STATUS OF DEVELOPMENT OF THE TAILORED CERAMIC HIGH-LEVEL NUCLEAR WASTE FORM

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INTRODUCTION

There is a continuing interest in disposal of high-level nuclear wastes (HLW) from defense and commercial reactors. Research and development worldwide on use of borosilicate and other glasses for immobilization of these HLW's has advanced to the point where this waste form is generally judged by the technical community to be satisfactory for the purpose. It is currently considered the reference waste form against which an alternate waste form (AWF) should be judged.

Because of the concern of some about the safe disposal of immobilized waste, and because of certain technical shortcomings of the borosilicate glass waste form pointed out by some investigators(1) (primarily, devitrification in ground water systems), development and evaluation of alternate waste forms has been undertaken by the U.S. DOE.

As one alternative to borosilicate glass, crystalline ceramics have been proposed by a number of investigators including McCarthy(2) and Ringwood.(3) Based on the supercalcine ceramic concept developed at the Pennsylvania State University's Materials Research Laboratory for Battelle Pacific Northwest Laboratory, a broader, more inclusive "Tailored Ceramics" concept has been formulated and is the subject of our current investigation.

Tailored Ceramics are inherently stable, consolidated assemblages of compatible crystalline phases. Their processing involves starting with the nuclear waste to be immobilized, adding selected tailoring agents, preparing a dry feed, and consolidating this into a dense ceramic.

The factors involved in phase selection are listed in Table I. Selection of a "Tailored Ceramic" phase assemblage for a given waste is not unique. For Savannah River Plant (SRP) defense wastes, a phase formulation involving silica tailoring was recently proposed.[4] The major effort on our project has utilized the alumina present in the waste, along with additions of rare earth and silica, for tailoring.[5] Others favor tailoring with titania.[3] These tailoring formulations all lead to "Tailored Ceramics" made with the same waste. In our current work, the composition of the waste itself and the geologically stable phases that form naturally by consolidating the untailored waste have served as a guide to phase selection. Specifically, the high Al content of much of the SRP waste led to selecting a high-alumina Tailored Ceramic for these wastes. This permits the alumina in the waste to be utilized for tailoring, which, in turn, leads to a potentially higher waste loading in the final form.

TABLE I

FACTORS INVOLVED IN PHASE SELECTION

- Chemical Composition of the Waste
- Consolidation Process Requirements
- Geologic Stability (of the Phase or its Mineral Analog)
- Anticipated Repository Conditions

The scope of Tailored Ceramic phase selection feasible for the SRP wastes is indicated in Table II. The silica (and phosphate) tailoring was characteristic of the supercalcine ceramics.[2] It may be noted that the three ceramic types shown have a number of phases in common.

Our Tailored Ceramics project, part of the Department of Energy's Long-Term High-Level Waste Management Program (under DOE-SRO Contract DE-AC09-79ET41900 with Rockwell's Energy Systems Group) is a coordinated effort involving Rockwell International organizations (Science Center; Energy Systems Group, Research and Engineering; and Hanford Operations) and the Pennsylvania State University's Materials Research Laboratory (PSU/MRL). The major contributions of each to the program are shown in Table III.

TABLE II

SCOPE OF TAILORED CERAMIC PHASE SELECTION

High Silicate-Phosphate Ceramics	High Alumina Ceramics	High Titania Ceramics
. Monazite	. Corundum	. Hollandite
*. Nepheline	*. Spinel	. Zirconolite
. Feldspar	. Al-Perovskite	. Ti-Perovskite
*. Pollucite	. Magnetoplumbite	*. Spinel
*. Fluorite Structures	*. Fluorite Structures	. Ilmenite
. Scheelite	*. Pseudobrookite	*. Pseudobrookite
	*. Nepheline	*. Nepheline
	*. Pollucite	*. Pollucite

*Common to several ceramic groups

FORMULATION AND CONSOLIDATION STUDIES

The major emphasis on this project has been on Savannah River Plant (SRP) wastes in accordance with the priorities assigned by the National Program.(6) For this work, three SRP waste compositions were furnished to the alternate waste form developers.(7) Working with the compositions without aluminum removal, which permits this aluminum to be used for tailoring, tailoring formulas and consolidation techniques have been developed at Rockwell's Science Center (RSC) for each of the three SRP compositions.

For the high-Al and composite SRP wastes, fine-grained, fully dense ceramic bodies have been prepared with a minimum of tailoring additives. Of the various formulations tested, the one using addition of rare earth oxides (REO) to form the magnetoplumbite phase and minor amounts of TiO_2 to aid consolidation is currently preferred. The ceramics produced are relatively simple crystalline phase assemblages. When properly tailored, only three phases are present--spinel, magnetoplumbite, and uraninite. If an excess of any tailoring additive is used, other stable, inert (nonradiophase), compatible phases appear. For example, excess Al_2O_3 yields a corundum phase; excess REO leads to a RE-Al perovskite,

TABLE III

TAILORED CERAMICS PROJECT ACTIVITIES

Site	Pennsylvania State University Materials Research Laboratory	Rockwell International Science Center	Rockwell International Energy Systems Group Research and Engineering	Rockwell International Energy Systems Group Hanford Operations
Principal Activities	Optimum host phases for selected radionuclides Dissolution mechanisms and kinetics Encapsulation concepts Inert-phase barrier Cement-matrix composites Fundamental radiation effects	Multiphase formulations Consolidation processes Characterization Evaluation	Process evaluation and definition Process development Radiation and transmutation effects	Hot formulations Geologic strata compatibility Engineering support

$RE(Al,Fe)O_3$, while excess TiO_2 will produce pseudobrookite $(Fe,Ti,Al)_2TiO_5$. The only negative result of overtailoring is the resultant slight reduction in waste loading.

It is significant to note that a naturally occurring four-phase material containing corundum, spinel, magnetoplumbite, and thorianite $(Th,U)O_2$ (an analog of the the uraninite of the four-phase Tailored Ceramic), has been found in alluvial deposits in Madagascar.(8) Therefore, this phase assemblage is known to be compatible as well as stable over geologic time scales.

Consolidation by sintering, uniaxial hot pressing, or hot isostatic pressing (HIPPING) requires reactive powders. These may be produced in the laboratory by drying, calcining, and milling the tailored synthetic sludge. Comparable powders have been prepared on a larger (2 kg/h) scale by spray calcining. Laboratory studies on these spray-calcined powders have shown that by simply heating to progressively higher temperatures (up to ~1100^{o}C), fine crystallites of the phases form; these are identified by XRD. Periodic use of this powder sintering and XRD technique during processing may provide a tool for quality assurance in actual waste processing.

A bright field transmission micrograph of a sample Tailored Ceramic (prepared from high-Al synthetic SRP) waste is shown in Fig. 1. The four phases present (spinel, magnetoplumbite, uraninite, and corundum) are indicated. Also, some of the elements identified as being contained in each of the phases are listed. It may be seen that the magnetoplumbite hosts a wide variety of elements; this arises from its unique structure with cation lattice sites of varied coordination.(9) In this structure, neither glassy phases nor microcracks were found.

Loss of volatile waste species, especially radionuclides, in processing is generally a matter of serious concern. However, in Tailored Ceramics, the volatility of radionuclides such as cesium is reduced by chemically incorporating them into host phases during processing. Within the experimental error of the neutron activation analysis method used, all the cesium was retained in tailored simulated SRP defense wastes in their consolidation by hot pressing in a nickel container at temperatures up to 1300^{o}C.

Uranium in the waste must be reduced and retained in the +4 oxidation state so that it and other transuranics are hosted in the uraninite phase. For the wastes containing a significant

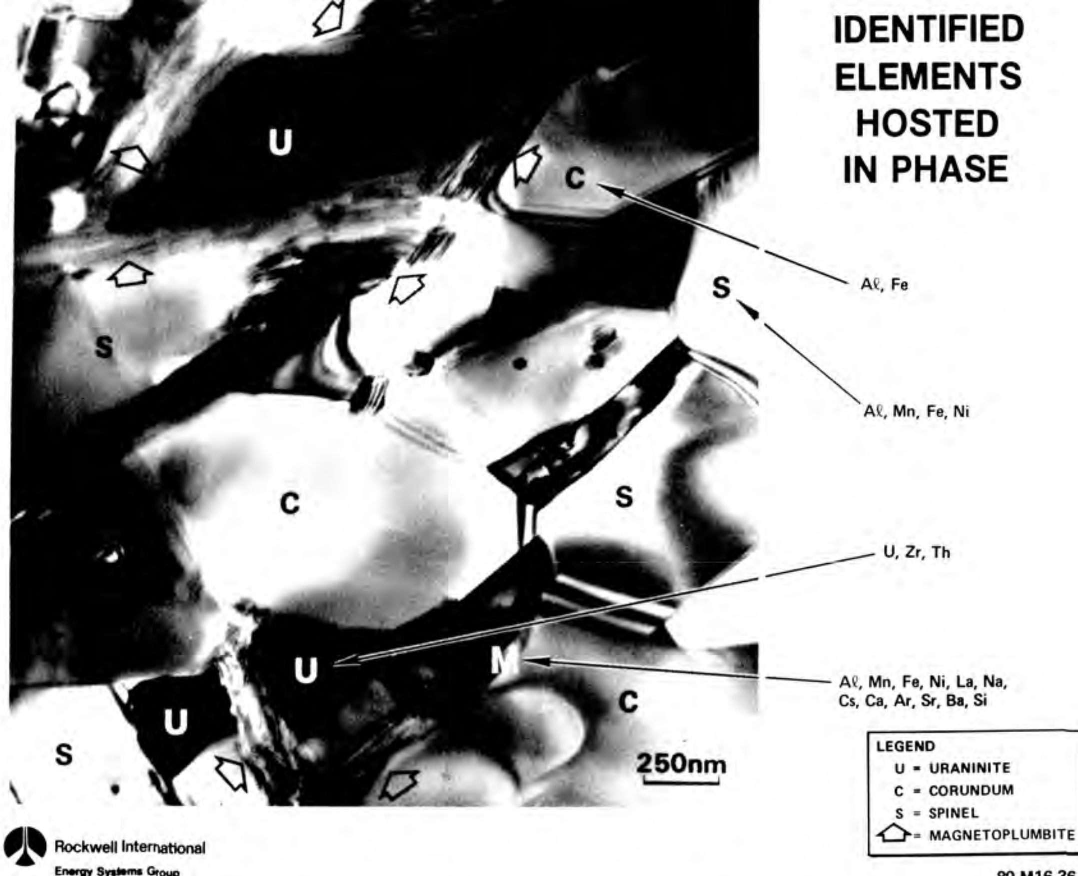

Fig. 1 Bright Field Transmission Micrograph of High Alumina Tailored Ceramic (Sample HASR 1)

quantity of iron (e.g., the composite and high-Fe SRP wastes), partial reduction of Fe(III) to Fe(II) is also required to achieve a Tailored Ceramic with the proper phases. In the laboratory, iron metal has been used successfully to obtain the PO_2 of the Fe-FeO buffer for this purpose. For full-scale processing, use of other reducing agents is under investigation.

For the high-Fe SRP waste, as well as the composite SRP waste, alternative tailoring formulations using alumina and silica as the principal additives have been studied. With this tailoring, nepheline, a naturally occurring mineral, forms as the primary sodium host phase, with spinel solid solutions taking up the bulk of the transition metals. Uranium can be formed into a fluorite-structure solid solution or can be tailored into other stable mineral phases (e.g., pyrochlore). The magnetoplumbite phase is compatible with both nepheline and pollucite, which serve to host, respectively, sodium and cesium. For the higher iron content wastes, and with the sodium levels expected to be encountered in the SRP wastes with currently planned processing methods, the alumina-silica Tailored Ceramic will show a higher waste loading than the comparable alumina-rare earth Tailored Ceramic.

Initial short-term leaching studies have been completed on some developmental alumina-REO-TiO_2-tailored specimens. Comparative studies using MCC-1 static leach tests indicate that component leach rates are 5 to 1000 times lower than in borosilicate glass.

Studies[10] on ion-thinned ceramic specimens, using STEM, have shown the importance of proper tailoring to avoid the formation of intergranular glassy phases in ceramic forms. Such amorphous intergranular material tends to accumulate cesium and other radionuclides. If continuous, the glassy phase tends to leach more readily than the desired crystalline phases.

Currently, formulation activities are directed toward optimizing the tailoring for high waste loading in SRP waste-containing ceramics.

GENERIC, FUNDAMENTAL, AND SUPPORT STUDIES

Besides some basic work on phase formulation for the high-Fe SRP HLW, researchers at PSU's MRL have looked for optimum host phases for selected radionuclides, studied dissolution mechanisms and kinetics, examined cement matrix ceramics, and evaluated radiation and transmutation effects in selected radiophases.

Phase relations in the quaternary [fluorite] system (UO_{2+x}-CeO_2-ZrO_2-ThO_2) have been studied at 1200°C; this work directly relates to the Tailored Ceramic uraninite (UO_2) phase and its stabilization by small additions of ZrO_2. Of the iodine hosts examined, I-sodalite has proven the most promising. Host phases for Tc are under study.

Dissolution studies on pollucite, sodalite, nepheline, and Sr-feldspar show diverse mechanisms operative, though all show a strong pH rate dependence. Monazite, which may serve as the transuranic host phase in some Tailored Ceramic formulations, has been shown to have extremely high leach resistance. Cement-matrix consolidation may serve as an alternative to hot consolidation (e.g., by hot pressing). Composites of (synthetic) SRP waste calcine with high alumina cements show leach resistance comparable with that of glass; these studies are continuing.

Initial experiments have indicated that oxides show greater resistance to radiation damage than do phosphates, silicates, or titanates. Fission fragment damage effects on dissolution and recrystallization are under study. A method was formulated for study of radiation and transmutation effects by doping specimens with ^{6}Li or ^{10}B and irradiating them. Li-doped magnetoplumbite specimens have been prepared for reactor irradiation.

The potential impact of repository environments on Tailored Ceramic waste forms and related matters are under investigation at Rockwell Hanford Operations.

PROCESS ASSESSMENT

As part of the project, an effort is underway to assess the feasibility of producing Tailored Ceramics safely and reliably under large-scale remote operating conditions. For this, key process steps in a process flowsheet specifically applicable to SRP high-level wastes have been identified and are being evaluated for engineering feasibility.

The current flowsheet is shown in simplified form in Fig. 2. It is based on the most recent information on the planned SRP Defense Waste Processing Facility (DWPF) utilizing borosilicate glass as the reference waste form. A major difference between the glass and ceramic process is that the latter does not have an aluminum removal step for reasons noted above (Section II). Ceramic processing, as currently envisioned, does involve a few

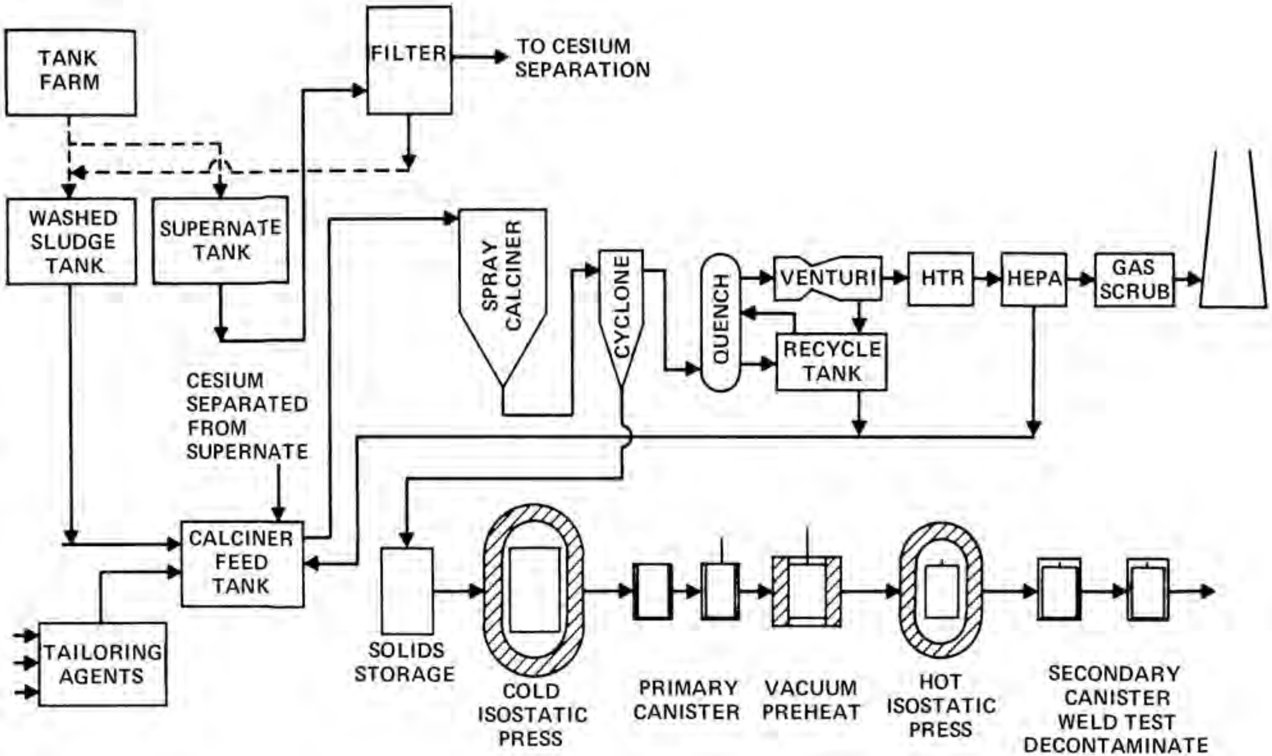

Fig. 2 Tailored Ceramics Preliminary Flow Diagram

more steps in preparation of the final in-canister product than does the reference glass product. Studies to date have examined the process steps of spray calcination, preconsolidation, consolidation, and cesium recovery from the supernate and feed to the ceramic processing stream. Some work has also been undertaken to control the redox state of U and Fe.

A direct-combustion, gas-heated spray calciner has been used for preparation of powders from synthetic SRP sludge for the formulation and consolidation work, as well as for evaluation and assessment of the process step per se. With exit gas temperatures in the range of 650-700°C, the powder product contains essentially no moisture or nitrates. With the short residence times involved (of the order of a few seconds), no appreciable oxidation (e.g., of Fe(II)) or reduction occurs. The product powder from sludge feed is much denser than that from solution feed. In all cases, the powders are suitably reactive for consolidation.

For full-scale operation, hot isostatic pressing (HIPPING) is the present reference consolidation method, with preconsolidation by cold isostatic pressing to achieve the requisite initial density (40 to 60% of theoretical). A recent suggestion(11) to add and tamp to compress the powder directly into the HIPPING container merits further study.

Uranium and iron reduction prior to the spray calcination step appears to be the most practical approach to redox control in full-scale operation. Once the proper oxidation states for U and Fe have been attained, care must be taken to maintain them in subsequent processing. Methods to accomplish this redox control are currently under study, but no significant results are available to report here.

The reference DWPF process calls for Cs^+ separation from the HLW supernate by ion exchange and feed to the immobilization process adsorbed on a zeolite. Properly size-reduced, the components of this zeolite are readily incorporated into Tailored Ceramic phases. If, for some reason, it is desired to process this zeolite separately, it should be noted that studies at PSU's MRL have shown that on calcining this material, the Cs^+ ends up as $CsAlSi_5O_{12}$, which, in preliminary leach testing, shows promising results.

Recent results from the SRL DWPF process studies have suggested that a modified ion exchange process may be selected in which the Cs^+ would be eluted with formic acid for feed into the immobilization stream. In this case, cesium would be incorporated into either magnetoplumbite or pollucite in the final Tailored Ceramic product.

As part of the overall Tailored Ceramic process assessment, a comparison was made of materials throughput with that of the reference borosilicate glass. Some of those parameters are shown in Table IV. In summary, because of the higher projected waste loading and product density, the waste volume requiring disposal as a Tailored Ceramic is only one-third that of the reference glass.

TABLE IV

PROJECTED PROCESS THROUGHPUT PARAMETER COMPARISON
(For SRP Composite Composition)

Parameter	Reference (glass)	Tailored Ceramic ($5\%\ Na_2O$)
Quantity of Waste (tons)	4,830	4,830
Additives Required (tons)	8,400	3,600
Waste Loading (%)	25	50
Waste Form Produced (tons)	11,200	7,200
Salt Cake Produced (tons)	129,000	106,100
Water Evaporated (10^6 gal)	53	34
Waste Volume (10^3 ft^3)	151	58

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