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

V. M. Oversby

September 1982

Lawrence
Livermore
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UCRL-53326
Distribution Category UC-70

UCRL--53326

DE83 002464

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Manuscript date: September 1982

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ABSTRACT

SYNROC C is a titanate ceramic waste form designed to contain the waste generated by the reprocessing of commercial nuclear reactor fuel. The properties of SYNROC C are described with particular emphasis on the distribution of chemical elements in SYNROC, the fabrication of good quality specimens, and the chemical durability of SYNROC. Data obtained from testing of natural mineral analogues of SYNROC minerals are briefly discussed. The information available on radiation effects in SYNROC in relation to structural alteration and changes in chemical durability are summarized.

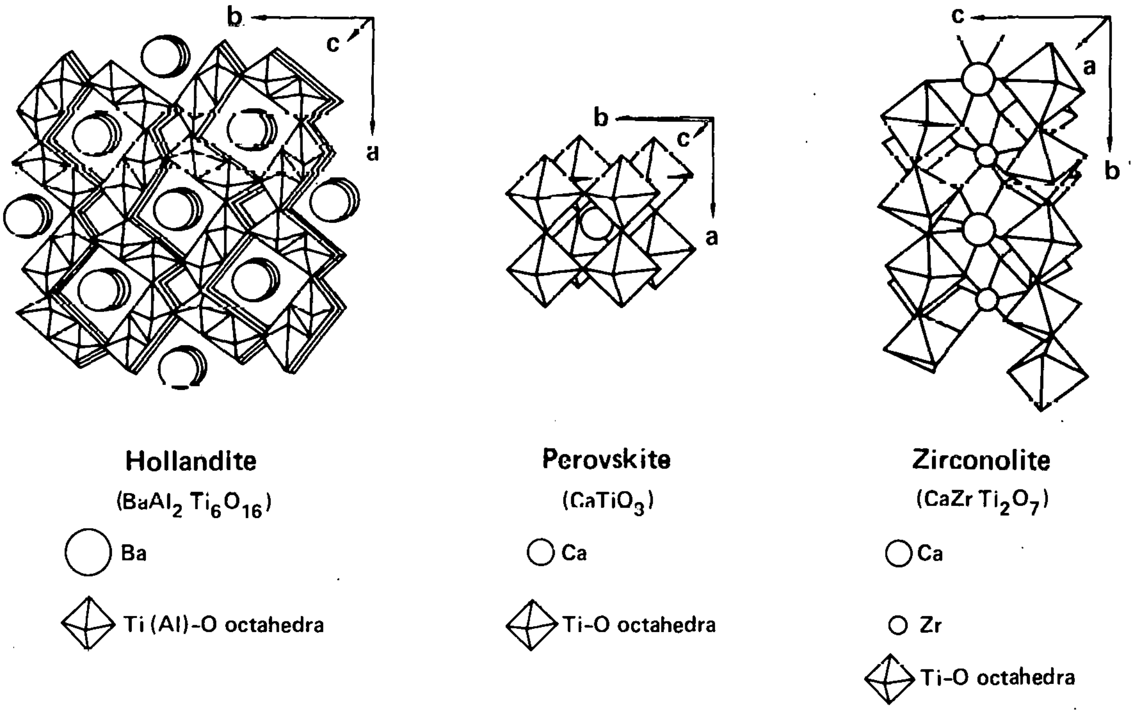
INTRODUCTION

SYNROC (<u>syn</u>thetic <u>roc</u>k) is a titanate ceramic waste form designed to immobilize high-level nuclear reactor wastes. SYNROC was first proposed and developed as a waste form by Ringwood.[1] Early development work led to improvements in the waste form mineralogy and elimination of phases which had inferior resistance to leaching.[2,3] SYNROC was designed to immobilize the acid stream waste resulting from PUREX reprocessing procedures. SYNROC containing PUREX type waste (or simulated waste) is called SYNROC C (C for commercial, since waste of this type would be generated by reprocessing of commercial nuclear power reactor fuels). SYNROC made with the same chemical composition, but without real or simulated waste, is referred to as SYNROC B. The original, superseded formulation is SYNROC A. A specialized formulation with different mineralogy was designed for the high Na-, Al-, Fe-containing wastes produced at the Savannah River defense reprocessing facility. The defense waste formulation is called SYNROC D. A detailed description of SYNROC D fabrication and properties has been given by Campbell et al.[4] This report will deal exclusively with SYNROC B and C.

SYNROC was proposed as an alternative to borosilicate glass as a medium for high-level waste immobilization. The advantages claimed for SYNROC over glass included the use of low solubility titanate minerals as the host for waste immobilization, incorporation of waste as dilute solid solutions in the resistant host minerals, and the use of minerals which occur in nature. The latter feature meant that natural minerals could be studied to aid in prediction of long-term behavior of SYNROC under geologic storage conditions.

The mineral assemblage in SYNROC B and C consists of three minerals which act as hosts for the waste elements, a metal phase which contains some fission products, and rutile (TiO_2) which does not contain waste elements. The SYNROC minerals are zirconolite ($CaZrTi_2O_7$), perovskite ($CaTiO_3$), and Ba-hollandite ($BaAl_2Ti_6O_{16}$). Crystal structures of these minerals are shown in Fig. 1 (modified from Ref. 4). The waste elements are incorporated into the minerals by substitution for Ca, Zr, Ti, Ba, or Al, thus forming dilute solid solutions in the mineral phases.

This report will summarize the available information on SYNROC C fabrication, phase chemistry, physical properties, behavior in aqueous solutions, and response to radiation dosage.



Hollandite ($BaAl_2Ti_6O_{16}$)

Perovskite ($CaTiO_3$)

Zirconolite ($CaZrTi_2O_7$)

Figure 1. Crystal structure of SYNROC minerals.

DESCRIPTION OF COMMERCIAL HIGH-LEVEL WASTE

The exact composition of high-level radioactive waste, both in terms of chemical and isotopic composition, depends on a number of variables. These variables can be divided into two main types: those which are determined by the history of the fuel element and those which are controlled by the reprocessing method.

In 1977 Mendel et al.[5] described the range of expected compositions in high-level radioactive waste. Two examples of their estimates are given in Table 1. Both examples presume fuel which originally contained 3.3% ^{235}U and which was burned to 33,000 MWd/MTU. PW-4b represents waste from a PUREX plant operating under optimized conditions resulting in recovery of 99.9% of the U and Pu from the fuel. PW-7a assumed 99.0% removal of U and Pu from the waste stream and includes some Intermediate Level Waste (ILW) which contributes large amounts of Na and P. Work on SYNROC has generally used the PW-4b type waste, frequently simplified by elimination of trace components such as Ag and Cd, and by combination of rare earth elements into a few representative elements. Actinide elements are represented in simulated waste compositions by natural or 235-depleted uranium.

Slate et al.[6] have recently reviewed the types of waste to be expected in the reprocessing of commercial reactor fuels. Their reference waste composition is given in Table 1 labelled as RWC. This composition is based on the operational flow sheet for the Allied General Nuclear Services (AGNS) plant at Barnwell, South Carolina, which also was the basis for the PW-7a composition. The AGNS flow sheet combines high-level waste (HLW) which contains 99% of the fission products, Np, Cm, and Am, plus 1% or less of the U and Pu originally present in the spent fuel with ILW generated by clean-up procedures carried out on the purified U + Pu fraction, solvent regeneration procedures, process vessel flushes, and decontamination procedures. In the combined HWL + ILW composition (RWC), the true high-level waste consitutes 54.2% of the waste, and the nonradioactive process chemicals are 45.8% of the waste. By contrast, for "clean" PUREX waste which does not contain ILW, the process chemicals account for only 6.5% of the final HLW waste stream. Thus, addition of ILW to HWL increases by a factor of approximately 1.9 the amount of waste which must be treated as HLW.

Table 1. Estimated high level waste composition, kg/MTU.

	PW-4b	PW-7a	RWC
Process chemicals			
Gd_2O_3	--	10.360	25.827
Fe_2O_3	1.511	3.022	1.143
Cr_2O_3	0.345	0.345	0.292
NiO	0.141	0.141	0.127
MnO_2	--	--	0.221
ZrO_2	--	--	0.338
P_2O_5	0.672	6.339	5.007
Na_2SO_4	--	--	0.037
NaCl	--	--	0.181
Na_2O	--	6.872	6.634
Sub Total	2.669	27.079	39.807
Fission Products			
SeO_2	--	--	0.077
Rb_2O	0.354	0.354	0.371
SrO	1.059	1.059	0.946
Y_2O_3	0.598	0.598	0.564
ZrO_2	4.944	4.944	4.723
MoO_3	5.176	5.176	4.938
Tc_2O_7	1.291	1.291	1.196
RuO_2	2.972	2.972	2.871
Rh_2O_3	0.480	0.480	0.572
PdO	1.483	1.483	1.613
Ag_2O	0.088	0.088	0.085
CdO	0.097	0.097	0.128
SnO_2	--	--	0.116
TeO_2	0.725	0.725	0.599
Cs_2O	2.880	2.880	2.621
BaO	1.567	1.567	1.762

Table 1. (Continued).

	PW-4b	PW-7a	RWC
La_2O_3	1.480	1.480	1.407
CeO_2	3.323	3.323	2.859
Pr_6O_{11}	1.482	1.482	1.329
Nd_2O_3	4.522	4.522	4.628
Pm_2O_3	0.123	0.123	0.044
Sm_2O_3	0.924	0.924	0.961
Eu_2O_3	0.200	0.200	0.166
Gd_2O_3	0.137	0.137	0.127
Sub Total	35.905	35.905	34.703
Actinides			
U_3O_8	1.169	11.689	11.278
NpO_2	0.865	0.865	0.497
PuO_2	0.010	0.103	0.093
Am_2O_3	0.181	0.181	0.465
Cm_2O_3	0.040	0.040	0.027
Sub Total	2.265	12.878	12.360
Grand Total	40.839	75.862	86.870

The following options are available to the operators of a reprocessing facility:

1. Combine ILW and HLW streams and solidify as one product.
2. Separately treat ILW and HWL giving--
   a. Solidified HLW containing fission products plus actinides.
   b. Solidified ILW containing process chemicals plus a small amount of actinides.

Separately solidified ILW would contain much lower levels of radioactivity than either HLW alone or combined ILW + HLW, but it would probably contain sufficient activity to be classified as a transuranic waste (TRU, containing greater than 100 nCi of alpha-emitting actinides other than uranium per gram of waste). This TRU waste would probably require geologic repository disposal. The most cost effective treatment of waste streams if all costs including packaging, handling, and ultimate repository storage are considered is not obvious. We must, therefore, consider that commercially produced HLW might have any composition between the extremes represented by PW-4b and RWC.

PREPARATION OF SYNROC C SAMPLES

There are two fundamentally distinct chemical methods which have been used to prepare SYNROC C samples. The first method, which will be referred to as the Oxide Route, involves mixing of Al, Zr, Ca, Ba, and Ti as finely divided solids by either simple mixing or techniques such as ball milling under alcohol. The chemical forms generally used are anatase (TiO_2), finely divided ZrO_2, $Al(OH)_3$, $CaCO_3$ and $BaCO_3$. If carbonates are used, the oxide-carbonate precursor is mixed with water to form a slurry, and nitric acid is added to decompose the carbonates. Waste solutions are then added to the oxide-nitrate slurry, and the mixture is dried by flash evaporation, spray drying, or fluid bed calcining. In the case of the first two methods, the nitrates are then decomposed by heating in air at approximately 600°C. For some samples oxidation state is then controlled by heating in a reducing atmosphere such as Ar-4% H_2 or CO/CO_2 gas mixtures at approximately 800 to 850°C.

The second fabrication method was developed by R. G. Dosch of Sandia Laboratories,[7] and will be referred to as the "Sandia Process." This process involves the use of organometallic compounds of Ti and Zr to make a SYNROC precursor material. Waste solutions are added to the precursor material with sufficient excess water to make a mixture with the texture of wet sand. Typically, the precursor will absorb 2 to 3 times its weight of liquid. The precursor plus waste mixture is dried at approximately 100°C to remove the bulk of the water, and then calcined in air at 650 to 750°C. Redox control may be achieved by a further calcination at 800 to 850°C in a reducing atmosphere, or by adding 2 to 3% of fine Ti metal to the SYNROC plus waste after calcining.

Densification of SYNROC samples may be accomplished by several methods. The most frequently used technique is hot uniaxial pressing in graphite dies, either with or without a metal container for the sample. Densities which are 99% or more of theoretical density can be easily achieved provided care is taken to establish the correct pressing temperature. Sandia process SYNROC with 10% simulated waste produced high density samples when pressed at 1170°C. Oxide route samples require 1200°C to produce equivalent densities. For samples with 20% waste, pressing temperatures are 20 to 30C° lower than those for 10% waste samples. Pressures used have been in the range 1000 to 4000 psi.

Other hot pressing techniques are being investigated for commercial scale SYNROC fabrication. They include hot isostatic pressing and "in-can" hot pressing. In-can hot pressing is a uniaxial pressing method being developed by the Australian Atomic Energy Commission.[8] Small cans of SYNROC are loaded into a larger outer canister which serves as the support during pressing, replacing the conventional graphite die. Samples with final dimensions of 11.5-cm diameter by 90-cm length have been produced with density close to theoretical density (Reeve[9]).

An investigation of SYNROC densification by sintering has recently been carried out at Argonne National Laboratory.[10] Sintering was done in a controlled atmosphere of CO/CO_2 gas with ratios ranging from $CO/CO_2 = 0.005$ to 100. High-density samples were achieved when CO/CO_2 was greater than or equal to 10. As will be seen in later sections, the properties of samples sintered under these conditions are similar to those of good quality hot pressed samples.

Several chemical compositions have been recommended as "optimum" for SYNROC precursor. In addition, each laboratory has added its own variations to the basic recipe. Table 2 lists some of the more frequently used compositions. As will be seen in subsequent sections, variations in starting material with the ranges given in Table 2 do not seem to affect product quality.

The chemical compositions of simulated waste solutions used to make SYNROC samples have generally been similar to PW-4b (see Table 1). Again, variations have occurred due to elimination of some elements (such as Tc, Ru, Ag, Se), combination of rare earth elements into a representative subset to simplify later chemical analysis, increasing U content to allow for less efficient extraction during PUREX operations, and addition of Re to act as an analog for Tc. Table 3 gives the composition of SYNROC samples with waste loadings ranging from 9 to 16% made from the ANU basic composition (see Table 2), but two different waste solutions. Again, no differences in product performance during leach testing could be seen due to variations in the waste composition.

Table 2. SYNROC composition, wt% before waste addition.

	TiO_2	ZrO_2	Al_2O_3	CaO	BaO	Reference
AAEC[a]	59.5	11.4	6.0	15.9	7.2	8
ANL[b]	57	11	10	13	9	10
ANU[c]	58.8	10.8	7.5	15.0	7.8	11
LLNL[d]	57.2	12.8	5.5	16.2	8.3	12

[a] AAEC = Australian Atomic Energy Commission.
[b] ANL = Argonne National Laboratory.
[c] ANU = Australian National Laboratory.
[d] LLNL = Lawrence Livermore National Laboratory.

Table 3. SYNROC compositions in wt% after waste addition.

Oxide or element	SP[a] - 9%[b]	Oxide or element	SP - 16%	OX - 10%
TiO_2	57.65	TiO_2	57.65	56.41
Al_2O_3	6.10	Al_2O_3	4.82	4.68
CaO	12.18	CaO	9.62	12.40
ZrO_2	9.47	ZrO_2	8.99	10.20
BaO	6.65	BaO	5.69	6.04
La_2O_3	0.23	P_2O_5	0.34	0.21
Pr_2O_3	0.22			
Nd_2O_3	0.76	Nd_2O_3	2.61	1.63
Sm_2O_3	0.18	Sm_2O_3	0.53	0.33
Gd_2O_3	1.60			
Eu_2O_3	0.03			
Fe_2O_3	0.34	FeO	0.64	0.40
NiO	0.02	NiO	0.10	0.06
Rb_2O	0.06	Rb_2O	0.14	0.09
SrO	0.14	SrO	0.45	0.28
Y_2O_3	0.09	Y_2O_3	0.26	0.16
Ag_2O	0.01			
CdO	0.03			
U_3O_8	1.79	UO_2	0.96	0.60
Cs_2O	0.41	Cs_2O	1.23	0.77
Cr_2O_3	0.04	Cr_2O_3	0.14	0.09
Ce_2O_3	0.45	CeO_2	2.05	1.28
Rh	0.08			
Ru	0.32	ReO_2	1.26	0.79
MoO_3	0.80	MoO_2	2.21	1.38
Pd	0.23			
TeO_2	0.10	TeO_2	0.30	0.19
SeO_2	0.003	Ti		2.0
	100.00		100.00	100.00

[a] (SP = Sandia Process chemistry; OX = Oxide route chemistry. Percentage given is %waste in sample).

[b] Composition supplied by R. G. Dosch, Sandia Laboratories: Cs verified by ANU using atomic absorption on dissolved sample; Ti, Al, Ca, Zr, Ba, U verified by electron microprobe analyses.

MINERAL PHASE CHARACTERIZATION

The mineral assemblage produced in properly prepared SYNROC C samples contains five major phases. Perovskite, hollandite, and zirconolite are formed in roughly equal amounts and constitute about 80% of the sample. Rutile is generally present as 5 to 10% of the sample, and a mixed metal phase accounts for about 5% of the sample. The remaining 5% consists of minor phases such as aluminates and Ti_3O_5 which is formed when large amounts of Ti metal are used for redox control. The excess Ti metal which is not required for reducing elements (such as Mo, Ru, and Tc) to the metallic state reacts with Ti^{+4} to form Ti^{+3}. Some Ti^{+3} replaces Al^{+3} in the hollandite structure, and the released Al^{+3} forms aluminates. If large amounts of Ti^{+3} are present a Ti_3O_5 phase forms. The presence of ZrO_2 as a separate phase indicates an unequilibrated sample. This problem can occur due to use of too low a temperature for densification, or may be due to insufficient mixing during precursor preparation. Samples containing ZrO_2 as a separate phase usually have inferior leaching properties.

Table 4 shows the distribution of waste elements among the SYNROC phases. Rutile, aluminates, and Ti_3O_5 do not contain significant amounts of waste elements. For elements which can exhibit more than one oxidation state the primary host mineral may be different for different oxidation states. The oxidation states which are expected in properly prepared SYNROC C are (III) for all rare earth elements except Eu which will be (II), (III) for all actinides except U and Th which will be (IV), Np which may also be (IV), and (0) for Mo and Tc.

Hot pressing conditions which are used to prepare SYNROC samples with high chemical durability give mineral grain sizes of a micron or less. These fine-grained samples are not suitable for electron microprobe chemical analyses. In order to study the distribution of chemical elements between phases, samples were prepared at ANU in a Boyd piston cylinder apparatus using slightly higher temperatures than normal hot pressings to give larger grain growth. Electron microprobe data for these samples (B8654, 275, 8803 and 8806) are given in Tables 5 through 8. Sample SO8HIP1A was prepared at LLNL by hot isostatic pressing at 1200°C and yielded grains of sufficient size for microprobe analysis.

Table 4. Distribution of principal high-level waste elements between coexisting SYNROC phases.[a]

Hollandite	Zirconolite	Perovskite	Metal
Cs	U (IV)[b]	Na	Ru
Rb	Th (IV)	Sr	Tc
K	Pu (IV)	Pu (III)	Mo
Ba	Cm (IV)	Am (III)	Ni
Fe (II)	Am (IV)	Cm (III)	Pd
Cr (III)	Np (IV)	Np (III)	Rh
[Ni][c]	[ACT[d] (III)]	REE (III)	Te
[Mo (IV)]	[REE[e] (III)]	[ACT (IV)]	S
	[Sr]		[Fe]

[a] Data from Ref. 13.
[b] (II), (III), (IV) are oxidation state numbers.
[c] Values in [] indicate secondary host which will contain smaller amount of element than primary host.
[d] ACT = Actinide Elements.
[e] REE = Rare Earth Elements.

Table 5. Perovskite compositions in SYNROC samples, wt% oxide.

	Sample[a]				
	1	2	3	4	5
TiO_2	55.6	56.1	60.1	59.7	55.4
ZrO_2	0.2	0.2	0.8	0.6	0.5
UO_2	0.2	<0.1	0.4	0.5	1.4
Al_2O_3	1.1	0.7	1.3	1.0	<0.1
REE_2O_3	5.5	5.6	--[b]	--[b]	6.7
FeO	3.1	1.3	0.1	0.2	0.1
CaO	34.8	35.0	37.1	37.6	29.7
SrO	0.2	0.6	1.1	1.4	0.7
BaO	--[c]	--[c]	--[c]	--[c]	0.3

[a] Sample descriptions:

1.	B8654	10% waste, Fe capsule, oxide mix + 5% Fe metal.
2.	275	10% waste, Fe capsule, oxide mix, no Fe metal.
3.	8803	10% waste, Fe capsule, oxide mix + 1% Ti metal.
4.	8806	10% waste, Fe capsule, oxide mix + 2% Ti metal.
5.	S08HIP1A	10% waste, Ni capsule, oxide mix, no metal added.

Analysts:
Samples 1 through 4, N. Ware, Australian National University.
Sample 5, F. Ryerson, Lawrence Livermore National Laboratory.

[b] Not analysed for.

[c] Below detection limits.

Table 6. Zirconolite compositions in SYNROC samples, wt% oxide.

	Sample[a]				
	1	2	3	4	5
TiO_2	46.2	45.5	51.2	51.5	48.7
ZrO_2	31.1	32.5	28.7	27.7	34.5
UO_2	1.8	1.3	1.3	1.4	0.7
Al_2O_3	2.2	2.5	2.8	2.1	2.2
REE_2O_3	~1	1.1	--[b]	--[b]	0.8
FeO	5.1	2.8	0.4	0.5	0.3
CaO	12.6	13.4	14.9	15.0	13.8
SrO	--[c]	0.3	0.2	0.2	0.1
BaO	--[b]	--[b]	--[b]	--[b]	0.2

[a] For descriptions of samples, see Table 5.
[b] Not analysed for.
[c] Below detection limits.

Table 7. Hollandite compositions in SYNROC samples, wt% oxide.

	Sample[a]		
	1	2	5
TiO_2	69	71	66.5
ZrO_2	0.3	0.3	0.6
MoO_2	<0.1	<0.1	--
Al_2O_3	4.6	5.1	9.8
FeO	6.5	2.8	0.8
CaO	0.3	0.4	0.9
BaO	18	18	18.5
Cs_2O	0.8	1.4	1.25

[a] Hollandite in samples 3 and 4 too fine-grained to analyse.
[b] For sample descriptions, see Table 5.

Table 8. Aluminate compositions in SYNROC samples, wt% oxide.

	Sample[a]				
	1	2	3	4	5
TiO_2	28.2	13.8	19.8	21.1	9.6
Al_2O_3	46.3	70.8	70.8	68.7	78.9
FeO	14.1	8.7	2.8	2.7	4.1
CaO	9.8	6.3	6.5	6.8	4.4

[a] For sample descriptions, see Table 5.

The composition of minerals in SYNROC depends on the metal used to achieve redox control as well as on the redox state during pressing. The mineral composition data shown in Tables 5 through 8 cover four basic situations:

- Sample 1 - High Fe content produced by the combination of Fe capsule plus added Fe; strongly reducing conditions (Fe/FeO).
- Sample 2 - Moderate Fe produced by Fe capsule; strongly reducing conditions (Fe/FeO).
- Samples 3 and 4 - Low Fe, redox control by adding Ti metal; strongly reducing conditions (Ti^{+3}/Ti^{+4}).
- Sample 5 - Low Fe, redox control by Ni capsule; mildly reducing conditions (Ni/NiO).

Samples run in Fe capsules with Ti metal showed very little tendency for Fe to migrate from the capsule into the sample during the run. Samples run in Fe capsules without added Ti, but with or without added Fe, always showed strong migration of Fe from the capsule into the samples. This meant that samples 1 and 2 had higher total FeO content in the finished samples than did samples 3 through 5. Comparison of perovskite, zirconolite, and hollandite mineral analyses in Tables 5, 6, and 7 clearly shows the effect of the higher FeO in these samples. Also, the aluminate phases found in samples 1 and 2 (Table 8) contain higher FeO than those found in samples 3 through 5.

The nature of the aluminate phase found in SYNROC depended strongly on redox state and FeO content of the sample. The aluminate formed when Ti metal is used as the reducing agent (samples 3 and 4, Table 8) probably contains Ti^{+3} substituting in the Al^{+3} sites and is probably the same structural phase as the higher Al, lower Ti phase formed in the nickel capsule sample (sample 5, Table 8). Samples run in Fe capsules without Ti metal produced aluminates which varied in composition and probably represented several different crystal structures. Sample 2 contained a dispersed metal phase which contained Fe, Mo, and Re. Rhenium was included in the sample because its chemical behavior is almost identical to that of Tc. It is not possible that the FeO shown in the aluminate analysis for sample 2 contains any Fe^{+3} in the Al^{+3} site since this would be incompatible with the presence of Fe metal. It is also unlikely that the higher FeO in that sample represents any included metal phase since several microprobe analyses of different grains gave the same composition. Therefore, the aluminate in sample 2 is probably a distinct mineral, different in structure from that found in samples 3 through 5.

Perovskite analyses show that partitioning of Sr into perovskite was most efficient in samples 3 and 4. The high FeO content in samples 1 and 2 may have affected the ability of the structure to accept Sr. The UO_2 content of the perovskite in sample 5 is higher than that in the other samples, and the partitioning of uranium between zirconolite and perovskite favors the perovskite in that sample. All other samples show U preferentially distributed into the zirconolite phase by a factor of at least 3. The reason for the unusual U distribution in sample 5 is not well understood, but may be due to a long calcination step involving 120 h at 800°C (Ryerson[14]).

Rare earth elements are preferentially taken into the perovskite structure over the zirconolite structure in all samples. Analyses for samples 3 and 4 did not include measurements for rare earth elements. The normalization procedure used to reduce data for these samples has resulted in TiO_2 and CaO values which are about 5 relative percent too high for the perovskite analyses. This procedure produced totals without REE_2O_3 which approximate 100% even though the perovskite probably contained about 5% REE_2O_3 component.

MECHANICAL AND THERMAL PROPERTIES OF SYNROC C

Mechanical and thermal properties have been measured on samples of SYNROC C and B (recall that B is the base composition for C before addition of waste elements or simulated waste). The data are summarized in Table 9. Details of sample preparation are given in the original references quoted in Table 9. The data set for SYNROC C is incomplete, but comparison of existing results where data are available for both B and C suggests that physical properties of SYNROC are rather insensitive to waste loading. Most of the results quoted in Table 9 were discussed by Campbell et al.[4] and the data were compared there to physical properties of SYNROC D.

Jardine et al.[15] have measured the extent of production of respirable fine fragments (diameter less than 10 microns) produced by impact which delivers an energy density of 10 J/cm^3. He found about 0.15 wt% of material with diameter less than 10 microns for SYNROC B, and similar results for SYNROC D and borosilicate glass.

CHEMICAL DURABILITY OF SYNROC C

The chemical durability of nuclear waste forms is conventionally measured by using "leach tests." Two types of tests are commonly used. The first is a procedure developed by the Materials Characterization Center which uses small discs of the waste form.[17] This procedure is a static leach test where fresh discs (called monoliths) are contacted with the leach solutions at fixed temperature for various lengths of time.

The second commonly used leach test is that proposed by the International Organisation for Standarisation (ISO). This test is a "dynamic" leach test in that a single test specimen is exposed to a series of fresh leach solutions.[18] The draft standard procedure specifies the use of a monolithic sample. This test procedure was modified in the case of SYNROC C testing to use a sized fraction of crushed material.[8,11] This modification was necessary because leach rates of most elements from SYNROC were too low to produce measurable quantities in solution for monolithic samples in reasonable amounts of time.[11]

The MCC-1 test specifies leach periods of 3, 7, 14 and 28 days. The results are an average leach rate over the duration of the test. A

Table 9. Physical properties of SYNROC B and C.

Property	SYNROC B	SYNROC C	References
Density	4.23 g/cm^3	4.35 g/cm^3	12, 11
Longitudinal velocity	7949 m/s		12
Shear velocity	4329 m/s		12
Thin-rod velocity	6949 m/s		12
Poisson's ratio	0.289	0.29	12, 10
Bulk Modulus	1.62×10^5MPa	1.52×10^5MPa	12, 10
Shear Modulus	7.92×10^4MPa	7.59×10^4MPa	12, 10
Young's Modulus	2.04×10^5MPa	1.93×10^5MPa	12, 10
Flexural strength	295 MPa		12
Compressive strength	575 MPa		12
Microhardness, HKN$_{50}$	1.1×10^3kg/mm^2		12
Thermal expansion coefficient	1.0×10^{-5} °C^{-1}		12
Thermal conductivity at room temperature	2 W/m°C	2 W/m°C	12, 16
Heat capacity, C_p, at 200°C	0.8 J/g K		8

differential leach rate can be estimated by subtracting results for 14-day tests from those obtained for 28-day tests. This eliminates the effects of any initial release and gives a better estimate of the long-term behavior of the samples. The differential leach rate may then be compared to the measured rates obtained by the ISO procedure.

A third type of leach testing procedure is the single-pass continuous-flow test.[19] This test is a truly dynamic test because fresh leach solutions are continuously passed over the test specimen. One drawback of this procedure is that it is difficult to adapt the method to temperatures greater than 75°C.

Results of leach testing of SYNROC C using all three test procedures will be presented in this section. Rather than duplicate completely the extensive data sets, results for representative samples will be compared at a few fixed time points. Complete data may be found in the original sources quoted in Tables 10 through 13. All results are presented as "normalized elemental leach rates," NELR. These rates are calculated using the relationship:

$$NELR = m_i/(f_i)(SA)(t),$$

where

m_i = mass of element i in the leach solutions (g)
f_i = mass fraction of i in the total sample
SA = geometric surface area of the sample (m^2)
t = time of contact between the leach solution and the solid sample (d).

Where necessary, data from the original sources have been recalculated to fit this form. Normalized elemental leach rates are sometimes referred to as "bulk sample" leach rates. This is true in the sense that the total sample would dissolve at the rate given by the NELR(i) if the sample consisted of pure component i.

For several elements in SYNROC C the leach rate is strongly dependent on the redox conditions used during sample preparation. The effect of redox conditions is clearly shown in Table 10 for samples prepared by sintering under controlled CO/CO_2 atmospheres.[10] The density of the sintered sample also depended on redox state. The relatively high Ca leach rate at low CO/CO_2 is probably due more to low sample density than to high oxidation state. The Cs and Mo leach rates are the most clearly affected by high oxidation state since they form a soluble cesium molybdate compound under oxidizing conditions. Westsik et al.[20] prepared a low-density (approximately 80% of theoretical density) sample of SYNROC by cold pressing and sintering in N_2 gas at 1300°C. This procedure produced an oxidized specimen with poor leaching characteristics for Cs and Mo.

Leach testing of SYNROC C samples always shows a relatively large release of most elements during the first few days of leaching. Leach rates then decrease as leaching proceeds, and eventually level out at a "plateau" leach rate for most elements. This behavior is shown in Fig. 2 for a SYNROC C sample containing 9% simulated waste tested by a modified ISO procedure.[11] The variation in leach rate with time can be handled for comparison purposes by comparing initial leach rates (which strongly depend on fabrication

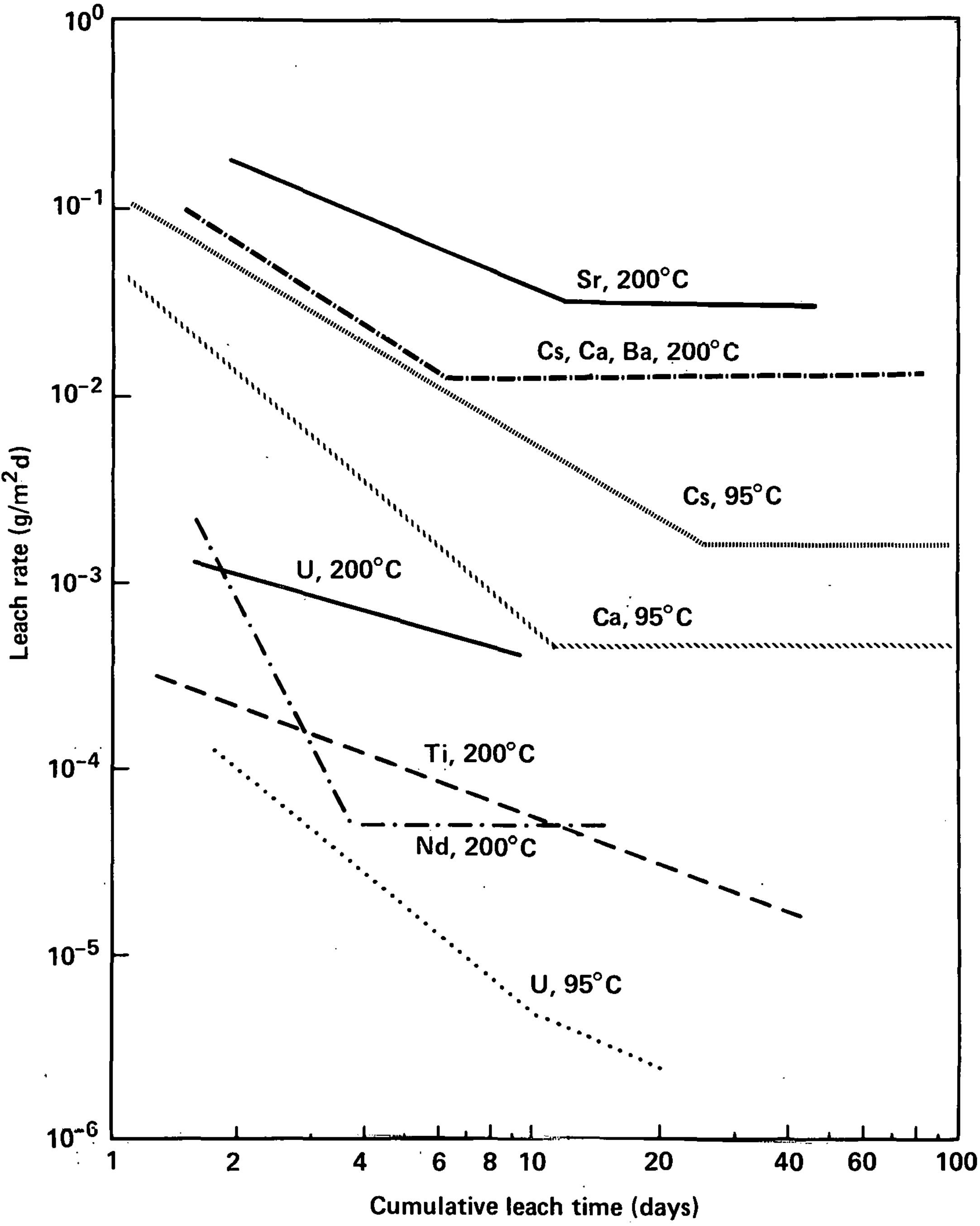


Figure 2. Normalized elemental leach rates for SYNROC C as a function of time (data from Ref. 11).

Table 10. Leach rates for sintered SYNROC C as a function of CO/CO_2 during fabrication.[a]

CO/CO_2	Density, % of theoretical	Leach rate, g/m^2d				
		Cs	Mo	Ca	Al	Ba
0.01	0.89	22	6.1	0.12	0.008	0.32
0.1	0.91	15	3.9	0.14	0.008	0.33
1.0	0.95	0.7	0.02	0.015	0.077	0.15
10	0.98	0.17	0.26	0.018	0.076	0.08
100	0.99	0.26	0.31	0.01	0.07	0.13

[a] Test conditions: MCC-1, 90°C, deionized water. Leach rates are normalized elemental leach rates based on the element listed, averaged over the 28-day leaching period; data from Ref. 10.

techniques and sample density) and long-term or plateau leach rates. At 90°C, the plateau level has been reached for most elements after 14 days of leaching. Therefore, for MCC-1 data, the long term leach rate was recalculated by using the 14- to 28-day differential rate as discussed above.

Initial leach rates at temperatures between 75 and 95°C for SYNROC C samples prepared by oxide and Sandia processes are given in Table 11. The Sr leach rate was not measured for the Sandia process sample, but was inferred from the Ca measurements. The Cs leach rate for the 95% density oxide sample is rather high, probably as a result of the oxidation state during sample preparation. The Sandia process sample shows the lowest initial Cs leach rate; however, as will be seen in Table 12, this difference is not present in the long term leach rates. The initial Sr leach rates are in excellent agreement for all samples.

Long-term leach rates for SYNROC C samples at temperatures between 75 and 200°C are given in Table 12. Data for two samples of a Ca-titanate waste form prepared by Sandia process chemistry are also given for comparison. These samples have phase assemblages very similar to SYNROC C. Data for all sample types and test methods are in good agreement for the 90 and 100°C tests. Again, the low-density sample tested at 75°C shows inferior performance relative to the higher density samples. No difference is seen in this temperature range (90 to 100°C) between samples prepared by Sandia process chemistry and oxide process chemistry.

Table 11. Initial leach rates for SYNROC C.[a]

Sample preparation	Density % theoretical	Leaching temperature °C	Normalized elemental leach rate, g/m^2d Cs	Sr	Reference
Oxide	95	75	4	0.2	19
Oxide	99	75	0.6	0.2	8
Oxide	99	90	0.9	0.25	8
Sandia	99	95	0.3	(0.2)[b]	11

[a] Test conditions: Reference 19: continuous flow, single-pass method.
References 8, 11: modified ISO method.

[b] Inferred from Ca leach rate.

Table 12. Long-term leach rates for SYNROC C and Ca-titanate waste form.[a]

Sample type	Density % theoretical	Temperature of leach, °C	Normalized elemental leach rate, g/m^2d Cs	Sr	Ba	Reference
SYNROC oxide	95	75	0.2	0.03	0.003	19
SYNROC oxide	99	90	0.05	0.002	0.015	16A
SYNROC oxide	99	100	0.004	0.003	--[b]	16B
SYNROC Sandia	99	95	0.005	0.002	0.004	11
Ca-titanate	--[b]	90	0.003	0.0006	--[b]	21
Ca-titanate	--[b]	150	0.006	0.02	0.3	21
SYNROC Sandia	99	200	0.01	0.04	0.008	11

[a] Testing conditions: 11 - Modified ISO method on 100- to 200-micron powders.
16A - MCC-1 on monoliths, average of 14- to 28-day rate for Cs, Sr; average of 1- to 28-day rate for Ba.
16B - Modified ISO on 100- to 150-micron powders.
19 - Single-pass, continuous-flow on 150- to 300-micron powders.
21 - Modified ISO on monoliths.

[b] Data not given in reference.

Table 13. Normalized elemental leach rates for uranium, rare earch elements and matrix elements from SYNROC C and Ca-titanate waste forms.[a]

Sample	Leach temp., °C	Normalized elemental leach rate, g/m^2d			
		U	REE	Ti	Zr
SYNROC	95	5×10^{-5}	8×10^{-5}	3×10^{-5}	2×10^{-5}
Ca-titanate	150	$<1 \times 10^{-4}$	8×10^{-5}	$<1 \times 10^{-4}$	--[b]
SYNROC	200	3×10^{-4}	5×10^{-5}	3×10^{-5}	4×10^{-5}

[a] References: SYNROC data, 11; Ca-titanate data, 21.
[b] Not analysed.

Data for Sandia process SYNROC at 200°C and Ca-titanate at 150°C show that there is very little dependence of long-term leach rate on temperature over the range 90 to 200°C. The high value for Ba leach rate in the Ca-titanate waste form may be due to the presence of a Ba mineral other than hollandite in this sample.

Data for leaching of uranium, rare earth elements (Nd in SYNROC and Gd in Ca-titanate), and matrix elements are given in Table 13 for SYNROC at 95 and 200°C and Ca-titanate at 150°C. These are average leach rates for several samples over the entire leaching time. Both waste forms show very low leach rates for these elements. Again, there is very little dependence of leach rate on temperature.

RADIATION EFFECTS

Radiation can cause changes in the physical state of waste forms, and these changes can affect the chemical durability of the waste form. Radiation damage can be studied by inducing damage via external bombardment by neutrons or charged particles, by doping waste forms with short lived radionuclides to induce damage over a short time scale, or by studying natural materials which have accumulated damage over an extended period of time.

Two of the SYNROC minerals, zirconolite and perovskite, occur with reasonable frequency in natural rocks. Zirconolite samples generally contain substantial amounts of U and Th, and have been subjected to large internal radiation doses. These zirconolites have been studied to determine the extent of structural damage[22] and the effects of the damage on the chemical durability of the samples.[23,24]

Van Konynenburg and Guinan[25] summarized the data available on structural effects of radiation in natural and synthetic SYNROC minerals. In order to compare the results they chose two fixed points in the damage scale: (1) the dose to cause a 1% increase in sample volume, and (2) the dose to cause the sample to become x-ray metamict. A representative selection of data from their summary is given in Tables 14 and 15. Perhaps the most interesting conclusion from their analysis is that the damage depends on total dose and is insensitive to dose rate. Also, the damage produced by fast neutrons is in good agreement with that produced by natural alpha decay.

Table 14. Radiation dose to produce one percent increase in volume.[a]

Sample	Radiation type	Dose, dpa[b]	Dose rate dpa/yr	Equivalent alpha/g
Zirconolites				
$CaZrTi_2O_7$	Fast neutrons	0.13	10	2.6×10^{18}
Kaiserstuhl	Natural U + Th	0.10	10^{-8}	2.0×10^{18}
Cubic $CaPuTi_2O_7$	^{238}Pu	0.034	1	6.8×10^{17}
$CaZrTi_2O_7$ + 3% Cm	^{244}Cm	0.049	0.1	1.0×10^{18}
Perovskites				
$CaTiO_3$	Fast neutrons	0.11	10	2.9×10^{18}
Baikal	Natural U + Th	0.07	10^{-9}	1.4×10^{18}
$^{244}CmAlO_3$	^{244}Cm	0.02	10	4.0×10^{17}
Hollandite				
$BaAl_2Ti_6O_{16}$	Fast neutrons	0.25	10	5×10^{18}

[a] Data from Ref. 25.
[b] dpa = displacements per atom.

Table 15. Radiation exposure to become x-ray metamict.[a]

Sample	Radiation type	Dose, dpa	Dose rate dpa/yr	Equivalent alpha/g
Zirconolites				
Kaiserstuhl	Natural U + Th	>0.20	10^{-8}	$>4 \times 10^{18}$
Jacupiranga	Natural U + Th	<0.42	10^{-9}	$<8.4 \times 10^{18}$
$CaZrTi_2O_7$ + 3% Cm	^{244}Cm	0.20	0.1	4×10^{18}
$CaZrTi_2O_7$	3 Mev Ar^+	0.3 - 0.8	10^3	$5\text{-}16 \times 10^{18}$
Perovskites				
$CaTiO_3$	Fast neutrons	>0.21	10	$> 4 \times 10^{18}$
$CmAlO_3$	^{244}Cm	0.20	10	4×10^{18}
Loparite	Natural U + Th	<0.37	10^{-9}	$<7.4 \times 10^{18}$

[a] Data from Ref. 25.

The structural state of the waste form (whether it is crystalline, metamict, or glassy) is important only if structural state affects the ability of the waste form to isolate waste elements. Natural samples of zirconolite and perovskite have been examined using lead isotopic methods to determine the extent to which the minerals have retained the products of U and Th decay.[23] Some of these samples were also studied by leach testing methods to determine the effects of radiation damage on chemical durability of these minerals under hydrothermal conditions.[24] Table 16 gives the age, accumulated alpha dose per gram, and the time required for this dose to accumulate in SYNROC minerals for a waste form containing 10% radioactive waste elements.

The samples listed in Table 16 are those for which chemical leaching data are available. All of these samples except Kaiserstuhl have also been studied by lead isotopes to determine whether they have remained closed systems. (The Kaiserstuhl sample is too young for the lead isotope test to be used.) Within the precision of the isotopic measurements, all of these samples remained closed systems for U, Th, and all daughter products from the time of mineral formation to the present day. The extremely large radiation dose accumulated by the Sri Lanka samples appears to have had little or no effect on the ability of these zirconolites to retain U, Th, and their daughter products.

Table 16. Ages and radiation doses of natural mineral samples analogous to SYNROC phases.[a]

Sample	Age 10^6 yr	Radiation dose alpha/g	Time to accumulate equivalent dose in SYNROC[b] 10^6 yr
Perovskite			
Baikal	460	2×10^{18}	0.01
Zirconolites			
Kaiserstuhl	16	1×10^{18}	0.001
Jacupiranga	130	8×10^{18}	0.5
Sri Lanka (83800)	555	1×10^{20}	500
Sri Lanka (SL3/12)	546	9×10^{19}	300

[a] Data from Ref. 23.
[b] Assumes 10% waste loading.

Leach rates were determined for Ca at 95 and 200°C from the four natural zironolites. The plateau leach rates are given in Table 17. For three of the sample the U leach rate was also measured at 200°C. The Ca data do not show any clear trend with radiation damage. In fact, the low damage Kaiserstuhl sample has an unexpectedly large Ca leach rate at 200°C. The U leach rate for this sample at 200°C is much lower than the Ca leach rate and is in good agreement with the value measured for synthetic SYNROC C (see Table 13). The Sri Lanka zirconolites have U leach rates slightly higher than the Kaiserstuhl sample. This may be due to radiation damage in the Sri Lanka samples, but data are needed on other samples of intermediate damage before this can be confirmed.

Three natural perovskites have been studied for Ca leach rate at 95°C. The plateau leach rates are in good agreement for the three samples. Only one sample, the Lake Baikal perovskite, was tested at 200°C, and the results show a much higher leach rate for this sample at 200°C compared to 95°C. As was the case for the Kaiserstuhl zirconolite, the U leach rate for the Baikal perovskite at 200°C is much lower than the Ca leach rate. The other samples of perovskite do not contain enough U to allow measurement of the U leach rate.

Table 17. Plateau leach rates for natural mineral samples.[a]

Sample	Normalized elemental leach rate, g/m^2d		
	Ca, 95°C	Ca, 200°C	U, 200°C
Perovskites			
Magnet Cove	3.5×10^{-3}	--[b]	--[b]
Wolgidee Hills	2.5×10^{-3}	--[b]	--[b]
Lake Baikal	2×10^{-3}	0.3	3×10^{-4}
Zirconolites			
Kaiserstuhl	4×10^{-3}	0.1	4.1×10^{-4}
Jacupiranga	--[b]	1.5×10^{-3}	--[b]
Sri Lanka, 83800	--[b]	7×10^{-3}	1.7×10^{-3}
Sri Lanka, SL3/12	2×10^{-3}	5×10^{-3}	2.1×10^{-3}

[a] Data from Ref. 24.
[b] Not determined.

All samples of natural minerals were examined by electron microprobe before and after leaching. Only two samples had sufficient leaching occur to produce a detectable leached layer on the mineral grains. Data for electron microprobe analyses for these samples are given in Table 18. Low totals for leached samples are due to the presence of hydrated alteration products. Leaching of the Baikal perovskite at 200°C produced some grains with 10- to 20-micron-thick rim structure with composition shown in Table 18; other grains appeared to dissolve congruently. The rims formed on the Kaiserstuhl zirconolite were about 8 microns thick, and could be removed by treating the sample with 1.2 N HCl at 90°C for 1 h.

Palmour et al.[26] report leach testing results for U at room temperature on SYNROC samples containing 10% waste. Their samples were prepared by sintering in air at 1195°C; these conditions would produce an oxidized specimen and are not recommended for production of high-quality SYNROC samples. Palmour et al.[26] measured leach rates for U in the presence of a gamma radiation field of 2 to 7 × 10^5 rads/hr. The pH of the leach solution dropped due to gamma radiolysis effects, but the U leach rates for irradiated samples after 25 days were approximately 1 × 10^{-4} g/m^2d. This was the same rate as that found by Palmour et al. for leaching without the gamma radiation.

Table 18. Chemical changes on leaching natural zirconolite and perovskite.[a]

	Baikal perovskite[b]		Kaiserstuhl zirconolite[b]	
	Core	Rim	Core	Rim
Nb_2O_5	0.7	0.6	12.2	14.3
Ta_2O_5	<0.1	<0.1	0.5	0.7
TiO_2	55.3	78.4	25.0	30.4
ZrO_2	0.3	0.2	34.9	26.8
ThO_2	<0.1	<0.1	4.0	7.0
UO_2	<0.1	<0.1	0.5	0.7
Al_2O_3	0.1	1.6	<0.1	<0.1
FeO	1.1	2.0	7.0	4.2
CaO	40.8	3.7	12.0	0.9
REE_2O_3	2	3	4	8
MnO	<0.1	<0.1	0.2	0.1
MgO	<0.1	<0.1	0.3	<0.1
Totals	100.3	89.5	100.6	93.1

[a] Data originally reported in Ref. 13, but identification of perovskite sample and duration of leaching are incorrectly given there.

[b] Leaching times: Baikal, 28 d at 200° C.
Kaiserstuhl, 31 d at 200° C.

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