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Support for DOE Program in Mineral Waste-Form Development

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Support For DOE Program in
Mineral Waste-Form Development

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by
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SUPPORT FOR DOE PROGRAM IN
MINERAL WASTE FORM DEVELOPMENT

I. INTRODUCTION

This research investigation relates to sintered simulated ceramic waste forms of the generic SYNROC compositional type. Though they have been formulated with simulated wastes only, they serve as prototypes for potential "hot," processed, crystalline waste forms whose combined thermodynamic stability and physical integrity are considered to render them capable of long term immobilization of high level radwastes under deep geologic disposal conditions.

In several earlier studies in the U. S. and in Australia, it has been demonstrated that by incorporating the various radwaste ions directly into the molecular structures of one or more of the three crystalline phases which make up the titanate-based SYNROC phase assemblage, very low leach rates can be maintained under simulated deep geologic groundwater conditions. Stability in strong radiation fields has also been demonstrated.

The high level radwastes under consideration would stem from the reprocessing of commercial nuclear power fuels. Since different types of nuclear fuels as well as different types of chemical reprocessing are likely to be involved, the compositions of specific waste streams are expected to differ from one another. For best stability and highest resistance to leaching under long-term disposal conditions, it therefore may also be necessary to adjust (or tailor) the SYNROC matrix composition to the particular needs (phase demands) of a specific waste stream.

The problems involved are nontrivial, largely because of the very complex nature of the radwastes: a typical waste stream would contain more than 31 cation species. When the stabilizing matrix constituents are included, the final batch composition must successfully account (and find substitutional "holes" for some 35 different cation species. One of the important objectives of this study thus has been to develop a computer-based method for simulating these complex ion substitutions, and for calculating the resultant phase demands and batch formulations.

Primary goals of the study have been (1) use of that computer simulation capability to incorporate rationally the radwaste ions from a specific waste stream (PW-7a) into the available SYNROC lattice sites and (2) utilization of existing ceramic processing and sintering methodologies to assure (and to understand) the attainment of high density, fine microstructure, full phase development and other features of the sintered product which are known to relate directly to its integrity and leach resistance. Though improved resistance to leaching has been a continuing goal, time and budget constraints have precluded initiation of any leachability studies of these new compositions during this contract period.

Background

The SYNROC concept was developed in Australia by Ringwood.^{1,2} Since its introduction in 1978, SYNROC has been the subject of intensive investigation, particularly in Australia and in the U.S. Most of the active research groups, (e.g., at Lucas Heights in Australia and at Lawrence Livermore National Laboratory in the U.S.) have continued to utilize various adaptations of Ringwood's originally-proposed in-can hot pressing and/or hot isostatic pressing methods for densification.

The sintering approach for SYNROC undertaken at N.C.S.U. was initiated at University expense in 1979, and as a part of a national program on Alternative Wastes, subsequently received DOE support through the Savannah River Operations Office during FY-'80* and FY-'81.[†] That earlier effort, which has resulted in a number of publications,³⁻¹⁸ mostly made use of the supposedly sodium-free^{††} simulated radwaste spray calcines PW-4b and PW-4b-7, obtained from Battelle's Pacific Northwest Laboratories.

*"Stabilization of Simulated High Level Radioactive Wastes in Sintered Ceramic Forms," Contract DE-AC09-80ET-41902, for the period May 15, 1981 September 30, 1981.

†"Stabilization of Radioactive Wastes in Sintered Ceramic Forms," Contract DE-AC09-81SR-10957, for the period February 4, 1982 - September 30, 1982.

††During this study, it has been shown the initial soda-free presumption for PW-4b materials was not well founded. This point is discussed in later sections.

For FY-'83, the coordination of all DOE-supported SYNROC activity in the U. S. shifted from Savannah River to the Lawrence Livermore National Laboratory, with the NCSU effort being continued under LLNL Subcontract. At the request of LLNL's Technical Monitor, Dr. Clarence Hoenig, a number of questions relating to compositional design, sinterability and phase development of SYNROC ceramics containing simulated PW-7a radwaste additions have been addressed during this contract period. The methods employed and the results obtained are treated in following sections of this report.

II. EXPERIMENTAL APPROACH

A. Preliminary Experiments

1. Effect of atmosphere-temperature-time precalcine treatments on densification of SYNROC ceramics containing simulated PW-4b-7 radwastes.

a. Rationale. Though the early SYNROC studies at NCSU had employed a precalcine step;^{3,4} later methods successfully employed for densification of NCSU SYNROC compositions did not include a calcination step under reducing conditions in the 775-900°C range. Although previous leach results for those NCSU compositions have in general been quite good, the most recent high density samples thus produced showed relatively poor results when leach tested (MCC-3) at LLNL. Based on other LLNL studies, the observed leachabilities were most probably attributable to that lack of the calcination step.¹⁹

To test the effect of precalcination, two calcination temperatures were chosen: 775°C and 900°C, with a 4h hold in Ar-4% H₂. In addition, both Ar and Ar-4% H₂ atmospheres were used after the calcination to investigate the phase development (particularly the metallic phases) and the sintering characteristics. The heating rates and temperatures employed given in Table I were consistent with previous experiments.

b. Results. The sintering results are summarized in Table II. Schedules B, C, F and H yielded the best (and comparable) densities. It should also be pointed out that these densities were the best yet achieved for this particular batch.

X-ray diffraction results showed normal phase development in the best samples.

TABLE I
Firing Schedules for NCSU Sintering Study

Firing Schedule	Heating Rate(°C/min)	Calcine			Solid State Sintering		
		Soak			Soak		
		Temp(°C)	Time(hrs)	Atm	Temp(°C)	Time(hrs)	Atm
A	10	775	4	Ar-4%H ₂	1260	2	pure Ar
B	10	775	4	Ar-4%H ₂	1260	2	Ar-4%H ₂
C	10	900	4	Ar-4%H ₂	1260	2	Ar-4%H ₂
D	10	900	4	Ar-4%H ₂	1260	2	pure Ar
E	10	900	4	Ar-4%H ₂	500-1260	2	pure Ar
A'	repeat of A						
D'	repeat of D						
F	10	900	4	Ar-4%H ₂	1235	2	Ar-4%H ₂
G	10	900	4	Ar-4%H ₂	1210	2	Ar-4%H ₂
H	10	900	4	Ar-4%H ₂	1210	4	Ar-4%H ₂
I	10	900	4	Ar-4%H ₂	1220	2	Ar-4%H ₂
J	10	900	4	Ar-4%H ₂	1220	4	Ar-4%H ₂
K	10	no calcine			1260	2	Ar-4%H ₂

TABLE II
Comparison of NCSU & LLNL Calcine Temperatures and Atmosphere Conditions

*Sample Number	Firing Schedule	Mean Density(p/cc)	**Fract. Density	Water Absorbed(g)
48-1	A	4.0825	0.9278	0.0003
49-1	A	4.0307	0.9161	0.0004
48-2	B	4.2133	0.9576	0.0003
49-2	B	4.1885	0.9519	0.0005
48-3	C	4.2291	0.9612	0.0003
49-3	C	4.2333	0.9621	0.0002
48-4	D	3.6575	0.8313	0.0000
49-4	D	3.4761	0.7900	0.0001
49-5	A'	3.9764	0.9037	0.0003
49-6	E	3.9665	0.9015	0.0001
49-7	D'	3.5291	0.8021	0.0001
49-8	F	4.1978	0.9541	0.0005
49-9	G	4.0744	0.9260	0.0007
49-10	H	4.1624	0.9460	0.0004
51-1	I	4.2036	0.9571	0.0004
51-2	J	4.2364	0.9628	0.0004
40-1	K	4.1800	0.9500	0.0005

*Batch 48, 49, & 51 are identical except each was milled in different but comparable jar mills.

**Based on a theoretical density of 4.4 g/cc.

The following conclusions were drawn from the data in Table II:

1. Calcination at 900°C has a greater positive effect on attainable density than does calcination at 775°C .
2. A higher density is obtained by using the Ar-4% H_2 atmosphere during the entire firing. The pure Ar atmosphere retards the sintering, also promoting a "skin" effect as evidenced by the low water absorption at low density.
3. With the 900°C Ar-4% H_2 calcining step, a technically dense product can be achieved at a sintering temperature of 1220°C , lower than previously obtained for this composition. A minimum firing temperature of $1200\text{--}1210^{\circ}\text{C}$ is considered feasible if a somewhat longer soak period is used.

Based on these findings, all subsequent compositions, including those formulated with simulated PW-7a radwastes, utilized the 900°C calcination step in Ar-4% H_2 as a normal part of the firing schedule.

2. Effect of sodium and phosphorus additions on SYNROC ceramics containing simulated PW-4b-7 radwastes.

a. Rationale. Because of the uncertainty in phase formation kinetics with the inclusion of sodium and phosphorous in the waste, the densification behavior and phase formation in SYNROC-B type compositions with sodium and phosphorus additions was examined in detail (see Appendix I).

The following compositions were formulated following our standard procedure:

1. 3% Na_2O in Modified SYNROC-B.
2. 3% P_2O_5 in Modified SYNROC-B.
3. 3% Na_2O in Modified SYNROC-B with 7% PW-4b-7.
4. 3% P_2O_5 in Modified SYNROC-B with 7% PW-4b-7.
5. $\left. \begin{array}{l} 1.5\% \text{ Na}_2\text{O} \\ \text{ \& } \\ 1.5\% \text{ P}_2\text{O}_5 \end{array} \right\}$ in Modified SYNROC-B with 7% PW-4b-7.

b. Results. X-ray diffraction studies revealed:

1. Composition #5 showed no difference in phases formed when compared with previous materials.
2. The sodium additions (#3, #2) showed very faint extra unidentified lines with a few minor peaks in composition #3.
3. The phosphorus compositions (#2, #6, particularly #2) showed extra lines, identified as a calcium phosphate.

The densification behavior was affected by the inclusion of these cations, and particularly so with sodium. These results are shown in Table III.

Table III. Densification Behavior of Doped SYNROC-B containing added Na_2O and P_2O_5 .

	<u>Temp.</u>	<u>Time</u>	<u>Density</u>	<u>Fractional Density</u> <u>(4.4 g/cm³ basis)</u>
#1	1195°C	4h	4.0506	0.944
3	1195°C	4h	4.0650	0.923
	1260°C	2h	3.7916	0.8617
2	1195°C	4h	3.942	0.9189
4	1195°C	4h	3.973	0.903
	1260°C	2h	4.116	0.936
5	1195°C	2h	4.114	0.935
	1260°C	2h	3.928	0.893

The effect of phosphorus on the densification behavior was minor. Densities were slightly lower than normal ($D = 0.95$). On the other hand, sodium-containing samples were very much overfired at 1260°C , and probably so even at 1195°C . The samples at 1260°C showed warping, deformation, and cracking as well as discoloration (black area). Both additions (#5) showed intermediate behavior, with satisfactory results at 1195°C .

The examination of the microstructures revealed the following:

1. With the addition of P, small regions rich in calcium and phosphorus were found. It is believed these contribute minor x-ray peaks identified as a calcium phosphate.

2. With the addition of Na, a thin platy phase with a Na-Al-Ca-Ti composition was observed. This phase became blockier at 1260°C .

c. Summary*

1. At the 3% level, neither P or Na was completely incorporated in SYNROC-B. However, these "forced" doping levels are more than twice the level to be encountered with 10% PW-7a doping.

2. The presence of the PW-4b-7 radwaste (7%) in the SYNROC-B allows better incorporation of both N and P, presumably through charge compensation effects.

3. At the 1.5% level, P and Na are readily incorporated in SYNROC batches doped with PW-4b-7 without detectable changes in the x-ray pattern. With Na and P additions, the material densified at a lower temperature, and the morphology of at least one of the final phases was changed.

4. Sodium additions alter the densification behavior rather significantly.

* These findings preceded our discovery of substantial quantities of Na_2O (at approximately the 5% level^{20,21}) in the PW-4b-7 simulated radwaste² calcine which had been employed in preparing these 7% doped SYNROC compositions. The sodium contents in the Na-doped batches, therefore, were even greater than those discussed here. Similarly, real differences in performance between PW-4b-7 and PW-7a calcines attributable to sodium content obviously will be less than heretofore expected.

On the basis of this preliminary study, incorporation of the somewhat more complex Na-and P-bearing PW-7a radwaste in SYNROC by making use of the known behavior of the HPZ phase assemblage as a starting point, coupled with the existing knowledge of fabrication and processing previously developed for sintered HPZ SYNROC, was deemed the best approach.

B. Compositional Studies

1. Computer Programs.

The calculations for waste loadings and batch adjustments for possible radwaste stream compositions (e.g., PW-4b, PW-7a, etc.) have been studied with the aid of computer programs designed to estimate site location and compute the resultant phase demands (HPZ or other) and finally the resultant batch additions. Some simple programs of this sort had been utilized in earlier studies with PW-4b.⁴ A more sophisticated set of programs was written early in this contract period and used to produce the most recent SYNROC batches for PW-7a simulated radwastes described in this report (Table IV and Appendix II).

The program set consists of four parts:

1. Phase and Waste Entry
2. Valence Entry
3. Substitutional Schemes and Phase Demand
4. Batch and Cation Site Calculations for Target Loadings and Phase Ratios

a. Phase and Waste Entry. The phase and waste compositions can be entered in any form (atomic, weight or oxide %) and are stored on disks as phase and waste files. The entry system also creates and maintains directory files accessible for the substitutional and batching programs. The current version of the program does not allow entry of other forms (nitrates, carbonates, etc.) although this improvement could easily be added.

The phase entry program requires the valence of all cations, and the ion sizes are computed from the valence.

b. Valence Entry. The expected valence in a given waste (properly adjusted for the firing conditions employed) is entered and the ion sizes computed. Many valence lists for a given radwaste can be saved to explore changes in substitutional schemes as a function of the degree of reduction expected during calcining or densification.

c. Substitutional Scheme and Phase Estimation. The critical aspects of the substitutional calculations are (1) the ratios of radwaste ions in the various sites as a function of size and valence difference, and (2) the bookkeeping operations which sum the total amount of each phase required.

Two principal schemes have been employed so far in making the site selection. The first partitions the ion strictly according to size, so that the site for a given cation is the best fit sizewise, with allowance for multiple sites for the same ion (e.g., Ti and Ca ions fit in two or more HPZ phases). The second scheme is a somewhat more elaborate method which accords a 10/1 ratio for fitting of ions into sites with a size difference of 10%. For example, in this way, 9.1% are apportioned into a site 10% too small or too large, but 91% into an exact match. In addition, some attention is given to a valence mismatch, so that exact valence matches are given a higher priority than mismatches, even though the size may be (slightly) better for the non-valence-matched cation. In most cases, the choice between these two partitioning methods does not have a strong influence on the final composition.

The radwaste ions are placed one by one into the sites, and the valence differences are employed to compute site demand. For a given phase, the site with the highest demand (ratioed by their numbers in the phase crystal structure) determines the loading of that phase. The sites which have been less in demand then require the addition of the standard phase cations (i.e., from matrix, rather than radwaste) to bring about the proper stoichiometry for the "maximum conceivable loading" case. The subsequent calculations for each phase also produce the ratio of site demands for each phase, which can be translated into phase demand on a site, formula, weight, and volume basis.

d. Dilution and Batch Calculation. The final batch calculation is based on factors which can be varied as desired. The waste loading in oxide weight percent and the phase balance desired are entered, and the batch requirements are computed, which is a rather complex calculation but one well suited to the computer.

Although it is logical to suppose that the particular phase demand supplied by part 3 of the program should be employed, it may well be that a considerably greater dilution at a problem site (such as Na in the Ca site) might be prudent, so the program anticipates that the relative amount of the phases employed may need to be changed selectively. This is the case in adapting the HPZ system to incorporate Na-rich PW-7a radwaste, as explained below.

2. Composition Calculations for SYNROC Phases Doped with PW-7a.

Using the valence list (see Table I in Appendix II), this four-part set of programs was employed to partition the radwaste ions into eight cation sites in the three HPZ phases. The maximum conceivable waste loading was computed to be just about 40 weight percent (see Table II of Appendix II). The numbers in the first column are the atomic % (including oxygen) for the particular waste cation. The second column adjusts for the valence, such that a trivalent ion in a divalent site would create 3/2 times the demand for the matched case.

Several examples can be pointed out which illustrate the substitutional method. Sr^{+2} is apportioned between the Ca^{+2} sites in the P and Z phases and the Ba^{+2} site in the E phase as it matches the valence and is intermediate in size. It should also be pointed out that some ions, such as P, do not fit at all well according to the rules of structural inorganic chemistry. Even so, the "best" place, (i.e., substituting for Al^{+3}), was selected.

With this waste (when lacking in Gd and U), Na is the dominant radwaste ion (32% of the cations) and therefore its fate is considered to be critical to the success of this material formulation.

The phase demand and "maximum" loading (see Table III of Appendix II) reflects primarily the sodium and other major ion apportionments. The greatest uncertainty probably comes from the Mo, which under reducing conditions tends to form a discrete metallic phase rather than be entirely stabilized by any oxide phase.

The columns of interest in the maximum loading site statistics are the valence differences and size differences for the substituted sites. It is clear that the indicated negative valence average shows too many ions to fit, whereas a positive number would show unoccupied sites as cation defects. The compensational method was not considered. The average computed size difference in the fit is not worrisome.

To improve the chances for obtaining high loadings without producing undesirable phases, two other feasible computation approaches are (1) to adjust the batch by dilution with excess matrix phase oxides in the proper ratio and (2) to add small amounts of compensating ions to the waste to balance the valence and size demand produced by certain "difficult" ions in the radwaste composition.

To compensate for monovalent Na, adding some trivalent ion such as Gd (which, like Na, is also near Ca in ion size) is one such logical step. Another possible compensating dopant for this system is Be^{+2} , chosen to offset the valence and size mismatch of the P^{+5} ion.

Although it is probably not realistic to expect to be able to predict precisely the amounts of the various radwaste ions actually partitioning into each site, there appears to be great value in running this type of simulation program with a variety of assumptions, since differences in the results or batch computations will quickly show which information about partitioning options is important. Note that the purely empirical batch-fire-analysis alternative would be both expensive and difficult, especially so because of the inherent experimental difficulty in homogeneously distributing the radwaste ions during processing, and subsequently, in adequately analyzing the results in sufficient quantitative and statistical detail.

Given this uncertainty, and in view of the short time available for

active experimentation in this contract period, the following strategy for compositional design was adopted.

1. Deliberate dilution to the 10% loading level, to minimize errors in the assumptions. Greater loadings which cut the demand for BaO could result in low yields of Hollandite and/or higher leachability rates.

2. Deliberate biasing in the direction of excess TiO_2 . This was accomplished by assuming the $\text{TiO}_2 : \text{Al}_2\text{O}_3$ ratio in H composition would be 6:1. Formation of free TiO_2 as rutile (or similarly, of free ZrO_2) was not considered to be as serious a risk as the possibility of creating phases with higher ratios of divalent cations.

3. Incorporation of small additions of compensating ions, such as Gd^{+3} or Be^{+2} , to deal with the "problem" ions of Na and P, respectively, as discussed above.

4. Dilution of Zirconolite demand in the interests of better sintering. We have found that the more Hollandite, the lower the sintering temperature. The phase ratio planned is around 65% H, with the rest divided between P and Z. At 15% total radwaste loading, this assures that no site would be more than 50% loaded with radwaste cations (see Table IV of Appendix II).

Using the programs described above, 10wt% waste loadings were computed for the compositions shown in Table IV. The batches selected were (1) similar to previous Modified SYNROC-B compositions for PW-4b-7, (2) a high Gd^{+3} modified batch designed to charge-compensate for Na^+ ions in Ca^{+2} sites, (3) a high Hollandite formulation designed for easier sintering, and (4), a 20% waste loading similar to batch 1.

Figure 1 illustrates the decreasing demands for all phase oxides (except TiO_2) as a function of waste loading, based on the previously described computer program calculations. The Ba and Ca demand levels decrease most rapidly, since the radwaste-related phase demand is greatest for the Ba and Ca sites.

The principal difference between the (a) and (b) plots in Fig. 1 is a reduction in the Zr level in going from 65 to 70% H.

Figure 2 shows the approximate positions in the HPZ SYNROC doped with (1) PW-4b-7, (2) PW-7a, (3) PW-7a with Gd and (4) PW-7a + U + Gd. Note the increase in Z demand for the fully loaded waste (case 4).

a). HPZ 70-15-15

b). HPZ 65-15-20

Fig. 1. Batch Formulation with Increasing Radwaste Loadings.

TABLE IV
Computed Compositions

Compound	Weight Percents				
	Batch 53	Batch 54	Batch 56	Batch 57	Batch 58
Al ₂ O ₃	8.109	7.263	8.828	7.040	8.282
CaO	6.263	4.851	5.414	3.787	6.188
TiO ₂	58.841	56.327	58.782	57.089	58.064
ZrO ₂	6.456	8.085	4.567	5.231	6.438
BaO	10.330	8.814	11.410	6.854	11.029
Gd ₂ O ₃	-	4.66	-	-	1.17
U ₃ O ₈	-	-	-	-	1.17
PW-7a waste	11.79	11.52	11.79	23.58	7.76

Fig. 2.

PHASE DEMANDS AND COMPOSITIONS IN HPZ SYNROC

TABLE IV

Sintered Densities of SYNPOC Doped with PW-7a

Sample Number	Furnace Type	Sintering		Density	
		Time(hrs)	Temp(C)	g/cm ³	Fractional
53-1	tube	2	1260	4.294	0.976
54-1	tube	2	1260	4.398	0.977
56-1	tube	2	1260	4.282	0.973
53-5,6,7	tube	2	1230	4.244	0.965
54-5,6,7	tube	2	1230	4.363	0.970
56-5,6,7	tube	2	1230	4.274	0.971
53-8	dilatometer	2	1235	4.264	0.969
54-8	dilatometer	2	1235	4.352	0.967
56-8	dilatometer	2	1235	4.246	0.965

C. Fabrication

Batches of the compositions given in Table IV were prepared using well-established materials, facilities and methods described elsewhere. The laboratory powder processing method employed involves intensive dry ball-milling, introduction and distribution of organic binder and lubricant with further dry milling, and screening to yield a flowable, lightly agglomerated intimately mixed powder.

Disc specimens (typically 1 or 2g), were dry pressed at 10,000psi. Binder/lubricant burnout was accomplished in air on a controlled temperature-time schedule (to ~400 C in 18 hr).

D. Densification

1. Conventional Sintering.

a. Densification. Samples fabricated with the composition described in the previous section with 10% and 20% PW-7a additions were sintered conventionally in the controlled atmosphere tube furnace facility to test the densification behavior attributable to the PW-7a addition.

After burnout, the discs were loaded into alumina refractory boats on small ZrO_2 setters (or bed of bubble ZrO_2). Boats were then introduced gradually (~45 min) into the tube furnace at a holding temperature of ~500°C in an atmosphere of flowing Argon. After the boat reached the center tube position position, the end cap was sealed in place, and the tube flushed with flowing Ar, 4% H_2 . Temperature-time cycles (up-and-down) were programmed by DataTrak^R and were very closely controlled in this three-zone Globar^R heated tube furnace (Mellen type 55-211-3). After cooling to the holding temperature, the atmosphere was again switched to Argon, and the boat removed in a gradual stepwise manner, etc.

The initial schedule employed was the standard firing schedule (1260°C + 2h) incorporating the 900 C calcining hold, which had been reduced to two hours because of the small sample size. Samples were subsequently fired at 1230 C to check sinterability at lower temperatures. The results are summarized in Table V.

The fractional density of the high Gd waste was computed from an estimated theoretical density of 4.5 g/cm³, as compared to the 4.40 g/cm³ normally used. These fractional densities compared well with those from

other studies with PW-4b-7, were consistent with the observed microstructures. (Fig. 3)

There were only minor differences among the samples, with a slight drop in density in going from 1260 C to 1230, indicating that 1230 C is near the optimum temperature for conventional firing schedules. These densities were also reproduced (within $D = \pm 0.005$) by similar firings in the dilatometer.

b. Microstructure. The microstructure revealed in SEM in these samples is shown in Fig. 3. The pore structure is typical of past SYNROC materials and did not indicate any departure from the normal structure previously encountered. Pore size and amount is not greatly altered and is thought to result from calcium and/or barium carbonate breakdown. This type of pore distribution has been linked with calcium carbonate particle size, being principally developed by CO_2 removal in areas where large CaCO_3 particles or agglomerates were located.

The large euhedral grains observed in Figure 3a and 3c are quite similar to those observed for the preliminary sodium additions described in section II-A-2 (See Appendix I). These were also visible in the backscattered images. (See IIE3). Liquid phases, even when present in small amounts, are known to favor the growth of such large, straight-sided grains²².

With the Gd^{+3} addition, no such large grains were observed (Fig. 3b). This is viewed as evidence that the Gd^{+3} is aiding the "fit" of Na^{+1} into existing Ca^{+2} sites in the crystalline phases present, thereby eliminating (or at least sharply reducing) the formation of Na-rich glassy phases.

The successful sintering of PW-7a doped SYNROC also was investigated in greater detail with the controlled atmosphere dilatometer (See IIC2).

(a) Sample 53
600X

(b) Sample 54
(High Gd)
600X

(c) Sample 56
(High H)
600X

Fig. 3. Microstructures of PW-7a doped SYNROC showing pore distributions.

2. Dilatometry.

a. Background. To facilitate understanding and control of the sintering behavior of SYNROC ceramics, dilatometry has been employed in the past, but because of prior equipment limitations which restricted such studies to air atmosphere environments, those efforts had mostly been confined to compositions not doped with simulated radwastes. In a few instances, doped SYNROC specimens in quasi-reducing environments (Pt foil-wrapped, Y-buffered) were studied dilatometrically.¹

The need for a controlled atmosphere dilatometer of high quality to support and extend these SYNROC sintering studies had been identified at the outset of the NCSU program in 1979. Planning, development, design, construction and/or acquisition of components for such a facility, and more recently, system checkout and programming of microcomputer software for control, data logging, data reduction and graphics display functions, have been underway since late 1979 under various combinations of DOE and University funding.

At the beginning of this contract period, the hardware items were complete, much of the control software was written, and system checkout was well advanced. Some continuing problems were still being experienced with stability of the power supply and with its digital interface to the Apple II microcomputer, but they were satisfactorily resolved during May, 1982. Since then, steady and significant progress has been made in checking out, fine-tuning and calibrating the facility, and in completing, testing and "bullet-proofing" the various software programs for the microcomputer. To gain greater precision and quicker readout via BCD circuits together with direct visual monitoring of the key temperature and displacement parameters, two new, very stable DORIC Trendicator^R units have also been installed.

The facility has now met or exceeded all technical performance expectations, and all its software programs, including operation in the rate controlled sintering mode, are now operational. This dilatometer system, shown in Figs. 4-8 and discussed briefly in sections (b) and (c), is being described in greater detail elsewhere.^{23,24}

Fig. 4. Functional hot components of the dilatometer. All structural parts are made of C-axis sapphire.

Fig. 5. Alumina refractory ceramic tube enclosing hot dilatometer components. Tube is impermeable and hermetically sealed.

Fig. 6. Dilatometer assembly, constructed of Invar, shown in place on water-cooled base plate. Upper "cold end" fittings for sapphire support rods, thermocouples, and gas injection tube are shown, along with the counter-balanced support system for the LVDT core and central sapphire probe rod. Multiport collar and bell jar complete the hermetic enclosure above the water-cooled base plate.

Fig. 7. Side view of the dilatometer; pneumatic actuator lowers furnace ~35 inches to provide access to the closed-end refractory tube (Fig. 5) and to gain access to the dilatometer stage assembly (Fig. 4).

Fig. 8. Power supply/control cabinet and Apple II microcomputer.

b. Dilatometer Control Programs. Many laboratory applications involving the control of a sophisticated instrument in traditional and even more powerful ways have been made possible by the advent of the low-cost microcomputer. The adaptability and power of the microcomputer has allowed it to replace more traditional and expensive control equipment. In this instance of a controlled atmosphere dilatometer, the microcomputer not only replaced more expensive control equipment, but allowed the dilatometer to be used in experiments that had only been approximated heretofore.

The traditional dilatometer control had a standard temperature (thermocouple, usually) controller of the 3-mode variety. This controller was connected to a variable power supply, which applied power to the furnace heating elements, and a programmer which would allow the user to set a temperature profile for the controller to follow. The microcomputer combines the controller and programmer into one function and still keeps the same external connections to the power supply and thermocouple, although in slightly different form.

The connection to the power supply consisted of a special interface card tied to a custom 16 bit D-A converter mounted in the power supply. The connection to the thermocouple was through a standard digital panel meter (which allowed external verification of the temperature) and used the meter's BCD interface to connect to an interface card in the microcomputer. The same was true for the connection of the LVDT.

In operation, the microcomputer allows the user to input a multi-segmented profile with the improved accuracy of a digital input (i.e., no more little handdrawn cards or templates) that assures the user that the profile he wants is the one that he will get from the dilatometer. With the exception of curved segments (which can be approximated using small segments) the microcomputer operates exactly like a normal temperature programmer. Once the profile is set, other operating parameters are entered. For example, the data logging interval is entered (the time interval for taking the precision digital data and storing it on diskette).

With the completion of all of the "set-up" tasks outlined above, the dilatometer actually begins to operate. The microcomputer display shows the current digital readings along with a graphics display that closely mimics the operation of a chart recorder. This scrolling "chart recorder" display allows the operator to have a "feel" for how the dilatometer is operating by giving him a time history of the temperature and LVDT readings. The dilatometer will operate at this point without further operator intervention, following the profile set by the operator, storing data at the prescribed intervals, and finally shutting the dilatometer down when the profile is finished.

It should be pointed out that by having the microcomputer store the data from the dilatometer directly onto a diskette that further data analysis is greatly enhanced. There is no entering the data into the microcomputer with its associated tedium and chances for error. And the amount of data stored by the microcomputer is probably greater than would or could be entered by hand.

Up to this point, the microcomputer has only done the job of replacing standard control equipment in a highly precise and very flexible manner. But it is also capable of control that is very exotic. To control a piece of equipment such as a dilatometer by using the RATE OF CHANGE of the LVDT (a concept that is central to rate-controlled sintering RCS) as a control signal is one that cannot be readily achieved with normal control equipment. At this point the microcomputer becomes indispensable.

In achieving RCS, the controller must be capable of normal temperature profile control, and at onset of shrinkage, also be capable of switching smoothly to control based on rate of change of the sample height. In addition, the rate of shrinkage of the sample must be put on a profile much the same way as the temperature is done in normal dilatometry, with one exception. The changes in the heating/rate segments are dictated by preset temperatures. In RCS the segment changes are dictated by the absolute sample shrinkage, not the rate. The complexities of such control are achievable with a microcomputer, and can be done with precision comparable to standard control equipment working in the conventional temperature mode.

Fig. 9. Dilatometer firing schedule

Fig. 10. Sintering behavior of PW-7a doped SYNROC, sample 53.

Fig. 11. Sintering behavior of PW-7a doped SYNROC, sample 54.

Fig. 12. Sintering behavior of PW-7a doped SYNROC, sample 56.

c. Results. The sintering behavior was investigated in detail with the dilatometer, using the firing schedule shown in Figure 9, involving a heating rate of $10^{\circ}\text{C}/\text{min}$ with a programmed hold for 1 hr at 900°C and a 2 hr hold at 1235°C . All three materials were examined in this way.

The densification behavior for all three materials is best shown on density-time and densification rate-time plots obtained directly by the computer from the data file which can precisely convert shrinkage information with additional information such as initial length, density and final density into the density-time-temperature display modes.

Densification behavior is shown in Figures 10, 11 and 12 for all three materials. In each case, the early part of the sintering curve shows a characteristic drop in density, i.e., a negative $\frac{dD}{dt}$, at about 750°C (before the calcination soak). It is known from TGA experiments that this expansion occurs after the waste loses residual anions (principally NO_2), and the CO_2 is removed from CaCO_3 and BaCO_3 . The expansion thus is linked with early phase formation, though it is not known whether it is some intermediate, or P, or H, or both. Zirconolite formation is known to start at about 1000°C .

All the samples show the characteristic acceleration of the densification rate to high values, followed by deceleration before the onset of the soak. However, there were subtle differences among the various materials. Sample 56 (High H) showed a somewhat slower densification rate at some temperatures (see Fig. 13), but did not exhibit continued densification during the soak. The higher Hollandite material reached maximum density essentially at the end of linear heating rate portion, consistent with earlier observations regarding the improved sinterability of higher Hollandite materials.

Finally, the high Gd sample showed a "bump" (see Figs. 11 and 13) which somehow must be linked with the incorporation of the Gd_2O_3 powder added to the batch to produce the higher loading of Gd. The effect of the Gd was to retard the sintering slightly.

Fig. 13. Comparison of Densification Rates During Sintering of PW-7A Doped SYNROC

It is evident from this data (and from sintering results on other compositions) that there are only minor effects on sintering if the phase ratio is held nearly constant. In all varieties of compositions investigated in this laboratory (including those containing deliberately added excess CaO , TiO_2 , ZrO_2 , BaO , or Al_2O_3)* the basic sintering characteristics have been quite similar. The only noteworthy departure was with very high Na, which considerably lowered the sintering temperature range. [Experiments involving (1) higher Z, lower H; (2) 20% waste loading; and (3) (fully doped) U_3O_8 added are nearing completion at the writing of this draft.]

2. X-Ray Diffraction Analyses

Patterns were obtained from all compositions with the use of a high resolution Guinier camera, described previously. Because the automated data acquisition system (as described in Appendix III) has not yet been fully implemented here at N. C. State, films were obtained and read manually/visually. The peak 2θ angles were then entered to disk files for analyses by the search-match system, as described in Appendix III.

Software developed for phase identification (described in Appendix III) was employed on compositions studied during this period, including compositions with sodium and phosphorous (see Section II-A1) and three of the compositions shown in Table VI. Major phases (HPZ) were easily identified, even with deliberate sodium additions, and it was expected there would be little difficulty in establishing the major phases (HPZ) in the PW-7a-doped SYNROC. Table VI shows output for phase analysis for these three materials. In the case of samples 54 and 56, the phases found were nominally the same as those studied previously, except that Zirconolite did not appear to fit quite as well as TiZrO_2 , in contrast to earlier work. This is indicated by the lower figures of merit (intensity and position). The Zirconolite pattern was characterized by a conspicuous lack of the double peak at about $d = 1.91\text{\AA}$, and in fact most of the Z peaks could have been accounted for equally well by

* Done as a laboratory exercise under Dr. Hare's direction, in a Materials Engineering Course 310, "Examinations of Materials," Spring Term, 1982.

TABLE VI

Search Match Results for SYNROC Doped with PW-7a

Analysis of file "53-1"

Search Parameters*:

Error-window width multiplier: 1

Offset angle: 0 degrees

Summary:

Phases Found	Lines Found	Figures-of-merit			'Uniqueness:'	
		Intensity	Position	Offset	Lines Found	Int. Ratio
Hollandite	14	0.95	1.00	0.05	5	1.00
Al ₂ O ₃	13	0.92	0.86	0.00	8	0.11
CaTiO ₃	14	0.91	1.00	0.07	7	0.33
BaO	8	0.78	0.81	0.09	4	0.24
TiZrO ₄	12	0.71	0.84	-0.06	3	0.19
CaZrTi ₂ O ₇	10	0.64	0.60	-0.11	3	0.71
Na ₂ TiO ₃	8	0.60	0.61	-0.01	1	0.01

Analysis of file "56-1"

Search Parameters*:

Error-window width multiplier: 1

Offset angle: -.1 degrees

Summary:

Phases Found	Lines Found	Figures-of-merit			'Uniqueness:'	
		Intensity	Position	Offset	Lines Found	Int. Ratio
Hollandite	14	0.95	1.00	0.10	7	1.00
Al ₂ O ₃	13	0.92	1.00	0.11	9	0.11
CaTiO ₃	13	0.89	1.00	0.09	9	0.62
TiZrO ₄	11	0.71	0.93	0.01	1	0.25
CaZrTi ₂ O ₇	10	0.66	0.34	-0.11	2	0.32

Analysis of file "54-1"

Search Parameters*:

Error-window width multiplier: 1

Offset angle: -.1 degrees

Summary:

Phases Found	Lines Found	Figures-of-merit			'Uniqueness:'	
		Intensity	Position	Offset	Lines Found	Int. Ratio
Hollandite	14	0.95	1.00	0.11	7	0.79
CaTiO ₃	14	0.91	1.00	0.13	10	0.30
Al ₂ O ₃	12	0.90	1.00	0.13	8	0.09
TiZrO ₄	13	0.88	0.90	-0.01	4	0.17
CaZrTi ₂ O ₇	12	0.85	0.52	-0.13	3	1.00

*Minimum lines for positive match = $\frac{8}{15}$ for all search match results.

the TiZrO_4 pattern. However, EDX analyses have shown the presence of localized areas corresponding to the correct Ca-Zr-Ti ratio for Zirconolite. Ti-Zr regions corresponding to TiZrO_2 regions have never been seen in EDX analyses, although the presence of very fine grains of such a phase could not be ruled out.

Additional phases such as BaO and Na_2TiO_3 were also listed as "possible," though a few of their major peaks were missing. At this point, to resolve the issue, slowscan analyses in target d-spacing regions would need to be performed, and combined with more extensive microscopy.

Continuous stripping of the pattern showed that Hollandite, Perovskite, and Zirconolite, with $\alpha\text{-Al}_2\text{O}_3$ as a minor phase, accounted for all but a few minor lines, particularly at large d-spacings. The "possible" candidate minor phases (Na_2TiO_3 , BaO) could not be confirmed.

3. EDX and Backscattered Images

Appendix IV shows how the combination of EDX analysis with the backscattered images can be used as a powerful tool to investigate over a fairly wide area the microstructure features revealed by both techniques.

Figures 14 and 15 show backscattered images. For each composition, many of the dark areas have been identified either as pore areas or as "chips" from alumina milling balls. In some cases, dark phases appeared to be nearly entirely TiO_2 , possibly with some alumina or Na_2TiO_3 (instrument resolution for sodium is poor).

In backscattered images, only two levels of grey, identified as light and dark grey phases, respectively, were observed and can be clearly identified in the X2000 pictures (Fig. 15). It was not possible to correlate positively any particular phase with either shading, as done previously with PW-4b-7-doped SYNROC (see Appendix III).

Even though many areas were large enough (3-5 μm), the elemental "fingerprint" generally observed was almost identical to the overall composition, i.e., containing some Ca, Zr, Ti, and Al (Ba is marked). The Zirconolite (identified by a specific Ca-Zr-Ti) pattern only was observed in the light

(a) Sample 53
600X

(b) Sample 54
(High Gd)
600X

(c) Sample 56
(High H)
600X

Fig. 14. Microstructures of PW-7a doped SYNROC.
Backscattered image.

(a) Sample 53
2000X

(b) Sample 54
(High Gd)
2000X

(c) Sample 56
(High H)
2000X

Fig. 15. Microstructures of PW-7a doped SYNROC.
Backscattered image.

grey (high atomic number) areas. Although Perovskite was a clearly identified phase by x-ray diffraction, it was extremely difficult to resolve by EDX. Hollandite was apparently present in both light and dark areas. In sample 56 (High Gd), the Gd intensity was relatively higher in the light areas.

Based on this limited study, the microstructure revealed by the back-scattered image was not well correlated with specific phases, as had been observed in earlier studies (see Appendix III). The definite structured areas observed are therefore considered to multiphase areas having locally similar average atomic numbers, probably associated with locally different ratios of phases and/or levels of waste incorporation.

E. DISCUSSION

SYNROC-B waste forms have been shown to be readily sinterable to technical density, with reasonably controlled fine microstructures. This sinterability has been consistently observed with a variety of waste types and over a range of waste additions up to ~20%. When well processed, most SYNROC specimens sinter at or below 1230°C, both in this most recent investigation with PW-7a simulated radwaste, and in earlier studies based on PW-4b-7. Compositions have been selected which include high U, Gd and Na wastes as well as power wastes with high Cs and Mo, and the indications over the whole range are that technical density can be achieved by sintering well down in the subsolidus range (although some transient liquid formation has not been ruled out).

It has been found that, in general, the more Hollandite, the better the sintering characteristics. In this latest work, however, it was shown that a composition containing 70% H may in fact sinter more slowly than the nominal composition (65% H, 15% P, 20% Z) previously studied. There may in fact be an optimum phase balance for best densification, though it may not be congruent with the best phase balance for waste incorporation.

Under constant heating rate conditions, densification occurs rather rapidly over a rather narrow temperature range (850-1200°C) indicating possible problems if the heating rate chosen is too fast. The application of rate controlled sintering (in progress) can, for example, serve to

reduce possible rate-related stress on the compact. In addition to its well documented effects in optimizing densification and refining microstructure in other materials, rate controlled sintering is also expected to assist in limiting loss of volatiles during sintering of SYNROC systems.

Proper formation of the major candidate phases (H,P,Z) has been easily accomplished, although there is some indication that minor phases are formed and the Zirconolite is not as readily formed as with PW-4b-7 type wastes. Much more detailed x-ray diffraction and analytical STEM work would need to be done to confirm several of these possibilities. We believe the actual phase arrangement at the microstructural level is not fully reflected by x-ray diffraction data and is probably much more complex than previously believed.

The proper direction for future compositional adjustment and/or process refinements must be related to leachability characteristics so that possible problems can be related to improvements in composition design and process methodology in an iterative manner. Given proper composition design and material processing, the present findings clearly indicate that there will be no difficulty in adequately sintering conceivable HPZ-based SYNROC compositions at temperatures below the solidus.

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APPENDIX I

A STUDY OF THE EFFECTS OF SODIUM AND PHOSPHORUS
ADDITIONS ON DENSIFICATION BEHAVIOR, PHASE FORMATION,
AND ELEMENTAL DISTRIBUTION IN MODIFIED SYNROC-B

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INTRODUCTION

Subsolidus sintering of Modified SYNROC-B has successfully produced the three needed major phases: Hollandite, Perovskite and Zirconolite without the formation of undesirable residual minor phases. The addition of 10 wt% simulated PW-4b-7 radwaste (which contains a large variety of oxides) to Modified SYNROC-B has made densification somewhat more difficult and enhanced the possibility for undesirable phase formation. Although no significantly detrimental effects have been encountered with the addition of PW-4b-7, the use of a modified version of this type of radwaste, specifically PW-7a and/or PW-7a-2 which contains some higher levels of possible problem elements (Na and P, as well as Gd and U) may present considerable problems. Oxide compositions of Modified SYNROC-B containing PW-4b-7, PW-7a, and PW-7a-2 radwastes are listed in Appendix I.

It is the purpose of this study to observe the effects of the addition of 3 wt% Na, 3 wt% P, and 1.5 wt% Na plus 1.5 wt% P on densification behavior, phase formation, and elemental distribution in Modified SYNROC-B. With this information, it should be possible to determine whether any unacceptable effects should arise with the use of PW-7a or PW-7a-2 radwastes.

PROCEDURE

Batches

A total of five Modified SYNROC-B batches were prepared for the purpose of this study:

1. 3.0 wt% Na based on the total batch added to standard undoped Modified SYNROC-B composition in the form of Na_2CO_3 .
2. 3.0 wt% Na added to standard doped Modified SYNROC-B composition in the form of Na_2O_3 bringing the total Na content of the entire batch to 3.8 wt%.
3. 3.0 wt% P based on the total batch added to standard undoped Modified SYNROC-B composition in the form of $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

4. 3.0 wt% P added to standard doped Modified SYNROC-B composition in the form of $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ bringing the total Na content of the entire batch to 3.2 wt%.
5. 1.5 wt% Na plus 1.5 wt% added to standard doped Modified SYNROC-B composition in the form of Na_2CO_3 and $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, respectively. Bringing the total Na and P contents of the entire Batch to 2.3 and 1.7 wt%.

NOTE: Calculations for batches containing Phosphorous included subtraction of excess Ca contained in $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

The following processing procedure was carried out for each of the five batches:

...The weighed batch was added to a polyurethane-lined ball mill with 1.9 cm dia 99% alumina milling balls (~14.8 g each) in a 20:1 ball:charge weight ratio. After milling for 6 hr at a speed of approximately 115 rpm, 2.5 wt% carbowax dry binder was added to the batch which was then screened and remilled for an additional 6 hr. Following this milling, 2.5 wt% lubricant (oleic acid) was added to the mixture which was then screened and remilled for an additional 6 hr.¹

At the completion of the milling process, the batch was screened and ready for pressing.

Pellet Pressing

Approximately 12 pellets, each weighing 2 g, were pressed from each of the five SYNROC batches in a 5/8" diameter hardened steel die. A small hydraulic press was used, and after a brief (10 sec.) application of light pressure, a constant pressure of 10,000 psi was applied on the pellet for exactly one minute.

Green Densities

Following pressing, the pellets were weighed, and their height and diameter measurements were taken with a micrometer. Using this data, geometric density calculations were made and recorded.

Binder Burnout

Next, the pellets were placed in a "Blue M" drying oven for careful binder/lubricant burnout. To prevent thermal degradation, the samples were heated to ~450°C over an 18 hr period. Geometric density data was again taken and recorded.

Firing

An already well established controlled atmosphere firing procedure was employed:

The specimens were placed on zirconia chips in an alumina boat and fed slowly into a controlled atmosphere tube furnace, which was already at 500°C. To avoid thermal shock, the boat was fed into the furnace at a rate of $\frac{1}{4}$ "/3 min for ~50 min followed by 1"/3 min for 15 min, and then pushed directly into the "central hot zone." The tube was then sealed and flushed with Ar for 20 min followed by a 20 min flush Ar/4% H₂.

The temperature of the furnace was increased manually 10°C/min until the desired hold temperature was reached (1195 or 1260°C). The samples were held at temperature for the required time (either 2 or 4 hr) and the furnace was then cooled down at 10°C/min. When the temperature decreased to below 800°C, the gas was switched back to Ar, and the boat was removed following the same procedure for entry.²

Archimedes Densities

Measurements for archimedes densities were taken after firing. Dry weights were recorded first, and then the pellets were placed in a vacuum atmosphere for one minute. About 25 ml of H₂O was then released into the vacuum atmosphere, submerging the pellets. The specimens remained submerged in this atmosphere for 3 min, at which time the vacuum was released, and the specimens were placed in a container of H₂O.

Weight measurements were taken by suspending the pellets in a beaker of water by an extremely thin polyurethane coated Cu wire, which was attached to the balance. The pellets were then dried off with a kimwipe until no visible trace of moisture remained on their surface and conventionally weighed again to establish the amount of H₂O retention.

Dry, suspended and saturated weight values obtained were used to calculate fired densities.

Sample Preparation for SEM Analysis

The first step in preparing the samples for SEM examination involved cutting sections from the pellets for mounting. A center transverse section was cut from each specimen selected using a Buehler low speed saw with a circular diamond blade.

The sections were placed in a 1" ring mold and mounted in epoxy resin. A steel lapping plate which was charged with 3 μ diamond paste was then used to reduce surface scratches to 3 μ and insure a flat specimen surface within its mount.

Following the lapping procedure, the specimens were polished using 1 μ diamond paste on a Syntron vibratory polishing unit. Polishing took place for approximately 6 hr at a speed of @ 1 rev/min. The samples were removed from the mounts by soaking them in methanol, and their surfaces were thoroughly cleaned using an acetone, methanol, ethanol sequence. After being cemented to an appropriate metallic stub, the polished surface of each specimen was carbon coated in vacuo using a Denton coating system, and the samples were then ready for SEM analysis.

SEM Analysis

Scanning electron micrographs of the SYNROC-B samples were taken on the JEOLCO JSM-II instrument in the backscattered composition mode. A variety of magnifications was used ranging from 200x to 6000x, at a setting of 15kv. The micrographs taken were located at the center position of the specimens. Selected EDX spot analyses were also performed to determine qualitative compositions of unidentified phases in the microstructures.

X-ray Diffraction Analysis

Pellets having the lowest suspended density value from their respective firing schedules were crushed into a powder of 200 mesh fineness. Guinier X-ray diffraction patterns were made of the specimens using Cu K_{α} radiation and an X-ray source setting of 40kv and 10ma. The samples were exposed for 2 hr before the film patterns were developed. A light box film reader was used to read the 2θ values and relative intensities of the pattern lines.

RESULTS AND DISCUSSION

Sample designation is as follows:

UDN - Undoped SYNROC-B with 3 wt% Na added

DN - Doped SYNROC-B with 3 wt% Na added

UDP - Undoped SYNROC-B with 3 wt% P added

DP - Doped SYNROC-B with 3 wt% P added

DNP - Doped SYNROC-B with 1.5 wt% Na plus 1.5 wt% P added

SDS - Standard doped Modified SYNROC-B

I. Densification Behavior

The addition of 3 wt% Na greatly effects the densification kinetics of Modified SYNROC-B, while no appreciable change in densification behavior with the addition of 3 wt% P is observable.

The following table presents the density values and firing schedules for the various test specimens:

<u>Sample</u>	<u>Temp</u>	<u>Time</u>	<u>Density</u>	<u>Fractional Density</u>
UDN	1195°C	4 hr	4.0506	0.9442
DN	1195°C	4 hr	4.0650	0.9239
DN	1260°C	2 hr	3.7916	0.8617
UDP	1195°C	4 hr	3.9421	0.9189
DP	1195°C	4 hr	3.9727	0.9029
DP	1260°C	2 hr	4.1160	0.9356
DNP	1195°C	4 hr	3.9279	0.8927
DNP	1260°C	2 hr	4.1140	0.9350
SDS	1195°C	4 hr	3.8016	0.8640
SDS	1260°C	2 hr	4.2020	0.9550
SDS	1285°C	2 hr	4.1272	0.9380

NOTE: Density and fractional density values are an average of the best two out of three pellets. Also a presumed "theoretical" density of 4.4 g/cm³ was used to calculate fractional density values.

From the table values for samples containing phosphorus seem to approximately equal those of standard doped SYNROC-B, with the exception of a slight drop in density at 1260°C.

For doped SYNROC-B containing sodium and fired at 1260°C, a significant decrease in density with respect to standard doped SYNROC-B is observed. This decrease in densification is possibly due to an increase in pore size and volume (i.e., bloating) which results from overfiring. For samples containing sodium and fired at 1195°C, a considerable increase in density is obtained. These two deviations in densification from standard SYNROC-B values suggest that for the sodium-modified composition, the optimum firing temperature to achieve full densification is between 1195°C and 1260°C.

Doped SYNROC-B samples containing 1.5 wt% Na and 1.5 wt% P develop a densification behavior essentially equal to that of samples containing 3.0 wt% phosphorus.

Aside from the actual density values given in the table, it is important to note the physical appearance of the pellets. While the pellets containing phosphorus display no noticeable difference, the appearance of those containing sodium is drastically altered. The 3 wt% Na pellets fired at 1195°C are concave in the center with partially healed cracks extending inward from the edges. Those pellets containing 3 wt% Na fired at 1260°C are even more concave, with large separated cracks extending inward from the edges. On this basis alone it would not be advisable to continue experimentation or consideration of this level of Na (from NaCO₃) for possible use.

II. Phase Formation

X-ray patterns for all pellets containing sodium and/or phosphorus display the entire array of lines characteristic of standard Modified SYNROC-B, including the important major phases, Hollandite, Perovskite, and Zirconolite.

The only noticeable difference is the appearance of a few new faint lines occurring in the samples containing 3 wt% Na, and a few slightly stronger new lines appearing in those samples containing 3 wt% P.

No new lines appear in the samples containing both sodium and phosphorus due to the small levels of Na_2O and P_2O_5 added.

Undoped samples containing Na and those containing P produced patterns which contained more unidentified lines which were also stronger than those appearing in their doped counterparts. In addition, some broadening of Perovskite lines occurred in the undoped Na sample, which perhaps suggests an increased Perovskite content.

The reason for more differences showing up in the undoped samples could be due to the fact that the doped composition is better able to accommodate the P^{+5} and Na^+ ions. The presence of many types of ions already in the dopant cause distortions in the lattices of some of the phases present, making it easier for the P^{+5} and/or Na^+ ions to fit into the structure. These dopant ions are also thought to help compensate for charge differences which would need to be "adjusted" in fitting either Na^+ or P^{+5} into available crystal lattice sites.

The X-ray patterns indicate that additions of 3 wt% P or Na are too high to be completely accommodated in the standard SYNROC-B composition. Although unidentified at this time, the appearance of these faint new lines may well represent "potentially troublesome residual minor phases."³

III. Microstructural Results

Significant microstructural features uncommon to standard Modified SYNROC-B appeared in the polished sections of samples containing Na and/or P additions. These morphological and possible compositional differences can be seen in the SEM micrographs of Figs. 1-7.

Fig. 1 is the doped SYNROC-B specimen containing 3 wt% P fired at 1195°C . In addition to the three major SYNROC phases (HPZ) which can be seen in all seven micrographs, Fig. 1 shows a round black phase (Labeled A) inside a dark gray phase (Labeled B). EDX spot analysis suggests the composition of these two areas consists primarily of Ca and P, which implies a region of unreacted calcium phosphate. This assumption cannot be fully confirmed by analyzing only one spot in each area, which was the method ~~was~~ used on phases present in each specimen of this study.

The doped SYNROC-B specimen with 3 wt% P added which was fired at 1260°C (Fig. 2) contains the same black spot as in Fig. 1 and is taken to be of the same composition. "The small, bright phase observed in this micrograph appears in all doped SYNROC-B and is presumably a metallic phase composed of Mo and possible other alloying constituents (e.g., Ru, Rh, Pd, and Ag., etc.)"⁴

Fig. 3 is a micrograph of undoped SYNROC-B containing 3 wt% P. It is very similar to the doped specimens containing phosphorus, and shows the characteristic small black phase (presumed to be calcium phosphate). The most noticeable difference is its finer grain structure relative to the doped samples. However, this increase in grain growth is associated with the addition of PW-4b-7 and has routinely been observed.⁵

The most prevalent microstructural deviation relative to Modified SYNROC-B in the undoped Na specimen (Fig. 4) is the formation of black blocky phases. These phases as analyzed by EDX technique consistently show Ca-Na-Al-Ti. This phase type seems to be Perovskite with a high concentration of Na and Al substituting for part of the Ca, in other words [Ca, (Na, Al)] TiO₃.

The doped SYNROC-B samples containing 3 wt % Na fired at 1195°C and at 1260°C, as well as the doped samples containing 1.5 wt % Na plus 1.5 wt % P developed long, skinny, black plates or "flakes" in their microstructures as a result of the combination of PW-4b-7 and Na. As the firing temperature increases, these platelike phases become blockier which can be seen in a comparison of Fig. 5 with Fig. 6. "The elongation and development of 'straight' grain edges of these phases at lower temperatures may be attributed to the presence of a transient liquid phase."⁶ From the EDX analysis these flakes appear to be a complex Na-Al-Ca-Ti phase; however, a new set of X-ray diffraction peaks was not observed.

Since absolute phase identification of these flakes is impossible at this time, two logical hypotheses as to their composition can be made:

1. The flakes may be a high Na Perovskite with other EDX peaks interfering from background. In this case, the Na⁺ ions would be substituting for some of the Ca²⁺ ions since they are of the same atomic size (0.95Å) with Al³⁺ possibly compensating for charge differences.

2. An alternative explanation is that a totally new phase has formed containing Al, Na, Ca, Ti with a structure similar to H, P, or Z.

Finally, from the micrographs alone, the average pore size in some of these specimens (especially Figs. 4, 6 & 7) visually appears to have increased, which is certainly detrimental to densification behavior.

CONCLUSIONS

1. Addition of 3 wt% levels of sodium oxide considerably effects the densification of Modified SYNROC-B.
2. No appreciable change in densification behavior is encountered with addition of 3 wt% P or 1.5 wt% Na plus 1.5 wt% P to Modified SYNROC-B.
3. The optimum firing temperature to achieve complete densification in doped Modified SYNROC-B containing 3 wt% Na is at or below 1195°C.
4. The physical appearance of samples containing 3 wt% Na is drastically altered with the degree of alteration being particularly severe at 1260°C.
5. Undoped samples containing either 3 wt% Na or 3 wt% P developed more differences in their X-ray patterns than the doped specimens, implying the doped composition is better able to adjust to the sodium and phosphorus additions.
6. Significant new microstructural features developed in samples containing Na and/or P additions.
7. It is probable that an unreacted calcium phosphate phase is contained in the microstructures of specimens containing 3 wt% phosphorus.
8. A Ca-Na-Al-Ti phase was identified in the undoped specimen containing 3 wt% Na.
9. Doped specimens containing 3 wt% sodium developed a plate-like phase which may be a high sodium Perovskite or a new phase containing Al, Na, Ca, and Ti.
10. Addition of 3 wt% Na or 3 wt% P is too high to be completely incorporated into the standard Modified SYNROC-B composition.
11. Samples containing 1.5 wt% P plus 1.5 wt% Na and PW-4b-7 show no conclusive evidence that they cannot be accommodated in Modified SYNROC-B.
12. Based on the amounts of sodium and phosphorus contained in radwaste PW-7a or PW-7a-2, no significant problems in completeness of phase formation, density behavior or microstructure attained during densification should be encountered with the use of this radwaste. No conclusions can be formed concerning leachability.

FOOTNOTES

1. Hayne Palmour III, et. al., (North Carolina State University), "Subsolidus Sintering of SYMROC: II. Materials Selections, Process Improvements, Waste Form Evaluations." Topical Report NCSU-80-4, Contract DE-AC09-81SR 10957, July 1981, pp. 53-55.
2. Ibid, pp. 58-59.
3. Ibid, p. 34.
4. Ibid, p. 63.
5. Ibid, p. 63.
6. W. D. Kingery, Introduction to Ceramics, John Wiley and Sons, Inc., New York, 1960, p. 367.

GENERAL REFERENCES

1. Hayne Palmour III, et. al, "Subsolidus Sintering of SYNROC: II. Materials Selections, Process Improvements, Waste Form Evaluations," Contract DE-AC09-81SR 10957, July 1981.
2. Hayne Palmour III and T. M. Hare. "Sintering of SYNROC: Case History of Phase Formation and Densification of Complex Oxide Systems." Presented at 5th International Round Table Conference on Sintering, Portoroz, Yugoslavia, Sept. 1981.

APPENDIX I

OXIDE COMPOSITIONS OF MODIFIED SYNROC-B

<u>Oxide</u>	<u>+10 wt% PW-4b-7</u>	<u>+10 wt% PW-7a</u>	<u>+10 wt% PW-7a-2</u>
Ag ₂ O	0.019	0.019	0.017
Al ₂ O ₃	8.221	8.471	8.329
B ₂ O ₃	0.022	-	-
BaO	10.631	10.579	10.571
CaO	8.283	8.313	8.323
CdO	0.024	0.017	0.016
Ce ₂ O ₃	0.788	1.608	1.696
CO ₂ O ₃	0.003	0.055	0.052
Cr ₂ O ₃	0.105	0.073	0.071
CuO	0.009	0.021	0.017
Dy ₂ O ₃	0.004	0.518	0.240
Eu ₂ O ₃	0.047	0.012	0.006
Fe ₂ O ₃	0.412	0.813	0.778
Gd ₂ O ₃	0.047	0.171	0.129
K ₂ O	-	0.187	0.171
La ₂ O ₃	0.374	0.786	0.970
Li ₂ O	0.004	-	-
MgO	0.015	0.017	0.015
MnO ₂	0.004	-	-
MoO ₃	1.445	1.119	1.050
Na ₂ O	0.791	1.122	1.175
Nd ₂ O ₃	1.102	0.666	0.872
NiO	0.043	0.175	0.166
P ₂ O ₅	0.182	0.475	0.468
PbO	0.013	-	-
PdO	0.367	-	-
Pr ₆ O ₁₁	0.279	0.075	0.084

OXIDE COMPOSITIONS OF MODIFIED SYNROC-B
(continued)

<u>Oxide</u>	<u>+10 wt% PW-4b-7</u>	<u>+10 wt% PW-7a</u>	<u>+10 wt% PW-7a-2</u>
Rb ₂ O	0.068	-	-
Rh ₂ O ₃	0.089	-	-
RuO ₂	0.687	-	-
SiO ₂	0.150	0.049	0.058
SrO	0.251	0.172	0.167
TeO ₂	0.152	0.112	0.111
TiO ₂	57.171	57.170	57.169
ZnO	0.016	0.005	0.005
ZrO ₂	7.380	7.091	7.016
Cs ₂ O	0.656	0.001	0.001
Y ₂ O ₃	0.148	0.109	0.261

UNDOPED BATCHES

For 3 wt% :

$$\frac{x}{100+x} = .03$$

$$x = .03(100+x)$$

$$x = 3 + 0.3x$$

$$x - .03x = 3$$

$$.97x = 3$$

$$x = 3.09278g$$

BATCH #1: Undoped Modified SYNROC-B + 3 wt% Na₂O

$$\text{Na}_2\text{CO}_3 \text{ FW} = 105.99 \text{ g/mole}$$

$$\text{Na}_2\text{O} \text{ FW} = 61.97 \text{ g/mole}$$

$$\frac{3.09278g \text{ Na}_2\text{O}}{61.97g \text{ Na}_2\text{O/mole}} = 0.4990 \text{ mole}$$

$$(0.4990 \text{ mole}) \times (105.99g \text{ Na}_2\text{CO}_3/\text{mole}) = 5.2897g \text{ Na}_2\text{CO}_3$$

BATCH #2: Undoped Modified SYNROC-B + 3wt% P₂O₅

$$\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O} \text{ FW} = 252.07 \text{ g/mole}$$

$$\text{P}_2\text{O}_5 \text{ FW} = 141.9426 \text{ g/mole}$$

$$\frac{3.09278g \text{ P}_2\text{O}_5}{141.9426g \text{ P}_2\text{O}_5/\text{mole}} = .0217889 \text{ mole}$$

$$(.0217889 \text{ mole}) \times (252.07g \text{ CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}/\text{mole}) = 5.492g \text{ CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$$

$$\frac{1 \text{ mole CaO}}{1 \text{ mole CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}} \times \frac{1 \text{ mole CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}}{252.07g \text{ CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}} \times \frac{56.08g \text{ CaO}}{1 \text{ mole CaO}} = \frac{.2224779g \text{ CaO}}{1g \text{ CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}}$$

$$\frac{.2224779g \text{ CaO}}{1g \text{ CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}} \times (5.4923g \text{ CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}) = 1.2219 \text{ g CaO EXCESS}$$

$$\frac{1 \text{ mole CaCO}_3}{1 \text{ mole CaO}} \times \frac{1 \text{ mole CaO}}{56.08g \text{ CaO}} \times \frac{100.09g \text{ CaCO}_3}{1 \text{ mole CaCO}_3} = \frac{1.78477175g \text{ CaCO}_3}{1g \text{ CaO}}$$

BATCH #3: Doped Modified SYNROC-B with calculations based on 3 wt% Na added, yet recent ICP analysis shows PW-4b-7 contains ~ 8 wt% Na₂O therefore the actual Na content is 3.8 wt% of the total batch.

<u>Oxide</u>	<u>PW-4b-7 10 wt% dopant</u>	<u>CO₃</u>
Al ₂ O ₃	8.18	8.81
BaO	10.31	13.27
CaO	8.25	14.72
TiO ₂	57.16	57.16
ZrO ₂	6.10	6.10

$$\frac{1.7848\text{g CaCO}_3}{1\text{g CaO}} \times (7.0281\text{g CaO}) = 14.7246\text{g CaCO}_3$$

$$(7\text{g PW-4b-7}) \times (1.23001 \text{ MF}) = 8.61007\text{g PW-4b-7}$$

$$\frac{3.00\text{g Na}_2\text{O}}{61.97\text{g Na}_2\text{O/mole}} = .0484105 \text{ mole Na}_2\text{O}$$

$$(.0484105 \text{ mole Na}_2\text{O}) \times (105.99\text{g Na}_2\text{CO}_3/\text{mole}) = 5.1310\text{g Na}_2\text{CO}_3$$

Batch #4: Doped Modified SYNROC-B with calculations based on 3 wt% P added, yet recent ICP analysis shows PW-4b-7 contains ~ 2 wt% P₂O₅ therefore the actual P content is 3.2 wt% of the total batch.

<u>Oxide</u>	<u>PW-4b-7 10 wt% dopant</u>	<u>CO₃</u>
Al ₂ O ₃	8.18	8.18
BaO	10.31	13.27
CaO	7.03	12.54
TiO ₂	57.16	57.16
ZrO ₂	6.10	6.10

$$\frac{1.7848\text{g CaCO}_3}{1\text{g CaCO}_3} \times (7.0281\text{g CaO}) = 12.54375\text{g CaCO}_3$$

$$\frac{3.00 \text{ g } P_2O_5}{141.9426 \text{ g } P_2O_5/\text{mole}} = .0211353 \text{ mole } P_2O_5$$

$$(.0211353 \text{ mole } P_2O_5) \times (252.07 \text{ g } CaH_4(PO_4)_2 \cdot H_2O/\text{mole}) = 5.3276 \text{ g } CaH_4(PO_4)_2 \cdot H_2O$$

APPENDIX II

TABLE I.

Assumed Valence States for Radwaste Cations

in PW-7a

<u>Z</u>	<u>SYM</u>	<u>AT%</u>	<u>VALENCE</u>	<u>ION SIZE</u>
8	O	56.9465	2.0	1.4000
11	Na	14.0660	1.0	0.9500
12	Mg	0.1638	2.0	0.6508
13	Al	2.2176	3.0	0.4990
14	Si	0.3168	4.0	0.4094
15	P	2.6002	5.0	0.3450
19	K	1.5424	1.0	1.3300
20	Ca	0.4364	2.0	0.9922
22	Ti	0.0486	4.0	0.6788
24	Cr	0.3732	3.0	0.6154
26	Fe	3.9559	2.0	0.7399
29	Cu	0.1025	2.0	0.8072
30	Zn	0.0238	2.0	0.7399
38	Sr	0.6449	2.0	1.1315
39	Y	0.3750	3.0	0.9400
40	Zr	3.1246	4.0	0.8010
43	Mo	3.0204	4.0	0.6834
47	Ag	0.0637	1.0	1.2600
48	Cd	0.1566	2.0	0.9772
52	Te	0.2726	4.0	0.6025
55	Cs	0.0035	1.0	1.6900
56	Ba	0.6815	2.0	1.1725
57	La	1.8745	3.0	1.1383
58	Ce	3.8065	3.0	1.1055
59	Pr	0.1712	4.0	1.0336
60	Nd	1.5379	3.0	1.0728
63	Eu	0.0264	3.0	1.0318
64	Gd	0.3665	3.0	1.0145
66	Dy	1.0790	3.0	0.9909

TABLE II.

Ion Site Allocation for PW-7a

in Hollandite, Perovskite and Zirconolite

note: Site demand total from all phase cation site sums to AT% in TABLE I. The valence adjusted site demand is for charge compensation. Size difference is (waste ion - site ion)/waste ion.

PHASE/ION	SITE DEMAND	VAL. ADJUSTD	VAL. DIFF	SIZE DIFF
WASTE ION - NA				
VALENCE- 1	SIZE- .35			
HOL-TI	0.0002	0.0000	-3.0000	0.0074
HOL-BA	0.0084	0.0442	-1.0000	-0.2342
PER-CH	0.0057	3.4928	-1.0000	-0.0414
PER-TI	0.0002	0.0000	-3.0000	0.2054
ZIR-LA	0.0057	3.4928	-1.0000	-0.0414
ZIR-TI	0.0002	0.0000	-3.0000	0.2054
ZIR-ZR	0.0052	0.0013	-3.0000	0.1386
WASTE ION - HG				
VALENCE- 2	SIZE- .65			
HOL-AL	0.0085	0.0043	-1.0000	0.2320
HOL-TI	0.0521	0.0260	-2.0000	-0.0430
PER-TI	0.0521	0.0260	-2.0000	-0.0430
ZIR-TI	0.0521	0.0260	-2.0000	-0.0430
ZIR-ZR	0.0006	0.0007	-2.0000	0.1307
WASTE ION - AL				
VALENCE- 3	SIZE- .5			
HOL-AL	2.2174	2.2174	0.0000	0.0000
WASTE ION - SI				
VALENCE- 4	SIZE- .41			
HOL-AL	0.3164	0.4219	1.0000	-0.0151
HOL-TI	0.0001	0.0001	0.0000	-0.6577
PER-TI	0.0001	0.0001	0.0000	-0.6577
ZIR-TI	0.0001	0.0001	0.0000	-0.6577
WASTE ION - P				
VALENCE- 5	SIZE- .35			
HOL-AL	2.5997	4.3329	2.0000	-0.4468
HOL-TI	0.0001	0.0002	1.0000	-0.9674
PER-TI	0.0001	0.0002	1.0000	-0.9674
ZIR-TI	0.0001	0.0002	1.0000	-0.9674

TABLE II continued

WASTE ION - K				
VALENCE- 1	SIZE- 1.33			
HOL-BA	1.4173	0.7088	-1.0000	0.1184
PER-CA	0.0625	0.0312	-1.0000	0.2538
ZIR-CA	0.0625	0.0312	-1.0000	0.2538
WASTE ION - CR				
VALENCE- 2	SIZE- .99			
HOL-BA	0.0033	0.0033	0.0000	-0.1816
PER-CA	0.2165	0.2165	0.0000	0.0000
ZIR-CA	0.2165	0.2165	0.0000	1.0000
WASTE ION - TI				
VALENCE- 4	SIZE- .88			
HOL-TI	0.0181	0.0181	0.0000	0.2000
PER-TI	0.0181	0.0181	0.0000	0.0000
ZIR-TI	0.0181	0.0181	0.0000	0.0000
ZIR-ZR	0.0002	0.0002	0.0000	-0.1799
WASTE ION - CR				
VALENCE- 3	SIZE- .62			
HOL-AL	0.1174	0.1174	0.0000	0.1888
HOL-TI	0.0849	0.0837	-1.0000	-0.1029
PER-TI	0.0849	0.0837	-1.0000	-0.1029
ZIR-TI	0.0849	0.0837	-1.0000	0.1029
WASTE ION - FE				
VALENCE- 2	SIZE- .74			
HOL-AL	0.0324	0.0216	-1.0000	0.3253
HOL-TI	0.0863	0.4331	-2.0000	0.0826
HOL-BA	0.0008	0.0008	0.0000	-0.3845
PER-CA	0.2265	0.2265	0.0000	-0.3409
PER-TI	0.0863	0.4331	-2.0000	0.0826
ZIR-CA	0.2265	0.2265	0.0000	-0.3409
ZIR-TI	0.0863	0.4331	-2.0000	0.0826
ZIR-ZR	0.8704	0.4352	-2.0000	-0.0824

TABLE II continued

WASTE ION - CU

VALENCE- 2 SIZE- .81

HOL-TI	0.00 3	0.0006	-2.0000	0.1591
HOL-BA	0.0001	0.0001	0.0000	-0.4524
PER-CA	0.0270	0.0270	0.0000	-0.0231
PER-TI	0.00 3	0.0006	-2.0000	0.1591
ZIR-CA	0.02 0	0.0370	0.0000	-0.0291
ZIR-TI	0.0013	0.0006	-2.0000	0.1591
ZIR-ZR	0.0442	0.0321	-2.0000	-0.0077

WASTE ION - ZN

VALENCE- 2 SIZE- .74

HOL-HL	0.00 1	0.0001	-1.0000	0.0000
HOL-TI	0.00 2	0.0026	-2.0000	0.0026
PER-CA	0.00 3	0.0013	0.0000	-0.0013
PER-TI	0.00 2	0.0026	-2.0000	0.0026
ZIR-CA	0.00 3	0.0013	0.0000	-0.0013
ZIR-TI	0.00 2	0.0026	-2.0000	0.0026
ZIR-ZR	0.00 2	0.0026	-2.0000	-0.0026

WASTE ION - SR

VALENCE- 2 SIZE- 1.13

HOL-BA	0.50 6	0.5076	0.0000	-0.0061
PER-CA	0.0006	0.0006	0.0000	0.1231
ZIR-CA	0.00 6	0.0006	0.0000	0.1231

WASTE ION - Y

VALENCE- 3 SIZE- .94

HOL-HL	0.0001	0.0001	0.0000	0.4009
HOL-TI	0.0010	0.0007	-1.0000	0.2773
HOL-BA	0.0021	0.0031	1.0000	-0.0472
PER-CA	0.1744	0.2616	1.0000	-0.0555
PER-TI	0.0010	0.0007	-1.0000	0.2773
ZIR-CA	0.1744	0.2616	1.0000	-0.0555
ZIR-TI	0.0010	0.0007	-1.0000	0.2773
ZIR-ZR	0.0207	0.0155	-1.0000	0.1479

WASTE ION - ZR

VALENCE- 4 SIZE- .8

HOL-TI	0.0055	0.0055	0.0000	0.1525
PER-CA	0.0001	0.0002	2.0000	-0.2387
PER-TI	0.0055	0.0055	0.0000	0.1525
ZIR-CA	0.0001	0.0002	2.0000	-0.2387
ZIR-TI	0.0055	0.0055	0.0000	0.1525
ZIR-ZR	0.0077	0.0077	0.0000	0.0000

TABLE II continued

WASTE ION - NO

VALENCE- 4 SIZE- .68

HOL-AL	0.0032	0.0003	1.0000	0.2635
HOL-TI	0.9993	0.9993	0.0000	0.0067
PER-TI	0.9993	0.9993	0.0000	0.0067
ZIR-TI	0.9993	0.9993	0.0000	0.0067
ZIR-ZR	0.0222	0.0222	0.0000	-0.1730

WASTE ION - AG

VALENCE- 1 SIZE- 1.36

HOL-BA	0.0593	0.0206	-1.0000	0.4634
PER-CA	0.0022	0.0011	-1.0000	0.2124
ZIR-CA	0.0022	0.0011	1.0000	0.2124

WASTE ION - CD

VALENCE- 2 SIZE- .93

HOL-BA	0.0011	0.0011	0.0000	-0.1936
PER-CA	0.0777	0.0777	0.0000	-0.0150
ZIR-CA	0.0777	0.0777	0.0000	-0.0153

WASTE ION - TE

VALENCE- 4 SIZE- .6

HOL-AL	0.0031	0.0042	1.0000	0.1715
HOL-TI	0.0095	0.0095	0.0000	-0.1266
PER-TI	0.0095	0.0095	0.0000	-0.1265
ZIR-TI	0.0095	0.0095	0.0000	-0.1265
ZIR-ZR	0.0000	0.0000	0.0000	-0.3292

WASTE ION - CS

VALENCE- 1 SIZE- 1.63

HOL-BA	0.0030	0.0015	-1.0000	0.3962
PER-CA	0.0002	0.0001	-1.0000	0.4128
ZIR-CA	0.0002	0.0001	-1.0000	0.4122

WASTE ION - BA

VALENCE- 2 SIZE- 1.17

HOL-BA	0.6441	0.6441	0.0000	-0.0000
PER-CA	0.0186	0.0186	0.0000	0.1537
ZIR-CA	0.0186	0.0186	0.0000	0.1537

TABLE II continued

WASTE ION - LA

VALENCE- 3 SIZE- 1.14

HOL-TI	0.0002	0.0002	-1.0000	0.4036
HOL-BA	1.5480	2.3221	1.0000	-0.0360
PER-CA	0.1610	0.2416	1.0000	0.1203
PER-TI	0.0002	0.0002	-1.0000	0.4036
ZIR-CA	0.1610	0.2416	1.0000	0.1203
ZIR-TI	0.0002	0.0002	-1.0000	0.4036
ZIR-ZR	0.0033	0.0025	-1.0000	0.1367

WASTE ION - CE

VALENCE- 3 SIZE- 1.11

HOL-AL	0.0002	0.0002	0.0000	0.7131
HOL-TI	0.0011	0.0000	-1.0000	0.3753
HOL-BA	2.1300	3.2350	1.0000	0.0005
PER-CA	0.0187	1.2280	1.0000	0.1024
PER-TI	0.0011	0.0000	1.0000	0.7131
ZIR-CA	0.0187	1.2280	1.0000	0.1024
ZIR-TI	0.0011	0.0000	-1.0000	0.7131
ZIR-ZR	0.0152	0.0114	-1.0000	0.2754

WASTE ION - PR

VALENCE- 4 SIZE- 1.03

HOL-TI	0.0041	0.0041	0.0000	0.7472
HOL-BA	0.0051	0.9102	2.0000	-0.1747
PER-CA	0.0450	0.0000	2.0000	0.0400
PER-TI	0.0041	0.0041	0.0000	0.3432
ZIR-CA	0.0450	0.0000	2.0000	0.0400
ZIR-TI	0.0041	0.0041	0.0000	0.3432
ZIR-ZR	0.0635	0.0635	0.0000	0.1650

WASTE ION - NO

VALENCE- 3 SIZE- 1.07

HOL-AL	0.0001	0.0001	0.0000	0.3746
HOL-TI	0.0006	0.0005	-1.0000	0.3672
HOL-BA	0.3739	0.5698	1.0000	-0.0009
PER-CA	0.5731	0.8597	1.0000	0.0750
PER-TI	0.0006	0.0005	-1.0000	0.3672
ZIR-CA	0.5731	0.8597	1.0000	0.0750
ZIR-TI	0.0006	0.0005	-1.0000	0.3672
ZIR-ZR	0.0094	0.0070	-1.0000	0.2533

TABLE II continued

WASTE ION - EU				
VALENCE- 3	SIZE- 1.03			
HOL-BA	0.0013	0.0013	1.0000	-0.1763
PER-CA	0.0124	0.0187	1.0000	0.0383
ZIR-CA	0.0124	0.0187	1.0000	0.0383
ZIR-ZR	0.0001	0.0001	-1.0000	0.2237
WASTE ION - GO				
VALENCE- 3	SIZE- 1.02			
HOL-TI	0.0001	0.0001	-1.0000	0.3315
HOL-BA	0.0085	0.0128	1.0000	-0.1546
PER-CA	0.1776	0.2664	1.0000	0.0238
PER-TI	0.0001	0.0001	-1.0000	0.3315
ZIR-CA	0.1776	0.2664	1.0000	0.0238
ZIR-TI	0.0001	0.0001	-1.0000	0.3315
ZIR-ZR	0.0023	0.0017	-1.0000	0.3112
WASTE ION - DY				
VALENCE- 3	SIZE- .99			
HOL-TI	0.0003	0.0002	-1.0000	0.3149
HOL-BA	0.0090	0.0130	1.0000	-0.1832
PER-CA	0.5315	0.7973	1.0000	-0.0013
PER-TI	0.0003	0.0002	-1.0000	0.3149
ZIR-CA	0.5315	0.7973	1.0000	-0.0013
ZIR-TI	0.0003	0.0002	-1.0000	0.3149
ZIR-ZR	0.0066	0.0049	-1.0000	0.1916

TABLE III.

Maximum Possible Loading
Summary Statistics for Phase
Cation Sites

	PEROVSKITE		ZIRCONOLITE	
	VA DIFF	SZ DIFF	VA DIFF	SZ DIFF
HOLLANDITE				
AL	1.0351	-0.1536	0.3313	-0.0568
TI	-0.8779	0.0384	-0.0385	0.0017
BA	0.3719	-0.0063	0.3719	-0.0063
PEROVSKITE				
CA	-0.4430	-0.0163	-0.4430	-0.0163
TI	-0.8779	0.0384	-0.2306	0.0101
ZIRCONOLITE				
CA	-0.4430	-0.0163	-0.4430	-0.0163
TI	-0.8779	0.0384	-0.1107	0.0001
BA	-0.4430	0.0000	-0.4430	-0.0000

TABLE IV.

Loading Calculation for Synroc Formulation

H=0.65, P=0.15, Z=0.20, 15% waste

PHASE DEMANDFORMULA*****

PHASE	FORMULA	HEIGHT	VOLUME
HOLLANDITE	36.6197	66.1492	65.4629
PEROVSKITE	38.0281	12.7138	13.6196
ZIRCONOLITE	25.3521	21.1369	20.9175

PHASE DEMANDCATION*SITE*****

HOLLANDITE	65.0000%
PEROVSKITE	15.0000%
ZIRCONOLITE	20.0000%

PERCENT SITES OCCUPIED

PHASE	%	VAL DIFF	SZ DIFF
HOLLANDITE			
AL	16.1594	0.1491	-0.0008
TI	1.3041	-0.0145	0.0006
CA	36.7558	0.1367	-0.0023
PEROVSKITE			
CA	34.6392	-0.1734	-0.0039
TI	7.5353	-0.0738	0.0035
ZIRCONOLITE			
CA	51.9588	-0.2732	-0.0084
TI	5.6515	-0.0616	0.0027
ZR	22.6843	-0.1164	-0.0021

OXIDE BASIS BATCH

SOURCE	WASTE=100	PERCENT
WASTE	100.0000	15.0000
AL	50.4933	7.5730
CA	33.4397	5.0249
TI	388.4347	57.0652
ZR	38.9567	5.8435
GA	57.2820	8.5923

APPENDIX III

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An Automated X-ray Diffractometer for Detection and Identification
of Minor Phases

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In the preceding volume in this series, we described a stepping motor automation package for XRD data acquisition, based on the Apple microcomputer with an interface card that produces the stepping motor pulses and counts X-ray pulses from the normal X-ray detector and amplifier. We are presently using the system to automate a General Electric XRD-5 diffractometer mechanism, by replacing the original synchronous motor with the stepping motor, and installing a 10:1 reduction gear instead of the chain drive to drive the double worm gears. This gives 2500 steps of the motor per degree two theta. Motor pulses are counted by a small machine language routine which also handles accelerating the mechanism when slewing over long angular ranges.

X-ray Diffraction spectra are collected either by step scanning over a single long scan (perhaps 10-15,000 points) or a series of shorter step scans over the segments of the entire two-theta range which are of interest. In either case, as the data are acquired, they are stored (as dead time corrected counts per second) on floppy disk. They are also displayed on the computer's video monitor. Once recorded, the displays can be reexamined or printed out on a hard copy graphics printer, in the form of strip chart recordings with scale markings and peak identification.

Peaks can be located in the spectrum either by manual marking or automatic peak search. In the former case, the user views the displayed spectrum and positions a cursor using joystick or potentiometer knob. A multipoint parabola can be fitted to the data to locate peak centroids more accurately than the operator's eye. Alternately, the automatic peak search tracks changes in derivative to find peaks, and then locates centroids in the same way. The user enters a minimum peak width (defined as a number of steps), and a minimum peak to background ratio, to select peaks for storage. Up to 100 peaks are then written into a disk file as a list of d-spacings and normalised intensities for subsequent analysis and identification.

This system is being used to study phase development in SYNROC, a multiphase ceramic intended for use as a host for radioactive waste from power reactors, to immobilize the many (30 or more) ionic species for geological periods of time. The major phases in the host, before waste is added, are Hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$), Perovskite (CaTiO_3) and Zirconolite ($\text{CaZrTi}_2\text{O}_7$). By careful balance of the raw materials, it is possible to control the production of these phases without other minor phases appearing in the diffraction patterns when no waste is added. However, the addition of 10-15 weight percent of the waste ions affects the crystal structure. Many of the waste ions occupy either interstitial or substitutional sites in the crystal structure of the three phases (indeed, this is the reason for their selection). However, this produces some change in the lattice spacings and a corresponding changes in the measured diffraction patterns. The nonuniform distribution of the elements produces broadening of peaks as well as shifts.

Of great concern for the intended use of this material is the possibility that additional phases might be formed due to the presence of the waste. If these phases were less stable than the desired ones, they might be attacked (for instance by water leaching out the soluble ions) and cause release of the ions into the biosphere. Because the distribution of waste ions into the various phases is far from equilibrium, even a small amount of such a phase could be associated with significant release of the hazardous ions. By determining the presence and amount of such unwanted phases, the raw material proportions, fabrication and sintering processes can be tailored to eliminate them.

Patterns (sets of d and I values) for all of the likely or possible oxide forms of the various cations were stored in disk files for comparison to the measured unknown patterns. Many were taken from standard published sources, including the JCPDS files, and others were measured on carefully prepared single phase materials produced in our own laboratory. Up to 100 such patterns can be stored on a 5" floppy disk. A search match program compares the measured spectrum to the stored patterns to determine which of them may be present in the unknown.

To perform a search match, the operator enters the number of peaks to compare and the minimum number which must be present in the unknown for the compound to be considered further. Figure 1 shows the results when a search is made using the three most intense peaks and requiring that all three be present. The phases found include the three expected ones (Hollandite, $\text{CaZrTi}_2\text{O}_7$, and CaTiO_3). The Al_2O_3 and Na_2TiO_3 also appear possible based on visual comparison of the spectra. This is shown in Figure 2, comparing each of the phases to the unknown.

In the original search, a wide tolerance window for d-spacing mismatch was used. This is an operator parameter, which multiplies a tolerance curve that varies with d-spacing. The nominal acceptable error is ± 0.02 Å at $d=2.0$, and in this example the multiplier was 1.5. Narrowing the window results in the rejection of more peaks. Figure 3 shows a plot of the figure of merit (which will be defined shortly) as a function of this multiplier. As the spectrum is shifted slightly in two theta (to compensate for misalignment in the spectrometer or change in the lattice parameter), the smallest error window which does not reduce the fitting figure of merit changes. For the zirconolite, a shift of -0.2 degrees permits the window multiplier to be reduced to 0.75. Figure 4 shows that a similar shift, probably due to spectrometer misalignment, can be used to improve the results for most of the candidate minor phases.

Using this shift, the search match was repeated using the most intense 18 peaks for each standard pattern. The results (Figure 5) show the same candidate phases and a few others. The figure of merit shown is the sum of the fractional intensities of the peaks which match. A value of 1 indicates that all peaks were found. Values are reduced from one when a line is missing from the pattern, but the amount of reduction is greater if a major line is missing than if a minor line is absent. Notice that the first three phases, with figures of merit greater than 0.9, are the three expected host phases, followed by the same two possible candidate phases.

Figure 6 shows the comparison of the patterns from these phases with the residue after stripping away the peaks from the three major host phases. Note that several of the major peaks are missing due to removal along with the overlapping peaks from the major phases. The amount of intensity to remove from a line is scaled by the ratio of intensity in the unknown to that in the standard for the major peaks. A somewhat better indication of the possible amount of the phases present is shown in the table in Figure 7, which gives the ratio of intensity of the peaks in the unknown to those in the standard for only the uniquely matched peaks (only which only a single standard can account for). The numbers are consistent with the expected 50:25:25 proportion for the Hollandite, Zirconolite and Perovskite, and a trace amount of the Alumina.

The unequivocal detection of alumina is dependent on measuring a number of unique peaks attributable only to the major alumina peaks and distinct from the minor peaks of the identified major phases. By comparison, no unique peaks from the sodium containing phase were found with the full range scan. This did not rule out the presence of this phase, but rather identified the requirement for a second scan at slow speed over a small two-theta range to resolve the uncertainty. The pattern comparison in Figure 8

suggested which angle range should be used for this purpose, and in the scan no evidence of the phase was found.

For this material, the presence of about 1% of alumina (confirmed by quantitative metallographic techniques and point counting in the Scanning Electron Microscope) does not deleteriously affect the ceramic's properties. Another similar specimen showed the presence of a small amount of rutile (TiO_2), also using this method. The presence of the sodium titanate phase would have been extremely important because it is readily attacked by leachants.

This paper illustrates the utility of a rather simple, low cost computer control system for X-ray diffraction data acquisition and analysis, including search-match comparison of complex measured patterns to stored phases. Positive identification of minor phases can be made by combining the proper choice of simple search-match parameters with additional slow scan measurements over ranges selected with the aid of the analysis system.

Figure 1: Results from search match requiring 3/3 most intense peaks to match.

Phases found	# Peaks	F. M.
HOLLANDITE	3	1.0
CAZRTI207	3	1.0
CATIO3	3	1.0
AL2O3	3	1.0
NA2TIO3	3	1.0
TIZRO4	3	1.0
ZR02:CA0(85/15)	3	1.0

Figure 2: Comparison of measured spectrum (d,I data shown at bottom of each figure) with stored pattern for each matched compound. a) Hollandite, b) Zirconolite, c) Perovskite, d) Alumina, e) Sodium Titanate.

Figure 4: Optimum shift for each of the matched phases.

Phase	Offset	Multiplier
Hollandite	-0.1	0.5
CA2RTI207	-0.2	0.75
CATIO3	-0.2	0.5
AL2O3	-0.2	0.5
NA2TIO3	-0.2	0.75
TI2RO4	0	1.25
ZRO2:CAO(85/15)	-0.2	1.0

Figure 3: Variation of Figure of Merit with Window width multiplier for Zirconolite, as function of shift in pattern (angle in degrees two theta).

Figure 5: Search Match results using most intense 18 peaks.

Phases found	# Peaks	F. M.
HOLLANDITE	17	0.97
CAZRTI207	14	0.90
CATI03	13	0.90
AL2O3	14	0.79
TIZRO4	10	0.74
NA2TI03	7	0.67
BATIO3	8	0.55
ZRO2	10	0.55
BAO	7	0.52
ZRO2:CAO(85/15)	6	0.48
CATI205	7	0.46
TIO2 (RJT)	7	0.43
BETA-CA3 (P04)2	7	0.35
CAZRO3	6	0.31
TIO2 (ANA)	9	0.28

Figure 6: Comparison of candidate trace phase patterns to residual after stripping away of three major phases. a) Alumina, b) Sodium Titanate

Figure 7: Intensity ratio of uniquely matched peaks for phases found by search match procedure.

Phase	Peak Ratio
HOLLANDITE	32/64
CAZRTI2O7	15/40
CATiO3	15/50
AL2O3	4/100
NA2TiO3	4/70
TiZrO4	8/15
ZrO2:CaO(85/15)	8/45

APPENDIX IV

MULTIPOINT X-RAY ANALYSIS BY USE OF THE BACKSCATTERED ELECTRON SIGNAL AS A GUIDE

T. M. Hare, Dale Batchelor, and John C. Russ

The technique to be described here is applicable to the characterization of many multiphase materials. We shall illustrate it with a material of great interest to us, a fine-grained polycrystalline ceramic material (SYNROC) containing at least three major phases, intended for use as a repository for radioactive waste. That means that in addition to the five intended host oxides (of Al, Ca, Ti, Zr, and Ba) another 31 elements can be expected to present in small amounts. We want to find out by x-ray microanalysis (and other techniques) whether the three predicted phases are present and how they change with the introduction of the waste, whether any other phases appear, and where the minor element ions go (which phase acts as a host for which waste element). X-ray diffraction results can answer these questions only partially. There is some uncertainty about the patterns from several of the possible "pure" host phases, occurrence of some additional lines, and shifts with the introduction of dopants making the patterns more complex. In addition, because of the low intensity and probability of overlapping with lines of major phases, X-ray diffraction cannot reliably indicate the presence of minor phases (a few per cent by volume). We also want to know as much as possible about the local neighborhood around each grain, whether it is composed of grains of similar composition (both major and minor elements) or not, and how the radioactive ions distribute themselves during sintering throughout a large sample.

Classic energy-dispersive spectrometry is inadequate to answer these questions for a number of reasons. First, there is no such thing as a "typical" area which can be quantitatively analyzed. No two grains are exactly alike, and to analyze enough grains to draw conclusions about the ways in which one element substitutes for (or is found in conjunction with) another would require an enormous number of analyses, clearly precluding long analysis or computing times. Also, since the material is essentially impervious to etchants, the as-polished surface shows no easy guidelines to the discovery of individual grains, which are in any case so small (1-2 μm) that unequivocal analysis of single grains is undependable.

Cluster Analysis

We have previously reported on a technique that attempts to answer some of these questions by measuring x-ray intensities for the elements of interest, for short times (10-30 s), at a large number of randomly selected points on the sample surface.¹ The normalized intensity values are then plotted in an N-dimensional space (equal to the number of elements measured), and we expect to find (with computer assistance) clusters of points corresponding to individual phases. The number of points in each cluster yields an estimate of the relative volume fraction of the phase, the size and shape of the cluster (above and beyond purely statistical scatter) reflects the extent of substitution or other composition variation and grain size information, and the number of clusters tells us how many phases are present.

This method has given us some valuable information about the major phases. It has become necessary to model the change in the shape of the clusters with grain size, because they grow streamers or bridges toward other clusters if the region excited by the electron beam may cover more than one phase in this fine-grained material. Figure 1 illustrates the presence of clusters in two host materials with different grain sizes, to illustrate the effect of this bridging. This problem is surmountable (with enough

points measured), and indeed should in principle tell us something about the probability of two phases being adjacent.

The principal difficulty that remains is that with random point positioning, an inordinately large number of points must be analyzed to find minor phases that may be present. For instance, a phase amounting to 1% by volume would be very significant in terms of the properties (mechanical, thermal, and resistance to leaching out of the radwaste, if certain ions preferentially collected in the phase), but it would require the analysis of 10 000 locations for confident identification of its presence as a cluster. Even if the phase always occurred next to a particular host phase, or was significantly smaller in grain size, it might still be missed.

FIG. 1.--Plots of normalized intensities from random multipoint analysis of 10 kV. N-space distribution is projected onto a 2-D (two-element) plane (Ca vs Zr). (a) coarse-grained material (SYNROC, 2-5 μ m) with distinct clusters; (b) fine-grained material (SYNROC, 1-2 μ m) in which clusters have extensive bridging due to overlapping of analysis region onto several grains.

FIG. 2.--(a) Backscattered electron image of fine-grained radwaste-doped "SYNROC" multiphase ceramic. Contrast and black level suppression have been increased to cover gray scale of display with small variation in average atomic number; bright points are actually smaller than shown and have saturated display and film. (b) Histogram of brightness readings on backscattered electron image of peaks represent gray levels that correspond to points on surface with same average atomic number, and which thus may belong to a single phase.

Backscattered Electron Images

Although there is little or no relief on the polished surfaces placed in the SEM for analysis, so that secondary electron images show no detail except for occasional pores, pits, or scratches, it is possible to obtain contrast in the backscattered electron image. We use a segmented annular backscattered electron detector (GGW Model 30) which in independent tests has shown the ability to resolve average atomic number differences for elements in the $Z = 10-40$ range of about 0.1 to 0.2 Daltons. The fraction of incident electrons which backscatter increases monotonically with atomic number, so differences in average atomic number between the phases makes them distinguishable.

Figure 2(a) shows a representative backscattered electron image of a multiphase ceramic containing 10% simulated radwaste (nonradioactive isotopes of the expected elements, in the expected composition). There is clear visual evidence for several phases. By measuring the image brightness at each point (in a 256×256 -point array), we collect the histogram shown in Fig. 2(b). It shows the presence of several phases, which we can identify as at least five phases with subsequent x-ray microanalysis.

From the expected composition of the host phases, we would expect average atomic numbers as follows:

15.0	Zirconolite
13.6-14.6	Hollandite (depending on the barium-titanium ratio)
13.2	Perovskite

We have subsequently identified (by x-ray microanalysis) the small bright phase as heavy metals, chiefly the radwaste elements Mo and Rb, with an average atomic number of more than 40, and the darkest nonpore phase as alumina (resulting from inclusion of shattered grinding media), with a mean atomic number of 12.0. Note that the variation in the Hollandite allows it to cover the entire range between Perovskite and Zirconolite, and with the addition of even small amounts of heavy radwaste elements, to risk confusion with either.

EDX of Selected Grains

Using the backscattered electron image as a guide, we can position the electron beam stationary at the "center" of a region with a selected brightness (presumably a selected average atomic number) and perform an analysis using the energy dispersive spectrometer. This procedure may still cause penetration through to underlying phases of different composition, if the grain is thin (see our earlier paper on predicting the depth of analysis in this material),² but gives the best chance of getting a set of x-ray intensities characteristic of the selected phase by itself.

From many such points, with each one measured for 20 s at 15 kV, we can again plot the results in N-dimensional space to examine the clusters. The material has a grain size similar to that of Fig. 1(b). We have found that one particular brightness level (the light intermediate gray in Fig. 2) produces intensities that sorted themselves into two evident clusters, representing two different compositions, as shown in Fig. 3, in which it is evident that there are two phases, zirconolite and hollandite.

From the results, three main regions were identified in addition to the dark alumina and bright metal phases. These regions are shown in several two-dimensional projections in Figures 3(c) and (d). It is possible to distinguish the brightness levels of these phases in some cases, as shown in Fig. 4 (where a smaller area of the image was measured, with less variation in detection efficiency). It was also shown that the dark gray (not black) phase (perovskite) is the only phase that contains the radwaste element neodymium.

Conclusions

By combining the use of the backscattered electron image, to indicate phase boundaries, and rudimentary image analysis to find grain centers for beam positioning, one may obtain selected phases for compositional analysis by energy-dispersive x-ray measurement. This procedure is much more efficient than random-point analysis for measurement of minor phases. The variation in composition of phases, and the amounts of various minor elements in each, can be determined. In addition, measurements on the backscattered electron image can reveal the relative abundance (volume fraction) of the phases. This approach is an extremely efficient one for characterizing complex materials.

FIG. 3.--Normalized intensity plots from multipoint analysis using backscattered electron signal to select locations corresponding to chosen gray levels in Fig. 2(b). Points from light-gray region fall into two clusters, indicating two compositionally distinct phases with nearly equal average atomic numbers. (a) Ca vs Zr, light-gray area; (b) Zr vs Ti, light-gray area; (c) Ca vs Zr, light- and intermediate-gray areas; (d) Zr vs Ti, light- and intermediate-gray areas.

FIG. 4.--Brightness histogram showing two partially resolved peaks in light-gray area on Fig. 2(b), obtained by scanning over reduced area.

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