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High-Level Waste Program
Progress Report for April 1, 1980,
Through June 30, 1980

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NUCLEAR WASTE PROGRAMS

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HIGH-LEVEL WASTE PROGRAM PROGRESS REPORT
FOR APRIL 1, 1980, THROUGH JUNE 30, 1980

Program Manager: R. E. Blanco
Program Director: A. L. Lotts

Date Published: August 1980

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HIGHLIGHTS

1. Waste Management Analysis for Nuclear Fuel Cycles

As part of the continuing effort to update ORIGEN and its nuclear data libraries, a report was issued documenting broad-group macroscopic ANISN-formatted cross-section libraries to be used for fuel cycle shielding calculations. Final documentation of the P-T project has proceeded on schedule.

2. Fixation of Waste in Concrete

A leaching nomograph was developed to show the relationship between effective diffusivity, D_e , in cm^2/s and leach factor, L , in g/cm^2 day. Standard FUETAP concrete specimens containing high concentrations of ^{244}Cm continued to show much lower rates of radiolytic gas production than concrete cured under ambient conditions.

3. Study of Ceramic and Cermet Waste Forms

Operation of the large reactive spray calciner over a wide range of conditions has demonstrated its versatility and effectiveness in calcining wastes and additives in urea solutions.

The development of leach testing and analytical methods applicable to radiotracer-containing cermets has been essentially completed. The leach testing program will be initiated upon the imminent completion of the radiotracer laboratory facilities. The role of galvanic coupling in cermet leach resistance and durability is being investigated.

4. Alternative High-Level Waste Forms Development

Parametric runs were made using the internal gelation method to determine process conditions when making spheres of the Synroc-B composition. Batches of Synroc-B microspheres were sintered to densities greater than 92% of theoretical at temperatures as low as 1175°C .

5. High-Level Waste Container Development

Compatibility testing of candidate container materials with a number of waste forms has begun. The overall experiment includes 15 potential canister metals and 6 waste forms. The first two capsules, one each containing metal matrix Al-Si and FUETAP, have been assembled and are in test. The other capsules are being loaded.

1. WASTE MANAGEMENT ANALYSIS FOR NUCLEAR FUEL CYCLES
(Activity No. AP 05 25 10 0; ONL-WH01; WBS ON 1.1.3.2 AP)

J. O. Blomeke and A. G. Croff

1.1 Summary

Progress in updating the ORIGEN computer code and its data bases consisted of the following: (1) reference ORIGEN2 calculations for the once-through, U-Pu cycle CANDU reactor models were completed and documentation of the models is being prepared; (2) three U-Pu cycle LMFBR models have been completed and reference ORIGEN2 calculations are underway; (3) the user's manual and summary report documenting ORIGEN2 are in press; and (4) a report documenting updated gamma-ray-neutron cross sections for use in the shielding code ANISN was published. In addition, updated calculations of LWR and LMFBR spent fuels and wastes have been completed, and final documentation of the P-T project has proceeded on schedule.

1.2 ORIGEN Update

Auxiliary information for the once-through, U-Pu cycle CANDU reactor models was generated and installed in the appropriate libraries during this report period. Reference ORIGEN2 calculations for these two reactor models were completed and a rough draft report was written. At the present time, the draft is being typed and the models are available for use.

Generation of auxiliary information for three U-Pu cycle LMFBR models was completed and reference reactor calculations are currently underway. The reference calculations have proceeded far enough to permit re-activation of the special project described below. Reactor physics calculations have been initiated for the thorium cycle LMFBR models, but documentation of this latter work will not be initiated until all LMFBR models are completed.

Both the ORIGEN2 user's manual (ORNL/TM-7175) and the ORIGEN2 summary report (ORNL-5621) were completed during this report period and are currently in press. Upon completion, a complete version of ORIGEN2 and its libraries will be sent to the Radiation Shielding Information Center for formal distribution. Preliminary distribution of ORIGEN2 to Sandia Laboratory and HEDL resulted in favorable feedback from use of the code on other than IBM systems. Institution of ORIGEN2 on HEDL's Univac computer was facilitated by the changes made as a result of Sandia's earlier adoption of it for use on their CDC system.

A report (ORNL/TM-7038) documenting an updated and expanded shielding library was issued during this report period. This library contains coupled gamma-ray-neutron shielding cross sections for use in calculating

shielding thickness and dose rates with the ANISN computer code. This library was specifically designed with a gamma-ray group structure compatible with the photon output produced by ORIGEN2. The library also includes a much wider variety of materials than was previously available and is based on the most recent cross-section data available. This cross-section library is currently available from the Radiation Shielding Information Center, as is the ANISN computer code.

1.3 Special Projects

The completion of the U-Pu cycle LMFBR models allowed work on updated spent fuel and waste characteristics for PWRs, BWRs, and LMFBRs to proceed. Tables giving the characteristics (composition, radioactivity, thermal power, photon activity, and neutron activity) as a function of decay time have been generated, and a draft report describing the calculations and results has been written. These updated calculations are based on the updated and revised reactor models and on libraries developed for ORIGEN2.

1.4 Partitioning and Transmutation

Documentation and dissemination of the results of the ORNL P-T project was the primary activity during this report period. The results of the program were presented at the Second Technical Meeting on the Nuclear Transmutation of Actinides held in Ispra, Italy, on April 21-24, 1980, and at the IAEA Coordinated Research Programme on "Environmental Evaluation and Hazard Assessment of the Separation of Actinides from Nuclear Wastes followed by Either Transmutation or Separate Disposal," which met immediately following the Second Technical Meeting. Domestically, a special session was organized at the June 1980 ANS meeting in Las Vegas to present the results of the P-T project. Six papers were given by people who had participated in key aspects of the project, along with a paper summarizing the European viewpoint.

The status of the final documentation of the P-T project is summarized as follows:

<u>Report</u>	<u>Description</u>	<u>Status</u>
ORNL-5566	Overall assessment report	Issued during June.
ORNL/TM-6982	Partitioning report	Issued during June.
ORNL/TM-6983	Transmutation report	Sent to printing during June.
ORNL/TM-6984	Miscellaneous aspects report	Awaiting editing.
ORNL/TM-6985	P-T facility design and costing (R. M. Parsons)	Issued during June together with its appendices.

ORNL/TM-6986	Short-term risk analysis (SAI)	Issued during June together with its appendices.
ORNL/TM-7987	Long-term risk analysis (LATA)	Additional corrections completed during June are currently being reviewed. Appendices issued during June.

In addition, the following P-T technical reports were published:

C. W. Forsberg, Computer Simulation of Displacement Cation Exchange Chromatography: Separation of Trivalent Actinides and Lanthanides, ORNL/TM-6738 (May 1980).

F. M. Scheitlin and W. D. Bond, Recovery of Plutonium from HEPA Filters by Ce(IV)-Promoted Dissolution of PuO₂ and Recycle of the Cerium Promoter, ORNL/TM-6802 (May 1980).

2. FIXATION OF WASTE IN CONCRETE

(Activity No. AP 05 25 10 0, ONL-WH02, WBS ON 1.3.1.1 AP)

J. G. Moore, S. Katz, E. Newman, and G. C. Rogers

2.1 Summary

The FUETAP process continues to hold much promise as an alternative waste form. During the past quarter, to eliminate some of the confusion in comparing leach results, a leaching nomograph was developed to show the relationship between effective diffusivity, D_e , in cm^2/s and leach factor, L , in $\text{g}/\text{cm}^2 \text{ day}$. FUETAP specimens containing ^{244}Cm continue to show much lower radiolytic gasification than ordinary concretes. Large numbers of small specimens of FUETAP concretes are being prepared for corrosion studies and the development of special characterization tests.

2.2 Introduction

This program was initiated to determine the technological feasibility and the acceptability of a process using FUETAP concretes to fix high-specific-activity waste as an alternative to existing concepts. In this process, solids containing the radioactive waste would be formed by curing cementitious mixtures containing specific admixtures to fix radionuclides for 24 h at temperatures $\leq 250^\circ\text{C}$ and pressures $\leq 4.1 \text{ MPa}$. After curing, the solids would be dewatered by heating to 250°C to diminish the

potential for future canister pressurization by radiolysis or heat after placement in a storage site or repository. During this report period, studies were made in the following areas:

1. leachability of waste forms,
2. radiolytic gasification,
3. specimen preparation, and
4. mix development.

2.3 Leachability of Waste Forms

Leach rates are usually reported as leach factor, L , in g/cm^2 day or effective diffusivity, D_e , in cm^2/s . Since these expressions are based on entirely different leach mechanism assumptions, they cannot be directly equated to each other. A leaching nomograph was developed to show the relationship between these two expressions using a calculated fraction of initially contained activity released during a given leach period as an index (Fig. 1).

Several assumptions were made in the construction of this nomograph. They are: (1) each of the mechanisms operates singly and not in concert with each other or with other mechanisms, (2) each mechanism remains constant, (3) the waste form is the size of a standard 200-liter drum and is treated as an infinite source, (4) the density of the waste form is 2 g/cm^3 , and (5) no correction for radioactive decay has been applied. Two examples of the use of the nomograph are shown by the dashed and dotted lines. The dashed line illustrates a bare 200-liter drum exposed to a leachant for 500 years. If a given nuclide has an effective diffusivity, D_e , of $1.0 \times 10^{-14} \text{ cm}^2/\text{s}$, the total fraction of the initially contained nuclide released during this period is approximately 1.3×10^{-3} . This corresponds to a waste form which has a leach factor of $1.6 \times 10^{-7} \text{ g/cm}^2$ day. The dotted line is an example of the use of the nomograph to determine the maximum leachability that would meet a total release criteria. In the case shown, the waste form may release no more than 1% of a given nuclide in 100,000 years of leaching. To comply with this restriction, the leach factor, L , should be $\leq 5.5 \times 10^{-9} \text{ g/cm}^2$ day or the diffusion coefficient, D_e , $\leq 2.6 \times 10^{-15} \text{ cm}^2/\text{s}$. Although not shown on the figure, we could use the nomograph to determine the maximum leach rates which would meet the conditions specified for geologic disposal of high-level wastes in the proposed NRC regulation (10 CFR 60). The release is specified as zero for the first 1000 years and a maximum total release of 1×10^{-5} per year thereafter. Thus the total fraction that could be released in 10,000 years would be 0.1. Under these conditions, the nomograph shows that the waste form could have a maximum leach factor, L , of $\sim 6 \times 10^{-7} \text{ g/cm}^2$ day or an effective diffusivity, D_e , of $\sim 3 \times 10^{-12} \text{ cm}^2/\text{s}$.

In other leach studies, we are currently collecting data to determine the leachability of 11 elements from FUETAP concrete. Preliminary data show the leachability of aluminum is less in spring water than demineralized water. Since aluminum compounds are known to be more soluble at

Fig. 1. Nomograph for the calculation of the total fraction of activity released from a 200-liter drum during a given leach period without decay correction. Comparison between the leach factor (L) and the effective diffusivity (D_e) resulting in the same release can be obtained from the appropriate intercepts.

higher pH values, the buffering action of the carbonate-bicarbonate system in the spring water that is producing a more neutral leachant may be responsible for the lower leach results.

Several additional leach studies were initiated this quarter to study the effects of temperature and high concentrations of cesium and strontium on the leachability of these elements. These results will be reported when data become available.

2.4 Radiolytic Gasification

The glove box studies continue in the investigation to determine the extent of radiolytic gas production in FUETAP concretes having a ^{244}Cm concentration of about 0.4 mg/g concrete. After approximately 150 days, the data indicate a gas production rate of 3 to 3.5 std cm^3/year in the FUETAP tests. For comparison, the production rate from a concrete specimen cured under ambient conditions and containing ferric oxide in the void volume of the container is 58 std cm^3/year and is decreasing with time. The initial data indicated a rate of 89 std cm^3/year . The increase in pressure and/or the seasonal increase in room temperature (~ 5 to 10°C) may be promoting increased recombination of the radiolytic decomposition products.

2.5 Specimen Preparation

A total of 270 specimens of the standard FUETAP concrete were prepared for use in corrosion studies in progress in the Metals and Ceramics Division. Using Teflon molds, right circular cylinder specimens were prepared that were 1.3 cm in diameter and approximately 3 cm long. These were cut to 0.6 cm in length using distilled water as the lubricant. About 4 kg of specimens, slightly shorter in length, and containing a specially prepared simulated waste mixture is being made for the Materials Characterization Center at the Pacific Northwest Laboratory. These will be used in the development of standard test methods at the center.

2.6 Mix Development

Studies were initiated to evaluate the effect of zeolites and various water reducers on the mixing and physical characteristics of FUETAP concrete. Preliminary results indicate at least 10.5 wt % zeolite may be accommodated in the standard FUETAP formulation by eliminating the clay and reducing the sand concentration. The first water reducing admixture examined (REOX-LP) showed no improvement over D-65, the material currently in use.

2.7 Presentations and Publications

J. G. Moore, G. C. Rogers, E. W. McDaniel, and H. E. Devaney, "Current ORNL Studies on Cementitious Hosts for Radioactive Waste," presented at the 1980 Annual Meeting of the American Ceramic Society in Chicago, Illinois, April 27-30, 1980.

J. G. Moore, "Status Report on FUETAP Concrete," presented at the HLW Technical Review Meeting in Atlanta, Georgia, May 8, 1980.

J. G. Moore, "A Survey of Concrete Waste Forms," presented at the Workshop on Alternate Nuclear Waste Forms and Interactions in Geologic Media in Gatlinburg, Tennessee, May 13-15, 1980.

G. C. Rogers, J. G. Moore, and M. T. Morgan, Scrubbing of Iodine from Gas Streams with Mercuric Nitrate - Conversion of Mercuric Iodate Product to Barium Iodate for Fixation in Concrete, ORNL/TM-7102 (June 1980).

H. W. Godbee, E. L. Compere, D. S. Joy, A. H. Kibbey, J. G. Moore, C. W. Nestor, Jr., O. U. Anders, and R. M. Neilson, Jr., "Application of Mass Transport Theory to the Leaching of Radionuclides from Waste Solids," Nucl. and Chem. Waste Man. 1, 29-35 (1980).

3. STUDY OF CERAMIC AND CERMET WASTE FORMS (Activity No. AG 30 20 01 0, ONL-WHO3; WBS ON 1.3.1.2 AG)

W. S. Aaron, T. C. Quinby, E. H. Kobisk, D. W. Ramey,
M. Petek, D. Thomas

3.1 Summary

Development and refinement of operating parameters for the reactive spray calciner are continuing. Coarsening of the calcine particle size range through "in situ" nozzle adjustments has been achieved to facilitate improved calcine collection while maintaining complete calcination of the feed solution. The reactive nature of urea solution calcination process provides exothermic heat to maintain centerline temperatures approximately equal to the calciner wall temperature and insures rapid calcination of feed droplets, thus preventing material accumulation on the calciner walls. The development of liquid phase sintering techniques for cermet densification has continued, as has preparation for leach testing of cermets under both static and flowing conditions. Initial results have been obtained in galvanic coupling experiments.

3.2 Continuous Calcination Technology

Investigations to optimize the reactive spray calcination of wastes and additives in molten urea solutions are continuing. The 23-cm ID calciner has been successfully operated using air or inert gas for injection of the feed solution. Complete calcination of the waste has been achieved in both modes of operation without any material buildup on the calciner walls or spray nozzle. Centerline temperatures are maintained at or slightly below the calciner wall temperature by the heat provided by the exothermic reaction of urea with the nitrate ion in the feed solution.

The major emphasis in recent work on the reactive spray calciner has been in the development of suitable calcine collection systems. This is being approached in two ways. The first procedure is to minimize the production of fines through the adjustment of the spray pattern, which can now be done in situ; the second procedure is the development of a more efficient collection system. Satisfactory calcination of a coarse spray has been accomplished and results in particle size and shape as shown in Fig. 3.1. These larger particles facilitate the separation of solids from the calciner off-gas. The separation of fines generated during spray calcination is accomplished by the apparatus shown in Fig. 3.2. The collection pot at the bottom of the calciner body and the cyclone separator are very efficient in collecting the calcined material. However, magnetic separation techniques are being developed to improve the collection of fines in the baffled collection chamber. Only a small amount of fines are formed. At this time, it is not known whether the fines are generated during the initial spray and calcination process or by abrasion of the particles following the particle formation. These simple and effective collection methods will greatly reduce the reliance on the off-gas filters.

3.3 Cermet Densification Technology

The simultaneous reduction and densification of cold-compacted calcine powder, using the recently developed liquid phase sintering technique,^{3.1} is being refined experimentally. The parameters required to develop an internal liquid phase in the proper proportion to enhance the sinterability of the cermet compact are dependent upon the specific formulation of the cermet. Therefore, different waste types and/or different cermet formulations require adjustments to sintering parameters for each particular type of cermet. The optimum conditions under which various cermets can be sintered using the liquid phase technique, are being explored. Additionally, for safety considerations, the proper conditions for liquid phase sintering using a 4% H₂/Ar atmosphere rather than a more highly enriched H₂ atmosphere are being investigated experimentally. Until new sintering furnaces arrive and are installed, a tube furnace has been converted for temporary use as a vertical sintering furnace.

Fig. 3.1. Particles resulting from the reactive spray calcination of waste feed solutions. In this case the use of inert injection gases resulted in substantial, if not complete, reduction of the metal oxides to form the ductile calcine spheres as evidenced by the higher magnification micrograph of a mechanically deformed spherical particle.

ORNL-DWG 80-11383R

Fig. 3.2. Schematic drawing of the operating reactive spray calciner emphasizing the collection system for the separation of calcined material from the off-gas.

3.4 Characterization of Cermet Waste Forms

Determination of leaching parameters of cermet waste forms is currently receiving major emphasis in the characterization aspects of this program. Methods for static leach testing of the modified IAEA-type have been tested and refined through preliminary experiments on previously fabricated radiotracer-containing cermet samples. Quantitative leach testing of samples representing products derived from improved processing techniques will be initiated when our radiotracer facility becomes operational. Concurrently, the system for single-pass, continuous flow leach testing is in the final stages of assembly and testing. Experimental details such as filter selection, flow-rate stabilization, and the general operation of the system are being refined.

Since cermets, by definition, include a metal phase, the role of galvanic coupling in leaching must be considered. This is not only of critical importance to canister material selection and other repository materials compatibility considerations, but must also be considered during laboratory leach testing. In the past, galvanic coupling between cermet samples and leach testing apparatus has interfered with the determination of leaching characteristics.^{3.2}

A series of experiments are in progress to determine the degree of galvanic coupling existing when cermet samples of two different alloy formulations are coupled with a variety of other metals in WIPP-B leachant solutions. Preliminary results from these experiments are summarized in Table 3.1. Since some instabilities were observed when direct coupling of the various galvanic pairs occurred, the potential values shown in Table 3.1 were measured for each material versus platinum to develop the galvanic series for these materials in WIPP "B" solution at 298°K. The investigation of these instabilities and the testing of a wider variety of galvanic couples is currently in progress.

3.5 References

- 3.1 High-Level Waste Program Progress Report for October 1, 1979, through December 31, 1979, ORNL/TM-7253 (March 1980).
- 3.2 High-Level Waste Program Progress Report for October 1, 1978, through March 31, 1979, ORNL/TM-6866 (May 1979).

Table 3.1 Preliminary Galvanic Series Results in WIPP "B" Solution

	<u>Material</u>	<u>Potential (V) vs. Pt</u>
Noble or	Pt	-
Cathodic	Ti	-0.190
	304 SS*	-0.350 (passive)
		-0.500 (active)
	Cermet (50 Fe-50 Ni)	-0.580
	Cu	-0.600
	Cermet (70 Fe-20 Ni- 5 Cu-5 Misc.)	-0.720
	Pb	-0.860
Active or	Zn	-1.375
Anodic		

*304 stainless occasionally suddenly becomes activated after which there is an exponential decay to the passive potential.

4. ALTERNATIVE HIGH-LEVEL WASTE FORMS DEVELOPMENT (Activity No. AR 05 15 10 0, ONL-WH04, WBS ON 1.3.1.3 AR) (Activity No. AP 05 25 10 0, ONL-WH09, WBS ON 1.3.1.3 AR)

W. J. Lackey, P. Angelini, A. J. Caputo, F. L. Layton,
D. A. Lee, D. P. Stinton, and J. S. Vavruska

4.1 Summary

Parametric runs were made using the internal gelation method to determine process conditions when making spheres of the Synroc-B composition. Various liquids were used for the immiscible liquid phase when forming large spheres. Additional tests of the water extraction method for producing crystalline waste forms were performed. Drying runs were made on internal gelation derived materials in order to test the influence of temperature and humidity on product characteristics. Batches of Synroc-B microspheres were sintered to densities greater than 92% of theoretical at temperatures as low as 1125°C. Comparisons were made between thermogravimetric and mass spectrometric data from gel-driven waste forms.

4.2 Sol-Gel Technology

Several parametric runs were made using the internal gelation method to determine conditions for preparing gel spheres of Synroc-B composition that were also suitable for coating studies after drying and sintering. The purpose of these runs was two-fold: (1) to evaluate the feasibility of using a solution containing 33 vol % perchloroethylene and 67 vol % 2-ethylhexanol (33 vol % PCE-2EH) as the immiscible liquid phase for forming large gel spheres ($\sim 4000 \mu\text{m}$ diam) that are needed for conversion to $\sim 1000 \mu\text{m}$ -diameter products and (2) to determine the percentage excess of calcium in the feed solution and the calcium concentration in the wash solution that are necessary for attainment of the desired calcium content in the product. Previous work had shown calcium was partially solubilized in the NH_4OH washing step. In addition, a few tests were initiated using the water extraction process to form Synroc gels.

Although the 33 vol % PCE-2EH was satisfactory for forming the spheres in 50-100 g amounts, the forming liquid phase became unstable after this amount of material had been produced. Further operation caused formation of an emulsion which appeared to result from the dispersion of a small amount of a second organic phase that was insoluble in the bulk organic phase. The second liquid phase may be caused by the extraction of water into the 33 vol % PCE-2EH. Initial gel sphere preparation tests using a PCE-hydrocarbon solution as the immiscible phase for dispersion of feed solution droplets showed this solution was satisfactory in regard to its stability.

The desired calcium content (13.5%) in the product was attained by employing a 25% excess of calcium in the feed solution and 0.25 g/liter of calcium hydroxide in the 0.5 M NH_4OH solution used for gel sphere washing. Microscopic examination of the dried gel spheres indicated that the gel spheres may not have been homogeneous with respect to calcium. Some of the spheres appeared to be coated with calcium hydroxide whereas others were not, although they belonged to the same batch preparation. Chemical analyses are being obtained on the two types of spheres, and the process conditions will be analyzed further.

The water extraction tests involved the preparation of a hydrosol feed solution followed by formation of gel spheres using 2EH as the forming liquid. To prepare the hydrosol feed, a basic codispersed hydrosol containing titania, zirconia, and alumina was prepared by precipitation peptization, and the BaCO_3 and CaCO_3 solids were slurried into the sol. The spheres that were formed from this feed were too soft, and the product showed a prohibitive amount of clumping together of the spheres. Based on previous experience with the preparation of nuclear fuel materials (UO_2 , ThO_2 , and PuO_2) by the water extraction method, extensive studies may have to be carried out on process variable studies in hydrosol preparation in order to evaluate the potential of the water extraction method. The purpose of these tests was to determine if a very simple approach might work for Synroc compositions.

4.3 Drying

The small laboratory oven was modified to permit the drying of small batches (10 g) of material with flowing air at a controlled relative humidity. Drying studies made at various levels of temperature and humidity resulted in sintered sphere densities of up to 93% theoretical. However, during this same period, considerable effort was expended investigating the conditions under which the spheres were formed in an attempt to obtain the desired overall Synroc composition. Thus, the effect of drying upon the spheres could not always be separated from the effects of forming conditions.

The initial testing of internal gelation derived spheres containing cesium revealed that the cesium was removed during the washing of the gel spheres with ammonium hydroxide. Additional drying studies have been initiated using spheres that have not been washed, that is, spheres as-formed in the organic liquid. Cesium is still present in these dried spheres. Initial testing has indicated that these spheres are more susceptible to cracking during processing. This is probably due to the greater amount of material (mostly organics) that must be removed from the spheres. This may or may not be a problem, depending on the desired final form of the waste material.

4.4 Sintering

For the first time, a large batch of Synroc-B microspheres was produced for sintering studies. It was determined that the heating rate (between 50 and 200°C/h) during sintering did not affect the final density of the microspheres. It was also found that batches could be sintered to densities greater than 92% of theoretical at temperatures as low as 1125°C. Work is continuing to further reduce the sintering temperature below 1125°C. Pellets made by pressing and sintering using crushed gel-derived materials achieved densities near 90% of theoretical. The microspheres from the large batch, however, when pressed into pellets and sintered, achieved densities of about 75% of theoretical. This points out that optimum gelation processing parameters may be very different depending on whether one desires microspheres or pellets as the final form. Additional testing will be performed to evaluate production of gel-derived materials suitable for cold pressing and sintering into pellets.

4.5 Thermal Analysis

During this period, the interfacing of the time-of-flight mass spectrometer (TOFMS) to the Macsym II microcomputer was completed. This device permits the operation of programmed thermal analysis by mass spectrometry without attention. The Macsym will initiate the scan of the spectra at every 5°C increase of the furnace temperature. Temperatures and scan data are recorded on a Decwriter and stored in the PDP 11/40 computer. At the end of the run, the Macsym will stop the heating program, stop the data collection, and call for the data file.

Many Synroc samples have been examined by thermal analysis. These samples include unwashed microspheres, washed microspheres, and microspheres dried by different methods. The methods used have been thermogravimetric analyses (TGA) and mass spectrometry. Comparisons have been made between the TGA thermograms and the mass spectra thermograms for the masses that appeared. Water was the major component involved. The thermograms revealed inner sphere, outer sphere, and dehydroxylation water, and the efficiency of drying procedures was noted. Deamination was evident from urea and hexamethylene-tetramine at two temperatures (170 and 240°C), especially from unwashed microspheres. There were many more masses in the spectra of unwashed microspheres than for those of washed microspheres. Carbon dioxide evolution was evident in two temperature ranges (250 and 600°C) for washed microspheres.

Other experiments with these materials are in progress including DTA studies to 1400°C and kinetic studies to determine reactions during drying and sintering.

4.6 Leaching

A number of leaching experiments are underway. Leaching studies on four melted Synroc samples containing ^{238}U and one or more of the following isotopes: ^{239}Pu , ^{241}Am , and ^{244}Cm , as well as leaching studies on two sintered Synroc pellets containing ^{238}U and ^{239}Pu , are continuing.

A short-term leaching test on two samples of coated and uncoated Synroc microspheres and one extruded Synroc pellet was carried out. The samples were leached with deionized water at temperatures of 23 and 70°C. Analyses of the leachants for Al, Ba, Ca, Ti, and Zr are underway. An actinide plateout study is being performed. Standard solutions of Pu, Am, and Cm were prepared in acid concentrations varying from 0.8 N to 8.0 N HNO_3 to determine at what acid concentration there would be no plateout of the actinides.

5. HIGH-LEVEL WASTE CONTAINER DEVELOPMENT

(Activity No. AR 05 15 10 1, ONL-WH06, WBS ON 1.3.1.4 AR)

(Activity No. AR 05 25 10 0, ONL-WH10, WBS ON 1.3.1.4 AR)

W. J. Lackey, J. H. DeVan, H. E. McCoy,
J. E. Mack, and P. Angelini

5.1 Summary

Activity on high-level waste container development during this past quarter has concentrated on the compatibility testing of candidate container materials with a number of different alternative waste forms. The objective of the tests is to identify a group of compatible container

materials for each waste form. Once final selection of the waste form is made, selection of a reference container material based on repository environment and cost-benefit analysis can then be made from this set.

5.2 Compatibility Tests

Compatibility tests are being assembled in which 15 potential canister metals and 6 waste forms will be contacted. The metals and the waste forms were described in considerable detail in the previous two reports in this series. During this report period, effort has continued in a few areas to complete preparation of the test materials.

We were unable to find a desirable commercial method for applying a diffused chromium layer to steels, so we simply put the steel discs in a capsule above chromium granules at 1300°C for 48 h in argon. The vapor pressure of chromium is sufficient at this temperature to transfer to the steel. The increased chromium concentration near the surface resulted in more pearlite and less ferrite. The affected depth was 100 to 150 μm .

We initially planned to apply titanium diboride to steel, but found that the deposited material was poorly adherent. Adherent deposits resulted when commercial grade titanium was used as the substrate. The corrosion samples prepared for study were titanium coated with about 0.5 μm of titanium diboride. The coatings are being evaluated further.

The FUETAP (concrete) waste pellets were prepared during this report period. The detailed chemical information is given in Table 5.1. The pellets were cured at 185°C and 160 psi and dewatered 24 h at 250°C. The Synroc-D pellets were successfully prepared, and the chemical composition of this material was reported previously. Work continued on preparing the glass samples.

Several details of the procedure used to load the corrosion capsules have been refined. Basically, a capsule consists of 30 metal discs (2 each of 15 types) and 30 waste pellets (all one composition). Each component is cleaned and weighed prior to placement in a quartz tube. The loaded quartz tube is then placed in a stainless steel tube. A spring placed on top of the samples provides the compressive force needed for contact between the waste form and the metallic specimen. The stainless steel cap is welded to the tube, and a 1/4-in.-diam tube penetrating the top of the cap is used evacuating and back-filling the capsule with the desired environment.

Two capsules, one each containing FUETAP and the metal matrix Al-Si, have been assembled and are in test. The other capsules are being filled.

Table 5.1. Composition of FUETAP Pellets

Components	Weight Percent
<u>FUETAP Mix 25S</u>	
Type I Cement	22.0
Kingston Fly Ash	11.0
Indian Red Pottery Clay	7.5
Waste Solids	15.0
NaNO ₃	0.75
D-65 (Water Reduced)	1.00
H ₂ O	15.0
Sand	27.75
<u>Waste Solids</u>	
Fe ₂ O ₃	75.18
Al ₂ O ₃	14.89
Cu ₂ O ₃	4.94
NiO	4.78
Sr	0.013
Ru(OH) ₃	0.027
CeO	0.037

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