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Properties of SYNROC-D Nuclear Waste Form: A State-of-the-Art Review

J. Campbell, C. Hoenig, F. Bazan,
F. Ryerson, M. Guinan,
R. Van Konynenburg, and R. Rozsa

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PROPERTIES OF SYNROC-D
NUCLEAR WASTE FORM:
A STATE-OF-THE-ART REVIEW

ABSTRACT

SYNROC is a titanate-based ceramic waste form being developed to immobilize high-level nuclear reactor wastes. SYNROC-D is a unique variation of SYNROC designed to contain high-level defense wastes, particularly those in storage at the Savannah River Plant (SRP). In this report, we review results from physical property and performance tests on SYNROC-D containing simulated SRP wastes. These results provide a data base for comparing SYNROC-D with other defense waste forms. The test data are grouped into three categories: 1) waste loading, 2) mechanical and thermal properties, and 3) leach resistance. We also examine the possible effects of radiation damage on SYNROC during long-term storage in a geologic repository.

The test data were collected from a series of SYNROC-D samples prepared as part of a comparative testing program initiated by Savannah River Laboratory. These samples were prepared by conventional ceramic hot-pressing techniques and then characterized by x-ray diffraction, scanning electron microscopy and electron microprobe analysis.

Whenever possible, standardized test procedures were used for evaluating the waste form properties. For example, leach rates were measured using the Material Characterization Center's (MCC) standard MCC-1 and MCC-2 tests.

INTRODUCTION

SYNROC (synthetic rock) is a titanate-based ceramic waste form currently being developed as an alternate to borosilicate glass for immobilizing high-level nuclear reactor wastes. The SYNROC concept was developed in 1978 by A. E. Ringwood of the Australian National University.^{1,2}

The SYNROC concept borrows heavily from nature; the suite of coexisting minerals in SYNROC has been designed to mimic those mineral assemblages/rocks in the earth's crust that contain radwaste-type elements and exhibit long-term stability.

The idea of putting radwastes into a synthetic mineral form is not new. In fact, it was originally suggested as far back as the early 50s.³ There are many natural minerals that can accept radwaste-type elements (Cs, Sr, and U) into their crystalline structure. Furthermore, several of these minerals possess the important property of having a very low solubility in groundwater and, thus, are strongly resistant to leaching and alteration in the geologic environment.

Ringwood's concept was unique in that he suggested: a) using a titanate-based mineral system of extremely low solubility, and b) incorporating the radionuclides into these "host" minerals at low concentrations (i.e., as dilute solid solutions).

The host minerals for the radwaste elements in SYNROC are zirconolite, perovskite, and hollandite (Fig. 1). Analogs of all three of these minerals can be found in nature. Many of the natural minerals contain radwaste elements (U and Th, for example) and have retained these elements in their crystal structure for up to 500 million years.⁴

The SYNROC composition originally proposed by Ringwood was designed for storage of commercial reactor wastes. This material is called SYNROC-C (C for commercial). At LLNL we are working on a modification of this original form for the storage of defense wastes. Ergo, the name SYNROC-D (D meaning Defense).⁵⁻⁷

There are two major crystal-chemical differences between SYNROC-C and SYNROC-D. First, an additional inert (i.e., contains no radionuclides) spinel mineral phase (Fig. 1) is formed from the large quantities of aluminum and transition metals (mainly Fe, Ni, and Mn) in the defense waste. Secondly, due to the presence of Na and Si in much of the defense waste, a silicate phase (nepheline) is also formed.* In this case, Cs partitions strongly into the nepheline phase and the more leach resistant hollandite phase is not formed. To demonstrate the difference between the two Cs hosts, we have made one waste form using nepheline as the Cs host, and another using hollandite.

The other radionuclides in the high-level waste substitute directly for various cations in the zirconolite and perovskite minerals (Fig. 1). The concentrations of the radionuclides are such that they are present as dilute, solid solutions in the mineral hosts.

*Some amorphous silicate phase also forms.

Figure 1. Crystal structures of the minerals in SYNROC. SYNROC-C is comprised of zirconolite, perovskite, and hollandite. SYNROC-D is composed of zirconolite, perovskite, nepheline, and spinel. Note that because of the Na and Si in the defense wastes, we have chosen to incorporate Cs in nepheline rather than hollandite.

We summarize product performance information on SYNROC-D containing simulated Savannah River Plant defense waste. The data are presented in a format enabling easy comparison with other waste forms. Wherever possible, we have tested our samples using standard tests prescribed by the Materials Characterization Center (MCC).

We first briefly describe the Savannah River waste and the way in which SYNROC-D is fabricated. Following this, the performance data are presented in five main sections: i) waste loading, ii) mineral phase characterization, iii) thermal and mechanical properties, iv) leach resistance, and v) effects of radiation damage.

DESCRIPTION OF SAVANNAH RIVER WASTES

The first high-level defense wastes to be immobilized are those generated as by-products from the production of plutonium and tritium, primarily for nuclear weapons, at the Savannah River Plant near Aiken, South Carolina.

The Savannah River Plant wastes are in tank storage and are composed of three components: sludge, salt cake, and a supernatant liquor. Chemically, the waste is very diverse. Table 1 lists the major component compositions of specific tanks that have order-of-magnitude differences in the major elements, i.e., iron, manganese, uranium, and aluminum. Also listed is the composite (average) composition for the total inventory.⁸ Minor element chemistry is also varied and diverse.⁸

Summarized in Table 2 are the principal radionuclides in the feed stream to the proposed waste solidification facility.⁹ These data are for the sludge, plus supernate feed (as calcine). ⁹⁰Sr is the major radionuclide in the sludge. There is only a minute amount of ¹³⁷Cs in it; however, the Cs activity in the supernatant liquid is roughly equivalent to that of ⁹⁰Sr in the sludge. Isotopes of plutonium are the major actinides in the waste.

PREPARATION OF SYNROC-D TEST SAMPLES

The method used to formulate and prepare the SYNROC-D samples is described in detail elsewhere.^{10,11} Figure 2 is a flow sheet showing the basic

Table 1. Major components in calcined SRP waste sludge.⁸ The columns labeled "High-Fe" and "High-Al" represent the compositional extremes possible while processing the sludge into a solid waste form (SYNROC). The composite is an average of the inventory at the Savannah River site.

Component	High-Fe (wt%)	Composite (wt%)	High-Al (wt%)
Fe ₂ O ₃	53.17	36.13	5.32
Al ₂ O ₃	4.89	28.26	76.05
MnO ₂	3.56	9.94	4.37
U ₃ O ₈	12.34	3.26	1.28
CaO	3.62	2.69	0.35
NiO	9.08	4.47	0.78
SiO ₂	0.40	0.85	0.56
Na ₂ O	4.52	5.08	1.96
Na ₂ SO ₄	<0.50	0.93	<0.50
Ion-Siv IE-95	8.82	8.93	9.33

Table 2. Major long-lived fission products and actinides in calcined SRP waste feed.⁹

Isotope	Activity (mCi/g)
⁹⁰ Sr	66.0
⁹⁰ Y	66.0
¹³⁷ Cs	60.9
²³⁸ Pu	1.6
²³⁹ Pu	1.5 x 10 ⁻²
²⁴⁰ Pu	9.7 x 10 ⁻³
²⁴¹ Pu	1.8
²⁴¹ Am	2.3 x 10 ⁻²

laboratory steps involved in preparing the samples. Figure 3 summarizes the oxide composition of the starting materials and final product mineral phases.

In brief, the preparation of SYNROC-D involves three basic steps.

STEP 1: MIXING AND SPRAY-DRYING

SYNROC ingredients are formulated based on the known sludge composition and then mixed and blended with the sludge as an aqueous slurry. The SYNROC ingredients are water-soluble nitrates with the exception of zirconium, which is added as ZrO_2 (derived from zirconyl decomposed at $300^{\circ}C$ in air), titanium added as pigment-grade anatase (TiO_2), and silica (SiO_2) added as colloidal silica. The combined slurry mixture is blended for about 16 hours. The slurry is then properly agitated to insure homogeneous particle suspension and spray-dried at $130^{\circ}C$ (exhaust gas temperature).

STEP 2: CALCINATION

The spray-dried powder is first air-calcined at $650^{\circ}C$ for approximately 16 hours. It is then redox-calcined at $800^{\circ}C$ in a 10-to-1 mixture of CO_2/CO to produce an Fe^{+2}/Fe^{+3} ratio of approximately 0.8-1.0.

STEP 3: HOT-PRESSING

The powder is hot-pressed to final form in a graphite die for 1 hour at $1050-1100^{\circ}C$ and 3000 psi. This gives a final sample density of about 4.0 g/cm^3 (98% theoretical density).

In the sample preparation scheme described above, Cs is incorporated directly into a nepheline host during the hot-pressing step. To evaluate hollandite as a Cs host we also prepared some SYNROC-D samples containing a presynthesized hollandite that we crushed and added to the calcined powder just prior to hot-pressing (thus, the hollandite appears as approximately 1-mm-diam particles in the SYNROC-D matrix). The purpose of preparing the SYNROC-D sample containing hollandite was twofold:

1. It allowed us to compare the integrity of the two different Cs hosts in a SYNROC-D matrix.
2. We were able to evaluate hollandite as a potential Cs host for use with low-sodium (acid) waste streams.

Figure 2. Schematic diagram showing the major steps in laboratory preparation of SYNROC-D. SYNROC additives are mixed and ground with the simulated waste slurry and then spray-dried, producing a freely flowing powder. This powder is calcined at 650°C in air to a constant weight and then reduced in a 10-1 mixture of flowing CO₂/CO. The reduced powders are finally hot-pressed in a graphite die at 1050-1100°C and 2000-4000 psi for 1 h.

Figure 3. Pie chart showing the composition of the starting materials and mineral products for preparation of SYNROC-D containing SRP composite sludge. The Cs host is nepheline (Sample S29).

The samples prepared by the above means and containing simulated composite SRP waste represent our "reference" SYNROC-D formulations. Therefore, any comparison of other defense waste forms with SYNROC-D should be on the basis of the performance data for these samples.

Table 3 lists the sample designation given key SYNROC formulations containing simulated SRP sludges.* The nominal oxide compositions of these samples are summarized in Tables 4 through 8.

Table 3. Summary of key SYNROC samples prepared for product performance study.

Sample designation	SRP sludge type ^a	Cs host phase	Density (g/cm ³)	Waste loading ^a		Equiv. curie (Ci/cm ³)
				(wt%)	g/cm ³	
S29	Composite	Nepheline	3.85	62.7	2.42	0.99
S21S18	Composite	Hollandite	3.94	59.2	2.33	1.00
S20S03a ^b	Composite	Hollandite	4.0	69.0	2.76	1.18
S30	High Fe	Nepheline	4.20	53.7	2.26	1.37
S26SAN	High Fe	Hollandite	4.36	50.6	2.21	1.26
S31	High Al	Nepheline	4.10	39.8	1.63	0.106

^a Without Al₂O₃ removal (unwashed sludge).

^b Sample used for mechanical tests.

* All of these samples were prepared as part of the Savannah River Laboratory Comparative Leach Test (CLT) conducted from 1980-81.

Table 4. Nominal oxide composition of SYNROC-D Sample S29 containing simulated SRP composite sludge and Cs in an in situ formed nepheline host.

Component oxide or salt	SRP composite sludge composition (wt%) ^a	SYNROC additives (wt%)	Total (wt%)
Fe ₂ O ₃	23.8	--	23.8
Al ₂ O ₃	18.6	--	18.6
MnO ₂	7.4	--	7.4
U ₃ O 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 ₂ O	3.3	--	3.3
Na ₂ SO ₄	0.6	--	0.6
Cs ₂ O	0.25	--	0.25
SrO	0.25	--	0.25
Ce ₂ O ₃	0.50	--	0.50
Nd ₂ O ₃	0.50	--	0.50
TiO ₂	--	18.8	18.8
ZrO ₂	--	<u>6.6</u>	<u>6.6</u>
Total wt%	62.7	37.3	100.0

^a Based on the unwashed composition as reported in Ref. 8 (zeolite removed).

Table 5. Nominal oxide composition of SYNROC-D Sample S21S18 containing simulated SRP composite sludge and Cs in a presynthesized hollandite host.

Component oxide or salt	SRP composite sludge composition (wt%) ^a	SYNROC additives		Total (wt%)
		Non- hollandite (wt%)	Hollandite (wt%)	
Fe ₂ O ₃	23.0	--	--	23.0
Al ₂ O ₃	18.0	--	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
TiO ₂	--	17.1	4.75	21.85
ZrO ₂	--	<u>5.8</u>	<u>--</u>	<u>5.8</u>
Total (wt%)	59.0	34.1	6.8	100.0

^a Based on an unwashed composition as reported in Ref. 8 (zeolite removed).

Table 6. Nominal oxide composition of SYNROC-D Sample S30 containing simulated SRP High-Fe sludge and Cs in an in situ-formed nepheline host.

Oxide or salt	Nominal SRP High-Fe sludge (wt%) ^a	SYNROC additives (wt%)	Total (wt%)
Fe ₂ O ₃	30.2	--	30.2
Al ₂ O ₃	2.8	5.2	8.0
MnO ₂	2.3	--	2.3
U ₃ O ₈	7.0	--	7.0
CaO	2.1	5.6	7.7
NiO	4.7	--	4.7
SiO ₂	0.2	6.5	6.7
Na ₂ O	2.6	--	2.6
Na ₂ SO ₄	0.6	--	0.6
SrO	0.3	--	0.3
Cs ₂ O	0.3	--	0.3
Ce ₂ O ₃	0.3	--	0.3
Nd ₂ O ₃	0.3	--	0.3
TiO ₂	--	18.4	18.4
ZrO ₂	--	<u>10.6</u>	<u>10.6</u>
Total	53.7	46.3	100.0

^a Based on composition as reported in Ref. 8 (zeolite removed).

Table 7. Nominal composition of SYNROC-D Sample S26SAN containing simulated SRP High-Fe sludge and Cs in a presynthesized hollandite host.

Oxide or salt	Nominal SRP	SYNROC additives		Total (wt%)
	High-Fe sludge (wt%) ^a	Non-hollandite (wt%)	Hollandite (wt%)	
Fe ₂ O ₃	28.9	--	--	28.9
Al ₂ O ₃	2.7	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	0.3	--	--	0.3
SrO	0.25	--	--	0.25
Cs 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	50.35	44.8	4.65	99.8

^a Based on composition reported in Ref. 8 (zeolite removed).

Table 8. Nominal composition of SYNROC-D Sample S31 containing simulated SRP High-Al₂O₃ sludge and Cs in an in situ-formed nepheline host.

Oxide or salt	Nominal SRP High-Al sludge (wt%) ^a	SYNROC additives (wt%)	Total (wt%)
Fe ₂ O ₃	2.4	32.5	34.9
Al ₂ O ₃	33.8	--	33.8
MnO ₂	1.5	--	1.5
U ₃ O 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 ₂ O	0.5	--	0.5
Na ₂ SO ₄	0.0	--	0.05
SrO	0.05	--	0.05
Cs ₂ O	0.05	--	0.05
Ce ₂ O ₃	0.13	--	0.13
Nd ₂ O ₃	0.15	--	0.15
TiO ₂	--	16.8	16.8
ZrO ₂	--	5.1	5.1
Total	39.8	60.2	100.0

^a Based on composition reported in Ref. 8 (zeolite removed).

WASTE LOADING IN SYNROC-D

Waste loadings of 60-65 wt% have been achieved for SYNROC-D containing SRP composite waste sludge; this corresponds to a waste concentration (volumetric loading) of approximately $2.3\text{--}2.5\text{ g/cm}^3$ (Table 3). The waste loadings for high Fe- and Al-content sludges are about 55 and 40 wt%, respectively (Table 3), and thus are somewhat lower than for the composite sludge.

Estimates of the curie content of the SRP wastes have recently been reported by Bernadzikowski¹² to be 0.69 and 0.39 Ci/g Fe_2O_3 for the sludge and supernate feed, respectively. Based on these values, we have calculated the equivalent curie loading in each of our SYNROC-D samples (Table 3). Note that the curie loading for the sample containing the high Al-content sludge is almost an order of magnitude less than for the other samples. This is primarily due to the lower Fe_2O_3 content and, hence, the associated lower radionuclide content.¹²

MINERAL PHASE CHARACTERIZATION

Radionuclides in the SRP waste sludge are immobilized as dilute solid solutions in the titanate minerals zirconolite ($\text{CaZrTi}_2\text{O}_7$) and perovskite (CaTiO_3). The Cs in the supernate is contained in nepheline (except for Samples S21S18 and S26SAN where Cs is in a presynthesized hollandite). The large excess of inert transition metals and alumina in the SRP waste reacts to form complex spinel solid solutions ($\text{Fe,Ni,Mn, [Al,Fe]}_2\text{O}_4 - [\text{Fe,Ni,Mn}]_2\text{TiO}_4$). Radionuclides have not been detected in the spinel phase(s).

Table 9 shows the distribution of radionuclides among the SYNROC phases. This distribution is based on the system crystal chemistry and has been verified by electron microprobe studies at several different laboratories.^{1,2,7,10} The distribution of Pu, Am, and Cm was experimentally confirmed by Angelini *et al.*¹³ using the three-phase SYNROC-B system.

Approximate values for the wt% and vol% of the final mineral phases in the SYNROC-D samples are given in Table 10. We have calculated the vol% values, using the densities of the individual mineral phases as a basis (Table 11).

Table 9. Distribution of principal HLW elements between coexisting phases of SYNROC-D. The parentheses indicate the secondary host phase for those elements.

Zirconolite	Perovskite	Spinel	Nepheline	Hollandite
U ⁴⁺	Na ⁺	Fe ²⁺	Na ⁺	Cs ⁺
Th ⁴⁺	Sr ²⁺	Ni ²⁺	K ⁺	Rb ⁺
Pu ⁴⁺	Pu ³⁺	Mn ²⁺	Rb ⁺	K ⁺
Cm ⁴⁺	Am ³⁺	Fe ³⁺	Ba ²⁺	Ba ²⁺
Am ⁴⁺	Cm ³⁺	Mn ³⁺	Cs ⁺	
Np ⁴⁺	Np ³⁺	Al ³⁺		
(ACT ³⁺) ^a	REE ³⁺	Cr ³⁺		
(REE ³⁺)	(ACT ⁴⁺) ^b			
(Sr ²⁺)				

^a ACT³⁺ = trivalent actinides.

^b ACT⁴⁺ = quadrivalent actinides.

Mercury porosimetry measurements of the SYNROC-D samples gave porosity values of less than 0.5%. These very low porosities were also qualitatively verified by SEM photos of internal sample surfaces. None of the photos showed any void spaces in the samples.

Figure 4 shows two scanning electron micrographs (SEM) of a SYNROC-D sample (S29) containing SRL composite sludge. As can be seen, the SYNROC-D matrix has a grain size less than 2 μm . Hence, quantitative compositional analysis by SEM or electron microprobe is not possible on these samples. To analyze the compositions of the perovskite and zirconolite phases, we have also prepared samples at a slightly higher hot-pressing temperature (above the solidus, yet below the liquidus temperature). These conditions produced larger mineral grain sizes, enabling us to quantitatively analyze the composition. Compositional analyses of zirconolite and perovskite in SYNROC-D produced under these conditions are given in Table 12. In these samples, we

Table 10. Calculated phase composition of SYNROC-D samples containing SRP simulated composite, High-Fe and High-Al waste sludges. Tables 4-8 contain the original SYNROC starting compositions.

Sample designation	SRP sludge type	wt% basis					vol% basis				
		Zir.	Per.	Neph.	Spinel	Holl.	Zir.	Per.	Neph.	Spinel	Holl.
S29	Composite	19	15	18	48	--	18	15	27	40	--
S21S18	Composite	19	14	16	44	7	17	14	25	38	7
S30	High-Fe	46	4	11	39	--	43	4	17	36	--
S26SAN	High-Fe	44	4	10	37	5	41	4	16	34	5
S31	High-Al	12	9	4	75	--	12	10	7	71	--

Table 11. Densities of major mineral phases contained in SYNROC-D.

Mineral phase	Density(g/cm ³)
Hollandite ^a	4.20
Zirconolite ^b	4.45
Perovskite ^c	4.04
Nepheline	2.63
Spinel ^d	4.65

^a Measured density of single-phase Ba,Cs-hollandite having a 9/1 mole ratio of BaO/Cs₂O. The (BaO, Cs₂O)/Al₂O₃/TiO₂ ratio was 1/1/6.

^b From Ref. 14; the zirconolite density was not corrected for the radionuclide substitution.

^c Densities determined from lattice parameters measured by x-ray diffraction.¹⁵

^d Density calculated using the spinel composition reported by Ringwood¹⁶ and a weighted average of densities for end-member components.¹⁷

used nearly equal amounts of Ce, Nd, Eu, and Gd oxides to represent the rare earth fission products, and uranium (IV) oxide to represent the actinides. Since our probe was only capable of analyzing for 13 elements at a time, we analyzed for only two of the four rare earths.

The data in Table 12 are grouped according to whether the elements detected were SYNROC additives, radionuclides (simulated) or miscellaneous, inert oxides in the sludge. Also, the far right-hand column in Table 12 lists the radionuclides' distribution coefficients ($K_{p/z}$) between perovskite and zirconolite. As expected, the distribution coefficients show that the rare earths and strontium preferentially partition into the perovskite phase, while uranium is strongly partitioned into zirconolite. However, it is important to remember that redox conditions during hot-pressing have an influence on the final element distribution. Some variations in $K_{p/z}$ values may be observed, therefore, depending on the sample preparation procedures used. (The samples in Table 12 were hot-pressed at 1100°C in nickel capsules at an oxygen fugacity corresponding to the Ni/NiO buffer.)

Figure 4. Scanning electron micrographs of SYNROC-D containing SRL composite sludge, showing the extremely fine grain size of the mineral phases. The scale (denoted by the length of the white bar on the lower margin of each picture) is 10 μm . Note that most of the mineral grains are less than 2 μm in size. The black regions here are nepheline, the white are zirconolite, and the light and medium-gray (indistinguishable in these pictures) are perovskite and spinel(s). Cs is incorporated in nepheline (Sample S29).

Table 12. Microprobe analyses of perovskite and zirconolite in SYNROC-D (grain size increased by heating above solidus, but below liquidus).

Oxide	Perovskite (wt%) ^a	Zirconolite (wt%) ^b	K _{p/z}
<u>SYNROC additives:</u>			
CaO	24.07	9.34	--
TiO ₂	48.12	29.11	--
ZrO ₂	<u>0.68</u>	<u>27.59</u>	--
Total	72.87	66.04	
<u>Simulated radionuclides:</u>			
SrO	0.37	BDL ^c	>10.0
UO ₂	1.66	9.52	0.17
Ce ₂ O ₃	4.76	0.43	11.0
Nd ₂ O ₃	4.87	1.01	4.8
Eu ₂ O ₃	NA ^d	NA	--
Gd ₂ O ₃	NA	NA	--
Total	11.66	10.96	
<u>Miscellaneous inerts:</u>			
SiO ₂	0.13	3.62	--
Al ₂ O ₃	1.49	3.77	--
FeO	3.21	5.47	--
MnO	0.91	2.01	--
NiO	0.71	0.63	--
Na ₂ O	<u>2.25</u>	<u>0.50</u>	--
Total	8.70	16.00	
Total for components analyzed	93.23	93.00	

^a Average of 3 analyses.

^b Average of 4 analyses.

^c BDL = below detection limit.

^d NA = not analyzed.

In a parallel set of experiments, we prepared a SYNROC-D sample at a temperature above the liquidus. (This sample also contained simulated SRP composite sludge.) We observed the same phase assemblage as in material prepared at subliquidus temperatures. The mineral grain sizes for the liquidus sample were large enough for compositional analysis (via the energy dispersive spectra from the SEM). These results are summarized in Table 13 for perovskite and zirconolite, as well as the spinels.

For easy comparison with the data in Table 12, we have again grouped these results according to whether they are SYNROC additives, simulated radionuclides, or miscellaneous inerts. Note that there is generally good compositional agreement between the same phases in the liquidus- and subliquidus-prepared samples. The absolute values of the radionuclide distribution coefficients (between perovskite and zirconolite) differ somewhat for the two samples. However, in general, actinides are preferentially partitioned into zirconolite, and rare earths into perovskite.

In preparing SYNROC-D, we had anticipated the formation of only one spinel. However, our analysis of the sample indicates two distinct spinels. As can be seen from the compositional data in Table 13, one of the spinels is rich in ulvöspinel (Fe_2TiO_4), while the other is rich in hercynite (FeAl_2O_4). A discussion of the mechanism leading to the formation of the two spinels in SYNROC-D is given elsewhere.⁷

An x-ray diffraction pattern (Fig. 5) of SYNROC-D containing composite SRP sludge shows the presence of the expected phases of zirconolite, perovskite, and nepheline. In agreement with the SEM data given above, the x-ray pattern showed two spinel phases. X-ray analysis also indicates the rich hercynite content of the one spinel, and the ulvöspinel-rich content of the other.

The agreement in compositional data for SYNROC-D samples prepared under three different conditions: i) subsolidus; ii) above the solidus, but below the liquidus; and, finally, iii) above the liquidus, indicates that we are at or near equilibrium. Thus, we can confidently state that our processing conditions produce fully dense samples of high integrity, which contain an equilibrium mineral phase assemblage.

The quantity of unknown crystalline material in SYNROC-D is very small, as indicated by the few unassigned peaks in the x-ray diffraction pattern (Fig. 5). There is also a small percentage of amorphous material present in

Table 13. Microprobe analyses of zirconolite, perovskite, and spinels in SYNROC-D (samples prepared by heating above liquidus).

Oxide	Perovskite (wt%)	Zirconolite (wt%)	Spinel 1 (wt%)	Spinel 2 (wt%)
<u>SYNROC additives:</u>				
CaO	25.68	16.26	NA ^a	NA
TiO ₂	49.15	35.60	20.61	5.78
ZrO ₂	<u>0.50</u>	<u>20.70</u>	<u>NA</u>	<u>NA</u>
Total	75.33	72.56	20.61	5.78
<u>Simulated radionuclides:</u>				
SrO	NA	NA	NA	NA
UO ₂	4.43	8.19	NA	NA
Ce ₂ O ₃	6.72	1.47	NA	NA
Nd ₂ O ₃	<u>NA</u>	<u>NA</u>	NA	NA
Total	11.15	9.66	--	--
<u>Miscellaneous inerts:</u>				
SiO ₂	NA	2.65	NA	NA
Al ₂ O ₃	2.14	5.03	24.28	47.39
FeO	2.79	4.21	41.33	30.23
MnO	2.84	2.02	10.47	7.16
NiO	1.03	0.09	1.32	1.12
Na ₂ O	<u>0.35</u>	<u>0.17</u>	<u>NA</u>	<u>NA</u>
Total	9.15	14.17	77.40	85.90
Total all components analyzed	95.63	96.39	98.01	91.68

^a NA = not analyzed.

Figure 5. X-ray diffraction pattern of the same SYNROC-D Sample (S29) discussed in Fig. 4 (containing SRL composite sludge). Although only the major peaks are identified in the figure, all peaks have been assigned to a SYNROC phase except those designated by an "X".

our samples due to relatively large quantities of Si and Na in the starting composition. A study is in progress to quantify the amount and composition of this amorphous material.

SEM and x-ray diffraction data were also recorded for the SYNROC-D containing composite sludge, but with Cs added in a presynthesized hollandite (Figs. 6 and 7). As expected, the only difference between the x-ray pattern for this sample and the one in Fig. 5, is the hollandite diffraction peaks.

The hollandite Cs-host in SYNROC Sample S21S18 (Fig. 6) is really a mineral assemblage of Ba,Cs-hollandite, and minor amounts of rutile, corundum, and a pseudobrookite analog (Al_2TiO_5). Actual proportions depend on the synthesis conditions. The hollandite grains in this assemblage are typically larger than 5 μm in diameter and, therefore, allow reliable quantitative analyses to be obtained (Table 14). These analyses indicate a $(\text{BaO,Cs}_2\text{O})/\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of 1/0.78/6.03 rather than the usual 1/1/6. The low Al_2O_3 content results from the replacement of Al^{+3} with Ti^{+3} ; the Ti^{+3} is formed by partial reduction of Ti^{+4} during hot-pressing in the graphite die. The replacement of Al^{+3} with Ti^{+3} does not affect sample quality.

During hot-pressing a minor interaction occurred at the interface between the SYNROC-D matrix and the presynthesized hollandite. This interaction resulted in the formation of ilmenite $[(\text{Fe,Mn})\text{TiO}_3]$ at the phase boundary. An iron x-ray map of the region (Fig. 7) indicates that iron migrated from the matrix to the hollandite boundary. The Ba,Cs-hollandite did not contain iron. Therefore, the chemical potential of iron was buffered at two different values in the hollandite and the SYNROC matrix, causing it to diffuse from one subsystem to the other. This produced the ilmenite growth at the boundary. This ilmenite rim contains no Cs and, thus, does not affect the leach resistance of the waste form.

Further work on the characterization of SYNROC-D samples is reported by Ryerson et al.¹⁸

MECHANICAL AND THERMAL PROPERTIES OF SYNROC

Extensive physical property measurements have been carried out on SYNROC-B, -C and -D.^{11,19-24} In this section we summarize the data from these various studies and compare the results. (Recall that SYNROC-B is the

Figure 6. X-ray diffraction pattern of SYNROC-D Sample S2LS18 containing composite sludge, but with Cs added in a presynthesized hollandite phase. The H-labeled peaks represent the diffraction lines from the hollandite, while the peaks designated with an "X" are unassigned. A comparison of this pattern with the one in Fig. 5 shows they are nearly identical except for the hollandite lines (Sample S2LS18).

Figure 7. Scanning electron micrograph showing a piece of presynthesized Ba,Cs-hollandite imbedded in the SYNROC-D matrix (Sample S21S18). Note the rim of ilmenite that has formed at the interface. The higher iron concentration in this rim is evident in the iron x-ray image. As in the case of sample S29 (Fig. 4), the grain size of the matrix material is quite small ($<2 \mu\text{m}$). (Sample S29 contained no hollandite.) Zirconolite, perovskite, nepheline, and spinel can be qualitatively identified from the light and dark regions (discussed in the caption to Fig. 4).

Table 14. Microprobe analysis of Ba,Cs-hollandite.^a

Oxide	Composition	
	(wt%)	(mol%)
TiO ₂	65.65	77.2
Al ₂ O ₃	10.81	10.0
BaO	18.26	11.2
Cs ₂ O	4.78	1.6
Total	99.95	100.0

^a Average of 7 points.

basic three-phase assemblage of zirconolite, perovskite, and hollandite without any radwaste; thus it can be thought of as a "reference" material with which to compare SYNROC-C and -D).

Hoenig *et al.*^{11,19,24} have recently reported mechanical and thermal property measurements on SYNROC-B and -D. In both studies, the test samples were prepared by hot-pressing in a graphite die at 2000 psi. The hot-pressing temperature was 1200°C for the SYNROC-B samples and 1050°C for SYNROC-D. The final hot-pressed material was in the form of disks with diameters of 15 cm (6 in.) and thicknesses of about 2.5 cm (1 in.). Samples for testing were cut from these disks. For many of the tests, duplicate samples were cut both from edge and center disc locations. This gave an indication of the uniformity of the physical properties across the diameter of the material.

MECHANICAL PROPERTIES

Table 15 is a summary of the LLNL mechanical property data for SYNROC-B and -D. Also given are data for SYNROC-C from Ringwood *et al.*²³ and Reeve *et al.*²⁰ The flexural and compressive tests performed at LLNL were done according to ASTM specifications. The tensile data reported by Reeve *et al.*²⁰ used the method of diametrical compression that produces tensile failure in a ceramic disc. Note that in the case of the strength measurements, the SYNROC-D has values roughly half those of SYNROC-B.

Table 15. Summary of mechanical properties of SYNROC.

Property	SYNROC-D ^c	SYNROC-C ^b	SYNROC-B ^a
<u>Strength:</u>			
Flexural strength ^d (psi) ^e	9.40×10^3	--	4.275×10^4
Tensile strength (psi)	--	1.1×10^4 h	--
Compressive strength (psi)	4.05×10^4	11.75×10^4	8.33×10^4
<u>Elastic constants:</u>			
Bulk modulus (psi) ^f	1.557×10^7	2.338×10^7	2.347×10^7
Shear modulus (psi) ^f	0.784×10^7	1.143×10^7	1.150×10^7
Young's modulus (psi)			
Ultrasonic	2.014×10^7	2.949×10^7	2.965×10^7
Modulus of rupture	2.30×10^7	--	2.935×10^7
Compression	1.50×10^7	--	4.18×10^7
Poisson's ratio	0.284	--	0.289
<u>Microhardness (kg/mm²):^g</u>			
HKN ₅₀	947	--	1094
HKN ₁₀₀	868	--	1023
HKN ₅₀₀	695	--	880
Density (g/cm ³)	4.00	4.35	4.234
Waste loading (wt%)	69	10	0

^a SYNROC-B data from LLNL;¹⁹ material taken from a 15.2-cm (6-in.)-diam x 2.5-cm (1-in.)-thick hot-pressing.

^b Except where noted, values are from Ringwood et al.²³

^c SRL composite sludge; 69 wt% loading; prepared at LLNL.

^d Modulus of rupture (4-pt loading, 3-in. span).

^e 1 psi = 6.895 kPa.

^f Ultrasonically measured.

^g Knoop hardness measured using a Leitz Duriment instrument.

^h Ref. 20.

Diametrical compression tests on SYNROC-C (10% PW-4b waste) have also been carried out by Sethi²⁵ at Argonne National Laboratory. He reports an average value of 1.04×10^4 psi (72 MPa). This agrees very well with the value of 1.10×10^4 reported by Reeve et al.²⁰ (Table 15) although Sethi does report a large amount of scatter ($\sigma \sim 28$ MPa) in his data set of 10 samples.

The compressive strength reported by Ringwood for SYNROC-C is greater than that for -B. We believe this value may be artificially high because of the low length-to-diameter ratio of the test specimen ($L/D = 1$).²³ The LLNL test samples had ratios greater than five, as specified by the ASTM. (We have observed compressive strengths as high as 12×10^4 psi when testing SYNROC-B samples with an L/D ratio of less than 5.)

The elastic moduli (Table 15) were determined using the "pulse-overlap" ultrasonic method developed by Papadakis.²⁶ Sample sizes of $1.3 \times 1.3 \times 0.4$ cm were used, and the frequencies were in the 5-20 MHz range. The longitudinal (V_L) and shear (V_s) velocities for SYNROC-B and -D were, respectively, $V_L = 7949$ and 6697 m/s, and $V_s = 4327$ and 3673 m/s. Hoenig et al.^{11,19} have found little variation in properties from center to edge in the 15.2-cm-diam, hot-pressed sample. Moreover, in the case of SYNROC-B, the measured flexural strength of 295 ± 31 MPa compares very well with a commercial grade 85 wt% Al_2O_3 ceramic. The elastic properties of SYNROC-B also compare well with commercial alumina.

The difference in mechanical properties of SYNROC-B and -C is minor, indicating that the addition of 10% high-level commercial waste does not appreciably alter the strength of SYNROC-C. On the other hand, high loadings (65 wt%) of SRP defense waste produce a decrease in mechanical strength for SYNROC-D vs -B. This change is probably due to the low strength of nepheline and not the waste loading, per se.

Sethi²⁵ has also measured the elastic moduli of SYNROC-C (containing 10% PW-4b waste) prepared by sintering (Table 16). The elastic moduli were determined from the longitudinal and shear velocities of 5 and 10 MHz acoustic waves using a pulse echo technique. The agreement is excellent between the Sethi²⁵ values and those reported by Ringwood²³ for SYNROC-C, and Hoenig et al.¹⁹ for SYNROC-B. Note further that the samples used by Hoenig et al. and Ringwood were hot pressed, whereas those from Sethi were prepared by sintering. Thus, the elastic properties of SYNROC are only minimally affected by consolidation as long as the final product has a high density ($>97\%$ TD).

Table 16. Comparison of elastic moduli measured by different laboratories for SYNROC-B and SYNROC-C.

Property	SYNROC-C ^a	SYNROC-C ^b	SYNROC-B ^c
Bulk modulus (psi)	23.79×10^6	23.38×10^6	23.47×10^6
Shear modulus (psi)	11.05×10^6	11.43×10^6	11.50×10^6
Young's modulus (psi)	28.65×10^6	29.49×10^6	29.65×10^6
Poisson's ratio	0.299	--	0.289

^a Average of two samples containing 10 wt% PW-4b prepared at Argonne National Laboratory (sintered at 1300°C in CO/CO₂ gas environment).²⁵

^b Samples prepared at Australian National University; 10 wt% simulated commercial waste (hot-pressed in Ni capsule at 1200°C).¹³

^c Samples prepared at Lawrence Livermore National Laboratory (hot-pressed in graphite die at 1200°C).¹⁹

The microhardness measurements (Table 15) were made with a Knoop indenter, using a Leitz Durimet hardness tester. Measurements were taken with 50-, 100- and 500-g loads, and average values were determined from three to six measurements.

The microhardness values show a characteristic decrease with increasing indenter load. As with the other physical property measurements, there was no significant variation from the sample edge to center in hardness. For the case of SYNROC-B the values taken under 100-g loads are of the order of 1000 kg/mm² and compare well with work by Hirthe *et al.*²⁷ on single-crystal rutile.

The hardness values for SYNROC-D are about 15-20% lower than those for SYNROC-B. Thus, the incorporation of 70 wt% SRP defense waste has only a small effect on the microhardness.

Jardine^{28,29} has carried out MCC-10-type impact tests on SYNROC-B and -D samples prepared at Livermore (Table 17, Fig. 8) Jardine adjusted the impact energy to insure delivery of a constant energy density (10 J/cm³) to the sample. He found that the amount of respirable fines (diam <10 μm) is nearly the same for SYNROC-B and -D. Jardine²⁸ also reported that impact tests run under the same conditions on the SRL borosilicate waste glass (SRL 131) gave approximately the same quantity of respirable fines (Fig. 9).

Table 17. Extent of respirable fines (<10 μm) produced during constant energy-density impact tests on SYNROC-B and SYNROC-D.^a

Sample	Total energy (J)	Sample size (g)	Energy density (J/cm ³)	Respirable fines (<10 μm) (wt%)
SYNROC-D ^b	138	53	10	0.16 $\pm$ 0.02
SYNROC-B ^c	146	60	10	0.15 $\pm$ 0.02

^a Tests performed by Jardine.^{28,29}

^b SRL composite sludge at 69 wt% loading (prepared at LLNL¹¹).

^c Sample prepared at LLNL.¹⁹

Impact friability tests on SYNROC-B and -C have also been carried out by Ramm and Ferenczy³⁰ using a total impact energy density of about 140 J/cm³. This energy density is more than an order of magnitude greater than that used by Jardine. Under these higher impact conditions considerably more fines were generated (Table 18). Ramm and Ferenczy's study evaluated the effects of waste addition (i.e., SYNROC-C vs -B) as well as the method of densification (sintering vs hot-pressing). The major difference observed was in the SYNROC-B prepared by hot-pressing. This material produced roughly half to a third as many fines as the other samples. They also determined the quantity of fines generated during similar impacts with borosilicate waste glass (ICM[PW-7-2(2.0)73-11]).

To compare his method with that of Ramm and Ferenczy, Jardine²⁹ also carried out tests at an impact energy density of 140 J/cm³ (Table 19). The results from the two studies are in close agreement.

THERMAL PROPERTIES

The thermal conductivity of LLNL SYNROC-D at 20⁰C is about 1.9 W/m⁰K. Values more than a factor of 2 greater have been reported by Reeve et al.²⁰ for SYNROC-C and -B (Table 20). They used a laser pulse technique and measured thermal diffusivity and specific heat as a function of temperature (Table 21).³¹

Table B-1. (Continued.)

License No.	Serial No.	Total resistance (Ω)	
		(Nov 79)	(7 May 81)
MBI121	3578-398	4858	4954
MBI122	3578-401	4835	4893
MBI123	3578-402	5009	5109
MBI124	3578-403	5235	5359
MBI125	3578-404	5154	5248
MBI126	3578-405	5050	5147
MBI131	3578-350	N/A	5330
MBI132	3578-351	5056	5116
MBI133	3578-352	4961	4950
MBI134	3578-353	5243	5306
MBI135	3978-563	5053	5179
MBI136	3978-564	5074	5253

Table 18. Extent of respirable fines ($<10\ \mu\text{m}$) produced during impact friability tests on SYNROC-C and SYNROC-B.^{20,30}

Size range (μm)	Air-sintered SYNROC-B (wt%)	CO/CO ₂ -sintered		Hot-pressed		Borosilicate waste glass, (ICM[PW-7]) (wt%)
		SYNROC-B (wt%)	SYNROC-C (wt%)	SYNROC-B (wt%)	SYNROC-C (wt%)	
<20	4.0	4.0	4.0	1.3	4.0	5.0
<10	2.0	2.0	2.0	1.0	1.1	2.5
<5	0.8	0.8	0.9	0.4	1.0	1.0

Table 19. Comparison of Jardine²⁸ impact tests with those by Ramm and Ferenczy³⁰ at an impact energy density of $140\ \text{J}/\text{cm}^3$.^a (SYNROC-B and SYNROC-D for the Jardine study was prepared by Lawrence Livermore National Laboratory.^{11,19})

Specimen	Preparation conditions	Respirable fines ($<10\ \mu\text{m}$) (wt%)
<u>Jardine (Argonne National Lab.):</u> ²⁹		
SYNROC-B	LLNL; hot-pressed	0.8 ± 0.1
SYNROC-C	LLNL; hot-pressed	1.2 ± 0.1
<u>Ramm and Ferenczy (Australian AEC):</u> ³⁰		
SYNROC-B	hot-pressed	1.0
SYNROC-B	CO/CO ₂ sintered	2.0
SYNROC-B	air-sintered	2.0
SYNROC-C	hot-pressed	1.1
SYNROC-C	CO/CO ₂ -sintered	2.0

^a Test conditions: $140\ \text{J}/\text{cm}^3$; 12.5-mm (nominal) cylinders; 10-kg drop-weight.

Table 20. Summary of important thermal properties of SYNROC.

Property	SYNROC-B	SYNROC-C	SYNROC-D
Thermal conductivity, (W/m ² ·K)			
20°C	3.4 ^a	3.0 ^b	1.85
200°C	--	--	1.91
400°C	--	--	1.95
Heat capacity			
25°C (J/g·K)	0.74 ^a	--	--
Thermal diffusivity			
25°C (m ² /s)	1.08 x 10 ⁻⁶ ^a	--	--
Thermal expansion coefficient ^c			
22-425°C	9.6 x 10 ⁻⁶	--	10 x 10 ⁻⁶
22-950°C	10.8 x 10 ⁻⁶	--	11 x 10 ⁻⁶
Solidus temperature (°C)	--	1340 ^b	1270

^a Ref. 31; value at 25°C.

^b Ref. 23.

^c Linear thermal expansion coefficient; $\alpha = (L/L_0)\Delta L/\Delta T$, Refs. 19 and 11.

Table 21. Thermal conductivity (k), diffusivity (α) and heat capacity (C_p) for SYNROC-B as reported by Reeve³¹ using a laser flash technique.

Temp (°C)	$\frac{\alpha}{2}$ (m ² /s)	k (W/m ² ·K)	C_p (J/g·K)
25	1.08 x 10 ⁻⁶	3.4	0.74
150	0.97 x 10 ⁻⁶	3.8	0.91
300	0.85 x 10 ⁻⁶	3.7	1.00

Hoenig *et al.*¹⁹ have also recently compiled thermal conductivity data on single-phase TiO_2 and Ca, Sr, and Ba titanates, and found values similar to those reported for SYNROC-B.

Plots of linear expansion vs temperature for SYNROC-B and -D are shown in Figs. 10 and 11, respectively. (The results from these runs are summarized in Table 20.) During the tests, the samples were heated in argon at a rate of about $3^\circ\text{C}/\text{min}$ up to 950°C . On reaching 950°C , the power was shut off and the samples cooled. The cooling rate was approximately $50^\circ\text{C}/\text{min}$ down to 600°C , and then about $15^\circ\text{C}/\text{min}$ down to 300°C . This is a much faster cooling rate than experienced during the original hot-pressing operation ($2\text{--}5^\circ\text{C}/\text{min}$).

To determine the degree of residual stress in the samples, the material was reheated through the same schedule. In the case of SYNROC-B the degree of residual stress was very small. This is indicated by the nearly identical expansion behavior observed during the first and second runs (Fig. 10). However, in the case of SYNROC-D, there is a significant difference observed between the first and second runs. The expansion coefficients for all temperature ranges are about 15-25% higher for the first run (Fig. 11). This behavior indicates that during the first run the sample was annealed during heating, relieving some internal stresses.

The behavior observed in the SYNROC-D samples during expansion heating seems to indicate the presence of a strained glassy phase. Bjerson¹⁸ has reported a nominal 25-vol% nepheline phase in SYNROC-D (Table 10) based on the Na and Si content. It is likely that some portion of this nepheline phase not yet fully crystallized may be responsible for the thermal expansion observed.

RESULTS FROM LEACH TESTS ON SYNROC-D

In this section we report results from standardized leach tests on SYNROC-D containing SRP composite sludge. A total of five different leach tests have been used (Table 22). These tests fall into the two broad categories of "dynamic" and "static" leaching, depending on whether the leachant is flowing through the sample container. The MCC-1 and -2 tests are static leach tests that differ mainly in the temperature used (i.e., 40°C and 90°C for MCC-1 vs 150°C for MCC-2). Thus, the MCC-2 test is often referred to as a high-temperature leach test.

Figure 10. Thermal expansion of SYNROC-B measured from 22-950°C. The test was repeated a second time (Run 2) to determine whether any residual stresses were present in the sample. Note that the behavior is nearly identical for both runs.

Figure 11. Thermal expansion of SYNROC-D (containing 69 wt% SRP composite sludge) measured from 22-950°C. The test was repeated a second time (Run 2) to determine whether any residual stresses were in the sample. The difference observed between the two curves (Run 1 vs 2) appears to indicate some stress developed during hot-pressing. This is discussed further in the text.

Table 22. Summary of leach tests used to evaluate SYNROC-D.

Test	Type	Temperature (°C)	SA/V ^a (cm ⁻¹)	Material form
MCC-1	Static, "low temp"	40,90	0.1	Monoliths
MCC-2	Static, "high temp"	150	0.1	Monoliths
MCC-3	Solubility	150	6.8 ^b	Crushed (150-300 μm)
MCC-4	Dynamic	75	variable ^c	Monoliths and crushed (150-300 μm)
IAEA	Pseudodynamic	95,75	variable ^c	Crushed (100-200 μm, and 150-300 μm)

^a Sample surface area/leachant vol.

^b Computer for 1 g crushed SYNROC in 10 cm³ of leachant. The surface area of the crushed sample was estimated from the sample density and the mean particle size (Eq. [3]).

^c The SA/V ratio is not constant for dynamic leach tests, but rather continuously decreases with time.

MCC-3 is also a high-temperature, static leach test, except that crushed (150- to 300-μm) samples of the waste form are used rather than monolithic specimens. The large increase in surface area caused by crushing makes it easier to detect elements of extremely low leachability. MCC recommends that the test be conducted until equilibrium is reached and that the results be reported as "solubilities" (i.e., grams of material per litre of leachant) rather than leach rates. In this work, however, we also report the data as leach rates since the results are for short time periods.

The leach resistance of SYNROC-D under dynamic conditions was evaluated using the single-pass, continuous-flow (SPCF) leaching method previously described by Coles³² and Coles and Bazan.³³ The SPCF test is a flow-through method very similar to the proposed MCC-4 test still under development. One difference between our test and the proposed MCC-4 is temperature. We used 75°C, whereas the MCC-4 calls for 90°C. Both monoliths and crushed samples have been tested by the SPCF method.

Our final test was a modified pseudodynamic IAEA at 95°C, in which the leachant was changed periodically. Only crushed material was used in the IAEA tests.

The following sections deal only with SYNROC-D-containing SRP composite sludge. Leach rates for SYNROC-D samples containing other SRP waste sludges are summarized in Appendix A.

It should be noted that the leach data presented here are for SYNROC-D only. A considerable base of leaching data has also been published on SYNROC-C (containing simulated commercial wastes).^{20,22,23,25,32-35} We will not attempt here to review the leach data on SYNROC-C.

Furthermore, we have purposely avoided presenting any modeling or other detailed physical or chemical analyses of the leaching mechanism. (This is addressed in a separate study.³⁶) Instead, our purpose has been to summarize the results from a series of standard tests performed on "reference" SYNROC-D samples (i.e., S29 and S21S18), and to present the data in a manner that can be used for performance comparisons with other waste forms.

LEACH RATE CALCULATIONS

Waste form leach rates are often reported in the literature without a clear explanation of the means by which they were calculated. To avoid such confusion (and to make comparison with other data sets easier), we briefly outline the simple methods used to calculate the SYNROC-D leach rates.

Perhaps the most straightforward means of presenting any leach data is in terms of the cumulative amount lost. In the MCC tests,³⁷ this quantity is referred to as the "normalized elemental mass loss" (NL_i) and is defined by

$$NL_i = m_i / f_i SA , \quad (1)$$

where

- m_i = cumulative mass of element i in the leachate solution (g),
- f_i = mass fraction of element i in the sample, and
- SA = geometric surface area of the sample (m^2).

NL_i values are reported for all the tests conducted on SYNROC-D. By plotting these data vs time, it is then possible to calculate either

"instantaneous" leach rates (from the slope of the line) or "average" leach rates (over the total duration of the test).

The average leach rate was computed by the method recommended in the MCC-1 test,³⁷ generally referred to as the "Normalized Elemental Leach Rate" (LR_i)

$$LR_i = \frac{NL_i}{t} = \frac{m_i}{f_i SA \cdot t} \quad (2)$$

Note that time (t) here refers to the total duration of the leaching experiment (in days) and, thus, LR_i represents the average leach rate for the entire experiment.

Values for f_i used in our calculations are given in Tables 4-8. (The values in Tables 4-8 are in wt% of equivalent oxide and, thus, must be put on an element basis before use in Eq. [2].)

Concerning the static leach tests, it is also possible to back-calculate the original elemental concentrations in the leachate from our tabulated leach rates:

$$C_i = (LR_i f_i t) \left(\frac{SA}{V} \right), \quad (3)$$

where

C_i = the solution concentration (g/m^3) and

SA/V = the sample surface area-to-leachant volume ratio (m^{-1}).

Since the surface area-to-volume ratio for the static MCC-1 and -2 tests (Table 22) is specified in the procedures, C_i can be readily calculated from the leach rates. This enables comparison of the SYNROC data with other waste forms, for which only concentration data may be available.

The MCC-3 static tests are not based on a fixed surface area-to-volume ratio, but rather on a fixed mass of crushed sample (1 g) in a fixed volume of leachant (10 cm^3). The MCC-3 data given here are reported as leach rates.

These rates are based on a surface area computed from the sample mean particle size and mass:

$$SA = \frac{6m_s}{\rho \bar{D}_p} \quad (4)$$

where

ρ = sample density (g/m^3),

$\bar{D}_p$ = mean particle diameter (m),

m_s = mass of sample (g).

Thus, for the MCC-3 test, Eq. (3) has the form:

$$C_i = \frac{6LR_i f_i t m_s}{\rho \bar{D}_p} \quad (5)$$

With the use of Eqs. (4) and (5), our MCC-3 leach rates can be converted back to the actual, measured solution concentrations.

Instantaneous leach rates (IR_{ij}) were computed via the expression:

$$IR_{ij} = \frac{m_{ij}}{f_i \cdot SA \cdot \Delta t} \quad (5)$$

where the subscript j refers to the j th leaching interval or j th water change, and Δt is the time interval $t_{j+1} - t_j$. The other variables have the same definitions as before. Note that IR_{ij} represents the leach rate at the time $(t_j + t_{j+1})/2$.

MCC-1 LEACH TESTS

Results from MCC-1 leach tests on the two SYNROC-D samples containing composite sludge (i.e., S29 and S21S18) are summarized in Tables 23-26. The data are compiled both in terms of the Normalized Elemental Mass Loss, NL_i (Tables 23 and 25) and the Normalized Elemental Leach Rate, LR_i (Tables 24 and 26). Recall that S29 has Cs in an in situ-formed nepheline phase, whereas S21S18 contains Cs in the presynthesized hollandite.

MCC-1 leach tests on SYNROC-D were carried out by both LLNL and the Materials Characterization Center at Pacific Northwest Laboratory (PNL).³⁸

Table 23. Normalized elemental mass loss (NL_1) measured via MCC-1 leach tests (90°C up to 28 days) on SYNROC-D containing simulated SRP composite sludge (Sample S29). The data are in units of g/m^2 .

Element	Deionized water				Silicate water	Brine
	3 d	7 d	14 d	28 d	28 d	28 d
A. LLNL results:						
Al	2.44	3.49	4.27	4.98	1.95	0.13
Fe	0.021	0.030	0.012	0.0095	0.012	--
Mn	0.260	0.400	0.406	0.609	0.056	--
Ni	--	0.336	0.795	1.267	0.208	--
Si	7.49	13.21	14.81	18.87	6.80 ^b	7.90
Sr	4.19	6.43	8.38	10.74	2.77	<2.9
Ca	2.34	3.05	3.58	4.38	1.72	--
Na	8.90	10.3	13.2	17.4	9.23 ^b	-- ^b
Cs	11.0	11.0	24.0	22.0	15.2	12.5
Ti	<0.0023	<0.0023	<0.0023	<0.0023	<0.0023	<0.053
Zr	<0.0096	<0.0096	<0.0096	<0.0096	<0.0096	<0.225
U	--	2.0×10^{-3}	2.0×10^{-3}	3.2×10^{-3}	0.0095	--
Ce	<3.1	<3.1	<3.1	<3.1	--	--
Nd	<0.23	<0.23	<0.23	<0.23	--	--
Mass loss (g/m^2)	1.86	2.00	2.90	3.63	1.20	0.88
pH ^a	6.0	6.0	6.0-6.2	6.5	8.0	6.2
ΔpH	+0.2	+0.2	+0.2-0.4	+0.7	+0.7	0.0
B. PNL (MCC) results:^c						
Al	2.40	2.66	3.36	4.20	1.48	<1.40
Fe	--	--	4.6×10^{-3}	7.8×10^{-3}	$<3.3 \times 10^{-3}$	<0.17
Mn	0.066	0.062	0.062	0.081	$<4.2 \times 10^{-3}$	<0.20
Ni	0.45	--	0.15	0.34	<0.11	<5.60
Si	8.31	8.40	9.10	14.0	3.64 ^b	<2.24
Sr	4.47	4.69	6.02	7.84	0.079	<5.60
Ca	1.77	1.89	2.38	3.10	0.84	<1.12
Na	7.80	8.40	9.94	12.9	10.0 ^b	-- ^b
Cs	7.27	12.6	--	19.9	6.16	<2.8
Ti	--	--	--	--	$<2 \times 10^{-3}$	<0.084
Zr	--	--	--	--	1.7×10^{-2}	<0.84
U	--	1.0×10^{-3}	1.7×10^{-3}	1.4×10^{-3}	5.9×10^{-3}	1.4×10^{-2}
Ce	--	--	--	--	<1.2	--
Nd	--	--	--	--	<0.56	--
pH	7.96	8.36	--	8.40	9.76	--

^a Measured by pH paper.

^b Leachant component; may affect accuracy of results.

^c Ref. 38.

Table 24. Normalized elemental leach rate (LR_i , $g/m^2 \cdot d$) via MCC-1 leach test ($90^\circ C$ up to 28 days) on monoliths of SYNROC-D containing simulated SRP composite sludge (S29).

Element	Deionized water				Silicate water	Brine
	3d	7d	14d	28d	28d	28d
A. LLNL results:						
Al	0.813	0.499	0.305	0.178	0.070	0.0046
Fe	0.007	0.0043	0.00086	3.4×10^{-4}	4.29×10^{-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	0.242^a	0.282
Sr	1.40	0.92	0.60	0.38	0.099	<0.1
Ca	0.78	0.44	0.26	0.16	0.061	--
Na	2.97	1.47	0.94	0.62	0.33^a	-- ^a
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}	3.4×10^{-4}	<0.0079
Ce	<1.03	<0.44	<0.22	<0.11	--	--
Nd	<0.0767	<0.0328	<0.0164	<0.0082	--	--
Mass loss ($g/m^2 \cdot d$)	0.62	0.29	0.21	0.13	0.043	0.031
B. PNL (MCC) results:^b						
Al	0.80	0.38	0.24	0.15	0.053	<0.05
Fe	--	--	3.3×10^{-4}	2.8×10^{-4}	$<1.2 \times 10^{-4}$	<0.006
Mn	0.022	8.8×10^{-3}	4.4×10^{-3}	2.9×10^{-3}	$<1.5 \times 10^{-4}$	<0.007
Ni	0.15	--	0.011	0.012	$<3.8 \times 10^{-3}$	<0.2
Si	2.77	1.20	0.65	0.50	0.13^a	<0.08
Sr	1.49	0.67	0.43	0.28	0.079	<0.2
Ca	0.59	0.27	0.17	0.11	0.030	<0.04
Na	2.60	1.20	0.71	0.46	0.36^a	-- ^a
Cs	2.42	1.8	--	0.71	0.22	<0.1
Ti	--	--	--	--	$<7.0 \times 10^{-5}$	$<3 \times 10^{-3}$
Zr	--	--	--	--	6.0×10^{-4}	<0.03
U	--	1.5×10^{-4}	1.2×10^{-4}	4.9×10^{-5}	2.1×10^{-4}	5.0×10^{-4}
Ce	--	--	--	--	<0.043	--
Nd	--	--	--	--	<0.02	--

^a Leachant component.

^b Ref. 38.

Table 25. Normalized elemental mass loss (NL_i , g/m^2) and pH change for SYNROC-D containing SRP composite sludge and Cs in presynthesized hollandite (Sample S21S18). Data are from MCC-1 leach tests conducted at $90^\circ C$ for up to 28 days.

Element	Unpolished samples						Polished samples					
	Silicate					Brine	Silicate					Brine
	Deionized water				water		Deionized water				water	
	3 d	7 d	14 d	28 d			3 d	7 d	14 d	28 d		
A. LLNL results:												
Cs	2.67	5.18	5.48	2.87	3.08	<2.6	3.09	2.52	2.70	1.57	3.53	<2.6
Sr	4.32	8.22	7.87	9.55	1.67	7.0	3.77	6.00	6.41	8.55	12.89	7.0
Ca	1.69	2.87	3.00	3.56	0.81	--	1.89	2.29	2.65	3.15	0.75	--
Ba	0.56	0.33	0.32	--	--	--	0.18	0.25	0.30	--	--	--
Al	2.22	4.00	4.36	4.82	1.40	0.97	2.24	3.15	3.41	4.11	1.34	1.13
Na	11.4	21.7	22.4	25.2	17.6 ^a	-- ^a	15.0	16.1	18.2	19.6	19.7 ^a	-- ^a
Si	10.2	16.0	16.8	20.0	7.34 ^a	4.15	8.82	14.6	15.6	19.1	8.6 ^a	4.45
Mn	0.097	0.101	0.104	0.129	0.013	0.253	0.050	0.091	0.131	0.158	0.013	0.294
Ni	1.02	0.872	0.944	1.16	--	--	0.276	0.960	0.820	0.796	--	--
Ti	<0.0023	<0.0023	<0.0023	<0.0023	<0.0023	<0.053	<0.0023	<0.0023	<0.0023	<0.0023	<0.0023	<0.053
Zr	<0.0096	<0.0096	<0.0096	<0.0096	<0.0096	<0.22	<0.0096	<0.0096	<0.0096	<0.0096	<0.0096	<0.22
U	<0.48	4.7 x 10 ⁻³	4.8 x 10 ⁻³	5.3 x 10 ⁻³	<0.48	--	<0.48	<0.48	<0.48	<0.48	<0.48	--
Mass loss (g/m ²)	1.6	2.1	2.3	2.6	1.1	2.8	1.8	2.3	1.9	2.9	0.9	1.4
pH	5.9	6.0	6.0	6.0	8.0	6.5	6.0	6.0	6.0	6.0	6.0	6.5
ΔpH	+0.1	+0.2	+0.2	+0.2	+0.8	0.0	+0.2	+0.2	+0.2	+0.2	+0.8	0.0
B. PNL (MCC) results: ^b												
Cs	6.06	6.23	10.5	7.28	4.48	<2.8						
Sr	3.90	5.25	6.72	7.28	2.0	<5.6						
Ca	1.56	2.03	2.52	2.80	1.62	<1.1						
Ba	0.36	0.30	0.29	0.36	0.09	<0.84						
Al	2.43	3.57	4.62	5.04	1.23	<1.7						
Na	4.47	--	7.70	8.96	5.32	-- ^a						
Si	7.83	10.8	13.2	14.6	2.41	<2.5						
Mn	0.78	--	0.088	0.11	4.2 x 10 ⁻³	<0.28						
Ni	0.25	--	0.42	--	0.31	<5.6						
Ti	3.6 x 10 ⁻³	<1.5 x 10 ⁻³	5.7 x 10 ⁻³	5.6 x 10 ⁻³	2 x 10 ⁻³	<0.084						
Zr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.84						
Zr	4.8 x 10 ⁻³	<3.1 x 10 ⁻³	6.3 x 10 ⁻³	6.4 x 10 ⁻³	0.018	0.098						
Ce	<1.1	<1.1	<1.1	<1.1	<1.1	<48						
Nd	<0.54	<0.64	<0.6	<0.6	<0.6	<28						
Fe	<0.02	--	0.017	0.015	6.7 x 10 ⁻³	<1.7						

^a Component in leachant.

^b Ref. 38.

Table 26. Normalized elemental leach rate (LR_i , $g/m^2 \cdot d$) for SYNROC-D containing SRL composite sludge and Cs in presynthesized hollandite (Sample S21S18). Data are from MCC-1 leach tests conducted at $90^\circ C$ for up to 28 days.

Element	Unpolished samples						Polished samples					
	Deionized water				Silicate water		Deionized water				Silicate water	
	3 d	7 d	14 d	28 d	28 d	Brine 28 d	3 d	7 d	14 d	28 d	28 d	Brine 28 d
A. LLNL results:												
Cs	0.89	0.74	0.39	0.10	0.11	0.09	1.03	0.36	0.193	0.056	0.13	0.09
Sr	1.44	1.17	0.56	0.34	0.06	0.35	1.26	0.86	0.46	0.31	0.066	0.35
Ca	0.56	0.41	0.21	0.127	0.035	--	0.63	0.33	0.19	0.11	0.028	--
Ba	0.19	0.047	0.023	--	--	--	0.06	0.036	0.021	--	--	--
Al	0.74	0.47	0.31	0.172	0.050	0.035	0.75	0.45	0.24	0.15	0.048	0.040
Na	3.8	3.1	1.6	0.9	0.63 ^a	-- ^a	5.0	2.3	1.3	0.7	0.70	--
Si	3.4	2.29	1.20	0.71	0.26 ^a	0.15	2.94	2.09	1.11	0.68	0.31	0.16
Mn	0.032	0.14	0.0074	0.0046	0.0046	0.009	0.017	0.013	0.0094	0.0036	0.00035	0.011
Ni	0.34	0.12	0.067	0.041	--	--	0.092	0.14	0.059	0.036	--	--
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	$<7.6 \times 10^{-4}$	$<3.3 \times 10^{-4}$	$<1.6 \times 10^{-4}$	$<8 \times 10^{-5}$	$<8 \times 10^{-5}$	<0.0019
Zr	<0.0032	<0.0014	<0.0007	<0.0004	<0.00034	<0.0079	<0.0032	<0.0014	<0.0007	<0.0004	<0.00034	<0.0079
U	<0.16	6.8×10^{-4}	3.4×10^{-4}	1.9×10^{-4}	0.017	--	<0.16	<0.06	<0.03	<0.02	0.017	--
Mass loss ($g/m^2 \cdot d$)	0.53	0.30	0.16	0.093	0.039	0.10	0.60	0.33	0.14	0.10	0.02	0.03
B. PNL (MCC) results:												
Cs	2.02	0.89	0.75	0.26	0.16	<0.1						
Sr	1.30	0.75	0.48	0.26	0.072	<0.2						
Ca	0.52	0.29	0.18	0.10	0.058	<0.04						
Ba	0.12	0.043	0.021	0.013	3.2×10^{-3}	<0.03						
Al	0.81	0.51	0.33	0.18	0.044	<0.06						
Na	1.49	--	0.55	0.32	0.19 ^a	-- ^a						
Si	2.61	1.54	0.94	0.52	0.086 ^a	<0.09						
Mn	0.26	--	5.3×10^{-3}	3.8×10^{-3}	$<1.5 \times 10^{-4}$	<0.01						
Ni	0.082	--	0.03	--	0.011	<0.2						
Ti	$<1.2 \times 10^{-3}$	$<2.2 \times 10^{-4}$	4.1×10^{-4}	2.0×10^{-4}	$<7.0 \times 10^{-5}$	$<3 \times 10^{-3}$						
Zr	$<6.6 \times 10^{-3}$	$<2.8 \times 10^{-3}$	$<1.4 \times 10^{-4}$	$<7 \times 10^{-4}$	6×10^{-4}	<0.03						
U	1.6×10^{-3}	7.3×10^{-4}	4.9×10^{-4}	2.3×10^{-4}	6.4×10^{-4}	3.5×10^{-4}						
Ce	<0.38	<0.16	<0.08	<0.04	<0.04	<2.0						
Nd	<0.18	<0.078	<0.04	<0.02	<0.02	<1.0						
Fe	6.7×10^{-3}	--	1.2×10^{-3}	5.5×10^{-4}	2.4×10^{-4}	<0.01						

^a Component of leachant; may affect accuracy of result.

^b Ref. 38.

For comparison, the data from both groups are summarized in Tables 23-26. In general, the agreement is quite good. The major exception is Mn in the S29 sample series; here the PNL result is about a factor of 10 lower at day 28.

The MCC-1 test procedure followed is identical to that recently published by the Materials Characterization Center.³⁷ In brief, monolithic samples of SYNROC were cut from a large piece of parent material. These samples were then leached under static conditions at 90°C for up to 28 days in three different leachants: 1) deionized water, 2) simulated silicate groundwater (silica and NaHCO₃; pH = 7.5), and 3) salt brine (sodium, potassium, and magnesium chlorides).

In the results presented here on SYNROC Sample S21S18 (Tables 25 and 26), we have tested both polished and unpolished samples. The polished samples were prepared from some of the unpolished material by hand grinding using a kerosene slurry of 0.25- μ m diamond grit. The results show that polishing the sample caused only a minor reduction in leach rate.

In Figs. 12 and 13, some of the MCC-1 leach rates are compared for the S29 and S21S18 SYNROC-D samples. As expected, the leach rates are nearly equivalent for the two samples except for the Cs rate. The Cs leach rates are somewhat lower for the S21S18 material due to the greater durability of the hollandite vs the nepheline phase as a Cs host.

Note that the MCC-1 rates in Figs. 12 and 13 represent an average rate over the whole leaching time (see Eq. [2]).

The leachability of the titanate phases (zirconolite and perovskite) can be contrasted with that of the silicate phase (nepheline) by comparing the Ti and Si leach rates at 28 days. The Ti leach rates* are more than 10⁴ lower than those for Si. Thus, the Si-containing material in SYNROC (i.e., nepheline plus any glassy phase) represents the least durable parts of the SYNROC matrix.

Some 28-day MCC-1 leach test data were also obtained at 40°C (Table 27). Due to the low leachability, only a few of the elements were able to be detected.

*Ti leach rates are lower than those listed in Tables 24 and 26; the listed values are based on the detection limits of our analytical method.

Figure 12. Comparison of MCC-1 normalized cesium and strontium leach rates (Eq. [2]) for SYNROC-D Samples S29 and S21S18. The S29 sample contained Cs in an in situ formed nepheline (silicate) phase, whereas in S21S18, Cs was added in a presynthesized hollandite. All leach data are for monoliths leached in deionized water at 90°C. Note that these data are not true rates, but rather averages over the duration of the leaching period.

Figure 13. Comparison of MCC-1 normalized uranium leach rates (Eq. [2]) for SYNROC-D Samples S29 and S21S18. Data are for monoliths leached in deionized water at 90°C. Note that these data are not true rates, but rather averages over the duration of the leaching period.

Table 27. Results from 28-day MCC-1 static leach tests (40°C) on monoliths of S21S18 and S29 SYNROC-D containing SRL composite sludge.

Element	Silicate water		Brine		Deionized water
	(S21S18)	(S29)	(S21S18)	(S29)	(S29)
<u>Normalized elemental mass loss, NL_i (g/m²)</u>					
Cs	2.70	5.04	<2.7	<2.7	10.5
Ca	0.14	0.61	<0.1	<0.1	1.52
Sr	0.84	0.92	<0.1	<0.1	2.4
Al	0.13	0.08	<0.1	<0.1	0.26
U	4.3×10^{-3}	2.6×10^{-3}	--	--	--
<u>Normalized elemental leach rate, LR_i (g/m²·d)</u>					
Cs	0.10	0.18	<0.1	<0.1	0.37
Ca	0.005	0.021	<0.004	<0.004	0.054
Sr	0.030	0.033	<0.004	<0.004	0.087
Al	0.005	0.003	<0.004	<0.004	0.009
U	1.6×10^{-4}	0.9×10^{-4}	--	--	--

It is interesting to compare the 28-day normalized elemental mass losses (NL_i) at 40 and 90°C for the silicate water leachant (Table 28). Note that the Al leach rate increases the most with temperature (roughly 10-25-fold with an increase in temperature from 40-90°C). Furthermore, the Cs leach rate for hollandite (in S21S18) depends much less on temperature than does the one for the nepheline phase (S29). In fact, the hollandite leach rate increases only about 15% with the 50°C temperature increase.

The data from the SYNROC-D MCC-1 tests generally show lower leach rates in silicate and brine leachants than in deionized water (Tables 23-26).

Jantzen et al.³⁹ have recently reported MCC-1 leach tests on a natural, pure-phase, nepheline sample. They report a normalized Si leach rate (28 days, 90°C, deionized water) of 0.48 g/m²·d. This value is in good agreement with the Si leach rates of approximately 0.5-0.7 g/m²·d observed for nepheline in SYNROC-D (Table 24). Tole and Lasaga⁴⁰ have recently published an extensive study of the dissolution kinetics and mechanism for nepheline. They varied both pH and temperature during their investigations (pH 3.0-11.0 and temperature from 25-80°C). Their reported nepheline leach rates at 80°C and 7 pH are in close agreement with the values we observed in SYNROC during the MCC-1 test.

Table 28. Comparison of MCC-1 normalized elemental mass loss (NL_1) at 90°C and 40°C for SYNROC-D containing composite sludge. Sample S21S18 contains Cs in a presynthesized hollandite, whereas S29 immobilized Cs in a nepheline (silicate) phase. (The leachant was a silicate water having a composition defined by the MCC-1 test.³⁷)

Normalized elemental mass loss after 28 d (g/m^2)						
Element	Sample S21S18			Sample S29		
	40°C	90°C	Ratio 90°C/40°C	40°C	90°C	Ratio 90°C/40°C
Cs	2.70	3.08	1.1	5.04	15.2	3.0
Ca	0.14	0.81	5.8	0.61	2.33	3.8
Sr	0.84	1.67	2.0	0.92	2.77	3.0
Al	0.13	1.40	10.8	0.08	1.95	24.3
U	0.0043	--	--	0.0026	0.0095	3.65

RESULTS FROM 150°C STATIC LEACH TEST ON MONOLITHS (MCC-2)

The MCC-2 test is a standard static leach test designed to evaluate the chemical durability of nuclear waste forms at temperatures between 110-190°C. As in the the case of the MCC-1 test, three standard leachants are used. These are silicate water, brine, and deionized water.

The MCC-2 leach tests are summarized in Tables 29 and 30. These data are for SYNROC-D Sample S29 (Cs in nepheline) and were reported by LLNL (Table 29) and Strachen³⁸ (Table 30).

A comparison of the 90 and 150°C normalized leach rates (28 days in deionized water) for several key elements shows an increase of three- to five-fold with the 60°C temperature increase (Fig. 14).

Arrhenius plots of Cs, Sr, and Ca leach rates from these static tests (Fig. 15) give effective activation energies of about 3-7 kcal/mole (Table 31). Surprisingly, the activation energy for Cs is lower than that observed for Sr in both deionized and silicate water leachant. Extrapolating the Arrhenius plots to higher temperatures indicates that the Sr leach rate should exceed that for Cs at temperatures above 180°C.

Table 29. MCC-2 static leach test results on SYNROC-D containing composite sludge (Sample S29). The tests were conducted on monoliths at 150°C. Results are from tests conducted at LLNL.

A. Normalized elemental mass loss (NL_i), g/m² during 28-day test:

Element	Deionized water	Silicate water	Brine
Al	13.3	5.44	<0.03
Fe	0.160	0.142	5.92
Mn	0.942	0.129	12.0
Ni	1.13	7.65	53.0
Si	80.4	26.7 ^a	75.1
Sr	51.0	13.8	42.9
Ca	17.6	5.19	14.4
Na	55.8	2.27 ^a	--
Cs	70.9	20.7	55.0
Ti	<0.0023	<0.0023	<0.053
Zr	<0.0096	<0.0096	<0.22
U	<0.48	<0.48	--
Mass loss (g/m ²)	12.8	3.64	6.48
pH	4.9	7.0	6.2
ΔpH	0.0	0.0	0.0

B. Normalized elemental leach rate (LR_i), g/m²·d:

Element	Deionized water	Silicate water	Brine
Al	0.475	0.194	<0.001
Fe	0.0057	0.005	0.211
Mn	0.034	0.005	0.429
Ni	0.040	0.273	1.89
Si	2.87	0.954 ^a	2.68
Sr	1.82	0.493	1.53
Ca	0.628	0.186	0.516
Na	1.99	0.081 ^a	-- ^a
Cs	2.53	0.740	1.96
Ti	<8.0 x 10 ⁻⁵	<8.0 x 10 ⁻⁵	<0.0019
Zr	<4.0 x 10 ⁻⁴	<4.0 x 10 ⁻⁴	<0.0079
U	<0.017	<0.017	--
Mass loss (g/m ² ·d)	0.46	0.13	0.23

^aComponent in leachant; may affect accuracy of result.

Table 30. MCC-2 static leach test results on SYNROC-D containing composite sludge (Sample S-29). The tests were conducted by Strachen³⁸ using monolith samples and deionized water at 150°C.

Element	Normalized elemental leach rate (g/m ² ·d)		
	3 d	7 d	14 d
Al	2.95	1.37	0.78
Ca	2.15	1.01	0.64
Cs	16.5	5.23	--
Fe	0.44×10^{-2}	0.38×10^{-2}	0.36×10^{-2}
Mn	2.0×10^{-2}	0.58×10^{-2}	0.48×10^{-2}
Na	11.1	4.77	3.12
Si	10.67	4.9	3.13
Sr	5.3	2.3	1.58
U	0.52×10^{-3}	0.69×10^{-2}	0.09×10^{-2}
pH	8.67	9.12	9.08

Table 31. Summary of effective activation energies determined from Arrhenius plots of Cs, Sr, and Ca leach rates in deionized and silicate waters. The rates used were average values over 28 days from static MCC-1 and -2 leach tests.

Element	Activation energy (kcal/mole)	
	Deionized water	Silicate water
Cs	4.6 ± 0.5	3.4 ± 0.7
Sr	7.3 ± 0.3	6.4 ± 0.7
Ca	5.9 ± 0.4	5.2 ± 0.2

Figure 14. Comparison of MCC-1 (90°C) and MCC-2 (150°C) 28-day normalized elemental leach rates for several elements in SYNROC-D (Sample S29).

Figure 15. Arrhenius plots of normalized elemental leach rates for monolith samples leached in a) deionized water and b) silicate water. Data are from 28-day MCC-1 and MCC-2 leach tests.

An Arrhenius plot of Al leach rates proved to be nonlinear. Although the temperature dependence of the Al leach rates paralleled that for Ca at higher temperatures (90-150°C, Fig. 14), there was a much sharper drop in rate between 90 and 40°C. Such a dramatic change in slope is often interpreted as a change in the rate-controlling step for the dissolution mechanism. However, it is probable that some degree of precipitation may be causing an artificially low Al leach rate at the lower temperature.

One must be cautious when comparing the activation energies reported here for static tests with values obtained from detailed kinetic measurements on single-phase material. The rates we have used are not instantaneous values, but rather averages over 28-day periods. Consequently, any approach toward solution saturation in these tests would cause a corresponding reduction in dissolution rate; this would make the effective activation energies reported here lower than the true values.

RESULTS FROM 150°C STATIC LEACH TESTS ON CRUSHED SAMPLES (MCC-3-TYPE)

At the time of this writing, the final MCC-3 test has not yet been approved. MCC-3 is proposed to be a high-temperature solubility test on crushed samples. The crushed material, of course, has a much greater surface area per gram than monoliths, making the concentration of elements in the leachate much higher. The object of the test is to reach an equilibrium between the aqueous phase and the waste form, allowing determination of waste form solubility for a given leachate volume.

We have carried out an MCC-3-type leach test on our SYNROC-D samples (Tables 32-34). The sample size was one gram and was sieved to a particle size range of 150-300 μm (having an equivalent geometric surface area of about 0.0068 m^2/g^*). During the test, the leachant and crushed SYNROC were continuously mixed by rotating the leaching vessel. A leachant volume of 10 cm^3/g of sample was used in all tests.

The results in Tables 32 and 33 are for Sample S21S18 (Cs in hollandite), and those in Table 34 are for S29 (Cs in silicate). We report the MCC-3-type

*Surface area based on mean equivalent spherical diameter (225 μm) of particles in the size fraction.

Table 32. MCC-3-type static leach test results on SYNROC-D containing SRL composite sludge (Sample S21S18). The tests were conducted on crushed samples ($150\text{--}300\ \mu\text{m}^a$) at 90°C using deionized water. The leachant and SYNROC were continuously mixed by rotating the leaching vessel.

Days	Element								
	Cs	Sr	Ca	Al	Na	Si	Ti	Zr	U
<u>Normalized elemental mass loss (NL_i), g/m^2</u>									
3	1.47	0.21	0.19	0.088	0.39	0.30	$<4 \times 10^{-5}$	$<2 \times 10^{-4}$	$<7 \times 10^{-3}$
7	1.69	0.38	0.33	0.176	0.66	0.60	$<4 \times 10^{-5}$	$<2 \times 10^{-4}$	$<7 \times 10^{-3}$
14	1.66	0.53	0.415	0.249	0.95	0.91	$<4 \times 10^{-5}$	$<2 \times 10^{-4}$	$<7 \times 10^{-3}$
<u>Normalized elemental leach rate (LR_i), $\text{g}/\text{m}^2 \cdot \text{d}$</u>									
3	0.49	0.070	0.063	0.029	0.13	0.10	$<1 \times 10^{-5}$	$<7 \times 10^{-5}$	$<2.3 \times 10^{-3}$
7	0.23	0.054	0.047	0.025	0.094	0.086	$<6 \times 10^{-6}$	$<3 \times 10^{-5}$	$<1 \times 10^{-3}$
14	0.11	0.038	0.030	0.018	0.068	0.065	$<3 \times 10^{-6}$	$<1.4 \times 10^{-5}$	$<5 \times 10^{-4}$
<u>Normalized "instantaneous" leach rate (IR_{ij}), $\text{g}/\text{m}^2 \cdot \text{d}$</u>									
1-3	0.49	0.070	0.063	0.029	0.13	0.10	$<1 \times 10^{-5}$	$<7 \times 10^{-5}$	$<2.3 \times 10^{-3}$
4-7	0.032	0.040	0.035	0.022	0.068	0.075	$<6 \times 10^{-6}$	$<3 \times 10^{-5}$	$<1 \times 10^{-3}$
8-14	--	0.024	0.012	0.010	0.041	0.044	$<3 \times 10^{-6}$	$<1.4 \times 10^{-4}$	$<5 \times 10^{-4}$

^aGeometric surface area (based on mean equivalent spherical diameter) is $0.0068\ \text{m}^2/\text{g}$. Data can be converted to solution concentrations via Eq. (3).

data in terms of normalized mass loss and leach rates. These data can be easily converted back to the original solution concentrations via Eq. (3).

An interesting comparison can be made between the MCC-2 and -3 data (Fig. 16). Both leach tests were conducted at 150°C under static conditions. The major difference between the two tests was the use of monoliths in MCC-2 and crushed samples in MCC-3.

Note that the leach rates for the monolith samples are far greater than those for the crushed material. A plot of the ratio of monolith-to-crushed sample leach rates is given in Fig. 17. These data show that initial leach rates are as much as 200 times greater for the monolith samples. However, the difference in leach rates between the two samples tends to decrease with time.

Table 33. Results from 28-day MCC-3-type static leach tests on SYNROC-D S21S18 (150-300 μm^a), containing composite sludge. Tests were carried out at 150°C and 90°C using brine and silicate water.

Element	Silicate water (28 days)		Brine (28 days)	
	150°C	90°C	150°C	90°C
<u>Normalized elemental mass loss, NL_i (g/m^2)</u>				
Cs	3.6	1.2	4.4	1.3
Ca	0.04	0.06	1.4	0.5
Sr	0.08	0.08	3.3	0.8
Al	0.21	0.05	0.008	0.005
Na	1.9	0.06	--	--
<u>Normalized elemental leach rate, LR_i ($\text{g}/\text{m}^2 \cdot \text{d}$)</u>				
Cs	0.13	0.043	0.16	0.46
Ca	1.4×10^{-3}	2.1×10^{-3}	0.05	0.018
Sr	2.8×10^{-3}	2.8×10^{-3}	0.12	0.029
Al	0.075	1.8×10^{-3}	2.9×10^{-4}	1.8×10^{-4}
Na	0.068	2.1×10^{-3}	--	--

^a Geometric surface area (based on mean equiv. spherical diam.) is $0.0068 \text{ m}^2/\text{g}$. These data can be converted to solution concentrations via Eq. (3).

Table 34. MCC-3-type static leach test results on SYNROC-D containing SRL composite sludge (Sample S29). The tests were conducted on crushed samples (150-300 μm)^a at 90°C using deionized water. The leachant and SYNROC were continuously mixed by rotating the leaching vessel.

Element									
Days	Cs	Sr	Ca	Al	Na	Si	Ti	Zr	U
<u>Normalized elemental mass loss (NL_i), g/m^2</u>									
3	1.74	0.17	0.081	0.044	0.42	0.24	$<4 \times 10^{-5}$	$<2 \times 10^{-4}$	$<7 \times 10^{-3}$
7	2.04	0.36	0.158	0.126	0.71	0.55	$<4 \times 10^{-5}$	$<2 \times 10^{-4}$	$<7 \times 10^{-3}$
14	2.29	0.52	0.232	0.208	1.01	0.86	$<4 \times 10^{-5}$	$<2 \times 10^{-4}$	$<7 \times 10^{-3}$
<u>Normalized elemental leach rate (LR_i), $\text{g/m}^2 \cdot \text{d}$</u>									
3	0.58	0.057	0.027	0.015	0.14	0.08	$<1 \times 10^{-5}$	$<7 \times 10^{-5}$	$<2 \times 10^{-3}$
7	0.29	0.051	0.023	0.018	0.10	0.08	$<6 \times 10^{-6}$	$<3 \times 10^{-5}$	$<1 \times 10^{-3}$
14	0.16	0.037	0.017	0.015	0.15	0.06	$<3 \times 10^{-6}$	$<1.4 \times 10^{-5}$	$<5 \times 10^{-4}$
<u>Normalized "instantaneous" leach rate (IR_{ij}), $\text{g/m}^2 \cdot \text{d}$</u>									
1-3	0.58	0.057	0.023	0.015	0.14	0.80	$<1 \times 10^{-5}$	$<7 \times 10^{-5}$	$<2 \times 10^{-3}$
4-7	0.077	0.048	0.019	0.021	0.073	0.078	$<6 \times 10^{-6}$	$<3 \times 10^{-5}$	$<1 \times 10^{-3}$
8-14	0.035	0.023	0.011	0.012	0.043	0.044	$<3 \times 10^{-6}$	$<1.4 \times 10^{-4}$	$<5 \times 10^{-4}$

^aGeometric surface area (based on mean equiv. spherical diam.) is $0.0068 \text{ m}^2/\text{g}$. These data can be converted to solution concentrations via Eq. (3).

Figure 16. Comparison of normalized elemental leach rates observed for monoliths vs crushed samples of SYNROC-D (S29) at 150°C in deionized water. The surface area for the crushed sample was based on the mean equivalent particle size. Note the much greater leach rates for the monolith samples.

Figure 17. Ratio of monolith/crushed sample leach rates vs time for SYNROC-D (S29). The ratios were determined from the data in Fig. 16.

The greater leach rates observed here for monoliths vs crushed samples of SYNROC-D have also been reported for SYNROC-C^{20,33} and PNL 76-68 glass.⁴¹ This particle size effect is probably due to the manner in which the sample surface area is measured. An indication of the variability of surface area measurements is given in Table 35, where geometric values are compared with BET measurements. As expected, the BET surface areas are greater than the corresponding geometric values in all cases. Surprisingly, however, the variability between the surface area measurements is lower for the crushed material. Note that the BET surface area is from 3-10 times greater than geometric surface area for the crushed material, but 18-91 times greater for the monoliths.

Our most important conclusion in this section is perhaps that the true leaching surface areas are probably incorrectly defined by geometric or BET values. Therefore, although comparisons of leach rates between different waste forms are possible (if all the tests are conducted in exactly the same manner), the mechanism of leaching cannot likely be obtained without exact knowledge of the nature (and extent) of the surface area.

MCC-4-TYPE LEACH TESTS

Like the MCC-3 test, MCC-4 has also not yet been approved in final form. The test is envisioned to be a single-pass, continuous-flow procedure using monolith samples. It is very similar to the test developed by Coles et al.^{32,33} for evaluating leach rates of glasses formed in cavities following underground nuclear tests.⁴²

In our evaluation of SYNROC-D we have used the Coles et al. single-pass flow test with deionized water at 75°C. The water flow rate was 30 cm³/d corresponding to superficial flow velocity of 38.6 m/y (i.e., superficial velocity of 0.106 m³/m²d). The test itself has been described in detail elsewhere.^{32,33} In brief, the waste form is placed directly in the path of the flowing water, with the rate of water flow set at some constant value. Peristaltic pumps control the flow rates and the leachant is directed from a supply carboy, through the pump, through a cell containing the waste form, and finally into a leachate collection vessel. The leachate is then analyzed for the elements or radionuclides of interest. This type of dynamic leaching experiment avoids the problem of solution saturation that may be encountered in static leach tests.

Table 35. Results from surface area analyses of SYNROC-D and SYNROC-C (data for SYNROC-C are from Ref. 33).

Sample	BET area (m ² /g)		$\frac{N_2}{Kr}$	Geometric area (m ² /g)	Ratio BET/geometric	
	$\frac{N_2}{N_2}$	Kr			$\left(\frac{N_2}{Geo}\right)$	$\left(\frac{K_r}{Geo}\right)$
<u>SYNROC-C</u>						
150-300 μm	0.246	0.101	2.4	6.55 x 10 ⁻³	37.6	15.4
Monoliths (cores)	--	0.017	--	6.25 x 10 ⁻⁴	--	27.2
<u>SYNROC-D</u>						
150-300 μm	0.063	0.034	1.85	6.8 x 10 ⁻³	9.3	5.0
Monoliths (cores)	0.036	0.007	5.14	3.96 x 10 ⁻⁴	91	18

Tables 36-38 summarize the results from single-pass flow tests on monolith and crushed samples of SYNROC-D containing SRL composite waste. Again, we have used the two SYNROC-D compositions (i.e., S29 and S21S18). Recall that in one, Cs is contained in a presynthesized hollandite host (S21S18), and in the other, Cs is immobilized in an *in situ*-formed nepheline (S29). In general, there is little difference in the leach rates of the two samples except for the Cs rates. (This will be discussed later in this section.)

The leach rates are tabulated as both instantaneous and normalized values (Eqs. [5] and [2]). We also report the cumulative amounts leached (i.e., normalized elemental mass loss, NL_i , see Eq. [1]).

The normalized elemental mass loss (NL_i) during these MCC-4-type tests is plotted for several elements in Fig. 18. (Since Ti, Zr, U, Nd, and Fe were all below detection limits, only the limited elemental data in Tables 36 and 38 are plotted.) The Na, Si, Sr, and Ca leach rates are about a factor of 2 greater for the S29 material than for the S21S18 sample (Fig. 18).

The Cs leachabilities differ markedly between the two SYNROC-D samples tested here (Fig. 19). This is because in Sample S29 the Cs has been immobilized in a silicate phase; the silicate phase is much less leach resistant than the hollandite (titanate) host (S21S18).

Table 36. Results from single-pass, continuous-flow test (MCC-4-type test) on monoliths^a of SYNROC-D containing simulated SRP composite sludge and Cs in hollandite (S21S18). The leachant was deionized water at 75°C.

A. Normalized elemental mass loss (NL_i) g/m²:

Days	Cs	Sr	Ca	Al	Si	Na	Mn	U
1	2.24	0.53	0.21	--	0.42	0.98	0.020	--
3	2.52	1.07	0.41	--	1.18	1.90	0.030	--
7	3.00	2.15	0.81	--	2.90	3.62	0.050	--
14	3.56	4.11	1.51	--	5.91	6.63	0.078	--
28	4.48	8.03	2.87	--	11.93	13.07	0.144	--
42	5.38	11.67	4.23	--	18.37	19.09	0.210	--
56	6.14	15.75	5.77	--	25.37	25.11	0.286	--
125	9.27	32.07	11.48	--	56.65	50.95	0.626	--

B. Normalized elemental leach rate (LR_i) g/m²·d:

Days	Cs	Sr	Ca	Al	Si	Na	Mn	U
1	2.24	0.53	0.21	--	0.42	0.98	0.020	--
3	0.84	0.36	0.14	--	0.39	0.63	0.010	--
7	0.43	0.31	0.12	--	0.41	0.52	0.007	--
14	0.25	0.29	0.11	--	0.42	0.47	0.0055	--
28	0.16	0.29	0.10	--	0.43	0.47	0.0051	--
42	0.13	0.28	0.10	--	0.44	0.45	0.005	--
56	0.11	0.28	0.10	--	0.45	0.45	0.005	--
125	0.074	0.26	0.092	--	0.45	0.41	0.005	--

C. Normalized "instantaneous" leach rate (IR_i) g/m²·d

Days	Mean time (d)	Cs	Sr	Ca	Al	Si	Na	Mn	U
1	0.5	2.24	0.53	0.21	--	0.42	0.98	0.020	--
2-3	2.5	0.14	0.27	0.10	--	0.38	0.46	0.005	--
4-7	5.0	0.12	0.27	0.10	--	0.43	0.43	0.005	--
8-14	10.5	0.080	0.28	0.10	0.020	0.43	0.43	0.004	--
15-28	21	0.066	0.28	0.097	0.017	0.43	0.46	0.005	$<4 \times 10^{-4}$
29-42	35	0.064	0.26	0.097	--	0.46	0.43	0.005	$<1.0 \times 10^{-5}$
43-56	49.0	0.054	0.29	0.11	--	0.50	0.43	0.005	--
57-125	91.0	0.046	0.24	0.084	--	0.46	0.38	0.005	1.2×10^{-5}

^a Geometric surface area = 3.96×10^{-4} m²/g.

Table 37. Results from single-pass continuous-flow leach test (MCC-4-type) on crushed SYNROC-D samples (150-300 μm^2) containing simulated SRP composite sludge and Cs in hollandite (S21S18). The leachant was deionized water at 75°C.

Normalized elemental mass loss (NL _i); g/m ²									
Days	Cs	Sr	Ca	Al	Si	Na	Mn	U	
1	1.0	0.13	0.10	0.023	0.095	0.20	0.0021	--	
3	1.15	0.29	0.28	0.053	0.32	0.46	0.0039	--	
7	1.27	0.55	0.54	0.117	0.72	0.86	0.0070	--	
14	1.37	0.97	0.72	0.201	1.33	1.46	0.0123	--	
28	1.54	1.73	0.98	0.327	2.49	2.54	0.0215	--	
42	1.71	2.50	1.32	0.495	3.76	3.76	0.0306	--	
56	1.84	3.28	1.63	0.68	5.09	4.93	0.0397	--	
125	2.40	7.28	3.01	1.51	12.82	11.35	0.0887	--	
Normalized elemental leach rate (LR _i); g/m ² ·d									
Days	Cs	Sr	Ca	Al	Si	Na	Mn	U	
1	1.00	0.13	0.10	0.023	0.095	0.20	0.0021	--	
3	0.38	0.097	0.093	0.018	0.11	0.15	0.0013	--	
7	0.18	0.079	0.077	0.017	0.10	0.12	0.0010	--	
14	0.098	0.069	0.051	0.014	0.095	0.10	8.8 × 10 ⁻⁴	--	
28	0.055	0.062	0.035	0.012	0.089	0.091	7.7 × 10 ⁻⁴	--	
42	0.041	0.060	0.031	0.012	0.090	0.090	7.3 × 10 ⁻⁴	--	
56	0.033	0.059	0.029	0.012	0.091	0.088	7.1 × 10 ⁻⁴	--	
125	0.019	0.058	0.024	0.012	0.102	0.091	7.1 × 10 ⁻⁴	--	
Normalized "instantaneous" leach rate (IR _{i,j}); g/m ² ·d									
Days	Mean time (d)	Cs	Sr	Ca	Al	Si	Na	Mn	U
0-1	0.5	1.00	0.13	0.10	0.023	0.095	0.20	0.0021	--
2-3	2.5	0.075	0.08	0.090	0.015	0.11	0.13	9.2 × 10 ⁻⁴	--
4-7	4.5	0.029	0.065	0.065	0.016	0.10	0.10	7.8 × 10 ⁻⁴	--
8-14	10.5	0.015	0.060	0.025	0.012	0.088	0.086	7.6 × 10 ⁻⁴	1.3 × 10 ⁻⁴
15-28	21.0	0.012	0.054	0.019	0.009	0.083	0.077	6.6 × 10 ⁻⁴	<5 × 10 ⁻⁵
29-42	35.0	0.012	0.055	0.024	0.012	0.091	0.087	6.5 × 10 ⁻⁴	<6 × 10 ⁻⁵
43-56	49.0	0.0094	0.056	0.022	0.013	0.095	0.084	6.5 × 10 ⁻⁴	--
57-125	91.0	0.0082	0.058	0.020	0.012	0.112	0.093	7.1 × 10 ⁻⁴	--

^aGeometric surface area $\pm 0.0068 \text{ m}^2/\text{g}$.

Table 38. Results from single-pass continuous-flow leach test (MCC-4-type test) on monoliths^a of SYNROC-D containing simulated SRP composite sludge and Cs in an in situ formed nepheline (S29). The leachant was deionized water at 75°C.

A. Normalized elemental mass loss (NL_i) g/m²

Days	Cs	Sr	Ca	Al	Si	Na	Mn	U
3	2.91	1.77	1.11	0.075	3.60	3.12	(0.03)	--
7	6.15	4.45	2.35	0.159	8.36	7.00	(0.07)	--
14	12.52	8.37	4.17	0.257	16.62	13.44	0.139	--
27	22.42	15.91	7.29	0.413	30.27	24.62	0.27	--
45	38.76	28.15	11.79	0.737	52.05	40.28	0.45	--
80	68.19	47.40	18.94	1.027	87.55	67.98	0.77	--
115	91.64	62.80	24.89	1.170	114.85	91.78	1.02	--
151	110.36	81.88	32.81	1.318	142.57	115.54	1.27	--

B. Normalized elemental leach rate (LR_i) g/m²·d

Days	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 x 10 ⁻⁴
45	0.86	0.63	0.26	0.016	1.16	0.90	0.009	<5 x 10 ⁻⁴
80	0.85	0.59	0.24	0.013	1.09	0.85	0.0096	--
115	0.80	0.55	0.22	0.010	1.01	0.80	0.0088	--
151	0.73	0.54	0.22	0.0087	0.94	0.77	0.0084	--

C. Normalized "instantaneous" leach rate (LR_i)_j g/m²·d

Days	Mean time (d)	Cs	Sr	Ca	Al	Si	Na	Mn	U
0-3	1.5	0.97	0.59	0.37	0.025	1.20	1.04	--	--
4-7	5.5	0.81	0.67	0.31	0.021	1.19	0.97	--	--
8-14	10.5	0.91	0.56	0.26	0.014	1.18	0.92	0.0099	--
15-27	21.0	0.80	0.58	0.24	0.012	1.05	0.89	0.0094	<4 x 10 ⁻⁴
28-45	35.0	0.88	0.68	0.25	0.018	1.21	0.87	0.010	<5 x 10 ⁻⁴
46-80	62.6	0.84	0.55	0.20	0.0083	1.01	0.79	0.0091	--
81-115	10.6	0.67	0.44	0.17	0.0041	0.78	0.68	0.0070	--
116-151	141	0.52	0.53	0.22	0.0041	0.77	0.66	0.0070	--

^a Geometric surface area = 3.86 x 10⁻⁴ m²/g.

Figure 18. Normalized elemental mass loss for samples (a) S21S18 and (b) S29 during single-pass, continuous-flow leaching at 75°C in deionized water.

Figure 19. Leach resistance of different Cs-host phases in SYNROC-D. The data are for Sample S29 (silicate Cs host) and S21S18 (titanate Cs host) taken during single-pass, continuous-flow leach tests at 75°C. The results are expressed as the normalized elemental mass loss.

Figure 20. Comparison of normalized, instantaneous leach rates observed during single-pass continuous-flow leach testing of crushed and monolith samples of SYNROC-D Sample S21S18. The sample geometric surface areas were used in the leach rate computations. The tests were done at 75°C using deionized water.

For SYNROC-D Sample S21S18, we conducted MCC-4-type tests on both the monoliths and crushed (150- to 300- μ m) material. A comparison of the leach rates for these two different particle sizes (Fig. 20) shows that the crushed sample leaches at a lower rate than the monoliths. Recall that this same observation was made for monoliths vs powdered material in static leach tests (see previous section). In the dynamic leach test, however, the difference between the two is not as great.

The data in Fig. 20 were computed on the basis of geometric surface areas.* If the data are replotted on the basis of BET surface areas, the leach rates for the two different samples (i.e., crushed vs monolith) agree very well (Fig. 21). This is illustrated even more clearly in Fig. 22 where just the Cs data are used as an example for comparison.

It can be argued that part of the difficulty in reporting rates based on geometric areas is due to the simplified way the crushed sample surface areas have been calculated. However, the method used probably underestimates the area. For example, studies of the sphericity[†] of granular solids⁴³ show that the average surface area of a particle is about 50% greater than that of a sphere of the same volume. Therefore, correcting the leach rates for the crushed material (to account for the larger area) would produce an even greater difference from those of the monolith samples.

Despite the fact that the dynamic leach rates for crushed and monolith samples agree well when calculated on the basis of a BET surface area, we do not advocate computing leach rates using BET areas. Rather, the "true" leaching surface should be properly determined, as should the effect of sample preparation on it.

MODIFIED IAEA LEACH TESTS

Modified IAEA tests on a crushed SYNROC-D sample (S21S18) were carried out at both LLNL and Australian National University (ANU).⁴⁴

*The geometric, equivalent surface area of the crushed sample is based on the mean, spherical diameter of the sieve fraction.

[†]Sphericity = ratio of the surface area of a sphere to that of a particle (both having equivalent volume).

Figure 21. Comparison of normalized, instantaneous leach rates observed for monolith vs crushed samples when computed using BET surface areas. The tests were conducted on SYNROC-D Sample S21S18 at 75°C in deionized water.

Figure 22. Comparison of normalized instantaneous Cs leach rates for monolith vs crushed samples, based on both geometric and BET surface areas. Note the much closer agreement observed if the rates are computed on the basis of BET areas (an effect discussed in more detail in the text). Tests were done at 75°C in deionized water on sample S21S18.

Figure 23. Normalized leach rates observed during modified IAEA leach testing of Sample S21S18. The data are for crushed samples (100- 200 μm) at 95°C in deionized water.

The results of these tests are summarized in Table 39. The LLNL data were obtained at 90°C, whereas ANU tests were performed at 95°C. A more complete description of the manner in which the tests were performed is given by Ringwood et al.²³

In general, the agreement between the two sets of tests is quite good; all values are within a factor of about 3. Note, in particular, the very good agreement for the Zr values.

The greater surface area associated with crushed material increases the cation concentrations in the leachate. Thus, by the IAEA test it was possible to measure rates for Ti, Zr, and Nd (Fig. 23). These elements are often below detection limits for leach tests using monoliths (e.g., MCC-1 and -2).

The absolute magnitude of the leach rates measured by the modified IAEA tests are probably not comparable to those from MCC tests. These differences stem primarily from the form of the sample (crushed vs monolith) and the water-change conditions. However, the relative differences between leach rates for the various elements generally seem to agree from one leach test to the next. For example, the Cs leach rate is about a factor of 10^3 higher than U for both the MCC-1 and the modified IAEA test. Thus, the modified IAEA tests are a stem primarily from the form of the sample (crushed vs monolith) and the water-change conditions. However, the relative differences between leach rates for the various elements generally seem to agree from one leach test to the next. For example, the Cs leach rate is about a factor of 10^3 higher than U for both the MCC-1 and the modified IAEA test. Thus, the modified IAEA tests are a good indicator of the relative leach rates for the least soluble species (e.g., Nd, Zr, and Ti) compared to the more soluble ones (e.g., Cs and Na).

Note that the modified IAEA data show Ti, Nd, U, and Zr leach rates to be dropping much faster with time than those of Na and Ca (Fig. 23).

Table 39. Results from modified IAEA leach tests at 90 and 95°C on SYNROC-D containing composite sludge (S21S18). The data are for crushed samples using deionized water and the rates are normalized "instantaneous" rates (Eq. [5]).

A. Normalized instantaneous leach rate ($\text{g}/\text{m}^2 \cdot \text{d}$); $T = 95^\circ\text{C}$; 100-200 μm :

<u>Days</u>	<u>U</u>	<u>Nd</u>				
1-3	8.8×10^{-4}	3.5×10^{-3}				
4-11	1.1×10^{-4}	2.9×10^{-4}				
	<u>Na</u>	<u>Al</u>	<u>Zr</u>	<u>Ti</u>	<u>Fe</u>	<u>Ba</u>
1	0.79	0.062	2.5×10^{-4}	9.7×10^{-3}	1×10^{-3}	0.09
2-3	0.98	0.10	1.3×10^{-4}	3.9×10^{-3}	2.7×10^{-4}	0.31
4-7	0.54	0.11	1.0×10^{-4}	4.1×10^{-4}	1.7×10^{-4}	0.061
8-13	0.38	0.061	6.7×10^{-5}	4.6×10^{-4}	1.2×10^{-4}	0.052
	<u>Cs</u>	<u>Ca</u>				
1	1.5	0.14				
2-3	0.30	0.14				
4-6	0.11	0.11				
7-10	0.10	0.11				

B. Normalized instantaneous leach rate ($\text{g}/\text{m}^2 \cdot \text{d}$); $T = 90^\circ\text{C}$; 150-300 μm :

<u>Days</u>	<u>Cs</u>	<u>Ca</u>	<u>Sr</u>	<u>Zr</u>
1-3	0.5	0.063	0.070	4×10^{-4}
3-7	0.03	0.033	0.040	5×10^{-4}
7-14	0.008	--	0.024	7.4×10^{-5}

RADIATION EFFECTS IN SYNROC AND SYNROC MINERALS

There are two general sources of information about radiation effects on SYNROC and its constituent minerals. The first is the study of naturally occurring minerals, analogous to the SYNROC phases. Many of these samples contain dissolved uranium and thorium, and have undergone alpha decay over geologic time. Figure 24 is from Ringwood *et al.*²³ and shows the radiation dose to be expected in zirconolite and perovskite in SYNROC containing 10% commercial high-level waste. Oversby *et al.*^{4,23} have studied naturally occurring samples assigned a location on the calculated curve (Fig. 24) according to the dose of alphas per gram they have received. Note that many of the samples have "equivalent SYNROC ages" greater than 100 million years.

The second source of information on radiation damage effects is irradiation of laboratory-synthesized SYNROC and SYNROC phases by various internal and external methods.

In this section, we offer a brief compilation of published damage on both the naturally occurring and synthesized SYNROC minerals and mineral analogs. The parameters measured include macroscopic swelling, variations in x-ray lattice constants and peak intensities, and changes in leach resistance.

STRUCTURAL EFFECTS

Data on swelling and metamictization (decrease in x-ray peak intensities) have recently been compiled by Van Konynenburg and Guinan⁴⁵ (summarized in Tables 40 and 41). Van Konynenburg and Guinan compared the number of displacements per atom (dpa) required to produce 1% swelling and x-ray metamictization for samples exposed to different displacement (damage) rates. As can be seen, even though the displacement rates varied by a factor of 1×10^{11} between the natural samples and the laboratory irradiations, the dpa from alpha decay required to produce either 1% swelling (Table 40) or to turn the sample x-ray metamict (Table 41) were within a factor of 4. This result is true for both zirconolite and perovskite.* This indicates that structural damage in the natural samples has not annealed significantly during their lifetimes.

* Zirconolite and perovskite are the SYNROC phases subject to alpha recoil damage.

Table 40. Exposure required to produce a 1% increase in volume.⁴⁵

Damage source	Ref.	Sample	Interpolated exposure	dpa	Equiv. alphas/m ³ (x10 ²⁴)	Ionization dose (MGy)	dpa/yr
A. Zirconolite:							
Reactor neutrons ^a	46	CaZrTi ₂ O ₇	4.0 x 10 ²³ n/m ²	0.13	10.6	1.5 x 10 ⁴	10 ¹
^{nat} U + Th alpha-decay	47	Kaiserstuhl zirconolites	8.2 x 10 ²⁴ alphas/m ³	0.10	8.2	1.5 x 10 ³	10 ⁻⁸
²³⁸ Pu alpha-decay	48	cubic CaPuTi ₂ O ₇	2.7 x 10 ²⁴ alphas/m ³	0.034	2.7	500	10 ⁰
²³⁸ Pu alpha-decay	48	Ca(Pu _{0.2} Zr _{0.8})Ti ₂ O ₇	2.7 x 10 ²⁴ alphas/m ³	0.034	2.7	500	10 ⁻¹
²⁴⁴ Cm alpha-decay	49	CaZrTi ₂ O ₇ + 3 wt% ²⁴⁴ Cm	4.0 x 10 ²⁴ alphas/m ³	0.049	4.0	800	10 ⁻¹
B. Perovskite:							
Reactor neutrons ^a	50	CaTiO ₃	2.5 x 10 ²³ n/m ²	0.08	6.6	10 ⁴	10 ¹
Reactor neutrons ^a	46	CaTiO ₃	3.5 x 10 ²³ n/m ²	0.11	9.3	1.5 x 10 ⁴	10 ¹
Reactor neutrons ^b	51	BaTiO ₃	2.5 x 10 ²³ n/m ²	0.03	2.1	10 ⁴	10 ¹
^{nat} U + Th alpha-decay	47	Loparite	3.4 x 10 ²⁴ alphas/m ³	0.04	3.4	700	10 ⁻¹⁰
^{nat} U + Th alpha-decay	47	Baikal + Jacupiranga	5.7 x 10 ²⁴ alphas/m ³	0.07	5.7	10 ³	10 ⁻¹⁰ - 10 ⁻⁵
²⁴⁴ Cm alpha-decay	52	²⁴⁴ CmAlO ₃	1.6 x 10 ²⁴ alphas/m ³	0.02	1.6	350	10 ¹

^a Energy > 1 MeV.

^b Energy > 0.05 MeV.

Table 41. Exposure required to eliminate powder or Laue pattern (x-ray metamict).

Damage source	Ref.	sample	Exposure	Calculated dpa ^b	Displacement equiv. ($\times 10^{25}$ alphas/m ³)	Ionization dose (MGy)	dpa/yr
A. Zirconolite:							
natU + Th alpha	47	Kaiserstuhl zirconolite	$>1.6 \times 10^{25}$ alphas/m ³	>0.20	>1.6	$>3 \times 10^3$	10^{-8}
natU + Th alpha	47	Jacupiranga zirconolite	$<3.4 \times 10^{25}$ alphas/m ³	<0.42	<3.4	$<7 \times 10^3$	10^{-9}
²³⁸ Pu alpha	48	CaPuTi ₂ O ₇	1.3×10^{25} alphas/m ³	0.16	1.3	2.5×10^3	10^0
²⁴⁴ Cm alpha	52	CaZrTi ₂ O ₇ 3 wt% ²⁴⁴ Cm	1.6×10^{25} alphas/m ³	0.20	1.6	3×10^3	10^{-1}
3 MeV Ar ⁺	53	CaZrTi ₂ O ₇	$2-6 \times 10^{19}$ ions/m ²	0.3-0.8	3-7	$1-3 \times 10^3$	10^3
1 MeV electron	54	CaZrTi ₂ O ₇	$>4 \times 10^{25}$ e ⁻ /m ²	>0.13	>1.1	$>10^6$	10^3-10^4
B. Perovskite:							
Reactor neutrons	50	CaTiO ₃	$>6.5 \times 10^{23}$ n/m ² (E > 1 MeV)	>0.21	>1.7	$>2.5 \times 10^4$	10^1
Reactor neutrons	51	BaTiO ₃	$>1.8 \times 10^{24}$ n/m ² (E > 0.15 MeV)	>0.18	>1.5	$>5 \times 10^4$	10^1
natU + Th alpha	47	Baikal perovskites	$>1.1 \times 10^{25}$ alphas/m ³	>0.13	>1.1	$>2.5 \times 10^3$	10^{-10}
natTh alpha	55	Irinite ^a	$<1.3 \times 10^{26}$ alphas/m ³	<1.6	<13	$<3 \times 10^4$	10^{-8}
natU + Th alpha	56	Loparite ^a	$<3.0 \times 10^{25}$ alphas/m ³	<0.37	<3.0	$<7 \times 10^3$	10^{-9}
²⁴⁴ Cm alpha	52	CmAlO ₃	1.6×10^{25} alphas/m ³	0.20	1.6	3.5×10^3	10^1
3 MeV Ar ⁺	53	CaTiO ₃	$10^{19}-10^{20}$ ions/m ²	0.1-1	1.0 - 10	$5 \times 10^2-5 \times 10^3$	10^3
1 MeV e ⁻	54	CaTiO ₃	$>4 \times 10^{25}$ e ⁻ /m ²	>0.13	1.1	$>10^6$	10^3-10^4

^a Exposures based on the most probable ages.⁵⁷^b dpa = displacements per alpha.

Figure 24. Calculated, total alpha dose vs age for SYNROC-C samples containing 10% commercial high-level waste; data are for storage times of 10^3 - 10^6 and 10^6 - 10^9 years. Also shown are equivalent SYNROC ages for natural samples; these ages are based on the alpha dose they have received through geologic time.²³

The damage level in SYNROC containing SRL defense waste is expected to be about 10^{18} alpha/g (5×10^{24} alpha/m³) in a million years. From the data compiled here, it appears that at one million years, both the perovskite and the zirconolite in SYNROC-D will be near the displacement level required to produce x-ray metamictization and, in their single-phase state, would be expected to swell about 2-3%. The volume change of SYNROC-D at this dpa level will depend on the microstructure (i.e., grain size, porosity, and presence of minor phases). It is not predictable from results with other samples. For example, cold-pressed and sintered samples of SYNROC-B swelled three times as much as hot-pressed samples of the same composition⁵⁸ during neutron irradiation.

EFFECTS OF RADIATION DAMAGE ON MINERAL LEACHING

Lead isotopic studies on natural zirconolites and perovskites by Oversby and Ringwood⁴ show that these minerals possess remarkable ability to retain uranium, thorium, and their decay products even after suffering a large degree of radiation damage. By measuring U, Th, and Pb concentrations, and Pb isotopic compositions in these minerals, Oversby and Ringwood calculated three ages using the $^{207}\text{Pb}/^{235}\text{U}$, $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios (Table 42). These calculated ages agreed closely and, thus, are concordant. Concordant ages occur only if the system has been closed with respect to U and Pb since the mineral first crystallized. Thus, concordant Pb/U ages for zirconolites and perovskites indicate that these minerals have retained essentially all their U, Pb, and intermediate daughter products since the minerals formed.

All the zirconolite samples, except one from Sri Lanka (Z5) and another from Jacupiranga (C) were of concordant ages (Table 42). Ringwood *et al.*²³ report the Jacupiranga zirconolite (C) was a crystal extracted from highly decomposed rock; the younger age (compared to A and B) indicated 10% loss of Pb. They point out that this Pb loss is minor when contrasted with the extreme weathering of the host rock. The Sri Lanka Sample Z5 is a fine-grained mixture of zirconolite, baddeleyite, and rutile. These authors suspected the presence of another high U phase (possibly pyrochlore) that contributed to the slight discordance.

The ages of the two perovskite samples from Lake Baikal were concordant. However, a small amount of Pb loss (less than 10%) cannot be completely discounted due to uncertainties in the Pb isotope measurements.

Table 42. Isotopic lead-uranium and lead-lead ages for some naturally occurring perovskite and zirconolites.⁴

Sample	Age ($\times 10^6$ years)		
	$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{207}\text{Pb}/^{206}\text{Pb}$
<u>A. Perovskites</u>			
Baikal	A 464 $\pm$ 2	472 $\pm$ 19	509 $\pm$ 69
	B 461 $\pm$ 3	469 $\pm$ 19	508 $\pm$ 46
<u>B. Zirconolites</u>			
Stavern	296 $\pm$ 2	295 $\pm$ 3	290 $\pm$ 20
Larvik	294 $\pm$ 2	292 $\pm$ 3	272 $\pm$ 22
Jacupiranga	A 133.5 $\pm$ 1.5	130 $\pm$ 5	--
	B 128.5 $\pm$ 1.5	125 $\pm$ 5	--
	C 115 $\pm$ 2	113 $\pm$ 6	--
Russian A	646 $\pm$ 2	648 $\pm$ 2	654 $\pm$ 7
Kola	376 $\pm$ 1	377 $\pm$ 1	379 $\pm$ 3
Sri Lanka	Z1 555 $\pm$ 2	555 $\pm$ 2	554 $\pm$ 2
	Z2 559 $\pm$ 2	560 $\pm$ 2	565 $\pm$ 3
	Z3 555 $\pm$ 2	554 $\pm$ 2	552 $\pm$ 7
	Z4 546 $\pm$ 1	546 $\pm$ 1	543 $\pm$ 3
	Z5 494	503	542 $\pm$ 14

Ringwood et al.²³ report that in leach tests on natural zirconolites and perovskites, at 95 and 200°C, "plateau" (steady state) leach rates were generally established after 7-10 days. Table 43 and Fig. 25 summarize some of the leach rates at 95°C for Ca and at 200°C for Ca and U. The uranium leach rates at 200°C are quite low, all falling between 2×10^{-3} and 3×10^{-4} g-mineral/m²·d. Metamict samples from Sri Lanka have higher leach rates than the younger Kaiserstuhl zirconolite, suggesting a slight U leach rate dependence on radiation dose. (More detailed leach test results can be found in the recent work by Oversby and Ringwood.⁵⁹)

In addition to their work on natural samples, experimenters have investigated ion bombardment of SYNROC or related materials and found no significant increase in leaching due to displacement damage. (These data are summarized in Table 44.)

Barkatt⁶³ has recently reported an increase in SYNROC-D leaching with a gamma-ray field of 9×10^4 rad/h. This increase was accompanied by a pH drop from 5.7 to 4.6-4.9 at the end of each of five 3-day leaching periods. Apparently, these effects were due to radiolysis of the solution, the atmosphere above it, and/or the closed polypropylene centrifuge tubes, which had been used as leaching containers. The exact mechanisms involved are still under study. It is known that nitrogen in contact with an irradiated solution can be converted to nitric acid.⁶⁴ Also, polypropylene is susceptible to gamma radiolysis, which produces hydrogen. Very little air is likely to be available in a sealed repository environment, and there will be considerable chemical buffering in most repository waters. Although the effect observed by Barkatt may not be seen in the repository, it nonetheless needs further study.

In addition to this work, we are also conducting an ongoing laboratory program,⁶⁵ in which SYNROC-D samples are doped with a short-lived Pu isotope at a concentration high enough to create the expected long-term storage alpha decay (10^{18} alpha/g) within a few months. A high ionization dose is also delivered to some of the samples shortly after their preparation to simulate beta-decay in fission products during the first few hundred years. The procedure used for actinide doping was developed by the Materials Characterization Center (test MCC-6).⁶⁶ We will also use MCC-1 tests to evaluate the effects of damage on leach resistance.

Table 43. Results from leach tests of natural zirconolites and perovskites.⁵⁹

	Equiv. alpha dose (α/g)	Bulk sample leach rates ^a (g/m ² ·d)		
		200°C, based on		95°C based on
		Ca	U	Ca
<u>Zirconolites:</u>				
Kaiserstuhl	1.3 x 10 ¹⁸	1 x 10 ⁻¹	4 x 10 ⁻⁴	4 x 10 ⁻³
Sri Lanka, Z1	8.0 x 10 ¹⁹	7 x 10 ⁻³	2 x 10 ⁻³	not deter.
Sri Lanka, Z4	8.0 x 10 ¹⁹	5 x 10 ⁻³	2 x 10 ⁻³	2 x 10 ⁻³
Jacupiranga	7.6 x 10 ¹⁸	1 x 10 ⁻³	not deter.	not deter.
<u>Perovskite:</u>				
Baikal	2.6 x 10 ¹⁸	3 x 10 ⁻¹	3 x 10 ⁻⁴	2 x 10 ⁻³
Magnet Cove, Ark.	--	--	--	4 x 10 ⁻⁷
Wolgidee Hills, W. Aus.	--	--	--	2 x 10 ⁻⁷

^a Calculated by Oversby and Ringwood⁵⁹ using the expression: Leach rate = $(M_{aq}/M_s)(W/t \cdot A)$ where M_{aq} = quantity of ion in leach solution, M_s = quantity of ion in solid sample (adjusted for loss in previous leaching), W = initial weight of solid test sample, t = time, and A = surface area.

Figure 25. Leach rates (based on Ca and U) for some natural SYNROC mineral analogs. The leach test was a modified IAEA test using crushed material (100–200 μm) and deionized water.²³

Table 44. Summary of experiments involving ion bombardment followed by leaching.

Experimenters:	Sethi and Bates ⁶⁰	Primak ⁶¹	Northrup, Arnold and Headley. ⁶²
Material:	SYNROC-C (10% simulated waste loading)	SYNROC-B	Hydrous calcium titanate waste form.
Irradiating particles:	3.5 MeV He ⁺ 250 keV Kr ⁺	320 keV Xe ⁺	30-250 keV Pb ions.
Dose:	10 ²⁰ ions/m ² max	0.25-10 Microcoulombs/cm ²	10 ²² -10 ²⁵ alphas/m ³ (equiv).
Leachant:	Deionized water	Saline water	Deionized water.
Leaching method:	MCC-1; (28 d)	Pyrex containers (2 h)	Teflon containers, (24 h)
Leaching temperature:	90°C	Boiling	Room temp.
Diagnostic technique:	Leachate analysis by ICP, DCP, and AA	Sample surface examination	Rutherford backscattering from sample.
Results:	No significant increases in leach rate were observed.	No changes in surface contours were noted (leachate solutions were not analyzed).	No significant change in concentration profiles with depth; leachate not analyzed.

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APPENDIX A

RESULTS FROM LEACH TESTS ON
SYNROC-D CONTAINING SIMULATED
SAVANNAH RIVER SLUDGES

Table A1. Normalized elemental mass loss (NL_i ; g/m^2) and pH change for SYNROC-D containing simulated SRP High-Fe sludge and Cs added in presynthesized hollandite host (Sample S26SAN). Data are from MCC-1 leach tests at 90°C up to 28 days.

Element	Deionized water				Silicate	
	3d	7d	14d	28d	water 28d	Brine 28d
Al	4.41	7.38	7.88	9.52	3.76	2.00
Fe	0.010	0.012	0.11	0.005	0.012	0.086
Mn	0.073	0.084	0.021	0.062	0.010	--
Si	11.6	16.3	20.7	23.5	6.77 ^a	14.9
Sr	3.35	4.36	5.77	6.55	1.39	19.8
Ca	0.85	2.03	2.75	1.70	0.54	4.88
Na	10.2	15.7	23.3	23.0	3.32 ^a	-- ^a
Cs	2.96	1.39	1.34	3.00	2.87	<2.6
Mass loss (g/m^2)	1.92	1.87	3.76	3.07	4.20	2.18
pH ^b	5.8	5.8	5.8	6.0	8.0	6.2
Δ pH	0	0	0	+0.2	+0.8	0

^a Leachant component (may affect accuracy of result).

^b Measured by pH paper.

Table A2. Normalized elemental leach rates (LR_i ; $g/m^2 \cdot d$) for SYNROC-D containing simulated SRP High-Fe sludge and Cs added in presynthesized hollandite host (Sample S26SAN). Data are from MCC-1 leach tests at $90^\circ C$ up to 28 days.

Element	Deionized water				Silicate	Brine
	3d	7d	14d	28d	water 28d	28d
Al	1.47	1.05	0.56	0.340	0.13	0.071
Fe	0.0033	0.0017	0.0079	0.0002	0.0004	0.0031
Mn	0.024	0.012	0.0015	0.0022	0.0004	--
Si	3.87	2.33	1.48	0.84	0.24 ^a	0.53
Sr	1.12	0.62	0.41	0.23	0.050	0.71
Ca	0.28	0.29	0.20	0.061	0.019	0.17
Na	3.40	2.24	1.66	0.82	0.12 ^a	-- ^a
Cs	0.99	0.20	0.096	0.11	0.10	<0.093
Mass loss ($g/m^2 \cdot d$)	0.64	0.27	0.27	0.11	0.15	0.078

^a Leachant component (may affect accuracy of result).

Table A3. Normalized elemental mass loss (NL_i ; g/m^2) and pH change for SYNROC-D containing simulated SRP High-Fe sludge (Sample S30). Data are from MCC-1 leach tests at $90^\circ C$ up to 28 days.

Element	Deionized water ^a				Silicate water ^b	Brine ^b
	3d	7d	14d	28d	28d	28d
Al	4.62	5.50	5.78	9.25	3.17	1.34
Fe	0.034	0.025	0.020	0.019	--	0.12
Mn	0.14	0.21	0.30	0.44	0.13	0.25
Ni	0.51	1.01	0.76	1.43	0.36	5.24
Si	10.1	14.8	17.9	24.9	5.93 ^c	6.41
Sr	5.31	9.04	10.5	15.8	5.11	<25
Ca	1.51	2.22	2.57	3.72	1.62	--
Na	9.82	14.2	15.5	23.5	2.76 ^c	-- ^c
Cs	7.84	12.2	17.0	22.4	7.96	6.94
Mass loss (g/m^2)	1.58	2.16	2.73	3.39	0.84	1.28
pH ^d	5.8	5.8	5.8	6.0	7.2	6.2
ΔpH	0	0	0	+0.2	0	0

^a Average of two samples.

^b Average of three samples.

^c Leachant component (may affect accuracy of result).

^d Measured by pH paper.

Table A4. Normalized elemental leach rate (LR_i ; $g/m^2 \cdot d$) for SYNROC-D containing simulated SRP High-Fe sludge (Sample S30). Data are from MCC-1 leach tests at $90^\circ C$ up to 28 days.

Element	Deionized water ^a				Silicate water ^b	Brine ^b
	3d	7d	14d	28d	28d	28d
Al	1.54	0.79	0.41	0.33	0.11	0.048
Fe	0.012	0.004	0.001	0.0007	--	0.0043
Mn	0.044	0.031	0.022	0.016	0.0046	0.0090
Ni	0.17	0.15	0.054	0.051	0.013	0.19
Si	3.36	2.11	1.28	0.89	0.21 ^c	0.23
Sr	1.77	1.29	0.75	0.56	0.18	<0.9
Ca	0.51	0.32	0.18	0.13	0.058	--
Na	3.30	2.03	1.12	0.84	0.099 ^c	-- ^c
Cs	2.62	1.74	1.21	0.80	0.28	0.25
Mass loss ($g/m^2 \cdot d$)	0.525	0.309	0.195	0.121	0.030	0.046

^a Average of two samples.

^b Average of three samples.

^c Leachant component (may affect accuracy of result).

Table A5. Normalized elemental mass loss (NL_i ; g/m^2) and pH change for SYNROC-D containing simulated SRP High-Fe sludge (Sample S30). Data are from MCC-1 leach tests at 40°C and 28 days.

Element	Deionized water ^a	Silicate water ^a	Brine ^a
	28d	28d	28d
Al	0.196	0.196	0.504
Fe	<0.014	0.0056	0.040
Mn	0.039	0.028	--
Ni	0.644	0.577	2.60
Si	3.98	1.29	--
Sr	1.43	0.53 ^b	<13.3
Ca	0.518	0.143	0.59
Na	3.50	9.02 ^b	--
Cs	3.22	0.644	2.52
Mass loss (g/m^2)	0.491	0.243	0.253
pH ^c	5.8	7.2	6.2
Δ pH	0	0	0

^a Average of three samples.

^b Leachant component (may affect accuracy of result).

^c Measured by pH paper.

Table A6. Normalized elemental leach rates (LR_i ; $\text{g/m}^2 \cdot \text{d}$) for SYNROC-D containing simulated SRP High-Fe sludge (Sample S30). Data are from MCC-1 leach tests at 40°C and 28 days.

Element	Deionized water ^a	Silicate water ^a	Brine ^a
	28d	28d	28d
Al	0.007	0.007	0.018
Fe	<0.0005	0.0002	0.0014
Mn	0.001	0.001	--
Ni	0.023	0.021	0.093
Si	0.142	0.046 ^b	--
Sr	0.051	<0.019	0.47
Ca	0.019	0.005	0.021
Na	0.125	0.322 ^b	--
Cs	0.115	0.023	0.090
Mass loss ($\text{g/m}^2 \cdot \text{d}$)	0.0175	0.0087	0.0090

^a Average of three samples.

^b Leachant component (may affect accuracy of result).

Table A7. Normalized elemental mass loss (NL_i ; g/m^2) and pH change for SYNROC-D containing simulated SRP High-Fe sludge (Sample S30). Data are from MCC-2 leach tests at $150^\circ C$ and 28 days.

	Deionized water ^a	Silicate water ^b	Brine ^a
Element	28d	28d	28d
Al	16.0	47.0	0.34
Fe	0.017	0.31	1.48
Mn	0.56	2.29	3.11
Ni	0.34	2.68	6.72
Si	79.8	112.3 ^c	80.4
Sr	45.6	75.6	50.9
Ca	12.3	16.9	15.1
Na	74.8	104.4 ^c	-- ^c
Cs	79.5	105.3	60.2
Mass loss ($g/m^2 \cdot d$)	23.90	18.29	4.47
pH ^d	6.0	5.7	6.2
ΔpH	+0.2	-1.5	0

^a Average of two samples.

^b Average of three samples.

^c Leachant component (may affect accuracy of result).

^d Measured by pH paper.

Table A8. Normalized elemental leach rates (LR_i ; $g/m^2 \cdot d$) for SYNROC-D containing simulated SRP High-Fe sludge (Sample S30). Data are from MCC-2 leach tests at $150^\circ C$ and 28 days.

Element	Deionized water ^a	Silicate water ^b	Brine ^a
	28d	28d	28d
Al	0.57	1.68	0.012
Fe	0.0006	0.011	0.053
Mn	0.020	0.082	0.11
Ni	0.012	0.096	0.24
Si	2.85	4.01 ^c	2.87
Sr	1.63	2.70	1.82
Ca	0.44	0.60	0.54
Na	2.67	3.73 ^c	-- ^c
Cs	2.84	3.76	2.15
Mass loss ($g/m^2 \cdot d$)	0.855	0.653	0.160

^a Average of two samples.

^b Average of three samples.

^c Leachant component (may affect accuracy of result).

Table A9. Summary of results from 28-day MCC-1 leach tests on SYNROC-D samples containing simulated SRP composite, High-Fe, and High-Al waste sludges. Tests were conducted at 90°C. The normalized elemental leach rates ($\text{g/m}^2 \cdot \text{d}$) are shown.

Element	Composite		High-Fe		High-Al
	S21S18 ^a	S29 ^b	S26SAN ^a	S30 ^b	S31 ^b
A. Deionized water					
Al	0.17	0.18	0.34	0.33	0.022
Si	0.55	0.54	0.84	0.89	1.70
Na	0.90	0.62	0.82	0.84	3.46
Cs	0.10	0.79	0.11	0.80	3.86
Sr	0.34	0.38	0.23	0.56	<0.13
Ca	0.13	0.16	0.060	0.13	0.079
U	1.9×10^{-4}	1.1×10^{-4}	<0.005	<0.005	<0.07
B. Silicate water					
Al	0.050	0.070	0.13	0.08	0.021
Si	0.20	0.19	0.24	0.15	0.64
Na	0.63	0.33	0.12	0.07	1.24
Cs	0.11	0.54	0.10	0.20	2.95
Sr	0.06	0.099	0.05	0.13	<0.13
Ca	0.035	0.061	0.019	0.04	0.020
U	6.4×10^{-4}	3.4×10^{-4}	<0.005	<0.005	<0.07
C. Brine					
Al	0.035	0.0046	0.071	0.03	ND
Si	0.12	0.22	0.53	0.16	ND
Na	ND ^c	ND	ND	ND	ND
Cs	0.09	0.45	<0.09	0.17	1.50
Sr	0.25	<0.1	<0.7	0.05	<3.2
Ca	ND	ND	ND	ND	ND
U	3.5×10^{-3}	--	<0.005	<0.005	<0.07

^a Cs contained in presynthesized hollandite phase.

^b Cs contained in in situ-formed nepheline phase.

^c ND = not detected.