MASTER

DEVELOPMENT OF TAILORED CERAMICS
FOR
GEOLOGIC STORAGE OF NUCLEAR WASTES

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CONTENTS

	<u>Page</u>
1.0 PROJECT DESCRIPTION AND OBJECTIVES.....	1
2.0 SUMMARY AND HIGHLIGHTS.....	2
2.1 Tailored Ceramic Waste Form Development and Characterization.....	2
2.2 Tailored Ceramic Process and Equipment Development....	2
3.0 TECHNICAL PROGRESS.....	4
3.1 Tailored Ceramic Waste Form Development and Characterization.....	4
3.1.1 Generic and Fundamental Studies.....	4
3.1.2 Formulation and Consolidation Studies.....	16
3.1.3 Radiation and Transmutation Effects.....	19
3.1.4 Geologic Strata Compatibility.....	21
3.2 Tailored Ceramic Process and Equipment Development....	21
3.2.1 Engineered Containment.....	21
3.2.2 Process Evaluation and Definition.....	21

1.0 PROJECT DESCRIPTION AND OBJECTIVES

A multitask program is being carried out for the development and characterization of Tailored Ceramics as a waste form for the geologic storage of radioactive wastes. The feasibility of producing the waste form safely and reliably under large-scale remote operating conditions is being assessed, and the long-term stability of the ceramic form is being evaluated vis-a-vis borosilicate glass.

Tailored Ceramics are crystalline assemblages made by high-temperature and pressure consolidation of a nuclear waste with selected additives. The specific crystalline phase assemblages produced by the waste tailoring process closely approximate those found in natural minerals which have persisted for geologic ages. These consolidated ceramic forms provide a total volume reduction for the waste and are extremely hard, dense materials with low surface areas and potential for high leach resistance.

The program involves basic studies at the Pennsylvania State University's Materials Research Laboratory, applied research at Rockwell International's Science Center, process and remote fabrication technology development at Rockwell International's Energy Systems Group, and engineering development support at Rockwell's Hanford Operations. This integrated effort is directed toward advancing Tailored Ceramic technology to the state where it provides a viable alternative waste form for use at the SRP and other installations.

2.0 SUMMARY AND HIGHLIGHTS

2.1 TAILORED CERAMIC WASTE FORM DEVELOPMENT AND CHARACTERIZATION

Generic and Fundamental Studies (Task 2) are underway on (1) crystalline phases for Savannah River Plant (SRP) sludges, and phases for iodine and fluoride fixation, (2) cement matrices for Tailored Ceramic phases, (3) mechanism and kinetics of dissolution of pollucite, Sr-feldspar, and nepheline, and (4) fundamental transmutation effects. Simulated SRP sludge yielded spinel and, depending on additives, $\alpha\text{-Al}_2\text{O}_3$, UO_2 , cristobalite, and mullite. Nd monazite appears to be compatible with a variety of high silica and high alumina cements. $\text{CsFeSi}_2\text{O}_6$ appears promising as resistant to the ^{137}Cs to ^{137}Ba transmutation.

Formulation and Consolidation Studies (Task 3) have established an initial tailoring formula based on alumina, yielding a four-phase crystalline assemblage: corundum, spinel, magnetoplumbite, and uraninite. Hard, dense hot-pressed ceramic pellets have been prepared in the laboratory, and host phase identification for various species of concern is underway.

The initial Radiation and Transmutation Effects (Task 4) effort has included the establishment of a program plan and key contacts with other researchers in the field, the initiation of a detailed literature review of the radiation damage field as applied to nuclear waste forms, and a start on formulating the program's first radiation damage experiments. Task 5 Geologic Strata Compatibility studies had not been initiated during the quarter.

2.2 TAILORED CERAMIC PROCESS AND EQUIPMENT DEVELOPMENT

Under Engineered Containment (Task 6), current technology is under review and assessment, and a report library has been established.

Under Process Evaluation and Definition (Task 7); the unit operations needed to carry out steps in the Tailored Ceramic process are under evaluation. Hot pressing, hot isostatic pressing, and calcination are the operations of immediate interest in conjunction with the processing concept in which the alumina in the waste is retained to serve as a tailoring ingredient in forming a consolidated Tailored Ceramic waste form.

3.0 TECHNICAL PROGRESS

3.1 TAILORED CERAMIC WASTE FORM DEVELOPMENT AND CHARACTERIZATION

3.1.1 Generic and Fundamental Studies

Task 2, "Generic and Fundamental Studies," is devoted to the development and characterization of new materials capable of either containing the desired radionuclide as an essential part of the crystal structure (the high-loading option) or taking some quantity of the radionuclide into stable solid solution (the low-loading option).

3.1.1.1 Optimum Phases for Tailored Ceramics

This aspect of the work is with the crystalline phases that can be formed from a Savannah River Plant (SRP) sludge and with new crystalline waste forms specifically designed for the radionuclides in other high-level wastes.

Work has been started on phases for strontium, cesium, iodine, and rare earth elements. In each case, the approach is to first identify crystalline hosts that will accept the radionuclide(s) in question, then address questions of thermal stability during synthesis and processing, and then investigate mutual compatibility of phases that must coexist in the final ceramic product.

3.1.1.1.1 Crystalline Phases from Fired Simulated Savannah River Sludge

Since these materials are rich in aluminum and iron, there appears to be a very good possibility of forming ceramics directly by firing the sludge. Ceramic bodies were made by drying solutions or slurries at $\sim 120^{\circ}\text{C}$, calcination at 600°C , grinding, pelletizing using a pressure of $\sim 3 \times 10^4$ psi, and firing at $900\text{--}1200^{\circ}\text{C}$. On firing a simulated sludge

at 900-1200°C, a spinel of undetermined constitution was the dominant phase, but many other unidentified X-ray lines were observed.

Use of silica, alone and with other additives, was then studied for tailoring of the SRP sludge. A mixture of nitrate solutions (of cation composition similar to the previous simulation) plus Ludox (colloidal SiO_2) was made. X-ray data similar to those for the additive-free simulation were obtained with ceramics fired at 1000-1200°C.

The effect of fairly large quantities of tailored additions to the nitrate-based simulation was studied, the additions being (1) 60 mole % SiO_2 , (2) 280 mole % Al^{3+} + 60 mole % SiO_2 , and (3) 60 mole % PO_4^{3-} . The SiO_2 and H_3PO_4 additions (1 and 3 above) produced melting on subsequent firing at 1200°C. The mechanical properties of pellets made with all of these additives were poor, while those of the addition-free material seemed satisfactory.

Addition of sodium, a potentially damaging additive from a leaching standpoint, was explored, as was that of calcium. The additions to the nitrate-base simulation were (1) 60 mole % Na^+ , (2) 60 mole % Ca^{2+} , and (3) 60 mole % Na^+ + 60 mole % Ca^{2+} . As found by McCarthy for commercial wastes, sodium additions improved the mechanical properties. Calcium addition produced somewhat less of an improvement, but the addition (3) produced a poorly crystallized and mechanically weak "ceramic" even on firing at 1200°C. Spinel was a dominant phase in (1) and (2) but was absent in (3). No nepheline or sodium silicate phases were observed.

A second nitrate + Ludox mixture was made up with enhanced uranium and strontium concentrations to try to clarify the phases bearing these elements. The hydroxides were precipitated with excess NH_4OH and then calcined and fired as usual. The effect of 10 mole % additions of calcium or aluminum was trivial as far as X-ray diffraction was concerned, but the addition of 10 mole % SiO_2 was to promote the formation of UO_{2+x} as against a presumed uranate phase.

Spinel was observed in most cases. High SiO_2 led to an amorphous phase and cristobalite formation. High Al led to $\alpha\text{-Al}_2\text{O}_3$ formation, while high Al plus Si led to formation of $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite). With high PO_4^{-3} additions, no phase identifications were obtained.

The spinel was not noticeably suppressed by (so is, therefore, presumably compatible with) Al_2O_3 and SiO_2 additions. Moreover, as there was a large fraction of unreacted (albeit crystallized) Al_2O_3 and SiO_2 , there appears to be no impediment to the formation of Sr-feldspar and pollucite to tie up ^{90}Sr , ^{134}Cs , and ^{137}Cs .

As expected, firing in a reducing atmosphere promoted the formation of the UO_{2+x} phase rather than U_3O_8 or the presumed uranate phase. However, the chemical details of why adding SiO_2 to the second nitrate simulation promoted UO_{2+x} as against the uranate phase are not clear.

3.1.1.1.2 Iodine Fixation

A candidate crystalline host for ^{129}I is boracite. The mineral boracite is $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$. However, there are many isostructural compounds in which magnesium is replaced by other intermediate-size cations and chlorine is replaced by bromine or iodine. The halogen in the boracite structure is encapsulated within a three-dimensional framework of boron-oxygen polyhedra, suggesting that this structure may be useful for immobilizing iodine. So far, synthesis of an iodine boracite has not been successful.

Fe-I-boracite crystals, grown elsewhere by chemical transport techniques, were unaffected by a γ -dose of $\sim 10^9\text{R}$, but decomposed on heating in air at 900°C , $\alpha\text{-Fe}_2\text{O}_3$ being the major decomposition product detected by X-ray diffraction. Some evidence was obtained that Fe-I-boracite is unstable on prolonged heating at 300°C . If substantiated, this result severely jeopardizes Fe-I-boracite as a candidate iodine

fixer. Although iodine would be processed separately from the main nuclear waste, an iodine fixer would be buried in the same repository as high-level waste, and thus it would experience near-field temperatures of $\geq 100^{\circ}\text{C}$, even though β , γ -heating in the iodine fixer itself would be negligible because of the long half life of ^{129}I .

3.1.1.1.3 Fluoride Fixation; Thorex Wastes

McCarthy showed that fluoride-bearing phases could not be accommodated in "supercalcine" Tailored Ceramic phases based on PW-4b and PW-7 high-level nuclear wastes. It was shown that $\text{Ca}_5(\text{PO}_4)_3\text{F}$ was thermally stable up to $\sim 1000^{\circ}\text{C}$, although chemical analysis showed the F content to be only about 50% of the theoretical value. After heating at 1200°C , the F content was only about 1.5% of the theoretical value, but the X-ray patterns were apparently virtually unchanged. In the present work, heating the fluorapatite phase at 1350°C caused complete decomposition to $\alpha\text{-Ca}_3(\text{PO}_4)_2$.

$\text{Sr}_2\text{FeO}_3\text{F}$ is reportedly stable at temperatures of up to 1200°C . Well crystallized $\text{Sr}_2\text{FeO}_3\text{F}$ was produced by drying, calcination, and firing mixed nitrate and NH_4F solutions. A firing temperature of $\sim 900^{\circ}\text{C}$ seemed to be optimum, although phase-pure material was not obtained. However, heat treatment for 1 week at 1050°C produced complete decomposition into SrFe_2O_4 plus unknown phases.

3.1.1.2 Tailored Ceramic Composites

Commercial and modified cements are being considered as matrices or bases for ceramic waste forms. To test their suitability, samples were prepared for controlled curing and leaching experiments. Individual Tailored Ceramic waste form phases are being examined to delineate their behavior in cement matrices more precisely. An alumina based cement (Secar 71) and two silicate cements (Class C and Class H) were chosen.

NdPO_4 is a monazite structure compound (where neodymium is a model rare earth and a stand-in for the actinides) which is the first Tailored Ceramic phase being tested for compatibility in cement compounds.

Samples were prepared with cement as-received and modified as follows:

- 1) NdPO_4 plus 20 wt % of the cement
- 2) Compositionally adjusted with amorphous SiO_2
- 3) Addition of SiO_2 and NdPO_4 .

Addition of SiO_2 was intended to approximate tobermorite for the silicate cements and feldspar + Al_2O_3 for the aluminate cement.

Each cement formulation was cast to permit sampling at intervals during isothermal curing (60°C). Accelerated hydrothermal leach testing, and characterization of the solids by X-ray diffraction and SEM, were performed on samples taken after 28 and 56 days. Interpretation of the data from X-ray diffraction is underway.

Hydrothermal leaching was conducted for 28 days at 200°C and 30.4 MPa overpressure on subsamples of approximately 0.05 gm (total solids) sealed in noble metal tubes with 0.5 gm deionized water. Solutions were analyzed by atomic emission. Solids remaining after leaching were studied by X-ray diffraction and scanning electron microscopy. Refinement of these studies is continuing.

For all cement composites analyzed, and the presence of NdPO_4 did not appear to alter the hydration products of the cement. Grains of the NdPO_4 remained tightly bonded in the cement, even through leaching, and no alteration of the structure or chemistry of the monazite structure compound was detected. Some of the desired phases were achieved with the compositionally adjusted cements. Experiments on samples cured longer than 28 days should be conclusive.

No neodymium was detected in any of the leachates. The amounts of phosphorus detected were less than that available from the starting cements. Accelerated leaching of NdPO_4 in deionized water under the same conditions has been undertaken to determine its proclivity to release phosphorus without the complicating presence of the cements.

3.1.1.3 Dissolution of Tailored Ceramics

A three-pronged investigation of the stability, dissolution, leaching, and dissolution mechanisms of the crystalline phases which are candidate components for Tailored Ceramics is underway, including (1) measurement of the dissolution of these materials at low temperatures including a study of the dissolution mechanism, (2) measurement of the dissolution and possible breakdown of the solid phases at hydrothermal temperatures, and (3) an investigation of the surface chemistry and surface reaction layers of the leached solid phases utilizing sputter-induced optical spectroscopy as the primary characterization tool.

3.1.1.3.1 Low-Temperature Dissolution of Pollucite

Pollucite (ideal formula $\text{CsAlSi}_2\text{O}_6$) is still one of the leading crystalline hosts for the immobilization of ^{137}Cs . Natural pollucite ground to -45 to -60 mesh was used for the initial experiments. In water at 25°C and at neutral pH, the uptake of cesium into solution resulted in concentrations after 14 days on the order of 0.05 to 0.3 ppm--about at the threshold of the analytical methods. Accordingly, dissolution experiments at low pH where dissolution rates are expected to be much higher were undertaken, with the idea to gradually increase pH and then extrapolate the dissolution rates into the neutral pH range. Under highly acid conditions, cesium, aluminum, and silicon all appear in solution apparently governed by parabolic (dissolution kinetics) rate laws.

3.1.1.3.2 Other Dissolution-Related Studies

Strontium feldspar is being considered as a possible host for ^{90}Sr in a ceramic waste form. As it is not known to occur naturally, it must be synthesized. Several methods for synthesis are being tried to determine the optimum one.

Some literature survey and other preliminary work has been done with a view to determining the stability and alkali extraction from the nepheline (ideally NaAlSiO_4 , usually $\sim\text{Na}_{0.75}\text{K}_{0.25}\text{AlSiO}_4$) phase.

3.1.1.3.3 High-Temperature, High-Pressure Dissolution Apparatus

To simulate conditions in an open system environment, candidate crystalline materials will be leached in a flowthrough system at controlled pressures and temperatures (Figure 3.1). Water from a reservoir is pumped by a pneumatic pump into the system at a predetermined pressure. It is circulated by a metering piston pump through the reaction vessel which is heated in a furnace. Effluent from the reaction vessel may be sampled before or after the quench chamber. Solid samples may be retrieved from reaction vessel and quench chamber at the end of a run.

Several modifications were made to the equipment to extend the period between repairs and to facilitate the repairs. Also, a modification was made to improve the high-temperature sampling.

3.1.1.3.4 Surface Chemistry

Another aspect of the dissolution work is to determine how the surface chemistry of Tailored Ceramics influences dissolution processes. Sufficiently surface sensitive techniques such as sputter-induced photon spectrometry (SIPS), ion scattering spectrometry (ISS), and Auger electron spectrometry (AES) are used to determine changes in surface composition

Figure 3.1. Circulating hydrothermal apparatus from H.L. Barnes, C.W. Burnham and W.F. Downs (1978) "Experimental Evaluation of Geochemical Conditions in Geothermal Energy Systems," Final Report on National Science Foundation Grant No. AER-08473.

due to ion-exchange and/or readsorption (complexing) with solubilized species. Initial work has been undertaken using polished faces of natural monazite single crystals.

3.1.1.4 Fundamental Transmutation Effects

Combined radiation and transmutation effects may be deleterious to crystalline material under a certain combination of circumstances. The experimental design to investigate this is for first examining recognizable crystal structure effects through transmutations induced in synthetic crystalline materials. Since neutron-induced transmutations are easier to introduce in the short term than radioactive decay-induced transmutation, this program will examine the potentials of transmutation effects through the former, using Tailored Ceramic crystalline structures.

The following have been chosen as suitable for this study: Cs → Ba, Sr → Y, Tc → Ru, In → Sn, Lu → Hf, Hf → Lu, Rb → Sr, and Hf → Ta. Of these, depending upon the ready availability of enriched stable isotopes, the Tc → Ru and Hf → Lu transmutations will be examined initially. Some detailed calculations on these isotopes have been completed. The problems associated with performing X-ray diffraction studies on radioactive materials are being examined using the results of these calculations. A typical set of calculated results for the transmutation experiment,

shows that it is possible to achieve about 12% conversion of the ^{174}Hf in 25 days' irradiation. This would amount to about 2.5% of total conversion of all Hf → Lu in the crystalline matrix. Another isotope of this element ^{181}Hf is available with an artificial enrichment of 95%. This isotope undergoes the following neutron transmutation induced changes:

A 100-day irradiation of a crystalline matrix containing ^{181}Hf results in about 3.5% change in the total hafnium. Allowing adequate decay time following irradiation, this can be converted to tantalum in the crystal matrix.

A special glove box facility with a furnace is being set up to incorporate ^{99}Tc in crystalline ceramics. Pending arrival of some of the materials, radiation effects of similar materials are being examined using a fission product spectrum source (a reactor in a shutdown mode) and a combined neutron, gamma, and electron flux of a research reactor.

$\text{CsAlSi}_2\text{O}_6$ (pollucite) has been put forward as a promising Cs fixer, because it is refractory and has a high leach resistance. However, the $\text{Cs} \rightarrow \text{Ba}$ transmutations could degrade the crystal integrity in a few years. Barium has low solubility in $\text{CsAlSi}_2\text{O}_6$. It seems possible, however, that the isomorphous compound $\text{CsFeSi}_2\text{O}_6$ might have host potential since the $\text{Cs}^+ \rightarrow \text{Ba}^{2+}$ transmutation could be accommodated by a $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ transformation. One-day Soxhlet tests on $\text{CsFeSi}_2\text{O}_6$ showed ~5 wt % loss for a preparation fired for 6 hr at 1100°C and ~1 wt % loss for preparations fired (1) 25 hr at 1100°C , (2) 16 hr at 1330°C , and (3) 28 hr at 1400°C . Further losses of ~1 wt % per day were obtained for (2) and (3) after subsequent 3-day Soxhlet tests. These values are far too high to be acceptable.

The preparation (3) was found to be phase-pure by X-ray diffraction, and an uncompact sample of $\text{CsFeSi}_2\text{O}_6$ powder remained single phase after a DTA run to a maximum temperature of 1470°C was carried out. These results show that the thermal stability of $\text{CsFeSi}_2\text{O}_6$ is satisfactory. A heat treatment of 10 hr in N_2 at 1000°C did not cause an observable departure from phase purity.

Mn, Ni, and Co analogs of pollucite were prepared, although not as yet in phase-pure form. Assuming, as found for $\text{CsFeSi}_2\text{O}_6$, that the

lattice parameters were insensitive to the starting stoichiometry, the parameters of the Mn, Fe, Co, and Ni pollucites were found as 13.76, 13.85, 13.69, 13.68 (all ± 0.02) Å, respectively.

A natural pollucite (Smithsonian Institute, Sample 135267) was found to display no evidence for either Fe^{2+} or Fe^{3+} in solid solution. Heating for 1/2 hr in air at 600°C was sufficient to render the initially clear crystal completely opaque. This result was presumably due to dehydration, by analogy with similar known phenomena in beryl and cordierite which occur on heating at $\sim 800^\circ\text{C}$. The associated change in the lattice parameter was $< 0.3\%$ after heating to 600°C , and no further change in the parameter ensued on heating at temperatures to 1200°C .

No effects on the X-ray patterns of $\text{CsAlSi}_2\text{O}_6$ and $\text{CsFeSi}_2\text{O}_6$ were observed after a small dose of γ -irradiation (10^9 R). Samples are presently being neutron-irradiated to a dose of $\sim 2 \times 10^{18}$ nvt (fast) and further samples, either mechanically mixed with U_3O_8 or with the U dispersed as an X-ray amorphous phase, have been prepared for fission-fragment irradiation.

A crystalline material that will accommodate ^{90}Sr and its decay products is being designed. The host must satisfy the usual requirements of a nuclear waste form plus the two criteria of being able to accommodate the decrease in ionic radius upon decay of radioactive $^{90}\text{Sr}^{+2}$ (1.26 Å) to radioactive $^{90}\text{Y}^{+3}$ (1.02 Å) to stable $^{90}\text{Zr}^{+4}$ (0.84 Å), and being able to accommodate the change in valence states as shown above through some charge compensation mechanism.

One possible way to do this is to incorporate Sr into a crystalline solution phase that can also dissolve appreciable amounts of Y and Zr. The first attempt was to try to incorporate SrO into crystalline solution with ZrO_2 . SrO was found to be insoluble (less than 1 mole percent) in ZrO_2 forming a two-phase mix of SrZrO_3 and ZrO_2 at all compositions investigated.

The second attempt sought to determine the limits of crystalline solubility of SrO , Y_2O_3 , and ZrO_2 in the rare earth (RE) oxides La_2O_3 , CeO_2 , Nd_2O_3 , Gd_2O_3 , and Y_2O_3 . Again, however, SrO was found to have negligible solubility forming a two-phase mixture of RE_2O_3 and an unknown $\text{SrO-RE}_2\text{O}_3$ compound of low symmetry. These unknown compounds have been synthesized and are being characterized by powder diffraction techniques.

The third attempt at finding a suitable host for ^{90}Sr fixation was to try to incorporate Sr into a synthetic garnet of the approximate composition $\text{SrCa}_2\text{Fe}_2\text{Si}_3\text{O}_{12}$. Experimental work has commenced and is now underway.

Monazite appears to be very resistant to metamictization from dissolved α -emitters, but after a critical radiation dose monazite might be rendered semi-amorphous and then not recrystallize as recognizable monazite when annealed.

Ce and La monazites, doped with up to 5 mole percent natural U, are presently being irradiated with neutrons. U-doped huttonite and zircon, produced by the usual calcination/firing technique, are being similarly irradiated.

Nine natural monazites from various sources were annealed at 950 and 1100°C and in most cases an X-ray volume contraction of ~1%, together with sharpening of the diffraction lines, was observed. If this result can be associated with α -recoil damage, rather than chemical zoning effects, monazite is clearly not completely immune to radiation damage.

Zirconolite ($\text{CaZrTi}_2\text{O}_7$), doped with U, has been prepared for fission-fragment irradiation. Numerical calculations have been made of the α -recoil damage which would be measured by the TRU-bearing phases in high-level waste. As an indication, if zircon incorporated all the TRU ions (hypothetically), it would be rendered amorphous (with a density decrease of ~16%) after $\sim 10^4$ years.

3.1.2 Formulation and Consolidation Studies

Efforts have been focused on developing a suitable crystalline phase assemblage for simulated Savannah River Plant (SRP) defense waste which will provide a high quality Tailored Ceramic with a minimum of additives. In the initial efforts, a number of samples representing the range of compositions for simulated waste called out in the July 5, 1979, SRL letter from J. A. Kelley to D. L. McIntosh in both untailored and tailored* forms have been made up, hot pressed, and analyzed for phase and microstructural content. The information obtained from these runs has been used to design phase compatibility studies, direct the development of new tailoring schemes, and to orient geochemical stability studies.

With aluminum and iron being the bulk cations in the SRP waste, these elements have to a great extent controlled the properties of the hot-pressed ceramics. Tailored waste samples with the Al/Fe ratio ranging from 0.14 to 22.3 have thus far been examined. Results show that at the lower extreme of Al/Fe, crystalline spinel determines the ceramic properties, while α -alumina (sapphire) dominates at the other extreme. The characterization results from these samples have shown the high Al composition to provide the most promising physical and chemical characteristics for a Tailored Ceramic waste form.

The hot-pressed pellets formed (see Figure 3.2) from the high Al tailored waste composition (Al_2O_3 = 65 to 85 mole percent of calcine) are extremely hard with a density greater than 93% that of theoretical. The crystalline grains are small (2000-10,000 Å) and show a very high degree of crystalline microstructural isolation. Figure 3.3 shows a bright field transmission micrograph of a hot-pressed sample made up

*That is, with selected additions to produce a ceramic with the desired phase assemblage.

Figure 3.2. One inch diameter hot-pressed multiphase ceramic, HASR1
Mole percent composition (Calcine)

Fe_3O_3	3.8%
Al_2O_3	84.8
MnO_2	5.7
U_3O_8	0.17
CaO	0.68
NiO	1.1
Na_2O	3.60
Cs_2O	0.009

Pressing T&P: 1400°C , 3820 PSI
Calculated Density: 3.7833 G/CC
Archimedes Density: 3.826 G/CC
% Theoretical Density: >93%

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NiO	1.1
Na_2O	3.60
Cs_2O	0.009

Pressing T&P: 1400°C , 3820 PSI
Calculated Density: 3.7833 G/CC
Archimedes Density: 3.826 G/CC
% Theoretical Density: >93%

Figure 3.3. Bright field transmission micrograph of high alumina composition simulated SRP waste, sample HASR1.

U = Uraninite

C = Corundum

S = Spinel

↑ = Magnetoplumbite

Figure 3.3. Bright field transmission micrograph of high alumina composition simulated SRP waste, sample HASR1.

- U = Uraninite
- C = Corundum
- S = Spinel
- ↑ = Magnetoplumbite

from Kelley's high Al (without Al removal) composition and without the addition of Ion Siv IE95. The micrograph illustrates the dense, polyphase nature of the ceramic. The four constituent phases present are (Fe,Mg)-spinel (hercynite) labelled S, α -alumina (sapphire) labelled C, UO_2 uraninite labelled U, and magnetoplumbite shown with arrows. No continuous intergranular glassy phase is present and each phase is microstructurally isolated from others of the same type. SIMS analysis of this sample showed Cs to be retained during hot pressing and STEM analysis indicated that it is primarily located in the magnetoplumbite structure. Work is continuing with a number of high Al compositions to optimize hot-pressing parameters and to determine the effects of adding ranges of trace elements and Ion Siv IE95.

To establish the basic phase compatibility relationships controlling the ceramic formation, studies have been initiated on the $\text{CaO-Fe}_2\text{O}_3\text{-Nd}_2\text{O}_3$ and $\text{CaO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ phase diagrams. Preliminary leach testing experiments at 90°C in distilled water have been started on samples of hot-pressed high Al waste.

3.1.3 Radiation and Transmutation Effects

This task was initiated to study the effects of nuclear decay radiation and transmutations on Tailored Ceramic waste forms now under development. The objective is to carry out a series of irradiation experiments that simulate radiation and transmutation effects in proposed Tailored Ceramic materials on an accelerated time scale. The results will be used to assess the durability of Tailored Ceramics in isolating nuclear waste nuclides from the environment over a geologic time scale.

Results of the initial program effort included the establishment of a program plan and key contacts with other researchers in the field, the initiation of a detailed literature review of the radiation damage field as applied to nuclear waste forms, and a start on formulating the program's first radiation damage experiments.

A literature review on radiation and chemical effects on nuclear waste forms was initiated during the report period. The objective of this background research is to establish a firm foundation for planning the experimental program and the interpretation of the results. The literature review emphasizes the simulation of radiation effects in high-level nuclear waste forms; radiation effects on covalent (plus some ionic) metal oxides which are basic constituents of proposed Tailored Ceramic waste oxide compositions; the formation and properties of the metamict state; and the effects of alpha particles on naturally occurring minerals. A draft report entitled "The Simulation of Radiation Effects in High-Level Nuclear Waste Forms" is in preparation. This review covers work on glass as well as crystalline waste forms. A second draft report reviewing radiation damage effects in naturally occurring minerals has been initiated.

Work has begun on formulating the program's first radiation damage experiments. It appears at present that these experiments will be reactor neutron irradiations of doped Tailored Ceramic crystalline phases, with the dopants consisting of one or more isotopes with large thermal-energy neutron cross sections. The major effects these experiments will simulate include alpha-decay and recoil nucleus damage and transmutation damage. The phases to be investigated, and the dopants and doping procedures to be used, will depend in large measure on those phases selected under the Task 2 and Task 3 program efforts to host key waste radionuclides. Attractive choices at present include ^6Li doping of a spinel phase and ^{10}B interstitial doping in monazite.

A spent thermoelectric generator with a ^{90}Sr heat source has been located with the cooperation of the Department of Energy. The ^{90}Sr is incorporated in the crystalline phase $^{90}\text{SrTiO}_3$, a form of the mineral phase perovskite. This mineral is similar to some crystalline phases proposed in Tailored Ceramics formulations. About 35% of the ^{90}Sr in the source has decayed to the stable nuclide ^{90}Zr in the 20 years since

this source was manufactured. The source thus appears to provide an ideal opportunity to study transmutation damage in a single-phase crystalline material. Means to acquire this source are now being pursued.

3.1.4 Geologic Strata Compatibility

This task had not been initiated during the quarter being reported.

3.2 PROCESS AND EQUIPMENT DEVELOPMENT

3.2.1 Engineered Containment

The results of the trade study currently in progress will be used to guide the development of the process(es) for consolidation of Tailored Ceramics and the loading of canisters with the dense ceramic bodies. The process will be constrained to mate with the SRL process flow diagram and to utilize both the waste materials separation processes and the final clean canister handling process.

Investigations of current technology have begun with the review and assessment of published reports. In conjunction with this review, a file has been established for the collection and cross-referencing of pertinent report data.

A trade study whose thrusts are to identify the critical process parameters involved in the production and the containment of consolidated Tailored Ceramic waste forms, and to optimize the canister size, weight, heat load, and matrix material selection combinations has been initiated.

3.2.2 Process Evaluation and Definition

Process flow diagrams of increasing complexity will be prepared for promising process sequences leading to the issuance of a report at the

end of the fiscal year. Order of magnitude cost estimates will be prepared on the more promising process sequences. In all cases, these sequences will utilize the existing SRL front-end waste removal and stream separation process steps.

Calcination studies of waste compositions containing aluminates will be performed to evaluate the feasibility of producing a calcine which can be consolidated at an acceptable temperature to form a dense Tailored Ceramic body.

Waste technology reports have been assessed for their applicability to the Tailored Ceramic process. Information on the specific wastes to be immobilized is undergoing evaluation. The need for the removal of aluminum from the waste is in question, with the thought that its ceramic end products, Al_2O_3 and Al-spinels, are very stable ceramic species and are quite acceptable as final chemical forms. One critical parameter in these considerations is the minimum satisfactory consolidation (sintering) temperature at which a dense closed-pore ceramic containing possible high amount of Al_2O_3 either as corundum or in a spinel can be formed from the waste calcine.

Preliminary flow diagrams and material balances are being developed for processes in which the alumina is not removed from the waste. These sequences involve the use of the existing SRL plan for removing the supernate and the sludge fractions from the waste tanks, an additive "tailoring" step, a calcination step, and a calcine densification step (such as extrusion or cold pressing) to form a body which is hot pressed (either uniaxially or isostatically). The logistics of the sizes and the numbers of pressings, and of process lines, are being examined in the Task 6 trade study.

In the considerations of the "alumina-in" process sequence, it is evident that a highly sinterable alumina must be produced in the calcination step in order that the final hot pressing be possible at tractable temperatures (1200°C, as a nominal maximum). Accordingly a test study of the calcination process step has been initiated using guidance from Task 3.

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