# THE APPLICATION OF SYNROC TO HIGH-LEVEL U.S. DEFENSE WASTES

W. B. Durham, C. L. Hoenig, F. J. Ryerson, and J. D. Tewhey
Lawrence Livermore Laboratory

## INTRODUCTION

There are a very large number of natural minerals which can accept radwaste-type elements (Cs, Sr, U, REE, etc.) into dilute solid solution in their crystalline structure. A subset of these minerals possesses the important property of being very sparingly soluble in aqueous solutions. This latter group of minerals typically displays a staunch resistance to leaching and alteration in a wide range of crustal and surfacial geologic environments. The radwaste-type elements in solid solution in these minerals thereby tend to be quantitatively retained within the host phase for eons under varying geologic conditions.

## THE SYNROC CONCEPT

The SYNROC (synthetic rock) concept for incorporating radwaste elements in solid solution in minerals was introduced in 1978[1] by Professor A. E. Ringwood of the Australian National University in Canberra. 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 which contain radwaste-type elements and exhibit long-term stability. In the search for the optimum mineral assemblage for the incorporation of nuclear waste components, the fulfill-ment of certain requirements has been sought:

a. The mineral assemblage must exhibit thermodynamic stability and mutual compatibility of the individual phases with respect to chemical and physical properties.

b. The waste form should have low synthesis temperatures ($\leq$ 1300°C) so as to minimize volatilization and facilitate production technology.

c.   The bulk chemical system must be capable of being completely
     crystallized into well-formed crystals.  Glass phase(s)
     should not coexist with the mineral assemblage.

d.   The coexisting mineral phases should be capable of effect-
     ively immobilizing the radwaste elements present in high-
     level nuclear waste.

A program is currently underway at Lawrence Livermore
Laboratory to develop a SYNROC waste form for application to
U.S. defense wastes.  The LLL program involves four principal
areas of research:  1) waste form development including powder
preparation techniques, synthesis by means of sintering, hot
pressing and HIP and phase equilibria studies, 2) waste form
characterization by means of XRD, SEM, STEM and electron
microprobe analysis, 3) stability assessment of the waste form
by means of high temperature-pressure leaching, ambient
temperature-pressure leaching, radiation effects and physical
properties studies, and 4) assessment and development of
production technology for large-scale processing of SYNROC.

CHARACTERISTICS OF SYNROC B AND SYNROC C

A chemical system which is compatible with the requirements
is the $TiO_2-Al_2O_3-ZrO_2-CaO-BaO$ system.  The amount of each com-
ponent in a SYNROC B[a] formulation is given in Fig. 1.  The three
principal phases in SYNROC B are:

"hollandite"- $BaAl_2Ti_{5-6}O_{14-16}$
perovskite  - $CaTiO_3$
zirconolite - $CaZrTi_2O_7$

The stoichiometries of perovskite and zirconolite in SYNROC
are essentially the same as those found in nature.  However,
the hollandite-type phase in SYNROC is a structural isotype of
the natural mineral $(BaMn_8O_{16})$.  Pseudobrookite $(Al_2TiO_5)$,
rutile $(TiO_2)$ and corumdum $(Al_2O_3)$ are common accessory phases
which result from excess alumina and titania that are present
in the formulation to facilitate incorporation of the radwaste
components in the host phase.  The small amount of nickel in
SYNROC B acts as a sink for excess oxygen thereby controlling the
redox conditions during synthesis.  The three principal SYNROC
phases are capable of extensive solid solution.  The specific
distribution of radwaste elements in SYNROC is given in Table I.

Table I.  Summary of Distribution of Radwaste Elements among
          SYNROC B Phases[2]

| "Hollandite" | Zirconolite | Perovskite |
|---|---|---|
| $Mo^{4+}$ | $U^{4+}$ | $U^{4+}$ |
| $Tc^{4+}$ | $Th^{4+}$ | $Th^{4+}$ |
| $Cr^{3+}$ | $Pu^{4+}$ | $Cm^{4+}$ |
| $Ni^{2+}$ | $Cm^{4+}$ | $Pu^{4+}$ |
| $Fe^{2+}$ | $Am^{4+}$ | $Am^{3+}$ |
| $K^+$ | $Y^{3+}$ | $Y^{3+}$ |
| $Cs^+$ | $REE^{3+}$ | $REE^{3+}$ |
| $Rb^+$ | $Na^+$ | $Sr^{2+}$ |
| $Na^+$ | | $Na^+$ |

(a)

SYNROC B:  The basic SYNROC formulation.  The principal components
are $TiO_2$-$Al_2O_3$-$ZrO_2$-CaO-BaO and the principal phases are
"hollandite", perovskite and zirconolite.  SYNROC B contains no
radwaste elements.  The microstructure of SYNROC B is shown in
Fig. 2.

SYNROC C:  C=Commercial High-Level Waste.  Same chemistry and
mineralogy as SYNROC B except that radwaste elements are
included in solid solution in quantities up to ten weight percent.
A microprobe analysis of SYNROC C is given in Table II.

SYNROC D:  D=Defense High-Level Waste.  SYNROC formulation which
incorporates up to 70 weight percent of defense waste sludge.
Principal phases are "hollandite", zirconolite, perovskite
and Al-Fe-Mn spinel ($A^{2+}B_2^{3+}O_4$).  Microstructure and microprobe
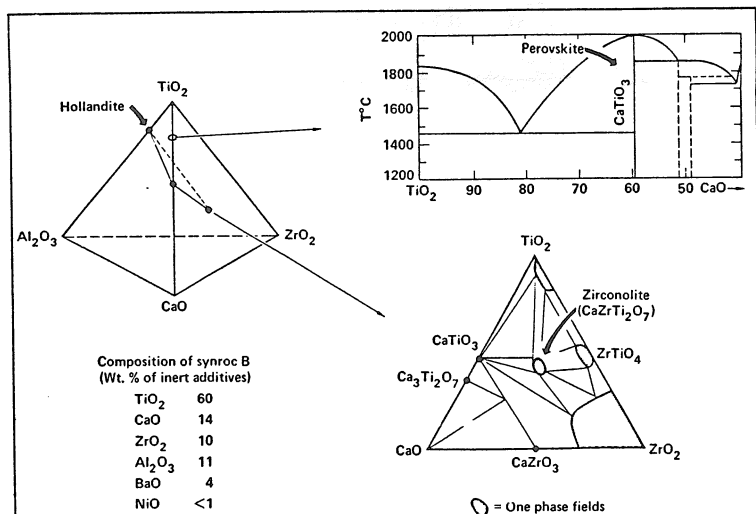analyses of SYNROC D are given in Fig. 3 and Table IV.

Phase diagrams and composition of SYNROC B

Table II.  Microprobe Analysis of SYNROC C (weight percent).

|          | Hollandite | Perovskite | Zirconolite | Pseudobrookite |
|----------|-----------|-----------|-------------|----------------|
| $TiO_2$  | 68.2      | 54.5      | 47.4        | 52.6           |
| $Al_2O_3$| 10.4      | 1.2       | 3.6         | 47.4           |
| $CaO$    | 0.3       | 33.7      | 15.6        | 0.8            |
| $ZrO_2$  | 0.4       | 0.6       | 23.4        | 0.4            |
| $BaO$    | 20.8      | 1.3       | 0.2         | 2.4            |
| $NiO$    | 0.2       | ---       | ---         | ---            |
| $CS_2O$  | <1.0      | ---       | ---         | ---            |
| $SrO$    | ---       | <2.0      | <1.0        | ---            |
| $UO_2$   | 0.2       | 2.8       | 3.8         | ---            |
| $REE$    | ---       | <2.0      | <2.0        | ---            |
|          | 101.5     | 98.1      | 97.0        | 103.6          |

Sample was hot pressed in graphite dies at 1300°C for one hour. Starting material was made by coprecipitation from a molten urea solution[3]. Powder was calcined at 600°C for 38 hours. $Cs_2O$, SrO and REE determined by EDS.
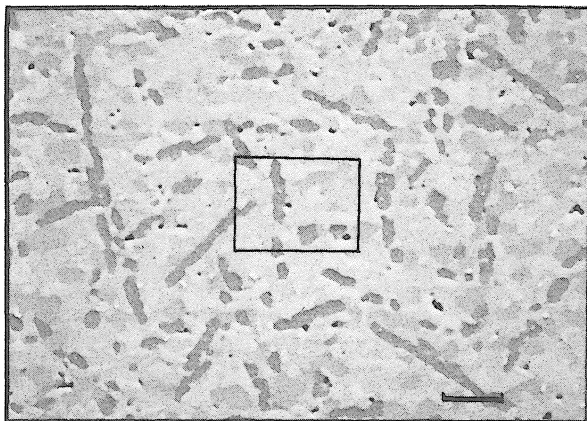
**Fig. 2a.** Backscattered electron photomicrograph of SYNROC B. Sample was hot pressed at 1300°C for one hour. Magnification 1000X. Scale bar is ten microns. Sample is >99% of theoretical density.
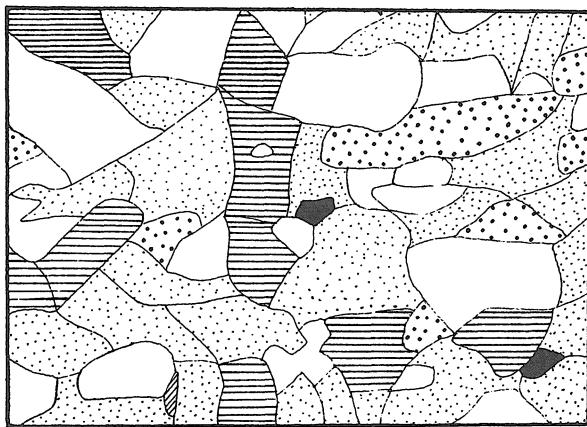


**Fig. 2b.** Microstructure and phase identification of indicated area of Fig. 2a. White=zirconolite, light stipple=hollandite, heavy stipple=perovskite, horizontal lines=pseudobrookite, black=voids, diagonal lines=nickel.

## CHARACTERISTICS OF U.S. DEFENSE WASTES

U.S. defense wastes exist as sludges in tank storage at Savannah River, South Carolina, and Hanford, Washington. The defense wastes at Idaho Falls, Idaho, exist as dry calcine. The SRP sludges, the current focus of waste form research at LLL, consist of Fe, Al and Mn oxides and hydroxides in varying proportions along with 1-10 weight percent fission products and actinides. Table III gives an indication of the large tank-to-tank compositional variability of sludge. The high-iron and high-aluminum compositions are from specific tanks that represent the compositional extremes. The radionuclides, with the exception of Cs, are strongly partitioned into the sludge portion of the waste. Cesium is partitioned into the supernatant liquid coexisting with the sludge. The reference process for SRP wastes calls for the Cs to be removed from the supernatant on an ion exchange medium. The Cs and exchange medium would then be incorporated with the sludge for waste form processing (Ion-Siv in Table III).

Table III. Major Components in SRP Waste Calcines

| Component | High Fe | Composite | High Al |
|-----------|---------|-----------|---------|
| $Fe_2O_3$ | 53.17 | 36.13 | 5.32 |
| $Al_2O_3$ | 4.89 | 28.26 | 76.05 |
| $MnO_2$ | 3.56 | 9.94 | 4.37 |
| $U_3O_8$ | 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 |
| $Na_2O$ | 4.52 | 5.08 | 1.96 |
| $Na_2SO_4$ | <0.50 | 0.93 | <0.50 |
| Ion-Siv* | 8.82 | 8.93 | 9.33 |

* Ca-K-Na zeolite ion exchange medium

### SYNROC D

SYNROC D formulations consist of up to 70 weight percent of SRP sludge, the remainder being inert additives which consist of SYNROC B components that are not present in the sludge ($TiO_2$ BaO, $ZrO_2$ and CaO). For washed sludge compositions with $\leq 1.5$ weight percent $Na_2O$, the SYNROC D formulation consists of perovskite, zirconolite spinel and ilmenite. "Hollandite"

cannot accommodate large amounts of sodium into its crystal structure, therefore, if the $Na_2O$ content of the sludge is not reduced by washing and remains at 4-5 weight percent, the preferred SYNROC D formulation consists of perovskite, zirconolite, nepheline ($NaAlSiO_4$), spinel and ilmenite. The substitution of nepheline for "hollandite" is accomplished by using $SiO_2$ as an inert additive rather than BaO.

SYNROC D has been found to exhibit exceptional flexibility with respect to the compositional variability of SRP sludges. Synthesis experiments for the three sludge compositions in Table III have shown that the stoichiometries of the principal SYNROC phases do not differ appreciably in the three formulations. On the other hand, the spinel phase has been shown to be exceptionally "forgiving", in that the composition differs significantly in the three formulations. It is the spinel phase, which contains no radionuclides, that accommodates the order-of-magnitude variation in FeO, $Al_2O_3$ and NiO. Therefore, the composition of the inert additives does not have to be sharply tailored to the differing sludge compositions. This greatly facilitates the production processing of the sludge into a SYNROC waste form. Photomicrographs and microprobe analyses of a SYNROC D formulation for a low sodium composite sludge are given in Fig. 3 and Table IV.

Table IV. Microprobe Analysis of SYNROC D (weight percent).

|  | "Hollandite" | Perovskite | Zirconolite | Spinel |
|---|---|---|---|---|
| $TiO_2$ | 66.1 | 53.2 | 49.2 | 2.8 |
| $Al_2O_3$ | 7.7 | 1.1 | 2.1 | 58.3 |
| BaO | 0.7 | 0.7 | 0.1 | --- |
| FeO | 7.1 | 1.9 | 1.4 | 13.3 |
| $ZrO_2$ | 3.1 | 0.3 | 24.9 | --- |
| CaO | 4.1 | 32.9 | 11.4 | 0.1 |
| MnO | 2.7 | 1.4 | 1.1 | 4.5 |
| $Na_2O$ | 0.1 | 0.2 | --- | --- |
| NiO | 3.2 | 0.2 | 0.5 | 21.0 |
| $UO_2$ | 0.7 | 1.7 | 3.5 | --- |
| $Cs_2O$ | <1.0 | --- | --- | --- |
| SrO | --- | <2.5 | <1.0 | --- |
| REE | --- | <2.0 | <2.0 | --- |
|  | 96.5 | 98.1 | 97.2 | 100.0 |

Sample was hot-pressed in a nickel capsule at 1270°C for one hour. Starting material was made by coprecipitation from a molten urea solution[3]. Powder was calcined at 1000°C for 24 hours. $CS_2O$, SrO and REE determined by EDS.
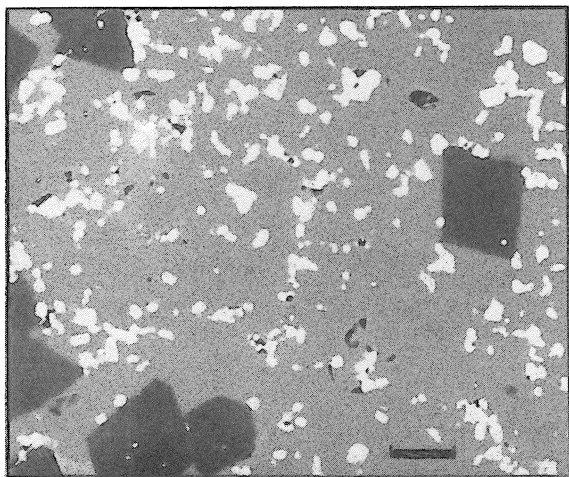


**Fig. 3.** Backscattered electron photomicrograph of SYNROC D. Sample is the same as reported in Table IV. Scale bar is ten microns. Black phase=spinel, white phase=zirconolite, grey (undifferentiated)=perovskite and hollandite.

# REFERENCES

1. A. E. Ringwood, "Safe Disposal of High-Level Nuclear Reactor Wastes: A New Strategy," Australian National University Press, Canberra, 64p, 1978.

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