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Preparation and Properties of Synroc D Containing Simulated Savannah River Plant High-Level Defense Waste

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CONTENTS

Foreword	ii
Abstract	1
Introduction	1
Description of Savannah River Plant Waste	2
The Comparative Leach Testing Program	6
Synroc D Formulations	8
General Background	8
Composite Waste Forms (S21, S29, S20) and Hollandites (S18, S03a)	15
High-Iron Waste Forms (S26, S30) and Hollandite (SAN)	18
High-Aluminum Waste Form (S31)	20
Waste Form Preparation	20
S29--The Reference Synroc D Composite Waste Form	20
Starting Materials	22
Slurry Preparation	25
Spray Drying and Calcination	26
Hollandite Preparation	34
Hot Pressing	35
Mechanical and Thermophysical Properties	44
Ultrasonic Elastic Constants	44
Flexural Strength	47
Compression Strength	49
Thermal Expansion	49
Thermal Conductivity	52
Microhardness	53
Leaching Characteristics	54
References	57
Appendix A.	61
Appendix B.	67

FOREWORD

The information provided in this report summarizes the procedure for preparing the Synroc D test samples used in the Comparative Leach Test Program of FY81; results from some leaching, mechanical, and thermophysical property tests are also reported. As with any large experimental endeavor, the success of the efforts depends on contributions from a number of scientific, engineering, and technical support personnel. Those members of the LLNL Synroc project team whose efforts made this report possible include:

Program Managers:	Jack Campbell and John Tewhey.
Ceramic Processing:	Herb Newkirk, Conrad Yu, Carolyn Rossington, Bill Wade, Ralph Smith, Ken Deas, and Gene Hammeral.
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PREPARATION AND PROPERTIES OF SYNROC D CONTAINING SIMULATED SAVANNAH RIVER PLANT HIGH-LEVEL DEFENSE WASTE

ABSTRACT

We describe in detail the formulation and processing steps used to prepare all Synroc D samples tested in the Comparative Leach Testing Program at the Savannah River Laboratory. We also discuss how the composition of the Savannah River Plant sludge influences the formulation and ultimate preparation of Synroc D. Mechanical properties are reported in the categories of elastic constants, flexural and compressive strengths, and microhardness; thermal expansion and thermal conductivity results are presented. The thermal expansion data indicated the presence of significant residual strain and the possibility of an unidentified amorphous or glassy phase in the microstructure. We summarize the standardized (MCC) leaching results for both crushed Synroc and monoliths in deionized water, silicate water, and salt brine at 90°C and 150°C.

INTRODUCTION

Defense wastes represent most of the high-level nuclear waste in the United States.¹ These wastes are presently stored in three DOE facilities: the Savannah River Plant near Aiken, SC, the Hanford Plant near Hanford, WA, and the Idaho Chemical Processing Plant near Idaho Falls, ID. A total of about $2.8 \times 10^5 \text{ m}^3$ (75 million gallons) of waste containing about $1.3 \times 10^9 \text{ Ci}$ has been generated as a result of producing plutonium and tritium for nuclear weapons. By 1990, the projected inventory of defense waste is expected to reach $1.8 \times 10^9 \text{ Ci}$ --an increase of about 38%.

In comparison, commercial wastes in the United States (mostly in the form of unprocessed spent reactor-fuel elements) represent a slightly larger inventory of about $5 \times 10^9 \text{ Ci}$. By 1990, this commercial inventory is expected to reach $23 \times 10^9 \text{ Ci}$ --an increase of about 360%.

The Mineral Waste Form Program at the Lawrence Livermore National Laboratory (LLNL) was established to develop techniques to immobilize

radioactive wastes at the Savannah River Plant (SRP), which has operated since 1953. These acid wastes have been neutralized with sodium hydroxide and are presently stored in large underground tanks as precipitated sludge, alkaline salt cake, and supernate.

In 1977, the Energy Research and Development Administration (now Department of Energy) completed a site-specific study for SRP as a step toward establishing long-range goals and policies to insure safe permanent disposal of these wastes. Twenty-three separate plans for the processing and storage of SRP wastes were evaluated in this study.² At that time, the only solid waste forms under consideration were glasses, concrete, dry sludge, and salt cake. Borosilicate glass was eventually selected as the reference form for waste immobilization. Subsequent additional studies were also initiated on 11 solid waste forms as alternates to glass.³ This became known as the Alternate Waste Form Program. As a part of this program, LLNL was designated the lead laboratory to evaluate the Synroc⁴ concept and its potential to immobilize SRP waste. An important part of the evaluation process was the Comparative Leach Testing Program (CLT) in which all participants supplied waste-form samples to the SRP for evaluation using standardized leach tests.

This report summarizes the method we used to prepare the Synroc D samples submitted for CLT and presents the results of thermal- and mechanical-property tests we made on these samples.

DESCRIPTION OF SAVANNAH RIVER PLANT WASTE

The 1980 inventory¹ of stored SRP waste was $1 \times 10^5 \text{ m}^3$ (25 million gallons) of sludge, alkaline salt cake, and supernate. About 85% of this waste is supernate/salt that contains most of the radioactive cesium and some of the strontium. The balance, about 15%, is sludge, an alkaline mixture of hydrous oxides produced by neutralizing acid wastes with excess NaOH (Fig. 1). Because about 95% of the soluble salts can be removed from the sludge by washing,^{5,6} each cubic metre of waste yields 180 kg (i.e., 1.5 lb/gal) of washed and dried sludge. Hence, the total approximate dried solid-waste equivalent in the 1980 inventory was 2,550 metric tons. With a processing throughput goal of one ton/day, it would take from seven to eight years to convert all present SRP waste into a waste form suitable for storage.

Figure 1. High-level radioactive sludge stored at the Savannah River Plant in (a) Tank No. 7 and (b) Tank No. 15. The sludge, which represents about 15% of the radioactive waste at SRP, is an alkaline mixture of hydrous oxides produced by neutralizing acid wastes with excess NaOH.

Detailed descriptions of the radionuclide content² and the processing steps³ for the reference glass waste form may be found in earlier reports.

The 1980 reference-glass process consists of three input feed streams:

1. The major feed stream is a slurry of washed sludge containing hydrous oxides of elements such as iron, aluminum and manganese. Washing removes about 95% of the soluble salts, and the sludge contains most of the radionuclides in the waste, including ^{90}Sr , ^{239}Pu , and rare-earth fission products. About 75% of the aluminum is removed by caustic washing; this step is desirable for the reference borosilicate glass process but is not required for the Synroc waste form.

2. The second feed stream is a slurry of aluminosilicate zeolite grains (ion exchange column) containing ^{137}Cs adsorbed from the supernate fraction

of SRP waste. The volume and mass of this stream is relatively small, but it contains nearly all of the ^{137}Cs radionuclide.

3. The third stream, also minor, contains dissolved Na-EDTA, the eluting agent for ion-exchange separation of ^{90}Sr from the supernate fraction of SRP waste. This stream, labelled "Sr concentrate," contains only a small part of total ^{90}Sr .

The reference-glass process is continuously evolving; consequently, some of these feed streams may change in the future. Table 1 lists the average major-element compositions of the waste stream, given as oxide/salt equivalents. Compositions with and without aluminum are also given because aluminum removal by caustic washing was an added step required by the reference borosilicate glass process. Contractors studying the alternate waste forms were allowed to choose compositions from either category in order to optimize their waste-form performance for CLT; we chose the composition from which aluminum had not been removed.

In Table 1, each category consists of three compositions: high iron, high aluminum, and composite. The high-iron and high-aluminum compositions are thought to represent the compositional extremes whereas the "composite"

Table 1. Compositions of SRP waste calcines.^{a,b}

Component	Without aluminum removal (wt%)			With aluminum removal (wt%)		
	High Fe	Composite	High Al	High Fe	Composite	High Al
Fe ₂ O ₃	53.17	36.13	5.32	55.99	47.16	14.80
Al ₂ O ₃	4.89	28.26	76.05	1.29	9.24	50.77
MnO ₂	3.56	9.94	4.37	3.74	12.98	12.16
U ₃ O ₈	12.34	3.26	1.28	12.98	4.25	3.57
CaO	3.62	2.69	0.35	3.80	3.51	0.97
NiO	9.08	4.47	0.78	9.54	5.84	2.17
SiO ₂	0.40	0.85	0.56	<0.40	1.12	1.57
Na ₂ O	4.52	5.08	1.96	4.75	6.63	5.41
Na ₂ SO ₄	<0.50	0.93	<0.50	<0.50	1.21	<0.50
Zeolite ^c	8.82	8.93	9.33	8.00	8.05	8.53
	100.90	100.54	100.50	100.90	99.99	100.50

^a Values taken from Ref. 2.

^b Only the major elements are listed.

^c Ion-Siv IE-95; mixture of CaAl₂Si₄O₁₂•6H₂O and (NaKCa)₃Al₃SiO₂₄•8H₂O.

composition represents an average of the total tank inventory at SRP. During processing, extensive blending of the SRP waste is planned, which will give greater importance to the composite compositions. However, because significant variations in tank feed are possible, the waste form must also be able to accommodate the extreme high-iron and high-aluminum compositions.

The glass reference process calls for an aluminosilicate ion-exchange media (zeolite) to separate cesium from the salt/supernate. Other ion-exchange media such as titanates, which are more compatible with the Synroc process, are also acceptable as a substitute for zeolite.

Uranium oxide (U_3O_8) is the only radioactive compound listed in Table 1. The total fraction of other radionuclides constitutes about 3% of the calcinated SRP waste. Table 2 lists weight-percent ranges for 37 minor elements that have also been identified. Some of these elements (such as C, Cl, Hg, P, Pb, Ag, and F) may affect both waste-form synthesis and performance, but in this initial development program, these elements were not included in the waste formulation. Simulated waste supplied to us by SRP

Table 2. Minor elements in SRP waste sludges.^{a,b}

Element	Range (wt%)	Element	Range (wt%)
Ag	0-0.3	Nb	0.02-0.1
B	0-0.05	Nd	0.3-1.0
Ba	0.1-0.25	P	0.03-0.3
C	0-16.8	Pb	0.1-0.5
Cd	0-0.05	Pd	0-0.03
Ce	0.05-1.0	Pm	0-0.04
Cl	0-2.0	Pr	0.04-0.2
Co	0-0.01	Rh	0-0.05
Cr	0.01-0.45	Ru	0.03-0.5
Cs	0-0.06	S	0.02-0.5
Cu	0.03-0.15	Sm	0-0.05
Eu	0-0.02	Sr	0-0.15
F	0-0.15	Th	0-0.18
Hg	0.1-2.8	Ti	0-0.1
K	0.02-0.14	V	0-0.01
La	0.04-0.3	Y	0.01-0.05
Mg	0.06-0.3	Zn	0.04-0.5
Mo	0-0.01	Zr	0.1-0.5

^a Values taken from Ref. 2.

^b Value is wt% in washed, dried sludges.

contained only uranium, strontium, neodymium, and cerium as radwaste elements; we added enough cesium to make its concentration equal to that of strontium.

The concentration of sodium in SRP sludge is about 5% (see Table 1). Sodium concentrations are of concern because Synroc minerals have a limited capacity to accommodate sodium. As will be shown, we immobilize sodium in a silicate phase (nepheline). This phase has much poorer leach resistance than the normal titanate Synroc phases. Also, the large amount of sodium and the silica additive used to make nepheline increase the chance for formation of amorphous phases in our ceramic waste form.

THE COMPARATIVE LEACH TESTING PROGRAM

The CLT program⁷ was initiated by SRL to provide the performance information needed to select one alternate waste form (in addition to borosilicate glass) for further development in FY 82-83. The program was designed to provide test data by August 1981, when the alternate waste form would be selected for further hot-cell testing and engineering studies.

All waste-form developers were asked to provide input to SRL before the plan was finalized. The LLNL response⁸ dealt with our concerns about leaching temperatures, neutron activation of test samples before leaching, emphasis on composite, high-iron, and high-aluminum compositions, leach solutions that simulate geochemical conditions, and surface-preparation procedures.

Once the final CLT plan was adopted,⁹ SRL sent the plan and three specially prepared sludge compositions (composite, high iron, and high aluminum) to the waste-form developers. Each sludge contained a mixture of strontium, cerium, neodymium, and uranium to simulate fission products and actinides in the waste. Each developer was allowed to add cesium from the supernate in any form desired with the proviso that the concentration of cesium and strontium be equivalent and that the method of addition be based on the actual plant process. The plan included a detailed description of the methods used to prepare these simulated SRP sludges (Appendix A).

The plan also included instructions and guidelines on sample preparation and leach testing. It required that final waste-form samples for testing be in the form of large pieces or fragments that could be core-drilled or sawed into monoliths for leach testing.

Both the SRL developers of the reference glass and six off-site waste-form developers submitted samples incorporating the three simulated compositions. These seven waste forms were:

- Borosilicate glass, from the DWPF reference process (SRL).¹⁰
- High-silica glass, from a porous glass matrix process (CUA).¹¹
- Tailored ceramic derived from the supercalcine concept (RES).¹²
- Synroc, a titanate-based ceramic (LLNL).¹³
- Coated ceramic pellets (PNL).¹⁴
- Coated sol-gel spheres (ORNL).¹⁵
- FUETAP (Formed Under Elevated Temperature And Pressures) concrete (ORNL).¹⁶

These six waste forms were tested and evaluated at SRL. Leaching tests using neutron activation at SRL were complemented with off-site leach testing by the Materials Characterization Center (MCC) and by the waste-form developers. CLT samples were tested using the standardized Materials Characterization Center (MCC) tests.^{17,18} Furthermore, in the case of Synroc, we at LLNL characterized the microstructure, mineralogy, radwaste distribution among the various phases, mechanical and thermophysical properties of our waste form. We also evaluated the probable effects of radiation damage.¹⁹

In preparing our Synroc D samples for the CLT program, we intensively studied surrogate waste compositions to establish the correct additives and processing conditions. Most of our work was devoted to the SRP composite waste composition. Three spray-dried composite compositions (S07, S10, and S11) were needed to optimize the final conditions necessary before the samples were prepared for CLT. In the case of the compositional extremes in SRP wastes, two spray-dried compositions [S12 (high iron) and S14 (high aluminum)] were evaluated before the CLT samples were prepared.

During October and November 1980, SRL shipped about 2 kg of simulated composite sludge (air dried and hydrated) and about 1.3 kg of both "high iron" and "high aluminum" to LLNL. These sludges were analyzed at LLNL and the composition compared with the "as-made" values reported by SRL (Appendix A).

We sent our first Synroc composite CLT waste form [with cesium added as a hollandite solid solution--(S21-S18)] to SRL in January 1981. The high-iron waste form with cesium added as a hollandite solid solution (S26-SAN) was shipped in April 1981. The high-aluminum waste form with cesium mineralized in situ as nepheline or pollucite was shipped in June 1981.

At the request of SRL, we sent two additional waste-form samples to SRL during this period. These two samples were not prepared using SRL simulated waste because we had insufficient SRL material. Instead, we prepared a nearly identical substitute by adding the radwaste components strontium, cesium, cerium, neodymium, and uranium to simulated sludges prepared by Southwestern Analytical Chemicals, Inc. (Austin, TX). The major oxide components were similar to the simulated waste supplied by SRL. Compositions were again confirmed by analyses at LLNL.

Our first alternate sample (S29) was a composite sample with cesium mineralized in situ as nepheline (or possibly pollucite); it was shipped in May 1981. Preparation of this sample involved a different processing concept. In making the first sample (S21-S18), cesium had been mineralized first as a hollandite solid solution and then added to the bulk waste. (If this concept is adopted, cesium will be processed separately from the sludge stream but using the same equipment. This approach may have merit for the two-stage processing schedule now envisioned for SRP waste.) In preparing sample S29, however, cesium was added to the sludge stream as a water-soluble salt and mineralized in situ in nepheline (or pollucite).

Our second alternate sample (S30-HP3A) was a high-iron sample; it was shipped in June 1981. We submitted this sample because our first sample (S26-SAN) exhibited cracking. We determined that the high-magnetite phase component in this waste form was highly susceptible to localized nonisothermal heating effects when the sample was inductively hot pressed. These effects could be eliminated entirely by resistive hot pressing, and we submitted sample S30-HP3A as a replacement for the high-iron sample. Also, the resistively hot pressed sample more closely represents the reference Synroc process in which hot isostatic pressing (HIP) is used for densification.

SYNROC D FORMULATIONS

GENERAL BACKGROUND

Exploratory phase-equilibria studies by Ringwood⁴ showed that adding TiO_2 , ZrO_2 , CaO , and SiO_2 to the three SRP simulated waste compositions yielded three radwaste host phases: zirconolite ($\text{CaZrTi}_2\text{O}_7$), perovskite (CaTiO_3), and nepheline ($\text{NaAlSi}_2\text{O}_6$). The remaining phases, which did

not act as radwaste hosts, were iron-aluminum spinel-solid solutions ($\text{MO} \cdot \text{M}_2\text{O}_3$) of varying compositions. Ringwood made hot pressings of small samples at 0.5 GPa (73 ksi) at temperatures between 1000 and 1300°C and at different oxygen fugacities using platinum, iron, and nickel capsules. For all compositions, the solidus temperatures were in the range of 1150 to 1200°C. Only those samples hot pressed at or above 1150°C had crystallite sizes sufficiently large to allow accurate phase compositions to be determined using the electron microprobe. Ringwood reported difficulty in achieving phase equilibrium in his mixed oxide samples at temperatures below 1100°C.

Table 3 summarizes phase compositions determined by Ringwood for the three SRP compositions. In this study, Ringwood reported the partitioning behavior of only two radwastes (uranium and samarium). Uranium, reported as UO_2 , partitioned predominantly into zirconolite regardless of the sludge composition. The concentrations of UO_2 in zirconolite were in the range of 4 to 5.5 mol%. Smaller amounts of UO_2 (0.7 to 1.3 mol%) also partitioned into perovskite. Ringwood made the general observation that uranium and other tetravalent actinides partition in zirconolites and perovskites in ratios (zir/per) varying from 2 to 5, depending on the early mineralization history and oxygen fugacity. Ringwood suggested that if time-temperature conditions are favorable to early perovskite formation, then subsequent redistribution of uranium into zirconolite may be more difficult.

The only data for rare-earth partitioning reported by Ringwood was for the composite sludge. Table 3 shows that Sm_2O_3 partitioned into both zirconolite (0.7 mol%) and perovskite (1.5 mol%) in the ratio of 0.5 (zir/per). Ringwood described similar partitioning behavior for other rare earths and also postulated that Am^{+3} and Pu^{+3} would partition in this manner.

Ringwood gave no data for cesium and strontium in his report. However, on the basis of his work with Synroc, he believed that strontium and cesium would partition strongly into perovskite and nepheline, respectively. Ringwood indicated his general preference for hollandite over nepheline as a cesium waste form except when sodium levels in the sludge were high.

Another feature of Ringwood's data (Table 3) is the importance of the iron oxidation state in iron oxide. Depending on the sludge composition, the iron oxidation state is important in controlling the spinel mineralogy and composition if the amount of titania (TiO_2) consumed in spinel formation is to be minimized. When the sludge contains sufficient alumina to react

Table 3. Phase compositions of Synroc D containing simulated SRP sludges from Ringwood.^a

Phase	Estimated amount of phase in waste composition (wt%)											
	Composite ^b			High iron ^c			High aluminum ^d					
Zirconolite	16			15			16					
Perovskite	11			11			13					
Nepheline	18			15			16					
Spinel	55			59			55					

Oxide	Oxide content of phase in each waste composition (mol%)											
	Zirconolite			Perovskite			Nepheline			Spinel		
	Comp.	Fe	Al	Comp.	Fe	Al	Comp.	Fe	Al	Comp.	Fe	Al
TiO ₂	40.6	42.1	35.8	49.9	46.0	47.1	0.4	0.4	0.2	15.7	10.0	6.2
ZrO ₂	26.5	19.7	29.6	<0.1	0.8	0.4	-	-	-	0.2	-	0.2
CaO	17.5	25.0	21.2	45.3	49.8	48.0	1.0	-	-	0.4	-	-
UO ₂	4.1	5.5	5.0	<0.8	0.7	1.3	-	-	-	<0.03	-	-
Sm ₂ O ₃	0.7	-	-	1.5	-	-	-	-	-	-	-	-
Na ₂ O	1.1	0.3	3.6	<0.6	-	-	24.7	23.6	24.7	<0.14	-	-
SiO ₂	-	-	-	-	-	-	48.7	49.2	49.1	-	-	-
Al ₂ O ₃	1.0	0.4	1.0	0.1	1.1	0.2	24.7	24.6	25.0	14.8	7.9	40.3
Fe ₂ O ₃	4.4	4.7	-	1.3	0.7	-	0.5	2.3	-	11.2	28.9	-
FeO	-	-	5.5	-	-	2.3	-	-	0.8	37.8	27.3	44.4
MnO	1.3	2.4	1.2	0.3	0.8	0.7	-	-	0.2	13.3	12.8	8.7
NiO	2.8	-	-	0.2	0.2	-	-	-	-	6.7	13.1	0.4
Totals	100.0	100.1	99.9	100.1	100.1	100.0	100.0	100.1	100.0	100.3	100.0	100.2

^a Ref. 4.

^b Composite sludge was hot pressed in a nickel capsule at 5 kbar and 1150°C for 1 h; doped with 1-2% Sm₂O₃.

^c High-iron sludge was hot pressed in a platinum capsule at 5 kbar and 1150°C for 1 h.

^d High-aluminum sludge was hot pressed in an iron capsule at 5 kbar and 1200°C for 1 h.

Table 4. Nominal composition for Synroc D simulated composite sludges (S11, S21 and S29).

Chemical ingredient	S11 (wt%)	S29 (wt%)	S21 (wt%)	Average sludge composition (wt%) ^a
<u>Composite sludge</u>				
Fe ₂ O ₃	26.2	23.8	24.7	27.1
Al ₂ O ₃	20.4	18.6	19.3	21.2
MnO ₂	8.1	7.4	6.0	6.1 (MnO)
CaO	1.4	1.8	1.7	2.0
NiO	3.3	3.0	3.2	3.4
Na ₂ O	3.6	3.3	2.8	3.8
Na ₂ SO ₄	0.6	0.6	1.4	0
SiO ₂	0.6	0.6	0.5	0.6
	<u>64.2</u>	<u>59.1</u>	<u>59.6</u>	<u>64.2</u>
<u>Radioactive waste compounds</u>				
U ₃ O ₈	2.4	2.1	2.3	2.3
Cs ₂ O	0	0.25	0	0
SrO	0.4	0.25	0.26	0
Ce ₂ O ₃	0.4	0.50	0.54	1-2% Sm ₂ O ₃
Gd ₂ O ₃	0.4	0	0	0
Nd ₂ O ₃	0.4	0.50	0.54	0
Eu ₂ O ₃	0.4	0	0	0
	<u>4.4</u>	<u>3.6</u>	<u>3.6</u>	<u>4.3</u>
<u>Synroc additives</u>				
CaO	3.7	5.3	5.4	4.9
ZrO ₂	5.3	6.6	6.2	4.0
TiO ₂	15.4	18.8	18.4	15.0
SiO ₂	7.0	6.6	6.7	7.5
	<u>31.4</u>	<u>37.3</u>	<u>36.7</u>	<u>31.4</u>
Totals	<u>100.0</u>	<u>100.0</u>	<u>99.9</u>	<u>100.0</u>

^a From Ringwood, Ref. 4.

completely with iron oxide (to form a hercynite-type spinel, FeAl₂O₄), then redox conditions near the Fe/FeO buffer were employed to reduce all iron oxide to FeO. These conditions exist in the case of the high-aluminum sludge, and the iron oxide component for this sludge is reported as FeO (Table 3). In the case of high-iron sludges, less powerful reducing conditions at the Ni/NiO buffer are needed to form magnetite (Fe₃O₄). Ringwood described the composite-sludge spinel as a complex solid solution between the ferrite and

hercynite spinels. For the high-iron and composite spinels shown in Table 3, the $\text{FeO}/\text{Fe}_2\text{O}_3$ mol ratios were 1.0 and 3.4, respectively.

The composite waste forms that we hot pressed at 1050°C contained two spinels instead of one. One spinel was rich in hercynite whereas the other was rich in ulvospinel (Fe_2TiO_4) and magnetite. The high-aluminum and high-iron waste forms prepared at LLNL showed single-spinel formation. A detailed discussion of the phase equilibria responsible for our double-spinel waste form was given previously.²⁰ Basically, we believe that the two spinels formed early at the 800°C calcination step and that subsequent hot pressing to 1050°C for 1 h was insufficient to completely equilibrate the waste form into a single-phase spinel.

In our formulations of Synroc D for CLT samples, we relied on Ringwood's work⁴ (Table 3), especially in the case of spinel compositions and uranium-rare earth partitioning. However, we extended his work with our own syntheses and phase analyses for composite waste forms (S11 and S21) containing UO_2 , SrO , and rare earth oxides. Table 4 shows the nominal composition for S11, S21, S29, and Ringwood's composite sludge. The nominal compositions of all Synroc D samples sent to SRL for testing are listed in Appendix B.

We prepared samples S11 and S21 to study their phase characteristics. The components were first slurry-mixed and then spray dried to a powder that was calcined in air to constant weight.

To make S11, titanium powder was added directly to air-calcined powder to allow in situ redox control during hot pressing. The amount of titanium added was calculated to adjust the mol ratio of $\text{FeO}/\text{Fe}_2\text{O}_3$ to about 3.4, similar to that reported by Ringwood in Table 3. During hot pressing in a nickel capsule, the sample (S11-HP3A) was first held at 800°C (a temperature just below the onset of densification) for 60 min to allow redox equilibration. The sample was then heated to 1100°C and held for 50 min at 27.6 MPa (4 ksi). During this period, the temperature fluctuated between 1070 and 1140°C as a result of power-control problems. Because we observed large grain growth in the microstructure, we believe that the sample may have reached the solidus temperature momentarily during this period (Fig. 2a).

To make S21, the air-calcined powder was then calcined in a reducing gas environment of flowing CO/CO_2 . In this case, titanium additions were unnecessary. The sample S21-HP3A was hot pressed above the solidus

Figure 2. Scanning electron microscope photographs of composite Synroc D samples. (a) Sample S11-HP3A after hot pressing in a nickel capsule to 1100°C at 27.6 MPa (4 ksi) for 50 min. (b) Sample S21-HP3A after hot pressing in graphite to 1200°C at 6.9 MPa (1 ksi) for 30 min.

temperature at 1200°C to promote large grain growth for the purpose of microstructural analysis (Fig. 2b).

Table 5 lists the electron-microprobe phase characterizations for S11 and S21. A more detailed and inclusive phase- and microstructural-characterization study of Synroc D was made by Ryerson and Smith.²¹ A comparison of the

Table 5. Microprobe analyses^a of perovskite, zirconolite and spinel phases in two composite Synroc D samples.^b

Oxide	Composition (mol%)					
	Zirconolite		Perovskite		Spinel	
	S11-HP3A	S21-HP1A	S11-HP3A	S21-HP1A	S21-HP1A	
					No. 1	No. 2
TiO ₂	36.0	39.4	50.3	49.8	20.9	6.8
ZrO ₂	22.1	14.8	0.5	0.3	0	0
CaO	16.4	25.6	35.9	37.1	0	0
NiO	0.8	0.1	0.8	1.1	1.4	1.4
MnO	2.8	2.5	1.1	3.2	12.0	9.4
FeO	7.6	5.2	3.7	3.1	46.5	39.2
Al ₂ O ₃	3.7	4.4	1.2	1.7	19.3	43.3
SiO ₂	5.9	3.9	0.1	0	0	0
Na ₂ O	0.8	0.2	3.1	0.5	0	0
UO ₂	3.5	2.7	0.5	1.3	0	0
SrO	c	0.8 ^d	0.3 ^d	0.1 ^d	0	0
Ce ₂ O ₃	0.1	0.4	1.2	1.7	0	0
Nd ₂ O ₃	0.3	e	1.2	e	e	e
Eu ₂ O ₃	e	f	e	f	f	f
Gd ₂ O ₃	e	f	e	f	f	f
Totals	99.9	100.0	100.0	99.9	99.9	100.0

^a LLNL analyses by R. Ryerson.

^b S11-HP3A was hot pressed in a nickel capsule at 4 ksi and 1100°C for 1 h. S21-HP1A was hot pressed in graphite at 1 ksi and 1200°C for 0.5 h.

^c Below detection limit.

^d Estimates.

^e Not analyzed.

^f Not added.

phase compositions for major constituents in S11 and S21 with those reported by Ringwood⁴ (Table 3) showed good agreement for TiO₂ and ZrO₂ in perovskite and zirconolite. The agreement for CaO was only fair. Both S11 and S21 contained about 30 mol% perovskite vs 45 mol% reported by Ringwood. For UO₂, our analysis showed good agreement with Ringwood's values for both the perovskite and zirconolite phases. Overall, we believe our analyses agree very well with those of Ringwood.

COMPOSITE WASTE FORMS (S21, S29, S20) AND HOLLANDITES (S18, S03a)

We prepared three composite waste-form samples (Appendix B). Two samples (S21-S18 and S29) were sent to SRL for CLT. The third sample (S20-S03a) was used in mechanical and thermophysical property studies at LLNL. A portion of this third sample was sent to Argonne National Laboratory (Argonne, IL) for brittle fracture impact studies. The S20-S03a waste form was nearly identical to the S21-S18 sample.

The two composite waste-form samples for CLT differed mainly in the way cesium was added. In S21-S18, the cesium was first incorporated in hollandite (S18) and then added to the main waste-form starting powder (S21). In S29, cesium was added directly to the main waste form as a water-soluble salt (CsNO_3) and then immobilized as nepheline/pollucite in the final synthesis step.

A more complete description of the formulation procedures used to prepare CLT samples may be found in a report by Ryerson, Burr, and Rozsa.²² As one example, we show the formulation of S29 in Table 6. The nominal S29 sludge composition without Synroc additives was taken from Appendix B and is expressed as moles of oxide per kilogram of sludge. Both uranium and manganese oxides were converted to the reduced oxides UO_2 and MnO , respectively; all sodium was converted to Na_2O . We arbitrarily added a slight excess of each Synroc component as a safety margin.

The following steps were used to determine the amount of each additive that must be added to the composite sludge to make S29:

1. Na_2O and Cs_2O in Nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). We first determined the amount of SiO_2 and Al_2O_3 needed to give a mol ratio of 2.0 [$\text{SiO}_2 / (\text{Na}_2\text{O} + \text{Cs}_2\text{O})$]. For example, 0.94 mol of $\text{Na}_2\text{O} + \text{Cs}_2\text{O}$ required 1.88 mol of SiO_2 and 0.94 mol of Al_2O_3 . Because the sludge already contained 0.17 mol SiO_2 and 2.91 mol Al_2O_3 , only 1.71 mol of SiO_2 was needed. We added 1.75 mol of SiO_2 , which included a slight excess.

2. UO_2 in Zirconolite ($\text{CaO} \cdot \text{ZrO}_2 \cdot 2\text{TiO}_2$). We used the data in Tables 3 and 5, which give the UO_2 concentrations in zirconolite for the composite sludge as 4.1, 3.5 (S11), and 2.7 (S21) mol%, respectively. Uranium can substitute for zirconium in the zirconolite lattice, and the $\text{UO}_2 / (\text{ZrO}_2 + \text{UO}_2)$ ratios from Ringwood's composite (Table 3) and S11 and S21 (Table 5) were 0.13, 0.14, and 0.15, respectively. This was remarkably good agreement. We

Table 6. S29 Reference Synroc D formulation for SRL composite sludge.

Oxide	Composition of sludge with additives (wt%)	Oxide present (mol/kg sludge)	Amount needed to form mineral phase (mol/kg sludge)			
			Nepheline ^b	Zirconolite ^c	Perovskite ^d	Spinel ^e
<u>Oxide sludge, unwashed</u>						
FeO	-	-				1.8
Fe ₂ O ₃	38.0	2.38				0.5
Al ₂ O ₃	29.7	2.91	0.94			0.7
MnO ₂	11.8	1.36 ^f				0.7
U ₃ O ₈	3.3	0.12 ^g		0.12		
CaO	2.9	0.52		0.5		
NiO	4.8	0.64				0.3
SiO ₂	1.0	0.17	1.7			
Na ₂ O	5.3	0.93 ^h	0.93			
Na ₂ SO ₄	1.0					
Cs ₂ O	0.4	0.01	0.01			
SrO	0.4	0.04			0.04	
Ce ₂ O ₃	0.8	0.02				
Nd ₂ O ₃	0.8	0.02				
	100.2					
<u>Synroc additives</u>			<u>Moles addedⁱ</u>			
TiO ₂		3.8		1.2	1.5	0.7
ZrO ₂		0.9		0.8		
CaO		1.6			1.5	
SiO ₂		1.8	1.7			

^a Unwashed composite sludge from Southwestern Analytical Chemicals, Inc. containing additives from LLNL to simulate DP-1545.

^b Na₂O·Al₂O₃·2SiO₂; the mol ratio of SiO₂/(Na₂O + Cs₂O) is 2.0.

^c Table 4, composite.

^d Contains 1.3 mol% of strontium.

^e Table 4; the ratio of FeO/Fe₂O₃ is 3.4.

^f MnO.

^g UO₂.

^h Total Na₂O.

ⁱ Slight excess added.

used Ringwood's composite composition for zirconolite to determine the TiO₂, ZrO₂, and CaO additions for S29. Our composite sludge contained 0.12 mol/kg UO₂, which required that 2.9 mol of zirconolite be added. This in turn required adding 1.2 mol/kg TiO₂, 0.8 mol/kg ZrO₂, and 0.5 mol/kg CaO. Because the sludge already contained 0.5 mol/kg of CaO, only the amounts of TiO₂ and ZrO₂ are listed as Synroc additions (Table 6).

3. SrO in Perovskite (CaO·TiO₂). We could only use our estimates of SrO concentrations (Table 5) as a guide because we had difficulties analyzing the low strontium concentrations in these compositions. For S29, we

arbitrarily set the molar concentration of SrO in perovskite at 1.3 mol%, which is higher than the value reported in Table 5. Using this criterion, 0.04 mol/kg of SrO requires that 3.0 mol of perovskite (1.5 mol/kg of TiO_2 and 1.5 mol/kg of CaO) be made to immobilize SrO. Since the CaO initially present in the sludge was already committed to forming zirconolite, both TiO_2 and the additional CaO are listed in Table 6 as Synroc additives.

4. TiO_2 , ZrO_2 and CaO in Spinel. Our microprobe analyses showed insignificant amounts of ZrO_2 and CaO (Tables 3 and 5) in the spinel phase. However, there were significant amounts of TiO_2 in the spinel phases that must be taken into account. Our average TiO_2 concentration for the two spinels was about 14 mol% (Table 5) vs Ringwood's value of 10 mol% for a single-phase spinel (Table 3).

We used Ringwood's analysis to calculate the amount of TiO_2 required to form the spinel phases. In this case, we first determined that the $\text{FeO}/\text{Fe}_2\text{O}_3$ mol ratio in composite spinel listed in Table 3 was 3.4; we then converted the 2.38 mol/kg Fe_2O_3 for S29 in Table 6 to 0.54 mol/kg Fe_2O_3 and 1.84 mol/kg FeO. The mol ratio of TiO_2/FeO from Table 3 was 0.4. Therefore, the amount of TiO_2 required for the spinel phase in S29 was 0.71 mol/kg.

Finally, Table 6 gives the molar concentration of Al_2O_3 needed to form the composite spinel (0.7 mol/kg). Formation of both the spinel and nepheline requires 1.66 mol/kg of Al_2O_3 --well below the 2.91 mol/kg that is available in the sludge. However, for high-iron formulations, the Al_2O_3 concentrations in the sludge were low, requiring that additional Al_2O_3 be added as a Synroc ingredient.

5. Rare Earth Oxides Ce_2O_3 and Nd_2O_3 . We did not specifically calculate Synroc additives for rare earth oxides in S29. As shown in Tables 3 and 5, the rare earth oxides partition into both zirconolite and perovskite phases to the extent of 2-3 mol% (total rare earths). We believed that the amounts of zirconolite and perovskite already added to S29 to immobilize UO_2 and SrO would adequately accommodate the rare earth oxides.

The compositions of S21-S18 and S20-S03a were formulated in the same manner except that hollandite rather than nepheline was selected as the mineral host for cesium. Table 7 shows the composition and process description of S18 hollandite and a second improved hollandite designated SAN. This improved hollandite was added to the high-iron waste form and is discussed below.

Table 7. Hollandites (S18, SAN, and S03a) added to Synroc D composite (S21-S18 and S20-S03a) and high-iron (S26-SAN) waste forms.

Hollandite type	Oxide		Hollandite added (g/kg Synroc D oxide sludge)	Process conditions
	(wt%)	(mol%)		
S18-HP3A ^a	TiO ₂	67.4	77.6	Oxide/salts: [TiO ₂ (anatase), Al(OH) ₃ , Ba(OH) ₂ ·8H ₂ O, CsNO ₃] spray dried, air calcined at 900°C for 15 h, ball milled, hot pressed in graphite at 1200°C and 3 ksi for 2 h.
	Al ₂ O ₃	12.4	11.2	
	BaO	16.8	10.1	
	Cs ₂ O	3.4	1.1	
		100.0	100.0	
SAN-HP4A ^b	TiO ₂	72.3	81.4	Tetraisopropyl titanate (TIPT) reacted with methanol solution of CsOH + Ba(OH) ₂ . Then reacted with aq. Al(NO ₃) ₃ . Air dried and calcined at 650°C; hot pressed at LLNL in graphite at 1200°C and 3.5 ksi for 1 h.
	Al ₂ O ₃	13.0	11.5	
	BaO	9.1	5.3	
	Cs ₂ O	5.6	1.8	
		100.0	100.0	

^a Crushed; particle size = 1.00-0.42 mm, density = 4.23 g/cm³, porosity = 5.1%. S03a Hollandite was prepared by a similar procedure.

^b Crushed, particle size = 1.00-0.42 mm, density = 4.15 g/cm³. Prepared by R. G. Dosch, Sandia National Laboratories, Albuquerque, NM. (Ref. 24).

HIGH-IRON WASTE FORMS (S26, S30) AND HOLLANDITE (SAN)

We prepared two high-iron waste form samples (S26-SAN and S30) for CLT. The overall compositions are listed in Appendix B. As in the case for composite waste forms, the primary difference between S26-SAN and S30 is the manner in which cesium was added. For example, Table 8 shows the S30 formulation. Although the formulation process used for high-iron sludge was similar to that used for the composite sludge, there were some important differences:

1. Because the uranium oxide concentration in high-iron sludge was considerably higher than in the composite, more zirconolite was required in this waste form. To determine the zirconolite components needed, we used Ringwood's analysis⁴ for high-iron sludge (Table 3). In his analysis, the UO₂ concentration in zirconolite was slightly higher than that used in our S29 composite zirconolite. The UO₂/(ZrO₂ + UO₂) ratio for Ringwood's high-iron material was 0.22 vs 0.13 for our S29 composite material.

Table 8. S30 Reference Synroc D formulation for SRL high-iron sludge.

Oxide	Composition of sludge with additives (wt%) ^a	Oxide present (mol/kg sludge)	Amount needed to form mineral phase (mol/kg sludge)			
			Nepheline ^b	Zirconolite ^c	Perovskite ^d	Spinel ^e
<u>Oxide sludge, unwashed</u>						
FeO	-	-				1.7
Fe ₂ O ₃	56.2	3.52				1.8
Al ₂ O ₃	5.2	0.51	0.9			0.5
MnO ₂	4.3	0.50 ^f				
U ₃ O ₈	13.0	0.46 ^g		0.46		
CaO	3.9	0.70		2.1		
NiO	8.8	1.18				
SiO ₂	0.4	0.07	2.00			
Na ₂ O	4.8	0.85 ^h	0.85			
Na ₂ SO ₄	1.1	0.08 ^h				
Cs ₂ O	0.56	0.02	0.02			
SrO	0.56	0.05			0.05	
Ce ₂ O ₃	0.56	0.02				
Nd ₂ O ₃	0.56	0.02				
	99.90					
<u>Synroc additives</u>						
		<u>Moles added</u>				
TiO ₂		4.3		3.5	0.5	0.6(0.3) ⁱ
ZrO ₂		1.6		1.6		
CaO		1.9 ^j		1.4	0.45	
Al ₂ O ₃		1.0 ^j	0.4			0.5
SiO ₂		2.0 ^j	1.9			

^a Unwashed high-iron sludge from Southwestern Analytical Chemicals, Inc. containing additives to simulate DP-1545.

^b Na₂O·Al₂O₃·2SiO₂; the mol ratio of SiO₂/(Na₂O + Cs₂O) is 2.3.

^c Table 4, high iron.

^d Contains 5.0 mol% of strontium.

^e Table 4; the ratio of FeO/Fe₂O₃ is 0.9.

^f MnO.

^g UO₂.

^h Total Na₂O.

ⁱ Formation of spinel required 0.6 mol/kg and 0.3 mol/kg were added.

^j Slight excess added.

2. A slight excess of SiO₂ was added to insure complete synthesis of nepheline.²³ The SiO₂/(Na₂O + Cs₂O) ratio was 2.3 vs 2.0 in the S29 composite waste form.

3. The concentration of SrO in perovskite was increased from 1.3 mol% to 5.0 mol%.

4. The iron oxide in the spinel phase was not reduced as much as in the composite waste form. The FeO/Fe₂O₃ mol ratio was 0.9 according to Ringwood (Table 3) vs 3.4 in our composite.

5. We formulated S30 with less TiO_2 in the spinel phase than was used in S26. We added 4.3 mol TiO_2 /kg of sludge (Table 8). Of this amount, 4.0 mol/kg was allocated to zirconolite and perovskite, leaving the balance (0.3 mol/kg) to spinel--even though 0.6 mol/kg was needed for a high-iron spinel, according to Table 3. We formulated S26 in accordance with Table 3 using a small overall excess of TiO_2 .

6. There was insufficient Al_2O_3 in the sludge, which required that we add 0.9 mol Al_2O_3 /kg sludge as a Synroc additive.

Table 7 gives the composition and process description of the hollandite (SAN) that was added to S26. This hollandite precursor powder was prepared at Sandia National Laboratory by Dosch²⁴ and then hot pressed at LLNL.

HIGH-ALUMINUM WASTE FORM (S31)

In our high-alumina waste form (S31), we adjusted the initial composition by adding Fe_2O_3 to nearly duplicate the composite sludge and adopted the same formulation procedure used for the composite waste form S29. Because of this Fe_2O_3 addition to S31, the radwaste components were more dilute than in the S29 composition.

The overall composition is given in Appendix B.

WASTE FORM PREPARATION

S29--THE REFERENCE SYNROC D COMPOSITE WASTE FORM

We designated S29 as our reference waste form. On the basis of our experience gained by preparing several waste compositions, we believe that S29 demonstrates the potential for a procedure for the large-scale remote processing of high-level defense waste. Ref. 25 gives a more detailed description of large-scale Synroc processing.

In Fig. 3, a basic flow diagram shows the processing steps for preparing S29. Precise formulation and microstructural characterization were not a major requirement. Good mixing and homogenization at the slurry-powder preparation stage using conventional spray-drying technology was successful; grinding and milling steps were not required. The redox control of the iron

Figure 3. Processing steps for preparing sample S29, the reference Synroc D composite waste form.

oxidation state was very flexible. The final step of densification and mineralization was achieved at very modest temperatures and time periods, which permits the application of conventional, well-understood ceramic technology in the fields of sintering and hot isostatic pressing.

We generally used the same procedure to prepare all Synroc D CLT samples. In the following sections, we use S21 powder with SRL simulated waste as an example. It was the first powder prepared for CLT and its preparation is representative of Reference S29 and all subsequent preparation steps except that:

1. The mineral host selected for cesium was changed from hollandite to nepheline (except for high-iron S26-SAN).

2. Powder grinding proved unnecessary for adequate mixing and was eliminated in all subsequent CLT preparations.

3. Redox calcination temperatures were reduced from 965°C to 800°C in all later CLT preparations because the lower temperature is more desirable for large-scale processing, and it reduced the risk of forming unwanted precursor mineral phases such as ilmenite.

STARTING MATERIALS

In Table 9, we categorize all spray-dry batches according to the type of sludge used and the salt/oxide components added to make up the slurry mixtures for spray drying. The preparation of dried sludges by SRL is discussed in Appendix B. Table 10 compares the results of our chemical analyses of sludges received from SRL listed in Table 10 to the nominal SRL compositions (taken from Appendix B). The values generally agree well except that our values for rare earth oxides Ce_2O_3 and Nd_2O_3 in the composite sludge were about 0.5 wt% vs 1.0 wt% nominal reported by SRL. We used the SRL values in our formulated composite compositions.

For the additive salts listed in Table 9, we determined in advance the oxide equivalents of each salt. The SRL sludges were powders derived from slurry solutions that had been dried by an air sparge using low heat to evaporate the water. We conducted an initial test of the SRL powder for water-soluble oxides on only the "as-received" composite sludge. About 1.5 g of sludge powder was stirred in 100 ml of distilled water at room temperature for 16 h. Table 11 shows the spectrochemical analysis of the leachate. The

Table 9. Starting materials for Synroc D waste-form preparation.

Sludge type		Spray-dry batch number							
		Composite			High iron		High aluminum	Hollandite	
		S20	S21	S29	S26	S30	S31	S18	S03a
SRL composite			x						
SRL high iron					x				
SRL high aluminum							x		
SAC composite ^a		x		x					
SAC high iron ^a						x			
<hr/>									
Oxide equivalent	Salt additive								
TiO ₂	TiO ₂ (anatase) ^b	x	x	x	x	x	x	x	x
ZrO ₂	Zr(NO ₃) ₄ ^c	x	x	x	x	x ^d	x ^d		
CaO	Ca(NO ₃) ₂ ·H ₂ O	x	x	x	x	x	x		
BaO	Ba(OH) ₂ ·8H ₂ O							x	x
Al ₂ O ₃	Al(NO ₃) ₃ ·9H ₂ O	x	x	x	x	x	x	x ^e	x ^e
Fe ₂ O ₃	Fe(NO ₃) ₃ ·9H ₂ O						x		
SiO ₂	Colloidal silicate ^f	x	x	x	x	x	x		
Na ₂ O	NaNO ₃			x					
Na ₂ O·SiO ₂	NaO·SiO ₂ ·H ₂ O	x							
Na ₂ O	Na ₂ SO ₄	x				x			
UO ₂	UO ₂ (NO ₃) ₂ ·6H ₂ O	x		x		x			
Cs ₂ O	CsNO ₃			x		x	x	x	
SrO	Sr(NO ₃) ₂	x		x		x			
Ce ₂ O ₃	Ce(NO ₃) ₃ ·6H ₂ O ^g	x		x		x			
Nd ₂ O ₃	Nd(NO ₃) ₃ ·5H ₂ O ^g	x		x		x			
Eu ₂ O ₃	Eu(NO ₃) ₃ ·6H ₂ O ^g	x							
Ge ₂ O ₃	Ge(NO ₃) ₃ ·5H ₂ O ^g	x							

^a Simulated sludge prepared by Southwestern Analytical Chemicals, Austin, TX.^b Pigment Grade Titanox 1000, supplied by NL Chemicals Co., South Amboy, NJ.^c Prepared by BDH, England, and supplied by Gallard Schlesinger, Carle Place, NY.Calcined at 300°C to ZrO₂ before adding to sludge.^d Zirconium added as the nitrate.^e Added as Al(OH)₃.^f Supplied as ammonium-stabilized Ludox colloidal silica by E.I. du Pont de Nemours and Co., Wilmington, DE.^g Supplied by Research Chemicals, Phoenix, AZ.

Table 10. Chemical analyses^a of "as received" dried sludges^b from the Savannah River Laboratory.

Oxide/salt	Composition (nominal wt%)					
	Composite sludge		High-iron sludge		High-aluminum sludge	
	SRL	LLNL	SRL	LLNL	SRL	LLNL
Fe ₂ O ₃	49.93	51.2	58.60	59.3	15.95	18.4
Al ₂ O ₃	9.79	10.2	1.35	1.4	54.69	53.0
MnO ₂	13.74	12.4	3.93	3.8	13.10	11.9
U ₃ O ₈	4.51	4.7	13.60	14.3	3.84	3.7
CaO	3.72	3.6	3.98	2.7	1.05	1.7
NiO	6.19	6.7	10.00	10.7	2.34	2.7
SiO ₂	1.19	1.2	0.42	0.4	1.70	1.7
Na ₂ O	7.02	5.7	4.99	4.0	4.12	3.8
Na ₂ SO ₄	1.28	2.9	0.52	0.5	0.53	0.6
SrO	0.53	0.43	0.52	0.47	0.53	0.40
Ce ₂ O ₃	1.05	0.55	1.04	1.12	1.07	1.03
Nd ₂ O ₃	1.05	0.47	1.04	1.25	1.07	1.15
Totals	100.00	100.02	99.99	99.94	99.99	100.08
Loss in air after 16 h at 800°C (wt%)	28.3 ^c	26.2	29.5 ^c	28.5	31.3 ^c	31.6

^a Atomic absorption analyses were performed by Bob Lim, and x-ray fluorescence analyses were performed by Richard Ryan, both at LLNL.

^b Data taken from Appendix A.

^c SRL weight losses in air after 96 h at 900°C.

leachate indicated very low concentrations of all elements except sodium, which was expected. On the basis of 200 µg Na₂O/100 ml leachate, we estimated that about 1.8 wt% of Na₂O was leached from the powder vs the 5.7 wt% initially present in the starting sludge. This low rate of sodium dissolution may result from the fact that the simulated SRL sludge was dried at low temperatures.

To demonstrate the differences between formulated and mixed compositions for a large batch of sludge, we compare three different analyses of random samples in Table 12. These samples were taken from about 2.2 kg of S21 composite powder after redox calcination to a FeO/Fe₂O₃ mol ratio of 2.1. In Table 13, we show the analyses of two hot-pressed composite samples (S21-S18 and S29) and one high-iron sample (S26-SAN). There is generally good

Table 11. Spectrochemical analysis of aqueous phase after separation from simulated SRL composite sludge/water slurry after stirring 16 h at room temperature.

Elements detected			
Element	Concentration ^a ($\mu\text{g/ml}$)	Element	Concentration ^a ($\mu\text{g/ml}$)
Na	>200 ^b	Ba	0.1
U	>30 ^c	Fe	0.1
Al	20	B	0.06
Ca	6	Sr	0.06
Zn	5	Mg	0.02
Si	0.4	Ag	<0.006
Cr	0.2	Cu	0.006

Elements not detected	
Element	Limit of detection ($\mu\text{g/ml}$)
Sm, Tb	<2
Dy, Gd, Ge, Ho, La, Lu, Nb, Nd, Pr, Sb, Sc, Zr	<0.2
Er, Eu, Ni, Pb, Tm, V, Y	<0.06
Bi, Cd, Sn, Ti, Yb	<0.02
Be, Co, Mo, Mn	<0.006

^a 1.4 g dried, simulated sludge leached in 100 ml water.

^b About 1.8 wt% Na_2O .

^c About 0.002 wt% UO_2 .

agreement between nominal and measured compositions in both the calcined powder and hot pressed stages of Synroc D synthesis. Since then, we have prepared batches of up to 65 kg of powder and have observed little or no variation in composition within the batch.

SLURRY PREPARATION

To prepare simulated SRL composite sludge for slurry mixing and spray drying, 2 kg of the powder was first divided into four 500-g portions. Each

Table 12. Analyses of S21 composite waste-form powder after redox calcination in a carbon monoxide-carbon dioxide (10:1) gas environment at 965°C for about 10 h in a rotary kiln.^a

Oxide	Composition (wt%)			
	As formulated	Atomic absorption	X-ray fluorescence	
Fe ₂ O ₃	24.7	26.1	28.3	24.4
Al ₂ O ₃	19.3	19.6	18.5	-
MnO ₂	6.0	6.2	6.5	7.3
U ₃ O ₈	2.3	-	2.4	1.9
CaO	7.2	7.5	9.1	8.4
NiO	3.2	3.2	3.1	2.3
Na ₂ O	3.4 ^b	3.4	3.8	-
SiO ₂	7.2	-	10.1	-
SrO	0.25	0.21	0.21	0.19
Ce ₂ O ₃	0.50	-	0.61	-
Nd ₂ O ₃	0.50	-	0.57	-
TiO ₂	18.4	14.9	13.9	21.9
ZrO ₂	6.3	-	6.0	5.3
Totals	99.3		103.1	

^a Three batches were cone-blended for 2 h before sampling. The mol ratio of FeO/Fe₂O₃ was 2.3.

^b Total Na₂O reported, which includes 1.4 wt% Na₂SO₄.

portion was then combined with about 870 g of an oxide/salt mixture containing the appropriate amounts of each ingredient. Each batch of powder (about 1.4 kg) was then combined with about 6 l of water and tumbled with a small number of alumina balls for about 16 h in a large 5-gal plastic container. The container was removed from the roller mill just before spray drying. When using sludges prepared as aqueous slurries from Southwestern Analytical Chemicals, Inc., slurries were mixed homogeneously in barrels before removing known aliquots for subsequent combination with the required additives.

SPRAY DRYING AND CALCINATION

After the sludge and additives have been slurried, the measured pH was 3 to 5. At these pH levels, the hydrogen-ion concentrations were still quite low and probably insufficient to dissolve significant amounts of the suspended

Table 13. Analysis of composite (S21-S18 and S29) and high-iron (S26-SAN) waste forms^a after hot pressing in graphite.

Oxide	Composition (wt%)							
	S21-S18-HP8A ^b				S29-HP8A ^c		S26-SAN ^d	
	Nominal	Atomic absorption	X-ray fluorescence	Electron microprobe ^e	Nominal	X-ray fluorescence	Nominal	X-ray fluorescence
Fe ₂ O ₃	23.0	23.3	25.0	22.8	23.8	25.3	28.9	29.0
Al ₂ O ₃	18.9	18.7	20.0	22.1	18.6	23.3	6.9	7.7
MnO ₂	5.6	5.6	5.8	5.6	7.4	7.6	1.9	1.9
U ₃ O ₈	2.1	-	2.3	2.3	2.1	2.4	6.7	6.5
CaO	6.6	7.4	6.6	7.7	7.1	7.1	7.3	7.2
NiO	3.0	3.0	3.1	2.7	3.0	3.2	5.2	5.4
Na ₂ O	3.2	2.8	2.9	4.6	3.6	3.2	2.0	2.2
SiO ₂	6.7	-	8.2	11.7	7.2	9.0	4.4	5.7
Cs ₂ O	0.24	-	0.22	-	0.25	0.20	0.25	0.20
SrO	0.24	-	0.12	-	0.25	0.14	0.25	0.13
Ce ₂ O ₃	0.50	-	0.55	0.38	0.50	0.58	0.50	0.61
Nd ₂ O ₃	0.50	-	0.55	0.54	0.50	0.50	0.50	0.50
TiO ₂	21.85	17.9	18.5	21.2	18.8	15.3	24.0	18.8
ZrO ₂	5.8	-	5.9	6.2	6.6	6.6	10.4	8.5
BaO	1.18	-	1.5	0	0	0	0.4	0.6
Total	99.41		101.24		99.7	104.42	99.60	94.94

^a After hot pressing, samples were crushed to -300 μ m powder for analysis.

^b Hot pressed at 1050°C for one hour at 20.7 MPa (3 ksi).

^c Hot pressed at 1025°C for one hour at 20.7 MPa (3 ksi).

^d Hot pressed at 1100°C for one hour at 20.7 MPa (3 ksi).

^e Electron microprobe broad-beam analysis of S21 matrix phase only. Values normalized to exclude 7.04 wt% hollandite for S21-S18 comparison.

SRL sludge in the slurry. In this regard, we believed that the preferential dissolution of radwaste components in actual SRP sludges could make an important contribution to homogeneous mixing before the material was spray dried and that this possibility should receive additional study. We were also concerned that no water-soluble titanium salt was available, which required us to add titanium as pigment-grade TiO_2 consisting of submicron-sized particles. We found, however, that we could achieve good densification and mineralization using dried SRL simulated sludges and pigment-grade TiO_2 .

A portable spray dryer with centrifugal atomization and single-point collection in a cyclone separator (Niro Atomizer, Columbia, MD) was used to process all waste-form slurries (Fig. 4). In order to provide feed for spray drying, portions of the slurry were transferred to a large 4-l beaker and stirred mechanically. The slurry supply to the dryer was about $70 \text{ cm}^3/\text{min}$, which allowed an exit-gas temperature in the range of $132\text{--}136^\circ\text{C}$. In some cases, however, temperature excursions did occur to a maximum of 150°C and a minimum 125°C . Dried powder was collected at the base of the cyclone separator in 500-ml bottles (Fig. 4a). The powder production rates of dried uncalcined powder ranged between 9 and 13 g/min (6 to 9 g/min of oxide equivalent, based on an average 30%-weight losses incurred during calcination).

In the laboratory, the spray-dried powders were calcined in two stages: air calcination and redox calcination. Two-stage calcination made it easier to dispose of decomposition gases; the powders were first air calcined in furnaces inside vented enclosures and then redox calcined in a rotary calciner. In actual processing of defense wastes, a single calcination step would be used.

A total of 4.4 kg of S21 powder was produced by the spray dryer. The total solids input to the spray dryer was:

Sludge	2.0 kg
Aluminum nitrate	3.3
Calcium nitrate	0.7
TiO_2	0.6
ZrO_2	0.2
SiO_2	<u>0.7</u>
Total	7.5 (3.0 kg oxide equivalent)

Figure 4. (a) Portable spray dryer with centrifugal atomization that was used to process all waste-form slurries. (b) Cyclone separator; dried powder was collected at the separator's base in 500-ml bottles.

Assuming total loss of water of hydration during drying, the powder yield would have been 5.33 kg. Our yield of 4.4 kg indicates that some nitrate decomposition in addition to dehydration occurred during drying.

The spray-dried powders were then loaded into large alumina crucibles so that each one was half full and contained about 1 kg of powder. The powders were calcined in air to constant weight at 650°C for periods of 40 to 53 h. We had previously determined that smaller samples heated in air at 650°C achieved a constant weight in 16 hours. The temperature of 650°C was selected because earlier work had shown that some mineralization begins at higher calcination temperatures; because we did not want spinel to form under the oxidizing conditions of an air calcine, temperatures at this stage were limited to 650°C.

The average weight loss for S21 batches was $38.2 \pm 0.1\%$. The total oxide weight was 2.7 kg vs 3.0 kg oxide calculated from the original formulation. This represents a possible 10% stack loss (neglecting minor handling losses) in the spray-dryer operation. Since the spray-dryer specifications indicate only a nominal 95% recovery using this equipment, we were satisfied with our recovery.

The 2.7 kg of air-calcined S21 powder was then redox calcined in a rotary kiln-type furnace system (Fig. 5). The reaction vessel was heated in a three-zone split-hinged furnace (Model 54657, Lindberg Furnace Co., Chicago, IL) having Cr-Al-Fe alloy heating elements capable of 1200°C. The reaction vessel (Fig. 6) was rotated at about one rpm. The powder load limit for this chamber (filled a third full) was about 1 kg. Three batches of S21 powder were calcined at 965°C for periods of 5-16 hours in a carbon dioxide-carbon monoxide (10:1) reducing atmosphere at a total flow rate of about 46 l/h. Calcination times varied with batch size (0.85 to 1.0 kg) and each batch was redox calcined until the $\text{FeO}/\text{Fe}_2\text{O}_3$ mol ratio was about 2.1, as determined by wet-chemical analysis.²⁶

After redox calcination, all three powder batches were blended for 2 h in a rotating-cone blender with a rapidly rotating disintegrator bar traveling at 2800 rpm (Patterson Industries, Inc., East Liverpool, OH). Samples were then taken for x-ray analysis and some small-scale test hot pressings.

The x-ray analysis of redox-calcined S21 powder indicated some crystallinity. The major phases were two spinels ($a^\circ = 8.45 \text{ \AA}$ and $a^\circ = 8.18 \text{ \AA}$) and perovskite; secondary phases were ilmenite (FeTiO_3) and ZrO_2 . Because

Figure 5. Rotary kiln-type furnace system used to redox calcine air-calcined powders. The reaction vessel was heated in a three-zone split-hinged furnace capable of 1200°C.

Figure 6. Reaction vessel (316 stainless steel) in which air-calcined powders were redox calcined. The vessel, filled about one-third full, was rotated in the furnace at about one rpm at 965°C for 5-16 hours while a carbon dioxide-carbon monoxide (10:1) reducing atmosphere flowed through it at flow rates of about 46 l/h (AAA81-101445-00).

we were concerned about the formation of ilmenite in our calcined powder, we made small-scale hot pressings of this powder at 1000 and 1050°C in graphite at 27.6 MPa (4 ksi) to evaluate the consequences of ilmenite in our calcined powder.

X-ray analysis of these hot-pressed samples showed good Synroc phase formation and no ilmenite. Leach-screening tests also indicated no adverse behavior. However, microstructural analysis indicated some free ZrO_2 as a

minor phase. X-ray analysis did not show free ZrO_2 . We elected to grind S21 powder in a Sweco Vibro-Energy mill (Model M18L, Sweco Inc., Los Angeles, CA). Powders were milled with alumina balls in isopropyl alcohol for 46 h. Weighing the alumina balls before and after milling indicated no loss of alumina. Additional hot pressings were made of this milled powder, and misrostructural analysis indicated that all the ZrO_2 had been incorporated into zirconolite. We did not find it necessary to grind any of the remaining CLT powder batches. Additionally, the redox-calcination temperature for all remaining waste-form powders was reduced from 965 to 800°C, eliminating ilmenite formation.

After the S21 powders were ground, they were blended a second time. During blending, the powders naturally granulated into free-flowing spheroidal shapes 0.5-1.5 mm in diam (Fig 7a). This same powder when dispersed

(a)

0.8 mm

(b)

0.6 μm

Figure 7. The S21 powders (a) after grinding, blending a second time, and granulation into free-flowing spheroidal particles 0.5-1.5 mm in diam and (b) after ultrasonic dispersion in a liquid medium.

ultrasonically in a liquid medium is shown in Fig. 7b. We cannot tell in Fig. 7b if all agglomerates have been dispersed, but we can say that all particles are less than 1 μm in diam. The S21 powder density measured by helium pycnometry was 4.07 g/cm^3 . The S21 powder surface area, determined by nitrogen gas adsorption (BET), was 7.59 m^2/g . This powder was now ready to be blended with our crushed S18 cesium-hollandite waste form to make S21-S18.

HOLLANDITE PREPARATION

In preparing hollandite (S18), a base composition of $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{TiO}_2$ having a $\text{BaO}/\text{Cs}_2\text{O}$ mol ratio of 9/1 was mixed as an aqueous slurry of TiO_2 (pigment-grade anatase), barium and aluminum hydroxides, and cesium nitrate. This slurry was spray dried and air calcined at 900°C for 15 h. An x-ray analysis indicated hollandite and anatase. The surface area of the calcined powders by nitrogen BET was 8.29 m^2/g . An earlier study²⁷ of hollandite preparations of this kind showed no cesium loss during air calcination. This was later confirmed by an analysis of hot-pressed material. Initially, a small amount of powder (S18-HP1A) was hot pressed in graphite at 1200°C for 2 h at 27.6 MPa (4 ksi) for screening leach tests.

Screening leach tests were conducted in deionized water at 150°C for 1, 2 and 3 days on crushed aggregate (-48 to +100 mesh, 300-150 μm). They showed cesium losses of 2.2, 1.5, and 1.1% for each successive day. In an effort to improve the cesium leach behavior, the air-calcined powder was milled a second time in isopropyl alcohol for 71 h. The additional grinding increased the surface area from 8.29 to 12.48 m^2/g . A second small hot pressing (S18-HP2A) was completed in graphite at 1200°C for 2 h at 27.6 MPa (4 ksi). The finer particle size resulted in a higher pressed density that was 99.0% of theoretical. However, the leaching behavior of this material was not improved.

The balance of S18 powder (about 400 g) was then hot pressed in preparation for the S21-S18 formulation. This larger sample (S18-HP3A) was inductively hot pressed in graphite at 1200°C for 2 h at 20.7 MPa (3 ksi).

The sample was then crushed to -16 to +35 mesh (0.4 to 1.0 mm) and submitted for characterization. Figure 8 shows crushed S18-HP3A hollandite. The helium pycnometric density of the aggregate was 4.23 g/cm^3 . The surface area was 0.042 m^2/g . About 160 g of hollandite aggregate containing 3.3 wt%

Figure 8. S18-HP3A hollandite crushed to -16 to +35 mesh (0.4 to 1.0 mm) particles.

Cs_2O was cone blended with 2100 g of S21 powder to make up the final S21-S18 waste-form composition. This mixture was then uniformly blended for 1 h before hot pressing. We selected a temperature of 1050°C for the hot pressing of S21-S18 because of our concern that higher temperatures would cause extensive hollandite-S21 matrix interactions that could have detrimental effects on leaching. Ryerson²⁸ studied the hollandite-Synroc D boundary in samples hot pressed in graphite at 1050°C for 1 h at 2 ksi. He identified a minor 1-2 μm reaction layer of ilmenite. No radwaste elements were found in this boundary, and it did not affect the leach resistance of S21-S18.

HOT PRESSING

Small test samples (about 10 g) were densified with a resistance-heated hot press (Fig. 9). In this system, electrical currents are passed directly through the insulated graphite pressing die. A calibrated thermocouple (Pt/Pt + 10% Rh) was placed in a tight-fitting hole next to the sample. The thermocouple hole was not drilled through the graphite wall. Gold point calibrations were made at the melting point (1063°C) and were accurate to $\pm 10^\circ\text{C}$. The approximate power to reach temperatures of 1100 to 1200°C was 8.1 kW at 4.5 V and 1800 A.

Figure 9. Resistance-heated hot press used to densify small test samples of about 10 g.

Figure 10 shows the graphite die punches and metal capsule inserts. Metal capsules were used in some experiments where closely controlled redox conditions were needed. This was not the case for Synroc D that had been redox calcined. Figure 10 also shows coatings of Y_2O_3 made on the inside die wall and on one metal capsule to prevent metal-graphite reactions at higher temperatures. We found this necessary only when nickel capsules were

Figure 10. (a) Graphite die punches and metal capsule inserts used in experiments requiring closely controlled redox conditions. The inside die wall and one metal capsule were coated with Y_2O_3 to prevent metal-graphite reactions at higher temperatures. (b) When metal capsules were used, the lid was electron-beam welded after powder loading, and a small graphite mid-punch was inserted into the lid. Once maximum temperature was attained, the full pressure was applied, breaking the welded seal and pushing the lid into the can, thus hot pressing the powder to full density.

heated to more than 1300°C in graphite. When metal capsules were used, the lid was electron-beam welded after powder loading. Then a small graphite mid-punch shown at the center of Fig. 10a was inserted into the lid. The mid-punch was designed to apply pressure only on the lid and not the can wall. After maximum temperature was attained, the full pressure was applied, breaking the welded seal and pushing the lid into the can, which hot pressed the powder to full density.

Most of the CLT samples were densified in an induction hot press (Fig. 11). A 7.62-mm-diam die was coated with Y_2O_3 before loading the powder as a precaution to prevent sample-die reactions. Figure 12 shows a

Figure 11. Induction hot press used to densify CLT samples.

Figure 12. Typical CLT sample after removal from the die; the Y_2O_3 coating is still visible. A calibrated optical pyrometer was inserted in the black-body hole in the die to measure the temperature.

Figure 13. Five samples of S21-S18 composite waste after hot pressing. Four cylinders are shown with core drillings removed; these core drillings were used for leach testing and characterization.

typical CLT sample after removal from the die. The Y_2O_3 coating was still visible and was easily removed from the surface by brushing. Also shown in Fig. 12 is the black body hole for temperature measurement with a calibrated optical pyrometer.

Five samples of S21-S18 composite waste were hot pressed and sent to SRL for testing (Fig. 13). The weights and immersion densities of each sample are given in Appendix B. In Fig. 13, two samples have a small amount of Y_2O_3 coating remaining that was not brushed off. Four cylinders are shown with core drillings removed; these core drillings were used for leach testing and characterization at LLNL.

All S21-S18 composite samples were hot pressed in graphite dies at 1055°C for 1 h at 13.8 MPa (2 ksi). This temperature is well below 1180°C, where a major phase change (as determined by differential thermal analysis) occurs in the composite composition. All hot-pressed samples achieved densities (measured by immersion) greater than 3.93 g/cm³. Mercury porosimetry showed a total open porosity of 0.2% down to a pore size of 0.0146 μ m and a maximum pressure density of 3.953 g/cm³. On this basis, we assign 4.0 g/cm³ as the theoretical density of S21-S18, and all CLT samples were >98% of theoretical.

Table 14 gives a complete account of typical hot-pressing parameters for S21-S18-HP8A, and Fig. 14 plots density and temperature as functions of time.

In addition, S21-S18 samples HP10A, HP11A, and HP12A were annealed at 800°C for 30 min during cooling. All samples lost about 1.3% of their weight during hot pressing.

The data plotted in Fig. 14 are typical for waste-form compositions covered in this report except that some compositions were hot pressed at a slightly higher temperature (1100°C). The data show that no significant densification occurred until temperatures of about 900°C were reached. If full pressure [13.8 MPa (2 ksi)] had been applied at the onset, the threshold temperature for densification would have been lower. These data compare very well with results reported earlier for composite Synroc D.²⁰ In that work, density-vs-time plots for small samples (10 g) of Synroc D without hollandite addition were given at three pressures: 27.6, 13.8, and 6.9 MPa (4, 2, and 1 ksi, respectively). The hollandite aggregate additions had little effect on the hot-pressing behavior.

Samples were taken from both edge and center positions on one CLT sample (S21-S18-HP8A) for x-ray and microstructural analysis. We could find no

Table 14. Hot-pressing parameters for Synroc D composite S21-S18-HP8A.^{a,b}

Time (min)	Temperature (°C)	Pressure (ksi)	Percent theoretical density
0	23	1	47
51	740	1	47
65	810	1	47
85	940	1	47
95	997	1	52
106	1050 ^c	2	76
110	1054	2	86
113	1052	2	89
116	1055	2	93
120	1055	2	95
125	1055	2	97.0
130	1055	2	97.5
140	1055	2	98.0
155	1056	2	98.5
167	1050 ^d	0	98.5
170	1004	0	
175	950	0	
180	895	0	
185	850	0	
190	820 ^e	0	

^a The sample was hot pressed in a 7.62-cm-diam graphite die under a flowing argon atmosphere.

^b All S21-S18 hot pressings (8A, 9A, 10A, 11A and 12A) were hot pressed under similar conditions except that 10A, 11A, and 12A were annealed for 30 min at 800°C during cooling.

^c Begin 1-h hold at maximum pressure.

^d End 1-h hold; power turned off and pressure released.

^e Overnight cooling to room temperature.

significant compositional differences between these locations. Figure 15 shows x-ray patterns of samples from both positions. As indicated, all peaks in a 2 θ span of 10 to 74 have been identified except for a few small peaks. In addition, the edge-section x-ray pattern shows the presence of a metallic iron alloy, which indicates that more graphite reduction does occur in the outer regions of the sample. We did not find any difference in the leaching behavior of samples taken from both locations.

The microstructural characterization of this waste form is discussed in an earlier report.²⁸ Table 13 shows the results of chemical analysis of a sample of ground hot-pressed material. We did not determine the Fe⁺²/Fe⁺³ ratio of the hot-pressed materials.

Figure 14. Hot pressing data for Synroc D composite (S21-S18-HP8A). Densification (a) and temperature (b) as functions of time at an initial pressure of 6.9 MPa (1 ksi) and a final pressure of 13.8 MPa (2 ksi).

Figure 15. X-ray patterns of a CLT sample (S21-S18-HP8A) taken from (a) center and (b) edge locations. Except for a few small peaks, all peaks in the 2θ span of 10 to 74 were identified, and we found no significant compositional differences between these locations.

Just before preparing samples for CLT using SRL sludges, we formulated a larger batch of Synroc D composite called S20-S03a. This was done both as a final preparation step for the CLT program and also to prepare larger samples for mechanical- and thermophysical-properties studies.

For S20-S03a, we used a simulated sludge supplied by Southwestern Analytical Chemical, Inc. A composite composition equivalent to about 3.5 kg of oxide was made up in three slurry batches, spray dried, and air calcined at 650°C to constant weight. The powders were then redox calcined in 0.7-to-1.0-kg batches at 800 to 915°C and analyzed for iron oxidation state. Powder batches were then blended before adding crushed hollandite (S03a, -16 to +35 mesh) and hot pressing.

Two smaller 3-in.-diam hot pressings (S20-S03a-HP1A and S20-S03-HP2A) were prepared for the impact studies at Argonne National Laboratory (Appendix B). A larger 6-in.-diam hot pressing (S20-S03a-HP4A) was also prepared for mechanical-property studies at LLNL. Figure 16 shows the hot press and gives the time-temperature history of this sample. Figure 17 shows the sample after hot pressing; about 1.6 kg powder with hollandite was hot pressed in a 6-in.-diam graphite die at 1050°C in vacuum at 13.8 MPa (2 ksi) for 1 h. Temperatures were measured both optically and with a thermocouple. A calibrated optical pyrometer was manually sighted into a black-body hole drilled into the die wall. A sheathed thermocouple was positioned so that it touched the outer surface of the graphite die. After hot pressing, the large disk was cut with a diamond saw and cores were drilled into smaller test specimens to measure flexural and compressive strengths, ultrasonic elastic constants, thermal expansion, and thermal conductivity. Figure 18 shows some of these test samples.

MECHANICAL AND THERMOPHYSICAL PROPERTIES

The general test procedures for this property study of Synroc D were described in an earlier report²⁹ in which we evaluated Synroc B in a similar manner.

ULTRASONIC ELASTIC CONSTANTS

Water-immersion densities and ultrasonic elastic constants were measured on four samples (Fig. 18a) taken from separate regions of the large

Figure 16. (a) Time-temperature history of a 6-in.-diam hot pressing (S20-S03a-HP4A). The sample, containing 1.6 kg powder with hollandite, was hot pressed in an evacuated graphite die coated with Y_2O_3 ; it was heated at about $8^\circ\text{C}/\text{min}$ and cooled at the following rates: $5^\circ\text{C}/\text{min}$ from 1055 to 600°C , $2^\circ\text{C}/\text{min}$ from 600 to 300°C , $0.8^\circ\text{C}/\text{min}$ from 300 to 100°C , and $0.1^\circ\text{C}/\text{min}$ from 100 to 50°C . (b) The hot press used to prepare this sample.

Figure 17. The sample after hot pressing.

Figure 18. Smaller test specimens cut from the disk and cores. (a) Samples on which water-immersion densities and ultrasonic elastic constants were measured. (b) Samples cut for flexural-strength testing. (c) Samples cut for linear thermal expansion studies. (d) Samples prepared for compressive testing.

hot-pressed sample. These samples (E-1 to E-4) were 1/2 in square and 0.150 in. thick, and the large faces were ground flat and parallel to <0.0005 in. deviation across the flat surfaces. Table 15 lists the results of these measurements. The mean density of $4.00 \pm 0.01 \text{ g/cm}^3$ indicates good density homogeneity throughout the sample. Ultrasonic measurements were made at 20 MHz (longitudinal) and 10 MHz (shear). The mean values and errors calculated as the standard deviation from the mean also indicated good homogeneity across the sample in regard to elastic properties. The average Young's Modulus of 138.93 GPa compares well with an average ferrite body³⁰ having a modulus of about 140 GPa ($P = 4.7 \text{ g/cm}^3$, ~7% porosity).

FLEXURAL STRENGTH

Figure 18b shows two of the four samples cut for flexural-strength testing. Sample dimensions were nominally 4.00 by 0.50 by 0.19 in., and tests were conducted in four-point bending with a 3-in. span. After samples were tested with a 3-in. span, four broken segments were tested a second time with a 1.5-in. span. Results of 3-in.-span testing are available for only two of the four specimens because of equipment malfunctions. Only the data for

Table 15. Immersion density and ultrasonic elastic constants of Synroc D composite (S20-S03a-HP4A)^a

Sam- ple No.	Thick- ness (mm)	Density (g/cm ³)	Longi- tudinal velocity (m/s)	Shear velocity (m/s)	Poisson's ratio	Bulk modulus (GPa)	Shear modulus (GPa)	Young's modulus (GPa)
E-1	3.860	3.992	6688	3683	0.282	106.4	54.14	138.86
E-2	3.870	3.998	6691	3676	0.284	106.9	54.03	138.72
E-3	3.879	4.009	6725	3677	0.287	109.0	54.21	139.50
E-4	3.713	4.012	6684	3667	0.285	107.3	53.96	138.63
Mean value		4.00	6697	3676	0.285	107.4	54.09	138.93
σ^b		± 0.01	± 19	± 7	± 0.002	± 1.1	± 0.11	± 0.39

^a Longitudinal frequency = 20 MHz, shear frequency = 10 MHz (A. E. Brown, Lawrence Livermore National Laboratory, Livermore, CA, Materials Test Engineering Report No. 81-149, March 27, 1981).

^b Standard deviation.

3-in.-span testing meets the required specifications of ASTM³¹. Data were taken over the shorter span only to demonstrate the degree of homogeneous strength throughout the samples (Table 16). The mean strengths were 65 and 55 MPa (9.4 and 8.0 ksi) for 3-in. and 1.5-in. spans, respectively. Both values fall within the error band of the 1.5-in. span. Accordingly, we averaged all six values to give a mean value of 59 ± 12 MPa (8.5 ± 1.7 ksi) for the flexural strength. The values for bulk modulus, however, varied significantly for the two spans. We believe the bulk modulus of 159 MPa (23,000 ksi) for the 3-in. span is the more reliable value because samples tested at the shorter 1.5-in. span are subjected to relatively high shear forces that are present at the support fixtures.

Table 16. Flexural strength of Synroc D composite (S20-S03a-HP4A).^a

Sample No. ^b	Support span (in.)	Width (in.)	Depth (in.)	Fracture load (lb)	Fracture stress (ksi)	Bending modulus (10^{-3} ksi)
3A	3.0	0.4002	0.1882	45.6	9.7	23.0
4A	3.0	0.5073	0.1773	47.6	9.0	23.0
Mean value					9.4	23.0
σ^c					± 0.5	
1A-2	1.5	0.4018	0.1928	65.6	6.6	14.7
2A-2	1.5	0.5080	0.1890	79.2	6.6	14.2
3A-2	1.5	0.4002	0.1882	101.6	10.8	16.3
4A-2	1.5	0.5073	0.1773	85.8	8.1	14.5
Mean value					8.0	14.9
σ^c					± 2.0	± 0.9

^a Data taken from R. L. Brady, Lawrence Livermore National Laboratory, Livermore, CA, Materials Test Engineering Report No. 81-183, ET #6775, May 7, 1981.

^b Samples 3A-2 and 4A-2 tested using a 1.5-in. support span were taken from broken samples 3A and 4A.

^c Standard deviation.

COMPRESSION STRENGTH

Figure 18d shows two long core-drilled samples prepared for compressive testing are shown. These two samples were then cut into smaller sizes (13.2 mm diam by 63.5 mm long) according to ASTM test specifications.³² Also shown in Fig. 18d are rectangular bearing blocks cut from the same material in order to match the elastic moduli at the loading points. Copper was also used as a bearing block in some tests. Table 17 gives the results of these tests. The average compressive strength was 353 ± 30 MPa (51.2 ± 4.3 ksi). For comparison, the compressive strengths of porous ferrites²⁷ ($P = 4.7 \text{ g/cm}^3$, 7% porosity) fall between 400 to 700 MPa.

THERMAL EXPANSION

Figure 18c shows two samples (25.4 by 4.8 by 4.8 mm) cut from the same location for linear thermal expansion studies. The equipment and test procedures have been described in an earlier report.²⁹ Measurements were performed in accordance with ASTM E-228-71 for a Vitreous Silica Dilatometer.

Table 17. Compressive strength of Synroc D composite (S20-S03a-HP4A).^a

Sample No.	Diameter (in.)	Length (in.)	Length/diameter ratio	Maximum load (lb)	Compressive strength (ksi)	Compressive elastic modulus (10^{-3} ksi)
1	0.524	2.477	4.7	11,750	54.6	15.3
2 ^b	0.525	2.476	4.7	18,600	86.1	15.4
3	0.527	2.381	4.5	10,100	46.4	15.5
4 ^b	0.526	2.407	4.6	11,430	52.6	17.3
Mean value					51.2	15.9
σ^c					$\pm 4.3^d$	± 1.0

^a Data taken from R. L. Brady, Lawrence Livermore National Laboratory, Livermore, CA, Materials Test Engineering Report No. 81-183, ET #6787, May 19, 1981.

^b Copper metal was used as bearing block material instead of Synroc D.

^c Standard deviation.

^d The high value for specimen No. 2 was not included in the average and standard deviation calculations.

Figure 19 shows one sample heated to 950°C that maintained excellent structural integrity after testing; the hollandite inclusions are clearly visible.

Four thermal expansion runs for two samples (C-1 and C-2) are plotted in Fig. 20. Thermal expansion coefficients calculated at several temperature intervals are tabulated in Table 18. Overall the expansion coefficients listed in Table 18 fall in the range of coefficients reported for MnZn ferrites ($\alpha = 11 \times 10^{-6}$, 0-200°C) and for NiZn ferrites ($\alpha = 8 \times 10^{-6}$, 0-200°C).³⁰

As shown in Fig. 20a, the first and second runs of sample C-1 (heated to 950°C) differ significantly. The expansion coefficients for all temperature ranges are on the order of 17-25% higher in the initial test run than in the second test run. This behavior indicates that an annealing effect (relieving internal stresses) took place during the initial run. This same behavior is typical of strained glass where differences as small as 5% in the thermal expansion coefficients have been measured between strained and annealed soda-lime-silica glasses.³³ In these tests to 950°C, the cooling rates were approximately ten times faster than the original hot-pressed cooling rate shown in Fig. 17. Therefore, some of the internal stress shown in Fig. 20a may have been induced during the rapid cooling after run 1.

Figure 19. Synroc D composite (S20-S03a-HP4A) sample C-1 after two thermal expansion runs in argon to 950°C.

Figure 20. Thermal expansion and thermal cycling effects of sample S20-S03a-HP4A as a function of temperature. (a) The first and second runs of test sample C-1 differ significantly, indicating that annealing occurred during the initial run. (b) Repeat of the runs in (a) except that C-2, the second test sample, was heated under argon to only 650°C in the initial run; in this case, no significant difference in the expansion behavior of runs 1 and 2 was observed.

Table 18. Linear thermal expansion coefficients^a for Synroc D composite (S20-S03a-HP4A).

Temperature range (°C)	Expansion coefficient ($\alpha \times 10^6$)			
	Sample C-1		Sample C-2 ^b	
	Test No. 1	Test No. 2	Test No. 1	Test No. 2
22-79.8	6.92	5.71	8.65	6.23
22-207.1	9.19	6.81	9.40	8.70
22-319.3	9.92	7.90	9.89	9.42
22-425.0	10.77	8.51	10.15	9.80
22-526.8	10.72	8.82	10.36	10.16
22-625.7	11.07	9.34	10.40	10.40
22-721.4	11.22	9.37	-	10.74
22-814.3	11.15	8.99	-	10.68
22-949.0	10.57	9.06	-	10.82

^a Two tests were performed under an argon atmosphere on each sample. Testing was performed by R. C. Lum. Mechanical Engineering Department, Lawrence Livermore National Laboratory, Livermore, CA.

^b Test No. 1 was taken to 650°C only.

As a test to explore the temperature dependence of stress relief, the second specimen, C-2, was heated to only 650°C in the first run. As shown in Fig. 20b, there was no significant difference in the expansion behavior of runs 1 and 2. Also, the expansion coefficients for both runs 1 and 2 are nearly the same as the initial run for sample C-1.

These results indicate that in the temperature region of 650 to 950°C, internal stresses can be relieved and that cooling rates in this temperature interval are important in the preparation of a stress-free Synroc D waste form of this composition. We believe that these data indicate the presence of a strained glass matrix in our Synroc D composite waste form. In an earlier report,²⁸ we reported a nominal 25-vol% nepheline phase in Synroc D, and there is a strong likelihood that some of this nepheline phase may not have fully crystallized.

THERMAL CONDUCTIVITY

The thermal conductivity of S21-S18 composite Synroc D was measured at room temperature using a thermal comparator. In this method, the cooling rate

of Synroc D is determined by touching the surface of the sample with the tip of a heated probe. This rate is then compared to those of standard materials of known thermal conductivity. The details of this method were covered in an earlier report²⁹ in which the thermal conductivity of Synroc B was given as 2.0 W/m-K.

A large sample of S21-S18 with a polished surface was used for these tests. Nine determinations gave an average value of 1.7 ± 0.2 W/m-K for Synroc D.

MICROHARDNESS

We measured the Knoop microhardness of both S18 hollandite as single-phase material and the combined S21-S18 Synroc D composite. In the latter case, measurements were made at edge and center locations to assess sample homogeneity. Three indenter loads (50, 100, and 500 g) were used in the evaluation to assess loading effects. Table 19 lists the mean values and calculated errors. The hardness typically decreases with increasing load for all samples. We found no significant difference between the edge and center values of two S21-S18 samples nor any difference in hardness between the

Table 19. Microhardness of hollandite (S18) and Synroc D composite (S21-S18).

Sample number	Metallograph number ^a	Microhardness (kg/mm ²) ^b		
		HKN ₅₀	HKN ₁₀₀	HKN ₅₀₀
Hollandite S18-HP3A	2450	959 $\pm$ 23	841 $\pm$ 6	774 $\pm$ 5
Synroc D S21-S18-HP8A	2466 (center)	953 $\pm$ 20	867 $\pm$ 25	689 $\pm$ 21
Synroc D S21-S18-HP12A	2472 (edge)	941 $\pm$ 24	869 $\pm$ 13	701 $\pm$ 10
Synroc B ^c	(center)	1109 $\pm$ 13	1017 $\pm$ 10	875 $\pm$ 21
	(edge)	1079 $\pm$ 35	1028 $\pm$ 9	884 $\pm$ 37

^a Metallographic filing number. Measurements were made by Al Ulrich.

^b Error calculated as the standard deviation from the average of three values.

^c Reference 27.

single-phase hollandite (S18) and the composite waste form (S21-S18) after hollandite additions.

Table 19 also shows the microhardness values of Synroc B taken from an earlier report.²⁹ Synroc B is significantly harder than Synroc D. This is not surprising since the other mechanical properties reported for Synroc B²⁶ were about 50% greater than Synroc D properties.

LEACHING CHARACTERISTICS

Bazan has already presented leaching data on S21-S18 composite,²⁸ and, in Ref. 34, he gives additional detailed CLT leach results on all of the Synroc D samples covered in this document.

We have only summarized some of the data, which are given in Tables 20 and 21.³⁴ In Table 20, we chose to list our high-temperature (150°C) leaching data for strontium, cesium, and uranium in deionized water for all waste forms. These data were taken using a MCC-3 type test in which hot-pressed monoliths were crushed and sized to 150-300 μm . A mean equivalent spherical diameter was used to calculate surface areas for determining leach rates (LR) normalized to the initial elemental concentration. Leach rates are given for each day in three successive days of testing.

In Table 21, we have listed only the 28 day normalized elemental LR for MCC-1 testing at 90°C. For these experiments, unpolished monoliths were tested and geometric surface areas were used to calculate leach rates. Leaching data for three leachants (deionized water, silicate water, and salt brine) are reported.

Figure 21 shows monolithic leaching samples after leaching for S21-S18. Before leaching, core-drilled cylinders were wax mounted on a metal rod. Thin disks about 3 mm thick were then sliced with a diamond saw. Finally, the disks were cut again to give the proper geometric area for the leach tests. The surfaces of composite samples were tested in both the unpolished and polished state. All samples exhibited excellent structural integrity after testing.

Table 20. MCC-3-type^{a,b} static leach rates^c on crushed Synroc D at 150°C using deionized water.

Synroc D waste form	Initial concentration in Synroc D (wt%)								
	Strontium			Cesium			Uranium		
S21-S18-HP8A	0.14			0.23			1.3		
S29-HP8A	0.15			0.22			1.4		
S26-SAN7A	0.15			0.23			4.2		
S30-HP3A	0.19			0.22			4.2		
S31-HP1A	0.029			0.046			0.24		

Synroc D waste form	Leach rate (LR) (g/m ² •d)								
	Strontium			Cesium			Uranium		
	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
S21-S18-HP8A	0.14	0.15	0.16	1.85	1.10	0.79	<0.007	<0.007	<0.007
S29-HP8A	0.26	0.24	0.30	3.73	0.74	0.51	<0.008	<0.008	<0.008
S26-SAN7A	0.10	d	d	0.46	d	d	d	d	d
S30-HP3A	0.53	0.48	0.48	1.87	1.20	1.20	d	d	d
S31-HP1A	0.40	0.44	d	3.97	2.35	d	d	d	d

^a Leaching studies were done by C. Bazan and S. McLean.

^b Crushed size range was 150-300 μm . A geometric surface area (SA) of 0.0068 m²/g for leach-rate calculations was derived using a mean spherical diameter of 225 μm and a density of 3.94 g/cm³.

^c The leach rates (LR) were normalized for each elemental mass fraction according to

$$LR = \frac{M_i^0}{f_i^0 \cdot SA \cdot (1 \text{ day})}$$

where

M_i^0 is the elemental mass loss (in g) during each day (1, 2, and 3) of leaching,

f_i^0 is the initial mass fraction of element,

SA is the geometric surface area (m²).

^d Not analyzed.

(a)

(b)

Figure 21. Monolithic leaching samples (S21-S18) after leaching for 28 days at 90°C (magnified 5x). (a) S21-S18-HP9A after leach testing; unpolished, silicate solution. (b) S21-S18-HP8A after leach testing; polished, deionized water.

Table 21. MCC-1 static leach rates ^{a,b} on Synroc D monoliths ^c in deionized water, silicate water, and brine. ^d

Synroc D waste form	Leach rate (LR) (g/m ² ·d)								
	Deionized water			Silicate water ^e			Brine ^f		
	Sr	Cs	U	Sr	Cs	U	Sr	Cs	U
S21-S18	0.35	0.11	0.00019	0.06	0.11	0.00016	<0.2	0.09	g
S29	0.38	0.79	0.00011	0.099	0.54	0.00034	<0.1	0.45	<0.00025
S26-SAN7A	0.23	0.11	g	0.05	0.10	g	<0.7	<0.1	g
S30	0.56	0.80	g	0.15	0.20	g	0.05	0.17	g
S31-HP1A	<0.13	3.86	g	<0.13	2.95	g	<3.2	1.50	g

^a Leaching studies were done by C. Bazan and S. McLean.

^b Normalized leach rates were calculated according to Table 20, footnote c.

^c Monoliths were sliced using a diamond saw from core drills taken from larger 7.62-cm-diam CLT samples having geometric surface areas (SA) of 400 mm² and leachant volumes of 10 cm³.

^d Samples were leached 28 days at 90°C.

^e Simulated silicate ground water (silica and NaHCO₃; pH = 7.5).

^f Salt brine containing sodium, potassium, and magnesium chlorides.

^g Not analyzed.

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PREPARATION DETAILS
SIMULATED SAP SLUDGE - 12 lb. BATCH SIZE

The details shown below are those actually used for the preparation of each batch. While the preparation procedure is the same for each batch, the details of preparation vary due to different settling rates of the three sludges, number of washes required to remove the NaNO_3 , and time required to dry each batch.

SLUDGE TYPE: Composite, with Aluminum Removal

1. KMnO_4 Solution (3.9 wt %)
Mixed 484.7 g KMnO_4 with 7250 g (ml) H_2O .
2. $\text{Mn}(\text{NO}_3)_2$ Solution (9.5 wt %)
Mixed 1811 g of a 50 wt % solution of $\text{Mn}(\text{NO}_3)_2$ in H_2O with 7621 g H_2O .
3. Added the KMnO_4 solution to the $\text{Mn}(\text{NO}_3)_2$ slowly with vigorous mixing. Mixed for 1 hour after completing addition.
4. Added 15.53 L of H_2O to the MnO_2 slurry.
5. Added 6168 g of 60wt % $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. Added the remainder of the metal nitrate salts. Mixed for 2 hours.
6. Added ~27,700 g (22.4 L) of 12 wt % NaOH solution slowly, with mixing. Monitor pH carefully, taking care not to exceed pH 9.5.
7. Added sufficient pH 9.5 water to bring total volume to 300 L, and mixed for 2 hours. Let mixture settle overnight.
8. 1st wash: Decanted 150 L of clear solution. Added pH 9.5 H_2O to bring to 300 L. Agitated 3 hours and let settle overnight.
2nd wash: Decanted 150 L of clear solution. Added pH 9.5 H_2O to bring back to 300 L. Agitated 3 hours and let settle overnight.
3rd wash: Decanted 150 L. Added pH 9.5 H_2O to bring to 300 L, mixed 2.5 hours and let settle over weekend.
4th wash: Decanted 250 L.
9. Added soluble salts to the remaining solution (50 L). Mixed for 2 hours to dissolve salts.
10. The slurry solution was dried for 7 days, using four 500-watt air blowers. The solution was agitated during drying by an air sparge.

11. The dried sludge was pulverized in a rotary ball mill for 4 hours, using ~2 lb lots, using Al_2O_3 ceramic balls. The pulverized material was sieved through a 6 mesh screen, with the larger particles re-ground.

12. Yield from SRL preparation

The High Aluminum sludge weighed 16.7 lb. after grinding and sieving. The sludge had 31.3 % weight loss on calcining at 900°C for 96 hours.

13. Calculation of Na_2O

The amount of Na_2O in the High Aluminum sludge is:

$$\text{wash factor: } \frac{170}{300} \times \frac{130}{300} \times \frac{150}{300} \times \frac{150}{300} \times \frac{150}{300} \times \frac{130}{300} = 0.0133$$

$$\text{moles NaNO}_3/100 \text{ g oxide} = 3.881$$

$$\text{moles NaNO}_3/100 \text{ g oxide left after washes} = 3.881 \times 0.0133 = 0.0516$$

$$\text{moles Na}_2\text{O}/100 \text{ g oxide (from NaNO}_3) = 0.0258$$

$$\text{moles Na}_2\text{O}/100 \text{ g oxide:}$$

$$\circ \text{NaNO}_3 = 0.0258$$

$$\circ \text{Na}_2\text{SiO}_3 = 0.0261$$

$$\circ \text{NaNO}_2 = 0.0008$$

$$\circ \text{Na}_2\text{C}_2\text{O}_4 = 0.0001$$

$$\circ \text{Na}_2\text{CO}_3 = \underline{0.0087} \quad (50.29 \text{ Na}_2\text{CO}_3 \text{ added})$$

$$.0615$$

PREPARATION DETAILS
SIMULATED SRP SLUDGE - 12 lb. BATCH SIZE

The details shown below are those actually used for the preparation of each batch. While the preparation procedure is the same for each batch, the details of preparation vary due to different settling rates of the three sludges, number of washes required to remove the KNO_3 , and time required to dry each batch.

SLUDGE TYPE: High Iron, with Aluminum Removal

1. KMnO_4 Solution (5.9 wt%)
Mixed 139.4 g KMnO_4 with 2332 g (ml) H_2O .
2. $\text{Mn}(\text{NO}_3)_2$ Solution (9.6 wt %)
Mixed 523 g of a 50 wt % solution of $\text{Mn}(\text{NO}_3)_2$ in H_2O with 2196 g H_2O .
3. Added the KMnO_4 solution to the $\text{Mn}(\text{NO}_3)_2$ slowly with vigorous mixing. Mixed for 1 hour after completing addition.
4. Added 29.165L of H_2O to the MnO_2 slurry.
5. Added 856.6g of 60wt % $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. Added the remainder of the metal nitrate salts. Mixed for 2 hours.
6. Added ~ 26,400B (4 21.3 L) of 27 wt % NaOH solution slowly, with mixing. Monitor pH carefully, taking care not to exceed pH 9.5.
7. Added sufficient pH 9.5 water to bring total volume to 300 L, and mixed for 0.75 hours. Let mixture settle over weekend.
8. 1st wash: Decanted 150 L of clear solution. Added pH 9.5 H_2O to bring to 300 L. Agitated 2 hours and let settle overnight.
2nd wash: Decanted 150 L of clear solution. Added pH 9.5 H_2O to bring back to 300 L. Agitated 3 hours and let settle overnight.
3rd wash: Decanted 150 L. Added pH 9.5 H_2O to bring to 300 L, mixed 3 hours and let settle overnight.
4th wash: Decanted 150 L. Added pH 9.5 H_2O to bring to 300 L, mixed 3 hours and let settle over weekend.
5th rinse: Decanted 150 L.
9. Added soluble salts to the remaining solution (150 L). Mixed for 2 hours to dissolve salts.
10. The slurry solution was dried for 10 days, using four 100-watt air blowers. The solution was agitated during drying by an air sparge.

COAL COMPOSITION OF SIMULATED SRP SLUDGE SAMPLES

TYPE: Composite, with Aluminum Removal

Component, (a)	Reference Composition of SRP Waste Culture		Nominal Composition of SRP Simulated Sludge for Impregator Leach Testing Program		Amount relative to Fe_2O_3 -
	wt. % (b)	Amount relative to Fe_2O_3	12 lb. (3,464 g) batch	12 lb batch (69.9)	
Fe_2O_3	47.16	1.000	2,566	69.9	1.000
Al_2O_3	9.26	0.196	.501	9.79	.196
MnO_2	12.98	0.275	.706	13.74	.275
UO_2	4.25	0.090	.232	4.51	.090
CaO	3.51	0.074	.191	3.12	.075
NiO	5.84	0.124	.318	6.19	.124
SiO_2	-	-	.027	.53	.011
Ce_2O_3	-	-	.056	1.05	.021
Ba_2O_3	-	-	.056	1.05	.021
H_2SO_4	6.63	0.141	.161	1.07	.141
SiO_2	1.12	0.026	.066	1.28	.026
Iron-Siv	8.05	0.171	.061	1.19	.024
Total	99.99		5,139	100.00	

(a) Shown as most common stable compound, may not represent actual species present in natural sludge.

(b) wt. % as shown in Reference 1 and 2, with Al removal.

(c) Weight %s are different from the reference composition due to the addition of Fe_2O_3 & Mn oxides and deletion of the Iron-Siv material.

COAL COMPOSITION OF SIMULATED SRP SLUDGE SAMPLES

TYPE: High Iron, with Aluminum Removal

Component (a)	Reference Composition of SRP Waste Calcine		Nominal Composition of SRL Simulated Sludge for Comparative Leach Testing Program		
	wt. % (b)	Amount Relative to Fe ₂ O ₃	kg. of oxides in 12 lb. (5.44 kg) batch	wt. % in (c) 12 lb batch	Amount relative to Fe ₂ O ₃
Fe ₂ O ₃	55.90	1.000	3.042	58.60	1.000
Al ₂ O ₃	1.29	0.023	.070	1.35	.023
H ₂ O ₂	1.74	0.067	.204	3.93	.067
H ₂ O ₄	12.98	0.232	.706	13.60	.232
CaO	3.80	0.068	.207	3.98	.068
H ₂ O	9.54	0.171	.519	10.09	.171
SiO ₂	-	-	.027	0.52	.009
Cr ₂ O ₃	-	-	.054	1.04	.018
Na ₂ O ₃	-	-	.054	1.04	.018
H ₂ O	4.75	0.085	.259	4.99	.085
Na ₂ SO ₄	0.50 (d)	0.009 (d)	.027	0.52	.009
SiO ₂	0.40 (d)	0.007 (d)	.022	3.42	.007
Iron-Sil-	8.00	0.143	-	-	-
Total	100.90		5.191	99.99	

(a) Shown as most common stable compound, may not represent actual species present in calcined sludge.

(b) wt. % as shown in References 1 and 2, with Al removal.

(c) Weight %'s are different from the reference composition due to the addition of Sr, Co, & Ni oxides and deletion of the Iron-Sil material.

(d) Upper limit.

11. The dried sludge was pulverized in a rotary ball mill for 4 hours, using 1/2 lb 100, using Al₂O₃ standard balls. The pulverized material was sieved through a # 20 mesh screen, with the larger particles re-ground.

12. Yield from SRL preparation

The High Aluminum sludge weighed 16.2 lb. after grinding and sieving. The sludge had 31.3 % weight loss on calcining at 900°C for 96 hours.

13. Calculation of Na₂O

The amount of Na₂O in the High Aluminum sludge is:

$$\text{wash factor: } \frac{120}{300} \times \frac{150}{300} \times \frac{150}{300} \times \frac{130}{300} \times \frac{130}{300} \times \frac{130}{300} = 0.0133$$

$$\text{moles NaNO}_3/100 \text{ g oxide} = 3.881$$

$$\text{moles NaNO}_3/100 \text{ g oxide left after washes} = 3.881 \times 0.0133 = 0.0516$$

$$\text{moles Na}_2\text{O}/100 \text{ g oxide (from NaNO}_3) = 0.0258$$

$$\text{moles Na}_2\text{O}/100 \text{ g oxide:}$$

$$\begin{aligned} & \text{NaNO}_3 = 0.0258 \\ & \text{Na}_2\text{SiO}_3 = 0.0261 \\ & \text{NaNO}_2 = 0.0008 \\ & \text{Na}_2\text{C}_2\text{O}_4 = 0.0001 \\ & \text{Na}_2\text{CO}_3 = 0.0087 \end{aligned}$$

$$\begin{aligned} & \text{(50.29 Na}_2\text{CO}_3 \text{ added)} \\ & \hline & .0615 \end{aligned}$$

PREPARATION DETAILS
SIMULATED SRP SLUDGE - 12 lb. BATCH SIZE

The details shown below are those actually used for the preparation of each batch. While the preparation procedure is the same for each batch, the details of preparation vary due to different settling rates of the three sludges, number of washes required to remove the NaNO_3 , and time required to dry each batch.

SLUDGE TYPE: High Aluminum, with aluminum removal

1. KMnO_4 Solution (5.9 wt%)
Mixed 454 g KMnO_4 with 7244 g(ml) H_2O .
2. $\text{Mn}(\text{NO}_3)_2$ Solution (9.6 wt %)
Mixed 1696 g of a 50 wt % solution of $\text{Mn}(\text{NO}_3)_2$ in H_2O with 7140 g H_2O .
3. Added the KMnO_4 solution to the $\text{Mn}(\text{NO}_3)_2$ slowly with vigorous mixing. Mixed for 1 hour after completing addition.
4. Added 6.0 L of H_2O to the MnO_2 slurry.
5. Added 33,892g of 60wt % $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. Added the remainder of the metal nitrate salts. Mixed for 7 hours.
6. Added ~38,000 g (~33.0 L) of 22 wt % NaOH solution slowly, with mixing. Monitor pH carefully, taking care not to exceed pH 9.5.
7. Added sufficient pH 9.5 water to bring total volume to 300 L, and mixed for 0.75 hours. Let mixture settle 16 hours.
8. 1st wash: Decanted 150 L of clear solution. Added pH 9.5 H_2O to bring to 300 L. Agitated 2 hours and let settle over weekend.
2nd wash: Decanted 170 L of clear solution. Added pH 9.5 H_2O to bring back to 300 L. Agitated 3 hours and let settle overnight.
3rd wash: Decanted 150 L. Added pH 9.5 H_2O to bring to 300 L, mixed 3 hours and let settle 40 hours.
4th wash: Decanted 150 L. Added pH 9.5 H_2O to bring to 300 L, mixed 3 hours and let settle overnight.
5th rinse: Decanted 150 L. Added pH 9.5 H_2O to bring to 300 L. Mixed 1 hour and let settle over weekend.
6th wash: Decanted 170 L H_2O .
9. Added soluble salts to the remaining solution (150 L). Mixed for 7 hours to dissolve salts.
10. The slurry solution was dried for 10 days, using six 500-watt air blowers. The solution was agitated during drying by an air sparge.

11. The dried sludge was pulverized in a rotary ball mill for 4 hours, using ~2 lb lots, using Al_2O_3 ceramic balls. The pulverized material was sieved through a 9 mesh screen, with the larger particles re-ground.

12. Yield from SRL preparation

The High Iron sludge weighed 15.80 lb. after grinding and sieving. The H₂ Fe sludge had 79.5 % weight loss on calcining at 900°C for 96 hours. The calcined sludge would therefore weigh 11.14 lbs(5053g).

13. Calculation of Na_2CO_3 addition

The amount of Na_2CO_3 added in Step 9 was calculated as follows:

$$\text{wash factor} = \frac{150}{300} \times \frac{150}{300} \times \frac{150}{300} \times \frac{150}{300} \times \frac{150}{300} = 0.0313$$

$$\text{moles } \text{NaNO}_3/100 \text{ g oxide} = 2.845$$

$$\text{moles } \text{NaNO}_3/100 \text{ g oxide after washes} = 2.845 \times 0.0313 \\ = 0.0889$$

$$\text{moles } \text{Na}_2\text{O}/100 \text{ g oxide} = 4 \times 0.0889 = 0.0445$$

$$\text{Goal amount of } \text{Na}_2\text{O} = 0.0766 \text{ moles}/100 \text{ g oxide.}$$

$$\text{Moles of } \text{Na}_2\text{O}/100 \text{ g oxide:}$$

$$o \text{ } \text{KAlO}_2 = 0.0445$$

$$o \text{ } \text{Na}_2\text{SiO}_3 = 0.0066$$

$$o \text{ } \text{NaNO}_2 = 0.0016$$

$$o \text{ } \text{Na}_2\text{C}_2\text{O}_4 = \frac{0.0001}{0.0528}$$

$$\text{Goal } \text{Na}_2\text{O} = 0.0766$$

$$= \underline{0.0528}$$

$$, 0.0528 \text{ moles } \text{Na}_2\text{CO}_3/100 \text{ g oxide to add.}$$

$$0.0528 \text{ moles}/100 \text{ g oxide} \times 5.44 \text{ kg oxide} \times 100 \text{ g/mole}$$

$$= 137.2 \text{ g } \text{Na}_2\text{CO}_3$$

**STARTING MATERIALS FOR
PREPARATION OF SIMULATED SRP SLUDGE SAMPLES - 12 lb. BATCHES**

Compound Used	Composite	Quantity, g	
		High Iron	High Aluminum
KMnO ₄	484.7	139.4	454.0
Mn(NO ₃) ₂	905.4	260.7	848.0
Al(NO ₃) ₃ ·9H ₂ O	3,700.0	514.1	20,335.0
Fe(NO ₃) ₃ ·9H ₂ O	12,989.3	15,394.0	4,076.0
UO ₂ (NO ₃) ₂ ·6H ₂ O	413.9	1,262.0	348.0
Ca(NO ₃) ₂ ·4H ₂ O	804.5	870.0	221.0
Ni(NO ₃) ₂ ·6H ₂ O	1,237.3	2,020.0	459.0
Sr(NO ₃) ₂	55.6	55.7	55.7
Ce(NO ₃) ₃ ·6H ₂ O	144.0	144.1	144.0
Nd(NO ₃) ₃ ·6H ₂ O	141.8	141.7	142.0
NaOH	6,100.0	~6,000	~8,400
NaSiO ₃ ·9H ₂ O	288.4	102.1	404.0
Na ₂ CO ₃	190.4	137.2	50.2
NaNO ₂	5.9	5.9	5.9
Na ₂ SO ₄	65.9	27.0	27.0
Na ₂ C ₂ O ₄	0.7	0.7	0.7

GOAL COMPOSITION OF SIMULATED SRP SLUDGE SAMPLES

TYPE: High Aluminum, with Aluminum Removal

Component (a)	Reference Composition of SRP Waste Calcine		Nominal Composition of SRP Simulated Sludge for Comparative Leach Testing Program		Amount relative to Fe ₂ O ₃
	wt. % (b)	Amount Relative to Fe ₂ O ₃	kg. of oxides in 12 lb. (5.44 kg) batch	wt. % in (c) 12 lb batch	
Fe ₂ O ₃	14.80	1.000	0.806	15.95	1.000
Al ₂ O ₃	50.77	3.430	2.763	54.69	3.428
MnO ₂	12.16	.822	.662	13.10	.821
U ₃ O ₈	3.57	.241	.194	3.94	.241
CaO	0.97	.066	.053	1.05	.066
NiO	2.17	.147	.118	2.34	.147
SrO	-	-	.027	.53	.033
Ce ₂ O ₃	-	-	.054	1.07	.067
Nd ₂ O ₃	-	-	.054	1.07	.067
Na ₂ O	5.41	.366	.208	4.12	.258
Na ₂ SO ₄	0.50 (d)	.034 (d)	.027	.53	.033
SiO ₂	1.57	.106	.086	1.70	.106
Ion-Siv	8.58	.580	-	-	-
Total	100.50		5.052	99.99	

(a) Shown as much common stable compound, may not represent actual species present in calcined sludge.

(b) wt. % as shown in References 1 and 2, with Al removed.

(c) Weight %'s are different from the reference composition due to the addition of Sr, Ce, & Nd oxides and deletion of the Ion-Siv material.

(d) Upper limit.

APPENDIX B

February 6, 1981
0112R

Dr. John A. Stone
E. I. DuPont
Savannah River Laboratory
Fuel Cycle Technology Division
Aiken, SC 29801

Dear Dr. Stone:

We shipped our composite waste form to you on January 29, 1981, by Federal Express (Way Bill No. 0157412500). The purpose of this letter is to give a summary description of the preparation and composition of the waste form. A more detailed report will follow at a later date.

We wish to emphasize that these samples of Synroc do not necessarily represent a fully optimized waste form. We believe that some improvements may still be made in the overall performance of Synroc as applied to U. S. Defense Waste.

The shipment consisted of four (4) hot pressed cylinders and one half cylinder (photo attached). The dimensions were nominally 7.6 cm diameter x 2.5 cm height and the total mass was approximately 1.911 kg. Based on an average immersion density of 3.93 g/cc the total volume of sample was 486 cc. In your letter dated October 17, 1980, you requested at least 300 cc of material so that 15 mm diameter cores could be taken for testing. Some of our samples have a few visible cracks. However, we believe that a sufficient number of cores can be taken in the uncracked portions to provide 300 cc of test material. We think the cracking was caused by non-uniform heating in our early core drill procedure. Cylinders were secured to a ceramic plate with low melting wax prior to core drilling by means of a hot plate. When samples were heated uniformly in a small oven the cracking disappeared.

A breakdown of the nominal compositions of as received SRL composite waste, Al_2O_3 additive to convert to unwashed waste and Synroc additions are listed in Table 1. Analyses of some of the important simulated radwaste oxides and immersion densities are shown in Table 2. Additional analyses will be available at a later date. Immersion density measurements indicate closed porosity in all samples. Mercury porosimetry measurements are in progress.

The preparation steps used were as follows:

STEP 1: MIXING AND SPRAY DRYING

Synroc ingredients formulated from a known sludge composition were mixed and blended with the sludge as an aqueous slurry. The Synroc ingredients were water soluble nitrates with the exception of zirconium which was added as ZrO_2 derived from zirconyle decomposed at 3000°C in air, titanium which was added as pigment grade anatase (TiO_2) and silica (SiO_2) which was added as colloidal silica. The combined slurry mixture was blended for about 16 hours. The slurry was then properly agitated to insure homogeneous particle suspension and spray dried at 1350°C.

STEP 2: CALCINATION AND GRINDING

The spray dried powder was first air calcined at 650°C for approximately 16 hours to a constant weight. The powder was then redox calcined to an Fe^{+2}/Fe^{+3} weight ratio of 1:1. Using our rotary calciner we have found that a one kilogram batch of air calcined powder can be adequately reduced in approximately 12-16 hours at 965°C and CO_2/CO ratio of 10/1. The total gas flow rate during this period is approximately 46 liters/hour. The reduced powder was then slurry ground in a Vibro Energy mill using iso-propyl alcohol.

Normally grinding would not be necessary depending on the nature of the sludge. We found in preliminary hot pressing evaluations of spray dried material that some minor heterogeneities were present which were eliminated by the grinding step.

STEP 3: HOT PRESSING

The redox calcined powder was then blended homogeneously with crushed hot pressed Ba/Cs hollandite. The hollandite particle density was >98% of theoretical (4.2 g/cc) and the particle size range was 0.4 to 1.0 mm.

Nickel powder was not added because the Fe^{+2}/Fe^{+3} ratio had been adequately adjusted in the previous calcination step. The powders were then hot pressed to final form directly in graphite at 1050°C, 1 hour, 3000 psi to a density >98% of theoretical (4.0 g/cc). The amount of powder loaded for each hot pressing was limited in amount so that the final L/D ratio of the sample is <0.75.

Dr. John A. Stone

-3-

February 6, 1981

Approximately 15 cc of sample S21518HPBA has been sent to Dr. D. E. Clark at the University of Florida for leaching studies as requested by Mr. T. A. Bernadzikowski in his letter dated January 21, 1981.

Sincerely,

Clarence Hoenig

Clarence Hoenig
Materials Science Division
Chemistry & Materials Science Department

CH:rr
Attachments

Copy to:

Bender, C.
Campbell, J. A.
Holt, J. B.
Johnson, O.
Landingham, R. L.
Mara, G./Cline G.
Newkirk, H.
Ringwood, A. E.
Ross, R.
Ryerson, R.
Shock, R.

Table 1
Nominal Composition of Synroc - SRL
Composite Waste Form S21518

Weight Percent Oxide or Salt	Nominal SRL Composite As Rec'd	Al ₂ O ₃ Addition to convert to unwashed DP-1545	Synroc Additives (Mon- Hollandite)	Synroc Additives (Hollandite, 0.4 - 1.0 mm)	Total
Fe ₂ O ₃	23.0				23.0
Al ₂ O ₃	4.6	13.4		0.87	18.87
MnO ₂	5.6				5.6
U ₃ O ₈	2.1				2.1
CaO	1.6		5.0		6.6
NiO	3.0				3.0
SiO ₂	0.5		6.2		6.7
Na ₂ O	2.6				2.6
Na ₂ SO ₄	1.3				1.3
SrO	0.24				0.24
Cs ₂ O				0.24	0.24
Ce ₂ O ₃	0.50				0.50
Nd ₂ O ₃	0.50				0.50
BaO				1.18	1.18
Y ₂ O ₃			17.1	4.75	21.85
ZrO ₂			5.8		5.8
Total	45.54	13.40	34.1	7.04	100.1

Table 2

Radwaste Analyses, Hot Pressed Densities and Weights of Synroc - SRL

Composite Waste Form S21S18

Sample No.	Weight (grams)	Immersion(1) Density (g/cc)	SiO ₂	Weight Percent(2) Cs ₂ O	U ₃ O ₈
S21S18HP0A	178.38	3.938	0.16	0.23(c)	1.5
			0.16	0.21(E)	1.5
S21S18HP0A	434.11	3.929	0.15	0.24	1.5
S21S18HP10A	432.15	3.930	0.16	0.22	1.5
S21S18HP11A	431.98	3.940	0.15	0.26	1.5
S21S18HP12A	434.45	3.931	0.16	0.26	1.6

1. Theoretical density is taken as 4.0 g/cc.
 2. Analysis by XRF, Accuracy $\pm 10\%$
 c = Center location, E = Edge location
 other analyses at intermediate locations.

February 18, 1981

Dr. Leslie Jardine
 Argonne National Laboratory
 9700 So. Cass Avenue
 Chicago, Illinois 60439

Dear Dr. Jardine:

Under separate cover we are sending you samples of SYNROC D for your brittle fracture impact studies. We expect this material to have mechanical properties similar to the SYNROC D composite sent to SRL for comparative leaching. The hollandite in these samples does have different leaching characteristics. Therefore, we ask that this material not be used for any leaching studies.

For reference the LLNL sample designations are S20SO3allP1A and S20SO3allP2A. They were prepared by Clarence Hoening from our Material Science Division. Sample descriptions are as follows:

- A. Sample Designation: S20SO3allP1A
 Density: 3.98 g/cm³
 % Theoretical Density: 99%
 Mass of Samples: 82.0 gram total (contains 1.7 g D-38 oxide)
 No. of Samples: one 1" diameter
 two 1/2" diameter
 Preparation: Samples hot pressed in graphite die at 1100°C/5 minutes/4000 psi
- B. Sample Designation: S20SO3allP2A
 Density: 3.78 g/cm³
 % Theoretical Density: 94%
 Mass of Samples: 125.9 gram total (contains 2.6 g D-38 oxide)
 No. of Samples: two 1" diameter
 four 1/2" diameter
 Preparation: Samples hot pressed in nickel capsule at 1050°C/one hour/2000 psi

Please note that the density of S20SO3allP2A (hot pressed at 1050°C) is lower than that of S20SO3allP1A (hot pressed at 1100°C). This may have some effect on the brittle fracture behavior of the material.

The chemical composition of both samples is shown in Table 1. The hollandite phase was first hot pressed as a separate waste form then crushed to 0.2-1.00mm particle size and added to the composite sludge for final hot pressing.

We will be anxious to learn about the results of your study. Please feel free to call me if you any questions.

Best regards,

 Jack H. Campbell
 Project Leader
 Mineral Waste Form Development Project

A. Sample Designation: S20503aHP1A
 Density: 3.96 g/cm³
 % Theoretical Density: 99%
 Mass of Samples: 82.0 gram total
 (contains 1.7 grams D-38 oxide)
 Number of Samples: one 1" diameter
 two 1/2" diameter
 Preparation: Samples hot pressed in graphite die at
 1100°C/5 minutes/4000 psi

B. Sample Designation: S20503aHP2A
 Density: 3.76 g/cm³
 % Theoretical Density: 94%
 Mass of Samples: 125.9 gram total
 (contains 2.6 grams D-38 oxide)
 Number of Samples: two 1" diameter
 four 1/2" diameter
 Preparation: Samples hot pressed in nickle capsule
 at 1050°C/one hour/2000 psi

TABLE 1. Nominal Composition of Simulated SYNROC - SRL Composite Waste Form
 S20503aHP1A and S20503aHP2A

Weight % Oxide or Salt	Simulated SRL Composite Unwashed Waste	SYNROC Add. Non-Hollandite	SYNROC Add. Hollandite (0.42-1.00mm)	TOTAL
Fe ₂ O ₃	24.2			24.2
Al ₂ O ₃	18.9		1.0	19.9
MnO ₂	7.5			7.5
CaO	1.3	3.4		4.7
NiO	3.1			3.1
MgO	3.4			3.4
Nb ₂ SO ₄	0.6			0.6
UO ₂	2.1			2.1
SiO ₂	0.5	6.0		6.9
ZrO ₂		4.9		4.9
TiO ₂		14.2	4.5	18.7
BaO			1.4	1.4
SiO	0.4			0.4
Ca ₂ O			0.3	0.3
ICeO ₂	0.4			0.4
ICdO ₂	0.4			0.4
INd ₂ O ₃	0.4			0.4
Eu ₂ O ₃	0.4			0.4
TOTAL	63.6	28.9	7.2	99.7

April 15, 1981

Dr. John A. Stone
E. I. DuPont
Savannah River Laboratory
Fuel Cycle Technology Division
Aiken, SC 29801

Dear John:

We shipped our high Fe SYNROC waste form to you on April 10, 1981 by Federal Express (Way Bill No. 353311885). Our letter of February 6 gave a summary description of the preparation steps for our composite waste form. This description also applies in a general sense to our high Fe waste form. There are some exceptions, however. The shipment consisted of two hot pressed cylinders. The dimensions were nominally 7.8 cm diameter x 2.5 cm height, and the total mass was 765.5 grams. Based on an average immersion density of 4.36 g/cc, the total volume of sample was 175 cc. Core drilled samples have been taken for our tests at LLNL.

The high Fe material has different microstructure than the composite waste form. Large grain boundaries were developed during the hot pressing step using magnetic induction heating. The dominant spinel phase in this composition is a form of magnetite (Fe_3O_4). The samples are, in fact, magnetic. We believe that magnetic coupling occurred within the sample during hot pressing, which caused this unusual grain boundary development. This was not the case in the composite waste form.

Our leaching studies do not show any adverse effects due to this large grain development. However, we have found that the material has lower strength than the composite waste form. This makes it more difficult to prepare samples for leach testing. Follow-up tests using our large Centor resistance hot press indicate that microstructures comparable to our composite waste form can be achieved with the high Fe composition if resistance rather than induction heating methods are used during hot pressing.

A breakdown of the nominal compositions of as-received SRL composite waste, Al_2O_3 additive to convert to an equivalent unwashed waste and SYNROC additions are listed in Table 1. Analyses of some of the important simulated radwaste oxides and immersion densities are shown in Table 2. Additional analyses will be available at a later date. Immersion density measurements indicate closed porosity in all samples. Mercury porosimetry measurements are in progress.

Dr. John A. Stone
April 15, 1981
-2-

The preparation steps used were as follows:

Step 1: Mixing and Spray Drying

SYNROC ingredients formulated from a known sludge composition were mixed and blended with the sludge as an aqueous slurry. The SYNROC ingredients were water soluble nitrates with the exception of zirconium, which was added as ZrO_2 derived from zirconyle, decomposed at 300°C in air; titanium, which was added as pigment grade anatase (TiO_2); and silica (SiO_2), which was added as a colloidal silica. The combined slurry mixture was blended for about 16 hours. The slurry was then properly agitated to ensure homogeneous particle suspension and spray dried at 110°C .

Step 2: Calcination and Grinding

The spray-dried powder was first air calcined at 650°C for approximately 16 hours to a constant weight. The powder was then redox calcined to an $\text{Fe}^{+2}/\text{Fe}^{+3}$ weight ratio of approx. 0.4. The reduced powder was then slurry ground in a Vibro Energy mill using iso-propyl alcohol.

Normally, grinding would not be necessary, depending on the nature of the sludge. We found in preliminary hot pressing evaluations of spray dried material that some minor heterogeneities were present; they were eliminated by the grinding step.

Step 3: Hot Pressing

The redox calcined powder was then blended homogeneously with crushed hot pressed Ba/Ca hollandite. The hollandite particle density was 98% of theoretical (4.2 g/cc), and the particle size range was 0.4 to 1.0 mm. The hollandite for this waste form was prepared from a material with potential as a titanate ion exchange for cesium (R. G. Dosch, Sandia Laboratory). We have found that the leach resistance of this hollandite is equal to that prepared by the spray dry method and used in our composite waste form.

Nickel powder was not added because the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio had been adequately adjusted in the previous calcination step. The powders were then hot pressed to final form directly in graphite at 1025°C , 1 hr, 3000 psi, to a density of 4.36 g/cc. The amount of powder loaded for each hot pressing was limited in amount so that the final L/D ratio of the sample is 0.75.

Jack Campbell
Jack H. Campbell
Project Leader
Mineral Waste Form Development Project

TABLE 1: NOMINAL COMPOSITION OF SYNROC-SRL HIGH FE WASTE FORM S26SAN

Weight Percent Oxide or Salt	Nominal SRL High Fe As Rec'd	Al ₂ O ₃ Addition to convert to unweathered CP-1545	SYNROC Additives (Non- Hollandite)	SYNROC Additives (Hollandite, 0.4-1.0 mm)	Total
Fe ₂ O ₃	28.9	-	-	-	28.9
Al ₂ O ₃	0.7	2.0	3.6	0.6	6.9
MnO ₂	1.9	-	-	-	1.9
U ₃ O ₈	6.7	-	-	-	6.7
CaO	1.3	-	6.0	-	7.3
NiO	5.2	-	-	-	5.2
SiO ₂	0.2	-	4.2	-	4.4
Na ₂ O	1.9	-	-	-	1.9
Na ₂ SO ₄	0.1	-	-	-	0.3
SrO	0.25	-	-	-	0.25
Ca ₂ O	-	-	-	0.25	0.25
Ce ₂ O ₃	0.50	-	-	-	0.50
Nd ₂ O ₃	0.50	-	-	-	0.50
BaO	-	-	-	0.4	0.4
TiO ₂	-	-	20.6	3.4	24.0
ZrO ₂	-	-	10.4	-	10.4
TOTAL	48.35	2.0	44.8	4.65	99.8

TABLE 2: RADWASTE ANALYSES, HOT PRESSED DENSITIES AND WEIGHTS OF SYNROC

SRL HIGH FE WASTE FORM S26SAN

Sample No.	Weight (grams)	Immersion ¹ Density (g/cc)	Wt. % ²		
			SrO	Ca ₂ O	U ₃ O ₈
S26SAN#7A	388.3	4.361	0.17	0.24	4.7

¹ Theoretical density is taken as approx. 4.36 g/cc

² Analysis by XRF, accuracy $\pm 10\%$. Analyses on cored samples taken at intermediate locations.

May 6, 1981

Mr. John A. Stone
E. I. duPont de Nemours and Company
Savannah River Laboratory
Fuel Cycle Technology Division
Aiken, South Carolina 29801

Dear John:

Our work on a second SYNROC D composition formulation in which cesium has been added in situ has progressed very well.

We shipped a single sample S29HP8A to you on May 6, 1981, by Federal Express. The dimensions were nominally 7.6cm diameter x 2.0cm height and the total mass was approximately 250 grams.

We have taken two core drills for our leaching studies. We had no difficulty coring the sample. In fact, this material appears to have greater mechanical strength than our earlier samples in which cesium was added as hollandite.

The nominal composition of this material is as follows:

Wt% Oxide or Salt	SRL Composite (unwashed)	SYNROC Additives
Fe ₂ O ₃	23.8	--
Al ₂ O ₃	18.6	--
MnO ₂	7.4	--
U ₃ O ₈	2.1	--
CaO	1.8	5.3
NiO	3.0	--
SiO ₂	0.6	6.6
Na ₂ O	3.3	--
Na ₂ SO ₄	0.6	--
Ca ₂ O	0.25	--
SrO	0.25	--
Ce ₂ O ₃	0.50	--
Nd ₂ O ₃	0.50	--
TiO ₂	--	18.8
ZrO ₂	--	6.6
	62.7	37.3

Mr. J. A. Stone
May 6, 1981
Page 2

The preparation steps used were as follows:

Step 1: Mixing and Spray Drying

SYNROC ingredients formulated from a known sludge composition were mixed and blended with the sludge as an aqueous slurry. The SYNROC ingredients were water soluble nitrates with the exception of zirconium, which was added as ZrO₂ derived from zirconyle, decomposed at 300°C in air; titanium, which was added as pigment grade anatase (TiO₂); and silica (SiO₂), which was added as colloidal silica. The combined slurry mixture was blended for about 16 hours. The slurry was then properly agitated to ensure homogeneous particle suspension and spray dried at 130°C.

Step 2: Calcination and Grinding

The spray-dried powder was first air calcined at 650°C for approximately 16 hours to a constant weight. The powder was then redox calcined to an Fe²⁺/Fe³⁺ weight ratio of approximately 0.8.

Step 3: Hot Pressing

Nickel powder was not added because the Fe²⁺/Fe³⁺ ratio had been adequately adjusted in the previous calcination step. The powders were then hot pressed to final form directly in graphite at 1100°C, 1 hour, 3000 psi, to a density of 3.85 g/cc.

Sincerely,

Jack H. Campbell

Jack H. Campbell
Project Leader
Mineral Waste Form Development Project

June 12, 1981

Dr. John A. Stone
E. I. duPont de Nemours and Company
Savannah River Laboratory
Fuel Cycle Technology Division
Aiken, South Carolina 29801

Dear John:

We shipped for comparative leach testing our high Al SYNROC and a second high Fe SYNROC (both with in-situ cesium) by Federal Express (SRL No. NPM31240, Waybill No. 353315826) on June 4, 1981.

The high Al sample (S31HP1A) was nominally 7.8 cm diameter x 2.5 cm height with a cord section removed for our samples. The total mass was 32u.4 g and the nominal composition is given in Table 1. In this composition, we have added a substantial amount of Fe_2O_3 to react with the large percentage of Al_2O_3 in the unwashed sludge. Thus, we have converted the waste form to a composite-like composition. The conversion of the high Al to a composite-like sludge (by Fe_2O_3 addition) reduces the SYNROC waste loading to 40% (see table 1). In an ongoing research program, we have also investigated the use of MgO addition to react with Al_2O_3 . MgO has the advantage of giving higher waste loadings (50-60%) due to its lower molecular weight and invariant oxidation state (+2). However, because it is still in the research stage we chose not to prepare the CLT sample in this manner.

It has also been brought to our attention that in all likelihood the sludge will be washed at the tank farm regardless of the waste form selected. In this case the Al_2O_3 concentration for high Al_2O_3 sludge will be substantially reduced.

The high Fe sample (S30HP3A) was taken from a large 15.2 cm diameter sample, hot pressed with resistive heating rather than inductive heating. The sample was nominally 5 cm x 4.5 cm x 1.3 cm. The total mass was 142.3 grams and the nominal composition is given in Table 2.

An earlier sample S26SANHP7A (see letter dated April 15, 1981) was hot pressed with inductive heating and exhibited some internal cracking. We believe this cracking was caused by non-uniform heating which resulted from the internal coupling between the large amount of magnetite in this waste form and the magnetic force field used in inductive hot pressing. The fractured and cut surfaces of S30HP3A show no internal cracking by visual analysis. Therefore, we believe we have solved the problem of cracking exhibited in sample S26SANHP7A.

Mr. J. A. Stone
June 12, 1981
Page 2

The preparation steps used for both S30HP3A and S31HP1A were as follows:

Step 1: Mixing and Spray Drying

SYNROC ingredients formulated from a known sludge composition were mixed and blended with the sludges as aqueous slurries. The SYNROC ingredients were water soluble nitrates with the exception of titanium which was added as pigment grade anatase (TiO_2) and silica (SiO_2), which was added as colloidal silica. Note that in all previous preparations the zirconium nitrate was first decomposed to oxide at 300°C to insure nitrate decomposition. We have found this is no longer necessary and zirconium has been added as a water-soluble nitrate in these compositions. The combined slurry mixtures were blended for about 16 hours. The slurries were then properly agitated to ensure homogeneous particle suspension and spray dried at 130°C.

Step 2: Calcination

The spray dried powders were first air calcined at 650°C for approximately 16 hours to a constant weight. The powders were then redox calcined at 800°C to an $\text{Fe}^{2+}/\text{Fe}^{3+}$ weight ratio in the range of 0.5 to 2.0. Note that we have found it unnecessary to grind either of these waste form powders; this is a significant processing improvement over earlier samples.

Step 3: Hot Pressing

Nickel powder was not added because the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio had been adequately adjusted in the previous calcination step. The powders were then hot pressed to final form directly in graphite at 1100°C, 1 hour, 2000 psi, to a density of 4.2 g/cc for S30HP3A (high Al) and 4.1 g/cc for S31HP1A (high Fe).

Sincerely,

Jack H. Campbell
Project Leader
Mineral Waste Form Development Project

JHC:ema

cc: C. Hoeng

Table 1. Nominal Composition of SYNROC - SRL High- Al_2O_3
Waste Form with In-Situ Cesium
Sample No. S31HP1A⁽¹⁾

Oxide or Salt	Nominal SRL As Rec'd High-Al Sludge (wt%)	Al_2O_3 Addition to Convert to Unwashed Sludge DP-1545 ⁽²⁾ (wt%)	SYNROC Additions, wt%	Total (wt%)
Fe_2O_3	2.4	--	32.5	34.9
Al_2O_3	6.8	27.0	--	33.8
MnO_2	1.5	--	--	1.5
U_3O_8	0.5	--	--	0.5
CaO	0.2	--	4.8	5.0
NiO	0.3	--	--	0.3
SiO_2	0.2	--	1.0	1.2
Na_2O	0.5	--	--	0.5
Na_2SO_4	0.05	--	--	0.05
SrO	0.05	--	--	0.05
Ce_2O_3	0.05	--	--	0.05
Ce_2O_3	0.13	--	--	0.13
Nd_2O_3	0.15	--	--	0.15
TiO_2	--	--	16.8	16.8
ZrO_2	--	--	5.1	5.1
TOTAL	12.8	27.0	60.2	100.0

(1) Hot pressed inductively in graphite at 1100°C and 2000 psi for one hour. The immersion density was 4.1 g/cc and the porosity was 0.55% measured by Hg porosimetry.

(2) Zeolite removed

Table 2. Nominal Composition of SYNROC - SAC⁽¹⁾ High-Fe
Waste Form with In-Situ Cesium
Sample No. S31HP3A⁽²⁾

Oxide or Salt	Nominal SAC As Rec'd (wt%)	Additives to Convert to Unwashed Sludge DP-1545 ⁽²⁾ (wt%)	SYNROC Additives (wt%)	Total (wt%)
Fe_2O_3	30.2	--	--	30.2
Al_2O_3	2.8	--	5.2	8.0
MnO_2	2.3	--	--	2.3
U_3O_8	--	7.0	--	7.0
CaO	2.1	--	5.6	7.7
NiO	4.7	--	--	4.7
SiO_2	0.2	--	6.6	6.7
Na_2O	2.6	--	--	2.6
Na_2SO_4	0.6	--	--	0.6
SrO	--	0.3	--	0.3
Ce_2O_3	--	0.3	--	0.3
Ce_2O_3	--	0.3	--	0.3
TiO_2	--	--	18.4	18.4
ZrO_2	--	--	10.6	10.6
TOTAL	45.5	8.2	46.3	100.0

(1) Synthetic High-Fe sludge received from Southwestern Analytical Chemicals, Inc., P.O. Box 423, Austin, Texas 78767

(2) Hot pressed by resistance heating in graphite at 1100°C and 2000 psi for one hour. Slow cooled at approximately $150^\circ\text{C}/\text{hour}$ to 800°C with a 40 minute hold at 800°C . The immersion density was 4.2 g/cc and the porosity is estimated to be less than 1%.

(3) Zeolite removed.