNWL-2144
- P. J. Pelto and W. L. Purcell, MFAULT, A Computer Program for Analyzing Fault Trees, BNWL-2145
- G. D. Seybold, RAFT: A Computer Program for Fault Tree Risk Calculations, BNWL-2146.

Figure 8.1 summarizes the input, output and interrelationships of the programs. ACORN analyzes the input logical structure of a fault tree and provides data for a CalComp plot of the tree. AND, OR, and INHIBIT gates are permitted, and basic events are drawn as diamonds, circles, or houses.

FIGURE 8.1. Risk Assessment Computer Package

Each component can have a descriptive label within a rectangle attached to the top of the symbol for the component.

MFAULT identifies the cut sets of a fault tree, calculates their probabilities, and screens the cut sets on the basis of specified cut-offs on probability and/or cut set length. The code is based on an

efficient upward-working algorithm for cut set identification. The probability calculations are based on the assumption of small probabilities and constant hazard rates (i.e., exponential failure distributions). Cut sets consisting of repairable components only, nonrepairable components only, or mixtures of both types can be evaluated. Components can be on-line or standby. Unavailability contributions from preexisting failures, failures on demand, and testing and maintenance downtime can be handled.

RAFT calculates release quantities and a risk measure based on the product of probability and release quantity for cut sets of fault trees modeling the accidental release of radioactive material from a nuclear fuel cycle facility. Cut sets and their probabilities are supplied as input to RAFT from an external fault

tree analysis code, e.g., MFAULT. Using the total inventory available of radioactive material, along with release fractions for each event in a cut set, the release terms are calculated for each cut set. Each release term is multiplied by the cut set probability yielding the cut set risk measure. The cut set probability term can be supplied as input or redefined within the code. RAFT orders the dominant cut sets on the risk measure. The total risk measure of processed cut sets and their fractional contributions are supplied as output. Input options are available to eliminate redundant cut sets, apply threshold values on cut set probability and risk, and control the total number of cut sets output. Hash addressing is used to remove redundant cut sets from the analysis.

9.0 NRC REQUESTED STUDIES

J. H. Jarrett - Project Manager

The objective of this study is to perform waste management studies upon NRC request.

SUMMARY

A program plan was prepared for ERDA-RL which provides for conversion of high-level liquid waste at the West Valley, New York, plant of Nuclear Fuel Services, Inc. (NFS) to a dry solid as soon as is reasonably feasible. The plan provides for selection of a recommended process about 1 year after authorization to begin the study; for completion of conceptual design, an environmental impact statement, and a preliminary

safety information report, all in support of a budget submittal package, in about 20 months; for initiation of detailed design in roughly 2-1/2 years; for start of construction, assuming a limited work authorization issued by NRC, in about 4-1/2 years; and for start of hot operations in about 6-1/2 years. This schedule would permit the first shipment of solidified NFS waste to a Federal repository in mid-1985, assuming initiation of the study in early fiscal year 1978.

10.0 WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

H. C. Burkholder - Project Manager
J. Greenborg, J. Stottlemire, D. J. Bradley,
J. R. Raymond and R. J. Serne - Task Leaders

The objectives of the Waste Isolation Safety Assessment Program (WISAP) are to:

- 1. develop the generic methods needed to assess the long-term safety of geologic isolation repositories*
- 2. obtain the generic and site-specific data necessary to apply the methods*
- 3. demonstrate the use of the methods for a specific site*
- 4. apply the methods to make safety assessments for sites of the National Waste Terminal Storage Program*
- 5. analyze societal acceptance issues and develop methods of communicating assessment results which enhance the rational resolution of those issues.*

During the quarter a document (PNL-2451) was issued summarizing the work in FY-1977. This work can be conveniently classed by whether it supported development of the generic assessment method or development of the generic data base. It is discussed here under these two major topics.

GENERIC ASSESSMENT METHOD DEVELOPMENT

Safety assessments for geologic isolation have six elements:

1. identification of the events and processes which could potentially cause breach of containment at the repository cavity
2. analysis of the ways these phenomena could combine to cause containment breaches
3. quantitative description of the radioactive release scenarios
4. prediction of radionuclide release rates from the repository cavity
5. prediction of the transport of released radionuclides to man

6. prediction of nuclide interaction with man.

Assessment method development activities related to the first three elements can be considered together under the term "Release Scenario Analysis." Those related to the last three elements can be considered together under the term "Release Consequence Analysis." Results of FY-1977 work in this sector are reported below under those headings.

Release Scenario Analysis

Identification of Disruptive Events and Processes

We first identified phenomena that could either individually or together cause a breach in containment at a geologic isolation repository.^(1,2) These were grouped into four classes:

1. natural, long period geologic processes

2. natural, short period geologic events
3. man-caused, short period events
4. repository-caused, long period processes.

Phenomena in all of these groups are listed in Table 10.1. Many of the phenomena are interrelated, and the distinction between short period and long period is sometimes unclear. Thus the classification shown here is somewhat arbitrary. Furthermore, we make no claim that the list of phenomena is all-inclusive.

Evaluation of Safety Analysis Methods

FY-1977 work included identifying, describing and evaluating the safety analysis methods available for analyzing the combined effect of the potentially disruptive phenomena and describing containment breach scenarios. Methods identified include expert opinion/Delphi, perspectives analysis, consequence analysis, stability analysis, fault/event trees, and Monte Carlo/Markov chain analysis. These methods are all briefly described in the next six paragraphs.

Expert opinion is a qualitative technique in which a recognized body of experts determines whether an activity is acceptably safe or not. This was the "original" waste isolation safety assessment method applied in 1957 by the National Academy of Sciences in recommending that high-level wastes be stored in bedded salt formations.⁽³⁾ Delphi is a formally structured method of obtaining expert

opinion which produces an estimate of the certainty of the safety conclusion in addition to the conclusion itself.^(4,5) This method has never been applied to the waste isolation safety assessment problem. Both methods have the advantage of simplicity but the disadvantage of subjectivity. Subjectivity has become increasingly suspect in the last decade because of the growing distrust of technology and technologists. Recently expert opinion has usually carried weight only when substantiated by the details of the logic and data of a quantitative assessment.

Perspectives analysis is a qualitative technique for comparing a safety attribute of a given activity with a safety attribute of some better understood or more familiar activity. This technique has been heavily used in the area of nuclear waste isolation to compare the potential hazard of the waste with those of the original ore from which it came and of other naturally occurring toxic materials.⁽⁶⁾ As with the other qualitative safety assessment methods, perspectives analysis has the advantage of simplicity and the disadvantage of subjectivity. A particular difficulty with this technique is that conflicting conclusions can result from the same analysis, depending on which attributes are compared and what assumptions are made in the comparison.

Consequence analysis is a quantitative method in which the safety assessment is based only on the consequences of assumed release scenarios. These release scenarios are simply postulated by expert opinion, and no consideration is given to their

TABLE 10.1. Potential Disruptive Phenomena for Waste Isolation Repositories

<u>Natural Processes</u>	<u>Natural Events</u>	<u>Man-Caused Events</u>	<u>Repository-Caused Processes</u>
Climatic fluctuations	Flood erosion	Improper design/operation:	Thermal, chemical potential, radiation, and mechanical force gradients:
Sea level fluctuations	New or undetected fault rupture	Shaft seal failure	
Glaciation	Seismically induced fracturing	Improper waste emplacement	Induced local fracturing
River erosion	Seismically induced shaft seal failure	Undetected past intrusion:	Chemical or physical changes in local geology
Sedimentation		Undiscovered boreholes or mine shafts	Induced groundwater movement
Tectonic uplift		Inadvertent future intrusion:	Waste container movement
Tectonic subsidence	Meteorite	Archeological exhumation	Increase in internal pressure
Volcanic extrusion		Weapons testing	Shaft seal failure
Igneous intrusion		Nonnuclear waste disposal	
Diapirism		Resource mining (mineral, hydrocarbon, geothermal, salt)	
Diagenesis		Storage of hydrocarbons or compressed air	
Motion on new or undetected fault		Intentional intrusion:	
Dissolution		War	
Aquifer flux variation		Sabotage	
		Perturbation of groundwater system:	
		Irrigation	
		Reservoirs	
		Intentional artificial recharge	
		Establishment of population center	

likelihood of occurrence. This method has been applied to estimate the consequences of groundwater intrusion into, and meteoritic exhumation of, a waste isolation repository in specific but hypothetical geologic and biologic settings.^(7,8) Consequence analysis has the advantage of estimating the quantitative impact of release scenarios and hence is a necessary part of all quantitative safety assessment methods. But when utilized by itself it has the disadvantage of biasing the safety assessment toward the low probability-high consequence release scenarios.

Stability analysis is a deterministic technique for analyzing whether important properties of the system of interest remain unchanged if the system is disturbed.⁽⁹⁾ Steps in the analysis include the development of a system model, the development of mathematical models for important processes at work within the model system, and the determination of the system's response to mathematically imposed disturbances. Unstable scenarios are further analyzed to determine the expected conditions of system failure. This analysis technique has not been applied to geologic isolation safety assessments. Stability analysis seems well suited for analyzing the processes but not for analyzing the events whose occurrences are difficult to model by continuum mathematics. Thus stability analysis is not a comprehensive technique but rather is a specialized method for analyzing a portion of the assessment problem.

Fault tree analysis is a deductive, deterministic technique by which the component failures leading to system failure can be logically deduced. Its application yields combinations of basic events whose occurrence causes the undesired system failure events. These event combinations are then evaluated by various screening techniques to determine the high-risk scenarios and their likelihood of occurrence. Historically the fault tree approach has received considerable attention in analyses of geologic isolation safety.^(1,10) Event tree analysis is an inductive, deterministic technique which reverses the fault tree approach; it starts with the basic failure events and works forward in time to display their logical propagation to system failure events.⁽¹¹⁾ This technique has not yet been applied to assessment of geologic isolation safety. The fault and event tree techniques can be combined into one integrated analytical method. For both techniques a consequence analysis is performed for the identified system failures. Because of its "binary" logic the fault/event tree approach is well suited for quantitatively analyzing the short period events which either occur or do not occur; however, it is not well suited for analyzing the long period processes which occur continuously at some finite rate. Furthermore, because of their deterministic nature, fault/event trees are not well suited for analyzing the interaction of the many different possible sequences of the potentially disruptive phenomena.

Monte Carlo analysis and Markov chain analysis are both stochastic techniques for analyzing system failures resulting from sequential events. A Monte Carlo analysis begins by listing the basic failure events and estimating their probabilities of occurrence. The analysis then steps through time assuming occurrence of these events according to their estimated probability distributions until a system failure occurs. Performing the simulation numerous times can determine a distribution of failures. Consequence analyses are then performed on this failure distribution. A Markov chain analysis begins by specifying the possible states of the system and determining the probabilities for transition between those states. Implicit in the analysis is the assumption that the transitional probability between two states is independent of earlier states of the system. The analysis then steps through time assuming probabilistic occurrence of the transitional events until a system failure occurs. Extensive mathematical formalism exists to reduce Markovian processes to analytical functional forms. Neither the Monte Carlo nor the Markov chain technique has been applied to safety assessments for geologic isolation. Both techniques are well suited to quantitatively analyzing the discrete events and, because of their stochastic nature, also to analyzing the complex interactions of these events. Monte Carlo analysis can be generalized to consider the continuous

processes by updating the state of the system for their effect at each time step. Markov chain analysis, on the other hand, does not appear applicable to the continuous processes because the states of the system must be specified a priori. Furthermore, the transition between states of a geologic system seems likely to be very dependent on previous state transitions, in violation of the basic assumption of Markovian processes.

In evaluating these techniques for use as the WISAP release scenario analysis method we applied three criteria:

- The method should yield quantitative information about potential release scenarios.
- The method should describe the many possible complex interactions and timing of the potentially disruptive phenomena.
- The method should analyze both discrete events and continuous processes.

We concluded that a generalized Monte Carlo analysis was the most applicable technique for assessing the safety of geologic isolation repositories and selected it as the base for construction of the WISAP assessment method, hereafter called "repository simulation analysis."

Development of Repository Simulation Analysis

Repository simulation analysis combines the expert opinion/Delphi,

fault/event tree analysis, stability analysis, and Monte Carlo analysis techniques. During FY-1977 the following steps for implementing the concept were defined:

1. Potentially disruptive natural and man-caused events and processes are listed (see Table 10.1).
2. The interdependencies of the processes are identified and their coupling relationships are quantified to the extent possible (e.g., worldwide warming trend, mean sea level increase, inundation of land over repository, renewed sedimentation and compaction, halokinetic diapirism, stress-induced overburden fracturing, groundwater penetration, and salt dissolution). This requires the expert analysis of geologists and geophysicists.
3. A stratified model of the site-specific geology is made using site exploration data.
4. The potential failure modes are identified.
5. Probabilities for the events and rates, durations, and lag times for the processes are determined by expert opinion from geologists and geophysicists.
6. Repository response curves (e.g., distance to the biosphere versus time) are derived for important system properties by simulating the combined effect of the continuous processes on the site-specific geologic model.
7. The occurrence probabilities of combinations of the events are determined by fault/event tree techniques.
8. The events and their combinations are allowed to occur according to their probability distributions (biasing techniques will be used to obtain proper statistics for very low probability events) on the model system, and their effect is superimposed on the repository response curves for the processes.
9. Containment failures are noted and the failure times are combined with information from the repository response curves to determine the boundary conditions for subsequent consequence evaluation.

A first-generation computer code to implement repository simulation analysis was completed during FY-1977.

Release Consequence Analysis

Evaluation of Consequence Analysis Methods

During FY-1977 we made an extensive compilation of computer models potentially applicable to describing the transport of radionuclides through the geosphere and biosphere and to calculating dose to man. Over 150 hydrologic, contaminant transport, water-dose, and air-dose models were identified.

Information about the hydrologic and contaminant transport models was obtained from a yet-to-be published international assessment of such models being performed by the Holcomb Research Institute. Information about the water-dose and air-dose models was obtained from recent compilations in open literature. The hydrologic and

contaminant transport models were categorized according to Table 10.2. The water-dose and air-dose models had considerable similarity and did not require a complex categorization.

Our evaluation of the hydrologic and contaminant models for the WISAP release consequences analysis modeling system was based on the following criteria:

1. The system should have several levels of modeling sophistication so that a range of data sophistication can be accommodated in a time and cost effective manner.
2. The system should have the capability to model saturated flow through heterogeneous geologic media.
3. The system should have the capability to model hydrodynamic dispersion, radioactive chain decay, equilibrium sorption and time variant leach rates.

These criteria directly follow from programmatic direction to ignore near-field effects. These effects were addressed in other parts of the National Waste Terminal Storage (NWTs) Program during FY-1977. Particularly in the case of the hydrologic models, several models were identified of essentially equal applicability according to these criteria. In these cases we chose models which could be most efficiently adapted to our computing system. Table 10.3 shows the characteristics of a number of the models chosen.

The WISAP system does not presently contain models to describe water flow in partially saturated systems. Such models will be added later if situa-

tions are identified where their use would lead to a substantially better prediction of release consequences. The contaminant models of the WISAP transport modeling system do not presently consider phenomena such as finite rate sorption, multiple chemical species of the same nuclide, chemical reactions among these multiple species, and irreversible mineralization. GETOUT and MMT will be extended to model these and other phenomena if the geochemical interaction data gathering activities of WISAP show that these phenomena are important for conditions of interest to geologic isolation safety assessments.

Our evaluation of dose models for the WISAP modeling system was based on the following criteria:

1. The system should model drinking water, terrestrial food, water immersion, external shoreline, and aquatic food doses.
2. The system should model chronic and acute air immersion and inhalation doses.
3. The system should calculate both individual and population doses.

For both water-dose and air-dose several models were identified of essentially equal applicability according to these criteria. As with the hydrologic and contaminant transport models, we chose models most adaptable to our computing system.

Development of Integrated Modeling System

Work to convert all computer codes for the WISAP release consequence analysis system to a common computing

TABLE 10.2. Format for Categorizing Hydrologic and Contaminant Transport Models

[illegible]

TABLE 10.3. Characteristics of WISAP Transport Models

HYDROLOGIC

- PATHS - Two-dimensional, analytical/numerical method, homogeneous geology, saturated flow⁽¹²⁾
- VTT - Two-dimensional, numerical method, heterogeneous geology, saturated flow⁽¹³⁾
- DAVIS FE - Three-dimensional, numerical method, heterogeneous geology, saturated flow⁽¹⁴⁾

CONTAMINANT TRANSPORT

- GETOUT - One-dimensional, analytical method, chain decay, single speciation, equilibrium sorption, constant leach rate, dispersion⁽¹⁵⁾
- MMT - Three-dimensional, numerical method, single speciation, equilibrium sorption, time variant leach rate, dispersion⁽¹⁶⁾

WATER DOSE

- ARRRG - Drinking water, immersion, external shoreline, and aquatic food doses⁽¹⁷⁾
- FOOD - Terrestrial food dose⁽¹⁸⁾

AIR DOSE

- KRONIC - Chronic external dose⁽¹⁹⁾
- SUBDOSIA - Acute external dose⁽²⁰⁾
- DACRIN - Chronic or acute inhalation dose⁽²¹⁾

language (FORTRAN) was begun in FY-1977. We plan to integrate the system so that the output-input formats of interfacing codes are the same.

GENERIC DATA BASE DEVELOPMENT

Safety assessments for geologic isolation require data of six general types:

1. geologic and geophysical data for estimating disruptive event frequencies and disruptive process rates and durations
2. waste form and container property data for estimating radionuclide release rates under the conditions of potential repository release scenarios
3. geohydrologic data for estimating the origin, direction and velocity of groundwater flow for potentially disruptive scenarios
4. geochemical data for estimating the degree to which radionuclides are retarded during groundwater transport through geologic media

5. geographic and demographic information about sites of interest to the NWTS Program
6. biologic, biochemical and biophysical data concerning radionuclide transport processes in the biosphere.

Data base development activities in FY-1977 were concentrated on measuring radionuclide leach rates for glass waste forms and sorption properties for geologic media of interest to the NWTS Program.

Waste Form Release Rate DataPreparation of Doped Glass Waste Forms

As a compromise between the reality of cracked glass monoliths and the powdered glass frequently studied in accelerated leach testing, we chose glass beads as the sample waste form for study. Two methods of preparing these samples were developed. A resistance-heated unit was installed in a glove box for preparation of doped glasses, and an induction heated

system was set up for hot cell use. Both units involve heating a comparatively large volume of glass to the melt temperature, continuously forming droplets at the end of a nozzle, and collecting the solid beads on a heated metal plate. The beads are flattened hemispheres, well suited to geometric determination of their surface area. The major value of this bead making approach lies in the ease and reproducibility of sample preparation.

Doped glass samples containing ^{99}Tc , ^{233}U , ^{237}Np , ^{239}Pu , ^{243}Am and ^{244}Cm were produced by these techniques, and characterization comparisons with the undoped glass were made. The metallography, x-ray diffraction, and alpha autoradiography analyses show that the dopants were homogeneously distributed and that the doping/waste form manufacturing process does not significantly change the glass from its original form with the exception of small increases in porosity.

Leaching of Doped Glass Waste Forms

The leaching procedure for the doped glasses is based on the standard IAEA method and uses five different solutions:

1. salt brine based on the analysis of a deionized water dissolved core from the WIPP facility (300 g/l NaCl)
2. high ionic strength calcium groundwater (2.206 g/l $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)
3. high ionic strength sodium groundwater (1.76 g/l NaCl)
4. high ionic strength bicarbonate groundwater (2.52 g/l NaHCO_3)

5. deionized water.

The experiments will be performed with both air and nitrogen atmospheres. The latter condition more closely simulates the anoxic conditions of some geologic isolation situations.

The experimental information obtained during FY-1977 shows that the leach rates of all nuclide dopants are decreasing with time. This occurs presumably as the resistance to diffusion of the radionuclides through the waste depleted glass matrix near the surface of the beads becomes increasingly dominant. The high pH bicarbonate solution (pH = 9) shows higher leach rates for all nuclides than do the low pH solutions. This is presumably caused by an increased dissolution rate of the glass matrix itself.

Radionuclide Geochemical Interaction Data

Evaluation of Sorption Measurement Methods

Several methods can be used to measure the sorption of radionuclides by geologic media. During FY-1977 we began investigating them to determine their precision, simplicity, time and cost effectiveness, and limitations. The methods studied included: 1) batch, static, shaking or jar tests, 2) low-pressure, flow-through column experiments, 3) axial filtration, and 4) soil channel chromatography. Preparations were also made to study the high-pressure, intact core, flow-through column method.

In the batch method a solution of known radionuclide concentration is placed in a container with geologic medium of known weight and/or surface area. The liquid phase is sampled until its radionuclide concentration, macroconstituents, and pH are constant with time. The phases are then separated and counted. From this information the distribution of radionuclide between the two phases is calculated (K_d or K_a). This information can then be used together with knowledge about the bulk density, porosity, and fracture characteristics of the geologic medium in its in-situ state to estimate the retardation factor, K , for groundwater transport of that radionuclide (the quantity needed for the assessment model calculations) using either of the two equations below:

$$K \equiv 1 + \frac{K_d \rho}{\epsilon} \text{ (unconsolidated media)} \quad (1)$$

where:

K_d = distribution coefficient

$$\left[\frac{\text{activity of nuclide in sorbed state}}{\text{mass of medium}} \right] \div \left[\frac{\text{activity of nuclide in dissolved state}}{\text{volume of pore space}} \right]$$

ρ = bulk density of medium

$$\left[\frac{\text{mass of medium}}{\text{volume of medium}} \right]$$

ϵ = void fraction

$$\left[\frac{\text{volume of pore space}}{\text{volume of medium}} \right]$$

$$K \equiv 1 + K_a R_f \text{ (fractured media)} \quad (2)$$

where:

K_a = distribution coefficient

$$\left[\frac{\text{activity of nuclide in sorbed state}}{\text{surface area}} \right] \div \left[\frac{\text{activity of nuclide in dissolved state}}{\text{volume of fracture}} \right]$$

R_f = surface to volume ratio of fracture system $\left[\frac{\text{surface area}}{\text{volume of fracture}} \right]$

Advantages of the batch method include simplicity, nominal cost, short duration, ability to perform many experiments simultaneously, ability to use crushed rock, chunks, shards, or rock tablets, ability to calculate K_d 's on either a mass or surface area basis, ability to monitor pH, Eh, K_d time dependence, and reversibility. Disadvantages include inability to address multiple oxidation states and species, difficulty in solid-liquid phase separation, unrealistically high solution to solids ratios, disregard of hydrodynamic or flow effects, and alteration of geologic material by crushing and grinding.

In the low-pressure column method a column of known length is loaded with the geologic medium of known density and porosity, and groundwater is pumped through the column at constant velocity. After steady state is reached, either a pulse or continuous injection of radionuclide solution is injected into the flowing groundwater. The experiment continues until the radionuclide discharges from the column. From the length of the column, the velocity of the water, and the time for discharge of the radionuclide, the retardation factor (K)

can be calculated. The distribution coefficient (K_d) is then back-calculated using Equation 1. The low-pressure, flow-through column method permits the nuclide migration rates to be measured directly for porous materials with little alteration of sample. Reversibility, multiple oxidation states or species, and physical transport of colloids and fine particulates can be studied under realistic solution to solids ratios. Porous and fracture flow experiments are possible. Disadvantages include lengthy experiments, inability to create practical flow rates in rock materials with low permeability, experimental phenomena such as channeling, greater difficulty in control of Eh and pH, and data reduction difficulties for non-ideal discharge curves.

The axial filtration method uses a rotating cylindrical filter enclosed in a coaxially-mounted pressure vessel. Solution flows into the outer chamber, through the filter into the cylindrical space within the filter, and finally out through a tube mounted on the axis of rotation. A slurry of the adsorbing geologic material is first placed in the outer (reaction) chamber and the system brought to steady state. The radionuclide solution is then introduced into the system as either an impulse or step change in the inflow concentration, and the radionuclide concentration in the outflow is recorded with time. The relative transport rates of the radionuclide with adsorbent present and absent are compared and the retardation factor is calculated. The distribution coefficient is then back-

calculated using Equation 1. The principal advantages of this method are the ease and rapidity with which distribution coefficient determinations may be made and the capability to determine the reversibility of the sorption. Variable oxidation states or multiple species can be identified. Eh, pH can also be monitored and controlled. Disadvantages include the necessity of using unconsolidated geologic media and potential interpretation problems on unsymmetric data peaks.

In the soil channel chromatography method, soils or ground rock material are slurried with water until moderately fluid and then applied to chemical chromatography plates using a conventional spreader. Strips of blotter paper are used as wicks for transporting the radionuclide solution to the layered soil in the channels. The radionuclide is introduced into the column chromatograph either through the feed solution or by spotting the radionuclide directly onto geologic media. The velocities of movement of both the eluting water and the nuclide are recorded. The retardation factor is calculated, and the distribution coefficient is back-calculated. Advantages of soil channel chromatography include the ability to rapidly compare the migration rate of nuclides through numerous geologic media, the ability to study several wetting and drying cycles nondestructively, and the ability to study multiple-oxidation states or species. Disadvantages include the need to use crushed materials, the lack of control of flow rates, and the complexity in data reduction techniques.

Sorption Measurements for Generic Data Bank

During the year we made a large number of sorption measurements using the methods described previously for many nuclides and generic geologic materials. The nuclides investigated included Tc, I, Sr, Cs, Np, Am, Pu, Eu, Co, Ce, Sb, U, Nb and Ru. The geologic materials included limestone, dolomite, marble, sandstone, siltstone, shale, tuff, soapstone, anhydrite, galena, chalcopryrite, greenstone, granite, gneiss, basalt, rock salt, montmorillonite, illite, kaolinite, vermiculite, quartz, apatite, argillite, albite, anorthite, microcline, biotite, hornblende, enstatite, pyroxine, chalk and bentonite. We are establishing a data bank to collect and organize these data from the more than 300 sets of isotopes and conditions investigated. Table 10.4 shows the information to be included with the data bank entries.

Analysis of Generic Sorption Data

Using information from the data bank about the geologic material properties, groundwater properties, and experimental conditions, it should be possible to develop empirical relationships between the measured sorption values and the independent experimental variables. Such relationships can then be used to predict sorption behavior in situations similar to, but not the same as, the situations investigated. We are investigating two statistical methods for accomplishing this task, nonlinear regression and adaptive learning networks.

Although our generic data base is not complete, several preliminary comparisons can be made. Table 10.5 compares the strontium, cesium, americium and plutonium sorption data for basalt with two plagioclase feldspars. Basalt contains labradorite, an intermediate composition plagioclase feldspar. The K_d for strontium appears

TABLE 10.4. Information Requirements for Generic Data Bank

<u>Geologic Material Properties</u>	<u>Independent Variables</u>		<u>Dependent Variables</u>	
	<u>Groundwater Properties</u>	<u>Experimental Conditions</u>	<u>K_d or K_a</u>	<u>Uncertainty Limits</u>
Mineralogy:	pH	Solution concentration		
Primary minerals	Eh			
Secondary minerals	Major cations	Nuclide valence state or species distribution		
$CaCO_3$	Major anions			
Hydrous oxides	Soluble organic composition	Contact time		
Organic content				
Cation-exchange-capacity	Soluble SiO_2	Measurement method		
Anion-exchange-capacity	Soluble minor species			
Surface area	Temperature			
Hydrology properties:				
Porosity				
Water velocity				
Percentage saturation				
Surface area to volume ratio for fracture system				

TABLE 10.5. Preliminary Distribution Coefficients for Strontium, Cesium, Americium and Plutonium with Basalt and Plagioclase Feldspars Similar to Those Present in Basalt

Material	Experiment	Groundwater	pH	Distribution Coefficients (K_d)				
				Sr	Cs	Am	Pu	
Columbia River basalt	Tablets (ANL)	Rock equilibrated	-	-	-	250	150	
	16-20 mesh (ANL)		-	-	-	83	88	
	30-40 mesh (ANL)		-	-	-	130	120	
	50-70 mesh (ANL)		-	-	-	180	130	
Umtanum basalt	Crushed (RHO)	0.003N NaHCO_3	8.6	-	300	-	-	
			7.9	150	-	-	-	
			8.8	-	-	230	20	
Albite	Crushed (PNL)	0.03N NaHCO_3	9.4	550	530	-	-	
			-	-	-	540	-	
Anorthite	Crushed (PNL)	0.03N CaCl_2	7.7	4	820	170	-	
		0.03N NaHCO_3	9.4	460	610	-	-	
			-	-	-	3800	-	
		0.03N CaCl_2	7.7	3	770	180	-	

sensitive to pH or HCO_3^- concentration, perhaps due to greater sorption by carbonate precipitation. The K_d for cesium does not appear to be as sensitive as strontium to solution pH. The americium data of the three groups compare well, but the ANL (Argonne) plutonium data are about five times larger than the RHO (Rockwell) data. The equilibrium water composition of the ANL data has not been specified, but it probably contains significantly less HCO_3^- ion capable of forming soluble complexes. Thus the lower K_d plutonium found by RHO could reflect soluble carbonate complexation. Plutonium tracer concentration and/or

speciation distribution could also be affecting the results. The pure mineral data for strontium suggest a strong effect of calcium concentration on strontium sorption.

Table 10.6 compares cesium sorption data from ORNL (Oak Ridge) and PNL for montmorillonite with salt brine. The ORNL cesium K_d is about a factor of ten lower than the PNL data. This difference may be caused by the difference in radionuclide concentration used. It may support the conclusion that a few selective sorption sites can cause a large K_d for some nuclides at very low concentrations (such as those expected in geologic isolation release scenarios).

TABLE 10.6. Preliminary Distribution Coefficients for Cesium with Montmorillonite

Material	Experiment	Groundwater	Cesium Concentration	$K_d \text{ Cs}$
Montmorillonite	Crushed (ORNL)	4N NaCl	10^{-3} M	3-10
		0.6N NaCl	10^{-3} M	11-35
	Crushed (PNL)	5N NaCl	10^{-11} M	33
		0.03N NaCl	10^{-11} M	1000

Table 10.7 compares strontium, cesium, americium and plutonium sorption data for granite with a major mineral constituent, quartz. The ANL and RHO data for americium do not compare well, possibly because the RHO material had a significant amount of apatite. However, the ANL apatite data (taken under somewhat different conditions) do not support the large RHO value. Groundwater composition and americium concentration should be more closely controlled in comparing rocks of similar composition. The quartz and Nevada Testing Site (NTS) granite data compare reasonably well for cesium.

Data were taken to compare the sorption of americium and plutonium for tablets and crushed materials. These measurements show higher sorption for the crushed materials and suggest that surface area can sometimes be an important parameter.

Validation Studies

An important consideration is the relationship between results of short-

term laboratory experiments and of long-term in-situ behavior. We have collected thermodynamic data for elements with long-lived isotopes. Plots of nuclide activity in solution versus pH and Eh have been constructed. These data are being incorporated into a computer program to facilitate rapid calculation of nuclide activities for any groundwater composition. Future work may compare the laboratory results to the nuclide behavior observed at Oklo and NTS, and in uranium ore deposits and to the waste management experience at many sites.

Sorption Mechanism Studies

A more complete understanding of the controlling sorption mechanisms for important nuclides in geologic environments relevant to waste isolation will increase our ability to predict radionuclide behavior at one site from data taken at another site. This in turn can result in savings of time and cost during subsequent site-specific investigations. We began investigations to study the effects of

TABLE 10.7. Preliminary Distribution Coefficients for Strontium, Cesium, Americium and Plutonium with Granite Rocks, a Major Constituent, Quartz, and a Minor Constituent, Apatite

Material	Experiment	Groundwater	pH	Distribution Coefficients (K_d)			
				Sr	Cs	Am	Pu
Granite (N.C.)	Tablets (ANL)	Rock equilibrated	-	-	-	10	37
Granite (NTS)	Crushed (ANL)	Rock equilibrated	-	-	-	21	2,100
Quartz monzonite porphyry (NTS)	Crushed (RHO)	0.004N NaHCO_3 0.007 CaSO_4	8.0	5.5	650	60,000	5,400
Apatite	Crushed (ANL)	Apatite equilibrated	-	-	-	9,400	-
Quartz	Crushed (PNL)	0.03N NaHCO_3	9.4	350	37	130	-
		0.03N CaCl_2	7.7	0	34	0	-

solution ionic strength on nuclide sorption, microstructural configuration of sorption sites on specific geologic materials, and controlled

pH-Eh sorption experiments for plutonium. These studies have not advanced far enough to yield significant results.

REFERENCES

1. K. J. Schneider and A. M. Platt, eds., High-Level Waste Management Alternatives. BNWL-1900, Battelle, Pacific Northwest Laboratories, Richland, WA, 1974.
2. S. F. Logan, chmn., Workshop on Geologic Data Requirements for Radioactive Waste Management Assessment Models. Y/OWI/SUB-76/81726, Office of Waste Isolation, Oak Ridge, TN, 1976.
3. Disposal of Radioactive Wastes on Land, Publication 519, National Academy of Sciences, Washington, DC, 1957.
4. T. J. Gordon and O. Helmer, Report on a Long-Range Forecasting Study. Rand Paper P-2982, Rand Corporation, Santa Monica, CA, 1964.
5. H. A. Linstone and M. Turoff, eds., The Delphi Method: Techniques and Applications, Addison-Wesley Publishing Co., Reading, MA, 1975.
6. J. Hamstra, "Radiotoxic Hazard Measure for Buried Solid Radioactive Waste." Nuclear Safety 16: 180, 1975.
7. H. C. Burkholder, M. O. Cloninger, D. A. Baker and G. Jansen, "Incentives for Partitioning High-Level Waste." Nuclear Technology 31:202, 1976.
8. H. C. Claiborne and F. Gera, Potential Containment Failure Mechanisms and Their Consequences at a Radioactive Waste Repository in Bedded Salt in New Mexico. ORNL-TM-4639, Oak Ridge National Laboratory, Oak Ridge, TN, 1974.
9. H. C. Burkholder, J. A. Stottlemire and J. R. Raymond, "Safety Assessment and Geosphere Transport Methodology for the Geologic Isolation of Nuclear Waste Materials." Risk Analysis and Geologic Modeling in Relation to the Disposal of Radioactive Wastes into Geologic Formations, OECD Nuclear Energy Agency, Paris, France, 1977.
10. G. Bertozzi, M. D'Alessandro, F. Girardi and M. Vanossi, "Evaluation de la Sûreté du Stockage des Déchets Radioactifs en Formations Géologiques: Une Application Préliminaire de la Fault Tree Analysis à des Formations Salines." Risk Analysis and Geologic Modeling in Relation to the Disposal of Radioactive Wastes into Geologic Formations, OECD Nuclear Energy Agency, Paris, France, 1977.
11. Reactor Safety Study, U.S. Nuclear Regulatory Commission, Washington, DC, 1975.
12. R. W. Nelson, Evaluating the Environmental Consequences of Groundwater Contamination. BCSR-6/UC-11, Boeing Computer Service, Richland, WA, 1976.
13. K. L. Kipp, A. E. Reisenauer, C. R. Cole and C. A. Bryan, Variable Thickness Transient Groundwater Flow Model Theory and Numerical Implementation. BNWL-1703, Battelle, Pacific Northwest Laboratories, Richland, WA, 1972, updated 1976.
14. S. K. Gupta, K. K. Tanji and J. N. Luthin, A Three-Dimensional Finite Element Ground Water Model, University of California at Davis, Davis, CA, 1975.
15. D. H. Lester, G. Jansen and H. C. Burkholder, "The Migration of Radionuclide Chains Through an Adsorbing Medium." AICHE Symposium Series No. 152, Adsorption and Ion Exchange, 71:202, 1975.
16. S. W. Ahlstrom, H. P. Foote, R. C. Arnett, C. R. Cole and R. J. Serne, Multicomponent Mass Transport Model: Theory and Numerical Implementation (Discrete-Parcel-Random-Walk Version). BNWL-2127, Battelle, Pacific Northwest Laboratories, Richland, WA, 1977.

17. J. K. Soldat, N. M. Robinson and D. A. Baker, Models and Computer Codes for Evaluating Environmental Radiation Doses. BNWL-1754, Battelle, Pacific Northwest Laboratories, Richland, WA, 1974.
18. D. A. Baker, G. R. Hoenes and J. K. Soldat, FOOD - An Interactive Code to Calculate Internal Radiation Doses from Contaminated Food Products. BNWL-SA-5523, Battelle, Pacific Northwest Laboratories, Richland, WA, 1975.
19. D. L. Streng, E. C. Watson, KRONIC - A Computer Program for Calculating Annual Average External Doses from Chronic Atmosphere Releases of Radionuclides. BNWL-B-264, Battelle, Pacific Northwest Laboratories, Richland, WA, 1973.
20. D. L. Streng, E. C. Watson and J. R. Houston, SUBDOS - A Computer Program for Calculating Individual External Doses from Accidental Atmospheric Releases of Radionuclides. BNWL-B-351, Battelle, Pacific Northwest Laboratories, Richland, WA, 1975.
21. D. L. Streng, DACRIN - A Computer Program for Calculating Organ Dose from Acute or Chronic Radionuclide Inhalation: Modification for Gastrointestinal Tract Dose. BNWL-B-389, Battelle, Pacific Northwest Laboratories, Richland, WA, 1975.

11.0 MONITORING AND PHYSICAL CHARACTERIZATION OF UNSATURATED ZONE TRANSPORT

S. J. Phillips - Project Manager

The objective of this project is to develop monitoring instrumentation systems and burial media-waste characterization methods to evaluate the migration of contaminants from disposal sites for low-level solid waste.

SUMMARY

Sediment chemistry and hydrodynamic flow analyses have been made prior to evaluating unsaturated transport of radionuclide flux from shallow land waste disposal sites.

Physical models and laboratory radionuclide counting apparatus have been used to initially evaluate porous media flow of single-phase flux in isotropic homogeneous isothermal systems.

In-situ monitoring activities are continuing in order to develop an accurate system for use in evaluating atmospheric and geohydrologic parameters controlling uncontaminated and radioactive waste materials transport.

A draft document has been initially prepared and reviewed which covers theoretical and empirical developments used in simulations and monitoring transport of radionuclide waste constituents.

TASK 1 - LABORATORY ANALYSIS -

R. J. Serne, S. J. Phillips and
G. W. Gee

The transport of low-level radionuclides from waste disposal sites is

controlled by those physiochemical interactions among environmental factors, the burial media, the transport media, and the radionuclides. Under conditions of partial saturation from the ground surface to the saturated groundwater domain, evaluation of transport becomes exceedingly complex. Studies are continuing to evaluate radionuclide transport parameters of two generic Hanford sediments.

X-ray diffraction analysis of these sediments has been conducted on particle size distributions of less than 2 μ . Typically each sediment comprises the same clay mineral suite; however, the degree of crystallinity and relative proportionality of each mineral differs. The coarse-textured generic sediment was found to contain poorly crystallized smectite with minor amounts of hydromica and trace amounts of kaolinite. The fine-textured equivalent, with a factor of about three times more or less than the 2- μ particles, however, contains well crystallized smectite and minor amounts of micaceous and kaolinitic crystalline material. Typical x-ray diffractograms of these soils are illustrated in Figures 11.1 and 11.2. Diffraction traces of <2 μ (equivalent spherical

FIGURE 11.1. X-Ray Diffractogram of $<2\text{-}\mu$ Fraction of Fine-Textured Generic Sediment

diameter) oriented material represented include: I - magnesium saturation, II - magnesium saturated ethylene glycol treatment, III - potassium saturated heat treatment (105°C), IV - potassium saturated, and V - potassium saturated heat treatment (500°C).

A rigorous analysis of the $<2\text{-}\mu$ fraction of all sediments is required because radionuclide adsorption-

FIGURE 11.2. X-Ray Diffractogram of $<2\text{-}\mu$ Fraction of Coarse-Textured Generic Sediment

desorption phenomena typically increase with decreased particle size.

To better understand the macrochemical reactions occurring in the soil systems, we measured the ion exchange selectivity constants for sodium, potassium, calcium, and magnesium. Binary exchange reactions were determined from mass-action laws, and empirical selectivity constants were calculated. Because the rigorous mass-action equation requires the determination of solid components' activities, which is not possible for heterogeneous solids, an empirical approach is used. Three binary systems (Na-Ca),

(Na-K), and (Mg-Ca) were studied using batch sorption experiments with two sediments. The data derived from the batch experiments on binary systems are used to model the transport of radionuclides by simultaneous calculation of the four-component system (Na, Ca, K, Mg). The mass-action equations which represent the three binary systems studied are:

where X represents the soil matrix. The equivalent relationships from which empirical selectivity constants and solid-phase activity corrections can be calculated are:

$$K_{K-Na} = \frac{(\gamma_{Na})(Na^+)}{(\gamma_K)(K^+)} \left[\frac{KX}{NaX} \right]^P \quad (4)$$

$$K_{Na-Ca} = \frac{(\gamma_{Ca})(Ca^{+2})}{(\gamma_{Na})^2(Na^+)^2} \left[\frac{Na_2X}{CaX} \right]^P \quad (5)$$

$$K_{Mg-Ca} = \frac{(\gamma_{Ca})(Ca^{+2})}{(\gamma_{Na})^2(Na^+)^2} \left[\frac{MgX}{CaX} \right]^P \quad (6)$$

where:

K_{a-b} = empirical selectivity constants

γ = activity coefficients

P = solid-phase activity correction.

For all experiments, the generic sediments were pretreated to remove calcium carbonate and then saturated at pH 7 with either calcium or sodium. In the K-Na system, sodium saturated sediment was contacted overnight with solutions with (30 ml) of Na-K-Cl with a total ionic strength of 0.03 normal at pH 7 (variable Na/K ratios). After centrifugation, the effluent solutions (assumed to be at equilibrium) were analyzed by atomic absorption for sodium and potassium. The decrease in potassium concentration is used to calculate the amount of replacement of potassium for sodium on the sediment.

Similar binary solutions of Na-Ca-Cl and Mg-Ca-Cl were contacted with calcium-saturated sediments to determine the K_{Na-Ca} and K_{Mg-Ca} , respectively.

The batch exchange experiments yield the equilibrium ratio of cations in solution and on the sediment matrix. By taking the logarithm of both sides of Equations 4-6, a straight line expression is obtained. For example, using Equation 5:

$$\log \frac{(\gamma_{Ca})(Ca^{+2})}{(\gamma_{Na})^2(Na^+)^2} + P \log \frac{Na_2X}{CaX} =$$

$$\log K_{Na-Ca}$$

$$\log \frac{(\gamma_{Ca})(Ca^{+2})}{(\gamma_{Na})^2(Na^+)^2} = \log K_{Na-Ca} - P$$

$$\log \frac{Na_2X}{CaX}$$

$$(Y = b + mX)$$

$$\text{where } \log \frac{(\gamma_{\text{Ca}})(\text{Ca}^{+2})}{(\gamma_{\text{Na}})^2(\text{Na}^+)^2} = Y$$

$$\log K_{\text{Na-Ca}} = b$$

$$\log \frac{\text{Na}_2\text{X}}{\text{CaX}} = X$$

$$P = -m.$$

A plot of the logarithms of the ratios of equilibrium solution and sediment-bound cations should yield a straight line with an intercept equal to the log K and a slope equal to (-P).

Figure 11.3 shows the plot for the batch ion exchange sediments for one sediment. The initial binary solutions and final logarithm values are shown in Table 11.1.

FIGURE 11.3. Plot of Na-K Exchange for Fine-Textured Sediment

TABLE 11.1. Ion Exchange Results for Na-K

Soil A- Na-Saturated
Na-K Selectivity

	Initial Solution	$\log \frac{KX}{NaX}$ X	$\log \frac{\gamma_{Na}}{\gamma_K} \frac{Na}{K}$ Y
Na	0.0154M	-0.810	1.79
K	0.0013M	-0.810	1.79
		-0.785	1.95
Na	0.0126M	-0.501	1.337
K	0.0027M	-0.501	1.350
		-0.485	1.395
Na	0.0076M	-0.084	0.870
K	0.0055M	-0.084	0.870
		-0.084	0.861
Na	0.0107M	-0.012	0.789
K	0.0067M	+0.022	0.810
		+0.017	0.808
Na	0.0050M	+0.434	0.207
K	0.0113M	+0.441	0.207
		+0.521	0.232
Na	0.0097M	+0.087	0.702
K	0.0070M	+0.086	0.715
		+0.095	0.702

Binary exchange equation parameters:

$$m = -1.203$$

$$b = 0.790$$

$$4 = 0.996$$

TASK 2 - PHYSICAL MODELING OF
CONTAMINANT TRANSPORT - L. Kannberg
and S. J. Phillips

Field data and those data derived by laboratory experimentation and subsequent mathematical modeling concerning flow in porous media often are inconsistent. These inconsistencies may prove to be a function of the analytical approach. To evaluate

this problem, simultaneous laboratory analyses of sediment samples and large one-dimensional physical models are being conducted. Scaling of real and prototype variables, dimensional analysis and similitude requirements have been developed for several partially-saturated flow systems. For one-dimensional, homogeneous, isotropic isothermal flow of single-phase incompressible fluids has been evaluated and computer codes formulated. In addition, a formulation of two-phase homogeneous isotropic incompressible flow has been numerically analyzed.

Laboratory analysis of single-phase drainage, imbibition and wetting front migration has been conducted. Multichannels gamma spectroscopy of sediment fluid attenuation has provided fluid content accuracy of greater than 2% and spatial resolution of about 5 mm. Diffusivity determinations on partially-saturated, one-dimensional columns have been completed and subsequent numerical analysis using cubic spline least squares fitting techniques has been made. These data are used to evaluate the total diffusivity and the contributions of vapor- and liquid-phase constituents.

TASK 3 - FIELD MONITORING AND DATA EVALUATION - S. J. Phillips and G. W. Gee

To accurately evaluate the factors controlling transport of

mobile materials in radioactive waste burial sites, environmental and subterranean parameters must be monitored in-situ. Two three-dimensional arrays of instrument access and thermal and potentiometric transducers have been installed adjacent to a waste burial site. A data logger capable of recording porous media flow and environmental parameters has been acquired and is being modified and interfaced to specific electronic components. In addition, thermopile heat flux plates used in determining thermal inertia and flux in partially-saturated geohydrologic systems have been fabricated, and calibrated and tested prior to in-situ installation.

Significant micrometeorological parameters controlling evaporation and coupled evapotranspiration have been evaluated. Provisions for interfacing climatological sensors to existing recording systems have also been made. Weighing lysimetry is an accurate method to monitor short-duration vapor- and liquid-phase flux across the sediment-atmosphere interface. Prior to installation of these devices, the system has been evaluated.

A draft document describing theoretical, numerical analysis, laboratory analysis, and in-situ monitoring has been written and initially reviewed.

.

.

.

.

.

.

.

.

12.0 DETECTION AND CHARACTERIZATION OF MOBILE ORGANIC COMPLEXES OF FISSION PRODUCTS

J. A. Franz - Project Manager

The objective of this program is to determine the important mobile or volatile organic complexes of fission and activation products formed in the storage of low-level waste in shallow land burial.

SUMMARY

A detailed review of the chemistry and stability of technetium complexes was written. A detailed review of the chemistry and stability of niobium complexes was started. Experiments were performed to determine conditions where $Zr(OH)_4$ precipitation is reversible and to compare hydrolyzed zirconium's reactivity with unhydrolyzed zirconium's reactivity. Potentiometric titrations of zirconium mixed ligand solutions indicated that tartaric acid or gluconic acid prevents precipitation of zirconium at high pH. Ni-complex, soil elution experiments were performed which indicate the dependence of absorption on the form of reacting ligand, stability, and charges of resultant complexes.*

TASK 1 - IDENTIFICATION OF NUCLIDES AND COMPLEXING AGENTS - D. J. Wiggins and J. A. Franz

A detailed review of the stability of nickel complexes was completed and written during the third quarter

of FY-1977. The detailed review of the stability of technetium complexes was also started during this period.

The detailed review of technetium complex stability was completed and written during the fourth quarter of FY-1977. A detailed review of niobium complex stability was started during this quarter.

This latter review revealed several key features of aqueous niobium solutions:

- aqueous Nb(V) is essentially insoluble at pH 0-7⁽¹⁾
- Nb(V) has a pronounced affinity for oxygen donors⁽²⁾
- 5-membered rings form the most stable Nb(V) chelate rings⁽³⁾
- Nb(v) bonds with either two hydroxyl groups simultaneously or one hydroxyl and one carboxyl⁽³⁾
- EDTA⁴⁻ and protocatechuic acid²⁻ form the most stable complexes with niobium (Log K ~40.78 and 63.1, respectively).⁽⁴⁾

The review of the known chemistry of organic complexes of technetium revealed another key feature of aqueous technetium solutions:

- Tc(IV) - NTA³⁻, - EDTA⁴⁻, and - DATA⁴⁻, have fairly large stability constants (~20) at pH 1.5.⁽⁵⁾

* For the background of this total program, see BNWL-2290 and BNWL-2377-2.

TASK 2 - STUDY OF MOBILITY CHARACTERISTICS OF ORGANIC COMPLEXES -

D. J. Wiggins and J. A. Franz

Several experiments were performed during the fourth quarter of FY-1977 in an attempt to determine whether there are conditions where the irreversible precipitation of $\text{Zr}(\text{OH})_4$ is reversible. Preliminary results indicate that $\text{Zr}(\text{OH})_4$, if not heated, can be resolubilized by tartaric acid or gluconic acid by refluxing the $\text{Zr}(\text{OH})_4$ in the presence of either one of these acids. Experiments were also performed to ascertain the relative tendency of hydrolyzed zirconium to complex or polymerize as compared with unhydrolyzed zirconium. Preliminary results indicate that ligands which require more than two coordination sites will not bond in the same manner with hydrolyzed zirconium as unhydrolyzed zirconium. The degree of zirconium hydrolysis will have a significant impact on the stability and solubility of the complexes which it forms.

Potentiometric titrations of various combinations of ligands and zirconium revealed that the precipitation of zirconium or destruction of the complex at high pH can be eliminated by the presence of only tartaric or gluconic acid ("protolyzed zirconium"). This probably has something to do with their glycol-type structure which becomes available for bonding at high pH. One investigator proposed that zirconium, EDTA, and tartaric acid (citric or lactic acid) form an overall complex which is more stable to alkaline destruction than the zirconium-EDTA complex.⁽¹⁾

With high-performance liquid chromatographic instrumentation, 11 soil elution studies have been performed during the third and fourth quarter of FY-1977. Two types of soil were used, soil A, a fine soil which is found at the bottom of a shallow land burial trench, and soil B, a coarse soil which is used to fill in over the buried waste. Experiments were conducted at the pH of distilled water (pH 6-7). The complexes are made at pH 1.0, where the likelihood of hydrolysis is minimal. The pH is then increased with base until the pH of water is obtained. Two concentrations of complex were used: 0.1M and 0.001M. The effluent flow rate was maintained at 2 ml/min.

In Figure 12.1, the elution results of three nickel-gluconate complexes are shown. In all three cases, much of the complex is absorbed by soil. Soil A can absorb much more of the complex than can Soil B because of its higher ion exchange capacity:

Soil A 12.0 ± 0.1 meq/100 g

Soil B 5.0 ± 0.1 meq/100 g

The nickel-gluconate complex is absorbed at low pH entirely, but if the pH is allowed to increase, the complex will eventually elute. The following equation probably represents the unfavored formation of the nickel-gluconate complex at low pH:

As the pH is raised, the following equation represents the formation of a neutral complex which is not absorbed by the soil:

Nickel-EDTA is a very stable complex and is not absorbed by soil to a significant extent (0 to 10% absorbed).

FIGURE 12.1. Elution Curves of Nickel-Gluconate Complex from Hanford Soils at pH 6-7: Soil B, 72.87% Absorbed; Soil A, 99.78% Absorbed

The following probably represents the favored formation of nickel-EDTA complex:

As the pH is raised, a coordination site of the nickel could be usurped by a hydroxyl group as follows:

In Figure 12.2 the elution results of nickel-HEDTA and of nickel-DTPA are shown. The following equation probably represents the favored formation of nickel-HEDTA complex:

As with EDTA, a coordination site may be usurped by a hydroxyl group at higher pH:

The following equation probably represents the less favored formation of nickel-DTPA:

FIGURE 12.2. Elution Curves of Nickel-HEDTA and Nickel-DTPA from Hanford Soil. a. Nickel-DTPA, 20.16% absorbed. b. Nickel-HEDTA, 1.66% absorbed.

As the pH is raised, the following reactions probably occur:

As is evident from the above equations, the stability of the formed complex is very dependent on the pH

of the medium which controls the form of the complexing agent. And the absorption of the complex by soil is affected by the stability and the charge of the complex or mixture of complex products (if more than one form of the complex is present).

REFERENCES

1. G. A. Volkova, V. G. Sochevanov, "Complex Formation by Niobium Hydroxide with EDTA." Russ. J. Inorg. Chem., 12:222, 1967.
2. Ct. Konecny, "Studies on Complex Formation by Solvent Extraction Method II. Niobium(V) Complexes in Aqueous Solution." Z. Phys. Chem. (Leipzig), 235(1-2):39-48, 1967.
3. F. Fairbrother, J. B. Taylor, "Water-Soluble Complexes of Niobium and Tantalum. Part I. Complexes with α -Hydroxy Acids and Amines." J. Chem. Soc. (London), p. 4946, 1956.
4. A. E. Martell, compiler, Stability Constants of Metal Ion Complexes, Supplement, No. 1, part II, Spec. Pub. No. 25, The Chemical Society, Burlington House, London, 1971.
5. B. Gorski and H. Koch, "Über die Komplexbildung von Technetium mit Chelatbildenden Liganden-II." J. Inorg. Nucl. Chem., 32:3831-3836, 1970.

13.0 ELECTROPOLISHING FOR SURFACE DECONTAMINATION OF METALS

R. P. Allen and H. W. Arrowsmith - Project Managers

The objective of this program is to develop electropolishing as a large-scale decontamination technique for radioactive metal surfaces. Major program activities include 1) the establishment and operation of a demonstration decontamination facility and 2) laboratory studies to understand and optimize the decontamination process.

SUMMARY

The demonstration decontamination facility was tested with plutonium-contaminated material from the Hanford 231-Z Building. A total surface area of 1.86 m^2 (20 ft^2) was processed at one time, and the ability of electropolishing to decontaminate difficult areas was demonstrated with two stainless steel elbows 0.9 m (3 ft) long. Design work is under way to upgrade the demonstration facility's ventilation system.

A large plastic greenhouse was used to prepare such test materials as heavily corroded and contaminated mild steel pipe for initial decontamination studies. Four methods were used for sectioning the test materials: a large tubing cutter, two types of reciprocating saws, and a nibbler. Results showed that it is possible to section this kind of material without releasing contamination into the air. The greenhouse was later disassembled to prepare the area for a permanent sectioning/pretreatment prototype facility.

A pumped-stream in situ electropolishing probe was used to remove adherent contaminated oxide from

difficult-to-clean component areas. A current of 2 A reduced the radiation level of plutonium-contaminated spots from $15,000 \text{ dis/min/100 cm}^2$ to background in less than 2 min .

DEMONSTRATION FACILITY

Since completion of the major work on the demonstration decontamination facility, testing has been under way to determine the system effectiveness and capabilities and to identify necessary design changes. Modifications during the past quarter have included replacement of a leaking rotary seal pump with a sealless magnetically coupled pump. This pump failed after only 100 hr of service with the phosphoric acid electrolyte. These pump evaluation tests will continue, using a second type of zero-leakage pump with special acid-resistant alloy seals.

A splash shield has been installed in front of the electropolishing tank to provide additional protection for the operator, and design work has begun to upgrade the demonstration facility ventilation system. This effort will improve distribution of the airflow and permit use of the

second rinse tank as an alternative electropolishing cell for such special electrolyte studies as investigating the use of phosphoric-chromic solutions to decontaminate and passivate carbon steel items.

The electrical distribution system for the electropolishing tank has been upgraded with a remote switching system so that either the tank walls or an auxiliary electrode, or both, can be remotely selected to serve as the cathode for a particular component.

Plutonium-contaminated material from the Hanford 231-Z Building was used in testing the demonstration decontamination facility. Test pieces decontaminated included:

- Eight curved sections 0.8 m (2.5 ft) long by 0.4 m (1.3 ft) wide from a stainless steel duct 0.6 m (2 ft) in diameter (Figure 13.1). Three of these sections were processed at a time, representing a total surface area of 1.86 m^2 (20 ft^2). Electropolishing reduced the radiation level of 10,000 to 15,000 dis/min/ 100 cm^2 to background in less than 5 min and required removal of less than $5 \mu\text{m}$ (0.0002 in.) of surface material.
- Two stainless steel pipes (90° bend sections) 20 cm (8 in.) in diameter by 0.9 m (3 ft) long. The interior of each pipe was decontaminated from 115,000 dis/min/ 100 cm^2 to background in 15 min without using

PNL 7710315-5

FIGURE 13.1. Curved Sections from a Stainless Steel Duct (Figure 13.2). A total surface area of 1.86 m^2 (20 ft^2) was processed at one time.

an internal cathode. This further illustrates the throwing power or ability of electropolishing to decontaminate areas somewhat inaccessible or shielded from the cathode.

- A carbon steel pipe, 10 cm (4 in.) OD by 0.9 m (3 ft) long, that was both contaminated and pitted on the inside by exposure to plutonium-containing acid solutions. The radiation level was reduced from 750,000 dis/min/100 cm² to background in 10 min using an internal cathode.

PRETREATMENT FACILITY

A large plastic greenhouse--3.7 m (12 ft) square by 2.4 m (8 ft) high--adjacent to the electropolishing facility was used to prepare test material for initial decontamination studies in the 1500-liter (400 gal) demonstration system. More than 46 m² (500 ft²) of carbon steel and stainless steel ducting, 9 cm (3.5 in.) to 0.6 m (2 ft) in diameter, from the 231-Z Building was cut, or sectioned, into sizes suitable for processing in the electropolishing tank. Typical sectioning times were 10 min or less for the contaminated ducting.

The greenhouse was constructed of 5 by 5-cm (2 by 2 in.) aluminum angle with 0.04-mm (15 mil) plastic stretched over the outside of the aluminum frame. Major features included a change room for personnel to enter and exit and a port for introducing large pipes for sectioning into lengths about 0.9 m (3 ft).

The greenhouse was ventilated by approximately 14 m³ (500 ft³) of air/min flowing through a double layer of

fiberglass filters, through the down-draft facility, and into the contaminated exhaust of the building. No airborne contamination was ever detected by the constant air monitor installed to sample air from the sectioning facility.

Typical items processed through the sectioning facility were 10-cm- (4 in.) OD mild steel pipe. Inside the pipes were heavily corroded and highly contaminated to over 1 million dis/min/100 cm². Other material sectioned included a schedule 10 stainless steel pipe, 20 cm (8 in.) in diameter, used primarily for glove box exhausts. The contamination in the glove box exhaust pipes ranged from a few hundred to over a million dis/min/100 cm².

Four methods were used for sectioning the various materials mentioned. The first method used a large tubing cutter on the 10-cm-OD steel pipe. The tubing cutter was placed on the steel pipe, then gradually tightened and revolved about the pipe until the piece was sectioned from the large length of pipe. Neither the tubing cutter nor the surrounding area became contaminated. However, tubing cutters for tubing larger than 10 cm are very expensive and are complex to use.

The second method of sectioning both the mild steel pipe and the larger 20-cm-dia stainless steel pipe was the use of a heavy-duty reciprocating saw with 30- to 60-cm (12 to 24 in.) blades. This saw has a bracket that supports the weight of the saw, allowing the weight to pivot into the pipe being cut and thus reduce the force required

from operating personnel. A typical cutting time for a 20-cm-dia stainless steel schedule 10 pipe was about 5 min. A cutting oil helped to cool the reciprocating saw blade and to contain any contamination within the pipe near the cutting zone. About 30 m (100 linear ft) of 20-cm-dia pipe was sectioned using this technique. No airborne contamination was detected, and the only contamination on the saw blade was found around the cutting area. The rest of the contamination was contained within the pipes being sectioned.

The third method of cutting used a hand-held reciprocating saw with blades about 7.6 cm (3 in.) long. This tool also was able to cut the pipe, but blade life was shorter and the work was harder for the operators.

A fourth type of sectioning was done on about 4.6 m (15 ft) of highly contaminated stainless steel ducting 60 cm (2 ft) in diameter (Figure 13.2). The 0.08 mm (22-gauge) ducting was cut by using a nibbler device which has a scissor action. This device allowed the technicians to cut the material into pieces about 60 by 60 cm (2 by 2 ft).

After completion of the sectioning work, the cutting facilities inside the greenhouse were removed and were of low enough radioactivity to be wiped and reused. The greenhouse itself was uncontaminated and was easily disassembled to prepare the area for a permanent sectioning/pre-treatment prototype facility.

The permanent sectioning/pre-treatment prototype facility will include a glove box line consisting of a bead blaster, an ultrasonic cleaner, and a

PNL 775934-5

FIGURE 13.2. Ducting from Downdraft Facility, 22-gauge Stainless Steel, 60 cm in Diameter, Was Later Sectioned (Figure 13.1) in the Greenhouse in the Background

utility glove box. This glove box line is being installed to evaluate and develop optimum pretreatment techniques to remove paint, grease, corrosion layers, and gross surface contamination from components before decontamination by electropolishing. These glove boxes will be connected to the unpacking hood and electropolishing tank through a conveyor system 46 cm wide by 60 cm high by 6 m long (18 in. by 24 in. by 20 ft).

IN SITU DECONTAMINATION TECHNIQUES

PNL is developing in situ electropolishing techniques to decontaminate surfaces that cannot be transported to or immersed in a conventional electropolishing tank. This capability would be valuable in onsite decontamination and decommissioning operations for tanks, equipment, pipe interiors, and other large or immobile metal surfaces prior to dismantling.

Previous studies at PNL have demonstrated the ability to electropolish selected areas using higher voltage, pumped-stream and brush techniques. Now, in situ devices have been developed that can rapidly polish defined surface areas using high-current densities and normal electropolishing

voltages. For example, an area 20 cm^2 (3 in.^2) on a stainless steel surface can be electropolished in 5 min using phosphoric-sulfuric electrolyte, a current density of 0.06 A/cm^2 (550 A/ft^2), and an electrode potential of less than 12 V(dc). The ability to electropolish in situ at high-current densities and low voltages is important because it minimizes electropolishing time while retaining the safety of tank-type operation. Heat input to the electrolyte is minimized also at the lower electropolishing potentials.

A pumped-stream in situ electropolishing device was used to remove adherent contaminated oxide from component areas difficult to clean (Figure 13.3). A 1.3-cm- (0.5 in.) dia

PNL 78A458-6

FIGURE 13.3. Pumped Stream In Situ Electropolishing Probe Used to Remove Adherent Contaminated Oxide from Carbon Steel

stream of phosphoric acid electrolyte conducting a current of 2 A reduced the radiation level of plutonium-contaminated areas on a carbon steel component from 15,000 dis/min/100 cm² to background in less than 2 min.

RELATED PROJECTS

Experience has shown that the smooth surfaces produced by electropolishing are much easier to clean using standard decontamination techniques (chemical spray, soaking in nitric acid, or swabbing with tissue

and acetone) than are metal surfaces with a normal as-received finish. Because of this, significant interest is developing in using electropolishing to prepolish stainless steel laboratory ware, shipping and transfer containers, and other items that require routine decontamination. For example, 15 new 40-kg (90 lb) inter-area sample shipping containers were prepolished during the reporting period for the Rockwell Hanford Operations Company. These containers were specifically designed with accessible stainless steel surfaces to facilitate decontamination by electropolishing.

DISTRIBUTIONNo. of
CopiesNo. of
CopiesUNITED STATES

A. A. Churm
DoE Chicago Patent Group
9800 South Cass Avenue
Argonne, IL 60439

S. H. Smiley
Deputy Director for Fuels
and Materials
NRC Directorate of Licensing
for Fuels and Materials
4915 St. Elmo Ave.
Bethesda, MD 20014

W. P. Bishop
Assistant Director for Radioactive
Waste Management Branch
NRC Division of Materials and
Fuel Cycle Facility Licensing
Washington, DC 20555

W. G. Belter
DoE Division of Biomedical and
Environmental Research
Earth Sciences Branch
Washington, DC 20545

W. A. Brobst
DoE Division of Environmental
Control Technology
Washington, DC 20545

W. E. Mott
DoE Division of Environmental
Control Technology
Washington, DC 20545

G. W. Cunningham
DoE, Administrator for Nuclear
Energy Programs
Washington, DC 20545

R. B. Chitwood
DoE Division of Nuclear Power
Development
Washington, DC 20545

T. C. Chee
DoE Division of Waste Management
Washington, DC 20545

C. R. Cooley
DoE Division of Waste Management
Washington, DC 20345

C. H. George
DoE Division of Waste Management
Washington, DC 20545

C. A. Heath
DoE Division of Waste Management
Washington, DC 20545

G. Oertel
DoE Division of Waste Management
Washington, DC 20545

A. F. Perge
DoE Division of Waste Management
Washington, DC 20545

J. M. Taub
DoE Division of Waste Management
Washington, DC 20545

D. L. Vieth
DoE Division of Waste Management
Washington, DC 20545

R. D. Walton
DoE Division of Waste Management
Washington, DC 20545

DoE Idaho Operations Office
P. O. Box 2108
Idaho Falls, ID 83401

J. J. Schreiber
DoE Oak Ridge Operations Office
P. O. Box X
Oak Ridge, TN 37830

267 DoE Technical Information Center

A. P. Roeh, Manager
Process Evaluation Branch
Allied Chemical Corp.
550 - 2nd Street
Idaho Falls, ID 83401

R. A. Brown
Allied Chemical Corporation
550 - 2nd Street
Idaho Falls, ID 83401

C. A. Hawley
Allied Chemical Corporation
550 - 2nd Street
Idaho Falls, ID 83401

D. A. Knecht
Allied Chemical Corporation
550 - 2nd Street
Idaho Falls, ID 83401

Allied Chemical Corporation
(File Copy)
550 - 2nd Street
Idaho Falls, ID 83401

Distr-2

No. of
Copies

J. A. Buckham
Allied-General Nuclear Services
P. O. Box 847
Barnwell, SC 29812

A. Williams
Allied-General Nuclear Services
P. O. Box 847
Barnwell, SC 29812

J. L. Jardine
M. J. Steindler/L. E. Trevorow
2 Argonne National Laboratory
9700 South Cass Ave.
Argonne, IL 60439

Battelle Memorial Institute
505 King Ave.
Columbus, OH 43201

J. M. Batch
Battelle Memorial Institute
505 King Ave.
Columbus, OH 43201

2 Brookhaven National Laboratory
Reference Section
Information Division
Upton, Long Island, NY

Combustion Division
Combustion Engineering, Inc.
Windsor, CT 06095

2 M. A. Thompson
Rockwell International
Rocky Flats Division
Golden, CO 80401

M. D. Boersma
duPont Company, Aiken (DoE)
E. I. duPont DeNemours and Co.
Savannah River Laboratory
Aiken, SC 29801

C. H. Ice
duPont Company, Aiken (DoE)
E. I. duPont DeNemours and Co.
Savannah River Laboratory
Aiken, SC 29801

A. S. Jennings
duPont Company, Aiken (DoE)
E. I. duPont DeNemours and Co.
Savannah River Laboratory
Aiken, SC 29801

Leon Meyers
duPont Company, Aiken (DoE)
E. I. duPont DeNemours and Co.
Savannah River Laboratory
Aiken, SC 29801

No. of
Copies

P. H. Permar
duPont Company, Aiken (DoE)
E. I. duPont DeNemours and Co.
Savannah River Laboratory
Aiken, SC 29801

L. Henning
Electric Power Research Institute
3412 Hillview Ave.
P. O. Box 10412
Palo Alto, CA 94304

Environmental Protection Agency
Technology Assessment Div. (AW-559)
Office of Radiation Programs
U.S. Environmental Protection
Agency
Washington, DC 20460

R. G. Barnes
General Electric Company
175 Curtner Ave.
(M/C 160)
San Jose, CA 95125

L. H. Brooks
Gulf Energy and Environmental
Systems
P. O. Box 81608
San Diego, CA 92138

2 Central Research Library
Document Reference Section
Oak Ridge National Laboratory (DoE)
Oak Ridge, TN 37830

3 Los Alamos Scientific
Laboratory
P. O. Box 1663
Los Alamos, NM 87544

C. J. Kershner
Monsanto Research Corporation
Mound Laboratory
P. O. Box 32
Miamisburg, OH 45342

John Pomeroy
Technical Secretary
National Academy of Sciences
Committee of Radioactive Waste
Management
National Research Council
2101 Constitution Avenue
Washington, DC 20418

2 J. P. Duckworth
Plant Manager
Nuclear Fuel Services, Inc.
P. O. Box 124
West Valley, NY 14171

Distr-3

No. of
Copies

J. G. Cline, General Manager
NYS Atomic Space and Development
Authority
230 Park Avenue, RM 2425
New York, NY 10017

D. R. Anderson
Sandia Laboratories
Albuquerque, NM 87107

W. Weart
Division 1140
Sandia Laboratories
Albuquerque, NM 87107

J. Sivinski
Sandia Laboratories
Albuquerque, NM 87107

J. O. Blomeke
Union Carbide Corporation (ORNL)
Chemical Technology Division
P. O. Box Y
Oak Ridge, TN 37830

- 2 D. E. Ferguson
Union Carbide Corporation (ORNL)
Chemical Technology Division
P. O. Box Y
Oak Ridge, TN 37830

W. C. McClain
Union Carbide Corporation (ORNL)
Chemical Technology Division
P. O. Box Y
Oak Ridge, TN 37830

- 7 C. D. Zerby
Union Carbide Corporation
Nuclear Division
Office of Waste Isolation
P. O. Box Y
Oak Ridge, TN 37830

R. A. Beall
U.S. Department of Interior
Bureau of Mines
Albany Research Center
1450 W. Queen Ave.
Albany, OR 97321

R. G. Post
College of Engineering
University of Arizona
Tucson, AZ 85721

S. E. Logan
University of New Mexico
Albuquerque, NM 87131

No. of
Copies
FOREIGN

Rene Amavis
EURATOM
Health Physics Division
29, Rue Aldringer
Luxembourg, BELGIUM

K. D. B. Johnson
Atomic Energy Research
Establishment
Harwell, Didcot,
Berks, ENGLAND

D. W. Clelland
United Kingdom Atomic Energy
Authority
Risley, ENGLAND

P. J. Regnaut
Centre d'Etudes Nucleaires
de Fontenay-aux-Roses
Boite Postale 6
92 - Fontenay-aux-Roses
FRANCE

Y. J. Sousselier
Centre d'Etudes Nucleaires
de Fontenay-aux-Roses
Boite Postale 6
92 - Fontenay-aux-Roses
FRANCE

Bundesministerium für Forschung
und Technologie
Stressemannstrasse 2
5300 Bonn
GERMANY

Hans W. Levi
Hahn-Meitner-Institut
für Kernforschung Berlin (HMI)
Glienicke Strasse 100
1000 Berlin 39
GERMANY

Center for Atomic Energy
Documentation (ZAED)
Attn: Dr. Mrs. Bell
P. O. Box 3640
7500 Karlsruhe
GERMANY

H. Krause
Kernforschungszentrum Karlsruhe GmbH (KfK)
Postfach 3640
D7500 Karlsruhe
GERMANY

N. S. Sunder Rajan
Bhabha Atomic Research Centre
Waste Treatment Division
Trombay, Bombay, 400 085 INDIA

Distr-4

No. of
Copies

R. V. Amalraj
C.W.M.F. Project
P.O. Kalpakkam
Chingleput Dist.
Tamil Nadu, INDIA

- 2 International Atomic Energy
Agency
Kärtner Ring 11
P. O. Box 590
A-1011, Vienna, AUSTRIA

M. Tomlinson
Director of Chemistry and
Materials Science Division
Atomic Energy of Canada Ltd.
Whiteshell Nuclear Research
Establishment
Pinawa, Manitoba, CANADA

ONSITE

- 4 DoE Richland Operations Office

R. B. Goranson
M. J. Shupe
D. J. Squires
M. J. Zamorski

- 8 Rockwell Hanford Operations

H. Babad
R. A. Deju
R. J. Gimera
E. J. Kosiancic
C. M. Manry
J. H. Roecker
D. D. Wodrich
File Copy

Exxon
Richland, WA 99352

S. J. Beard

Joint Center for Graduate Study

J. Cooper

- 2 United Nuclear Industries, Inc.

T. E. Dabrowski
A. E. Engler

Westinghouse Hanford Company

A. G. Blasewitz

No. of
Copies

50 Battelle Northwest

R. P. Allen/H. W. Arrowsmith
T. W. Ambrose
N. E. Ballou
J. W. Bartlett
L. L. Burger
H. C. Burkholder
N. E. Carter
D. B. Cearlock
T. D. Chikalla
M. O. Cloninger
R. L. Dillon
R. F. Eggers
J. R. Eliason
J. W. Finnigan
J. C. Fox
J. A. Franz
J. J. Fuquay
R. L. Gordon
B. Griggs
K. M. Harmon
A. J. Haverfield
R. E. Heineman
E. R. Irish
J. H. Jarrett
R. S. Kemper
M. R. Kreiter
I. S. Levy
R. C. Liikala
R. P. Marshall
J. L. McElroy
R. D. Nelson
J. M. Nielsen/R. W. Perkins
R. E. Nightingale
D. E. Olesen
A. M. Platt
J. A. Powell
C. L. Simpson/C. E. Elderkin
G. L. Tingey
C. M. Unruh
H. H. Van Tuyl
E. J. Wheelwright
D. J. Wiggins
W. R. Wiley
L. D. Williams
W. K. Winegardner
Technical Information (5)
Technical Publications
Sharon Cozad
Bev Einarsson