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IMMOBILIZATION OF SAVANNAH RIVER HIGH-LEVEL WASTES IN SYNROC: RESULTS FROM PRODUCT PERFORMANCE TESTS*

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ABSTRACT

Large samples (up to 15cm diameter) of SYNROC D containing simulated Savannah River (SRL) waste sludge have been prepared and performance tested. Waste loadings of 60-65 wt% for the SRL composite sludge have been achieved; this corresponds to a waste concentration (volumetric) loading of approximately 2.3-2.5 g/cm^3. A typical SYNROC D sample has a density of about 4.0 g/cm^3 with less than 0.2% porosity. The compressive and flexural strengths of SYNROC D are 51,200 and 9,400 psi, respectively and Young's Modulus is 20.1 x 10^6 psi by ultrasonic measurement. The quantity of respirable fines (less than 10 μm) generated during a constant energy density impact (10J/cm^3) was less than 0.16 wt%. Values for the thermal conductivity (22°C) and the thermal expansion coefficient (22-950°C) were measured to be 1.7 W/m·K and 11 x 10^{-6} K^{-1}, respectively. Normalized elemental leach rates determined by 28-day MCC-1 tests (90°C) for Cs, Sr, U and Nd are 0.8, 0.4, 1x10^{-4} and < 8x10^{-3} g/m^2 · d, respectively.

INTRODUCTION

SYNROC is a titanate-based ceramic material currently being developed as a potential waste form for immobilizing high-level nuclear reactor wastes [1,2]. SYNROC D is a unique variation of this waste form that is being developed to contain high-level defense wastes** (particularly those in storage at the Savannah River Plant) [3-8].

This manuscript reviews the results from critical performance tests carried out on SYNROC D containing simulated SRP wastes. The performance data are broken down into three categories: (1) Waste Loading, (2) Mechanical and Thermal physical Properties, and (3) MCC Leach Test Results.

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** Currently there are three types of SYNROC:
(1) SYNROC B which is the Basic three-phase formulation containing no radwaste,
(2) SYNROC C which contains simulated, high-level Commercial waste, and
(3) SYNROC D which contains simulated, high-level Defense waste.
The major thrust of this manuscript is on the performance of SYNROC D.

These data were collected on a series of SYNROC samples specially prepared as part of a "comparative leach test" program initiated by Savannah River Laboratory (SRL) [7,9]. In short, this program required each waste form developer to incorporate simulated SRP sludges into their waste form. These samples were then subjected to a series of standard tests (conducted by both the developer and several outside laboratories) that were designed to test the quality and durability of the waste form.

After a brief description of how the SYNROC samples were prepared, the performance data from our tests are presented.

MATERIAL DESCRIPTION AND FORMULATION

The Savannah River Plant wastes are in tank storage and are composed of three components: sludge, salt cake and supernate liquor. Chemically the waste is very diverse. The major component compositions of the calcined waste from these tanks are given by Stone et al [10]. These are three compositions; two represent compositional extremes (high Fe, high Al) and the third (composite) represents the average composition of the total inventory. In this paper, we present data for SYNROC D containing the composite waste.

Radionuclides in the waste sludge are immobilized as dilute-solid solutions in the titanate minerals zirconolite ($CaZrTi_2O_7$) and perovskite ($CaTiO_3$). The large excess of "inert" components in the waste reacts to form spinel-solid solutions [$(Fe,Ni,Mn)(Al,Fe)_2O_4$ - $(Fe,Ni,Mn)_2TiO_4$] and nepheline ($NaAlSiO_4$). All of these phases show strong lines in the SYNROC x-ray diffraction pattern. Note that due to the high Na and Si content of the sludge, a small amount of an amorphous silicate phase also forms.

Cesium in the supernate liquor can be immobilized in one of two ways; either by direct incorporation into nepheline during the hot pressing or by adding as a presynthesized hollandite [$(Ba,Cs)Al_2Ti_6O_{16}$] that is blended into the SYNROC D powder prior to densification. We have prepared samples in both fashions.

Both perovskite and zirconolite are capable of incorporating the fission products and actinide elements in their crystal lattices as dilute solid solutions. Strontium has been found to partition mainly into perovskite. (Radionuclides do not partition into the spinel phases.) The phase composition of two SYNROC D samples containing simulated SRP composite waste are given in Table I; one sample (S21S18) contains hollandite as a Cs host and the other (S29) has Cs immobilized in nepheline.

In brief, SYNROC D is prepared by synthesizing minerals "in-situ" in a mixture of waste sludge and SYNROC additives which has been calcined both in air and a reducing atmosphere (CO/CO_2). The mixture is reacted and densified at high temperature, 1000-1100°C and under a modest confining pressure (2000-4000 psi). Details of the formulation and synthesis of SYNROC D are given by Hoenig et al [7] and Ryerson et al [8]. Table II lists the nominal composition of SYNROC D (sample S-29) containing simulated SRP composite sludge Cs incorporated in nepheline. Except for the hollandite addition, the composition of sample S21S18 is nearly identical to that in Table II.

WASTE LOADING IN SYNROC D

Waste loadings of between 60 to 65 wt% have been achieved for SYNROC D containing SRP composite waste sludge. This corresponds to a waste concentration (volumetric) loading of 2.3-2.5 g/cm^3. Estimates of the curie content for a given SRP waste loading can be calculated using the values reported by Bernadzikowski [11] of 0.69 Ci/g Fe_2O_3 and 0.39 Ci/g Fe_2O_3 for the sludge and supernate feed, respectively. Based on these values and our sample compositions we have calculated an equivalent curie loading in our SYNROC D of about 1.0 Ci/cm^3.

MECHANICAL AND THERMALPHYSICAL PROPERTIES

Rather extensive physical properties measurements have been carried out on SYNROC D [7]. Table II summarizes some of the data for several key properties. In general, the results are typical for many ceramic materials.

The flexural and compressive testing were done according to ASTM specifications with samples having a length-to-diameter ratio greater than five. The elastic moduli were determined using the pulse-overlap ultrasonic method developed by Papadakis [12]. Sample sizes of 1.3x1.3x0.4 cm were used and the frequencies were in the 5-20 MHZ range. The sample longitudinal (V_L) and shear (V_S) velocities were 6697 and 3673 m/s, respectively.

Constant energy density ($10J/cm^3$) impact friability tests carried out by Jardine [13] showed that SYNROC D produced less than 0.16 wt% "respirable fines" (i.e. paricles less than 10 μm in diameter).

TABLE I
Calculated phase composition for two SYNROC D samples containing SRP simulated composite sludge. Sample S21S18 has Cs added in the form of a presynthesized hollandite whereas S29 incorporates Cs in a nepheline phase formed during hot pressing [7].

Sample Number	Wt% Basis				
	Zirconolite	Perovskite	Nepheline	Spinel	Hollandite
S29	19	15	18	48	--
S21S18	19	14	16	44	7

TABLE II
Nominal oxide composition of SYNROC D (sample S29) containing simulated SRP composite sludge.

Component Oxide	SRP Composite Sludge Composition[a]	SYNROC Additives	Total
	wt%	wt%	wt%
Fe_2O_3	23.8	-.-	23.8
Al_2O_3	18.6	-.-	18.6
MnO_2	7.4	-.-	7.4
U_3O_8	2.1	-.-	2.1
CaO	1.8	5.3	7.1
NiO	3.0	-.-	3.0
SiO_2	0.6	6.6	7.2
Na_2O	3.3	-.-	3.3
Na_2SO_4	0.6	-.-	0.6
Cs_2O	0.25	-.-	0.25
SrO	0.25	-.-	0.25
Ce_2O_3	0.50	-.-	0.50
Nd_2O_3	0.50	-.-	0.50
TiO_2	-.-	18.8	18.8
ZrO_2	-.-	6.6	16.6
Total wt%	62.7	37.3	100.0

[a] Based on unwashed composite sludge composition as reported in Reference 10 (with zeolite removed).

TABLE III
Some key mechanical and thermal physical properties of SYNROC D containing SRL composite sludge [7].

Property	SYNROC D Composite
Mechanical	
Flexural Strength (psi)[a]	9.4×10^3
Compressive Strength (psi)	5.1×10^4
Elastic Constants:	
Bulk Modulus (psi)	15.6×10^6
Shear Modulus (psi)	7.8×10^6
Youngs Modulus (psi)	20.1×10^6
Poisson's Ratio	0.284
Microhardness (kg/mm^2)[b]	
HKN_{50}	947
HKN_{100}	868
HKN_{500}	695
Density (g/cm^3)	4.00
Thermal physical	
Thermal conductivity (W/m · K at 22°C)	1.9
Thermal expansion coeff (22-950°C)	11×10^{-6}

a Modulus of rupture (4 point loading, 2.5 cm span)
b Knoop hardness measured using a Leitz Durimet instrument

LEACH TEST RESULTS

Table IV summarizes the standardized leach tests that have been used to evaluate SYNROC D. Due to space limitations in this manuscript, we only report data from MCC-1 (static, 90°C), MCC-2 (static, 150°C), and MCC-4 (dynamic, 75°C) tests done on monolithic samples. (Further details of the results from these and the other leach tests listed in Table IV are given elsewhere [14]).

The average leach rate (Table V and VI) was computed by the method outlined in the MCC-1 test [15] and is generally referred to as the "Normalized Elemental Leach Rate" (LR_i)

$$LR_i = \frac{NL_i}{t} = \frac{m_i}{f_i \cdot SA \cdot t} \qquad (1)$$

where NL_i is the normalized elemental mass loss based on element i (g/m^2), m_i the mass of element i in the solution (g), SA is the geometric surface area (m^2) and f_i is the mass fraction of element in the sample. In this calculation t is the <u>total</u> duration of the leaching experiments (days) and thus it is important to realize that LR_i represents an <u>average</u> rate over this time.

Figure 1 compares 28-d normalized elemental leach rates for the four elements used to simulate the radionuclides in the waste. These data are from the MCC-1 tests. The value shown for Neodymium represents an upper bound since it is based on the detection limit of the analytical method.

The actinides (represented here by U) have the lowest leach rates in SYNROC D. This is due to the extreme durability of zirconolite. Since the actinides have such long half-lives it is important that they be immobilized in a very leach resistant phase.

The relatively high Cs leachability is due to the fact that it has been immobilized in a silicate (nepheline) phase in this SYNROC D sample. Figure 2 contrasts the Cs leachability for SYNROC D samples in which Cs is immobilized in nepheline (S29) vs. hollandite (S21S18). These data are from MCC-4 dynamic leach tests at 75°C in deionized water. Note that the SYNROC D sample that contained nepheline lost almost an order of magnitude more Cs over a 45-day period.

Normalized elemental leach rates (LR_i) from dynamic (MCC-4-type) single pass leach tests on SYNROC D are summarized in Table VII. These results are in a form such that they can be compared with the static leach test data. In general, the leach rates for the dynamic test are slightly higher than the static tests except for the case of Al [14].

In summary, the leach data show that the least durable material in SYNROC is the silica-containing phase. This is primarily comprised of two parts, nepheline and a small quantity of an amorphous phase. Recent leach data show that both parts leach at the same rate [14]. Cs is contained in the silicate material. The most durable phase is zirconolite followed next by the spinels and perovskite.

TABLE IV
Summary of Leach Tests Used to Evaluate SYNROC D

Test	Type	Temperature	V/SA[a]	Material Form
MCC-1	Static, "low temp"	40,90	10	Monoliths
MCC-2	Static, "high temp"	150	10	Monoliths
MCC-3-type	Solubility	150,90	0.15[b]	Crushed (150-300 μm)
MCC-4-type	Dynamic	75	variable[c]	Both monoliths and crushed (150-300 μm)
Modified IAEA	Pseudo-dynamic	95,75	variable[c]	crushed (100-200μm) and (150-300 μm)

a Leachant Volume/Sample Surface Area

b Computed for a crushed 1g SYNROC sample in 10 cm^3 of leachant. The surface area of the crushed sample was estimated from the sample density and the mean particle size.

c For these dynamic leach tests the V/SA ratio continuously increases with time.

TABLE V
Normalized Elemental Leach Rate (LR, $g/m^2 \cdot d$) via MCC-1 Leach Test (90°C, monoliths) for SYNROC D Containing Simulated SRP Composite Sludge (S29).

Element	Deionized Water 3d	Deionized Water 7d	Deionized Water 14d	Deionized Water 28d	Silicate Water 28d	Brine 28d
Al	0.81	0.50	0.31	0.18	0.070	0.0046
Fe	0.007	0.0043	0.00086	3.4×10^{-4}	4.3×10^{-4}	-.-
Mn	0.087	0.057	0.029	0.022	0.0020	-.-
Ni	-.-	0.048	0.057	0.043	0.0074	-.-
Si	2.50	1.89	1.06	0.67	0.24	0.282
Sr	1.40	0.92	0.60	0.38	0.010	< 0.1
Ca	1.05	0.59	0.34	0.21	0.083	-.-
Na	2.97	1.47	0.94	0.62	0.33	-.-
Cs	3.67	1.57	1.71	0.79	0.54	0.45
Ti	$< 7.6 \times 10^{-4}$	$< 3.3 \times 10^{-4}$	$< 1.6 \times 10^{-4}$	$< 8 \times 10^{-5}$	$< 8 \times 10^{-5}$	< 0.0019
Zr	< 0.0032	< 0.0014	< 0.0007	< 0.0004	< 0.0004	< 0.0079
U	-.-	2.8×10^{-4}	1.4×10^{-4}	1.1×10^{-4}	-.-	-.-
Ce	< 1.03	< 0.44	< 0.22	< 0.11	-.-	-.-
Nd	< 0.077	< 0.033	< 0.016	< 0.008	-.-	-.-
Mass loss ($g/m^2 \cdot d$)	0.0062	0.0028	0.0021	0.0013	4.3×10^{-4}	3.1×10^{-4}
pH	6.0	6.0	6.1	6.5	8.0	6.2
Δ pH	0.2	+ 0.2	+ 0.3	+ 0.7	+ 0.7	0.0

TABLE VI
MCC-2 Static Leach Test results on SYNROC D containing composite sludge (Sample S29). The tests were conducted on monoliths at 150°C for 28 days.

	Normalized Elemental Leach Rate (LR), $g/m^2 \cdot d$		
Element	Deionized Water	Silicate Water	Brine
Al	0.48	0.194	0.001
Fe	0.0057	0.005	0.2
Mn	0.034	0.005	0.43
Ni	0.040	0.27	1.89
Si	2.87	0.95	2.68
Sr	1.82	0.49	1.53
Ca	0.63	0.19	0.52
Na	1.99	0.081	-.-
Cs	2.53	0.74	1.96
Ti	$< 8.0 \times 10^{-5}$	$< 8.0 \times 10^{-5}$	< 0.0019
Zr	$< 4.0 \times 10^{-4}$	$< 4.0 \times 10^{-4}$	< 0.0079
U	9×10^{-4}	< 0.017	-.-
Mass Loss ($g/m^2 \cdot d$)	0.0046	0.0013	0.0023
pH	-.-	7.0	6.2
Δ pH	-.-	0.0	0.0

TABLE VII
Normalized Elemental Leach Rate LR_i [computed via eq (1)] for SYNROC D sample S29 containing simulated SRP composite sludge. The results are from MCC-4-type single-pass leach tests on monolithic samples at 75°C using deionized water.

	LR_i ($g/m^2 \cdot d$)							
Time (d)	Cs	Sr	Ca	Al	Si	Na	Mn	U
3	0.97	0.59	0.37	0.025	1.20	1.04	0.01	-.-
7	0.88	0.64	0.34	0.023	1.20	1.00	0.01	-.-
14	0.89	0.60	0.30	0.018	1.19	0.96	0.01	-.-
27	0.85	0.59	0.27	0.015	1.12	0.91	0.01	$< 4 \times 10^{-4}$
45	0.86	0.63	0.26	0.016	1.16	0.90	0.009	$< 5 \times 10^{-4}$

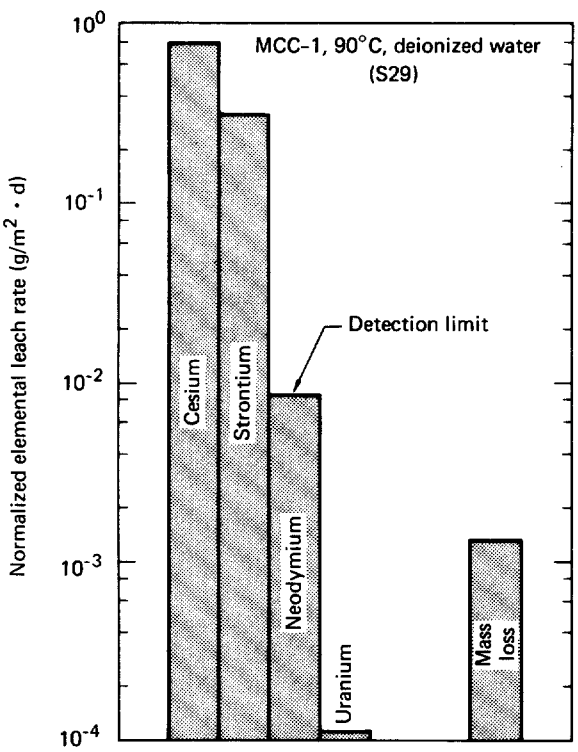

Fig. 1. Comparison of Normalized Elemental Leach Rates ($g/m^2 \cdot d$) for Cs, Sr, Nd and U in SYNROC D (S29). The results are from 28d MCC-1 tests (90°C) in deionized water. Also shown is the rate of mass loss. Note that the Nd value is an upper bound based on the detection limit of the analytical method.

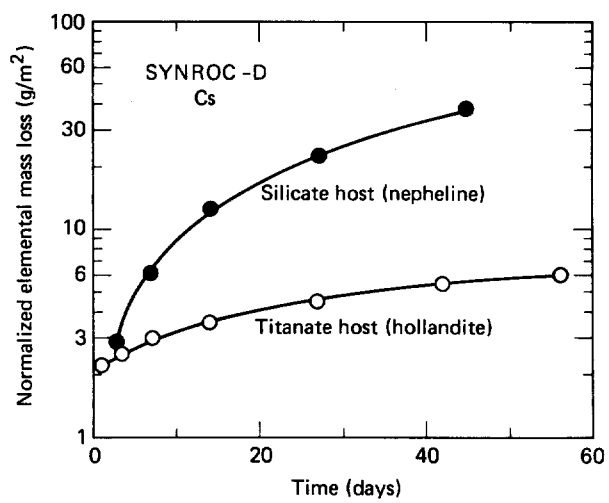

Fig. 2. Comparison of Cs leachability from nepheline (sample S29) vs. hollandite (sample S21S18) in SYNROC D. Data are expressed as normalized mass losses (NL in eq 1) rather than as rates.

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