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DEVELOPMENT OF TAILORED CERAMICS
FOR
GEOLOGIC STORAGE OF NUCLEAR WASTES

QUARTERLY PROGRESS REPORT
JANUARY 1, 1980 THROUGH MARCH 31, 1980

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
SAVANNAH RIVER OPERATIONS OFFICE
UNDER CONTRACT
DE-AC09-79ET 41900

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May 15, 1980

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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 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

In the second quarter of activities on developing Tailored Ceramic waste forms for SRP waste compositions, work has primarily been oriented towards determining the chemistry controlling the incorporation of the waste elements into the crystalline phases of the high-alumina content ceramic and the major factors affecting the consolidation process. Major advances in this quarter include:

- 1) The development of an initial rare earth tailoring formulation based on forming a "stuffed" magnetoplumbite structure to incorporate the major waste radionuclides.
- 2) Determining the compatibility relationships between the phases identified in the high-alumina Tailored Ceramic.
- 3) Description of the distribution of the major waste elements in the crystalline phases.
- 4) Microstructural characterization which has demonstrated that no continuous glassy phase is present in the hot-pressed high-alumina Tailored Ceramic.
- 5) Incorporation of an integral Al_2O_3 "cold" ceramic graded outer surface for the waste form to isolate the tailored waste from reactions with die surfaces, and to provide a nonradioactive surface for handling of the waste form.
- 6) Demonstration of the utility of spray calcining of sludges as a powder preparation technique for obtaining the desired mineralogy and reactive processing for high-alumina ceramic forms.
- 7) Initial measurements on cesium retention of powder during calcining and consolidated material during hot pressing.
- 8) Leach resistance and mechanical strength testing initiated.

During the quarter, under generic ceramic studies, research on the design and synthesis of oxide and phosphate ceramic waste forms has continued with most emphasis on fluorite-structure oxides and on rare earth phosphates with the monazite structure.

Three classes of potential host materials for the fixation of iodine have been investigated. Of these, the lead oxyiodides have proved to be unstable, and boracite structure compounds have proved to be difficult to prepare by ceramic processing techniques leaving sodalite structure materials as currently the most promising.

Research on calcine-cement composite waste forms suggests that such a material with a very low-leach rate can be prepared by low-temperature processes.

Studies are underway on the dissolution mechanisms of monazite, pollucite, nepheline, and several other crystalline ceramic components. Monazite continues to be stable under even the most extreme test conditions employed.

Progress on Radiation and Transmutation Effects during the quarter included the completion of two internal reports reviewing the literature on the simulation of radiation effects in high-level nuclear waste forms and on natural radiation damage in solids, further efforts to obtain a surplus thermoelectric generator with a $^{90}\text{SrTiO}_3$ heat source for radiation damage studies, and additional planning for the first radiation and transmutation effects experiments to be performed on Tailored Ceramic waste forms.

2.2 TAILORED CERAMIC PROCESS AND EQUIPMENT DEVELOPMENT

Based on a parametric study of packing ceramic waste forms into canisters, the intrinsic high-waste loading of the form is retained most simply by using a large, single consolidated piece closely fitting the canister. Because practical canister sizes range from 1 to 2 ft in diameter, hot isostatic pressing, which is capable of producing such a monolith, is a primary candidate for process study. A study of the effect of mass throughput requirements and required numbers of consolidation processing stations also pointed out the benefits of preparing large ceramics bodies.

A Tailored Ceramics processing concept, designed to exploit the high aluminum and iron content in the SRP waste, was derived. It is based on the

reference borosilicate glass DWPF process, and has been divided into nine subsystems for process design considerations. Current ceramic formulations point out the incentive to reduce sodium content in the waste. Accordingly, laboratory studies on lowering sludge sodium content were initiated. In addition, review of alternate methods for separation of cesium from the process liquor stream identified as feasible the use of a second duolite ion exchange unit to replace the reference process zeolite unit.

3.0 TECHNICAL PROGRESS

3.1 TAILORED CERAMIC WASTE FORM DEVELOPMENT AND CHARACTERIZATION

3.1.1 High-Alumina Tailored Ceramics

The current laboratory specimens of High-Alumina Tailored Ceramics are 1-in.-diameter pellets with an integral graded Al_2O_3 outer surface as shown in Figure 1. These samples are prepared from simulated dried hydroxide sludges similar in form to that shown at the left in the figure. The hydroxide sludges are prepared with the SRP "composite without Al removal" composition with a number of trace elements added along with exaggerated amounts of cesium and strontium to facilitate characterization. The dried hydroxide sludges are routinely ground in a mechanical chopping mill, then slurried in water with the tailoring agents. The tailored slurries are then either dried and furnace calcined or spray calcined. The calcines are further ground if necessary (not required for spray calcines), cold formed in a mechanical press with $\text{Al}(\text{OH})_3$ surrounding the calcined powder, and subsequently reactively hot pressed at 1250 to 1300°C in nitrogen or under vacuum.

The ceramic samples are nonporous (3.8 to 4 g/cm³) and show no continuous intergranular glassy phases as determined by dark field transmission electron microscopy. The grain size is typically submicron with excellent intergranular mixing of separate phases. This intergranular mixing provides microscopic encapsulation of the individual phases as shown in the example in Figure 2 for a 50% by weight composite waste loaded sample. Current research is being conducted on samples containing 30 to 60% by weight waste loading as oxides based on the SRP "composite" waste composition.

3.1.1.1 Formulation

Tailoring and Elemental Distribution

Untailored hot-pressed SR high-Al compositions (~85 mole % Al_2O_3) produced a phase assemblage of iron-manganese spinel (XY_2O_4), corundum (Al_2O_3), uraninite

Figure 1. Homogeneous dried hydroxide sludge reactively hot pressed into 1 inch diameter pellet with integral graded Al_2O_3 outer surface.

Figure 2. Transmission electron micrograph of 50% by weight "composite" waste loaded ceramic; showing intergranular mixing and microscopic encapsulation of individual grains (i. e. no continuous veins or exaggerated grains of a single phase).

(UO_2), and two hexagonal β -types, like β and β''' alumina. Since β -alumina types are fast ion conductors, subsequent SR compositions were tailored to promote the formation of stuffed magnetoplumbite types such as $\text{Na}_{0.5}\text{La}_{0.5}(\text{Al}, \text{Fe})_{12}\text{O}_{19}$.

The same four phases were identified by combined morphological appearance and elemental analysis using STEM. The corundum contained a small amount of iron in solid solution, the spinel hosted Al, Mn, Fe, and Ni, while the β phase acted as host for Al, Mn, Fe, Na, Cs, Ca, and Ni (Table 1). The presence of Ar was detected in the β phase; it came from the ion beam thinning process used to prepare the electron microscope sample. Normally, Ar is only detectable in glassy phases but here it indicates the open crystal structures of the β -types. Lattice fringe imaging of the β -types showed local stacking changes indicative of localized compositional variations from the hosted species.

The known compositional flexibility of magnetoplumbite-related structures permits chemical tailoring to combine large divalent ions with Al^{3+} and balance large monovalent ions with large trivalent ions, e.g., rare earths, to produce stuffed magnetoplumbite phases. This allows simple tailoring with alumina and rare earth (in excess of the amount of rare earth already present in the waste).

A 61 mole% Al_2O_3 composition with 1 mole% SiO_2 was tailored with rare earth and alumina: a spinel with higher Fe^{2+} content, uraninite with some Zr^{4+} and rare earth in solid solution, a nearly cubic $\text{RE}(\text{Al}, \text{Fe})\text{O}_3$ perovskite, and a hexagonal "stuffed" magnetoplumbite were found. A tailored composition aimed at maximizing the formation of magnetoplumbite contained 74 mole% Al_2O_3 and 3 mole% SiO_2 : a stuffed magnetoplumbite with minor iron-manganese spinel, corundum, and uraninite were found. The stuffed magnetoplumbite phase, therefore, does host significant amounts of Si^{4+} without the formation of nepheline or other high silica or glassy phases. However, when SiO_2 was present at greater than 4 mole% and tailoring was incorrect, i.e., excess sodium was present, nepheline was found as a fifth compatible phase.

TABLE 1
CURRENT HIGH Al TAILORED CERAMIC MINERALOGY
AND WASTE ELEMENT DISTRIBUTION

Phase	Nominal Composition	Elements Detected
Corundum	Al_2O_3	Al, Trace Fe, Ti
Spinel	$(Mg, Fe, Ni, Mn)(Al, Fe)_2O_4$	Al, Mn, Fe, Ni, Ti, Trace Mo, Si
Uraninite	UO_2	U, Trace Zr, Th
Magnetoplumbite	$XY_{12}O_{19}$ where $X=Ca, Sr, Ba, RE_{0.5}^{+}Na_{0.5}, etc.$ $Y=Al, Fe, Ti, Si, Ni, Mn, etc.$	Al, Mn, Fe, Ni, La, Na, Ca, Ti, Ar, Trace Sr, Cs, Ba, Si, Mo, Ce, K
Perovskite	$RE(Al, Fe)O_3$	La, Al, Fe, Trace Ca, Na, Ce
Pseudobrookite	$(Fe, Ti, Al)_2TiO_5$	Fe, Ti, Al

Several high-iron compositions were hot pressed, but magnetite and defect $(\text{Ca},\text{Na})\text{UO}_{4-x}$ phases formed. However, $(\text{Ca},\text{Na})\text{UO}_{4-x}$ is an undesirable phase as uranium is in valence states greater than 4. Also, since Na, Ca, Sr, and Cs go to to form this defect uranate, they are not available to form magnetoplumbite. However, the main problem is that the reduction of the U^{6+} present in the SRP sludge to U^{4+} , the only reasonably stable valence state for insoluble uranium compounds in a hydrothermal environment, is accompanied by a reduction of much of the iron to the ferrous state. For a desirable phase assemblage, this requires that the ferrous iron be crystal chemically associated with aluminum. Additional problems in producing a ceramic with the high iron compositions arose during hot pressing.

Each sample was analyzed by energy dispersive X-ray microanalysis with each of the elements in the Tailored Ceramic being detected in specific phases. The results of these elemental distribution analyses are shown in Table 1.

Phase Compatability

Phase relations in the high alumina region of the $\text{CaO}-\text{Nd}_2\text{O}_3-\text{Al}_2\text{O}_3$ ternary system were determined in air at 1300°C . This data was combined with existing information on the lower portion of the diagram to completely describe the phase compatibilities.

The experimental findings suggest that a partial solid solution exists between the calcium magnetoplumbite, $\text{CaAl}_{12}\text{O}_{19}$, and a high-temperature ($>1500^\circ\text{C}$) neodymium magnetoplumbite. At 1300°C , the high-temperature rare earth magnetoplumbite is metastable and three distinct compatibility regions exist (magnetoplumbite-perovskite, magnetoplumbite-corundum, magnetoplumbite-corundum-perovskite). The information in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{Nd}_2\text{O}_3$ ternary system can be used as a model for the alkali + alkaline earth- $\text{Al}_2\text{O}_3-\text{RE}_2\text{O}_3$ system. Since Mg spinel is known to be compatible with LaAlO_3 , and the compatibility of Mg, Fe, Ni-spinel with REAlO_3 is known from current results with hot pressing, then a quaternary tailoring diagram may be constructed as shown in Figure 3. The wide range of solid solution of the magnetoplumbite in the alkali + alkaline earth- $\text{RE}_2\text{O}_3-\text{Al}_2\text{O}_3$ face of the diagram makes the phase compatibility regions quadrilaterals rather

FIGURE 3. TAILORING SCHEMATIC FOR SR COMPOSITE
COMPOSITION WITHOUT AL REMOVAL.

than planar triangles through the tetrahedron (Figure 4). The newly determined defect nature of the perovskite phase and the STEM characterization, e.g., solid solubility of (Fe,Mg,Ni)O in magnetoplumbite, also increases the size of the compatibility quadrilaterals (Figure 4) and enables a wide variability of waste compositions to be accepted by a predetermined phase assemblage at a given waste loading. The phase equilibria determined in air at 1300°C are consistent with the phase assemblages produced during hot pressing except that UO_2 was not considered in the pure phase experiments.

3.1.1.2 Consolidation

Investigations have continued on determining the factors controlling the reactivity, phase formation, elemental distribution, and grain growth during consolidation of the high-alumina content Tailored Ceramics. Both hot pressing and sintering studies are being pursued to derive tailoring formulations suited to each consolidation method. The hot pressing studies are being conducted using both spray calcined and furnace calcined powders. These experiments have shown the spray calcined powders to have excellent reactivity, producing sub-micron grain formation in the ceramic products. The same phase composition and elemental distribution has been observed in the ceramic waste forms prepared from spray calcined powders as from ball-milled furnace-calcined material.

The hot pressed samples are currently being prepared with an integral graded Al_2O_3 outer layer formed by surrounding the simulated waste material with $\text{Al}(\text{OH})_3$ powder before hot pressing. As shown in Figure 1, this provides a cold outer coating which is an integral part of the ceramic form while preventing any contact of the graphite dies with the reactive elements in the simulated waste.

The usefulness of finely powdered $\text{Al}(\text{OH})_3$ (a material produced in multi-ton quantities during aluminum production) as a tailoring additive in adsorbing the slurried simulated waste has also been demonstrated. Mixing the $\text{Al}(\text{OH})_3$ with slurried, dried hydroxide composite waste compositions produces a fine grain, totally amorphous powder after calcining; this product is highly suitable for consolidation processing.

MAGNETOPLUMBITE - PEROVSKITE - CORUNDUM COMPATIBILITY

CASE A = IF MAGNETOPLUMBITE DID NOT EXHIBIT
SOLID SOLUBILITY

CASE B = IF MAGNETOPLUMBITE ONLY EXHIBITED
SOLID SOLUBILITY IN THE Al_2O_3 - RE_2O_3 -
ALKALI+ALKALINE EARTH SYSTEM

CASE C = MAGNETOPLUMBITE EXHIBITS SOLID SOLUBILITY
IN Al_2O_3 - RE_2O_3 -ALKALI+ALKALINE EARTH-(Mg, Fe, Ni)O
SYSTEM

FIGURE 4. EXAMPLE OF MAGNETOPLUMBITE-PEROVSKITE-CORUNDUM COMPATIBILITY

Cesium retention studies have been initiated on the calcined powders and hot pressed ceramic waste forms. Volatilization of the cesium has been shown by an atomic absorption technique to be retarded by the rare earth tailoring of the simulated waste material. Cesium has been shown to be completely retained by the simulated waste powders during calcining at 600°C and no significant volatilization of Cs up to 800°C was observed during calcining. Neutron activation analysis of a tailored high Al ceramic pellet, hot pressed at 1300°C, showed greater than 86% of the cesium to be retained in the ceramic. At the lower temperatures used for HIPing (Hot Isostatic Pressing) (<1200°C), it is expected that complete Cs retention will be readily achieved. The effects of lowering the hot pressing temperature and new tailoring formulations on Cs retention are being examined. In addition, new formulations using low levels of Ti to tailor the magnetoplumbite phase to accept a higher alkali loading have shown promise and reduce the temperature required for consolidation. Further studies using specific tailoring additions to lower consolidation temperatures and improve sintering characteristics are being pursued.

3.1.1.3 Candidate Waste Characterization

Work continued on physical and chemical characterization of site-specific candidate wastes. The Savannah River Plant was visited to discuss waste characterization and to view associated plant operations. Discussions were held regarding waste tank sampling, analytical sample preparation and analysis techniques, and laboratory quality control.

3.1.1.4 Future Work

New tailoring formulations to increase the alkali loading of the "stuffed" magnetoplumbite structures using Ti are being explored, and extensive leaching tests are being initiated for the third quarter of the program. Work will continue on studying the parameters controlling the consolidation processes in sintering, hot pressing, and hot isostatic pressing.

3.1.2 Generic Ceramic Studies

3.1.2.1 Ceramic Waste Form Design and Synthesis

The present main thrusts of the generic ceramic waste form design and synthesis are three:

- 1) Creation of ceramics with bulk compositions close to the composition of Savannah River Plant wastes, primarily based on high silicate phases.
- 2) Generic investigations of oxide and phosphate ceramic phases, notably those with fluorite and monazite structures.
- 3) Investigations of possible host phases for iodine and technetium.

Ceramic Phase Formation from Savannah River Sludges

Various further simulations of Savannah River Plant defense waste sludges were studied. In most cases, ~10 mole % Al and ~20 mole % Si were added to try to fix the Na as nepheline. Firing (in air) at 1050°C produced nepheline, spinel, hematite, and U⁶⁺-bearing phases, as found by X-ray diffraction. Firing at 1200°C essentially removed the nepheline and hematite and led to enhancements of the spinel and amorphous phases. Subsequent slow cooling over the 900-600°C range restored the phase assemblages observed on firing at 1050°C. Chemical spiking with Cs revealed pollucite formation at >2% Cs, but the nonlinearity of the pollucite intensities with Cs content implies that, at ~1% Cs, Cs was primarily incorporated in the nepheline.

Hot pressing at 1300°C of the Al-rich simulated sludges yielded a well-consolidated product with similar phase constitution to the sintered preparation, except that the U in the hot-pressed mixture was in the uraninite form. Hot pressing of Fe-rich simulations at ~1000°C yielded well-consolidated products.

Investigations of Synthetic Mineral Phases for Specific Radionuclides

Oxide Ceramics with the Fluorite Structure: Fundamental phase relation studies in the system U-Th-Ce-Zr-RE-O (RE = the rare earths, represented by Nd and Gd) have been continuing throughout the report period.

The system has been broken down into selected subsystems which are most relevant to waste forms. In particular, phase relation studies are being conducted on the systems $\text{UO}_{2+x}\text{-CeO}_2\text{-ThO}_2\text{-ZrO}_2$, $\text{Gd}_2\text{O}_3\text{-ThO}_2\text{-CeO}_2\text{-ZrO}_2$, $\text{Gd}_2\text{O}_3\text{-UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2$, and $\text{Nd}_2\text{O}_3\text{-UO}_{2+x}\text{-CeO}_2\text{-ZrO}_2$ at 1200°C in air. The study of the system $\text{UO}_{2+x}\text{-CeO}_2\text{-ThO}_2\text{-ZrO}_2$ is essentially completed.

Monazite: The main objectives were to (1) synthesize $\text{Ca}_{0.5}\text{U}_{0.5}\text{PO}_4$ (monazite), (2) examine the $\text{NdPO}_4\text{-Ca}_{0.5}\text{Th}_{0.5}\text{PO}_4\text{-Ca}_{0.5}\text{U}_{0.5}\text{PO}_4$ (UPTP) system, and (3) determine the appropriate conditions to maximize the monazite solid solution region within the UPTP (uranium phosphate-thorium phosphate) system.

The $\text{Ca}_{0.5}\text{U}_{0.5}\text{PO}_4$ (monazite) phase was prepared by firing a "wet method" prepared specimen in an argon atmosphere for 12 hours at 1150°C . The desired phase was not formed by reactive hot pressing at 3500 psi for 1/2 hour at 1110°C , 1200°C , or 1300°C .

Phase equilibria within the UPTP system were studied under three different conditions. When the UPTP mixtures were fired in air for 6 hours at 1200°C , the phase-pure monazite region extended down to the composition $0.2 \text{ Ca}_{0.5}\text{U}_{0.5}\text{PO}_4\text{-}0.8\text{NdPO}_4$ in the $\text{NdPO}_4\text{-Ca}_{0.5}\text{U}_{0.5}\text{PO}_4$ binary system. When the UPTP mixtures were fired in an argon atmosphere or in air within graphite crucibles, the phase-pure monazite region only extended down to $0.15 \text{ Ca}_{0.5}\text{U}_{0.5}\text{PO}_4\text{-}0.85\text{NdPO}_4$ within the $\text{NdPO}_4\text{-Ca}_{0.5}\text{U}_{0.5}\text{PO}_4$ system.

Thorite rather than huttonite was formed when 20 mole %, $\text{Li}_2\text{O/Li}_2\text{WO}_4$ flux was added to a ThSiO_4 calcine and the mixture fired at 1200°C for 72 hr. This result did not obtain when 2 mole % of the flux was added to the calcine or when either 2 or 20 mole % of $\text{Li}_2\text{O/Li}_2\text{MoO}_4$ flux was added. Minimum flux additives (including fluorides) for thorite formation are under investigation.

Ceramic Phases for Cesium Fixation: Cordierite, which in nature often contains cesium in structural channels, was synthesized easily by ceramic techniques at 1350°C in air. Infrared spectroscopy showed natural cordierites to contain significant amounts of CO_2 in addition to H_2O . Natural beryls and pollucites, on the other hand, did not contain detectable CO_2 . Hollandite formation was examined further. Although the lattice parameter varied as a function of the precise hot-pressing schedule, mixtures of TiO_2 and $\text{BaAl}_2\text{Ti}_5\text{O}_{14}$ were formed rather than hollandite. Cesium additions to air-fired preparations at $1000\text{--}1400^{\circ}\text{C}$ produced lattice parameter shifts, but it has not yet been verified whether cesium was retained rather than lost by volatilization.

Ceramic Phases for High-Fluoride Wastes

Thorex wastes would require different specially tailored crystalline phases because of the necessity of fixing fluorine in addition to the other waste constituents. This aspect of the work is an ongoing effort to find suitable fluorine-rich crystalline host materials.

Powder infrared studies of fluorapatite $[\text{Ca}_5(\text{PO}_4)_3(\text{F}^-, \text{OH}^- \dots)]$ made by calcination and firing of stoichiometric mixtures of $\text{Ca}(\text{NO}_3)_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ and NH_4F solutions showed extra absorption lines near 1000 cm^{-1} , in addition to absorptions reported by other workers on natural or hydrothermally produced fluorapatites. From the sensitivity of those lines to heat and fast neutron irradiation, a plausible assignment is OH^- for their origin. The tendency of fluorapatite to pick up anions other than F^- in wet preparations must be regarded as undesirable, for its use as a radwaste ceramic phase in F^- -bearing wastes.

Crystalline Hosts for the Fixation of Iodine

Sodalite: I-sodalite was found to be fairly stable after annealing at temperatures as high as 1350°C . No ion exchange was observed by X-ray diffraction when I-sodalite was ball-milled with 2M NaCl solution for several days and also when Cl-sodalite was similarly treated with 2M NaI solution. No ion exchange was observed when powdered natural Cl-sodalite was treated similarly with 2M NaI. No degradation of the natural Cl-sodalite was observed after a fast neutron dose of 2×10^{17} nvt.

Boracite: No change in X-ray patterns was observed after 10 days' ball milling of natural $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$ powder in 2M NaI solution. No wet preparations yielded boracite as a precipitate. 2×10^{17} nvt of fast neutrons had no observable effect on $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$.

Pb Oxyiodides and Chlorides: Complete reaction was observed between PbO and NaI, as expected, from the known reactions between PbO and NaCl, although the nature of the product of the NaI reaction is not yet known. The analogue experiments with NaCl gave various mixtures of blixite $[\text{Pb}_2\text{Cl}_2(\text{O},\text{OH})]$ and $8\text{Pb}_7\text{O}_6\text{Cl}_2$. Thermal stabilities of these products, however, were not good; 48 hr at $200\text{--}400^\circ\text{C}$ caused complete decomposition.

Although AgI remained crystallographically unaltered on heating for 1 day at temperatures close to the melting point (558°C), CuI, another very soluble iodide, transformed to CuO at temperatures above $\sim 200^\circ\text{C}$. ($\text{Ba}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$ was not studied as it is known to dehydrate at 200°C and consequently become quite soluble in hot water.)

3.1.2.2 Tailored Ceramic - Composites

Introduction

The scope of the research of this subtask as originally conceived included determining the chemical compatibility of a "fully" fired ceramic waste form with a cement matrix. Experimentation with dominant individual crystalline phases comprising the Tailored Ceramics was also initiated in order to place the understanding of the waste form compatibility on a more fundamental level. This combination also offers the practical possibility of using a cement matrix to consolidate calcined (i.e., crystalline) tailored waste at lower temperatures.

During this quarter, the scope of the investigation was expanded to include different types of waste forms typical of a calcined SRP sludge and the precursor to a commercial Tailored Ceramic formulation. In addition to the continuing research effort into the compatibility of monazite, an individual phase in

phosphate-based ceramics, the Cs and Sr containing phases, pollucite and scheelite, respectively, were incorporated into a suite of commercial and adjusted cementitious formulations.

Cured Cements

Commercial and compositionally adjusted calcium silicate and calcium aluminate cements were each separately cast with NdPO_4 , PSU-SPC-2+U, SRP calcines, and SrMoO_4 for long-term curing at 60°C . Sampling occurs at fixed intervals of 28 days, 56 days, 6 months, 1 year, or store. Samples at each interval are analyzed by X-ray diffraction and prepared for hydrothermal leaching for 21 or 28 days at 200°C , 300 bars. The resultant leachate and solids are analyzed and studied with the SEM. Leached samples of cementitious composites with NdPO_4 cured 6 months are undergoing analysis.

X-ray data from the solids after 6-month curing were compared with those from 1- and 2-month curing. Hydration of the cement phases is increasing as expected, but the patterns still exhibit distinct peaks for the waste phase. X-ray data from the cementitious composites cured 1 month with the calcines and with SrMoO_4 (scheelite structure) are being collected and analyzed.

Because of differences in their curing and chemical properties, the phosphate cement composites are being subjected to the same curing schedule. Phosphate cement has been cast with both calcines, and testing and analyses (including hydrothermal, modified Paige and Soxhlet leaching) were begun after 1 week of curing.

Hot-Pressed Cements

The first hot-pressed cementitious composites to be studied were calcium aluminate cements (Secar) with and without NdPO_4 (20 wt %). These samples were subjected to modified Paige and Soxhlet leaching, and the leachates were analyzed for cement and waste ions. NdPO_4 is still visible in the leached sample (at 50x). XRD and SEM analyses will follow.

Additional hot-pressed composites have been prepared and are currently undergoing the three above-mentioned leach tests. These composites include:

- 1) Calcium silicate cement (Class H)
- 2) Class H plus PSU-SPC-2+U
- 3) Class H plus $\text{CsAlSi}_2\text{O}_6$
- 4) Calcium aluminate cement plus SRP calcine.

Waste Forms

Baseline leach data (via solution analyses) for the five simulated waste forms currently under study are nearing completion. The waste forms were sealed in gold capsules with a ten-fold excess of water (same procedure as is used for cementitious composites) and held 21 days at 200°C , 300 bars. The leached solids will be analyzed by X-ray diffraction for comparison to preleach XRD data. Leachate analysis is being accomplished by plasma emission spectrophotometry.

3.1.2.3 Dissolution of Tailored Ceramics

Introduction

The stability of a ceramic waste form in the presence of aqueous solutions can be no better than the stability of the individual crystalline phases. Accordingly, the approach has been to investigate the dissolution behavior (mechanism and kinetics) of those crystalline forms that have already been identified as good candidate host phases for radionuclides. At a later time, it will be necessary to extend these studies to the integrated ceramic materials.

Two approaches have been used: (1) the determination of rate of solution in low temperature aqueous solutions by analysis of leach solutions as functions of time, temperature, and pH, and (2) investigations of the solid phases with surface and near-surface characterization techniques also as a function of time, temperature, and pH.

Dissolution Studies of Solid Crystalline Phases

During the past 3 months, leaching experiments have been conducted on five mineral phases which are prospective candidates for encapsulating radioactive waste. They are monazite $(\text{Ce,La,Th})\text{PO}_4$, pollucite $\text{CsAlSi}_2\text{O}_6$, sodalite $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{Cl}_2$, beryl $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$, and cordierite $\text{Al}_3(\text{Mg,Fe}^{+2})_2[\text{Si}_5\text{AlO}_{18}]$. These single crystalline samples were hydrated separately in deionized water in 200°C and 300°C for 24 hours. After hydration, the sample surfaces were examined by scanning electron microscopy and the concentration-versus-depth profiles obtained by sputter-induced photon spectrometry (SIPS).

The surfaces of pollucite, sodalite, and cordierite after hydration showed signs of etching even on visual examination. Figures 5(a) and 5(b) are scanning electron micrographs (mag. $\sim 1000\times$) showing the surface of a sodalite sample before and after hydration. The observed change in the surface topography is typical in all three samples of pollucite, sodalite, and cordierite, and we conclude that the surface must be dissolving congruently even in 200°C deionized water. The concentration-versus-depth profiles of Mg and Na in cordierite were measured by the SIPS technique. An Ar^+ ion beam sputtered the sample surface and the optical intensities of the Mg 2852 Å and Na 5891 Å lines emitted by the sputtered excited atoms were monitored as a function of time. The depth of the sputtered crater was determined by a Talysurf profilometer. Figure 6 shows the Mg and Na profiles in the hydrated cordierite surface. Mg and Na are depleted up to a depth of $1.5\ \mu\text{m}$ from the surface, indicating Mg and Na are leached out in exchange with in-diffusing H^+ ions. The surfaces of pollucite and sodalite were etched so extensively that we were unable to obtain satisfactory depth profiles.

In contrast to pollucite, sodalite, and cordierite, the surfaces of the monazite and beryl samples remained unchanged after hydration. Elemental depth-profiles for monazite and beryl also did not show any depleted regions, indicating that they were reasonably inert against attack by water at the temperature investigated.

Fig. 5(a) Sodalite surface before hydration.

Fig. 5(b) Sodalite surface after hydration at 200°C deionized water for 24 hours.

Fig. 6 Mg and Na depth-profiles in cordierite after hydration in 200°C deionized water for 24 hours. The leached depth is approximately 1.5 μm, indicated by the depletion of Mg and Na.

Dissolution Kinetics of Ceramic Phases in Aqueous Solutions

Monazite: NdPO_4 powder synthesized in the laboratory was selected as an experimental material. It was found that the rate of dissolution of NdPO_4 in deionized water was too slow for the uptake of Nd^{3+} in solution to be measured. Accordingly, the solutions were taken to extreme pH values to enhance solution rates.

At pH = 1.3 after 28 days at 25°C , 5 ppm Nd^{3+} was detected in the leach liquids. At pH = 10.2 after 22 days at 25°C , the Nd^{3+} concentration in the leach liquid remained below the limit of detectability.

Monazite appears to be extremely resistant to leaching, even under extreme pH conditions.

Pollucite: Natural pollucite crystals (with some admixed quartz) were used as an experimental material. The solubility of pollucite at 25°C and seven different pH conditions was determined.

One gram samples of pollucite, crushed to -60+100 mesh size, were reacted with 100 cm^3 of water. Both buffered and unbuffered solutions were used. Figure 7 gives some preliminary results. It can be seen that cesium extraction from the pollucite is rapid only at extremely low pH's. No cesium could be detected in a pH-5.8 leach solution, even after 50 days. No cesium was detected after 10 days in leach solutions with pH = 10.14 and pH = 12.34.

Strontium-Feldspar: The triclinic high temperature form of $\text{SrAl}_2\text{Si}_2\text{O}_8$ has been synthesized by dry-firing of oxide powders. The metastable orthorhombic and hexagonal polymorphs have been synthesized by hydrothermal techniques. The dissolution studies of the powder material are just underway.

Nepheline: The mechanism and rates of alkali extraction from nepheline ($\text{Na}_{0.75}\text{K}_{0.25}\text{AlSiO}_4$), a possible ceramic product phase from Savannah River Plant sludges, are being studied to determine for how long nepheline can withstand the continued action of hydrothermal solutions.

Figure 7. Concentration of cesium extracted from pollucite (1 gm pollucite in 100 cc. H₂O) after 40 days at 25° C.

Initial crude calculations from scanty literature data indicate complete disintegration of nepheline after ~300,000 years in 50°C slightly acid (pH = 5.8 at the start) solution. Experimental work is aimed at improving the reliability of these calculations, and extending the work to solutions of various pH, Eh, and solution composition conditions.

Natural nephelines have been selected and their chemical composition determined with the electron microprobe. A fairly pure nepheline of fairly uniform composition $(\text{Na}_{(0.75-0.78)}\text{K}_{(0.17-0.19)}\text{Al}_{(0.94-0.95)}\text{Si}_{(1.05-1.06)}\text{O}_4)$ will be used in the dissolution experiments.

3.1.3 Radiation and Transmutation Effects

The objective of the radiation and transmutation effects studies is to simulate radiation and transmutation effects in proposed Tailored Ceramics materials on an accelerated time scale. The results will be used to assess the anticipated durability of Tailored Ceramics in isolating nuclear waste nuclides from the environment over a geologic time scale.

Fundamental Studies

Some perovskite structures look promising for $\text{Cs} \rightarrow \text{Ba}$ and $\text{Sr} \rightarrow \text{Zr}$ transmutation resistance but have not as yet been verified in this regard. $\text{SrZrO}_3/\text{ZrO}_2$ mixtures look promising as vehicles for Sr fixation.

Various irradiated phases continued to "cool off" during the quarter, preparatory to X-ray examination; some γ -spectrometry to identify the active isotopes has been performed. Other TRU waste-bearing candidate phases have been prepared, doped with 1 mole % ^{235}U , for subsequent neutron irradiation.

Cs Fixation: Possible solid solutions of CsTaO_3 in BaZrO_3 are under study, the Cs fixation rationale being: $\text{CsTaO}_3 \rightarrow \text{BaTa}^{4+}\text{O}_3$. Initial results look promising, but more study is necessary to verify this system as a transmutation-stable Cs host.

No solubility of Ba was found in CsFeSiO_4 (rationale being $\text{CsFeSiO}_4 \rightarrow \text{BaFe}^{2+}\text{SiO}_4$) and, as in the case of iron pollucite, it would seem that tetrahedral Al sites have a strong resistance to Fe^{2+} substitution (such resistance appears to be well documented for beryl and cordierite).

Sr Fixation: Experiments were conducted to determine the replaceability of Sr^{+2} , Y^{3+} , and Zr^{4+} for Ca^{2+} in the anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) structure. An appropriate amount of ferric (3+) iron was substituted for Al^{3+} to act as a charge balancing ion by reduction to Fe^{2+} upon decay of $^{90}\text{Sr}^{2+}$ to Y^{3+} and Zr^{4+} . Mg^{2+} was used as a stand-in for Fe^{2+} so preparations could be fired in air, using a treatment of 72 hr at 1200°C .

In all cases, the triclinic polymorph of anorthite was formed readily. It was found that Sr and Fe could replace Ca and Al up to $x = 0.5$ with second phases appearing at greater values of x . Second phases were observed in all samples with Y and Zr. These results suggest that it would be necessary to go to Sr loadings lower than $x = 0.1$ to fix ^{90}Sr in the anorthite structure in this manner.

$\text{SrZrO}_3/\text{ZrO}_2$: SrZrO_3 in other studies apparently shows good leach resistance at temperatures up to 200°C and monoclinic ZrO_2 would be expected to be quite leach-resistant in view of the stability of the natural mineral, baddeleyite. The rationale in this system is that SrZrO_3 will decompose to oxygen-deficient ZrO_2 , which will be compatible with the stoichiometric encapsulant phase.

Literature Review

Two internal reports have been completed which summarize a literature review of radiation and chemical effects on nuclear waste forms and natural minerals. They are "Radiation Effects Simulation in High-Level Nuclear Waste Forms: A Literature Review" and "Natural Radiation Damage in Solids; A Literature Review." Both reports were written to provide background information for designing an experimental irradiation program for Tailored Ceramics nuclear waste forms.

The first report overviews experiments designed to simulate, at a greatly accelerated rate, radiation effects that would occur over a geologic time scale. Most of the data have been obtained on glass waste forms; only a few experiments on crystalline waste forms have been reported in the literature. Changes in physical properties such as crystal structure, stored energy, and density have been observed. In general, large changes in the latter two have not been observed. The principal chemical property of concern is the leach rate with water (or aqueous solutions). In low-temperature leach rate measurements, radiation does not appear to produce a significant effect.

The second report reviews studies made on the metamictization of natural materials. These materials provide valuable information for the evaluation of the long-term effects that result from radiation damage, particularly changes in physical properties. Several criteria are identified that can predict the stability of crystalline oxides under exposure to ionization and lattice displacement conditions.

Radiation Damage Effects on $^{90}\text{SrTiO}_3$

Efforts are continuing to acquire the SNAP-7E spent thermoelectric generator whose operation was based on a ^{90}Sr heat source. This generator is of interest because the ^{90}Sr is incorporated in the crystalline phase $^{90}\text{SrTiO}_3$, a mineral similar to some crystalline phases proposed in Tailored Ceramics formulations. About 35% of this nuclide has transmuted to ^{90}Zr . The source thus appears to provide an ideal opportunity to study transmutation damage in a single-phase crystalline material. During the present reporting period, further information has been obtained on the construction and temperature history of this source; the Navy personnel responsible for final disposal of the source have been identified and contacted, and procedures have been initiated to transfer the source from the Navy to the Department of Energy.

Experiment Planning

Efforts have continued on the planning for the first Tailored Ceramics irradiation experiments. A series of reactor experiments was identified,

beginning with the thermal-neutron irradiation of ^6Li -, ^{10}B -, and ^{235}U -doped single and multiphase materials and continuing with mixed spectrum (comparable thermal and fast neutron component) irradiations with additional dopants and phase compositions. However, the opportunity to obtain radiation effects data on a more immediate time scale than otherwise possible, using presently available equipment, has led to the examination of a helium-implementation experiment.

3.2 TAILORED CERAMICS PROCESS AND EQUIPMENT DEVELOPMENT

3.2.1 Engineered Containment

In order to take advantage of the potential of the Tailored Ceramics product to have high-waste loading, the product must fill a large fraction of the containment canisters. Obviously, the most effective packing of individual waste bodies in a cylindrical canister, for example, is accomplished if the outer diameter of each body is only slightly smaller than the inner diameter of the canister (i.e., the ratio of diameters is just below 1). As the diameter ratio falls below unity, the void fraction in the canister increases rapidly. For example, at a ratio of 0.9, the void becomes 19%, which thus reduces the net waste loading by a factor of 0.81. For single-sized cylindrical bodies whose length-to-diameter ratio, L/D , is unity, one finds a minimum net loading factor (about 0.18) at a diameter ratio just over 0.5, followed by an increase in loading factor as the diameter ratio falls below 0.5 to reach a nearly constant value in the range 0.42-0.45 for body-to-canister diameter ratios below about 0.15.

There is, therefore, an incentive to form large consolidated Tailored Ceramic bodies. Because canister sizes contemplated for SRP waste range from 12 in. to 24 in., and because the bodies should themselves approach full density, hot isostatic pressing (HIPing) is a primary candidate for consolidation process study.

Another consideration in canister loading is the number of major processing stations (consolidation presses or sintering furnaces) required to achieve a

given processing rate of the final consolidated product. The results of a computation involving D , the diameter of the consolidated body, t , the limiting processing time, and n , the number of bodies made per operation, all for a 100-lb/hr rate, are shown in Figure 8 with the ratio t/n (hours/body) as a definitive parameter. In this computation, the body length/diameter ratio (L/D) was taken as unity. Figure 8 shows the expected hyperbola-like trends from the (many small body) and (many stations) end of the scale to the (large body) and (few stations) end. Ideally, a single processing station (with a second station in reserve) would be preferred. This graph, therefore, gives some guidance on processing options. Processes for which n is small, such as uniaxial hot pressing, must handle large bodies, and must minimize processing times as well. If L/D values greater than unity are feasible, such as is the case for hot isostatic pressing (HIPing) (but not for uniaxial hot pressing), longer t -values can be permitted. For example, Table 2 shows a comparison of processing time and number of stations when L/D is varied, illustrating the advantage of increasing the L/D . Also shown is the effect of decreasing the waste form diameter. In the case shown, even when the L/D is increased to 7, two processing stations are required to accommodate the 100-lb/hr throughput, with a 20-hr pressing time. Thus Figure 8 also illustrates the incentive to prepare rather large bodies, in that only a few of them are needed, and the number of processing stations can be minimized. If small bodies must be considered, then large numbers must be simultaneously formed and consolidated in order to avoid the need for large numbers of processing stations.

Four companies currently marketing complete hot isostatic pressing (HIPing) systems in the U.S. have been contacted to determine what equipment is available and the suitability of that equipment for adaptation to a remote facility. All of them manufacture systems that could be used to press monoliths of the largest size being considered (2 ft in diameter by 8 to 9 ft long); one has had experience in sealing spent radioactive fuel rods in corundum capsules measuring 10 in. in diameter by 5 ft long. In addition, they have demonstrated the capability of sealing full-scale corundum capsules (greater than 1-1/2 ft in diameter and about 10 ft long). Although no difficulty is expected in adapting

Figure 8. Number of Processing Stations Required as a Function of Waste Body Size. (100 lb/hr of final waste product)
(Body lengths equal their diameter; $L/D = 1$)

TABLE 2
PROCESSING STATIONS FOR CONSOLIDATION OF A
CYLINDRICAL CERAMIC WASTE FORM
(Processing Rate: 100 lb Final Waste Product/hr)

Pressing Time (hr)	Number of Waste Form Bodies Produced Per Operation	Diameter of Body (cm)	L/D	Processing Stations
10 ⁽⁴⁾	1	54 ⁽¹⁾	1	1
20 ⁽⁴⁾	2	54 ⁽¹⁾	1	1
20	1	54 ⁽¹⁾	2	1
40	1	54 ⁽¹⁾	4	1
20	1	28 ⁽²⁾	7	2
10 ⁽⁴⁾	1000	6 ⁽³⁾	1	1

(1) 24-in. canister

(2) 12-in. canister

(3) Small body loaded in 24-in. canister

(4) From Figure 8

any of the available systems for a remote facility, none of these systems has been remotized to date. Methods of accomplishing this are being studied both for the HIPing unit and for the preparation of a suitable feed for the HIPing unit.

3.2.2 Process Evaluation and Definition

The current reference Tailored Ceramics process flow diagram is designed to be generally compatible with the existing DWPF glass product flow sheet (reference process). The Tailored Ceramics (TC) process sequence has been divided into nine subsystems, as illustrated in Figure 9. Subsystem 1 involves the preliminary separation of sludge and supernatant fractions in the tanks. This is to be accomplished in the fashion developed at SRL with the separated solution plus any redissolved salt being sent to Subsystem 3.

FIGURE 9
TAILORED CERAMICS
SCHEMATIC PROCESS FLOW DIAGRAM

In Subsystem 2, the sludge is washed to remove sodium, and the washings (which contain cesium and some strontium) are sent to Subsystem 3. This is a point of departure of the TC process from the SRL Reference Process in that the aluminum is not removed. Some of the tailoring chemicals may be added at this point, and then the washed, relatively low-sodium sludge is sent to Subsystem 5.

In Subsystem 3, the supernatant from the waste tanks plus the various washing streams is clarified to remove any residual solids. The solids stream is returned to Subsystem 2, and the clear solution is sent to Subsystem 4.

In Subsystem 4, ion exchange is used to separate the Cs and the Sr from the high-sodium liquor which follows the Reference Process separation concept, except that it may be advantageous to avoid the introduction of zeolite into the sludge stream. A liquid containing dissolved Cs and Sr with a minimum of sodium is the desired product to be directed to Subsystem 5. The decontaminated liquor stream is sent for evaporation/concentration and ultimate disposal.

In Subsystem 5, the remaining tailoring material is added to the washed sludge and Cs plus Sr streams. The mixture is thoroughly blended and diluted to form a pumpable stream to be calcined in Subsystem 6. In Subsystem 6, the feed-stock is evaporated and the resulting solids are calcined to decompose the hydroxides and nitrates. The offgases are stripped to remove the radioactive constituents to produce a releasable stack gas.

In Subsystem 7, the calcined product is preconsolidated, if necessary, and pressed or sintered to form the final dense consolidated waste bodies, which are then loaded into canisters in Subsystem 8. In addition, in Subsystem 8, the canisters are sealed (welded), cleaned to remove surface contamination, and transferred to local interim storage.

In Subsystem 9, the tailoring chemicals are blended and prepared for addition to the sludge stream.

This processing concept is designed to exploit the presence of relatively large amounts of aluminum (and iron, as hydroxides or hydrous oxides) in the

waste. The currently envisioned Tailored Ceramics waste form is a mixture of alumina-containing mixed oxides, which mixture has limited amounts of silica and sodium, and "tailoring" additions of rare earth and/or other polyvalent metal oxides. The end product is a dense (density approaching 4 gm/cu cm) polycrystalline ceramic body having a minimum surface area.

In one currently selected high-Al Tailored Ceramics crystal phase assemblage, species such as the rare earths are needed to stabilize the fission product cesium as well as all of the sodium remaining in the calciner feed. In addition, a large incremental amount of tailoring alumina is also required. It is, therefore, very desirable to reduce the sodium content of the sludge and of the Cs plus Sr stream. The effect of the amount of sodium in the calciner feed mixture on the final waste loading in the canisters and on the number of canisters required to contain the SRP composite mixture for a given tailoring formulation are shown on Figure 10a and Figure 10b, respectively. As indicated, the potentially high waste loadings of the Tailored Ceramics product can be attained only if the sodium content of the sludge is fairly low. Laboratory work, including laboratory testing, has therefore been initiated to determine practical procedures for removing sodium from synthetic sludge.

In addition, alternate methods of separating the cesium from the process liquor stream are being reviewed. The Reference Process, which removes cesium by a duolite ion exchange followed by elution and zeolite absorption is being compared with the following with regard to sodium return to the calciner feed stream (Subsystem 5):

- 1) Elimination of the zeolite absorption system and returning the total eluant from the duolite column
- 2) Sodium stripping and recycle from the duolite column. (This would require additional duolite ion exchange material (approximately 10% more) plus an additional evaporator.)*

*DP-79-125-1, "Waste Management Program, Technical Progress Report: January - March 1979," Dupont SRL, January 1980, pp 21-26.

Figure 10a
Waste Loading vs % Na₂O

Figure 10b
Number of Canisters Required
vs Waste Loading