Formulation of SYNROC-D Additives for Savannah River Plant High-Level Radioactive Waste

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FORMULATION OF SYNROC-D
ADDITIVES FOR SAVANNAH RIVER PLANT
HIGH-LEVEL RADIOACTIVE WASTE

ABSTRACT

SYNROC-D is a multiphase ceramic waste form consisting of nepheline, zirconolite, perovskite, and spinel. It has been formulated for the immobilization of high-level radioactive wastes now stored at the Savannah River Plant (SRP) near Aiken, South Carolina. This report utilizes existing experimental data to develop a method for calculating additives to these waste products. This method calculates additions based on variations of mineral compositions as a function of sludge composition and radionuclide partitioning among the SYNROC phases. Based on these calculations, a FORTRAN program called ADSYN has been developed to determine the proper reagent proportions to be added to the SRP sludges.

INTRODUCTION

SYNROC-D is a multiphase titanate-silicate ceramic designed to immobilize the radionuclides and processing contaminants contained in the hydroxide sludges and supernate solutions currently stored at DuPont's Savannah River Plant (SRP) near Aiken, South Carolina. The SYNROC-D phase assemblage consists of five major mineral phases: zirconolite ($\text{CaZrTi}_2\text{O}_7$), perovskite (CaTiO_3), spinel ($\text{MN}_2\text{O}_4\text{-M}_2\text{TO}_4$, M = divalent cation, N = trivalent cation, T = tetravalent cation), and nepheline (NaAlSiO_4). Minor sulfide, pollucite ($\text{CsAlSi}_2\text{O}_6$), and phosphate phases may also be present.

The sludges at SRP are chemically complex and variable. They contain the full complement of actinides, lanthanides, alkalis, and alkaline earths found in commercial reactor wastes (see Table 1, after Stone et al., 1979). However, their chemistry is dominated by inert processing contaminants including transition metals Ni, Fe, Mn, Cr, alumina, silica, and Na (see Table 2, after Stone et al., 1979). The High-Fe and High-Al are extreme end-member compositions, while the composite is the estimated average composition of all SRP sludges.

Table 1. Major components in simulated SRP waste calcines (after Stone et al., 1979).

Component	High-Fe	Composite	High-Al
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	1.28
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 O	4.52	5.08	1.96
Na ₂ SO ₄	<0.50	0.93	<0.50
Ion-Siv IE-95 ^a	8.82	8.93	9.33

^a Mixture of CaAl₂Si₄O₁₂ • 6H₂O and (NaKCa)₃Al₃SiO₂₄ • 8H₂O.

SYNROC-D is capable of incorporating all these elements as components in solid solution in the phases described above. To produce the SYNROC-D phase assemblage, the tailoring additives CaO, SiO₂, ZrO₂, TiO₂ and, in some cases, Al₂O₃ or Fe₂O₃ must be added to the sludges in prescribed amounts. In theory, the process of formulating additives consists simply of altering bulk composition such that the composition enters the desired phase volume. The phase volume is an n-dimensional polyhedron in compositional space, whose apices are defined by the compositions of the coexisting SYNROC phases. This is schematically displayed in Fig. 1 where S is the sludge composition and SA is the final composition (sludge plus additives) lying within the SYNROC phase volume. The direction of vector S-SA is determined by the proportions of the different additive components, and its magnitude is determined by their amount. The magnitude of S-SA is inversely proportional to the waste loading (weight of sludge/weight of sludge plus additives). In practice, the additive formulation must: 1) produce the desired phase assemblage; 2) maximize the waste loading; and 3) minimize the risk due to credible error.

This report presents the method by which SYNROC additives have been calculated for development at LLNL. Also included is a FORTRAN program,

Table 2. Minor components in SRP waste sludges
(Stone et al., 1979).

Element	Range (wt%)	Element	Range (wt%)
C	0-16.8	Nb	0.02-0.1
Nd	0.3-1.0	Hg	0.1-2.8
Zr	0.1-0.5	Y	0.01-0.05
Cr	0.01-0.45	Ag	0-0.3
Ru	0.03-0.5	Pm	0-0.04
Ba	0.1-0.25	Pb	0.1-0.5
Ce	0.05-1.0	Ti	0-0.1
K	0.02-0.14	Sm	0-0.05
Cl	0-2.0	Eu	0-0.02
Sr	0-0.15	V	0-0.01
La	0.04-0.3	Rh	0-0.05
S	0.02-0.5	F	0-0.15
P	0.03-0.3	Cs	0-0.06
Zn	0.04-0.5	Cd	0-0.05
Th	0-0.18	Pd	0-0.03
Mg	0.09-0.3	Mo	0-0.01
Cu	0.03-0.15	Eu	0-0.01
		Co	0-0.01

ADSYN,* that calculates additive components and reagents as a function of sludge composition. Also outlined are areas where improved experimental data are required for better modeling.

DATA BASE FOR SYNROC-D FORMULATIONS

INERT CONSTITUENTS

The SRP sludges are composed primarily of inert processing contaminants. Due to their predominance, these species play a major role in determining the

* See ADSYN Source Code microfiche, inside back cover.

Figure 1. Schematic of tailoring additives for SYNROC-D. The final SYNROC-D phase assemblage is represented by the n-dimensional polyhedron SP-NEPH-ZIRC-PER-POL, the apices of which represent the compositions of the mineral phases.

mineralogy and modal abundances in any SYNROC-D assemblage. The immobilization of these components is, therefore, the most immediate consideration.

As shown in Fig. 1, proper formulation of SYNROC additives depends on the relative position of the sludge and SYNROC phase volume in compositional space. The problem is trivial in a case where the starting composition is known and the phase volume apices are fixed in compositional space (i.e., the SYNROC phases show no compositional variability). This, of course, is not the case in SYNROC-D.

In SYNROC-D, the compositions of coexisting phases change as a result of synthesis conditions, sludge composition, and the proportions of additive components. Ideally, the calculation of additives should employ an iterative approach. In this manner, mineral compositions are first determined on the basis of sludge composition and the additives are calculated. On the basis of these additives, the mineral compositions are then refined and the additives are adjusted. This process continues until convergence is reached. Such an approach requires a detailed understanding of how mineral compositions are related to bulk composition and synthesis conditions. At this time, however, no such detailed data are available. A simpler technique has, therefore, been employed. This technique assumes that the compositions of some phases

(zirconolite and perovskite) remain constant over the specified ranges of SRP sludge compositions (High-Fe, composite, and High-Al).

The mineral compositions used in our calculations are derived from the work of Ringwood *et al.* (1979). In these experiments, simulated sludge calcines approximating the compositions of the SRP High-Al, High-Fe, and composite sludges (Table 3) were combined with TiO_2 , ZrO_2 , CaO , SiO_2 , and Al_2O_3 and pressed in Pt capsules in a solid-medium pressure apparatus. Run conditions were 1200°C at 500 MPa, and the O fugacity was close to that of the Ni-Ni oxide buffer. The additives in successive experiments were adjusted until only the desired phases (zirconolite, perovskite, nepheline, and spinel) were formed. The compositions of the coexisting phases were determined and combined in the approximate wt% ratios, 1:1:4:1; zir: per: sp: neph. These ratios maximize the loading while still allowing dilute solution of radionuclides in zirconolite and perovskite. The necessary additives were calculated from the final bulk composition.

Inspection of coexisting mineral compositions (Table 4) reveals some interesting features. The compositions of the phases, zirconolite, perovskite, and nepheline, are relatively constant in the three formulations, and they plot close to the ideal mineral compositions (Figs. 2 and 3).

Table 3. Simulated sludge compositions plus additives.

	High-Al			High-Fe			High-Fe		
	Calcined sludge	Addi- tives	Total	Calcined sludge	Addi- tives	Total	Calcined sludge	Addi- tives	Total
SiO_2	--	6.5	6.5	1.4	4.8	6.2	1.6	7.5	8.1
TiO_2	--	16.7	16.7	--	16.8	16.8	--	15.0	15.0
ZrO_2	--	4.2	4.2	--	4.0	4.0	--	4.0	4.0
UO_2	2.3	--	2.3	2.4	--	2.4	2.3	--	2.3
Al_2O_3	33.8	--	33.8	3.7	5.4	9.1	21.2	--	21.2
Fe_2O_3	17.7	--	17.7	36.8	--	36.8	27.1	--	27.1
MnO	5.3	--	5.3	6.1	--	6.1	6.1	--	6.1
NiO	0.6	--	0.6	6.6	--	6.6	3.4	--	3.4
CaO	2.1	5.5	7.6	1.9	5.0	6.9	2.0	4.9	6.9
Na_2O	3.4	--	3.4	3.2	--	3.2	3.8	--	3.8
F_p, A^a	2.0	--	2.0	2.0	--	2.0	2.1	--	2.1
TOTAL	67.0	33.0	100.0	64.0	36.0	100.0	69.0	31.0	100.0

^a F_p , A = Fission product plus actinides.

Table 4a. Compositions of coexisting phases (High-Fe).

A. wt% oxides	Zirconolite	Perovskite	Spinel	Nepheline
SiO ₂	--	--	--	40.6
TiO ₂	35.1	52.4	7.9	0.5
ZrO ₂	25.2	1.4	--	--
UO ₂	15.5	2.6	--	--
Al ₂ O ₃	0.4	1.5	8.1	34.4
Fe ₂ O ₃	7.8	1.6	43.5	5.0
FeO	--	--	20.7	--
MnO	1.8	0.8	9.0	--
NiO	--	0.2	9.7	--
CaO	14.6	39.8	--	--
Na ₂ O	0.2	--	--	20.1
Total	100.6	100.3	98.9	100.7
<u>B. Atoms/formula unit</u>				
Si	--	--	--	1.10
Ti	1.66	0.91	0.22	0.01
Zr	0.78	0.02	--	--
U	0.22	0.01	--	--
Al	0.03	0.04	0.35	1.10
Fe ³⁺	0.37	0.03	1.21	0.10
Fe ²⁺	--	--	0.64	--
Mn	0.09	0.02	0.28	--
Ni	--	0.02	0.29	--
Ca	0.99	0.99	--	--
Na	--	--	--	1.06
Total cations	4.14	2.03	3.00	3.37
No. oxygens/ formula unit	7.00	3.00	4.00	4.00

Table 4b. Compositions of coexisting phases (High-Al).

A. wt% oxides	Zirconolite	Perovskite	Spinel	Nepheline
SiO ₂	--	--	--	41.5
TiO ₂	30.1	53.2	5.8	0.2
ZrO ₂	38.5	0.7	0.3	--
UO ₂	14.2	4.8	--	--
Al ₂ O ₃	1.1	0.3	48.3	35.9
FeO	4.2	2.4	37.4	0.8
MnO	0.9	0.7	7.2	0.2
NiO	--	--	0.4	--
CaO	12.5	38.1	--	--
Na ₂ O	0.4	--	--	21.5
Total	101.9	100.2	99.4	100.1
<u>B. Atoms/formula unit</u>				
Si	--	--	--	0.99
Ti	1.45	0.95	0.13	0.01
Zr	1.20	0.01	--	--
U	0.20	0.03	--	--
Al	0.08	0.01	1.73	1.00
Fe	0.22	0.05	0.95	0.01
Mn	0.05	0.01	0.18	0.02
Ni	--	--	0.01	--
Ca	0.86	0.97	--	--
Na	0.05	--	--	0.99
Total cation	4.11	2.03	3.01	3.02
No. oxygens/ formula unit	7.00	3.00	4.00	4.00

Table 4c. Compositions of coexisting phases (composite).

A. wt% oxides	Zirconolite	Perovskite	Spinel	Nepheline
SiO ₂	--	--	--	41.0
TiO ₂	32.5	53.6	14.3	0.5
ZrO ₂	32.7	--	0.2	--
UO ₂	11.2	3.0	0.1	--
Al ₂ O ₃	1.1	0.1	17.2	35.2
Fe ₂ O ₃	7.1	2.7	20.5	1.1
Sm ₂ O ₃	2.5	6.8	--	--
FeO	--	--	31.0	--
MnO	0.9	0.3	10.8	--
NiO	2.1	0.2	5.7	--
CaO	9.8	34.1	0.2	0.8
Na ₂ O	0.7	0.5	--	21.4
Total	100.6	101.3	100.0	100.0
<u>B. Atoms/formula unit</u>				
Si	--	--	--	0.98
Ti	1.54	0.96	0.38	0.01
Zr	1.01	--	--	--
U	0.16	0.02	--	--
Al	0.08	--	0.71	0.99
Fe ³⁺	0.34	0.05	0.54	0.02
Sm	0.05	0.05	--	--
Fe ²⁺	--	--	0.90	--
Mn	0.05	0.01	0.32	--
Ni	0.11	--	0.16	--
Ca	0.67	0.87	--	0.02
Na	0.04	0.02	--	0.99
Total cation	4.05	1.98	3.01	3.01
No. oxygens/ formula unit	7.00	3.00	4.00	4.00

Figure 2. Composition of coexisting perovskites and zirconolites produced in densified SYNROC-D formulations for High-Al, composite, and High-Fe sludges (after Ringwood et al., 1979). The filled circles represent the ideal mineral stoichiometries, CaTiO_3 and $\text{CaZrTi}_2\text{O}_7$. The data indicate that the departure from ideal formulas is relatively small. Hence, the sludge components act essentially as dilutants and do not strongly alter the relative activity coefficients of CaO , ZrO_2 , and TiO_2 in these phases.

Figure 3. Compositions of raphelines produced in densified SYNROC-D assemblages for High-Al, composite, and High-Fe sludges. The ideal stoichiometry NaAlSiO_4 (fitted circle) compares favorably with those from SYNROC-D.

Zirconolite contains only 15 mole % of oxide constituents other than CaO , ZrO_2 , and TiO_2 . The additional constituents of importance are UO_2 and the transition metal oxides, FeO , MnO , and NiO . Perovskite contains only 5 mole % oxide constituents other than CaO and TiO_2 and plots quite close to the ideal composition. As in zirconolite, UO_2 and the transition metal oxides constitute the remainder of the perovskite. The case is even more extreme for nepheline, which contains a maximum of 2 mole % of constituents other than Na_2O , Al_2O_3 , and SiO_2 .

These data indicate that zirconolite, perovskite, and nepheline play a minor role in the incorporation of the inert components of the SRP sludge (with the exception of Na in nepheline). The compositions of these phases, therefore, show little variation as a function of sludge composition. In formulating the additives necessary to produce these phases, experts must place greater emphasis on the maintenance of safe (i.e., suitably dilute) radionuclide loading levels, rather than the effects of inert component variations. For instance, if the concentrations of inert components in zirconolite and perovskite are completely neglected, an error of only 2 mole % is incurred in formulating additives.

Large compositional variations in SRP sludge are not reflected in the compositions of perovskite, nepheline, and zirconolite. This leaves only spinel to incorporate compositional fluctuations in the sludges (Table 4). As such, the compositional variations in the sludges must be reflected in that of the spinels. The relationship between sludge components and spinel compositions is shown in Fig. 4. The High-Al sludge is characterized by high Al_2O_3 content, producing hercynitic (FeAl_2O_4) spinels. The High-Fe sludge is characterized by high Fe_2O_3 contents, which produce ferrite ($\text{M}^{2+}\text{Fe}_2\text{O}_4$) spinels. These types of spinels contain relatively little of the TiO_2 additive compared to the more complex spinels in the composite sludge (Fig. 5). The composite spinel is a solid solution of 26.8 mole % magnetite, 35.3 mole % hercynite, and 37.9 mole % ulvöspinel components (M_2TiO_4). The large ulvöspinel component in the composite spinel illustrates that a certain amount of TiO_2 must be allocated to these spinels when additives are formulated. The amount of TiO_2 varies with $\text{Fe}/(\text{Fe} + \text{Al})$ in both the spinel and (since the spinel reflects the overall bulk composition) the sludge (Fig. 5). The TiO_2 content reaches a maximum at the composite formulation. This trend in TiO_2 content mimics that of the variable,

Figure 4. Comparison of spinels in densified SYNROC-D for High-Fe, composite, and High-Al formulations, and the initial sludge compositions. The data are plotted in terms of atomic proportions of Fe, Mn + Ni, and Al* (= Al - Na to account for Al accommodated in nepheline). O is not plotted in the diagram, hence Fe_3O_4 plots at Fe. Sludge compositions are shown by filled symbols, spinel composition by open symbols.

Figure 5. Relationships between various spinel components, and spinel and sludge composition. The sludge compositions are represented as High-Al ($\square$), composite ($\circ$), and High-Fe ($\triangle$).

- The parameter $M = \text{mole \% } (\text{NiO} + \text{MnO} + \text{FeO}) - (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ and mole % TiO_2 in spinel display similar patterns vs $\text{Fe/Fe} + \text{Al}$ in spinel (spinel stoichiometry requires spinel TiO_2 content be proportional to the excess bivalent over trivalent cations in spinel, which approaches a maximum for the composite composition).
- Plot of M and TiO_2 in spinel vs $\text{Fe/Fe} + \text{Al}$ in the sludge mimics that in 5a due to close correspondence between $\text{Fe/Fe} + \text{Al}$ in spinel and sludge composition. The incorporation of alumina in nepheline has not been considered.
- Plot of $\text{Fe/Fe} + \text{Al}^*$ vs M and TiO_2 in spinel for the three sludge compositions. Al^* is equal to Al-Na , which accounts for the Al content of nepheline. M and TiO_2 in spinel reach a maximum for the composite composition. Straight lines have been used to interpolate spinel compositions for other sludges, and their equations (Table 5) are used in the ADSYN program.

$$\left[(\text{NiO} + \text{MnO} + \text{FeO}) - \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \right]_{\text{sp}},$$

which is equal to the sum of bivalent transition metal oxides that cannot be accommodated as either aluminate (MAl_2O_4) or ferrite (MFe_2O_4 ; M = bivalent cations). Using the relationship in Fig. 5 and Table 5, the amount of TiO_2 needed to form spinels may be calculated as a function of sludge composition. It should be noted that nepheline also requires Al_2O_3 , as does spinel. In this regard, the amount of Al_2O_3 present to form spinel is actually equal to

$$\text{Al}^* = \text{Al} - \text{Na} \quad . \quad (1)$$

This factor should be considered in formulating $\text{Fe}/(\text{Fe} + \text{Al})$ for any sludge.

An additional feature of the spinel compositions worthy of note concerns their oxidation state, $\text{Fe}^{3+}/\text{Fe}^{2+}$. A majority of the Fe in the sample is accommodated in spinel and, therefore, the oxidation state of the Fe and spinel reflects that of the entire sample. The oxidation state of the spinel (and of the sample) increases linearly as a function of $\text{Fe}/\text{Fe} + \text{Al}^*$ (Fig. 6.) This variation in redox state occurs even though the samples were prepared at the same O fugacity and temperature. Hence, the variation of redox state is solely a function of bulk composition.

Table 5. Linear equations relating spinel and sludge compositions.

Equation	Region of validity
$\text{M}^a = 93.5 \text{ Fe}/(\text{Fe} + \text{Al}^*)^c \text{ sludge}^{-14.1}$	$0.2 < \text{Fe}/(\text{Fe} + \text{Al}^*) \leq 0.50$
$\text{M} = -21.9 \text{ Fe}/(\text{Fe} + \text{Al}^*)^c \text{ sludge}^{+42}$	$0.50 < \text{Fe}/(\text{Fe} + \text{Al}^*) \leq 1.10$
$\text{TiO}_2^b = -42 \text{ Fe}/(\text{Fe} + \text{Al}^*)^c \text{ sludge}^{+8.1}$	$0.2 < \text{Fe}/(\text{Fe} + \text{Al}^*) \leq 0.50$
$\text{TiO}_2 = -10.2 \text{ Fe}/(\text{Fe} + \text{Al}^*)^c \text{ sludge}^{+20.9}$	$0.50 < \text{Fe}/(\text{Fe} + \text{Al}^*) \leq 1.10$

^a $\text{M} = \left[(\text{NiO} + \text{MnO} + \text{FeO}) - (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \right]$ in spinel as mole % oxide.

^b TiO_2 = mole % TiO_2 in spinel.

^c $\text{Al}^* = \text{Al} - \text{Na}$ in sludge.

Figure 6. $\text{Fe}/\text{Fe} + \text{Al}^*$ ($\text{Al}^* = \text{Al} - \text{Na}$) in the sludges bears a linear relationship to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of the spinel. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is calculated from spinel stoichiometry. The various sludges are represented by High-Fe ($\square$), composite ($\circ$), and High-Al ($\triangle$). The equation of the fit to these data is $(\text{Fe}^{3+}/\text{Fe}^{2+})_{\text{sp}} = 2.38 (\text{Fe}/\text{Fe} + \text{Al})_{\text{sludge}} - 0.64$.

Understanding the correct sample redox conditions as a function of composition is extremely important in determining the manner in which SYNROC-D samples are prepared. For instance, the presently preferred production scenario for SYNROC-D requires a reducing calcine of spray-dried powder followed by hot-pressing in graphite dies. Depending on sample size, these graphite dies may essentially act as inert containers due to rapid densification, low diffusivities and long diffusion paths. In this case, the proper redox state must be impressed on the sample during redox calcination. The relationship displayed in Fig. 6

$$\left[\text{Fe}^{3+}/\text{Fe}^{2+}\right]_{\text{sp}} = 2.38 \left[\text{Fe}/(\text{Fe} + \text{Al}^*)\right]_{\text{sludge}} - 0.64$$

can be used to determine redox ratios for a large range of sludge compositions.

RADIONUCLIDES: CRYSTAL CHEMISTRY OF ZIRCONOLITE AND PEROVSKITE

The important radionuclide-bearing phases in SYNROC-D are zirconolite, perovskite, and a Cs host phase (either pollucite or hollandite). Our formulations require that the radionuclides, U, Sr, Cs, and the rare earths be immobilized in these phases. Since the incorporation of radionuclides in these phases depends on their structure and crystal chemistry, important aspects of these parameters are summarized as follows.

The crystal structure of zirconolite has been described by Rossell (1980) and Gatehouse et al. (1981). They confirmed earlier work by Pyatenko and Pudovinka (1964) indicating that zirconolite is related to structures of the defect fluorite-type since it is derived by ordering CaF_{2-x} -type subunits. The monoclinic unit cell is eight times as large as the fluorite subunits and its structure is correctly expressed as $\text{Ca}_8\text{Zr}_8\text{Ti}_{16}\text{O}_{56}\square_8$ ($\square$ = O vacancy).

Rossell (1980) has found that the Ca atoms are coordinated to eight O atoms at the corners of a distorted cube. Zr is linked in seven-fold coordination to seven oxygens at the corner of a truncated cube (truncation due to O vacancy). Ti occupies three distinct lattice sites. In two of these, Ti is in octahedral coordination and linked to six O atoms. These O atoms are joined at apices to form six-membered and three-membered rings. Ti also resides in a five-fold site, in which the surrounding O atoms form a trigonal bipyramid.

Kesson and Ringwood (1981) have investigated the crystal chemistry of zirconolites by analyzing both naturally occurring zirconolites and those produced in synthesis experiments. Their experimental work in the system $\text{CaO-TiO}_2\text{-ZrO}_2$ at 1350°C has demonstrated that the zirconolite is quite intolerant to variations in Ca content, allowing only a few at.% deficiency. There is, however, considerable variation in the Zr/Ti ratio. The general formula can be written as $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$, and "x" varies from 0.9-1.3 at 1350°C . Wide variations in Zr/Ti are also known in naturally occurring zirconolites (Table 6). However, we know of no analyzed zirconolites that contain greater than two Ti atoms per formula unit. It is not uncommon to find Zr in excess of ideal stoichiometry. These patterns indicate that Zr^{4+} may be substituted into Ti sites and that Ti may be substituted into Zr sites. The partitioning of Ti into Zr sites is less likely, and usually not required by zirconolite stoichiometry.

Table 6. Analyses of natural zirconolites (after Kesson and Ringwood, 1981).

A. Loc.	Stavern	Stavern	Larvik	Jacu- piranga	Aldan	Kaiser- stuhl	Sri Lanka	Sri Lanka	Sri Lanka
	(brown)	(red)					(B20392)	(83800)	(S13-12)
Nb ₂ O ₅	18.9	15.6	8.0	11.3	4.6	15.6	3.6	3.9	0.2
Ta ₂ O ₅	0.4	0.2	0.7	0.2	0.1	1.2	--	--	0.1
TiO ₂	16.7	22.4	27.0	24.3	35.4	20.9	28.0	27.0	36.5
ZrO ₂	32.0	35.3	31.4	35.2	36.5	34.8	30.9	30.4	38.6
ThO ₂	3.7	0.6	4.1	7.4	1.2	2.9	20.5	21.8	0.9
UO ₂	1.9	0.3	1.3	0.5	0.5	1.5	2.1	1.7	4.6
FeO ^a	9.3	8.4	6.9	7.2	5.0	7.8	3.1	3.0	3.4
MnO	0.5	0.4	0.5	0.2	0.1	0.2	--	0.2	0.2
MgO	--	--	--	0.4	--	0.3	2.4	2.5	0.6
CaO	7.7	10.0	9.2	11.5	15.1	12.1	7.9	7.7	12.1
RE, Y	6.6	4.8	9.3	2.6	1.9	0.9	--	--	--
Total	97.7	97.8	98.4	100.8	99.2	98.2	98.5	97.2	96.9
B. Structural formulas based on 7 O atoms.									
Nb	0.596	0.463	0.243	0.332	0.126	0.464	0.113	0.125	--
Ta	0.008	--	0.013	0.004	--	0.022	--	--	--
Ti	0.876	1.105	1.366	1.186	1.611	1.034	1.456	1.433	1.718
Zr	1.089	1.129	1.030	1.114	1.077	1.117	1.042	1.047	1.178
Th	0.059	0.009	0.063	0.109	0.003	0.043	0.323	0.350	0.018
U	0.030	0.004	0.020	0.007	0.006	0.022	0.032	0.027	0.064
Fe ⁺²	0.543	0.461	0.388	0.391	0.253	0.429	0.179	0.118	0.178
Mn	0.030	0.022	0.029	0.011	--	0.011	--	0.012	0.011
Mg	--	--	--	0.039	--	0.029	0.247	0.263	0.056
Ca	0.576	0.703	0.663	0.800	0.978	0.853	0.585	0.582	0.811
RE, Y	0.159	0.109	0.216	0.058	0.040	0.020	--	--	--
Total	3.963	4.004	4.030	4.051	4.094	4.045	3.978	3.957	4.028

^a All Fe assumed to be FeO.

Kesson and Ringwood (1981) have also conducted experimental investigations of the mechanisms by which U⁴⁺ is substituted in zirconolite. They equilibrated samples with the composition CaU_{0.25}Zr_{0.75}Ti₂O₇ at 1400°C. These runs resulted in a U-rich pyrochlore and a relatively U-poor zirconolite (Table 7). These results set the U saturation limit in zirconolite at 12.6 wt% (calculated as UO₂). The zirconolite formula confirms the expected full occupancy of Ca and Ti sites. This requires the U⁴⁺ (cationic radius = 1.06Å) to be accommodated in the Zr⁴⁺ site (cationic radius = 0.86Å;

Table 7. Coexisting zirconolite and pyrochlore (after Kesson and Ringwood 1981).^a

<u>A. Microprobe analyses (wt%)</u>		
Oxides	Zirconolite	Pyrochlore
TiO ₂	42.3	37.3
ZrO ₂	29.1	18.9
UO ₂	12.6	28.0
CaO	<u>15.2</u>	<u>15.7</u>
Total	99.2	99.9

<u>B. Structural formulas based on 7 oxygen atoms.</u>		
Cations	Zirconolite	Pyrochlore
Ti	1.955	1.891
Zr	0.872	0.621
U	0.172	0.420
Ca	<u>1.001</u>	<u>1.134</u>
Total	4.001	4.067

^a Starting composition: CaU_{0.25}Zr_{0.75}Ti₂O₇; experimental conditions: 5 kbar, 1400°C, 1 h, Pt capsule.

Whittaker and Muntus, 1970). Hence, one mechanism by which U enters zirconolite is

Reference to the stoichiometry of naturally occurring zirconolites (Table 7) indicates that Zr per seven O atoms is greater than unity, and the amounts of excess Zr, Nb, Mg, Fe, and Ti are usually sufficient to fill all the Ti sites. The Ca site is deficient, however. This suggests that, in more complex systems, U may enter the Ca site.

Kesson and Ringwood (1981) investigated the partitioning of U into the Ca site by synthesizing materials along the join CaZrTi₂O₇-UZrMgTiO₇. The assumed substitution mechanism is

where U replaces Ca, and Mg replaces Ti to maintain charge balance. The zirconolites produced in the runs contain substantially more UO_2 than shown to be capable of entering the Zr site alone. Hence, some U^{4+} must be entering the Ca site, and some Mg^{2+} must be entering the Ti site, while the remaining portion of U enters the Zr site. The sum of these mechanisms allows a maximum of 10 mole % U to enter zirconolite.

Both U substitution mechanisms (Eqs. [2] and [3]) should operate in SYNROC-D since Fe^{2+} can replace Mg^{2+} in the coupled substitution mechanism, yielding maximum U solubility in zirconolite. The data in Table 4 demonstrate that both substitutions do, in fact, occur in SYNROC-D, but there is no apparent pattern to aid in determining which mechanism predominates. The zirconolites in the High-Fe formulation have completely filled Ca sites indicating that U^{4+} must be solely in the Zr site (low Fe^{2+} , Eq. [2] dominates). The zirconolites in the composite formulation possess full Zr sites (some Zr may actually be in the Ti sites) indicating that U^{4+} could be accommodated totally within the Ca site. In the High-Al formulation, U^{4+} must be present in both sites.

For the purposes of calculation, both maximum loading and product quality must be considered. Zirconolites are, therefore, never modeled with U concentrations higher than 5 mole % (the maximum that can be accommodated in the Zr site). Hence, only U/Zr is allowed to vary. Also, since UO_2 is strongly partitioned into zirconolite, it is safe to neglect UO_2 incorporation in perovskite (nonstoichiometric substitution $\text{U}^{4+} \rightleftharpoons \text{Ca}^{2+}$) as long as the zirconolite saturation level is not exceeded.

The rare earth elements in SYNROC are accommodated in a CaTiO_3 perovskite. Trivalent lanthanides (RE = lanthanides) can enter perovskite in a number of ways. Three mechanisms are shown below,

In the first mechanism (Eq. [4a]), a monovalent Na accompanies the trivalent rare earth in substituting for 2 Ca^{2+} . In the second mechanism (Eq. [4b]),

Al^{3+} enters the six-fold Ti site, with the rare earth filling the Ca site to maintain charge balance. In the final mechanism (Eq. [4c]), the RE is substituted directly into the Ca site. To maintain charge balance, a cation vacancy must exist for each two lanthanide atoms substituted. A recent study by Balachandran and Error (1981) has shown that single-phase perovskites with the formula $\text{La}_x\text{Sr}_{1-x}\text{O}_3$ may be synthesized where "x" equals 40 at.%. Hence, very little SrTiO_3 (or, by analogy, CaTiO_3) is needed to stabilize the $\text{La}_{2/3}\square_{1/3}\text{TiO}_3$ perovskites.

The SRP sludges contain ample Na and Al to accommodate the lanthanides in perovskite via the first two solution mechanisms (Eqs. [4a] and [4b]). Although there are no known data regarding the maximum concentrations of lanthanides for which these mechanisms are valid, reference to naturally occurring perovskites (Table 8) after Haaker and Ewing (1981) indicates they are sufficient to accommodate the lanthanide concentrations in the sludges. However, to maintain a margin of error (overestimation is preferable to underestimation), the additives should be modeled using the third mechanism. In this way, 1.5 mol TiO_2 should be added for every mole of lanthanide oxide. A further precaution can be added by considering the accommodation of lanthanides in zirconolite. This mechanism is simply

yielding a pyrochlore molecule, $\text{RE}_2\text{Ti}_2\text{O}_7$. For this substitution, 2 mol TiO_2 should be added for every mole of lanthanide oxide. Due to the additional margin of safety, our formulations use the pyrochlore calculation.

CS HOST PHASE

The manner in which the additions for Cs immobilization are calculated depends on the Cs host phase chosen. In some cases, Cs has been treated as a separate stream and immobilized as presynthesized Ba-hollandite. In this case, it can be ignored during the calculation. If Cs is to be immobilized in situ, it will reside in either pollucite or nepheline. Since the concentration of Cs in the sludges is small relative to the concentration in pollucite, the modal amount of pollucite necessary would be extremely small (<<10 wt%). In this regard, its presence in SYNROC-D assemblages has never

Table 8. Compositions of natural perovskites (after Haaker and Ewing, 1981).

A. Oxides	1 ^a	2 ^b	3 ^c	4 ^d	5 ^e	6 ^f
CaO	41.8	25.95	36.31	26.55	1.47	1.83
TiO ₂	58.2	10.05	53.87	51.47	39.28	46.45
Nb ₂ O ₅	--	43.90	0.36	2.50	3.95	6.31
Fe ₂ O ₃	--	8.74	1.77	1.87	--	0.88
Na ₂ O	--	4.03	1.29	1.74	6.36	6.41
K ₂ O	--	0.03	0.51	0.45	0.54	--
RE	--	2.03	2.58	10.70	31.28	24.00
MgO	--	2.20	--	--	--	--
MnO	--	0.77	--	--	0.02	--
SiO ₂	--	0.45	1.70	1.15	8.18	--
S	--	0.90	--	--	--	--
Te ₂ O ₃	--	--	--	--	2.46	--
ThO ₂	--	--	0.08	0.08	3.00	13.00
U ₃ O ₈	--	--	--	--	0.17	--
SrO	--	--	1.18	1.63	1.21	--
ZrO ₂	--	--	--	--	0.10	--
Al ₂ O ₃	--	--	--	1.30	0.60	--
Total	100.0	99.05	99.66	99.44	98.62	98.88

^a Ideal CaTiO₃ stoichiometry.

^b Niobian perovskite.

^c Perovskite.

^d Rare-earth-bearing perovskite.

^e Loparite.

^f Irinite.

Table 8. (Continued)

		Structural formula based on 3 O atoms					
B.	Cations	1 ^a	2 ^b	3 ^c	4 ^d	5 ^e	6 ^f
Ca		1.0	0.74	0.90	0.69	0.05	0.06
Ti		1.0	0.20	0.94	0.94	0.88	1.00
Nb		--	0.53	tr ^g	0.03	0.05	0.08
Fe		--	0.18	0.03	0.03	--	0.02
Na		--	0.21	0.06	0.08	0.04	0.35
K		--	--	0.02	0.01	0.02	0.24
RE		--	0.02	0.02	0.09	0.33	--
Mg		--	0.09	--	--	--	--
Mn		--	0.02	--	--	tr	--
Si		--	0.01	0.04	0.03	0.24	--
S		--	0.05	--	--	--	--
Te		--	--	--	--	0.03	--
Th		--	--	tr	tr	0.02	0.09
U		--	--	--	--	tr	--
Sr		--	--	0.02	0.02	0.02	--
Zr		--	--	--	--	tr	--
Al		--	--	--	0.04	0.02	--
Total		2.00	2.05	2.03	1.96	1.70	2.38

^a Ideal CaTiO_3 stoichiometry.

^b Niobian perovskite.

^c Perovskite.

^d Rare-earth-bearing perovskite.

^e Loparite.

^f Irinite.

^g tr = trace.

been verified (Ryerson et al., in progress). Due to this ambiguity, we have chosen to let Cs mimic the behavior of Na immobilized in nepheline.

FORMULATION OF SYNROC-D: SAMPLE CALCULATION

A sample additive calculation for a typical SRP composite sludge (Table 9) is presented below. For this calculation, mineral compositions similar to those determined by Ringwood et al. 1979 (Table 4c, this report) are employed. The ratio $U/(U + Zr)$ in zirconolite has been set at 0.13, and $Sr/Sr + Ca$ is set at 0.02 (Table 10). The experimenter could, of course, choose other values for these parameters that would alter waste loading and radionuclide concentrations in the SYNROC phases.

The first step is conversion of the sludge composition to moles of oxide/kg calcined sludge. In this conversion, U_3O_8 is reduced to UO_2 , and sulfate (Na_2SO_4 is the actual species) is reduced to sulfide. Also, Cs_2O is considered to be indistinguishable from Na_2O in the calculation.

The next step in the calculation is the assignment of sludge and additive constituents to the SYNROC phases described above. This is done by first determining the amount of a given phase required to immobilize a certain sludge constituent. Having done this, the amount of material necessary for phase formation (i.e., nepheline and perovskite) can be calculated. The amount of material necessary for phase formation is then compared to the amount present in sludge, and the excess components (or necessary additives) can be calculated. Each phase of the procedure just described is illustrated in the following table.

Nepheline is calculated first. The sludge contains 0.88 mol Na_2O plus Cs_2O /kg sludge. Since nepheline is 25 mole % Na_2O , 3.52 mol nepheline are required to immobilize Na and Cs.

Oxides	Amount necessary for nepheline formation (mol)	Amount present in sludge (mol)	Excess components in sludge (mol)	Necessary additives (mol)
SiO_2	1.76	0.15	--	1.61
Al_2O_3	0.88	2.94	2.06	--
Na_2O^*	0.88	0.88	0	--

Only part of the Al_2O_3 in the sludge is consumed in nepheline formation and 96.8 g (1.61 mol) SiO_2 must be added per kilogram of sludge calcined.

The anhydrous sludge contains 0.12 mol of UO_2/kg . This is all assigned to zirconolite (although some is actually accommodated in perovskite). The model zirconolite contains 4.1 mole % UO_2 requiring 2.93 mol of zirconolite for immobilization.

Oxides	Amount necessary for zirconolite formation (mol)	Amount present in sludge (mol)	Excess components in sludge (mol)	Necessary additives (mol)
TiO_2	1.21	--	--	1.21
ZrO_2	0.79	--	--	0.79
UO_2	0.12	0.12	0	--
Al_2O_3	0.03	2.06	2.01	--
Fe_2O_3	0.13	2.43	2.30	--
MnO	0.04	1.22	1.18	--
NiO	0.08	0.66	0.58	--
CaO	0.52	0.52	0	--

* $\text{Na}_2\text{O} + \text{Cs}_2\text{O}$

This consumes UO_2 , Al_2O_3 , Fe_2O_3 , MnO , NiO , and CaO from the sludge and requires the addition of 96.7 g (1.21 mol) TiO_2 and 97.3 g (0.79 mol) ZrO_2 to 1 kg of calcined sludge.

The immobilization of Sr is achieved by perovskite. The model perovskite contains 1 mole % SrO , and the sludge contains 0.03 mol SrO/kg . This requires 3 mol of perovskite. Perovskite formation requires the addition of 119.9 g TiO_2 and 82.4 g CaO reagent (equivalent oxide) to the sludge.

Oxides	Amount necessary for perovskite formation (mol)	Amount present in sludge (mol)	Excess components in sludge (mol)	Necessary additives (mol)
TiO_2	1.50	--	--	1.50
CaO	1.47	0	--	1.47
SrO	0.03	0.03	0	--

Table 9. Sludge and additive compositions used in sample calculation.

	1 ^a	2 ^b	3 ^c	4 ^d	5 ^e
SiO ₂	0.90	0.15	0.56	6.06	6.62
TiO ₂	--	--	--	20.12	20.12
ZrO ₂	--	--	--	6.09	6.09
U ₃ O ₈	3.50	0.12	2.19	--	2.19
Al ₂ O ₃	30.00	2.94	18.77	--	18.77
Fe ₂ O ₃	38.80	2.43	24.28	--	24.28
MnO ₂	10.60	1.22	6.63	--	6.63
NiO	4.90	0.66	3.07	--	3.07
SO ₄ ^f	1.00	0.10	0.63	--	0.63
CaO	2.90	0.52	1.81	5.16	6.97
Na ₂ O	5.40	0.88	3.38	--	3.38
Cs ₂ O	0.39	0.01	0.24	--	0.24
Ce ₂ O ₃	0.78	0.023	0.49	--	0.49
Nd ₂ O ₃	0.78	0.023	0.49	--	0.49
SrO	0.39	0.03	0.24	--	0.24
Total	100.34	--	62.78	37.43	100.21

^a Typical composite sludge in wt% oxide.

^b Typical composite sludge, "A", recast as mole of oxide, or metal/1000 g anhydrous sludge. U₃O₈, MnO₂, and SO₄ have been reduced to UO₂, MnO, and S, respectively.

^c wt% oxides of sludge in final formulation (U as U₃O₈, Mn as MnO₂, S as SO₄).

^d wt% oxide, additives.

^e wt% oxide, total bulk composition (U as U₃O₈, Mn as MnO₂, S as SO₄).

^f Sulfur is given as SO₄ (the actual species is Na₂SO₄, and the appropriate amount of Na₂O is included in the Na₂O value in column 1).

Table 10. Model mineral compositions for sample calculation (mole fractions).

	Zirconolite	Perovskite	Nepheline
SiO ₂	--	--	0.50
TiO ₂	0.414	0.500	--
ZrO ₂	0.270	--	--
UO ₂	0.041	--	--
Al ₂ O ₃	0.010	--	0.250
Fe ₂ O ₃	0.045	--	--
FeO	--	--	--
MnO	0.013	--	--
NiO	0.028	--	--
CaO	0.178	0.490	--
Na ₂ O	--	--	0.250
SrO	--	0.010	--
U/Zr + U ^a	0.130	--	--
Sr/Sr + Ca ^a	--	0.020	--

^a Atom ratios.

The sulfide content is small (0.1 mol) and, in our calculation, is assumed to combine with NiO to form NiS. This consumes 0.1 mol of NiO and does not require additives.

At this point in the calculation, excess transition metals are considered in calculating the additives necessary to form spinel. The excess components are illustrated in the table below.

Transition metal oxides (+Al ₂ O ₃)	Excess components in sludge (mol)	After reduction (mol)
Al ₂ O ₃	2.06	2.06
Fe ₂ O ₃	2.30	1.08
FeO	--	2.45
MnO	1.18	1.18
NiO	0.48	0.48
TiO ₂	--	--

From the second column (excess) we calculate $\text{Fe}/\text{Fe} + \text{Al}^*$ equal to 0.64. Using the relationship in Fig. 6,

$$(\text{Fe}^{3+}/\text{Fe}^{2+})_{\text{sp}} = 2.38(\text{Fe}/\text{Fe} + \text{Al}^*)_{\text{sludge}} - 0.64 \quad (6)$$

we obtain an $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the spinel equaling 0.88. Therefore, the sludge must be reduced to the condition given in the third column. For these calculations, the transition metal oxides are then combined as Fe_3O_4 (1.08 mol), FeAl_2O_4 (1.37 mol), MnAl_2O_4 (0.69 mol), Mn_2TiO_4 (0.24 mol), and Ni_2TiO_4 (0.24 mol). This results in a spinel with TiO_2 (6.33 mole %). The relation in Fig. 5c,

$$(\text{TiO}_2)_{\text{sp}} = 10.2 (\text{Fe}/\text{Fe} + \text{Al}^*)_{\text{sludge}} + 20.9 \quad , \quad (7)$$

which is valid for $0.50 < \text{Fe}/(\text{Fe} + \text{Al}^*) < 1.1$ can be used to estimate the TiO_2 content of the spinel at 14.4 mole %. To maintain a margin for error, the higher value is chosen, which requires the further addition of 1.21 mol or 97.5 g TiO_2/kg anhydrous sludge. If $(\text{Fe}/\text{Fe} + \text{Al}^*)$ had been less than 0.49, the relation

$$(\text{TiO}_2)_{\text{sp}} = 49.0 (\text{Fe}/\text{Fe} + \text{Al}^*)_{\text{sludge}} - 8.1 \text{ for } \sim 0.2 < \text{Fe}/(\text{Fe} + \text{Al}^*) < 0.50 \quad (8)$$

would have been applicable.

The lanthanides add up to 0.046 mol/kg. These components are cast as a pyrochlore ($\text{X}_2^{3+}\text{Ti}_2\text{O}_7$) molecule requiring 0.092 mol or 7.35 g of TiO_2 .

The total additives per kilogram of anhydrous sludge are

	<u>g</u>
TiO_2	321.5
ZrO_2	97.3
CaO	82.4
SiO_2	<u>96.8</u>
Total	598.0

This yields a waste loading of 62.6 wt% sludge; the final composition is given in Table 9. The expected mineralogy for this formulation is

	wt%
High Al ₂ O ₃	16.4
High Fe ₂ O ₃	19.1
Perovskite	13.7
Spinel	50.8

the Fe/Al ratio is 0.03, which is well below the recommended value of 0.4. Therefore, adjust this ratio to at least 0.4 by adding 810 g of Fe₂O₃ (see second column). The Fe₂O₃ must then be reduced to FeO to make FeAl₂O₄ component in spinel. This results in a Fe³⁺/Fe²⁺ lower than that predicted by the relation in Eq.(6), should be noted in preparing the high Al sample powder. Equation (8) can be used to calculate the necessary TiO₂ addition, and it specifies the addition of 140 g (1.76 mol) of TiO₂. Additives (g), can be added to increase the range of synthesis for single-phase spinels.

Transition metal oxides (+Al ₂ O ₃)	Excess components in sludge (mol)	Necessary additives (mol)
Al ₂ O ₃	7.98	--
Fe ₂ O ₃	0.25	5.07
FeO	--	--
MnO	0.19	--
ZnO	0.02	--
TiO ₂	--	1.76

The Fe/Al ratio is 0.03, which is well below the recommended value of 0.4. Therefore, adjust this ratio to at least 0.4 by adding 810 g of Fe₂O₃ (see second column). The Fe₂O₃ must then be reduced to FeO to make FeAl₂O₄ component in spinel. This results in a Fe³⁺/Fe²⁺ lower than that predicted by the relation in Eq.(6), should be noted in preparing the high Al sample powder. Equation (8) can be used to calculate the necessary TiO₂ addition, and it specifies the addition of 140 g (1.76 mol) of TiO₂. Additives (g), can be added to increase the range of synthesis for single-phase spinels.

An alternative method employs the addition of MgO to immobilize Al_2O_3 as MgAl_2O_4 spinel component. This method requires only 320 g MgO for the above composition and has the added advantages of higher waste loading and of requiring no redox control. Ringwood (private communication, 1981) has shown that this alternative produces spinels compatible with the other SYNROC phases. However, at this time, samples produced from this composition have not received the extensive leach testing given the Fe-bearing materials.

CONCLUSIONS

SYNROC additives to SRP sludge can be calculated so that high waste loading (approximately 60 wt%) and suitably dilute radionuclide concentrations (less than 50% of the saturation value of any radionuclide-bearing phase) are achieved. Compositional variations in SRP sludges are reflected in the composition of the spinels. Compositional trends in spinels X_{TiO_2} and $\text{Fe}^{+3}/\text{Fe}^{+2}$ can be described as the Fe/Fe + Al (atomic) ratio of the sludges. This feature is quite valuable in terms of automated additive calculations (i.e., the ADSYN program [see Appendix A]). To improve these additive calculations (should such improvement actually be necessary), a more diverse group of sludge compositions must be investigated. This would further our understanding of the relationship between sludge and mineral-phase composition.

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APPENDIX A

ADSYN: A COMPUTER PROGRAM FOR CALCULATION OF SYNROC ADDITIVES

ADSYN is an interactive FORTRAN program (see microfiche at the end of this report) that calculates the amounts of SYNROC additives and resulting nominal mineral compositions for a given input sludge composition. The program is now run on a Hewlett Packard Model HP 1000 computer system.

Here is a simplified flow sheet for ADSYN operation:

1. User input of sludge composition and desired solid solution limits for Sr and U.
2. Calculation of additives necessary to approximate DP1545 compositions.
3. Calculation of Cs and Na immobilization in nepheline.
4. Calculation of U immobilization in zirconolite.
5. Calculation of Sr immobilization in perovskite.
6. Calculation of S immobilization in nickel sulfide.
7. Calculation of lanthanides (Ce, Nd) as a "pyrochlore" (RETi_2O_7 ; rare earths are distributed between perovskite and zirconolite).
8. Calculation of Mn, Fe, Ni, and Al as spinel.
9. Output of quantities of reagent additives, equivalent oxide composition, nominal mineral compositions (as weight proportions).

Input can be entered by the user from an HP 1000 terminal or as a data file. The user can choose to: 1) adjust starting composition to a DP1545 reference composition (Stone et al. 1979), or 2) input his own reference composition. The second option is useful when the user wishes to examine the effects of varying quantities of individual components.

The required input is

1. Sludge composition (wt%).
2. Sludge weight in grams.
3. Reference composition type, i.e., DP1545 High-Fe, High-Al, composite or user input reference.
4. Whether or not all components are adjusted to DP1545 reference or just Fe and Al.
5. Whether Cs is included in the sludge.
6. Desired Sr/Sr + Ca ratio in perovskite.

7. Desired U/U + Zr ratio in zirconolite.
8. Desired percentage safety margin (over tailoring of TiO_2).

If the user wishes to input his own reference composition, he must also input

9. DP1545 sludge type closest to the composition.
10. Sludge composition.

A typical sequence of input/output at a terminal is shown in Fig. A-1.

It should be noted that, although the program asks for wet sludge composition and weight, the user may input dry compositions as long as consistency is maintained.

A user may want to repeat a number of tests with the same starting sludge composition or with only minor changes. With this in mind, the option is available for data file input. To run the program, all the user need do is specify the data file input option and give the name of the existing data file. The required data file format setup and a sample are shown in Fig. A-2.

To cut down on the number of user input steps in the interactive input, default "actual additives" (reagents) are assumed. If the user wishes to change the "actual additives," he must use the data file input option (Fig. A-2). A sample program output is shown in Fig. A-3.

The program outputs:

1. The spinel $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio and whether or not it was adjusted from the ratio equation: $\text{Fe}^{+3}/\text{Fe}^{+2} = 2.338 * [\text{Fe}/(\text{Fe} + \text{Al})] - 0.64$.
2. Sludge type.
3. Mineral compositions.
4. The TiO_2 safety factor, $\text{Sr}/(\text{Sr} + \text{Ca})$ and $\text{U}/(\text{U} + \text{Zr})$ ratios (these three are user inputs).
5. A composition table of:
 - a. Original sludge.
 - b. DP1545 (or reference) composition.
 - c. Additions to get to DP1545.
 - d. Working composition.
 - e. SYNROC additions.
 - f. Total (SYNROC + DP1545) additions.
6. A table of actual additives/100 g sludge and per user input of total sludge weight (the example shows 1000 g).
7. A table of anhydrous composition for original sludge, additives, and total.

WAITING FOR INPUT

:ADSYN ← *Type the name of the code to start.*

DO YOU WISH TO INPUT DATA FROM THE TERMINAL OR FROM A DATA FILE?NOTE:
IF YOU WISH TO CHANGE THE DEFAULT REAGENTS TO BE ADDED, YOU MUST USE DATA
FILE INPUT

INPUT 1 FOR TERMINAL OR 2 FOR A DATA FILE

1 ← *Specifies interactive input.*

INPUT SLUDGE COMPOSITION - WT% OF TOTAL (WET) SLUDGE

Fe2O3	=	44.3
Al2O3	=	31.7
MnO2	=	12.3
U3O8	=	0
CaO	=	1.7
NiO	=	4.8
SiO2	=	1.2
Na2O	=	1.4
Na23SO4	=	1.3
SrO	=	0
Md2O3	=	0
Ce2O3	=	0
Cs2O	=	0

INPUT TOTAL WET SLUDGE WEIGHT IN GRAMS 8596.

INPUT DESIRED DP1545 COMPOSITION:

- (1) NO AL REMOVAL, HIGH FE
- (2) NO AL REMOVAL, COMPOSITE
- (3) NO AL REMOVAL, HIGH AL
- (4) OTHER - TO BE ENTERED AT TERMINAL

INPUT 1,2,3, OR 4

4 ← *Specifies operator input of DP1545 composition.*

INPUT CLOSEST DP1545 TO DESIRED COMPOSITION FOR USE IN CALCULATING
MINERAL COMPS.:

- 1--HI FE
- 2--COMPOSITE
- 3--HI AL

2

SHOULD ALL COMPOUNDS BE ADJUSTED TO DP1545 OR JUST AL2O3 AND FE2O3?
ENTER 1 FOR ALL AND 2 FOR FE2O3 & AL2O3

1

SHOULD DP1545 INCLUDE Cs2O?

INPUT 1 FOR YES AND 2 FOR NO 1

INPUT DESIRED Sr/(Sr+Ca) RATIO .027

INPUT DESIRED U/(U+Zr) RATIO .13

Figure A-1. Example of running ADSYN code with interactive data input.

INPUT DESIRED SAFETY MARGIN FOR TIO₂. EX:

INPUT 1.0 IF NO ADDITIONAL TIO₂ ABOVE THAT CALCULATED SHOULD BE ADDED.

INPUT 1.1 IF 10% ADDITIONAL TIO₂ SHOULD BE ADDED FOR SAFETY.

1.

INPUT DESIRED STARTING COMPOSITION OTHER THAN DP1545

Fe ₂ O ₃	=	44.3
Al ₂ O ₃	=	34.65
MnO ₂	=	12.19
U ₃ O ₈	=	4.0
CaO	=	3.3
NiO	=	4.8
SiO ₂	=	1.04
Na ₂ O	=	6.23
Na ₂ SiO ₄	=	1.14
SrO	=	.49
Md ₂ O ₃	=	.98
Ce ₂ O ₃	=	.98
Cs ₂ O	=	.49

*The desired composition
was input to adjust the
DP1545 composition so
that no NiO would be
needed.*

*The results of the calculation are printed
into hardcopy.*

The output follows (Fig. 2).

Figure A-1. (continued)

- Row 1- Starting sludge composition, wt%:
Fe2O3, Al2O3, MnO2, U3O8, CaO, NiO, SiO2, Na2O, Na2SO4, SrO, Nd2O3, Ce2O3, Cs2O
- Row 2- Total sludge weight, grams
- Row 3- Desired reference composition (first three are DP1545):
1 - Hi Fe 2 - Composite 3 - Hi Al 4 - Other (see Row 4)
- Row 4- Other reference composition. This is only used if a 4 is entered in Row 3, but numbers (even if 0's) must be entered as space holders
- Row 5- Closest DP1545 to reference composition:
1 - Hi Fe 2 - Composite 3 - Hi Al
- Row 6- Reference adjustment to starting sludge:
1 - all compounds adjusted 2 - only Al2O3 and Fe2O3 adjusted
- Row 7- Should Cs2O be included?:
1 - yes 2 - no
- Row 8- Sr/(Sr+Cs) ratio in perovskite
- Row 9- U/(U+Zr) ratio in zirconolite
- Row 10 - TiO2 safety margin, see Fig. A-1
- Rows 11-25 - Actual additives and formula weights. Each additive name and name must be 16, and only 16, characters long (incl. spaces and punctuation). The additive name is followed by the formula weight. The additives must be input in the following order:
- Row 11 - Fe, Row 12 - Al, Row 13 - Mn, Row 14 - U,
Row 15 - Ca, Row 16 - Ni, Row 17 - Si, Row 18 - Na2O,
Row 19 - Na2SO4, Row 20 - Sr, Row 21 - Nd, Row 22 - Ce,
Row 23 - Cs, Row 24 - Ti, Row 25 - Zr
- Row 26 - Additive multiplication factors. This is the number of moles of additive that must be added to get 1 mole of principal component. For example: To get 1 mole of Fe2O3, 2 moles of Fe(NO3)3 9H2O must be added. Therefore, the multiplication factor is 2.0. Multiplication factors must be entered on one row and separated by commas or spaces, in the same order as the additives are entered in Rows 11-25.

Figure A-2. Data file input format with example.

0001	43.3,.1.0,2.8,10.0,2.0,7.8,0.3,2.9,.4,.4,.8,.8,0.0	
0002	1000.0	
0003	1	
0004	45.0,4.0,3.0,6.0,2.5,8.0,0.5,3.0,.4,.4,.8,.8,.5	
0005	1	
0006	1	
0007	2	
0008	.1	
0009	.2	
0010	1.1	
0011	FE(NO3)3.9H2O	403.87
0012	AL(NO3).9H2O	375.00
0013	MnO2	86.937
0014	UO2(NO3)2.6H2O	518.09
0015	Ca(NO3)2.4H2O	236.1
0016	NiO	74.69
0017	30%(SiO2SOLN9WT)	200.3
0018	NaNO4	85.01
0019	Na2SO4	142.037
0020	Sr(NO3)2	211.65
0021	Nd(NO3)3.6H2O	438.29
0022	Ce(NO3)3.5H2O	416.15
0023	CsNO3	194.92
0024	TiO2	79.9
0025	Zr(NO3)4	339.25
0026	2.0,2.0,1.0,3.0,1.0,1.0,1.0,2.0,1.0,1.0,2.0,2.0,2.0,1.0,1.0	

Figure A-2. (continued)

THE SPINEL FE+3/+2 RATIO IS 1.42
IT DID NOT NEED ADJUSTMENT

HIGH FE SLUDGE

MINERAL COMPOSITIONS

	NEPHELINE			ZIRCONOLITE			PEROVSKITE		
	MOLES	M. FRN.	WT. FRN.	MOLES	M. FRN.	WT. FRN.	MOLES	M. FRN.	WT. FRN.
FE2O3	0.000	0.00	0.00	.033	.047	.078	0.000	0.00	0.00
Al2O3	.062	.250	.359	.603	.604	.004	0.000	0.00	0.00
MnO	0.000	0.00	0.00	.017	.024	.022	0.000	0.00	0.00
CaO	0.000	0.00	0.00	.178	.251	.146	.035	.450	.354
NiO	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
SiO2	.125	.500	.423	0.000	0.00	0.00	0.000	0.00	0.00
Na2O	.062	.250	.218	0.000	0.00	0.00	0.000	0.00	0.00
S	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
SrO	0.000	0.00	0.00	0.000	0.00	0.00	.004	.050	.074
Nd2O3	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
Ce2O3	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
Ca2O	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
TiO2	0.000	0.00	0.00	.299	.422	.350	.039	.500	.568
ZrO2	0.000	0.00	0.00	.143	.202	.258	0.000	0.00	0.00
FeO	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
UO2	0.000	0.00	0.00	.036	.051	.142	0.000	0.00	0.00

	SULFIDE			LANTHANIDE			SPINEL		
	MOLES	M. FRN.	WT. FRN.	MOLES	M. FRN.	WT. FRN.	MOLES	M. FRN.	WT. FRN.
FE2O3	0.000	0.00	0.00	0.000	0.00	0.00	.139	.247	.403
Al2O3	0.000	0.00	0.00	0.000	0.00	0.00	.043	.076	.079
MnO	0.000	0.00	0.00	0.000	0.00	0.00	.016	.029	.026
CaO	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
NiO	.003	.500	.345	0.000	0.00	0.00	.102	.130	.137
SiO2	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
Na2O	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
S	.003	.500	.655	0.000	0.00	0.00	0.000	0.00	0.00
SrO	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
Nd2O3	0.000	0.00	0.00	.002	.165	.338	0.000	0.00	0.00
Ce2O3	0.000	0.00	0.00	.002	.169	.338	0.000	0.00	0.00
Ca2O	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
TiO2	0.000	0.00	0.00	.010	.667	.325	.068	.121	.099
ZrO2	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00
FeO	0.000	0.00	0.00	0.000	0.00	0.00	.197	.348	.256
UO2	0.000	0.00	0.00	0.000	0.00	0.00	0.000	0.00	0.00

Figure A-3. Sample output.

THE TiO2 SAFETY FACTOR IS 1.10
 THE SR/(SR+CA) RATIO IS .100
 THE U/(U+Zr) RATIO IS .200

	ORIG. SLUDGE/100 G. GRAMS	PER 100 G. OF WET SLUDGE		WORKING COMP.		SYNROC ADDNS.		TOTAL ADDNS. GRAMS
		DP1545 GRAMS	ADDN. TO GET DP1545 GRAMS	GRAMS	MOLES	MOLES	GRAMS	
FE2O3	43.30	43.30	0.00	43.30	.271	0.000	0.00	0.000
Al2O3	1.00	3.93	2.98	3.98	.039	.069	7.02	10.001
MnO2	2.80	2.90	.10	2.90	.033	0.000	0.00	.999
U3O8	10.00	10.05	.05	10.05	.012	0.000	0.00	.049
CaO	2.00	2.95	.95	2.95	.053	.160	8.96	9.907
NiO	7.80	7.39	0.00	7.80	.104	0.000	0.00	0.000
SiO2	.30	.33	.03	.33	.005	.119	7.16	7.181
Na2O	2.90	3.68	.78	3.68	.059	0.000	0.00	.731
Na2SO4	.40	.41	.01	.41	.003	0.000	0.00	.607
SrO	.40	.33	0.00	.40	.004	0.000	0.00	0.000
Nd2O3	.80	.65	0.00	.80	.002	0.000	0.00	0.000
Ce2O3	.80	.65	0.00	.80	.002	0.000	0.00	0.000
Ca2O	0.00	0.00	0.00	0.00	0.000	0.000	0.00	0.000
TiO2	0.00	0.00	0.00	0.00	0.000	.457	30.53	30.529
ZrO2	0.00	0.00	0.00	0.00	0.000	.183	17.65	17.650
FrO	0.00	0.00	0.00	0.00	0.000	0.000	0.00	0.000
UO2	0.00	0.00	0.00	0.00	0.000	0.000	0.00	0.000

Figure A-3. (continued)

ADDITIONS: SYNROC + DP1545
ACTUAL ADDITIVES - GRAMS

	PER 100 G WET SLUDGE	PER 1000.00 G WET SLUDGE
FE(NO3)3.9H2O	0.00	0.00
AL(NO3)3.9H2O	73.57	735.66
MnO2	.10	.99
UO2(NO3)2.6H2O	.09	.91
Ca(NO3)2.4H2O	41.71	417.11
NiO	0.00	0.00
30%SiO2 SOLN(WT)	23.94	239.40
NaN03	2.14	21.42
Na2SO4	.01	.07
Sr(NO3)2	0.00	0.00
Nd(NO3)3.6H2O	0.00	0.00
Ce(NO3)3.5H2O	0.00	0.00
CsNO3	0.00	0.00
TiO2	36.53	365.29
Zr(NO3)4	48.58	485.83

Figure A-3. (continued)

ANHYDROUS COMPOSITION

	WT. % SLUDGE	WT. % ADDITIVES	TOTAL
FE2O3	27.99	0.00	27.99
Al2O3	.65	6.46	7.11
MnO2	1.81	.06	1.87
U3O8	6.46	.03	6.50
CaO	1.29	6.40	7.70
NaO	5.04	0.00	5.04
SiO2	.19	4.63	4.84
Na2O	1.87	.50	2.38
Na2SO4	.26	.00	.26
SrO	.26	0.00	.26
Nd2O3	.52	0.00	.52
Ce2O3	.52	0.00	.52
Cs2O	0.00	0.00	0.00
TiO2	0.00	23.61	23.61
ZrO2	0.00	11.41	11.41
FeO	0.00	0.00	0.00
UO2	0.00	0.00	0.00
	<hr/> 46.86	<hr/> 53.14	<hr/> 100.00

MINERAL WT. PERCENTS (APPROX.)

NEPHELINE	11.82
ZIRCONOLITE	45.64
PEROVSKITE	3.63
SULFIDE	.42
LANTHANIDE	1.52
SPINEL	36.91

Figure A-3. (continued)