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DEVELOPMENT OF POLYPHASE CERAMICS
FOR THE
IMMOBILIZATION OF HIGH-LEVEL
DEFENSE NUCLEAR WASTE

DOE Research and Development Report

*Prepared for the United States
Department of Energy,
Savannah River Operations Office
under Contract Number DE-AC09-79ET41900*

Rockwell International
Energy Systems Group

MASTER

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NUCLEAR WASTE
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DEVELOPMENT OF POLYPHASE CERAMICS
FOR THE
IMMOBILIZATION OF HIGH-LEVEL
DEFENSE NUCLEAR WASTE

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FOREWORD

The report contains two major sections: Section I "An Improved Polyphase Ceramic for High-Level Defense Nucleation Waste" reports the work conducted on titanium-silica based ceramics for immobilizing Savannah River Plant waste. Section II "Formulation and Processing of Alumina Based Ceramic Nuclear Waste Forms," describes the work conducted on developing a generic alumina and alumina-silica based ceramic waste form capable of immobilizing any nuclear waste with a high aluminum content. Such wastes include the Savannah River Plant wastes, Hanford neutralized purex wastes, and Hanford N-Reactor acid wastes. The design approach and process technology in the two reports demonstrate how the generic high waste loaded ceramic form can be applied to a broad range of nuclear waste compositions.

SECTION I

AN IMPROVED POLYPHASE CERAMIC FORM FOR HIGH-LEVEL DEFENSE NUCLEAR WASTE

By

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ABSTRACT

An improved ceramic nuclear waste form and fabrication process have been developed using simulated Savannah River Plant defense high-level waste compositions. The waste form provides flexibility with respect to processing conditions while exhibiting superior resistance to ground water leaching than other currently proposed forms. The ceramic, consolidated by hot-isostatic pressing at 1040°C and 10,000 psi, is composed of six major phases, nepheline, zirconolite, a murataite-type cubic phase, magnetite-type spinel, a magnetoplumbite solid solution, and perovskite. The waste form provides multiple crystal lattice sites for the waste elements, minimizes amorphous intergranular material, and can accommodate waste loadings in excess of 60 wt%. The fabrication of the ceramic can be accomplished with existing manufacturing technology and eliminates the effects of radionuclide volatilization and off-gas induced corrosion experienced with the molten processes for vitreous form production.

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I. INTRODUCTION

The polyphase ceramic nuclear waste immobilization form has been developed over the past three years for Savannah River Plant type defense waste compositions as an alternative to borosilicate glass. Several ceramic formulations have been developed for the broad range of SRP waste compositions. In particular formulations using alumina based phases,¹ alumina-silica phases,² and titania-iron-silica phases.³⁻⁵ With the DoE selection of a ceramic as the alternative waste form to borosilicate glass for SRP waste in 1981, work has been focused upon the titanate-silicate based "Synroc-D" phase assemblage developed at Lawrence Livermore National (LLNL) Laboratory.⁴

The original Synroc-D ceramic form is an assemblage of crystalline phases including zirconolite phase, perovskite, two spinels (hercynite-type and an ulvospinel), nepheline and minor trace unknowns. This ceramic has the virtues of high waste loading and density while providing superior leach resistance to borosilicate glasses for uranium, and the actinides. The waste form did not, however, offer significant improvement over borosilicate glass for the short-lived radionuclides, Cs and Sr.⁶ In the fabrication of the titanate-silicate ceramic, a reduction step was called for using CO/CO₂ buffering at 600°C in a fluidized bed or the addition of metal powder, Fe or Ti, to insure the reduction of at least 50% of the waste iron to Fe²⁺. This reduction step caused the Fe to enter primarily the hercynite and ulvospinel phases. Hence the option of incorporating the iron as Fe³⁺ into the magnetoplumbite phase, an important potential host for Cs, Sr, and rare-earths, was not examined.

The practical necessity of using the silicate phase, nepheline, to accommodate the high soda content produces significant amounts of an amorphous phase in the ceramic. This intergranular material, which tends to include the highly basic elements such as Sr and Cs as well as such anions as Cl^- , SO_4^{2-} , and MoO_4^{2-} , is more soluble than the crystalline phases and can provide a short circuit leach path in the ceramic when present as a continuous phase.

It was originally proposed in this laboratory in 1980 that a more stable ceramic waste form, fabricated by a simpler process, could be achieved if the most stable phases of the alumina-silica ceramics were combined with the titania-silica based forms.⁵ This paper describes the resulting "improved" ceramic form resulting from such a formulation and compares its properties to those published for the S29 LLNL Synroc-D waste form.

II. OPTIMIZED CERAMIC DESIGN

The Synroc-D S29 ceramic form incorporates uranium in the 4^+ state into a zirconolite-type crystalline phase. This phase, as produced in the waste form at 1040°C , lacks many of the superlattice XRD lines of pure phase zirconolite,⁷ but shows excellent uranium retention in leaching tests and was selected for the optimized form. Nepheline, present in both the Rockwell alumina-silica based and Synroc-D type ceramics, while not a high-performance crystalline phase, was retained in the waste form to provide the sodium host phase required for high waste loading.

The remainder of the phases selected for the optimized defense waste ceramic were based upon the experience gained in the alumina-silica ceramics designed in this laboratory. In these ceramics, the magnetoplumbite phase, prototypically the mineral $\text{PbFe}_{12}\text{O}_{19}$ or Hibonite, $\text{CaAl}_{12}\text{O}_{19}$, was preferred as a host for Sr and Cs as well as rare earths, alkalis, and alkaline earths. In addition, a magnetite-type spinel was selected for the transition elements rather than the combination of the less stable ulvospinel-type with hercynite found in the Synroc-D formulation.

The formation of the magnetoplumbite phase requires that the iron in the SRP waste be retained as much as possible in the ferric state. Hence, the only reduction applied to the waste is that necessary to reduce uranium to the 4^+ state which can be simply accomplished by heating in an inert gas to approximately 800°C . These mild reduction conditions are possible because the $\text{U}^{6+} \rightleftharpoons \text{U}^{5+} \rightleftharpoons \text{U}^{4+}$ redox potential is not a constant but rather depends upon the crystal field stabilization of the valence states by host lattice sites. The availability of the zirconolite phase in the waste ceramic hence allows the reduction to the U^{4+} state to proceed under conditions which without Ti and Zr present would produce undesirable calcium uranates.

With this realization, the major phases designed into the ceramic were zirconolite, perovskite, nepheline, magnetoplumbite, and magnetite. Residual amounts of pseudobrookite can be expected as a buffer phase forming from excess of Ti over that required for the zirconolite. This modified waste form used the same basic chemical composition as the S29 LLNL-Synroc-D. The chemical composition of the simulated SRP "Composite Waste" used in the formulations is given in Table 1 and the initial formulation of the optimized ceramic is compared to that for the LLNL Synroc-D S29 in Table 2.

Table 1. Chemical Composition of the Simulated Savannah River Plant "Composite Waste" Used in this Study.

Component Oxide	Wt%
Fe ₂ O ₃	30.4
Al ₂ O ₃	30.0
MnO ₂	6.9
U ₃ O ₈	4.2
CaO	4.2
NiO	2.1
Na ₂ O	7.2
SiO ₂	10.2
ThO ₂	0.77
Ce ₂ O ₃	0.64
ZrO ₂	0.53
Na ₂ SO ₄	0.96
Na ₃ PO ₄	1.18
Cs ₂ O	0.34
SrO	0.38

Table 2. Comparison of the Composition of the LLNL-S29 Ceramic Form to the Improved RSC-S29 Form Developed at the Rockwell International Science Center

LLNL-S29[†]

Component Oxide	Wt%	Component Oxide	Wt%
Fe ₂ O ₃	23.80	Ce ₂ O ₃	0.50
MnO ₂	7.40	Nd ₂ O ₃	0.50
Al ₂ O ₃	18.60	Cs ₂ O	0.25
*CaO	7.10	SrO	0.25
NiO	3.00	*ZrO ₂	6.60
Na ₂ O	3.30	*SiO ₂	7.20
Na ₂ SO ₄	0.60	*TiO ₂	18.80
U ₃ O ₈	2.10		
			100%
			62.7 Wt% waste

RSC-S29

Component Oxide	Wt%	Component Oxide	Wt%
Fe ₂ O ₃	18.17	Cs ₂ O	0.20
MnO ₂	4.11	SrO	0.23
Al ₂ O ₃	17.87	SO ₄ ²⁻	0.39
*CaO	8.54	PO ₄ ³⁻	0.41
NiO	1.25	*ZrO ₂	7.94
Na ₂ O	4.94	*SiO ₂	9.98
U ₃ O ₈	2.51	*TiO ₂	22.62
ThO ₂	0.46		
Ce ₂ O ₃	0.38		
			100%
			60.0 wt% waste

*Elements added to the waste stream in addition to any amount present to promote the formation of the desired phases.

[†]Minor variations in the waste compositions are due to change in the SRL supplied reference "Composit SRP waste."

The major phases found in the consolidated ceramic were those expected: however a new cubic crystalline phase was found in the waste form. The XRD pattern of the optimized ceramic, RSC-S29, in Fig. 1 shows the major lines of the new phase, subsequently identified as a face-centered cubic structure believed to be related to murataite,⁸ with an approximate pure phase stoichiometry of $\text{Zr}(\text{Ca},\text{Mn})_2(\text{Fe},\text{Al})_4\text{Ti}_3\text{O}_{16}$, based on electron microprobe analysis.⁹ In addition to the elements in the nominal chemical formula, the cubic phase also incorporates a minor amount of uranium, rare earths, and sodium.

The XRD pattern in Fig. 1 also shows the presence of two trace phases hematite, Fe_2O_3 , and hauynite, nominally $\text{Ca}_2\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)_2$ or the related Cl^- containing form. The trace hauynite is a sodalite-like phase whose formation is associated with the presence of residual sulfate and chloride anions in the ceramic powders. The hauynite is easily leached and, therefore, undesirable. Subsequent to discovery of the hauynite phase, care was taken in anion removal during redox processing to avoid this potential problem.

The mineralogy and waste element distribution, as determined by XRD and analytical STEM, is shown in Table 3. The elemental distribution shows that the magnetoplumbite phase hosts the Sr as predicted, but that the cesium appears to preferentially associate itself with the nepheline phase. The zirconolite serves as the major host for uranium and frequently other tetravalents and trivalent transuranics. It should be emphasized that time has not permitted complete optimization of this form and

Fig. 1 XRD pattern of the RSC-S29 ceramic waste form, (Hauyne phase is not present in the optimized form).

Table 3. Waste Element Distribution in the RSC-S29 Ceramic as Determined by Analytical STEM and X-ray Microprobe. Elements are Listed in a Decending Order of Relative Concentration.

Phases	Elemental Content
<u>Phases</u>	
Nepheline	Si, Al, Na, Ca, Fe, K, Ti, Cs
Spinel (Magnetite-type)	Fe, Ti, Mn, Al, trace Ca, Ni
Zirconolite	Zr, Ti, Ca, U, Fe, Mn, Al
Perovskite	Ti, Ca, Fe, Mn, Zr, U, Sr, Si, Al, Na, Rare Earths
Murataite-type Cubic Phase	*Ti, Fe, Zr, Al, Mn, Ca, Ce, Nd, U, Si, Na, Ni
Magnetoplumbite	Fe, Al, Ti, Mn, Ca, Si, Na, Ni, Sr
Amorphous Material	Si, Al, Ca, Fe, Ti, Na
<u>Trace Phases</u>	
Pseudobrookite	(Fe ₂ TiO ₅)
Hematite	(Fe ₂ O ₃)
Trace Unknown	

*Microprobe analysis by F. Ryerson, LLNL.⁹

further improvements in the magnetoplumbite phase as a Cs host may well be possible by close control of the alkali/rare earth/silica ratios.

The magnetoplumbite phase adds a great flexibility to this assemblage as it can host many of the trace elements which might otherwise seek an intergranular phase. The XII fold lattice sites in the magnetoplumbite interspinel

layer have been shown to accommodate a wide variety of mono, di, and trivalent cations including alkalis, alkaline earths, transition elements, and rare earths. The details of this phase as a radwaste host structure have been discussed elsewhere.¹⁰

The RSC-S29 ceramic has a density of 3.97 g/cm³ at 60 wt% waste oxide loading. The approximate volume fraction of the observed phases content and theoretical density can be calculated based on pure phase densities and stoichiometries. This is shown in Table 4.

Table 4. Calculated Volume Percent Phase Composition of the Consolidated RSC-S29 Ceramic

Phase	Density (g/cm ³)	Volume %
Zirconolite	4.96 ^a	18
Magnetoplumbite	4.04 ^a	12
Murataite-type	3.44 ^b	26
Perovskite	4.04 ^b	8
Nepheline	2.63 ^b	22
Magnetite-type spinel	5.20 ^b	13
Amorphous	2.7 ^c	1 ^d
Calculated Density		3.9 (g/cm ³)
Experimental Density		3.97 (g/cm ³)

^a Calculated from x-ray lattice parameters and electron microprobe stoichiometry.

^b Measured from pure phase material.

^c Estimate

^d Estimate from STEM analysis.

III. PROCESSING

The simulated SRP "Composite" high-level defense waste used in these studies was obtained from several sources with the basic composition shown in Table 1, with some variation in trace elemental content. In this laboratory, the simulated waste was prepared by vacuum drying nitrate, hydroxide and alkoxide mixtures of the waste elements followed by partial denitration at 400°C in air, before mixing in the chemical additives. The use of alkoxides is especially convenient in that they form absorbant gelatinous "sludges" with the aqueous nitrate ingredients providing good mixing and easy handling. Other sources of the simulated composite waste were a batch supplied by the Savannah River Laboratory and bulk material prepared by the Western Chemical Company and supplied through Lawrence Livermore National Laboratory. In all cases the source of the simulated waste material was not found to effect significantly the final phases formed or the overall elemental release rates.

The RSC-S29 ceramic requires only three major processing steps, mixing of the SRP waste with the chemical additives, heating in an inert Argon gas environment to about 800°C and consolidation by hot isostatic pressing.

The mixing stage attempts to achieve near molecular mixing, using soluble or high surface area fine particle chemical additives with the waste stream. The redox control and denitration can be accomplished in a single heating step with an inert gas. The processing studies carried out at LLNL indicate that this can be readily accomplished with a fluidized bed calciner. The off gas system from the fluidized bed calciner will have to accommodate the water, nitrates, chlorides, sulfates, and mercury volatilizing

from the waste. However, there is no volatilization of Cs. The calcines pass from the fluidized bed into a steel vessel which, when welded under vacuum, will be consolidated by hot isostatic pressing (HIP). This process is shown schematically in Fig. 2.

Our processing studies have shown that adequate reduction of the uranium is obtained at calcining temperatures as low as 800°C. Cesium volatility in the pre-ceramic powders is undetectable at this temperature. Figure 3 shows a plot of Cs evolution versus temperature from the pre-ceramic powders, as determined by atomic absorption. The powders were heated in a graphite crucible in a nitrogen gas flow with an atomic absorption beam passing through holes in the crucible directly above the powder. This technique, described in detail elsewhere,¹¹ is highly sensitive and can be used to show the onset temperature for volatilization when a sufficiently slow heating rate is used for the sample. Figure 3 shows that over the range of heating rates used in this study no Cs volatilization was observed from the powders below 1100°C, well above the processing temperature.

In the proposed process the calcines will be vibratory packed into the HIP canisters to green densities of about 40% of the final form. The green density controls the amount of consolidation and hence the size of the final form, but it is not a limiting feature in the process. Full density of 3.97 g/cm³ has been obtained for laboratory specimens packed to as little as 25% green density at HIP operating conditions of 1040°C and 10,000 psi.

The effects of pressure and temperature have been investigated in the HIP consolidation of the waste form. A good temperature for the consolidation

Fig. 2 Schematic showing major process steps in fabricating the RSC-S29 ceramic waste form for SRP high-level waste.

Fig. 3 Plots of cesium evolution from RSC-S29 pre-ceramic powder, determined by atomic absorption as a function of temperature at four different heating rates.

process has been found to be about 1040°C. This temperature produces sufficient crystallinity, while at higher temperatures amorphous grain boundary material is observed to increase in the ceramic. The effect of pressure upon consolidation is shown in Fig. 4. Full density is obtained in the ceramic at pressures as low as 7000 psi; below this pressure lower final density is observed. At the selected HIP conditions of 1040°C and 10,000 psi, no improvement in the waste form crystallinity or density was observed through using temperature hold times longer than 30 minutes for the standard 150 g HIP samples or through using slow cool annealing. DTA has indicated that a eutectic exists at about 1000°C in this system, so that the HIP process is one of reactive densification in the presence of a liquid phase. This ensures rapid densification by the solution reprecipitation/grain boundary sliding mechanism.¹² Except for residual grain boundary layers or glasses, this generally allows good approach to thermodynamic equilibrium of the crystalline phases and explains the relatively low fabrication temperatures and pressures required for this ceramic.

IV. CHARACTERIZATION

The basic phase assemblage and elemental distribution of the RSC-S29 form have been given in Tables 2 and 3. Detailed microstructural and analytical analyses have been conducted on the form. Figures 5 and 6 show micrographs of ion-beam thinned foils of the RSC-S29 ceramic. The micrographs show the material to be extremely fine grained with some characteristic patterns of grain formation.

SC82-16740

Fig. 4 The effect of HIP pressure on the final density of the RSC-S29 ceramic form. Full density is reached at 7 ksi from an initial green density of about 25%.

Fig. 5 STEM micrograph of a region of the RSC-S29 ceramic form showing the fine grain size and preferential grouping of the lath-like magnetoplumbite grains. Magnetoplumbite = mp, Nepheline = N, Perovskite = P.

Fig. 6 STEM micrograph of the RSC-S29 ceramic showing nepheline, zirconolite, murataite-type, perovskite, and magnetoplumbite grains labeled N, Z, M, P, and MP, respectively. The nepheline grains show electron beam damage. The spinel phase is not present in the microscopic region.

The typical platelet magnetoplumbite grains, which in section appear lath-like, show a tendency to form clustered regions as shown in Fig. 5. A second characteristic feature is the formation of the nepheline grains within a thin glassy phase. The nepheline grains, labeled N in Fig. 6, exhibit electron beam damage which limits detailed analysis of their structure. On leaching the thin microscope foils in DI water,^{13,14} the intergranular material is removed as shown in Fig. 7 for a sample of LLNL LS04HP4A ceramic. The holes left by the leaching of the intergranular regions clearly outline the nepheline grains, demonstrating the pattern of formation for the intergranular glassy phase. This micrograph also reveals how the glassy phase can act as a short-circuit leach pathway into the ceramic form and controls the short term behavior observed in the laboratory leach testing by solution analyses. At higher magnification the foil, in Fig. 8, shows some nepheline dissolution also occurring.

One of the major advances in the RSC-S29 formulation over previous defense ceramic forms with silicate phases is that the intergranular material is minimized and does not preferentially concentrate radionuclides as observed in the Synroc-D samples for Sr. This is due to the availability of stable crystal lattice sites for the radionuclides and intimate mixing of the reactive chemical additives to enhance the formation of the desired phases.

Specific evidence of the success of the RSC-S29 form in avoiding the partitioning of the radionuclides into the amorphous intergranular phases comes from both the leach data and examination of the intergranular phase by X-ray photoelectron spectroscopy. XPS analysis of fracture surfaces of Synroc-type ceramics with a continuous glassy phase have demonstrated that

Fig. 7 STEM micrograph of ion-beam thinned foil of LLNL-LS04HP4A ceramic after immersion in DI water for 4 hours at 90°C. The amorphous intergranular phase has dissolved preferentially, leaving the holes in the foil that appear light. The nepheline grains also show some attack. The amorphous regions obviously form around the nepheline grains, probably as the nepheline crystallizes out of a liquid phase during consolidation.

SC82-18916

Fig. 8 Higher magnification micrograph of leached thin foil shown in Fig. 7. Note partial dissolution of nepheline grains in addition to removal of the amorphous phase. N = Nepheline, G = Glass.

cesium can be observed to preferentially concentrate in that phase.¹³ The RSC-S29 fracture surfaces shows no cesium at detectable levels with the Fe 3p lines clearly visible in the 700 to 750 eV binding energy region. The early Synroc-D samples exhibited a high Cs concentration in the exposed surface, overshadowing the Fe peaks though the bulk Cs concentration was equivalent to that in the RSC-S29 ceramic.

Microprobe analysis of individual grains was carried out when appropriate to confirm the stoichiometry of the crystalline phases. For example, the new cubic Murataite-type phase had the observed stoichiometry shown in Table 5.⁹ Similar analyses conducted on the magnetoplumbite phase show the cation/anion ratio to be quite close to the theoretical composition, $A^{2+}_8B^{3+}_{12}O_{19}$. Table 6 shows the measured stoichiometry of magnetoplumbite grains in a sample of the RSC-S29 ceramic. The large number of cations present in the grains confirms the flexibility of the magnetoplumbite structure for hosting the waste elements with several mechanisms of charge balancing.

Table 5. Electron Microprobe Atom Ratios of Elements Observed in the Murataite-type Cubic Phase in the RSC-S29 Ceramic Waste Form.*

Si	-	0.0723	Al	-	2.1982	Ti	-	4.0845
Na	-	0.2676	Zr	-	1.3518	Ca	-	1.5917
Mn	-	1.0546	Fe	-	3.4695	O	-	21.0000
Nd	-	0.0496	U	-	0.0847	Ce	-	0.0694

Approximate stoichiometry prepared as pure phase:

*Performed by F. J. Ryerson of LLNL.⁹

Table 6. Atom Ratios Determined by Electron Microprobe Analysis of the Magnetoplumbite Phase in the RSC-S29 Ceramic by F. J. Ryerson of LLNL.

Magnetoplumbite Stoichiometry = $\text{AB}_{12}\text{O}_{19}$

Normalized to O = 19

A Site Cations		B Site Cations	
Ca	0.544	Al	4.913
Sr	0.060	Fe	3.954
Na	0.415	Mn	1.152
Cs	0.005	Ni	0.291
Ce	0.013	Ti	1.630
Nd	0.010	Zr	0.045
		Si	<u>0.029</u>
ΣA	= 1.049	ΣB	= 12.014
Empirical stoichiometry $\text{A}_{1.05}\text{B}_{12.01}\text{O}_{19}$			

V. CRYSTAL CHEMISTRY

The phase formation in the titanate-silicate based ceramics for the SRP defense waste is a function of the chemical additives, the redox state of uranium and iron, and the consolidation temperature. The number of phases in the RSC-S29 form gives the chemistry a complex appearance. It can however be broken down into five fairly separate phase groupings for discussion purposes. These groupings are the fluorite type structures (zirconolite, murataite), the spinel related structures (magnetite, and magnetoplumbite), perovskite, the silicate phase (nepheline) and the inert buffer phases forming from excess additives (pseudobrookite, and hematite).

The zirconolite phase, prototypically $\text{CaZrTi}_2\text{O}_7$, provides the principal host lattice sites for the long-lived radionuclides U^{4+} , Th^{4+} , Np^{4+} , and secondary host sites for the trivalent actinides and rare earth, as well as Sr .¹⁵ The formation of the zirconolite phase requires that Ca and Ti be present in excess over the stoichiometric amount to accommodate the U^{4+} and added Zr^{4+} . The typical ratio of Zr to U has been selected as approximately 7 to 1 in the pre-ceramic powders. Critical to incorporation in this phase is the conversion of the uranium from the 6+ to the 4+ valence state.

Depending upon the availability of excess Ca^{2+} , Ti^{4+} , and Fe^{3+} the murataite-type cubic phase appears in the ceramic. In the RSC-S29 composition, the redox state of the iron controls the amount of this phase present. With high Fe^{3+} levels, Al, Ca and Ti can associate with excess Zr in the cubic phase, nominally $\text{Zr}(\text{Ca},\text{Mn})_2(\text{Fe},\text{Al})_4\text{Ti}_3\text{O}_{16}$. The relative equilibrium between murataite $\leftrightarrow$ zirconolite and other phases is quite complex. In related work

where uranium was left out it appeared that more murataite and less zirconolite was formed. Samples heated to higher temperatures in air also produced more of the murataite-type and it is surprising that this phase seems to be a very rare mineral in view of its ease of formation in this ceramic formulation.

Under the redox conditions of the LLNL Synroc-D where Fe^{2+} dominates, the two ferrous spinels, hercynite-type FeAl_2O_4 , and ulvospinel Fe_2TiO_4 , are formed. These phases do not contain radionuclides yet they make up a significant volume fraction of the waste form. The lesser stability of the ulvo-type spinel solid solution makes extensive reduction undesirable.¹⁶ With the Fe trivalent, the two spinel phases do not form. The Fe^{3+} and Al^{3+} readily combine with Ca^{2+} and Sr^{2+} , Ba^{2+} or $\text{Na}_{1/2} + \text{La}_{1/2}$ to form the magnetoplumbite solid solution, $\text{A}^{2+}(\text{Al},\text{Fe})_{12}\text{O}_{19}$, with some of the remaining trivalents going to a magnetite-type spinel and the murataite-type cubic phase. The discovery of ^{244}Pu fission tracks in meteoritic Hibonite,¹⁷ as discussed elsewhere,¹⁰ suggests magnetoplumbite as a host for Pu^{3+} , Am^{3+} , and Cm^{3+} . The stability of the $\text{Na}_{0.5}\text{La}_{0.5}\text{Al}_{12}\text{O}_{19}$ and $\text{Na}_{0.5}\text{Nd}_{0.5}\text{Al}_{12}\text{O}_{19}$ magnetoplumbites under highly aggressive acid conditions has also recently been reported by French researchers.¹⁸

A key simple test for whether magnetoplumbite, of the $\text{AB}_{12}\text{O}_{19}$ type, is formed is the measurement of the c/a ratio of the hexagonal unit cell.¹ For the RSC-S29 formulation, using the strong, easily distinguished, (220) and (20,11) lines, the values are: $a = 5.76\text{\AA}$, $c = 22.61\text{\AA}$, $c/a = 3.93$. This measurement confirms the 1:12:19 stoichiometry and is an easy scoping test for quality control.

The waste form as designed contains only one silicate phase, nepheline, $\text{NaAlSi}_3\text{O}_8$. However, the presence of residual chloride or sulphate anions, from incomplete calcining, or through the use of incorrect additives can produce sodalite or Nosean related phases such as hauynite. These phases require only small amounts of anion impurities to form and are quite soluble. Hence, some care must be taken in the powder denitration/reduction stage to volatilize these anions. It should be noted that the Hayne group contains many complex members¹⁹ including molybdates. At temperatures below 1000°C the nepheline phase does not fully form while at temperatures above 1100°C, additional amorphous material and/or carnegieite appear. Hence, the temperature range for optimizing the nepheline as well as overall densification centers around 1040°C.

To accommodate variations in the waste composition, excess levels of the chemical additives are normally included. The excess additives form "buffer" phases, useful internal indicators that tailoring is satisfactory. In the RSC-S29 formulation excess titanium forms pseudobrookite with Fe^{3+} , $(\text{Fe,Al})_2\text{TiO}_5$. Silica in excess substitutes into the magnetoplumbite matrix or forms silica-rich intergranular amorphous material. In those cases where insufficient Ti is present or mixing has not totally occurred during consolidation some trace hematite, Fe_2O_3 , may appear in the ceramic.

VI. LEACH PERFORMANCE

The RSC-S29 ceramic form has been extensively examined in static MCC-1, 2, and 3 type leach tests.²⁰ In all the tests, the RSC-S29 was found superior to the Synroc-D S29 phase assemblage. As described earlier, the

major form of attack upon the ceramic form by ground waters is the dissolution of exposed intergranular amorphous material followed by slow decomposition of the nepheline phase. The major radionuclide-containing phases, zirconolite, magnetoplumbite, murataite, and perovskite, show essentially no dissolution even in the MCC-tests with finely divided powders at 150°C.

Tables 7, 8, and 9 summarize the solution analyses observed in the static leach tests of the form. The brine data on the form is the least extensive due to the difficulties in conducting chemical analyses in the brine medium. As can be seen, the bulk of the dissolution occurs in the first 2 to 3 days of leaching as the high surface area exposed by cutting releases soluble species from exposed grain boundaries. After this, the only dissolution observed is attributable to the nepheline and surrounding glassy phases.

XRD, SEM, and XPS analyses of the leached surfaces, carried out through a separate study of the dissolution mechanisms of ceramic waste forms,²¹ has shown that surface layers slowly build up upon the ceramics. These surface layers have tentatively been identified as stratlingite ($\text{Ca}_2\text{Al}_2\text{SiO}_2 \cdot 8\text{H}_2\text{O}$), in silicate water and magnesium oxychloride ($\text{Mg}_2(\text{OH})_3\text{Cl}4\text{H}_2\text{O}$) in brine.

The extent to which the long-term dissolution of the ceramic form will be controlled by saturation effects versus solid-state diffusion will be a function of the flow rate of ground water in the ultimate repository and the penetration of ground water into the bulk ceramic via the dissolution of the nepheline and glassy phases. The short term (3 to 200 day) leach tests con-

Table 7. RSC-S29 Solution Analysis from MCC Leach Tests in DI Water

Normalized Release Rate g/m ² d												
MCC-1 90°								MCC-2 150°C		MCC-3 150°C		
Day	3	7	14	28	56	112	200	Day	28	Day	28	56
Na	2.37	1.30	0.78	0.40	0.22	0.17	0.10	Na	0.55	Na	0.27	0.47
Cs	2.83	1.83	0.53	0.29	0.26	7×10^{-2}	9×10^{-2}	Cs	0.43	Cs	$<8 \times 10^{-3}$	3.4×10^{-3}
Al	1.23	0.75	0.43	0.22	0.10	6×10^{-2}	4.5×10^{-2}	Al	0.23	Al	7.1×10^{-2}	9.8×10^{-2}
Si	5.15	1.99	1.11	0.60	0.30	0.18	0.13	Si	0.66	Si	3.2×10^{-2}	1.2×10^{-2}
Ca					5×10^{-2}	2×10^{-2}	3×10^{-2}	Ca	7.4×10^{-2}	Ca	1.3×10^{-3}	$<4 \times 10^{-5}$
Sr	0.35	0.15	8×10^{-2}	4×10^{-2}	1.9×10^{-2}	$<1 \times 10^{-2}$	4.8×10^{-3}	Sr	$<2.9 \times 10^{-2}$	Sr	$<5 \times 10^{-3}$	$<1.1 \times 10^{-3}$
U	$<8 \times 10^{-3}$	$<3.4 \times 10^{-3}$	$<1.7 \times 10^{-3}$	$<9 \times 10^{-4}$	3.6×10^{-4}	2.1×10^{-5}	9.3×10^{-5}	U	6.7×10^{-4}	U	1.4×10^{-4}	1.4×10^{-5}
Ce					$<1 \times 10^{-2}$	$<5.6 \times 10^{-3}$	$<3.1 \times 10^{-3}$	Ce	$<1.7 \times 10^{-2}$	Ce	$<3 \times 10^{-3}$	$<7 \times 10^{-4}$
Fe					$<3 \times 10^{-4}$	$<1.4 \times 10^{-4}$	$<7.8 \times 10^{-5}$	Fe	$<4.3 \times 10^{-4}$	Fe	$<7 \times 10^{-5}$	$<2 \times 10^{-5}$
La					$<1.2 \times 10^{-2}$	$<6.3 \times 10^{-3}$	$<3.5 \times 10^{-3}$	La	$<1.9 \times 10^{-2}$	La	$<3 \times 10^{-3}$	$<7 \times 10^{-4}$
Mn					$<1.4 \times 10^{-3}$	$<7 \times 10^{-4}$	$<3.9 \times 10^{-4}$	Mn	$<2.1 \times 10^{-3}$	Mn	$<3 \times 10^{-4}$	$<8 \times 10^{-5}$
Ni					$<3 \times 10^{-3}$	$<1.5 \times 10^{-3}$	$<8.4 \times 10^{-4}$	Ni	$<4.6 \times 10^{-3}$	Ni	$<7 \times 10^{-4}$	$<2 \times 10^{-4}$
Ti					$<3 \times 10^{-4}$	$<1.3 \times 10^{-4}$	$<7.3 \times 10^{-5}$	Ti	$<3.9 \times 10^{-4}$	Ti	$<6 \times 10^{-5}$	$<1.5 \times 10^{-5}$
Zr					$<6 \times 10^{-4}$	$<6 \times 10^{-4}$	$<3.4 \times 10^{-4}$	Zr	$<9 \times 10^{-4}$	Zr	$<1.4 \times 10^{-4}$	$<7 \times 10^{-5}$

Table 8. RSC S29 Solution Analysis From MCC Leach Tests in Silicate Water

Normalized Release Rate g/m ² d											
MCC-1 90°C					MCC-2 150°C				MCC-3 150°C		
Day	14	21	28	84	Day	14	28	56	Day	28	56
Na	<0.21	<0.14	<0.11	0.17	Na	<0.21	0.57	0.56	Na	0.43	0.35
Cs	$<6.9 \times 10^{-2}$	<0.12	$<8.8 \times 10^{-2}$	$<3 \times 10^{-2}$	Cs	0.48	0.20	0.21	Cs	$<8 \times 10^{-3}$	5×10^{-3}
Al	0.16	0.15	0.12	4×10^{-2}	Al	0.77	0.37	0.26	Al	7.7×10^{-2}	6.8×10^{-2}
Si	<0.21	<0.14	<0.11	0.13	Si	<0.21	0.54	0.38	Si	ND	ND
Ca	3.6×10^{-2}	4.9×10^{-2}	1.9×10^{-2}	1×10^{-2}	Ca	0.19	0.12	4.9×10^{-2}	Ca	1.9×10^{-3}	$<4 \times 10^{-5}$
Sr	$<7.7 \times 10^{-2}$	$<5.5 \times 10^{-2}$	$<3.9 \times 10^{-2}$	$<1.3 \times 10^{-2}$	Sr	$<7.5 \times 10^{-2}$	3.8×10^{-2}	2.8×10^{-2}	Sr	$<5 \times 10^{-3}$	$<1.1 \times 10^{-3}$
U	1.4×10^{-3}	1.2×10^{-3}	8.1×10^{-4}	2.5×10^{-4}	U	1.4×10^{-3}	9.1×10^{-4}	4.3×10^{-4}	U	2.8×10^{-4}	1.9×10^{-4}
Ce	$<4.6 \times 10^{-2}$	$<3.3 \times 10^{-2}$	$<2.3 \times 10^{-2}$	7.5×10^{-3}	Ce	$<4.5 \times 10^{-2}$	$<2.2 \times 10^{-2}$	2.2×10^{-2}	Ce	$<3 \times 10^{-3}$	$<7 \times 10^{-4}$
Fe	$<1.2 \times 10^{-3}$	$<8.3 \times 10^{-4}$	$<5.9 \times 10^{-4}$	$<2 \times 10^{-4}$	Fe	3.4×10^{-3}	1.1×10^{-3}	4.2×10^{-4}	Fe	$<7 \times 10^{-5}$	$<2 \times 10^{-5}$
La	$<5 \times 10^{-2}$	$<3.6 \times 10^{-2}$	$<2.6 \times 10^{-2}$	$<9 \times 10^{-3}$	La	$<5 \times 10^{-2}$	$<2.5 \times 10^{-2}$	$<1.2 \times 10^{-2}$	La	$<3 \times 10^{-3}$	$<7 \times 10^{-4}$
Mn	$<5.7 \times 10^{-3}$	$<4 \times 10^{-3}$	$<2.9 \times 10^{-3}$	$<9.4 \times 10^{-4}$	Mn	$<5.5 \times 10^{-3}$	$<2.8 \times 10^{-3}$	$<1.4 \times 10^{-3}$	Mn	$<4 \times 10^{-4}$	$<8 \times 10^{-5}$
Ni	$<1.2 \times 10^{-2}$	$<8.8 \times 10^{-3}$	$<6.2 \times 10^{-3}$	$<1.7 \times 10^{-3}$	Ni	$<1.2 \times 10^{-2}$	$<6 \times 10^{-3}$	$<3 \times 10^{-3}$	Ni	$<7 \times 10^{-4}$	$<1.7 \times 10^{-4}$
Ti	1.6×10^{-3}	$<1.2 \times 10^{-3}$	$<8.2 \times 10^{-4}$	$<7 \times 10^{-4}$	Ti	$<1.1 \times 10^{-3}$	$<5.4 \times 10^{-4}$	$<2.6 \times 10^{-4}$	Ti	$<6 \times 10^{-5}$	$<1.5 \times 10^{-5}$
Zr	$<2.5 \times 10^{-3}$	$<1.8 \times 10^{-3}$	$<1.3 \times 10^{-3}$	$<1.1 \times 10^{-3}$	Zr	$<2.5 \times 10^{-3}$	$<1.2 \times 10^{-3}$	$<1.5 \times 10^{-3}$	Zr	$<1.4 \times 10^{-4}$	$<7 \times 10^{-5}$

Table 9. RSC S29 Solution Analysis From MCC Leach Tests in Brine

Normalized Release Rate g/m ² d								
MCC-1 90°C				MCC-2 150°C		MCC-3 150°C		
Day	14	28	56	Day	56	Day	28	56
Na	-	-	-	Na	-	Na	-	-
Cs	<7.0	<3.4	<0.43	Cs	<0.43	Cs	0.18	0.12
Al	<8 x 10 ⁻²	<4 x 10 ⁻²	<9.5 x 10 ⁻³	Al	<9.5 x 10 ⁻³	Al	<4 x 10 ⁻⁴	<4 x 10 ⁻⁵
Si	<0.80	<0.39	5.8 x 10 ⁻²	Si	0.39	Si	7.4 x 10 ⁻³	2.9 x 10 ⁻³
Ca	0.97	0.41	3.8 x 10 ⁻²	Ca	0.19	Ca	0.16	0.30
Sr	<3.8	<1.90	<0.19	Sr	<0.19	Sr	0.11	0.10
U	<1.4 x 10 ⁻²	<7 x 10 ⁻³	2.1 x 10 ⁻²	U	3 x 10 ⁻²	U	8.1 x 10 ⁻⁴	4.1 x 10 ⁻⁴
Ce	<2.3	<1.1	<2.9 x 10 ⁻²	Ce	<2.8 x 10 ⁻²	Ce	<1.1 x 10 ⁻³	<6 x 10 ⁻⁴
Fe	<6 x 10 ⁻²	<3 x 10 ⁻²	<7.2 x 10 ⁻⁴	Fe	<7 x 10 ⁻⁴	Fe	<1.1 x 10 ⁻⁵	8 x 10 ⁻⁵
La	<2.6	<1.25	<3.1 x 10 ⁻²	La	<3.1 x 10 ⁻²	La	<1.2 x 10 ⁻³	<6 x 10 ⁻⁴
Mn	<0.28	<0.14	2.1 x 10 ⁻³	Mn	6.9 x 10 ⁻³	Mn	4.9 x 10 ⁻²	3.6 x 10 ⁻²
Ni	<0.6	<0.30	3 x 10 ⁻³	Ni	4.5 x 10 ⁻³	Ni	<3 x 10 ⁻⁴	<1.5 x 10 ⁻⁴
Ti	<6 x 10 ⁻²	<2.6 x 10 ⁻²	<2.7 x 10 ⁻⁴	Ti	<2.7 x 10 ⁻⁴	Ti	<3 x 10 ⁻⁵	<1.3 x 10 ⁻⁵
Zr	0.13	<6.5 x 10 ⁻²	9.2 x 10 ⁻²	Zr	0.12	Zr	<6 x 10 ⁻⁴	<3 x 10 ⁻⁵

ducted in this laboratory suggest that the microstructural isolation of nepheline grains by the insoluble phases could totally shut down the major dissolution processes with time in a monolith as could the formation of protective surface layers. In these cases, the release of all waste elements into the ground water would essentially be under diffusion control with surface ion-exchange and it is doubtful that any of the radionuclides would ever reach saturation levels in the repository ground waters from this waste form.

Summary

The combining of the high performance crystalline phases from the alumina-silica, and titanium-silica based ceramic waste forms has produced a significantly improved, if not optimized, defense waste ceramic. The RSC-S29 ceramic maintains high-waste loading, while improving the ceramic leach resistance and ease of fabrication.

The RSC-S29 ceramic takes advantage of both the zirconolite and magnetoplumbite phases as primary hosts for the long-lived radionuclides while also providing perovskite and murataite-type phases as secondary waste element host phases. The presence of multiple lattice sites for the major radionuclides gives a greater flexibility to the form for accommodating variations in the waste composition and processing parameters. The variety of coordination sites also offers a greater ability to accommodate the effects of transmutation in the form.

The processing requirements are compatible with remote operation; only mild reduction is required, no Cs volatilization occurs, and consolida-

tion can be accomplished at 1040°C and pressures less than 10,000 psi. The fabrication process for the RSC-529 ceramic is also compatible with the fluidized bed calciner technology being demonstrated at LLNL and used remotely at INEL/ICPP for 18 years.

In all testing the RSC-S29 appears to have the highest overall leach performance reported for any uncoated defense waste form at a waste volume reduction approximately a factor of three greater than the reference borosilicate glass form. The leach testing also indicates that the ceramic form's performance is such that additional engineered barriers such as geologic repository bentonite backfills are unnecessary with such a high quality basic form.

In summary this work supports the RSC-S29 formulation as the best ceramic form developed to date both with respect to processing and performance and shows the waste form to be a practical, permanent solution to the immobilization of high-level diffuse nuclear waste.

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REFERENCES

1. P. E. D. Morgan, D. R. Clarke, C. M. Jantzen, and A. B. Harker, "High-Alumina Tailored Nuclear Waste Ceramics," J. Am. Ceram. Soc. 64(5), 249-58 (1981).
2. A. B. Harker, C. M. Jantzen, P. E. D. Morgan, and D. R. Clarke, "Tailored Ceramic Nuclear Waste Forms: Preparation and Characterization," Scientific Basis for Nuclear Waste Management, Vol. 3 ed. by J. G. Moore (Plenum Press, N.Y. 1981) 139-146.
3. F. J. Ryerson, K. Burr, and R. Rozsa, "Formulation of Synroc-D Additives for Savannah River Plant High-Level Radioactive Waste," Lawrence Livermore National Laboratory, UCRL-53237 (1981).
4. J. Campbell, C. Hoenig, F. Bazan, F. Ryerson, M. Guinan, R. Van Konyneburg, and R. Roza, "Properties of Synroc-D Nuclear Waste Form: A State-of-the-Art Review," Lawrence Livermore National Laboratory, UCRL-53240 (1981).
5. A. B. Harker, P. E. D. Morgan, D. R. Clarke, and J. F. Flintoff, "Formulation and Processing of Polyphase Ceramics for High-level Nuclear Waste," Scientific Basis for Nuclear Waste Management, 4, in press (1982).
6. J. Stone, J. Allender, and T. H. Gould, Jr., "Comparison of Properties of Borosilicate Glass and Crystalline Ceramic Forms for Immobilization of Savannah River Plant Waste," E. I. DuPont de Nemours & Co., Savannah River Laboratory Report DP-1627 (1982).

7. H. J. Rossel, "Zirconolite, a Fluorite-Related Superstructure," *Nature* 283, 282-283 (1981)
8. J. W. Adams, T. Botinelly, W. N. Sharp, and K. Robinson, "Murataite, a New Complex Oxide from El Paso County, Colorado," *Am. Min.* 59, 172-176 (1974).
9. P. E. D. Morgan and F. J. Ryerson, "A New 'Cubic' Crystal Compound in Radwaste Ceramics," *J. Mater. Sci.* 1, 351-352 (1982).
10. P. E. D. Morgan and E. H. Cirlin, "The Magnetoplumbite Crystal Structure as a Radwaste Host," *J. Am. Ceram. Soc.* 65, C-114-115 (1982).
11. E. H. Cirlin and R. M. Housley, "Proceedings of the Lunar Science Conference," 3rd edition. Edited by E. H. King (Pergamon, New York, 1977) 3931-40.
12. R. Raj and P. E. D. Morgan, "Activation Energies for Densification, Creep, and Grain-Boundary Sliding in Nitrogen Ceramics," *J. Am. Ceram. Soc.* 64, C-143-145 (1981).
13. A. B. Harker, D. R. Clarke, C. M. Jantzen, and P. E. D. Morgan, "The Effect of Interfacial Material on Tailored Ceramic Nuclear Waste Form Dissolution," in *Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems*. Edited by J. Pasko and A. Evans (Plenum Publishing Co., 1981), 207-216.
14. D. R. Clarke, "Preferential Dissolution of an Intergranular Amorphous Phase in a Nuclear Waste Ceramic," *J. Am. Ceram. Soc.* 64, C-89-C-90 (1981).
15. A. E. Ringwood, S. E. Kesson, and N. G. Ware, "Immobilization of High-Level Nuclear Reactor Waste in SYNROC," *Nature* 278, 219 (1979).

16. C. M. Jantzen, D. R. Clarke, P. E. D. Morgan, and A. B. Harker, "Leaching of Polyphase Nuclear Waste Ceramics: Microstructural and Phase Characterization," J. Am. Ceram. Soc. 65, 292-300 (1982).
17. R. S. Rajan and A. S. Tamhane, "Evidence for ^{244}Pu Fission Tracks in Hibonites from Murchison Carbonaceous Chondrite," Lunar Plant. Sci., XII [3], 863-65 (1981).
18. J. P. Barret, A. Rafaoui, J. Thery, D. Vivien, and R. Collongues, "Sodium Lanthanides Mixed Aluminates." to be published Matl. Res. Bull. (1982).
19. R. R. Neurgaonkar and F. A. Hummell, "Substitutions in the $\text{Ca}_2\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)_2$ Hauyne Structure," Mater. Res. Bull. 11, 61-66 (1976).
20. J. E. Mendel, "Nuclear Waste Materials Handbook Waste Form Test Methods," Battelle Pacific Northwest Laboratory, DOE/TIC 11400 (1982).
21. A. B. Harker and D. R. Clarke, "Dissolution Mechanisms in Polycrystalline Ceramic Nuclear Waste Forms," Proceedings of the Battelle PNL, MCC Leaching Mechanisms Workshop held at Gaithersburg, MA, (May 1982).

SECTION II

FORMULATION AND PROCESSING OF ALUMINA BASED CERAMIC NUCLEAR WASTE FORMS

By

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ABSTRACT

A class of dense, high-alumina ceramics has been developed for the immobilization of Savannah River Plant defense nuclear waste. The ceramics, fabricated by hot isostatic pressing or reactive hot pressing, normally consist of four compatible crystalline phases - magnetoplumbite, spinel, uraninite, and corundum. A fifth compatible phase, nepheline, can be designed into the assemblage when high sodium levels are present in the waste. All radionuclides are incorporated into the magnetoplumbite and uraninite phases, with the nonradiophases providing microstructural isolation of the individual radiophase grains. The chemical formulation of the ceramic waste form and the processing requirements are discussed.

I. INTRODUCTION

The concept of immobilizing the radioactive elements of nuclear waste in an assemblage of mineral phases was originally introduced by Hatch¹ in 1953 and demonstrated by McCarthy between 1973 and 1976.^{2,3,4} This concept has been reviewed and conceptually extended by Roy.^{5,6} Since that time, several other mineralogical assemblages, notably the Sandia titanate-based ceramic⁷ and the zirconolite-hollandite-perovskite ceramic "Synroc" (also titanate-based), have been developed.^{8,9} Implicit in this concept is the idea of using additives to alter the composition of the waste: tailoring it chemically so that it will produce the desired crystalline phases after consolidation. Using this concept, another crystalline assemblage has been developed, based on alumina tailoring, for consolidating for eventual geologic storage the defense nuclear waste stored at the Savannah River Plant (SRP). The philosophy behind the tailoring approach for this phase assemblage takes as much advantage as possible of the existing chemical composition of the nuclear waste to minimize the required tailoring and produce a solid ceramic form with high waste loading and volume reduction, while reducing the required processing steps. The tailoring was designed to produce specific host phases (magnetoplumbite and uraninite) for the waste radionuclides such that the bulk of the ceramic form would be made up of phases containing no radioactive material (spinel, corundum, nepheline), thus providing microstructural isolation of the radiophases to improve the leach resistance of the form. This report describes the chemical composition, processing, microstructural characterization, and phase relationships of the new tailored waste form.

The starting compositions for the SRP defense waste were taken from six descriptions made up by the DuPont Savannah River Laboratories (SRL) to provide the mean and extreme compositions expected for the waste.¹⁰ Three of the compositions (Table 1) are for the existing waste, and three describe the expected waste compositions after proposed processing to remove aluminum compounds for volume reduction and easier processing into borosilicate glass. Since the aluminous nature of the existing waste is advantageous to producing a ceramic form, our work has concentrated on the SRL compositions without aluminum removal.

Table 1. Composition of Simulated Savannah River
Defense Waste Used in this Study

	Weight %		
	High Fe	Composite	High Al
<u>Major Components</u>			
Fe ₂ O ₃	50.74	34.59	5.10
Al ₂ O ₃	4.66	27.06	72.85
MnO ₂	3.45	9.52	4.19
U ₃ O ₈	11.88	3.12	1.23
CaO	3.48	2.58	0.34
NiO	8.66	4.28	0.75
SiO ₂	0.38	0.81	0.54
Na ₂ O	4.31	4.86	1.88
Na ₂ SO ₄	<0.48	<0.89	<0.48
Ion Sieve*	8.42	8.55	8.94
<u>Trace Elements</u>			
Cs ₂ O	1.38	Same for all compositions	
BaO	0.13		
MgO	0.27		
SrO	0.98		
ZrO ₂	0.17		
Cr ₂ O ₃	0.03		
RuO ₂	0.03		
PbO	0.04		
CeO ₂	0.07		
Nd ₂ O ₃	0.48		
ThO ₂	0.15		
*Nominally a mixture of: (wt%).			
Na ₂ O	1.7-9.1	K ₂ O	0.4-2.0
SiO ₂	66-69	MgO	0.5-2.5
Al ₂ O ₃	15.3-17.5	Fe ₂ O ₃	3.7-4.5
CaO	0.8-5.8		

II. TAILORING

The major radioisotopes of concern in the waste are ^{90}Sr , ^{137}Cs , uranium, plutonium, actinides (Am, Cm) and the rare earths (Sm, Eu, Ce). In low-concentration wastes such as SRP defense waste, the radioactive waste ions can be accommodated in solid solution in crystalline host lattices (radiophases). Moreover, any insoluble oxide or metal phase can act as both a physical and a chemical barrier to leaching by microstructurally isolating the radiophases. The number of inert phases is determined by the elements in the waste, the tailoring elements, the waste loading, and the consolidation technique.

A. Al_2O_3 + RARE EARTH OXIDE TAILORING

The primary tailoring concept introduced here for the alumina-based ceramic waste form is to add sufficient rare earth and alumina to facilitate the incorporation of the waste nuclides into a magnetoplumbite phase and to reduce the uranium in the preceramic powders to U^{4+} for the formation of uraninite, the uranium host phase (Table 2). If more alumina is added than required to form the magnetoplumbite and spinel phases, corundum will be formed. This has the intrinsic advantage that excess alumina may be added to provide microstructural isolation by forming both corundum and spinel.

The magnetoplumbite phase was selected as the basis of the mineralogical assemblage because magnetoplumbites are capable of containing both aluminum and iron¹¹ and also because they have a diverse crystal chemistry able to accept most of the radionuclides in the SRP waste. The magnetoplumbites,

Table 2. Tailored Ceramic Formulation and Calculated Phase Content Content for SRL High Al Defense Waste (Without Ion-Siv)

a. High Alumina ($2 \times \text{Re}_2\text{O}_3$)

Component Oxide	High Alumina Simulated Waste (wt. %)	Additives (wt %)
Fe_2O_3	5.05	
Al_2O_3	72.88	
MnO_2	4.18	
U_3O_8	1.22	
CaO	0.67	
NiO	0.75	
SiO_2	0.90	
Na_2O	0.91	
SrO	0.18	
Cs_2O	0.18	
Ce_2O_3	0.34	
Nd_2O_3	0.34	
La_2O_3		9.90
ZrO_2		0.50
TiO_2		<u>2.00</u>
Total wt %	87.60	12.40

b. Calculated Volumetric Phase Content

Phase	wt %	ρ g/cc	vol %
Magnetoplumbite	60.08	3.68	63.0
Spinel	21.37	4.11	20.1
Uraninite	1.69	9.84	0.7
Corundum	16.85	4.00	16.2

Calculated density = 3.86 g/cc

Observed density =

nominally $X(\text{Al},\text{Fe})_{12}\text{O}_{19}$ where $X = \text{Sr}, \text{Ba}, \text{Cs}_{0.5} + \text{La}_{0.5}, \text{Na}_{0.5} + \text{RE}_{0.5}$,¹² are accommodating structures because they are composed of spinel blocks that have the usual IV and VI coordinated sites for cations while interspinel layers have unusual V fold sites for small cations. The interspinel layers also accommodate large cations of ~ 0.115 to 0.184 nm radius, replacing oxygen in XII fold sites in the anion close-packed structure.¹³ These large ions may be monovalent, divalent, or trivalent with balancing charge substituents either in the interspinel layer (e.g., $\text{Na}_{0.5} + \text{La}_{0.5}$) or between the interspinel layer and the spinel block by balancing the spinel blocks (e.g., by La^{3+} and Mg^{2+} simultaneously replacing Ba^{2+} and Al^{3+} in $\text{BaAl}_{12}\text{O}_{19}$ to produce $\text{LaMgAl}_{11}\text{O}_{19}$).¹⁴

Tailoring for a magnetoplumbite phase to provide crystalline host sites for Cs and Sr involves supplying enough alumina to accommodate large divalent waste ions (e.g., $\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$) as well as supplying the large monovalent ions (e.g., $\text{Cs}^+, \text{Rb}^+, \text{Na}^+$) with large trivalent ions (e.g., rare earths La^{3+} , and Nd^{3+}) and sufficient alumina (as outlined above) to maintain charge balance. The alumina supply must also be sufficient to accommodate the divalent ions ($\text{Mg}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}$) in forming spinel. However, any remaining Fe^{3+} would substitute for Al^{3+} in magnetoplumbite or spinel and free Al^{3+} to produce an additional amount of corundum for microstructural isolation. Since the compatible crystalline assemblages all exhibit a wide range of solid solubility, wastes of variable composition can easily be accommodated. In addition to the $\text{Al}_2\text{O}_3 + \text{REO}$ tailoring, minor additives have been used to optimize the waste form. ZrO_2 is added to the formulation, at ~ 10 mole% of the expected UO_2 level, to form a fluorite structure solid solution. It has

been empirically observed that the dilution of the UO_2 with zirconium slightly improves in the leach resistance of the uraninite phase.

Titanium dioxide has been added to the SRL "High Al" composition (see Table 1) formulation to act as a consolidation aid. When added at a level of about 2 mole % of the Al in the waste form, it significantly lowers the required temperature for consolidation by reactive hot pressing (100 to 150°C). The addition of TiO_2 has not been a significant factor in establishing the consolidation temperature in hot isostatic pressing. The small level of TiO_2 is primarily incorporated into the magnetoplumbite and spinel phases.

The $\text{Al}_2\text{O}_3 + \text{REO}$ tailoring formulation currently used for the SRL waste compositions is given in Table 2. The basic waste compositions were those supplied by SRL in March 1981 based on the DP-1545 waste description.¹⁰

B. $\text{Al}_2\text{O}_3 + \text{SiO}_2$ TAILORING

The relatively low content of radioactive material in the SRP wastes makes it desirable to have a high waste loading in the consolidated form. Although the $\text{Al}_2\text{O}_3 + \text{REO}$ tailoring allows up to 90 wt % loading the High Al composition waste, loading is restricted by the amount of sodium present in the Composite and High Fe wastes to about 30 wt % of waste calcines.

To increase the loading of the Composite and High Fe wastes in the form, a fifth phase, nepheline can be added to the ceramic assemblage as a sodium host. Nepheline, nominally, NaAlSiO_4 , is one of the more stable crystalline sodium-containing phases in nature. The major advantage of nepheline in the waste form is that it contains a high percentage of Na in its

structure and allows loadings in the ceramic to be increased up to 50 to 75 wt % of Composite waste, depending on the redox state of the Fe in the precursor powders.

The $\text{Al}_2\text{O}_3 + \text{SiO}_2$ tailoring formulation consists of using the SiO_2 present in the waste, along with added Kaolin, to provide the correct nepheline stoichiometry. Then Al_2O_3 is added as required to form spinel and magnetoplumbite. The magnetoplumbite structure is still the designed host phase for strontium and cesium. A small amount of rare earth oxides is still required to balance the cesium in the magnetoplumbite phase, and ZrO_2 is again added to form a solid solution with UO_2 . The presence of the SiO_2 , Na_2O , and Al_2O_3 in the form invariably leads, at much lower temperatures than in the High Al cases, to the formation of a liquid phase during consolidation. Consolidation to full density in the SiO_2 tailored systems can occur at as low as 1000°C with hot isostatic pressing.

Tables 3 and 4 give two basic formulations for the nepheline containing ceramic using SRL Composite waste. The first at 60 wt % loading has all the Na present as nepheline, the second at 50 wt % loading splits the Na between the nepheline and magnetoplumbite phases. As noted in the description of the volumetric contribution of each phase in Tables 3 and 4, an intergranular amorphous phase is present in both compositions. This phase, formed by incomplete crystallization of the liquid phase during consolidation, lowers the leach resistance of the nepheline-containing forms with respect to the high-alumina ceramics for glass-modifying elements such as Ca, Na, and Cs.

Table 3. Tailored Ceramic Formulation and Calculated Phase Content for SRL Composite Waste With Nepheline as the Na Host (without Ion-Siv)

a. High Alumina

Component Oxide	High Alumina Sim. Waste (wt. %)	Additives (wt %)
Fe ₂ O ₃	23.18	
Al ₂ O ₃	18.13	33.83
MnO ₂	6.38	
U ₃ O ₈	2.09	
CaO	1.73	
NiO	2.87	
SiO ₂	0.82	5.72
Na ₂ O	2.80	
Na ₂ SO ₄	0.55	
SrO	0.24	
Cs ₂ O	0.24	
Ce ₂ O ₃	0.49	
Nd ₂ O ₃	0.49	
La ₂ O ₃		0.27
ZrO ₂		0.18
Total wt %	60.00	40.00

b. Calculated Volumetric Phase Content*

Phase	wt %	ρ (g/cm ³)	vol %
Magnetoplumbite	26.66	3.68	27.4
Spinel	55.48	4.24	49.5
Uraninite	2.26	9.84	0.9
Nepheline	51.03	2.63	21.6
Corundum	0.57	4.00	0.5

Calculated density = 3.80 g/cm³

Observed density = 3.78 g/cm³

* An amorphous intergranular phase was observed by transmission electron microscopy to be present in this composition.

Table 4. Tailored Ceramic Formulation and Calculated Phase Content for SRL Composite Waste With Both Nepheline and Magnetoplumbite Na Host Phases (without Ion Siv)

a.

Component Oxide	High Alumina Sim. Waste (wt. %)	Additives (wt %)
Fe ₂ O ₃	19.32	
Al ₂ O ₃	15.10	41.09
MnO ₂	5.32	
U ₃ O ₈	1.74	
CaO	1.44	
NiO	2.39	
SiO ₂	0.68	3.40
Na ₂ O	2.33	
SrO	0.18	
Na ₂ SO ₄	0.46	
Cs ₂ O	0.20	
Ce ₂ O ₃	0.41	
Nd ₂ O ₃	0.41	
La ₂ O ₃		5.34
ZrO ₂		<u>0.17</u>
Total wt %	50.00	50.00

b. Calculated Volumetric Phase Content

Phase	wt %	ρ g/cc	vol %
Magnetoplumbite	53.28	3.68	55.5
Spinel	35.57	4.50	30.3
Uraninite	1.88	9.84	0.7
Nepheline	9.27	2.63	13.5

Calculated density = 3.83 g/cm³

Observed density = 3.78 g/cm³

* An amorphous intergranular phase was observed by transmission electron microscopy to be present in this composition.

III. LABORATORY-SCALE PROCESSING OF SIMULATED SRL WASTE INTO TAILORED CERAMICS

In designing the powder preparation and ceramic consolidation procedures the aim was to fabricate a dense tailored ceramic, having a small ($<1\text{ }\mu\text{m}$) uniform grain size and containing no continuous intergranular amorphous phases. The small grain size is desired to prevent microcracking caused by differential or anisotropic thermal contraction or phase transformations from occurring during fabrication. Continuous intergranular phases are undesirable since they may act as short circuit leaching paths through the microstructure as well as be suitable hosts for Cs and Sr, both of which are known to be glass modifiers. A special consideration in the consolidation process is the need to form a dense ceramic at sufficiently low temperatures to minimize the loss of volatile species during fabrication. The techniques of hot isostatic pressing (HIPping) and reactive hot pressing¹⁵ were adopted since both are capable of producing full density at temperatures significantly lower than those of conventional hot pressing or sintering. In addition, it is known that natural high alumina phase assemblages may be formed by contact metamorphism (i.e., natural hot pressing) and also that they are stable over long geologic periods.¹⁶

As in previous studies,²⁻⁴ simulated sludges were prepared by using non-radioactive analogs of the important waste elements and using depleted uranium and thorium salts.

A. PREPARATION OF POWDERS

The starting powder is critical to the formation of fine-grain, fully dense ceramics. Ideally, the waste should be completely mixed at the atomic level with the anhydrous powders having a very small particle size (<250 mesh). Several techniques were used in this study both to approach the idealized situations and to simulate actual waste processing. These included (1) co-precipitation of nitrate mixtures of waste elements using tetramethylammonium hydroxide pentahydrate base followed by calcining at 650 to 800°C and ball milling, (2) spray calcining of nitrate mixtures, and (3) wet ball milling of the simulated waste sludge with fine powdered additives and nitrates.

The "standard" simulated wastes used in this study were either spray dried nitrates or mixed oxide-hydroxides as prepared by Stone and Pickett of SRL.¹⁷ In all cases total the weight loss calcining and the elemental content of the wastes were determined before processing.

B. POWDER PROCESSING

The simulated waste powders were normally wet ball milled with either water or isopropyl alcohol with the tailoring and redox control additives. $\text{Al}(\text{OH})_3$ and Kaolin were the major additives, with soluble nitrates being used for the minor constituents. When used, titanium was added as the isopropoxide. When chemical redox control was used, organic amines were mixed in during the initial ball milling. During this study monoethanol amine (MEA) and triethanol amine (TEA) were used as the organic redox control agents. After milling, the sludge was dried at 60°C in a vacuum oven.

After drying, the powders were either calcined in alumina crucibles in air or when chemical redox control was used, were heat treated in an argon atmosphere tube furnace. Calcination temperatures of 700 to 800°C were used in air calcining, while temperature programming in stages to 700 to 800°C was used when chemical redox control was desired.

Two basic means of redox control were used: metal - metal oxide buffers and organic reagents. Metal powder and metal mesh oxygen buffers gave satisfactory redox control, but the mechanical difficulties of mixing finely divided metal powders with the waste or obtaining intimate contact with coiled wire and meshes were determined to be unsatisfactory for remote operation. The use of chemical additives for redox control was found to have several advantages: it greatly reduces the amount of powder handling; using a liquid reagent allows complete mixing with the waste during the ball milling stage; and it permits one step "in-can" calcining and redox control.

The in-can technique consists of mixing the organic redox agent with the additives and waste, compacting either a gel or dried powders into the precursor form in the consolidation cannister, and heating under vacuum or inert gas atmosphere to reduce the material and drive off any volatiles. This process is shown schematically in Fig. 1. At laboratory scale, this technique gives good product uniformity, with no residual material from the organic being present after calcining.

The original concept for the organic redox control agent was to select a high-boiling-point material that would vaporize cleanly. MEA and TEA were selected for initial investigation since there were some existing data on

Fig. 1 Schematic of laboratory-scale powder process steps for fabricating tailored ceramic nuclear waste forms.

their performance.¹⁸ These amines, however, may not be the best for this purpose, and more research in selecting the best control agent needs to be carried out.

The laboratory preparation procedure for HIP consolidation of the ceramic form currently consists of:

- 1) The chosen waste sludge is thoroughly mixed with the additives and redox control agent by wet ball milling for up to 5 h.
- 2) The milled sludge is dried in a vacuum oven at 60°C.
- 3) The resulting dried powders are cold pressed into the desired preform and then cold isostatically pressed at 50,000 psi.
- 4) The preform is then heated in argon to 300 to 350°C and held at this temperature for 1 h.
5. The preform is then taken up to about 750°C for 2 h to drive off all volatiles.
6. The preform is wrapped in nickel and vacuum sealed into a stainless steel can for consolidation by HIPping.

C. REACTIVE HOT PRESSING

Reactive hot pressing refers to the densification of powders in which chemical reactions, decompositions, or phase transformations occur during hot pressing; the final ceramic has different phases than the starting powder. Densification generally occurs at a significantly lower temperature because of the ultrafine microstructures generated during these sequences and can result in a finer grain size than when the ceramic is produced from ground or "dead

burned" powders. As an example, submicrometer grain size MgO/CaO ceramic may be easily achieved by the reactive hot pressing of dolomite rock, $\text{CaMg}(\text{CO}_3)_2$, with the evolution of CO_2 ,¹⁵ modeling a possible natural process.

In the reactive hot pressing of the simulated waste sludge, the powders were highly reactive. Hot pressing was carried out from ambient to 1200 to 1300°C at 5 to 10°/min at 27.5 MPa and held for 1 h at 1200 to 1300°C in graphite dies, with the powders surrounded by nickel powder. The nickel powder was used to avoid further reduction of the powder by the graphite dies. The densification curves observed were similar to those of pure $\text{Al}(\text{OH})_3$, where no significant shrinkage is observed in the region of $\text{Al}(\text{OH})_3 \rightarrow \gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O}$ at approximately 300-500°C,¹⁵ but where shrinkage is observed to occur with increasing rapidity with the $\gamma \rightarrow \alpha$ type transformation at ~1000°C. An example is shown in Fig. 2. The hot-pressed samples have typical densities in the range from 90 to 98% of the calculated theoretical density.

The intermediate phases formed from very reactive powders during hot-pressing were observed by heat treating the Composite composition (Table 1) spray calcined nitrate solutions (representing an ideal tailored sludge calcine) at a variety of temperatures. The results are shown in the X-ray diffraction patterns and electron micrographs of Figs. 3 and 4. After heat treatment at 650°C, the powders were amorphous to X-ray analysis (curve a). After being heated to 950°C, the powder had crystallized to a $\gamma\text{-Al}_2\text{O}_3$ type with the nuclear waste ions in solid solution (curve b). An 8 h treatment at 1000°C (curve c) began the formation of the magnetoplumbite phase, and transmission electron microscopy, indicated the grain size to be <10 nm. In the

Fig. 2 Density as a function of temperature during the reactive hot pressing of a typical high-alumina tailored ceramic.

Fig. 3 X-ray diffraction patterns of a spray-calcined, high-alumina composition after heat treatment at the various indicated temperatures.

(a)

(b)

(c)

(d)

Fig. 4 Transmission electron micrographs of the same heat-treated, spray-calcined powder showing the development and growth of the crystalline phases with heat treatment. By 1000°C, small <10 nm, crystallites of the magnetoplumbite phase can be discerned by the presence of characteristic 2.2 nm lattice fringes. At 1050°C, the powder is fully crystallized.

transmission electron micrograph magnetoplumbite grains (revealed by the characteristic c-axis spacings in the lattice fringe image) of only two and three unit cells in size can be discerned. By 1050°C, the powder was completely crystalline (curve d), well developed crystallites could be seen, and the average grain size exceeded 10 nm. Differential thermal analysis (DTA), at 10°C/min, showed corresponding exotherms at 865°C and 1170°C, shifted to higher temperatures by the fast heating rate.

D. HOT ISOSTATIC PRESSING

Hot isostatic pressing is a ceramic processing technique that is currently finding extremely rapid commercial application. The technique is considerably simpler than uniaxial hot pressing and offers the advantage that large monoliths can be manufactured to predetermined shapes. In this laboratory, the waste pre-form is wrapped in nickel foil and sealed under vacuum in a stainless-steel canister for HIPping. The nickel foil prevents any reaction from occurring between the waste form and the steel canister, while making it simpler to separate the ceramic from the canister after consolidation for subsequent characterization. The HIP process consists of placing the sealed canister in a sealed furnace, pressurizing from 2000 to 9000 psi of argon, and then heating to the desired temperature. Final pressure in the furnace is regulated at a preset pressure from 10,000 to 30,000 psi. During the process, the steel canister collapses inward on the waste form, transferring the full pressure and consolidating the sample (Fig. 5).

Fig. 5 Photograph of the ceramic waste form at the various steps in consolidation by hot isostatic pressing.

E. Cs RETENTION DURING PROCESSING

The processing of a crystalline ceramic phase assemblage must avoid exceeding temperatures at which volatile elements such as Cs, and to a lesser extent Na, are either lost from their desired host phases or produce massive internal transport by evaporation-condensation, coarsening grain structures unduly and thereby inhibiting densification by other transport mechanisms. As a preliminary guideline to the limiting processing temperatures, the volatility of Cs in both crystallizing precursor powders and formed ceramics has been studied using a technique developed for the study of volatiles in moon rocks.^{19,20} The sample is heated, typically at 5°C/min, in a stream of argon in a pyrolytic graphite crucible with a cesium lamp beam entering and leaving the crucible through holes just above the sample. This adaptation of the atomic absorption technique can detect parts per million of Cs evolved as a function of temperature.

Pure Cs(NO₃), used as a reference, began to evolve Cs at 850°C. Maximum evolution rate occurred at 1050°C. A rare earth tailored powder, spray calcined at 650°C and lightly pressed into a pellet, began to evolve Cs at 1100°C with maximum evolution at 1250°C. A denser precipitated powder, also tailored with rare earths but precalcined to 600°C and pelletized, evolved Cs beginning at 1100°C and reached a maximum rate between 1450 and 1500°C. An untailored, hot pressed ceramic showed Cs loss beginning at 1000°C with a maximum at 1250°C; the equivalent rare-earth tailored, hot-pressed ceramic began Cs loss at 1100°C but did not reach a maximum rate until 1450° to 1500°C. These results were confirmed through Cs neutron activation analyses of both hot-pressed and HIPped waste samples. No cesium loss was detected with either consolidation technique.

IV. CHARACTERIZATION

The consolidated samples were all dense with little or no porosity evident by optical microscopy. In general, they had a uniform microstructure although some of the veining characteristic of hot-pressed samples could be discerned in oblique lighting. No microcracking was evident by optical or scanning electron microscopy. The grain size was typically less than 1 μm .

A. X-RAY DIFFRACTION - Al_2O_3 + REO TAILORING

X-ray diffraction (XRD) analysis indicated that the materials consisted of four phases: alumina, spinel, magnetoplumbite related solid solution type, and uraninite. A representative X-ray diffraction pattern of hot-pressed 100% untailored SRL "High Al" composition (Table 1) without ion seives is reproduced in Fig. 6. From the very low angle X-ray lines it was apparent that a β -alumina type (prototypically $\text{NaAl}_{11}\text{O}_{17}$) was forming. In addition, β''' -alumina or "W" type (prototypically $\text{NaMg}_2\text{Al}_{15}\text{O}_{25}$ (Ref. 21) and $\text{BaFe}_{18}\text{O}_{27}$) (Ref. 22) was found.*

Tailoring of the SRL Composite composition waste with a rare earth, La or Nd, so that each alkali ion (Cs or Na) is balanced by one rare earth ion, as for $\text{Na}_{0.5}\text{La}_{0.5}(\text{Fe,Al})_{12}\text{O}_{19}$, produced the phase assemblage in Fig. 7. A

* Because of the confusion in the literature in describing phases of the type $\text{NaMg}_2\text{Al}_{15}\text{O}_{25}$ and $\text{BaFe}_{18}\text{O}_{27}$, a modified Ramsdell notation is introduced here. It consists of the conventional Ramsdell notation followed by the number of layers in the spinel block in the unit cell placed in parentheses. Thus 2H(4S) and 2H(6S) represent two block hexagonal unit cells with four and six layer spinel blocks, respectively, and 3R(4S) represents a block rhombohedral unit cell with four layer spinel blocks.

Fig. 6 X-ray diffraction pattern, $\text{CuK}\alpha$ radiation, of hot-pressed untailored SRL high alumina composition. The diffraction peaks due to the corundum (c), spinel (s), uraninite (u), and magnetoplumbite related structures (mp) are indicated by shading.

Fig. 7 X-ray diffraction pattern of hot-pressed high alumina composition tailored with rare earth. $\text{CuK}\alpha$ radiation.

large fraction of magnetoplumbite-type phase is present, and the c/a ratio of the hexagonal unit cell, a distinctive indicator of the type of magnetoplumbite present, suggests a $XY_{12}O_{19}$ magnetoplumbite formulation. Verstegen and Stevels²⁴ have shown that c/a for β -type structures is approximately ~4.0 to 4.1;* for magnetoplumbites, it generally is approximately ~3.92 to 3.95. For the rare earth tailored rare earth magnetoplumbite type phase in Fig. 7, $a = 0.5612$ nm, $c = 2.2010$ nm, $c/a = 3.922$.

B. X-RAY DIFFRACTION- $Al_2O_3 + SiO_2$ TAILORING

XRD analysis of the ceramic forms, tailored with SiO_2 to produce nepheline as the sodium host, showed only five crystalline phases: spinel, nepheline, uraninite, magnetoplumbite, and corundum. As can be seen in Fig. 8, the use of nepheline as the major sodium host reduces magnetoplumbite to a minor phase (Tables 3 and 4). In the 60 wt % SRL Composite composition ceramic analyzed in Fig. 8, the magnetoplumbite serves only as a host for Sr, Ca, and Cs. The comparison between the High Al and Composite tailored ceramic XRD patterns demonstrates the flexibility of the waste form in accommodating vastly different levels of the major waste elements in only five crystalline phases.

* In further studies, we have found that the phase $Na_{0.5}La_{0.5}Al_{12}O_{19}$ definitely exists with a c/a of 3.948 contrasting with $NaAl_{11}O_{17}$ (~4.02) and $LaAl_{11}O_{19}$ (3.957).²¹ Also confirmed is the existence of $Cs_{0.5}La_{0.5}Al_{12}O_{19}$, $c/a = 3.940$.

Fig. 8 X-ray diffraction pattern of HIPped 60 wt % SRL Composite composition ceramic, tailored for nepheline as the Na host, compared to that of a rare earth tailored High Al composition ceramic.

C. ANALYTICAL ELECTRON MICROSCOPY ON Al_2O_3 + REO TAILORED CERAMICS

Samples for transmission electron microscopy were prepared by the standard method: a thin slice was cut, ground down to $\sim 50 \mu\text{m}$, and ion-beam thinned to electron transparency. The microstructures of the samples were examined in the conventional bright and dark field imaging modes, and regions of interest were analyzed by X-ray spectroscopy. In the microanalysis mode, the electron probe size was defined by varying the first condenser lens excitation, and the beam convergence was determined by the size of the second condenser lens aperture. In this way, regions as small as 4 nm could be selected electro-optically at 120 kV accelerating potential, although probe sizes of 10 nm and 40 nm were used in the majority of analyses. The size of the area from which the X-ray spectra originated was naturally larger than that defined electro-optically due to beam spreading within the foil, but in most cases the regions chosen for analysis were sufficiently thin to minimize the extent of beam spreading.

Figure 9 is a bright field transmission micrograph of a hot-pressed sample of rare earth tailored Composite composition waste, showing a region with a microstructurally isolated magnetoplumbite grain. The micrograph illustrates the dense polyphase nature of the ceramics. The grain size is $1 \mu\text{m}$ or less. The four constituent phases - alumina, spinel, magnetoplumbite and uraninite - were identified by their elemental contents. In Fig. 9, the four phases are labeled. The X-ray spectra recorded from the four phases are reproduced in Fig. 10. These indicate that the alumina phase does take some Fe into solid solution and that the spinel phase contains Fe, Ni, and Mn in solid solution. The uraninite phase contains principally U although other

Fig. 9 Bright field transmission electron micrograph of a rare earth and alumina tailored ceramic, illustrating the dense nature of the material. The selected region contains an isolated magnetoplumbite phase grain (mp), and the arrows point to grains of uraninite. Individual alumina (C) and spinel (S) grains are also labeled.

Fig. 10 X-ray microanalysis spectra recorded from the different phases in Fig. 9 demonstrating the elemental content of the four phases.
C = Corundum, S = Spinel, U = uraninite, and MP = magnetoplumbite.

small peaks are present in the spectrum that are a result from unavoidable beam spreading. The spectrum from the magnetoplumbite shows that it contains principally Al, Mn, Fe, and Ni. The elements Na, Cs, and Ca are present in smaller amounts as can be seen when the spectrum is displayed on a logarithmic scale (Fig. 11).

A Composite composition sample with Ion-Siv added was tailored specifically for the enhancement of the magnetoplumbite phase. The X-ray spectrum recorded from the tailored magnetoplumbite shows that it contained Al, Mn, Fe, Ni, La, Na, Sr, Cs, Si, Ce and K, the latter element introduced by the presence of the Ion-Siv.

The elements found by X-ray spectroscopy in the different constituent phases are summarized in Table 5.

Generally, the magnetoplumbite grains are readily identified by their long, lath-like morphology. At higher magnification, the basal plane periodicities can be observed visually and in electron diffraction patterns. The lattice fringe images clearly showed that the majority of the magnetoplumbite grains exhibited micro-syntaxy between the different polytypes. An example of this is shown in Fig. 12, where there is a region of the magnetoplumbite type 2H(6S) polytype surrounded by the 2H(4S) polytype. The observed change in stacking sequence reflects a local composition variation, as has been observed in the ferromagnetic magnetoplumbites²⁵ and demonstrated more recently in the compositionally controlled polytypes in the Mg-Si-Al-O-N system.²⁶

Fig. 11 The X-ray microanalysis spectrum from the magnetoplumbite phase recorded on a logarithmic vertical scale so as to emphasize the minor elemental constituents, Na, Ca, and Cs. The argon is implanted during the argon-ion beam thinning of the sample.

Table 5. Mineralogy and Waste Element Distribution

Phases	Nominal Composition	Elements Detected
<u>Principal</u>		
Spinel	(Mg,Fe,Ni,Mn) (Al,Fe) ₂ O 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. and Y = Al, Fe, Ti, Si, Mn	Al, Mn, Fe, Ni, La, Na, Ca, Ti, trace Sr, Cs, Ba, Si, Mo, Ce, K
<u>Present with excess tailoring</u>		
Corundum (Excess Al ₂ O ₃)	Al ₂ O ₃	Al, trace Fe, Ti
Perovskite (Excess REO)	RE(Al, Fe)O ₃	La, Al, Fe, trace Ca, Na, Ce
Pseudobrookite (excess TiO ₂)	(Fe, Ti, Al) ₂ TiO ₅	Fe, Ti, Al

Fig. 12 Lattice fringe image of a region of a magnetoplumbite type structured grain illustrating the microsyntax intergrowth between the 2H(6S) and 2H(4S) polytypes. The 2H(6S) and 2H(4S) polytypes have characteristic basal phase spacings of 3.2 nm and 2.2 nm, respectively.

In all the materials, the uraninite phase appears as finely divided particles uniformly distributed throughout the microstructure. This is illustrated by Fig. 13, a wide-aperture dark field micrograph, in which the uraninite phase appears as the dark, microstructurally discrete particles. Hence, the uraninite is microstructurally isolated by the surrounding phases, principally alumina and magnetoplumbite. No evidence of microcracking is visible.

D. INTERGRANULAR PHASES

It is often difficult to determine whether a continuous intergranular phase exists in the microstructure, as the literature on the intergranular phase in silicon nitride based alloys attests. However, three techniques of high resolution transmission electron microscopy have been developed^{27,28} for detecting thin (~1 nm) intergranular phases; lattice fringe imaging,²⁹ dark field imaging³⁰ and defocus imaging.³¹

Only two samples of the Al_2O_3 -REO tailored ceramics were unequivocally found to contain a detectable intergranular phase, and in both cases it appeared to be restricted to small regions of the material. One such region is seen in both bright and dark field in Fig. 14 (the noncrystalline intergranular phase appears bright in the dark field image). The large fraction of elements, such as K and Na, and which are also the principal components of the Ion-Siv found in the glassy phase by X-ray microanalysis suggests that the origin of the glass may be attributable to a partially dissolved, and hence unhomogenized, lump of the Ion-Siv.

Fig. 13 Large aperture dark-field electron micrograph of a rare earth tailored, high alumina composition illustrating the fine particle size of the uraninite (the black grains) and its microstructural isolation.

(a)

(b)

Fig. 14 Bright- and dark-field transmission electron micrographs of a high alumina tailored "composite" composition indicating the presence of a noncrystalline intergranular phase. The large concentration of K found in the glass suggests its is an unhomogenized piece of Ion-Siv. The dark grains are uraninite phases.

The other region containing an intergranular phase was detected in a Composite composition sample tailored to produce a high magnetoplumbite phase content. The intergranular phase is on a much finer scale than that of the above example and is shown arrowed in the dark field image of Fig. 15. (In contrast to the ideal imaging circumstances, several crystalline phases also appear bright in the dark field image on account of the unavoidable overlap of the diffraction intensities). The intergranular phase appears to be continuous, and, at the points arrowed F is calculated to be less than 2 nm thick. Its small dimensions precluded any X-ray microanalysis of its elemental composition.

E. $\text{Al}_2\text{O}_3 + \text{SiO}_2$ TAILORED CERAMICS

STEM characterization of the tailored ceramics with SiO_2 added to form nepheline showed there to be the expected crystalline phases and an amorphous intergranular phase. The extent of the intergranular phase can be seen in the transmission micrograph in Fig. 16. The intergranular phase undoubtedly forms as a result of the high volume fraction of liquid phase formed during consolidation of the alkali and silica rich waste.³²

X-ray microanalysis of the amorphous phase in the ceramic showed it to contain the glass modifiers Ca, Na, and Si, as well as the radionuclide cesium. This intergranular material is orders of magnitude more soluble than the major crystalline phases and degrades the overall leach resistance of the waste form.^{33,34} The preferential association of the radionuclide cesium with this amorphous phase further emphasizes its undesirability in a ceramic waste form.

Fig. 15 Dark-field transmission electron micrograph of a rare earth tailored, high alumina composition (as in Fig. 7). The long lath-shaped grains are magnetoplumbite. Thin intergranular glassy phases are indicated by the arrows. The thin films of glassy phase, F, are measured to be less than 2 nm thick. A three-grain junction pocket is at point P.

(a)

(b)

Fig. 16 Bright- and dark-field transmission electron micrographs of a 60 wt %, hot isostatically pressed, SRL Composite ceramic tailored with $\text{Al}_2\text{O}_3 + \text{REO} + \text{ZrO}_2$ (Table 3). The amorphous phase can be seen as small, bright intergranular regions in the dark field micrograph.

V. PHASE RELATIONS AND COMPOSITIONAL VARIABILITY

The $\text{CaO-Nd}_2\text{O}_3\text{-Al}_2\text{O}_3$ ternary system was chosen as a model for ascertaining some of the essential features of the alumina-magnetoplumbite phase assemblage expected from alumina - rare earth tailoring when iron was absent. The lower portion of the diagram had previously been determined³⁵ in connection with studies of radioactive waste disposal into cement.

Polyphase preparations in the ternary phase field $\text{CaO-Nd}_2\text{O}_3\text{-Al}_2\text{O}_3$ were made by slurring $\text{Al}(\text{OH})_3$ with pure nitrate solutions in a blender to achieve good homogeneity. The samples were dried at 120°C , lightly milled, cold isostatically pressed to 35 MPa, and sintered in air at 1300°C in platinum crucibles. The phases present were identified by powder XRD.

The results of this work³⁶ suggest that a partial solid solution exists between the calcium magnetoplumbite $\text{CaAl}_{12}\text{O}_{19}$ and the high temperature ($>1600^\circ\text{C}$) neodymium phase, $\text{NdAl}_{11}\text{O}_{18}$. At 1300°C , the temperature of the ternary section comparable to the hot-pressing temperature, the high temperature rare earth magnetoplumbite-related phase is metastable, and three distinct compatibility regions exist: magnetoplumbite-perovskite, magnetoplumbite-corundum, and magnetoplumbite-corundum-perovskite.

The ternary $\text{CaO-Nd}_2\text{O}_3\text{-Al}_2\text{O}_3$ system can be used as a model for the front face of a schematic ternary system, alkali + alkaline earth- $\text{Al}_2\text{O}_3\text{-RE}_2\text{O}_3$. Inclusion of a fourth apex, $(\text{Mg,Fe,Ni})\text{O}$, to represent the divalent ions in a reducing environment allows drawing a schematic quaternary tailoring diagram (Fig. 18a). Since spinel, MgAl_2O_4 , is known^{37,38} to be compatible

with LaAlO_3 and NdAlO_3 , it is assumed that a (Mg, Fe, Ni) spinel is also compatible with a (RE)AlO₃ type perovskite in the pseudo-ternary (Mg,Fe,Ni)O- RE_2O_3 - Al_2O_3 . The range of solid solution of the magnetoplumbite in the alkali + alkaline earth-(RE)₂O₃- Al_2O_3 face of the quaternary diagram illustrates that the phase compatibility regions are tetrahedrons rather than planar triangles through the quaternary system (Fig. 17a). However, the solid solubility of (Fe, Mg, Ni)O in magnetoplumbite, found by transmission electron microscopy in phase pure magnetoplumbite preparations, increases the size of the compatibility quadrilaterals formed between corundum-magnetoplumbite-spinel and magnetoplumbite-spinel-perovskite. These compatibility regions are then quadrilaterals and share the common face shown shaded in Fig. 17b. The enhanced size of the compatibility quadrilaterals, due to extensive solid solution of the component phases, allows a wide variability of waste compositions to be accepted by a predetermined phase assemblage at a given waste loading.

Adding SiO_2 to the tailoring scheme adds another dimension to the phase compatibility diagram. A Janecke diagram³⁹ depicting the additional complexity of the phase relations when silica, uranium, and zirconium are added is shown in Fig. 18. It is a schematic, and the complexities of the presence of PO_4^{3-} or Ti^{4+} are omitted. Magnetoplumbite extends over a range of compositions on the $\text{Na}_2\text{O}-(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)$ -CaO- Re_2O_3 plane in the shaded triangular region (Fig. 18). The true magnetoplumbites lie close to the $\text{CaAl}_{12}\text{O}_{19}$ - $\text{ReAl}_{11}\text{O}_{18}$ side of this triangle and extend toward the fabrication approximated by $\text{Na}_{0.5}\text{-La}_{0.5}\text{Al}_{12}\text{O}_{19}$. If insufficient rare earth is present to form the alkali-rare earth magnetoplumbite phase, $\text{Na}_{0.5}\text{La}_{0.5}\text{Al}_{12}\text{O}_{19}$, then $\beta\text{-Al}_2\text{O}_3$ can form. This is undesirable, as it is a known fast ion conductor

COMPATIBLE PHASES:

MAGNETOPLUMBITE, SPINEL, (RE)AlO₃

MAGNETOPLUMBITE, SPINEL, Al₂O₃

Fig. 17 Tailoring schematic for hot-pressed SRL Composite composition without the aluminum removal process step. (a) Tailoring diagram, representing reducing conditions, showing magnetoplumbite solid solution and the compatibility quadrilaterals for the phase assemblages produced during hot-pressing in graphite dies: Al₂O₃-magnetoplumbite-spinel and spinel-magnetoplumbite-(RE)AlO₃ perovskite. (b) Distorted view of the compatibility quadrilaterals showing the three-dimensional solid solution of magnetoplumbite (hatched region) and the magnetoplumbite-spinel plane (shaded) that the two compatibility quadrilaterals share in common.

Fig. 18 Janecke diagram indicating the possible phases crystallizing during processing of High Alumina tailored ceramic nuclear waste forms. The desired compatible phases are corundum-spinel-uraninite-magnetoplumbite and spinel-uraninite-magnetoplumbite-nepheline. Perovskite and pyrochlore are compatible and occur in the presence of excess RE and Zr. The magnetoplumbites are indicated by the shaded triangular region on the $\text{Na}_2\text{O}-\text{CaO}-(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)-\text{RE}_2\text{O}_3$ plane and lie in the region close to $\text{CaAl}_{12}\text{O}_{19}$ - $\text{REAl}_{11}\text{O}_{18}$. The $\beta\text{-Al}_2\text{O}_3$ related structure is undesirable, as in CaUO_{4-x} , due to poor leach resistance. The stripped pod near the SiO_2 apex indicates the undesired glass forming region (as discussed in the text).

and is leachable.^{40,41} Uraninite exists at the upper corner of the tent-shaped region and forms a solid solution with pyrochlore when large amounts of Sr^{4+} and RE^{3+} are present. If conditions are too oxidizing in the presence of the alkaline-earths, then $\text{CaUO}_4\text{-x}$ forms, which is not leach resistant.⁴¹ Corundum and spinel solid solutions share the Al_2O_3 , Fe_2O_3 apex, while RE-perovskites of the type REAlO_3 and REFeO_3 lie along the $(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)\text{-Re}_2\text{O}_3$ side of the tent shape. Nepheline, the alternate sodium host, lies on the left triangular face $(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)\text{-SiO}_2\text{-Na}_2\text{O}$ and exhibits a small range of solid solution⁴² which for clarity is not shown on the diagram for clarity. The stripped area extending from the SiO_2 apex toward Na_2O , UO_2 , CaO , and $(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)$ is the estimated region of glass formation. These elements are known glass network formers or modifiers. The known glass forming regions,⁴² the systems $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$, $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$, and $\text{SiO}_2\text{-Al}_2\text{O}_3$, have been used as models for the shape of this region.⁴² The refractory nature of $\text{SiO}_2\text{-Al}_2\text{O}_3$ compositions cause the observed concave depression in this glass forming wedge. The glass-forming region may be larger due to the presence of impurities such as Sr^{2+} , K^+ , and Ti^{4+} and PO_4^{3-} that are not shown on the diagram. The proximity of nepheline to the glass-forming region means that if insufficient Al^{3+} or Fe^{3+} is available, in the presence of silica, then glassy phases readily form from the U, alkaline earths, alkali, and silica. A schematic Janacke diagram such as this therefore serves (1) to distinguish the complex interrelationships between the waste species and the additives, and (2) to demonstrate the flexibility of the tailoring to produce the desired phases and minimize the undesired phases.

All the compatible crystalline assemblages exhibit a wide range of solid solubility; hence, wastes of variable composition can easily be accommodated, and similar tailoring formulations for commercial waste are anticipated.⁴³ Tailoring formulations will ultimately be determined by considerations such as leach resistance and mechanical strength, and empirical formulations that provide additional inert phases for microstructural isolation (e.g., spinel, corundum) will be advantageous.

VI. DISCUSSION

A. CRYSTAL CHEMISTRY

A dense tailored crystalline ceramic waste form consisting of alumina, spinel, magnetoplumbite, uraninite, and little or no continuous intergranular phase has been produced by reactive hot pressing and by hot isostatic pressing. The magnetoplumbite phase acts as a host for the radionuclides Sr and Cs. The compatible phases are analogous to a natural placer deposit assemblage of alumina-spinel-hibonite (magnetoplumbite)-thoria, in Fort Dauphin, Malagasy,⁴⁴ a locale of obvious and prolonged exposure to water. The phase assemblage is also significant in that sufficient rare earth tailoring is used to avoid the formation of calcium aluminates whose $\text{Al}_2\text{O}_3:\text{CaO}$ ratio is less than 6:1 since these forms are known from the cement literature to be readily hydrated.⁴⁵

Magnetoplumbite has utility as a nuclear waste host for monovalent ions because it is possible to combine large divalent ions with Al^{3+} , Fe^{3+} , and other spinel-forming ions and to balance large monovalent ions with large trivalent ions (e.g., rare earths), between the spinel blocks. The direct observation, by analytical electron microscopy, that the magnetoplumbite phase incorporates the elements Cs, Sr, Ba, La, Na, Si, Ce, and K into its crystal structure was expected because considerable work at the Philips Research Laboratories²⁴ on β -alumina and magnetoplumbite crystal structures for their luminescence properties had shown that these structure types could contain many of these elements singly or in combination. Further, they had demonstrated that true magnetoplumbites could exist over a range of axial c/a

ratios from 3.92 to 3.95, a range that encompasses the magnetoplumbite axial ratios obtained in the high alumina tailored ceramic. One particular advantage of the magnetoplumbite phase is that it is capable (as demonstrated by both the analytical microscopy and phase pure studies) of incorporating glass-modifying elements (Ti, Ba, Ca, Sr, Na, K and Cs) as well as glass forming elements (Si, Al, Zr), which may otherwise be expected to form glassy intergranular phases. A further advantage is that in some cases the complete solid solution range from $\text{XAl}_{12}\text{O}_{19}$ to $\text{XFe}_{12}\text{O}_{19}$ is achievable²⁴ and well understood (e.g., single crystal refinement studies of the site occupancies of Al and Fe have been reported for $\text{CaFe}_6\text{Al}_6\text{O}_{19}$ (Ref. 46) and $\text{SrFe}_7\text{Al}_5\text{O}_{19}$). (Ref. 47)

The formation of true magnetoplumbite analogs ($\text{XY}_{12}\text{O}_{19}$ or $\text{XY}_{18}\text{O}_{27}$, where X = large cations Ca, Sr, Ba, etc. and Y = small cations Al, Fe, Ni, etc.) instead of the β -alumina type analogues ($\text{XY}_{11}\text{O}_{17}$ and $\text{XY}_{17}\text{O}_{25}$) yield good (low) leach rates for sodium, strontium, and cesium.³³ (The latter β -alumina variants of the 2H(4S) or 2H(6S) varieties are not expected to show good leach resistance as this class of material is known to consist of fast ion conductors.) Moreover, magnetoplumbite analogs are known to be geologically stable; hibonite, close to $\text{CaAl}_{12}\text{O}_{19}$, is a placer mineral.⁴⁴ Even with β -alumina types, when alkali leaching does appear to replace it by H_3O^+ , the overall hexagonal framework is maintained,⁴⁸ and early results³³ indicate that crumbling or fracturing of the ceramic does not occur. The Cs retention data (Section III.E) indicate that tailoring to produce a magnetoplumbite related phase also decreases the loss of Cs. This supports the idea that the mobility of large monovalent cations, such as Cs, is lower in the rare earth magnetoplumbite $\text{X(Al,Fe)}_{12}\text{O}_{19}$ (where $\text{X} = \text{Alk}_{0.5}^+ + \text{RE}_{0.5}^{+3}$) structure than in an

untailored $X(\text{Al},\text{Fe})_{11}\text{O}_{17}$ β -type structure (where $X = \text{Alk}^+$). It also suggests that Cs is more thermodynamically stable in the former, since the vapor pressure of Cs is lower.

The phase equilibrium studies confirm that the system $\text{Al}_2\text{O}_3\text{-CaO-Nd}_2\text{O}_3$ can be used as a guide in understanding the phase compatibility in the high-alumina tailored ceramic waste form. The sub-solidus tie lines between the magnetoplumbite solid solution, alumina, spinel, and rare earth perovskite solid solution indicate the wide range of compositions that the waste form can tolerate when tailored to produce the desired phase assemblage.

Although tailoring with excess alumina has been emphasized here, extensions of this work have indicated that "overtailoring" with rare earth leads to the appearance of $\text{RE}(\text{Al},\text{Fe})\text{O}_3$ perovskite type as a compatible phase with magnetoplumbite, spinel, and uraninite. Furthermore, "overtailoring" with titanium (a useful sintering aid in alumina systems and one that provides approximately a 100 to 150°C reduction in hot-pressing temperature) leads to pseudobrookite, $(\text{Fe},\text{Al})_2\text{TiO}_5$, as a compatible phase with magnetoplumbite, spinel, and uraninite.

Using the nepheline phase has been shown to be feasible for increasing the loadings of SRL Composite composition waste in the ceramic form. Nepheline is compatible with the four phase "High Alumina" assemblage and, as a pure phase, shows acceptable leach resistance. Also, the presence of a significant level of liquid phase during consolidation of the SiO_2 tailored formulation leads to a 200°C reduction in the required consolidation temperature in HIPping. These features, while advantages from a processing

point of view, must be balanced against the overall loss in form leach resistance for those elements preferentially associated with the intergranular phase present in this form.

B. GRAIN SIZE EFFECTS

The ceramics produced all have had a small, fairly uniform grain size of less than 1 μm , as desired. Microcracking resulting from the residual stresses (generated by thermal contraction differences between the different constituent phases, anisotropic thermal contraction of the phases, or phase transformations, for instance) can be avoided only by producing a ceramic with such a fine grain size. Previous investigators⁴⁹⁻⁵² have found that to prevent microcracking requires keeping the scale of the microstructure (the grain size in single phase materials) below a "critical" size. The critical dimension, λ_c , can be expressed in the general form⁵³⁻⁵⁵

$$\lambda_c \approx \frac{k \Gamma_{gb}}{\langle E \rangle \epsilon^2}$$

where ϵ is the strain resulting from the differential thermal contraction, Γ_{gb} is the grain boundary fracture energy, and $\langle E \rangle$ is the mean elastic modulus of the material. The value of the constant k depends on the mechanism by which the residual stresses are generated and on the particular theoretical model adopted; it typically has a value between 8 and 24. The critical grain size for a wide range of ceramics ranges from a low of 2 to 5 μm for materials having the pseudo-brookite structure to 50-100 μm for pure alumina, suggesting that sub-micron grain sizes should be produced in tailored ceramics to prevent

microcracking. Furthermore, a fine grain size is necessary to avoid microcracking resulting from radiation-induced swelling of one or more of the constituent phases. Such a phenomenon is known to occur in irradiated BeO^{56,57} and has recently been reported⁵⁸ in a partially devitrified nuclear waste glass composition. The strain generated by swelling is then additional to that produced, for instance, by differential thermal contraction and, as can be seen from the equation, further reduces the critical grain size, λ_c .

C. PHASE DEVELOPMENT

The XRD and transmission microscopy observations (Figs. 3 and 4) of heat treated spray calcined powders clearly indicate that reactive hot pressing occurs by the decomposition and crystallization of a very reactive precursor. The precursors are substantially X-ray amorphous so that crystallization to the final phase assemblage occurs during hot-pressing, allowing advantage to be taken of the transient, extremely fine grain structures occurring during the transformation. This in turn minimizes the temperatures that must be used to obtain high density, at worst with closed pores, at best nearly theoretically dense, so that volatility effects, especially those of Cs, are minimized. These findings suggest that hot-pressing or hot isostatic pressing is to be preferred to sintering; hot pressing and HIPping can take advantage of extremely high reactivity in the starting powder, whereas sintering often suffers, mainly due to low green density, effects of nonuniform porosity because of aggregate effects and large differential shrinkages. Further encapsulation of the waste form in either alumina or graded ceramic structures would lead to essentially zero leach rate for radioisotopes. In

any hot isostatic pressing (HIPping) process, it will be necessary to achieve the correct oxidation states of uranium (U^{4+}), which is presently being accomplished using organic redox control agents.

D. INTERGRANULAR PHASES

The observation of noncrystalline intergranular material in the waste form is significant. The intergranular material dissolves more readily than the bulk of the ceramic and provides a short circuit leach path.³⁴ In the High Alumina tailored ceramics, the intergranular material can be controlled and minimized through correct processing. In the nepheline containing ceramics, however, more work needs to be done to optimize the form and reduce the content of glass. Proper tailoring and processing to avoid significant amounts of intergranular material are critical to obtaining the high level of leach resistance of which the crystalline ceramic form is capable.

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REFERENCES

1. L. P. Hatch, "Ultimate Disposal of Radioactive Wastes," *Am. Scientist* 41, 410-421 (1953).
2. G. J. McCarthy, "Quartz-Matrix Insulation of Radioactive Wastes," *J. Mat. Sci.* 8, 1358-1359 (1973).
3. G. J. McCarthy and M. T. Davidson, "Ceramic Nuclear Waste Forms: I. Crystal Chemistry and Phase Formation," *Bull. Am. Ceram. Soc. Bull.* 54, 782-786 (1975).
4. G. J. McCarthy, "High-level Waste Ceramics," *Trans. Am. Nucl. Soc.* 23, 168-169 (1976).
5. R. Roy, "Ceramic Science of Nuclear Waste Fixation (Abs.)", *Bull. Am. Ceram. Soc.* 54, 459 (1975).
6. R. Roy, "Rational Molecular Engineering of Ceramic Materials," *J. Am. Ceram. Soc.* 60, 350-363 (1977).
7. R. O. Schwoebel, "Stabilization of High Level Waste in Ceramic Form (Abs.)", *Bull. Am. Ceram. Soc.* 54, 459 (1975) or SAND-76-0105 (1976).
8. A. E. Ringwood, "Safe Disposal of High-Level Nuclear Reactor Wastes: A New Strategy," A.N.U. Press, Canberra, Australia (1978).
9. A. E. Ringwood, S. E. Kesson, N.G. Ware, W.O. Hibberson, and A. Major, "The SYNROC Process: A Geochemical Approach to Nuclear Waste Immobilization," *Geochem. J.* 13, 141-165 (1979).
10. J. A. Stone, S. T. Goforth, Jr., and P. K. Smith, "Preliminary Evaluation of Alternative Forms for Immobilization of Savannah River Plant High-Level Waste," SRL-DP-1545 (1979).

11. W. J. Croft, M. Kestigian, R. Borovicka and F. Gwabedian, "Unit Cell Dimensions in the System $\text{PbAl}_{12-x}\text{Fe}_x\text{O}_{19}$," Mater. Res. Bull. 2, 849-852 (1967).
12. R. N. Summergrad and E. Banks, "New Hexagonal Ferromagnetic Oxides," J. Phys. Chem. Solids 2, 312-317 (1957).
13. W. D. Townes, J. H. Fang, and A. J. Perrota, "The Crystal Structure and Refinement of Ferromagnetic Barium Ferrite, $\text{BaFe}_{12}\text{O}_{19}$," Z. Krist. 125, 437-449 (1967).
14. J. M. P. J. Verstegen, J. L. Somerdijk, and J. G. Verrite, "Cerium and Terbium Luminescence in $\text{LaMgAl}_{11}\text{O}_{19}$," J. Lumin. 6, 425-431 (1973).
15. P. E. D. Morgan, "Superplasticity in Ceramics," in Ultrafine Grain Ceramics, Eds. J. J. Burke, N. L. Reed, and V. Weiss, Syracuse University Press, 251-271 (1970).
16. W. E. Ford, "Dana's Textbook of Mineralogy," John Wiley and Sons, New York, p. 851 (1932).
17. J. B. Pickett and J. A. Stone, DuPont Savannah river Laboratory, private communication.
18. M. Dimitrov and I. Bakalova, God. Vissh. Khim-Tekhnol. Inst. Sofic. 1977 (Pub. 1978), 23(3), 257-265.
19. E. H. Cirlin and R. M. Housley, "A Flameless Atomic Absorption Study of the Volatile Trace Metalhead in Lunar Samples," Proc. Lunar Sci. Conf. 3931-3940 (1977).
20. E. H. Cirlin and R. M. Housley, "Scanning Auger Microprobe Atomic Absorption Studies of Lunar Volcanic Volatiles," Proc. Lunar Sci.

Conf., 341-354 (1979).

21. M. Bettman and L. Turner, "On the Structure of $\text{Na}_2\text{O}-4\text{MgO}-14\text{Al}_2\text{O}_3$, a Variant of β -Alumina," *Inorg. Chem.* 10, 1442-1446 (1971).
22. P. B. Braun, "The Crystal Structures of a New Group of Ferromagnetic Compounds," *Philips Res. Rep.* 12, 491-548 (1957).
23. J. Dexpert-Ghys, M. Faucher, and P. Caro, "Optical and Structural Investigation of the Lanthanum β -Alumina Phase Doped with Europium," *J. Solid State Chem.* 19, 193-204 (1976).
24. J. M. P. J. Verstegen and A. L. W. Stevels, "The Relation Between Crystal Structure and Luminescence in β -alumina and Magnetoplumbite Phases," *J. Lumin.* 9, 406-414 (1974).
25. J. D. M. McConnell, J. L. Hutchison, and J. S. Anderson, "Electron Microscopy of the Barium Ferrite Layer Structures," *Proc. Soc. London* A339, 1-12 (1974).
26. D. R. Clarke, "Determination of Grain Boundary Segregation by Combined X-ray Microanalysis and Lattice Fringe Imaging," *Scanning Electron Microscopy* 1, 77-84 (1978).
27. D. R. Clarke, "On the Detection of Thin Intergranular Films by Electron Microscopy," *Ultramicroscopy* 4, 33-44 (1979).
28. D. R. Clarke, "High Resolution Techniques and Application to Non-Oxide Ceramics," *J. Am. Ceram. Soc.* 62, 236-246 (1979).
29. D. R. Clarke and G. Thomas, "Grain Boundary Phases in a Hot-Pressed MgO Fluxed Silicon Nitride," *J. Am. Ceram. Soc.* 60, 491-95 (1977).
30. M. Ruhle, C. Springer, L. J. Gauckler, and M. Wilkens, "TEM Studies of Phases in Si-Al-O-N Alloys," *Proceedings of the 5th International*

Conference on High Voltage Electron Microscopy, 641-644 (1977).

Editors. T. Mura and H. Hashimoto, Japanese Society for Electron Microscopy.

31. D. R. Clarke, "Observation of Microcracks and Thin Intergranular Films in Ceramics by Transmission Electron Microscopy," J. Am. Ceram. Soc. 63, 104-106 (1980).
32. E. F. Osborn and A. Muan, "Phase Equilibrium Diagrams of Oxide Systems," J. Am. Ceram. Soc. and Edward Orton, Jr., Ceramic Foundation, 1960.
33. A. B. Harker, D. R. Clarke, and C. M. Jantzen, "Effects of Interfacial Material on Tailored Ceramic Nuclear Waste Form Dissolution," in Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems, Materials Science Research, Vol. 14, Eds. J. Pasko and A. Evans, Plenum Press, 207-216 (1981).
34. D. R. Clarke, "Preferential Dissolution of an Intergranular Amorphous Phase in a Nuclear Waste Ceramic," Am. Cer. Soc. Comm. 64, 89-90 (1981).
35. C. M. Jantzen and F. P. Glasser, "Solid-State Reactions in the System $\text{CaO-Nd}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$," Mater. Res. Bull. 14, 1601-1607 (1979).
36. C. M. Jantzen and R. R. Neurgaonkar, "Solid State Reactions in the System $\text{Al}_2\text{O}_3\text{-Nd}_2\text{O}_3\text{-CaO}$," submitted to Mater. Res. Bull.
37. N. A. Toropov and N. A. Zirazhiddinov, "The System $\text{MgAl}_2\text{O}_4\text{-LaAlO}_3$," Zh. Neorgan Khim. 9, 1300-1302 (1964).

38. N. A. Toropov and N. A. Zirazhiddinov, "The Phase Diagram of the System MgAl_2O_4 ," *Izv. Akad. Nauk SSSR, Utd. Khim. Nauk*, 374-376 (1963).
39. E. Janecke, "A New Form of Representation of Van't Hoff's Research on the Deposition of Ocean Salts," *Z Anorg. Allg. Chem.* 53, 319-326 (1907).
40. P. E. D. Morgan, D. R. Clarke, C. M. Jantzen, and A. B. Harker, "High Alumina Tailored Nuclear Waste Ceramics," *J. Am. Ceram. Soc.* 64, 249 (1981).
41. C. M. Jantzen, D. R. Clarke, P. E. D. Morgan, and A. B. Harker, "The Leaching of Polyphase Nuclear Waste Ceramics: I. Microstructural and Phase Characterization," to be published *J. Am. Ceram. Soc.* (1981).
42. E. M. Levin, C. R. Robbins, and H. F. McMurdie, Phase Diagrams for Ceramists, *J. Am. Ceram. Soc.* (1964).
43. P. E. D. Morgan, C. M. Jantzen, A. B. Harker, and D. R. Clarke, "Tailored Ceramic Formulations for Commercial High Level Waste," in preparation (1981).
44. H. Curien, C. Cuillemin, J. Orcel, and M. Sternberg, "La Hibonite, Nouvelle Espece Minerale," *C. R. Acad. Sci.* 242, 2845-2847 (1956).
45. F. M. Lea, The Chemistry of Cement and Concrete, Edward Arnold (Publ.) (1970).
46. M. Harder and Hk. Miller-Buschbaum, " $\text{CaFe}_6\text{Al}_6\text{O}_{19}$ with the Magnetoplumbite Structure," *Z. Naturforsch. Anorg., Chem.* 31B, 1148 (1976).
47. M. Harder and H. K. Miller-Buschbaum, "The Atomic Distribution in $\text{SrFe}_7\text{Al}_5\text{O}_{19}$," *Z. Naturforsch., Anorg. Chem.* 32B, 833-834 (1977).

48. M. W. Brieter, G. C. Farrington, W. L. Roth, and J. L. Duffy, "Production of Hydronium Beta Alumina from Sodium Beta Alumina and Characterization of Conversion Products," *Mat. Res. Bull.* 12, 895-906 (1977).
49. F. F. Lange, "Fracture Mechanics and Microstructural Design," in Fracture Mechanics of Ceramics, Eds, R. C. Bradt, D. P. H. Hasselman, and F. F. Lange, Vol. 4, Plenum Press, 779-819 (1978).
50. J. A. Kuszyk and R. C. Bradt, "Influence of Grain Size on Effects of Thermal Expansion Anisotropy in MgTi_2O_5 ," *J. Am. Ceram. Soc.* 56, 420-423 (1973).
51. R. W. Davidge and G. Tappin, "Internal Strain Energy and the Strength of Brittle Materials," *J. Mat. Sci.* 3, 297-301 (1978).
52. D. B. Binns, "Some Physical Properties of Two-Phase Crystal-Glass Solids," in *Science of Ceramics*, Ed., G. H. Steward, Academic Press 315-334 (1952).
53. F. J. P. Clarke, "Residual Strain and the Fracture Stress-Grain Size Relationship in Brittle Solids," *Acta Metall.* 12, 139-143 (1964).
54. A. G. Evans, "Microfracture from Thermal Expansion Anisotropy. I. Single Phase Systems," *Acta Metall.* 26, 1845-1853 (1978).
55. D. R. Clarke, "Microfracture in Brittle Solids Resulting from Anisotropic Shape Changes," *Acta Metall.* 28, 913-924 (1980).
56. B. S. Hickman and D. G. Waler, "Effect of Microstructure on the Irradiation Behavior of Beryllium Oxide," *J. Nucl. Mater.* 10, 243-245 (1963).

57. B. S. Hickman, T. M. Sabine and R. A. Coyle, "X-ray Diffraction Studies of Irradiated Beryllium Oxide," J. Nucl. Mater. 6, 190-198 (1962).
58. W. J. Weber, R. P. Turcotte, L. R. Burrell, F. R. Roberts, and J. H. Westsik, "Radiation Effects in Vitreous and Devitrified Simulated Waste Glass," in "Ceramics in Nuclear Waste Management," Proc. Intern. Symp. Eds., T. D. Chikalla and J. E. Mendel, Pub. US DOE Technical Information Center CONF-790420, 294-299 (1977).