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High-Level Waste Program Progress Report for January 1, 1980, Through March 31, 1980

R. E. Blanco
A. L. Lotts

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NUCLEAR FUEL AND WASTE PROGRAMS

HIGH-LEVEL WASTE PROGRAM PROGRESS REPORT FOR JANUARY 1, 1980, THROUGH MARCH 31, 1980

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

Date Published: May 1980

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HIGHLIGHTS

1. Waste Management Analysis for Nuclear Fuel Cycles

A report describing alternative fuel cycle PWR models for use with ORIGEN2 was published. Problems with CANDU depletion calculations have been resolved and auxiliary information required by ORIGEN2 for this reactor is currently being generated. The three Pu-U cycle LMFBR models for ORIGEN2 are nearing completion and the ORIGEN2 user's manual was submitted for editing. Work was initiated to update and expand calculations of spent LWR and LMFBR spent fuels and waste compositions. Progress on the seven reports constituting the final documentation of the P-T project is proceeding on schedule.

2. Fixation of Waste in Concrete

FUETAP concretes cured at 100°C and 0.1 or 0.6 MPa had essentially the same physical properties as those cured at higher temperatures and pressures. Standard specimens containing high concentrations of ^{244}Cm showed little, if any, gasification after 1 month.

3. Study of Ceramic and Cermet Waste Forms

The large (23-cm I.D.) spray calciner, offering greater operational flexibility, has been completed and is operating satisfactorily.

Preparations for the characterization of cermets produced by the new process flowsheet, especially the determination of leach rates, are proceeding as planned.

4. Alternative High-Level Waste Forms Development

Construction was completed on a sphere-forming system capable of producing 100-g batches of Synroc spheres by internal gelation. Several runs have been made to investigate feed compositions, forming, and washing conditions necessary to achieve the metal oxide composition in the dried spheres required by Synroc-B. A laboratory-scale drying oven has been modified to carefully examine the effect of humidity and drying time on the final sintered product.

5. High-Level Waste Container Development

Preparations for the compatibility tests are well underway. Metal coupons of each candidate alloy material have been fabricated. Several waste forms are now on hand, and others are being prepared. Loading of the test capsules will begin shortly.

1. WASTE MANAGEMENT ANALYSIS FOR NUCLEAR FUEL CYCLES (Activity No. AP 05 25 100; ONL-WH01; ON 1.1.3.2 AP)

J. O. Blomeke, A. G. Croff, and C. W. Alexander

1.1 Summary

A report describing alternative fuel cycle PWR models for use with ORIGEN2 was published. Problems with CANDU depletion calculations have been resolved and auxiliary information required by ORIGEN2 for this reactor is currently being generated. The three Pu-U cycle LMFBR models for ORIGEN2 are nearing completion and the ORIGEN2 user's manual was submitted for editing. Work was initiated to update and expand calculations of spent LWR and LMFBR spent fuels and waste compositions. Progress on the seven reports constituting the final documentation of the P-T project is proceeding on schedule.

1.2 ORIGEN Update

A report describing alternative fuel cycle PWR models was published: A. G. Croff and M. A. Bjerke, Alternative Fuel Cycle PWR Models for the ORIGEN Computer Code, ORNL/TM-7005 (February 1980). This report describes ORIGEN models for a high-burnup, enriched-uranium-fueled PWR and three thorium-cycle PWRs.

The discrepancy between our predicted CANDU spent fuel composition and that of Ontario Hydro was resolved during this report period by obtaining a third set of discharge compositions from Chalk River. The latter data differ significantly from those of Ontario Hydro and are much closer to our calculations. The differences are apparently due to Ontario Hydro's use of older computer codes and input data. The CANDU depletion calculations for both natural uranium and slightly-enriched uranium feeds have been completed. Work is currently underway to generate the auxiliary information required by ORIGEN2.

Progress in developing auxiliary information for three Pu-U cycle LMFBRs has been somewhat slower than expected due to the newness and complexity of the LMFBR fuel cycle as compared to the thermal reactor cycles considered previously. The LMFBR information is now about 90% complete, however, and is proceeding satisfactorily. Upon completion of the U-Pu LMFBR models, work will begin on thorium-cycle LMFBRs.

The results of testing of ORIGEN2 on the CDC computer at Sandia Laboratories were received and changes were made to the IBM version to maximize its compatibility with CDC computers. The draft ORIGEN2 user's manual (ORNL/TM-7175) was updated to reflect these changes and was submitted for editing. Meanwhile, due to the off-site demand for ORIGEN2. the computer code and a draft version of the user's manual were sent to the ORNL Radiation Shielding Information Center for distribution on request.

1.3 Special Projects

In December 1979, R. D. Walton, NEW/P, requested that we update and expand the calculations of spent fuel and waste compositions given in ORNL/TM-6008 and ORNL/TM-5427 by June 30, 1980. Test calculations of much of the requested data have been made, and final ORIGEN2 runs are scheduled pending completion of Pu-U cycle LMFBR models.

1.4 Partitioning and Transmutation

Documentation of the actinide partitioning and transmutation program has proceeded with the publication of the following report during this quarter:

> C. W. Forsberg, Separation of Americium, Curium, and Rare Earths from High-Level Wastes by Oxalate Precipitates: Experiments with Synthetic Waste Solutions, ORNL/TM-6445 (January 1980).

The status of the seven reports summarizing all major aspects of the P-T program are as follows:

Report	Description	Status
ORNL-5566	Overall assessment report	Revised to accommodate comments received since the first draft was released in January 1980. Revised draft issued March 17, 1980.
ORNL/TM-6982	Partitioning report	All reviews and editing complete; final typing underway.
ORNL/TM-6983	Transmutation report	All reviews complete; being updated.
ORNL/TM-6984	Miscellaneous aspects report	All reviews complete, but not yet incorporated into report.
ORNL/TM-6985 + Appendices	Conceptual design and costing report (R. M. Parsons Company)	Printed and awaiting distribution.
ORNL/TM-6986 + Appendices	Short-term risk analysis (Science Applications, Inc.)	Printed and awaiting distribution
ORNL/TM-6987 + Appendices	Long-term risk analysis (Los Alamos Technical Associates, Inc.)	Reviews complete and comments are being incorporated into ORNL/TM-6987. Appendices are printed and awaiting distribution.

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, studies showed that solids cured at 100°C and 0.1 or 0.6 MPa had essentially the same physical properties as those cured at higher temperatures and pressures. Although additional water had to be used to make a FUETAP concrete with simulated SRL waste containing zeolite, the resulting product still had a compressive strength of 37.4 MPa. Small scale dewatering studies indicated that free water was easily removed from cured specimens by heating at 250°C for 24 h. This heat treatment reduced the strength only about 20%. Glove box tests with standard FUETAP concretes containing ^{244}Cm indicated very little gasification after 1 month.

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°C and pressures $\leq$ 4.1 MPa. After curing, the solids would be dewatered by heating to 250°C to dimish 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. mix development,
2. dewatering characteristics,
3. radiolytic gasification, and
4. leachability of the waste form.

2.3 Mix Development

Investigations are in progress to determine the effect of curing conditions and the effect of waste composition on the properties of concretes made with the standard FUETAP formulation (Table 1). Initial curing studies with solids containing simulated NFS waste (Table 2) indicated that it may not be necessary to cure the solids at the higher temperatures and pressures. The physical properties of solids cured at 100°C and 0.1 or 0.6 MPa were essentially the same as those formed at the higher temperatures (Table 3).

Table 1. Standard FUETAP formulation

Ingredient	wt %
Type I cement	22.00
Kingston fly ash	11.00
Indian Red clay	7.50
Simulated waste	15.00
Sand	27.75
$NaNO_3$	0.75
D-65 (water reducer)	1.00
Water	15.00

Solids prepared with earlier FUETAP formulations and simulated SRL waste solids (SRL1, Table 2) indicated little effect of waste composition on the physical properties of the resulting solids. However, in current studies using a simulated waste containing zeolite (SRL2, Table 2), very thick grouts were produced with the standard FUETAP formula. To make the grouts pourable and to satisfy the high water demand of the zeolite and the amosphous silica, it was necessary to increase the water content of the mix from 15 to 18 wt % and the D-65 water reducer from 1 to 1.25 wt %. On curing the resulting mix at 100°C and 0.1 MPa, the solid had a compressive strength of 37.4 and a wet density of 2.11 g/cm^3. Additional variations in the formula will be made to determine the maximum SRL2 waste concentration (with and without zeolite present) that can be accomodated and still produce dense, high strength solids.

Table 2. Composition of simulated waste solids

Component	NFS (wt %)	SRL1 (wt %)	SRL2[a] (wt %)
Fe_2O_3	75.18	38.4	36.13
Al_2O_3	14.89	6.8	28.26
MnO_2		17.1	9.94
PbO[b]		16.5	3.26
CaO		1.0	2.69
NiO	4.78	6.5	4.47
Cr_2O_3	4.94	0.5	
Na_2O			5.00
Na_2SO_4			0.93
$Na_2SO_4 \cdot 10H_2O$		7.0	
NaF		2.0	
Na_2HPO_4		1.4	
SrO	0.14		
$Ru(OH)_3$	0.027		
CeO	0.037	2.5	
BaO_2		0.3	
SiO_2			0.85
Zeolite[c]			8.93

[a] Values taken from J. A. Stone, S. T. Goforth, Jr., and P. K. Smith, Preliminary Evaluation of Alternative Forms for Immobilization of Savannah River Plant High-Level Waste, DP1545 (December 1979).

[b] PbO substituted for U_3O_8.

[c] Ion-Siv IE-95.

Table 3. Effect of curing temperature and pressure on FUETAP concrete

Curing conditions[a]			Strength		
Heat up time (h)	Temperature (°C)	Pressure (MPa)	Compressive (MPa)	Tensile[b] (MPa)	Wet density (g/cm^3)
1.5	100	0.1	60.5	2.1	2.24
7.0	100	0.1	52.8	2.9	2.24
1.5	100	0.6	61.7	3.6	2.25
1.5	160	0.6	53.9	2.2	2.17
1.5	250	4.1	57.6[c]	2.6	2.23
7.0	250	4.1	61.0	*d*	2.26
e	*e*	*e*	48.9	*d*	2.24

[a] The standard FUETAP formulation containing NFS simulated waste solids was used with a total curing time (except where noted) of 24 h.

[b] The tensile strength was determined using the dog-bone technique and two specimens. Precision is very poor with this method.

[c] This is the average value for three determinations. All compressive strength values are based on a single determination.

[d] These values were not measured.

[e] These specimens were held 24 h at ambient temperature then heated to 250°C in 1.5 h and cured 22.5 h at 250°C and 4.1 MPa.

2.4 Dewatering of Standard FUETAP Concrete

The small scale dewatering studies were completed. The results indicated that at 250°C the free water in FUETAP concrete has a very high diffusion rate and may be adequately removed in $\leq$ 24 h. In tests using right circular cylinders ranging from 1 cm in dia x 1 cm high to 5 cm in dia x 15 cm high, 90% of the water that could be removed by heating 24 h at 250°C was removed during the first 3 h. The remaining 10% probably resulted from the decomposition of phases containing bound water.

Compressive strength tests on dewatered FUETAP specimens showed that on heating the solids at 250°C for 24 h, the strength was reduced from 62.5 MPa to 49 MPa. This is the strength equivalent to high-strength commercial concrete. A second specimen after dewatering at 250°C for

24 h was heated at 400°C and 900°C for an additional 24 h each. The strength of the resulting specimen was 14.1 MPa which is equivalent to the 28 days strength of a concrete made from Type IV or low-heat Portland cement. Equally significant was the fact that the specimen that had been heated to 900°C did not shatter or crumble during the compressive strength measurement. Although large cracks formed, the solid retained its original shape.

2.5 The Effect of Alpha Radiation on FUETAP Concrete

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. Initial results verify previous laboratory tests that had indicated that the catalytic activity of FUETAP concrete should be more than sufficient to recombine any radiolytically produced hydrogen and oxygen. After one month, the pressure produced by the radiolysis of a standard dewatered FUETAP specimen is too small to measure. For comparison, a control specimen (ordinary concrete cured under ambient conditions and not dewatered) generated 0.18 MPa pressure in 50 days and displayed a linear rate for the last 30 days of this time period. The gas was released and particles of Fe_2O_3 added to the chamber above the specimen. After 17 days at ambient temperature, the gas generation rate was about the same as it had been before the iron oxide was added.

2.6 The Leachability of FUETAP Concretes

Leach tests using the old formulations were discontinued and new studies initiated using the standard FUETAP formula. Initial short term results indicate cesium diffusivities in the order of 10^{-13} cm^2/s, 10^{-15} cm^2/s and 10^{-16} cm^2/s into Sandia brine, spring water and demineralized water, respectively. Analytical results are not yet available on the strontium leach tests in progress.

3. STUDY OF CERAMIC AND CERMET WASTE FORMS

(Activity No. AG 30 20 01 0, ONL-WH03; ON 1.3.1.2 AG)

W. S. Aaron, T. C. Quinby, E. H. Kobisk, D. K. Thomas

3.1 Summary

The transition of emphasis in this program from process development to product characterization is essentially complete. Construction of the large (23 cm i.d.) spray calciner has been completed and it is operating satisfactorily. Further refinements to it are being made during the course of preparing large quantities of calcined materials for use in the densification and characterization parts of the program. Evaluation of alternate densification techniques as they effect final cermet properties is continuing. Delays in the further development of the liquid phase sintering technique and sintering techniques, in general, have been encountered due to a lack of suitable sintering furnaces. This situation will be corrected shortly. The initial stages of the quantitative cermet leach testing program using radiotracers are proceeding as planned. This work is centered on NFS Acid Thorex and PW-4b type wastes along with Idaho calcine wastes, with no further efforts anticipated on the Savannah River sludge wastes.

3.2 Continuous Calcination Technology

Spray calcination of waste-urea solutions was shown to be successful during investigations with a small (10 cm i.d.) spray calciner.(3.1) The small size of this calciner, however, severely restricted any further development of operating parameters for this spray calcination process. A larger (23 cm i.d.) calciner, possessing greater operational flexibility, has been constructed and is currently being operated.

The feed system for the calciner is designed to pump the waste and additives, in a urea solution, through the spray nozzle, shown in Fig. 3.1., into the calciner. The design of this nozzle provides very effective atomization of the urea solution to facilitate calcination. Refinements to this nozzle are anticipated in an effort to maximize droplet size, and therefore calcine particle size for improved collection efficiency, while maintaining a small enough droplet size to permit complete calcination.

The droplet size is a function of nozzle design, and the physical properties of the urea solution. A typical feed solution having a density of 1.33 g/cc was shown to have a viscosity of 0.75 mPa·s at 333 K and a surface tension of 7.6×10^{-3} N/m at 347 K. These properties, coupled with maximum and minimum liquid flow rates and injection air flow rates yielded droplet sizes ranging from 8-56 μm. These droplets produced calcined particle sizes ranging from 0.3 μm to aggregates exceeding 355 μm in diameter. It has also been found that the spray pattern, shown in Fig. 3.2, provides droplets which are apparently completely calcined before they come in contact with the calciner wall since no buildup of material on the calciner walls has been experienced.

Monitoring of the temperature profiles in the calciner indicates that the cooling effects of injected air and feed solution are offset by exothermic reactions occurring during calcination. Calciner centerline temperatures are maintained at or just slightly below the wall temperature throughout the calcination tests. Studies are in progress to optimize the separation of the calcine particles from the calciner off gas. A cyclone separator is being used for the primary powder collection. By design, the off gas enters the cyclone at a velocity of 6-21 m/s which will effectively remove particles 5 μm in diameter and larger from the off gas. This velocity is then reduced to less than 1.5 m/s to facilitate separation of the fines from the off gas. In tests conducted thus far, approximately 5% of the powder escapes separation by the cyclone separator and must then be collected by a method suitable for separating fines from the off gas. Various methods are being studied to separate the fines quantitatively. One method involves taking advantage of the magnetic properties of the calcine to effect collection in a magnetic field. It has been found that if the off gas is kept hot until it passes through the cyclone separator, the condensation of water vapor from the slow moving exhaust stream is very effective in "scrubbing" the fines being carried by the off gas. These methods along with the use of baffles or impingment plates are being investigated to optimize separation of calcine powder without totally relying on high maintenance items such as filters.

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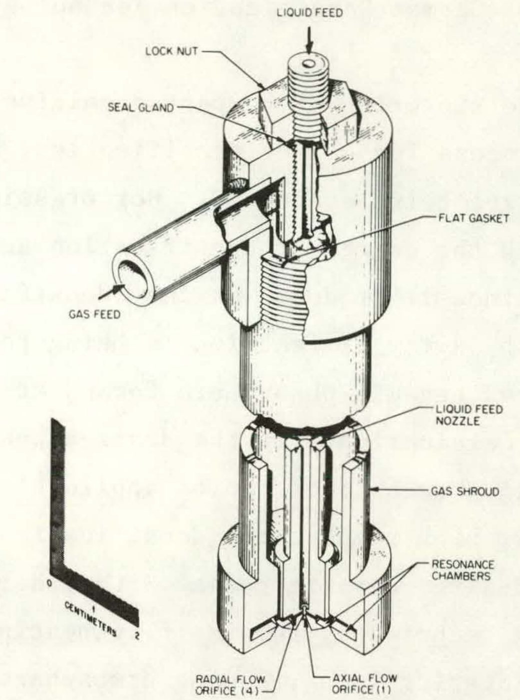

Fig. 3.1. Schematic of the nozzle used for the spray calcination of molten urea solutions.

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Fig. 3.2. The narrow, well atomized spray pattern provided by the above nozzle permits effective calcination of molten urea solutions.

3.3 Cermet Densification Technology

While liquid phase sintering of compacted calcine powder continues to be the reference process for cermet densification, alternate densification techniques are being evaluated. Hot pressing continues to be the basis against which the degree of densification achieved by alternate methods is compared, since it produces maximum densification. Analysis of spray-calcined powder by x-ray diffraction is being performed to determine whether the desired ceramic phases are formed at temperatures achieved during spray calcination. If the desired phases are formed, low temperature densification techniques can be applicable; in the case of batch-prepared powders, high temperature densification methods are required to form the desired ceramic phases. Consideration also is being given to rapid heating techniques, such as r.f. heating, for use with either liquid phase sintering in a reducing atmosphere or the rapid melting and solidification of the metal phase in a pre-reduced calcine compact. Suitable sintering furnaces for further development and application of liquid phase sintering are being procured. A small tube furnace is being modified to permit preparation of a limited number of samples for leach testing and rudimentary densification studies on spray-calcined powders.

3.4 Characterization of Cermet Waste Forms

Characterization efforts during this period have centered on the evaluation of spray-calcined powder. Preparations are in progress for quantitative determination of properties of the cermets produced using the new process flowsheet.(3.2) Of primary importance is the determination of leach rates for cermets under a variety of conditions. Both static and flowing leach tests will be used. Preliminary static tests with radiotracer-containing cermet samples at 300 K and 340 K in distilled water and WIPP-B brine are in progress to evaluate and refine the sampling and analytical methods to be used in our leach testing program. Cells for the flowing leach tests are being fabricated while other apparatus for these tests are being assembled and checked operationally. The static radiotracer tests are being performed in a temporary facility pending completion of a dedicated radiotracer laboratory and the receipt of approvals to operate that facility. This facility should be ready for use by the time the new leach systems are completed and tested. Necessary equipment for hydrothermal tests has been appropriated. Hydrothermal tests will be performed when deemed appropriate following initiation of other phases of the leach testing program described above.

References

3.1. "High-Level Waste Program Progress Report for October 1, 1979 through December 31, 1979," ORNL/TM-7253 (in press).

3.2. "Development and Characterization of Cermet Forms for Radioactive Waste," Scientific Basis for Nuclear Waste Management, Vol. 2 (in press), Plenum Press, New York, New York.

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

Construction was completed on a sphere forming system capable of producing 100 g batches of Synroc spheres by internal gelation. Several runs have been made to investigate feed compositions, forming, and washing conditions necessary to achieve the metal oxide composition in the dried spheres required by Synroc-B. Initial laboratory-scale tests were made to assess the applicability of several gel-sphere techniques for producing gels of the Savannah River Plant Frit-21 glass composition. A laboratory scale drying oven has been modified to carefully examine the effect of humidity and drying time on the final sintered product.

4.2 Introduction

Work is in progress to assess sol-gel techniques as a means of incorporating radioactive waste in both glass and crystalline forms. Variations of the internal gelation technique were examined this period in an attempt to better control the final composition of the microspheres. A system was constructed to assess the effect of several drying variables on the final sintered microspheres. Studies continued to determine the density and phases formed when sintering in different atmospheres.

4.3 Sol-Gel Technology — Glass

The feasibility of preparing spheres of Savannah River Plant's (SRP) preferred glass composition Frit-21 was evaluated. Initial tests involved the preparation of gel spheres of the Frit-21 composition without waste. Although scoping tests using external gelation and water extraction techniques were made, the most promising technique appeared to be internal gelation. Stable feed solutions were prepared from the salts of the Frit-21 metals. A typical feed solution for Frit-21 without silica is made from H_3BO_3, $Ca(NO_3)_2 \cdot 4\ H_2O$, $LiNO_3$, $NaNO_3$, and $TiCl_3$. To avoid premature gelation, urea was added to this solution until nearly saturated at room temperature. As a source of SiO_2, LUDOX-HS a sodium-stabilized colloidal silica was used. These two solutions were mixed at about 0°C followed by addition of chilled hexamethylenetetramine (HMTA) also at 0°C. This broth, which has a stability of about 30 min at 0°C, was formed into large, 4-mm droplets and gelled in a column of silicone oil at 95°C. Gelation rates were on the order of 2 to 4 s for this mixture. Relative to Synroc gels, the glass gels formed by internal gelation are softer and thus are more susceptible to damage and sphere clustering. These spheres were washed in 0.5 $\underline{M}$ NH_4OH — 0.025 $\underline{M}$ $(NH_4)_2CO_3$ followed by steam drying at oven temperatures of 90 and 225°C.

Limited tests to prepare spheres using sodium silicate as the source of silica were unsuccessful. Sodium silicate, a strong base when combined with acid solutions of the other metals, resulted in an immediate gelation. At the conditions investigated, the gelation is much more rapid than the mixing time required to form a homogeneous broth droplet. The use of sodium silicate in the silica catalyst bead industry is well documented, and with some development effort, could probably be applied to the preparation of borosilicate glass beads.

4.4 Sol-Gel Technology — Crystalline Forms

The effect of washing conditions on the final metal oxide compositions in dried spheres has been investigated. All Synroc sphere batches were prepared by internal gelation. It was determined by x-ray fluorescence analysis of the dried spheres that early batches of material showed deficiencies in BaO and CaO. Feed solutions prepared from the chloride salts of Ti and Zr and the nitrate salts of Al, Ca, and Ba, upon sitting at room temperature for several days, showed a slow precipitation of barium crystals. The precipitation can be avoided by preparing a separate solution of $Ba(NO_3)_2$ and a solution of the other metal salts, combining these just prior to the sphere forming step.

Deficiencies in CaO in the dried gel spheres are most likely attributed to the removal of Ca^{+2} during the aqueous washing step. The compositions of the dried gels were determined by x-ray fluorescence analyses. All early batches of Synroc gel spheres formed by internal gelation were washed with 0.5 $\underline{M}$ NH_4OH — 0.025 $\underline{M}$ $(NH_4)_2CO_3$. Carbonate was added to the wash solution because the solubilities of $BaCO_3$ and $CaCO_3$ are much lower relative to the hydroxides of these metals. The principle is that carbonate can diffuse into the gel during washing, thereby precipitating the dissolved Ba^{+2} and Ca^{+2} as carbonates in the gel. Later batches were made using variations in feed compositions and/or wash solution compositions. As an alternative to carbonate in the wash, two batches of spheres were washed in a solution containing ammonium oxalate [0.5 $\underline{M}$ NH_4OH — 0.03 $\underline{M}$ $(NH_4)_2C_2O_4$], because the solubilities of barium and calcium oxalates are even lower than the carbonates. The use of oxalate in the wash did inhibit the leaching of calcium and barium, however, the dried spheres from these batches were soft and powdery. The addition of excess Ca^{+2} to the feed solution appeared to yield a composition approaching the amount of CaO required by Synroc. One batch containing no excess Ca^{+2} or Ba^{+2} was washed in an ammonium hydroxide solution presaturated with $Ba(OH)_2$ and $Ca(OH)_2$ (IG-22C,D). The motivation for this approach was that no net loss of these cations from the gel should occur if the solution in contact with the gel spheres is already saturated with these cations. Of course a knowledge of the equilibrium distribution behavior between the gel and wash solution as a function of concentration would be necessary to verify this. Results indicate what appears to be an exchange of Ba and Ca in the gel showing an excessively large amount of BaO in the dried spheres. An alternate explanation for the high BaO composition is that a local buildup of dried $Ba(OH)_2$ may occur on the sphere surfaces from contact with the Ba^{+2}-rich solution.

Insufficient data are available to determine the effect of organic gelation liquid, gelation temperature, etc. on final product compositions. All the sphere forming runs in the semicontinuous system have been made using either silicone oil or 2-ethyl-1-hexanol as gelation media. Important advantages and disadvantages exist for each fluid with respect to broth droplet formation, sphere settling characteristics, hydraulic transportability, and ease of removal from the sphere surfaces.

4.5 Drying

The aging and drying of gel spheres appeared to have a significant effect upon the characteristics of the dried and/or sintered spheres. Therefore, an increased effort has been placed in this area. The rate at which moisture leaves the spheres affects not only sphere shrinkage (which affects final sphere size and sintered density) but also sphere cracking, shape, porosity, and surface effects. Various drying procedures have been tested in an attempt to determine the influence on crystallite size and growth, particle size, and product sinterability.

In the drying tests, the wet spheres were placed upon a 100 mesh screen in a covered container with only a small opening (3/16 in. diam) in the lid. Additional water could be placed beneath the wet spheres. The combination of additional water and a restricted opening in the lid aided in maintaining a humid atmosphere around the spheres while the spheres were heated to the desired drying temperature.

The amount of water placed beneath the spheres was varied in the first three drying runs of Batch SR-IG-15, but this did not significantly affect the sintered density and/or porosity. However, in other runs, the drying temperature was varied, and this had a significant effect upon both the sintered density and porosity. When the drying temperature was decreased from 230 to 145°C, the sintered density of the spheres increased from 3.59 g/cm^3 (85.6 % T.D.) to 3.87 g/cm^3 (92.2% T.D.). The corresponding open and closed porosity was lower at the higher densities. The spheres were placed into the oven at room temperature for all the previously mentioned runs. For one run, the oven was at temperature (230°C) when the spheres were added. This resulted in a lower sintered density and an increase in porosity. Batch SR-IG-15 was also evaluated by transmission electron microscopy. It is difficult to distinguish a crystal structure of the dried spheres even at a magnification of 100,000×. If the smallest particulates visible are "crystals," they are approximately 30–50 Å in diameter.

Since the runs using SR-IG-15 showed the drying temperature to have a significant effect upon density, Batch SR-IG-20 was tested for temperature effect. Three drying runs were made at temperatures of 225, 135, and 110°C. Naturally as the drying temperature was reduced, the drying time increased. The drying temperature did not have a significant effect upon the sintered density for this batch. A high sintered density (above 95% T.D.) was obtained in each of the drying runs.

4.6 Sintering

The analysis of sol-gel produced Synroc batches for phase formation after sintering has been quite confusing because of the loss of CaO and sometimes BaO. If batches are sintered in Ar-4% H_2, the desired phases seem to be formed but in unusual proportions because of the loss of CaO. Preliminary results show that sintering in air does not form the desired phases. Hollandite does not appear to form when sintering in air but leaves unreacted TiO_2. The desired phases of perovskite and zirconolite are formed when sintering in air. Sintering in a reducing atmosphere with water vapor present to control the partial pressure of oxygen does not appear to be acceptable. Hollandite again does not form under these conditions leaving unreacted TiO_2. Perovskite and zirconolite are normally formed when sintering in this atmosphere. Since there is a shortage of CaO in all batches, zirconolite and perovskite are not formed in the desired proportions. Furthermore in some batches with significant shortages of CaO ($\sim$45%), zirconolite and perovskite did not form at all.

4.7 Leaching of Synroc

The leachability of the waste form is the single most important property. In order to determine by what method the analysis of Synroc leaches for the major Synroc constituents could be best accomplished, a standard solution was prepared and submitted for analysis by x-ray fluorescence, inductively coupled plasma spectrometry, and either atomic absorption or flame emission spectrometry. The results from these tests are presently being collected.

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)

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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

The alternative waste forms to be used in the compatibility tests include Synroc, coated particles (carbon and carbon/silicon carbide coatings), metal matrix (lead-tin and aluminum-silicon), tailored ceramics, and concrete (FUETAP). Glass is included also primarily for purposes of comparison. Both metal matrices and coated particle types have been procured. The Synroc, glass, and FUETAP are currently being fabricated in pellet form suitable for the tests. Compositions of the waste forms containing simulated high-level waste sludge are shown in Table 5.1.

Metals coupons were made of all 15 alloy materials to be used in the compatibility tests. Compositions of these alloys are given in Table 5.2. Disks nominally 1/2-in. diam were stamped from sheet stock ranging from 1/16 to 1/8-in. thick. The disks were then annealed in argon and polished on each side to obtain a flat surface. The flat surfaces will be contacted with waste pellets during the corrosion test. The disks are currently being cleaned and weighed.

Table 5.1. Nominal Compositions of Alternative Waste Forms

Glass		Synroc "D"		Tailored Ceramic	
		Primary Host Constituents			
SiO_2	38.9%	Al_2O_3	21.2%	La_2O_3	11.2%
Li_2O	13.7%	TiO_2	15.0%		
B_2O_3	7.4%	SiO_2	8.1%		
Na_2O	7.4%	CaO	6.9%		
CaO	3.7%	ZrO_2	4.0%		
TiO	3.0%				
		Waste Constituents			
Fe_2O_3	13.3%	Fe_2O_3	27.1%	Al_2O_3	74.0%
MnO_2	3.6%	MnO_2	6.1%	Fe_2O_3	5.2%
Al_2O_3	2.6%	Na_2O	3.8%	MnO_2	4.3%
Na_2O	1.9%	NiO	3.4%	Na_2O	1.9%
NiO	1.7%	UO_2	2.3%	U_3O_8	1.2%
CeO_2	0.73%	CeO_2	1.0%	NiO	0.76%
Na_2SO_4	0.36%	Cs_2O	0.68%	SiO_2	0.55%
CaO	0.31%	SrO	0.50%	Na_2SO_4	0.50
SiO_2	0.29%			CaO	0.34%
IONSIV*	1.30%				

*Linde IONSIV IE-95. Mixture of CaAl, Si_4O_{12} · 6 H_2O and (NaKCa)$_3$ Al_3XiO_{24} · 8 H_2O.

In addition to the base metals, three coatings will also be evaluated. Test runs are under way to determine deposition time in applying titanium diboride over carbon steel blanks. Disks coated with nickel have already been prepared. A vapor deposition method is being tested for chromium.

Test furnaces for the 100 and 300°C long-term tests have been checked out and are ready to receive capsules. Preparation of furnaces for 800°C short-term tests are under way. All the capsule hardware has been received. Capsule loading will begin in April.

Table 5.2. Nominal Percent Compositions of Test Alloys

Alloy	Cr	C	Ni	Cu	Mn	Si	Mo	Fe	Others
Carbon Steel (A-516)		0.27 max			0.80-1.25	0.13-0.33		Balance	
304 L SST	18.00-20.00	0.03 max	8.00-11.00		2.00 max	1.00 max		Balance	
317 LM SST	18.00-20.00	0.03 max	12.00-16.00		2.00 max	1.00 max	4.00-4.50	Balance	
Inconel 600	14.00-17.00	0.10 max	72.00 min	0.50 max	1.00 max	0.75 max		6.00-8.00	1.75 Columbium + Ta
Inconel 625	20.00-23.00	0.10 max	Balance		0.50 max	0.50 max	8.00-10.00	5.0 max	3.15-4.15 Columbium + Ta, 0.40 max Al, 0.40 max Ti, 0.015 max S, 1.00 max Co
Inconel 690	30.0	0.03	Balance					9.5	
Monel 400		0.30 max	63.0-70.0	Balance	2.00 max	0.50 max		2.5 max	0.50 max Al, 0.02 max S
70-30 Cupronickel			29.0-33.0	65.0 min	1.00 max			0.70 max	1.15 max Sn, 1.0 max Zn, 0.05 max Pb
OFHC Copper				99.99 min					Trace impurities
5052 Aluminum	0.15-0.35			0.10 max	0.10 max	0.45 max Si + Fe		0.45 max Si + Fe	Balance Al, 2.2-2.8 Mg, 0.10 max Zn, Others 0.015 max total
Titanium									99.5 Ti
Ticode 12		0.08 max	0.6-0.9				0.2-0.4	0.30 max	0.25 max O, Balance Ti

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