000-2510-5

ADVANCED WASTE FORMS RESEARCH AND DEVELOPMENT

Annual Report

Gregory J. McCarthy
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

MASTER

June 11, 1975

PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION UNDER CONTRACT NO. E(11-1)-2510 IN
COOPERATION WITH THE BATTELLE PACIFIC NORTHWEST LABORATORIES.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

per T & W

~~DISTRIBUTION OF THIS DOCUMENT IS LIMITED~~
~~To Government Agencies and Their Contractors~~

OK. *[Signature]*
THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

~~DISTRIBUTION OF THIS DOCUMENT IS LIMITED~~

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

"This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Atomic Energy Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

As used in the above, 'person acting on behalf of the Commission' includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor."

Table of Contents

1.0	Introduction	1
2.0	Supercalcine Development	2
2.1	Phases for Cesium Fixation	2
2.2	Ruthenium Fixation	10
2.3	Cesium Aluminosilicates for Cs Fixation	13
2.4	Compatibility Studies	20
2.5	Supercalcine Formulations	31
3.0	Waste PSUW-4 and Supercalcine Formulation 75-1	38
3.1	Waste Formulation PSUW-4	38
3.2	Supercalcine Formulation 75-1	42
4.0	X-Ray Phase Analysis of PNL "Glass Sintered" Waste Form	43

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**DISTRIBUTION OF THIS DOCUMENT IS LIMITED
To Government Agencies and Their Contractors**

~~RESTRICTED - SECURITY INFORMATION~~

See

2B

1.0 Introduction

This document constitutes the annual report of research and development activities on advanced (i.e., alternatives to glass) nuclear waste forms. It describes work performed during the last five months but is meant to be more comprehensive than the two previous quarterly reports (COO-2510-1 and 3).

The three major FY 1975 research objectives (milestones) for this project have been met. The hot pressed ceramic waste form feasibility study was completed in April and a final report was issued as COO-2510-4. The crystalline phase formation on firing calcine of a simplified version of waste PW-4b was studied and a journal article based on this work (COO-2510-2, preprint) was accepted for publication in February. Our final objective was to develop a demonstration supercalcine^{*} formulation which will be evaluated on a larger processing scale at Battelle Pacific Northwest Laboratories (PNL). Some of our recent supercalcine formulations look very promising and based on these results, formulation 75-1 has been submitted to PNL.

Two new phases of the work which give essential background information for supercalcine development, "Cesium Aluminosilicate for Cs Fixation" and "Compatibility Studies", are introduced in this report.

* "Supercalcine" is a term for a crystalline ceramic waste form prepared by modifying with selected additives the composition of the liquid waste stream from the reprocessing of high level commercial power reactor spent fuel so that when it is dried, calcined and given additional heat treatment a series of thermodynamically stable, refractory and leach resistant crystalline phases are formed.

2.0 Supercalcine Development

2.1 Phases for Cesium Fixation (S. A. Gallagher)

Cesium is one of the most troublesome species present in radioactive waste because of its high heat producing capacity and its high volatility during waste solidification. The purpose of this work is to examine phases which will tie up the cesium in a refractory (stable to 1050°C), nonleachable, crystalline oxide compound or solid solution. Since Cs^+ is the second largest cation (radius = 1.88Å in XII coordination) known to exist, one is largely limited to oxides with the perovskite¹ ($\text{A}^{\text{XII}}\text{B}^{\text{VI}}\text{X}_3$), the scheelite² ($\text{A}^{\text{VIII}}\text{B}^{\text{IV}}\text{X}_4$), or the tectosilicate³ (aluminosilicate with large stuffing sites) structures which all contain highly coordinated sites that cesium could occupy.

Two preparation methods are used throughout these studies. In the "wet method", nitrate solutions of the various elements which are required are measured into a beaker in the proper proportions. The solution is stirred on a hot plate at 370°C until it has been reduced in volume through evaporation of the water to a gel-like material. This material is then dried at 125°C for 18 hours. After drying, the substance is ground, pelletized, weighed, and then denitrated at 600°C for 2 hours. After denitration, the pellet is reweighed to determine the weight loss. Then it is ground, and an X-ray diffraction slide is prepared to determine what phases are present. The sample is repelletized and weighed and then heat treatments of 850, 950 and 1050°C are conducted for several hours. After each heating, the pellet is weighed, ground, and the powder is subjected to X-ray diffraction analysis. Before each temperature increase, the sample is repelletized and weighed.

The "dry method" is used primarily when a nitrate solution or any other solution of a particular species cannot be found. This method begins with oxide, nitrate, or carbonate powders of the various elements which are required. These powders are weighed out in the proper proportions for making the compound of interest. The powders are then ground and shaken together and pelletized. The pellet is weighed and denitrated at 600°C for 2 hours. The procedure following the denitration step is identical to that of the "wet method".

1 Advanced Waste Forms Research and Development, Progress Report, C00-2510-1, September 18, 1974, p 46.

2 Galasso, Francis S, Structure and Properties of Inorganic Solids, Pergamon Press, New York, 1970, 7, p. 106; O. Muller and R. Roy, Major Ternary Structural Families, Springer-Verlag, New York, 1974, p 89 ff.

3 Wells, A. F., Structural Inorganic Chemistry, Oxford, New York, 1962, pp 808-816.

A number of oxides with the perovskite structure are known to be highly refractory such as SrZrO_3 , BaZrO_3 , and LaFeO_3 . If a solid solution could be formed between a cesium containing phase with the same stoichiometric ratio as the perovskite and with a melting point of 850 to 950°C and one of these refractory perovskite phases, there is a possibility of producing a product which has a higher melting point than the cesium phase (ideally greater than 1050°C). As a result of this increased melting point, the volatility of cesium should be reduced. Such a solid solution would then be tested for leachability.

With this objective in mind, the preparation of 10-90, 30-70, and 50-50 weight percent solid solutions of CsNbO_3 ⁴, a previously reported phase, with SrZrO_3 and BaZrO_3 was attempted using the "dry method". Cesium nitrate, Nb_2O_5 , SrCO_3 or BaCO_3 , and ZrO_2 powders were used as starting materials.

A typical example of what is happening in this system is seen in the attempt to prepare a 10-90 solid solution of CsNbO_3 with BaZrO_3 . The desired solid solution is not formed; however, the weight losses observed and the X-ray diffraction analyses indicate the following chemical reaction is probable:

There is 5% Cs_2O , 14% $\text{CO}_2 + \text{N}_2\text{O}_5$, 5% Nb_2O_5 , 34% ZrO_2 , and 42% BaO by weight. The percent weight loss for this system at each heat treatment temperature is shown below.

Temperature (°C)	Percent Weight Loss (%)
600	5
850	5
950	10
1050	1

Fourteen percent of the weight lost is due to the loss of CO_2 and N_2O_5 during the decomposition of CsNO_3 and BaCO_3 . This means that at 950°C 4% of the weight loss is due to CO_2 and N_2O_5 . The additional 6% is due to the loss of Cs_2O and other complex vapor species. An additional 1% is lost at 1050°C. The 5% Nb_2O_5 is at or just below the detection limit of X-ray diffraction analysis. This explains the fact that only BaZrO_3 is observed in the X-ray diffractogram.

4 Reisman, A. and J. Mineo, J. Phys. Chem., 65, 996-998, (1961).

All other weight loss data and X-ray diffraction analyses for these systems are shown in Table 1. For all the systems, the X-ray diffraction analyses after heating at 950°C and 1050°C indicates that the desired perovskite solid solutions were not formed. The weight losses at 950°C and 1050°C were appreciable in every case. In several diffractograms what could be the 100% peaks of either a 1:1 or a 2:15 stoichiometric ratio of Cs_2O to Nb_2O_5 were observed. Several perovskite solid solutions appear to be formed since a number of lines in the X-ray diffractograms could be indexed on a perovskite cell. The compositions of these perovskite solid solutions are uncertain. There were also several phases whose composition and structure could not be identified at this time.

Scouting runs to look for solid solutions of the hypothetical phases " CsMoO_3 " and " CsFeO_{3-x} " with LaFeO_3 were carried out at 10-90, 20-80, and 30-70 weight percents. It was not known that these species existed; however, when excess Fe was added to several of the supercalcine formulations less fogging of the silica tubes and lower weight losses were observed when pellets were heat treated. This was a promising sign of reduced volatilization of Cs. Solutions of CsNO_3 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were used for the preparation by the "wet method". No solid solutions were formed in these systems. The only phase observed in the X-ray diffractograms was LaFeO_3 . The Quarterly Report⁵ for September to December, 1974 indicates that Cs_2MoO_4 is likely to form in the waste because of its high thermodynamic stability below 950°C. Then why was no Cs_2MoO_4 , MoO_3 , or Fe_2O_3 seen in the diffractograms? The answer could be that Cs_2MoO_4 and Fe_2O_3 are present but in quantities too small to be observed by X-ray diffraction. Their presence was confirmed, however, by attempting to prepare the 50-50 solid solutions of " CsMoO_3 " and " CsFeO_{3-x} " in LaFeO_3 . At this ratio of the end members, the amounts of Cs_2MoO_4 and Fe_2O_3 are present in significant quantities to be seen in the diffractograms. The high weight losses in these system are, therefore, due to the loss of Cs_2O and to the loss of Cs_2MoO_4 which vaporizes above 950°C.

Several compounds with stoichiometry and, very likely structure, which are related to scheelite (CaWO_4 , SrMoO_4 etc.) and contain Cs have been reported by

5 Advanced Waste Forms Research and Development, Quarterly Progress Report, September 30 to December 31, 1974 Section 3.4.1.

Table 1
Cesium Fixation Studies and Results

MIXTURE	PERCENT WEIGHT LOSS (%) ^a	250°C X-RAY DIFFRACTION ANALYSIS	PERCENT WEIGHT LOSS (%) ^c	1050°C X-RAY DIFFRACTION ANALYSIS
10-90 CsNbO ₃ -SrZrO ₃	8	SrZrO ₃ +ZrO ₂	9	SrZrO ₃ + * (2:15Cs ₂ O-Nb ₂ O ₅)
30-70 CsNbO ₃ -SrZrO ₃	13	SrZrO ₃ +ZrO ₂ + * (2:15Cs ₂ O-Nb ₂ O ₅)	13	SrZrO ₃ +ZrO ₂ +Pss(a ₀ =4.06Å) + * (1:1 and 2:15 Cs ₂ O-Nb ₂ O ₅)
50-50 CsNbO ₃ -SrZrO ₃	40	*	43	*
10-90 CsNbO ₃ -BaZrO ₃	6	BaZrO ₃	7	BaZrO ₃
30-70 CsNbO ₃ -BaZrO ₃	13	BaZrO ₃ +ZrO ₂ + *	16	Ba ₃ Nb ₄ O ₁₅ +BaZrO ₃ +ZrO ₂ a ₀ =4.38Å
50-50 CsNbO ₃ -BaZrO ₃	21	Ba ₃ Nb ₄ O ₁₅ +ZrO ₂ +Pss(a ₀ =4.24Å)	28	ZrO ₂ +Pss a ₀ =4.24Å a ₀ =4.03Å
10-90 "CsFeO ₃ "-LaFeO ₃	13	LaFeO ₃	14	LaFeO ₃
20-80 "CsFeO ₃ "-LaFeO ₃	13	LaFeO ₃	14	LaFeO ₃
30-70 "CsFeO ₃ "-LaFeO ₃	19	LaFeO ₃	23	LaFeO ₃
10-90 "CsMoO ₃ "-LaFeO ₃	4	LaFeO ₃	6	LaFeO ₃
20-80 "CsMoO ₃ "-LaFeO ₃	3	LaFeO ₃	17	LaFeO ₃
30-70 "CsMoO ₃ "-LaFeO ₃	5	LaFeO ₃	28	LaFeO ₃
(Cs,La)MoO ₄ (wet)	1	Cs ₂ MoO ₄ +1/2La ₂ MoO ₆	49	La ₂ MoO ₆
(Cs,La)MoO ₄ (dry)	40	(Cs,La)MoO ₄ + *	76	La ₂ Mo ₃ O ₁₂
(Cs,La)WO ₄	1	(Cs,La)WO ₄	72	*
(Cs,Pr)WO ₄	2	*	88	*
(Cs,Nd)WO ₄	1	*	21	*
(Cs,Sm)WO ₄	2	*	4	*
10-90 (Cs,La)WO ₄ -SrWO ₄	4	SrWO ₄	7	SrWO ₄
20-80 (Cs,La)WO ₄ -SrWO ₄	4	SrWO ₄ +(Cs,La)WO ₄	7	SrWO ₄
30-70 (Cs,La)WO ₄ -SrWO ₄	8	SrWO ₄ +(Cs,La)WO ₄	12	SrWO ₄ +(Cs,La)WO ₄
10-90 (Cs,La)WO ₄ -BaWO ₄	<1	BaWO ₄ a ₀ =5.60Å c ₀ =12.60Å	1	BaWO ₄ a ₀ =5.60Å c ₀ =12.60Å
20-80 (Cs,La)WO ₄ -BaWO ₄	<1	BaWO ₄	1	BaWO ₄
30-70 (Cs,La)WO ₄ -BaWO ₄	1	BaWO ₄ +(Cs,La)WO ₄	3	BaWO ₄ +(Cs,La)WO ₄

a Weight loss above that calculated to be due to the loss of CO₂ and N₂O₅.

b An * indicates an unknown phase or phases. Pss indicates a perovskite solid solution.

c Total weight loss above that calculated to be due to loss of CO₂ and N₂O₅.

scientists in the USSR⁶⁻¹¹. Several cards for these compounds are included in the Powder Diffraction File (#23-892, 23-896, and 23-902). These compounds are of the type $(\text{Cs}, \text{RE})\text{MoO}_4$ and $(\text{Ca}, \text{RE})\text{WO}_4$ where RE stands for rare earth. The molybdates have melting points of about 950 to 1000°C while some of the tungstates melt as high as 1100°C. Both the "wet" and the "dry method" were used in attempts to prepare $(\text{Cs}, \text{La})\text{MoO}_4$ for leaching and thermal stability evaluation. Cs_2MoO_4 and La_2MoO_6 were formed at 950°C using the "wet method". Weight losses show that MoO_3 was lost in addition to the denitration products. The Cs_2MoO_4 vaporizes when the sample is heated to 1050°C since this is well above its melting point of 936°C¹². The "dry method" produces the desired product $(\text{Cs}, \text{La})\text{MoO}_4$ plus an unknown phase. During the 1050°C heating the Cs was lost along with MoO_3 . $\text{La}_2\text{Mo}_3\text{O}_{12}$ is seen in the X-ray diffractogram of the 1050°C sample confirming these losses. Therefore, $(\text{Cs}, \text{La})\text{MoO}_4$ is stable only to 950°C. (See Table 1).

When W is substituted for Mo in $(\text{Cs}, \text{La})\text{MoO}_4$, the melting point of the compound is reported to increase to 1040°C⁹. Cesium lanthanum tungstate was formed at 800°C using the "dry method". The weight loss at 950°C was insignificant, but as the melting point is exceeded at 1050°C, the sample decomposes and vaporizes. X-ray powder diffraction analysis was performed on this sample, and the diffraction pattern was indexed on a tetragonal cell using the unit cell parameters as reported by Russian scientists¹⁰. The hkl's, the d spacings (both calculated and observed), and the intensities are listed in Table 2. The least squares refined cell parameters are $a_0 = 6.553\text{\AA}$ and $c_0 = 9.642\text{\AA}$. The probable space group is $P4_2/\text{nmc}$ based on systematic absences.

- 6 Mokhosoev, M. V., et.al., Russ. J. Inorg. Chem. 14 (11), 1570, (1969).
- 7 Vinokurov, V. A., and P. V. Klevtsov, Soviet Phys. Cryst., 17, 102-6, (1972).
- 8 Plyushchev, V. E. and E. S. Razgon, Russ. J. Inorg. Chem. 19 (1), 47-49 (1974).
- 9 Rybahov, V. K. and V. K. Trunov, Russ J. Inorg. Chem. 18 (11), 1678-1680, (1973).
- 10 Ibid., 19 (2), 188-190, (1974).
- 11 Ibid., 16 (5), 698-701, (1971).
- 12 I.N. Belyaev and N. N. Chikova, Russ J. Inorg. Chem., 9 (12) 1483-1487, (1964).

By substituting praseodymium, neodymium, and samarium for lanthanum in $(\text{Cs},\text{La})\text{WO}_4$, the melting points are reported to increase to 1050°C^9 , 1110°C^9 and 1110°C^9 , respectively. These compounds were prepared using the "dry method" with starting materials of Cs_2CO_3 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , and WO_3 powders. The X-ray diffractograms obtained are not consistent with any of the reported patterns for $(\text{Cs},\text{Pr})\text{WO}_4$, $(\text{Cs},\text{Nd})\text{WO}_4$, or $(\text{Cs},\text{Sm})\text{WO}_4$ ^{8,9}. Weight losses are shown in Table 1. The weight losses at 950°C are small, and again as the melting point is approached at the 1050°C heating, the weight losses increase sharply.

A solid solution of one of these (probable) scheelite related phases containing Cs with a more refractory scheelite structure phase such as SrWO_4 or BaWO_4 should have greater thermal stability than the starting Cs phase. Attempts were therefore made to prepare solid solutions of 10-90, 20-80 and 30-70 weight percents of $(\text{Cs},\text{La})\text{WO}_4$ with SrWO_4 and BaWO_4 by the "dry method". Cesium carbonate, La_2O_3 , WO_3 , and SrCO_3 or BaCO_3 powders were the starting materials. No solid solutions were formed at any of the firing temperatures. The X-ray diffractograms showed the formation of both end members - either SrWO_4 and $(\text{Cs},\text{La})\text{WO}_4$ or BaWO_4 and $(\text{Cs},\text{La})\text{WO}_4$ (see Table 1). This resulted in small weight losses at both 950°C and 1050°C because only small amounts of the starting materials are lost. For the 10-90 ratio of $(\text{Cs},\text{La})\text{WO}_4$ to SrWO_4 , the amounts of $(\text{Cs},\text{La})\text{WO}_4$ formed was below the level of detection by X-ray diffraction. The 10-90 $(\text{Cs},\text{La})\text{WO}_4$ - BaWO_4 X-ray diffractogram showed a phase with lattice parameters ($a_0 = 5.60\text{\AA}$ and $c_0 = 12.60\text{\AA}$) only slightly shifted from those of pure BaWO_4 ($a_0 = 5.6134\text{\AA}$ and $c_0 = 12.720\text{\AA}$, PDF card #8-457). It is seen that the lattice parameters observed for this test are somewhat smaller than those for the pure phase, implying the substitution of a smaller cation into the structure. Since the ionic radius of Cs^+ ($1.88\text{\AA}$) is greater than that of Ba^{2+} ($1.35\text{\AA}$), Cs^+ is not the ion that has been substituted. The only alternative for substitution is La^{3+} ($1.15\text{\AA}$) which has a smaller radius. In order to substitute a 3^+ ion for a 2^+ ion some vacancies must be created to maintain charge balance. For other results see Table 1.

From the thermal stability standpoint, these cesium rare earth tungstate and molybdate samples seem to be the most promising studied so far. Leachability tests will be performed on $(\text{Cs},\text{La})\text{MoO}_4$, $(\text{Cs},\text{La})\text{WO}_4$, and $(\text{Cs},\text{Nd})\text{WO}_4$ if large enough grain sizes can be produced by hot pressing or sintering.

TABLE 2

X-Ray Powder Data for $\text{CsLa(WO}_4)_2$
 [Tetragonal, Space Group $P4_2/nmc$]
 $a_0 = 6.553(0)\text{\AA}$ $c_0 = 9.642(1)\text{\AA}$

hkl	d_{calc}	d_{obs}	I/I
002	4.82	4.81	2
110	4.63	4.62	3
112	3.34	3.34	100
200	3.28	3.28	40
202	2.710	2.708	2
212	2.504	2.505	3
004	2.410	2.409	7
220	2.317	2.316	20
213	2.165	2.165	1
222	2.088	2.088	1
311	2.026	2.026	1
302	1.990	1.990	<1
204	1.942	1.941	25
312	1.904	1.903	70
224	1.670	1.670	16
400	1.638	1.637	9
314	1.571	1.571	1
402	1.551	1.551	1
116	1.518	1.518	8
332	1.471	1.471	2
420	1.465	1.466	12
422	1.402	1.402	<1
404	1.3549	1.3551	12
316	1.27	1.27	14
207	1.27		
424	1.252	1.252	9
512	1.242	1.242	14
440	1.158	1.158	1
208	1.131	1.131	2
336	1.114	1.114	2
532	1.0945	1.0946	8
600	1.092	1.092	6

When the few remaining experiments are completed for the phases described above, our emphasis will be shifted to aluminosilicates for Cs fixation as described in the following Sections. In order to obtain the required background information for the supercalcine formulations, a systematic study of the phase relations, stoichiometry range, thermal stability, and leachability of the two known cesium aluminosilicate phases, $\text{CsAlSi}_2\text{O}_6$ (pollucite) and CsAlSiO_4 , will be undertaken.

2.2 Ruthenium Fixation (R.G. Johnston)

Gray at BPNL has shown that Ru volatilizes from PW-4b calcine (as RuO_4) at a significant rate at temperatures as low as 1000°C .^{*} RuO_2 is not a satisfactory phase for Ru fixation in supercalcine since it is unstable above $\sim 1000^\circ\text{C}$ in air and rapidly volatilizes as RuO_4 . Thus, phases for Ru fixation are being given special attention. Several ternary compounds and solid solution phases which could or do contain Ru as well as other waste ions are being examined in detail as possibilities for fixation of highly volatile Ru. Only those phases likely to be highly refractory are being considered.

The easily formed phase SrRuO_3 (5.5 hours at 920°C , $\text{SrCO}_3 + \text{RuO}_2$) has itself been investigated for possible decomposition with the loss of Ru by volatilization. This mixture was initially pressed into cylindrical pellets, weighed, and fired at 920°C (5.5 hours) and 1050°C (25.5 hours). The successive firings were carried out on the same pellet, which was weighed on a microgram balance, reground, pelletized and reweighed after each firing, with a small sample being removed for x-ray diffraction analysis of the phases present. Identification of the volatilized species, if any, was carried out indirectly by weight loss percentages with respect to the bulk composition and by determination of the phases remaining by x-ray diffraction analysis. No weight loss other than that attributable to CO_2 being driven off from the SrCO_3 was observed in the SrRuO_3 firings, nor were any phases other than SrRuO_3 seen in the x-ray diffractograms. The stability of the phase at 1200°C is currently being tested. Results from previous solid solution experiments with another batch of SrRuO_3 and other phases indicate that it should be stable at temperatures up to 1200°C . BaRuO_3 is also being prepared, both for investigation of its own behavior and use in possible solid solution compositions. Solid solution is the rule in supercalcine so we must know more about the solid solution behavior of SrRuO_3 and BaRuO_3 with other known supercalcine perovskite structure phases.

A number of possible solid solutions containing Ru and other waste ions, particularly those with the perovskite SrRuO_3 and the rare earth-containing pyrochlores $\text{RE}_2\text{Ru}_2\text{O}_7$, are currently being examined. The compositions prepared to date are listed in Table 3, along with firing, weight loss, and composition data. All of these mixtures were prepared from the stoichiometric oxides, and treated in the course of the firings as described above.

The $\text{RuO}_2\text{-ZrO}_2$ and $\text{RuO}_2\text{-TiO}_2$ mixes (RW44 and RW37 respectively) showed no solid solution. About 20% of the RuO_2 in the mixtures volatilized at

Table 3
Ruthenium Fixation Studies and Results

Run No.	Starting Composition	Firing Temperature, °C	Firing Duration(hr)	Wt. Loss (%)	X-ray Phase Analysis
RW37-1	$\text{RuO}_2 +$	880	22.0	<1	$\text{RuO}_2 - \text{TiO}_2$
-2	TiO_2	1050	26.25	11.81	$\text{RuO}_2 - \text{TiO}_2$
-3		1225	44.33	57.64	TiO_2
RW38-1	$0.25\text{SrRuO}_3 +$	880	23.75	<1	$\text{SrRuO}_3 + \text{BaTiO}_3$
-2	0.88BaTiO_3	1050	26.25	<1	Pss^*
-3		1225	24.33	<1	Single Tetragonal Phase
RW39-1	$0.25\text{SrRuO}_3 +$	880	24.67	<1	$\text{SrRuO}_3 + \text{SrTiO}_3^*$
-2	0.88SrTiO_3	1050	23.0	<1	Pss^*
-3		1225	24.0	<1	Pss^*
RW40-1	$0.25\text{SrRuO}_3 +$	880	24.67	<1	$\text{SrRuO}_3 + \text{NdFeO}_3$
-2	0.88NdFeO_3	1050	23.0	<1	$\text{NdFeO}_3 + \text{Pss}$
-3		1180	24.0	<1	$\text{NdFeO}_3 + \text{Pss}$
RW41-1	$0.25\text{SrRuO}_3 +$	880	24.67	<1	$\text{SrRuO}_3 + \text{NdCrO}_3$
-2	0.88NdCrO_3	1050	23.0	<1	$\text{Pss} + \text{NdCrO}_3$
-3		1180	24.0	1.03	$\text{Pss} + \text{NdCrO}_3$
RW42-1	$0.25\text{Sm}_2\text{Ru}_2\text{O}_7 +$	900	28.67	<1	$\text{Sm}_2\text{Ru}_2\text{O}_7 + \text{Sm}_2\text{Zr}_2\text{O}_7$
-2	$0.85\text{Sm}_2\text{Zr}_2\text{O}_7$	1040	26.0	<1	$\text{Sm}_2\text{Ru}_2\text{O}_7 + \text{Sm}_2\text{Zr}_2\text{O}_7$
-3		1215	45.75	12.66	$\text{Sm}_2\text{Zr}_2\text{O}_7 + \text{Unknown Phases}$
RW43-1	$0.25\text{Sm}_2\text{Ru}_2\text{O}_7 +$	900	28.67	<1	$\text{Sm}_2\text{Ti}_2\text{O}_7 + \text{Sm}_2\text{Ru}_2\text{O}_7$
-2	$0.85\text{Sm}_2\text{Ti}_2\text{O}_7$	1040	26.0	<1	$\text{Sm}_2\text{Ti}_2\text{O}_7 + \text{Sm}_2\text{Ru}_2\text{O}_7$
-3		1215	45.75	7.60	$\text{Sm}_2\text{Ti}_2\text{O}_7 + \text{Unknown Phases}$
RW44-1		900	28.67	1.39	$\text{RuO}_2 + \text{ZrO}_2$
-2	$\text{RuO}_2 + \text{ZrO}_2$	1040	26.0	11.87	$\text{RuO}_2 + \text{ZrO}_2$
-3		1215	45.75	43.13	ZrO_2
SR6-1		920	5.5	15.49**	SrRuO_3
-2	$\text{SrCO}_3 + \text{RuO}_2$	1050	25.5	1.52 **	SrRuO_3

* Pss = Perovskite Solid Solution

** CO_2 from SrCO_3

at 1050°C (in about 26 hours) and the remainder disappeared in the 1200°C heating. No additional phases were observed in these experiments.

Runs RW38 and RW39, mixes of BaTiO_3 and SrTiO_3 respectively with SrRuO_3 , show considerable promise. These perovskite-perovskite structure mixes exhibit negligible weight losses at all firing temperatures. RW38 exhibits the formation of a solid solution in the 1050°C firing, and apparently changes structure, becoming a single tetragonal phase, at 1200°C. The extent of the solid solution and the structure and stability of the 1200°C single phase are currently under investigation. The question of solid solution in RW39 is as yet unresolved. The major diffraction lines of SrRuO_3 and SrTiO_3 lie so closely together that they are very difficult to resolve on a diffractometer. This preparation will shortly be examined by the higher resolution Guinier technique.

RW40 and RW41, mixes of NdFeO_3 and NdCrO_3 with SrRuO_3 respectively, also showed negligible weight losses over the firing period. In RW40 a perovskite solid solution is formed, but its limits and cell parameters are difficult to determine due to the close proximity of the major diffraction peaks as in RW39. This run is also awaiting Guinier analysis. RW41 shows definite solid solution behavior, the extent of which is currently being examined.

RW42 and RW43 are mixes making use of a typical rare earth ruthenium pyrochlore structure phase, $\text{Sm}_2\text{Ru}_2\text{O}_7$. They are mixes with $\text{Sm}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{O}_7$. The rare earth ruthenium pyrochlores have been very difficult to form due to the double problem of slow reaction rates at 1050°C and below and high RuO_2 volatilization at the higher temperatures. The weight losses which occurred in these preparations can be seen in Table 3. Both showed no solid solution formation at 900 and 1050°C, nor were any other phases observed to form. At 1200°C $\text{Sm}_2\text{Ru}_2\text{O}_7$ partially or completely decomposed, and was hence absent from the x-ray diffractograms. The diffractograms showed the presence of the Ti and Zr pyrochlore phases and a number of as yet unidentified small peaks. We are taking one final look at $\text{Nd}_2\text{Ru}_2\text{O}_7$ and its solid solutions, if any, before closing out work on this structure type. However, it is apparent now that these phases are not especially promising for Ru fixation and our emphasis will be on the perovskite structure phases.

2.3 Cesium Aluminosilicates for Cs Fixation (G.J. McCarthy, D.E. Pfoertsch and C. A. Smith).

At this time it appears that aluminosilicates are the best candidates for fixing Cs in stable, leach resistant crystalline phases in supercalcine. There are many ways in which the necessary alumina and silica may be added to the liquid waste. It is expected that some alumina-silica sources will react with cesium more readily than others. We have begun to survey all readily available alumina-silica sources as candidates for Cs fixation and will determine the following:

- i. Which alumina-silica sources form suitable Cs aluminosilicates with the lowest energy input (i.e., at the lowest temperature for the shortest time) and with the least loss of Cs during formation.
- ii. Will pretreatment (e.g., dehydration) enhance Cs aluminosilicate formation.
- iii. Which of the promising alumina - silica sources will best form Cs aluminosilicate in complex waste mixtures. This is an important question since the alkaline earths readily form feldspar type aluminosilicates (e.g., celsians $\text{BaAl}_2\text{Si}_2\text{O}_8$, $\text{SrAl}_2\text{Si}_2\text{O}_8$ and anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$).

The third question will be discussed further under compatibility studies (Section 2.4). Finding the most suitable Cs aluminosilicate compositions is one of the aspects of the Cs fixation studies described above.

Three classes of alumina-silica sources will be surveyed: phyllosilicates (clays, alkali-exchanged micas), tectosilicates (zeolites, alkali exchanged feldspars and feldspathoids) and alumina-silica solutions-suspensions and dessicated gels. Clays and zeolites have long been used for Cs fixation in nuclear waste management and reports of any relevant studies are being collected and solicited.

Several experiments have been performed with a selection of clay minerals obtained from campus sources and collections:

Kaolinite - Commercial Georgia Kaolin - $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$

Halloysite - Wagon West, Colorado - $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$

Pyrophyllite-1 - Commercial LAVITE used in high pressure studies - $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$

Pyrophyllite-2 - Mineral specimen from Robbins, NC

Montmorillonite-1 - Belle Fourche, SC - nominally $(1/2 \text{ Ca}, \text{Na})_{0.67}\text{Al}_{3.33}\text{Mg}_{0.67}\text{Si}_8\text{O}_{20}(\text{OH})_4$; the Ca, Na, Mg are variable and it often contains small amount of Fe.

Montmorillonite-2 - Upton, Wyoming

Bentonite - "Volclay" Black Hills, SD - clays with exceptionally high cation exchange capacity whose main constituent is montmorillonite

It will be assumed at first that the small amounts of cation impurities in these clays will be incorporated by solid solution into any Cs aluminosilicates formed. The formula will be factored and written as $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ or $(x)\text{AlSi}_2\text{O}_5(\text{OH})$ to better show their compositional contribution to $\text{Cs}_2\text{Al}_2\text{Si}_2\text{O}_8$ (CsAlSiO_4) and $\text{CsAlSi}_2\text{O}_6$ (pollucite). Each of the clays was heated overnight at 150°C to remove adsorbed or loosely bound interlayer water.

The screening experiments for all alumina-silica sources will be similar. A portion of the solid material is mixed with a solution of CsNO_3 , then dried and fired at 500°C for two hours (to simulate calcining). The resulting powder is ground, pelletized and fired for two hours at 800, 950, 1050°C . These are some possible supercalcine sintering or crystallization temperatures. Weight loss on firing is recorded. Unfortunately this last data cannot be used quantitatively since the CsNO_3 is only partially decomposed by the 500°C -2 hr. "calcining" (CsNO_3 is present in every x-ray diffractogram after this heat treatment) and the clays dehydrate to varying degrees at this temperature. Selected samples will also be given the silica tube Cs - volatilization test described in the last report (COO-2510-3, pp 12-14).

Table 4 lists the results of the CsNO_3 -clay firings carried out during the last quarter, the most notable result is that a Cs aluminosilicate was formed in every case during the 1050°C - 2hr. firing. The weight losses in a given sample are similar for each firing temperature implying that the level of Cs retention is also similar. Cesium constitutes from 37 to 53 wt% of these samples so if Cs (or Cs_2O) were being volatilized rather than "fixed" the weight losses would be substantial and increase with firing temperature.

Two stoichiometric mixes were made for each clay. The first was the exact CsNO_3 to aluminosilicate mixture required to give either CsAlSiO_4 or $\text{CsAlSi}_2\text{O}_6$. Since it is likely that an excess of the stoichiometric ratio of aluminosilicate would be added in any supercalcine formulation a second mixture with a 50% excess above the stoichiometric amount of aluminosilicate was also tested. The fact that the x-ray diffractograms of the latter, Cs deficient, mixtures showed single aluminosilicate phases in most cases demonstrates that we are not dealing with strictly stoichiometric phases and when we write

Table 4
Cs Aluminosilicates for Cs Fixation

Bulk Starting Composition	Temperature (°C)	X-ray Phase Assemblage ^a	Weight Loss on Firing
2CsNO ₃ +Al ₂ Si ₂ O ₅ (OH) ₄ Kaolinite	800	Amorphous	13.9
	950	Amorphous	14.5
	1050	S-CsAlSiO ₄ (H) ^b	14.3
2CsNO ₃ +Al ₂ Si ₂ O ₅ (OH) ₄ Halloysite	800	Amorphous	16.3
	950	Amorphous	16.6
	1050	S-CsAlSiO ₄ (H)	16.1
CsNO ₃ +1.5Al ₂ Si ₂ O ₅ (OH) ₄ Kaolinite	800	Amorphous	7.0
	950	Amorphous	7.2
	1050	B-CsAlSiO ₄ (C) ^c	7.7
CsNO ₃ +1.5Al ₂ Si ₂ O ₅ (OH) ₄ Halloysite	800	Amorphous	8.5
	950	Amorphous	8.8
	1050	R-CsAlSiO ₄ (C)	9.4
CsNO ₃ +AlSi ₂ O ₅ (OH) _{0.5} Pyrophyllite-1	800	B-CsAlSiO ₄ (C)	21.6
	950	B-CsAlSiO ₄ (C)	18.3
	1050	S-CsAlSi ₂ O ₆ +B-CsAlSiO ₄ (C)	15.9
CsNO ₃ +AlSi ₂ O ₅ (OH) _{0.5} Pyrophyllite-2	800	B-CsAlSiO ₄ (C)+Py (Δ) ^d	22.8
	950	B-CsAlSiO ₄ (C)+Py (Δ)	21.7
	1050	W-CsAlSi ₂ O ₆ +B-CsAlSiO ₄ (C)	20.0

Bulk Starting Composition	Temperature (°C)	X-ray Phase Assemblage ^a	Weight Loss on Firing
.67CsNO ₃ +AlSi ₂ O ₅ (OH) _{0.5} Pyrophyllite-1	800	Amorphous	-
	950	Amorphous+W-CsAlSiO ₄ (C)	-
	1050	+W-Py(Δ)	-
.67CsNO ₃ +AlSi ₂ O ₅ (OH) _{0.5} Pyrophyllite -2	800	B-CsAlSiO ₄ (C)+Py(Δ)	18.3
	950	B-CsAlSiO ₄ (C)+Py(Δ)	17.6
	1050	B-CsAlSiO ₄ +Py(Δ)	16.0
CsNO ₃ +(x)AlSi ₂ O ₅ (OH) _{0.5} Montmorillonite	800	Amorphous+quartz	8.9
	950	S-CsAlSi ₂ O ₆	9.0
	1050	S-CsAlSi ₂ O ₆	9.2
CsNO ₃ +(x)AlSi ₂ O ₅ (OH) _{0.5} Bentonite	800	Amorphous+quartz	10.5
	950	S-CsAlSi ₂ O ₆	10.7
	1050	S-CsAlSi ₂ O ₆	10.7
.67CsNO ₃ +(x)AlSi ₂ O ₅ (OH) _{0.5} Montmorillonite	800	Amorphous+quartz	9.0
	950	Amorphous+quartz+Mt(Δ) ^e	6.7
	1050	M-CsAlSi ₂ O ₆ +quartz	6.8
.67CsNO ₃ +(x)AlSi ₂ O ₅ (OH) _{0.5} Bentonite	800	Amorphous+quartz	8.1
	950	Amorphous+W-CsAlSi ₂ O ₆ +quartz	7.7
	1050	S-CsAlSi ₂ O ₆	8.2

^a Appearance of reflections in diffractogram: S=strong and sharp, B=broad and strong, M=medium intensity, W=weak intensity.

^b CsAlSiO₄(H) = (proposed) hexagonal form of the phase with this nominal stoichiometry.

^c CsAlSiO₄(C) = cubic form; nominal stoichiometry only.

^d Py(Δ) = extra reflections due to heat treated pyrophyllite.

^e Mt(Δ) = reflections due to heat treated montmorillonite.

CsAlSiO_4 and $\text{CsAlSi}_2\text{O}_6$ we are giving an ideal composition only. In fact, this work clears up one point of controversy in the literature over the x-ray powder data of " CsAlSiO_4 ". In early descriptions* of this phase the powder data were indexed on a cubic cell similar to that of pollucite. A more recent report** gives powder data with significantly more reflections and indexed on a trial hexagonal cell (no single crystal data have been reported for this phase). As shown in Table 4, a cubic phase is observed when the starting mixture is Cs deficient while the hexagonal phase occurs in stoichiometric CsAlSiO_4 mixtures. Apparently the first work was on Cs deficient " CsAlSiO_4 ". The reflections of the cubic phases are always broad in our preparations compared to the hexagonal phase. This could be due either to the highly defective nature of the phase or to its being metastably formed at these temperatures. In the latter case it might transform to one or more other phases with additional heat treatment. The phase relations, stoichiometry range and symmetry of the Cs aluminosilicates will be studied in detail during the next year.

The results for CsNO_3 - pyrophyllite mixtures are instructive. First, these are the only mixtures which gave crystallization of a Cs aluminosilicate at 800°C . However, this phase is $\text{CsAlSiO}_4(\text{C})$ (cubic, Cs defective) instead of $\text{CsAlSi}_2\text{O}_6$ as required by the Al/Si ratio of 1/2. Only at 1050°C does the "stoichiometric" phase, pollucite, begin to appear. Even so, part of the $\text{CsAlSiO}_4(\text{C})$ has persisted metastably during the 2 hr firing. Finally, the weight loss on firing decreases in each case with increasing temperature. This could mean that a somewhat greater amount of Cs is lost at the lower temperature where the $\text{CsAlSiO}_4(\text{C})$ is formed than at the higher temperature where the "stoichiometric" phase, $\text{CsAlSi}_2\text{O}_6$, is beginning to form. We believe that this is only the first example of a topotactic (structural) rather than a stoichiometric control of phase formation and that others will be noted as more alumina - silica sources are surveyed.

Several pellets of the calcined-only batches were heated in silica tubes for 1 1/2 hrs at 1050°C . All samples showed some frosting of the silica glass (indicative of Cs loss from the sample and attack of the silica glass). This could simply mean that the silica glass has a greater Cs affinity than any of the alumina - silica sources studied so far. Considerably less frosting was noted for mixtures of 1.5X halloysite and bentonite which makes these the most promising sources to date.

* B. M. Barrier and N. McCallum, J. Chem. Soc. 4029 (A53)

** T.V. Soloveva et al. Russ. J. Inorg Chem. 15 909 (1970).

The x-ray diffractograms of the products of these silica tube runs shown in Figure 1 illustrate several points already made. Tracing A is for the stoichiometric mixture of CsNO_3 and halloysite. This is a sharp pattern of the "hexagonal" phase of CsAlSiO_4 . The firing of a mixture of $\text{CsNO}_3 + 1.5$ halloysite gives the Cs deficient cubic pattern of " CsAlSiO_4 " in tracing B. It can be seen that several sharp "hexagonal" reflections in A have formed broad "cubic" reflections in B. Tracing C is for $\text{CsNO}_3 + \text{Kaolinite}$ given identical heat treatment. However, compared to A, there is very little crystallinity even though the two mixtures are stoichiometrically identical. The chemical formula of the two clays are the same but halloysite has a fibrous habit compared to the platy kaolinite. Structural studies have indicated that halloysite has a greater degree of stacking disorder and usually has easily removed interlayer water. Thus, the 150°C drying could further disorder halloysite compared to kaolinite and contribute to its greater Cs reactivity. This is a second example of topotactic control over crystalline phase formation.

Differential thermal analysis was performed on all clay and clay + CsNO_3 samples. The thermograms of the former all had a broad endothermic feature in the range $500 - 750^\circ\text{C}$ due to the loss of structure (hydroxyl) water. This endothermic feature was broadened further with the addition of CsNO_3 (denitration has been added to dehydration) but in every case the thermal effect was completed by 800°C . This suggested another experiment. Several kaolinite and bentonite clay + CsNO_3 pellets from the 150°C - dried powders were slowly heated to 800°C and held there for 6 hrs. They were then weighed and fired at 1050°C for 2 hrs. Only negligible weight losses on firing were recorded (0.2-0.4 wt%). Since dehydration and denitration were essentially complete at 800°C , any weight losses at 1050°C could be attributed to Cs volatilization. Some Cs could have been lost during the 800°C firing but whatever Cs remained was effectively fixed by the clays during the 1050°C firing.

Based on the clay samples studied to date we concluded that there are no major differences in the ability of each of the clays to form aluminosilicates for Cs fixation at a typical supercalcine processing temperature (1050°C). However, montmorillonite and bentonite would be our first choices for forming $\text{CsAlSi}_2\text{O}_6$ (pollucite) and halloysite for forming CsAlSiO_4 based on the degree of crystallinity obtained and on the formation of the stoichiometric stable phase. These clays are being tested in compatibility studies and supercalcine formulations.

Figure 1 . CsNO_3 -Clay samples fired at 1050°C for 1.5 hrs.

($\text{CuK}\alpha$ radiation, $2^\circ 2\theta/\text{min}$)

- A. $2\text{CsNO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ [Halloysite]
- B. $\text{CsNO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ [Halloysite]
- C. $\text{CsNO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ [Kaolinite]

2.4 Compatibility Studies (G. J. McCarthy and M. T. Davidson)

In order to rationally design supercalcine formulations it is necessary to know which are the most stable phases formed in the complex oxide systems made up of waste and proposed additive cations. We described one approach to deriving this data in Report-Preprint C00-2510-2. There, increasingly more complex combinations of PW-4b oxides were studied for phase formation on firing. However, there is now a need to confirm some of the important observations with definitive phase formation experiments and to include into the oxide systems the most promising supercalcine additives. We introduce here a new class of experiments under the general heading of "compatibility studies".

The classical compatibility study of phase equilibria and materials compatibility research is illustrated in Figure 2. An experiment is performed to determine whether $(A + BC)$ or $(AB + C)$ is the most stable phase assemblage i.e., has the lowest free energy of formation. In simple ternary systems such as Figure 2 the availability of the appropriate thermodynamic data would allow for the prediction of the equilibrium phase assemblage without performing an experiment. However, these data are not generally available for the systems of interest in nuclear waste management so the experiments are necessary.

The fundamental assumption in a compatibility experiment, such as that illustrated in Figure 2, is that although the overall phase relations are ternary the behavior along the joins of interest is pseudobinary. That is, the composition of any phase on the join is defined in terms of the binary components at the ends of the join. For example, if a phase AC appeared in either of the phase assemblages in Figure 2 then the phase relations would no longer be pseudobinary. Although some of the experiments described below may seem to be as simple as the example in Figure 2, we expected, and found, that some were complicated by extraneous binary compounds, ternary compounds and both binary and ternary solid solution phases. Nevertheless, most of these runs gave us the necessary compatibility information.

The experimental procedure was chosen to simulate supercalcine processing. All components were mixed as solutions or combinations of solutions and suspensions of solids, dried and "calcined" at 600°C for 2 hrs. These powders were ground and fired at our standard supercalcine processing temperatures, 1050°C for 6 hrs. and 1200°C for 6 hrs.

Figure 2. At Bulk Composition "X", Either (AB + C) or (A + BC) is the Stable Phase Assemblage in this Simple Compatibility Diagram.

Weight losses were recorded in those cases where one or more of the possible products might volatilize at the firing temperatures. Phase analysis is carried out by X-ray powder diffraction.

Table 5 is a compilation of the reactions of interest in the products for each of the CS (compatibility study) runs completed to date. The following is an explanation of why the individual run is important to supercalcine development and an elaboration of the comments listed in the Table.

CS-1. Cs_2MoO_4 is a well established moderately thermally stable but water soluble Cs phase which is formed as a separate phase in certain waste containing glasses (in solid solution with Na_2MoO_4) as well as in simple calcine. Does kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) have a stronger Cs affinity than MoO_3 ? When the mixture specified in CS-1 is fired at 750 and 1050°C, a Cs aluminosilicate is observed but not the stoichiometric phase. Apparently small amounts of MoO_3 stabilize pollucite ($\text{CsAlSi}_2\text{O}_6$) rather than the stoichiometric CsAlSiO_4 phase. Much of the MoO_3 is volatilized at 1050°C emphasizing the need to form in supercalcine a molybdate phase of greater thermal stability than the oxide.

Table 5
Compatibility Studies and Results

RUN NUMBER	REACTIONS	X-RAY PHASE ASSEMBLAGE ^a AFTER FIRING AT T(°C)	COMMENTS
CS-1	$Cs_2MoO_4 + Al_2Si_2O_5(OH)_4 \xrightarrow{?} 2CsAlSiO_4 + MoO_3 \uparrow$	<u>750°</u> : Amorph+H-CsAlSi ₂ O ₆ <u>1050°</u> : S-CsAlSi ₂ O ₆ +H-X	CsAlSi ₂ O ₆ not the stoichiometric phase 1050° wt. loss indicates major MoO ₃ vaporization
CS-2	$Cs_2MoO_4 + Sr(NO_3)_2 \xrightarrow{?} Cs_2O + N_2O_5 \uparrow + SrMoO_4$	<u>500°</u> : S-CsNO ₃ +S-SrMoO ₄ <u>750°</u> : W-CsNO ₃ +S-SrMoO ₄	CsNO ₃ decomposing at 750°C
CS-3	$Cs_2MoO_4 + SrO + Al_2Si_2O_5(OH)_4 \xrightarrow{?} SrMoO_4 + 2CsAlSiO_4$ Kaolinite	<u>600°</u> : Amorph+SrMoO ₄ +CsNO ₃ +Cs ₂ MoO ₄ <u>1050°</u> : S-SrMoO ₄ +H-CsAlSiO ₄	Reaction Confirmed
CS-4	$Cs_2MoO_4 + Al_2Si_2O_5(OH)_4 + SrO + SiO_2 \xrightarrow{?}$ Kaolinite LUDOX $2CsAlSi_2O_6 + SrMoO_4$	<u>600°</u> : Amorph+SrMoO ₄ +CsNO ₃ <u>1050°</u> : S-CsAlSi ₂ O ₆ +S-SrMoO ₄	Reaction Confirmed
CS-5	$SrO + ZrO_2 + MoO_3 \xrightarrow{A} SrMoO_4 + ZrO_2$ $\xrightarrow{B} SrZrO_3 + MoO_3 \uparrow$	<u>1050 & 1200°</u> : S-SrMoO ₄ +S-ZrO ₂	Reaction A Confirmed
CS-6	$BaO + ZrO_2 + MoO_3 \xrightarrow{A} BaMoO_4 + ZrO_2$ $\xrightarrow{B} BaZrO_3 + MoO_3 \uparrow$	<u>1050 & 1200°</u> : B="BaZrO ₃ " (split reflections) + W - X	Reaction B Favored wt. losses indicate partial MoO ₃ vaporization
CS-7	$CeO_2 + NdO_{1.5} + FeO_{1.5} \xrightarrow{A} NdFeO_3 + CeO_2$ $\xrightarrow{B} 2(Ce_{0.5}Nd_{0.5})O_{1.75} + FeO_{1.5}$ (Fss)	<u>600°</u> : B-CeO ₂ <u>1050 & 1200°</u> : S-CeO ₂ +S-NdFeO ₃	Reaction A Confirmed
CS-8	$SrO + ZrO_2 + NdO_{1.5} \xrightarrow{A} SrZrO_3 + NdO_{1.5}$ $\xrightarrow{B} SrO + 0.5Nd_2Zr_2O_7$	<u>1050 & 1200°</u> : S-SrZrO ₃ +W-NdO _{1.5} +W-X (X=SrNd ₄ O ₇ +SrNd ₂ O ₄ ?)	Reaction A Favored phase assemblage not pseudobinary
CS-9	$BaO + ZrO_2 + NdO_{1.5} \xrightarrow{A} BaZrO_3 + NdO_{1.5}$ $\xrightarrow{B} BaO + 0.5Nd_2Zr_2O_7$	<u>1050 & 1200°</u> : S-BaZrO ₃ +H-NdO _{1.5} +H-X	Reaction A Favored phase assemblage not pseudobinary

RUN NUMBER	REACTIONS	X-RAY PHASE ASSEMBLAGE AFTER FIRING AT T(°C)	COMMENTS
CS-10	$\text{NdO}_{1.5} + \text{FeO}_{1.5} + \text{ZrO}_2 \xrightarrow{\text{A}} \text{NdFeO}_3 + \text{ZrO}_2$ $\xrightarrow{\text{B}} 0.5\text{Nd}_2\text{Zr}_2\text{O}_7 + \text{FeO}_{1.5}$	1050 & 1200°: S-Pss(5.19)+S-(Nd ₃ Fe ₅ O ₁₂) _{ss} + H-NdFeO ₃	Reaction A Favored phase assemblage not pseudobinary
CS-11	$\text{SrO} + \text{NdO}_{1.5} + \text{FeO}_{1.5} \xrightarrow{\text{A}} \text{NdFeO}_3 + \text{SrO}$ $\xrightarrow{\text{B}} \text{SrFeO}_3 + \text{NdO}_{1.5}$	1050 & 1200°: S-SrNdFeO ₄ +W-X	Ternary Phase(s) Formed
CS-12	$\text{BaO} + \text{NdO}_{1.5} + \text{FeO}_{1.5} \xrightarrow{\text{A}} \text{NdFeO}_3 + \text{BaO}$ $\xrightarrow{\text{B}} \text{BaFeO}_3 + \text{NdO}_{1.5}$	1050 & 1200°: S-BaNdFeO ₄ +H-NdO _{1.5} +W-X	Ternary Phase(s) Formed
CS-13	$\text{SrO} + \text{NdO}_{1.5} + \text{MoO}_3 \xrightarrow{\text{A}} \text{SrMoO}_4 + \text{NdO}_{1.5}$ $\xrightarrow{\text{B}} \text{SrO} + \text{Nd}_2\text{Mo}_3\text{O}_{12}$	1050 & 1200°: S-SrMoO ₄ +H-NdO _{1.5}	Reaction A Confirmed
CS-14	$\text{BaO} + \text{NdO}_{1.5} + \text{MoO}_3 \xrightarrow{\text{A}} \text{BaMoO}_4 + \text{NdO}_{1.5}$ $\xrightarrow{\text{B}} \text{BaO} + \text{Nd}_2\text{Mo}_3\text{O}_{12}$	1050 & 1200°: S-BaMoO ₄ +H-NdO _{1.5}	Reaction A Confirmed
CS-15	$2\text{CeO}_2 + \text{UO}_{2+x} + \text{SrO} \xrightarrow{\text{A}} (\text{Ce}_{.67}\text{U}_{.33})\text{O}_{2+x} + \text{SrO}$ $\xrightarrow{\text{B}} \text{SrUO}_x + 2\text{CeO}_2$ (x=3 or 4)	1050 & 1200°: S-CeO ₂ +S-X	Phase assemblage not pseudobinary
CS-16	$2\text{CeO}_2 + \text{UO}_{2+x} + \text{BaO} \xrightarrow{\text{A}} (\text{Ce}_{.67}\text{U}_{.33})\text{O}_{2+x} + \text{BaO}$ $\xrightarrow{\text{B}} \text{BaUO}_x + 2\text{CeO}_2$ (x=3 or 4)	1050 & 1200°: S-BaUO ₄ +S-CeO ₂	Reaction B Confirmed
CS-17	$2\text{SrO} + \text{NiO} + \text{MoO}_3 \xrightarrow{\text{A}} \text{Sr}_2\text{NiMo}_6$ $\xrightarrow{\text{B}} \text{SrMoO}_4 + \text{SrO} + \text{NiO}$	600°: S-SrMoO ₄ +W-NiO+S-X 1050 & 1200°: S-Sr ₂ NiMoO ₆ +W-X	Reaction B Favored at 600°C Reaction A Favored at 1050 & 1200°C phase assemblage not pseudobinary

RU RUNB	REACTIONS	X-RAY PHASE ASSEMBLAGE AFTER FIRING AT T(°C)	COMMENTS
CS-18	$\text{BaO} + \text{NiO} + \text{MoO}_3 \xrightarrow{\text{A}} 1/2 \text{Ba}_2\text{NiMoO}_6 + 1/2 \text{NiMoO}_4$ $\xrightarrow{\text{B}} \text{BaMoO}_4 + \text{NiO}$	1050 & 1200°C: BaMoO ₄ + NiO	Reaction B Confirmed
CS-19	$2\text{CsO}_{0.5} + 2\text{AlO}_{1.5} + 4\text{SiO}_2 + \text{SrO} + \text{MoO}_3 \xrightarrow{?}$ <p>(Nitrates) LUDOX</p> $\text{CsAlSi}_2\text{O}_6 + \text{SrMoO}_4$ <p>pollucite</p>	600°C: Amorph + M - CsNO ₃ 1050 & 1200°C: S - CsAlSi ₂ O ₆ + S - SrMoO ₄	Reaction Confirmed (no Cs stain on brick)
CS-20	$2\text{CsO}_{0.5} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{SrO} + \text{ZrO}_2 \xrightarrow{?} 2\text{CsAlSiO}_4 + \text{SrZrO}_3$ <p>Kaolinite</p>	1050 & 1200°C: S - CsAlSiO ₄ (H) ^b + M - SrZrO ₃	Reaction Confirmed (Cs stain on brick)
CS-21	$2\text{CsO}_{0.5} + 2\text{AlO}_{1.5} + 4\text{SiO}_2 + \text{SrO} + \text{ZrO}_2 \xrightarrow{?}$ $2\text{CsAlSi}_2\text{O}_6 + \text{SrZrO}_3$	1050°C: S - CsAlSi ₂ O ₆ + M - CsAlSiO ₄ (C) + W - ZrO ₂ + W - X 1200°C: S - CsAlSi ₂ O ₆ + M - SrZrO ₃ + W - ZrO ₂ + W - X	1050°C: incomplete reaction; Cs-deficient "CsAlSiO ₄ " formed Metastably; Sr-aluminosilicate(s) possible 1200°C: Reaction Favored - some Cs loss (Cs stain noted on brick) may have allowed Sr aluminosilicate formation with associated ZrO ₂ excess.
CS-22	$2\text{CsO}_{0.5} + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{SrO} \xrightarrow{\text{A}} 2\text{CsAlSiO}_4 + \text{SrO}$ $\xrightarrow{\text{B}} \text{SrAl}_2\text{Si}_2\text{O}_8 + \text{Cs}_2\text{O}^\dagger$ <p>Kaolinite</p>	1050°C: S - CsAlSiO ₄ (C) + M - Sr ₂ SiO ₄ (?) 1200°C: S - CsAlSiO ₄ (H) + S - Sr ₂ Al ₂ SiO ₇ + W - SrSiO ₃ (?) + W - Sr ₂ SiO ₄ (?)	(heavy Cs stain on brick) Neither Reaction Dominant
CS-23	$\text{CsO}_{0.5} + \text{AlSi}_2\text{O}_5(\text{OH}) + \text{SrO} \xrightarrow{?} \text{CsAlSi}_2\text{O}_6 + \text{SrO}$ <p>Pyrophyllite</p>	1050°C: Amorph + M - CsAlSi ₂ O ₆ + W - CsAlSiO ₄ (C) ^b 1200°C: S - CsAlSi ₂ O ₆ + M - CsAlSiO ₄ (H) + W - Sr ₂ Al ₂ SiO ₇	(slight Cs stain on brick) Proposed Reaction Dominant 1050°C: incomplete crystallization 1200°C: good crystallization; possibility of some Sr solid solution in Cs aluminosilicates
CS-24	same reaction with Bentonite instead of Pyrophyllite	1050 & 1200°C: S - CsAlSi ₂ O ₆ + W - CsAlSiO ₄ (H) + W - Sr ₂ Al ₂ SiO ₇	(slight Cs stain on brick) Proposed Reaction Dominant greater pollucite crystallization at 1050°C than in Cs-23

^a Intensity of reflections of phase in diffractogram: S=Strong, M=Medium, W=Weak, B=Broad; "Amorph" = broad maximum in diffractogram due to one or more X-ray amorphous phases; "X" = reflections due to unidentified phase or phases.

^b CsAlSiO₄(C) = cubic form; nominal stoichiometry only.
 CsAlSiO₄(H) = (proposed) hexagonal form of the phase with this nominal stoichiometry.

CS-2. As noted above, Cs_2MoO_4 is very likely one of the Cs phases in ordinary PW-4b calcine. Will Sr addition tie-up the MoO_3 and cause the formation of SrMoO_4 instead? In CS-2, when solutions of Cs_2MoO_4 and $\text{Sr}(\text{NO}_3)_2$ were mixed SrMoO_4 immediately precipitated. After drying and firing at 500°C the product consisted of well crystallized $(\text{CsNO}_3 + \text{SrMoO}_4)$ as shown by X-ray diffraction. The relative amount of CsNO_3 was reduced after the 750°C firings indicating that CsNO_3 is slowly decomposing and volatilizing. This run confirms the previously reported hypothesis that Sr has a greater Mo affinity than Cs in oxides.

CS-3, 4. Will the Cs released from Cs_2MoO_4 when SrMoO_4 is formed react with nearby alumina-silica sources to form a Cs aluminosilicate? More importantly, if they do, are SrMoO_4 and Cs aluminosilicates compatible at supercalcine formation temperatures? It is well known that Sr forms aluminosilicates, so the compatibility of SrMoO_4 with CsAlSiO_4 or $\text{CsAlSi}_2\text{O}_6$ has a direct bearing on the use of (Sr + alumina-silica sources) as supercalcine additives.

These two runs show that at 1050°C , SrMoO_4 plus the appropriate aluminosilicates form and are compatible.

CS - 5, 6. Zirconia is one of the major components of PW-4b calcine. In many of the supercalcine formulations studied to date, SrZrO_3 has been identified in the products when Sr had been used as a MoO_3 -fixation additive. Which oxide has a greater SrO affinity, SrMoO_4 or SrZrO_3 ? What is the situation if Ba rather than Sr is used as a MoO_3 -fixation additive?

Run CS-5 exhibits the simple behavior described in figure 2. SrO reacts preferentially with MoO_3 , leaving ZrO_2 unreacted. This means that in supercalcine formulations only the Sr necessary for MoO_3 fixation needs to be added without the need for concern that it will react with ZrO_2 rather than MoO_3 . The situation is quite the opposite in the case of Ba. Here BaZrO_3 is more stable than BaMoO_4 . However, the diffractograms indicate that " BaZrO_3 " is not a pure cubic perovskite structure phase from the broad but clearly split reflections. Probably some MoO_3 is taken into solid solution with BaZrO_3 , creating defects and lowering the symmetry. Weight losses indicate that only ~60% of the MoO_3 has volatilized. Other reflections in the diffractograms could not be indexed on any of the dozen or so binary phases in the BaO-ZrO_2 and BaO-MoO_3 systems. Here, as in every other CS-run, ternary phase equilibria and crystal chemistry have not been

previously studied. Thus, whenever the reactions are not pseudobinary, it is usually difficult to completely explain the observed phase assemblage.

These two runs show that Sr but not Ba can be used as a supercalcine additive for MoO_3 -fixation in the presence of Zr. In future runs we will explore the use of Ca (to form CaMoO_4) rather than Sr for this purpose. Ca sources are less expensive and would give higher waste loading in supercalcine compared to an equimolar amount of Sr.

CS-7. Does Nd_2O_3 (here written as $\text{NdO}_{1.5}$ for convenience in writing reactions) prefer to react with CeO_2 to form an Fss phase or with Fe_2O_3 ($\text{FeO}_{1.5}$) to form NdFeO_3 , a perovskite structure phase? This run shows that NdFeO_3 is more stable, confirming an observation made earlier (C00-2510-2).

CS-8, 9. Does the ZrO_2 in PW-4b calcine react with the alkaline earth oxides SrO and BaO to form perovskite structure zirconates or with $\text{NdO}_{1.5}$ to form the pyrochlore structure (ordered Fss) phase $\text{Nd}_2\text{Zr}_2\text{O}_7$?

In both run products the perovskites SrZrO_3 and BaZrO_3 are observed along with free $\text{NdO}_{1.5}$ but weak unidentified phases indicate that the phase assemblage is not pseudobinary. The free $\text{NdO}_{1.5}$ would be available to react with $\text{FeO}_{1.5}$ to form NdFeO_3 .

CS-10. It has been shown that the alkaline earths prefer to form molybdates so unless there is a large excess of SrO or BaO added to waste formulations there will be excess ZrO_2 available in the calcine. Will NdFeO_3 form in the presence of ZrO_2 or will the stable phase assemblage be $\text{Nd}_2\text{Zr}_2\text{O}_7 + \text{FeO}_{1.5}$?

The 1050 and 1200°C diffractograms of this run were complex but contained the same strong sharp reflections indicating a steady state if not equilibrium phase assemblage. NdFeO_3 was identified but was not the major phase. A Fss phase with $a_0 = 5.19\text{\AA}$ was present with even stronger reflections. After considerable effort all of the remaining phases were indexed on a body-centered cubic cell of $12.70\text{\AA}$. This, along with the relative intensities, immediately suggested a rare earth iron garnet structure phase, $\text{Nd}_3\text{Fe}_5\text{O}_{12}$. However, we tried unsuccessfully to prepare this phase several years ago. Also, the only report of this phase lists a cell parameter of $12.60\text{\AA}$.^{**} Apparently, ZrO_2 forms a partial solid solution in " $\text{Nd}_3\text{Fe}_5\text{O}_{12}$ " which stabilizes the garnet structure phase and expands the unit cell (Zr^{4+} is larger than Fe^{3+} ; note that allowance must be made for charge balance in the solid solution

* G. J. McCarthy et.al., J. Appl. Cryst. 5 377 (1972).

** G. P. Espinosa, J. Chem. Phys. 37 2344 (1962).

Figure 3. Compatibility Relations in a Partian of the System $\text{NdO}_{1.5}$ - ZrO_2 - $\text{FeO}_{1.5}$ at 1050°C . Dashed Lines are Postulated Compatibilities and Solid Triangle is the Experimentally Determined Compatibility.

model: vacancies? interstitials?). To our knowledge this solid solution has not been previously reported, which is surprising in light of many important magnetic device applications of this class of compounds.

The diffractograms of several CC-runs (see report C00-2510-2) with high Zr, Nd and Fe were checked but this new phase was not observed. In each of the CC-runs CeO_2 was also present and the available ZrO_2 formed instead a Fss with it.

As an illustration of the interpretation of phase formation we have plotted the results of this run in Figure 3. The solid solution regions in $\text{NdO}_{1.5}$ - ZrO_2 are new data obtained by W. Li of our laboratory in his current study of the system CeO_2 - ZrO_2 - $\text{NdO}_{1.5}$. The homogeneity range of " $(\text{Nd}_3\text{Fe}_5\text{O}_{12})_{\text{ss}}$ " is not known and is drawn schematically in the Figure. The bulk composition "X" of CS-10 was selected to find whether $(\text{NdFeO}_3 + \text{ZrO}_2)$ or $(\text{Nd}_2\text{Zr}_2\text{O}_7 + \text{FeO}_{1.5})$ was the compatible phase assemblage but the actual assemblage in this 1050°C isotherm consisted of the phases at the corners of the solid compatibility triangle. Many of the runs marked "phase assemblage not pseudobinary" could be given such an analysis as just described but, except for those of critical importance to supercalcine, the time needed is beyond the scope of the current program.

CS-11, 12: Sr and Ba are both known to form perovskite structure phases with Fe in the unusual tetravalent oxidation state. If Sr or Ba are present in large excess (as supercalcine additives) with Fe, will they compete with Nd in forming perovskite structure phases?

The products of CS-11 firings illustrate the formation not of a simple binary mixture of a ternary phase which had been previously observed. Joubert etal* have reported the formation of SrNdFeO_4 with the perovskite related K_2NiF_4 structure at 1350°C . Note that the Fe is trivalent. The three oxides of CS-11 combine to form this phase but the presence of a small amount of what is probably $\text{SrNd}_2\text{Fe}_2\text{O}_7$ (a structurally related phase) in the diffractograms implies incomplete reaction at the two firing temperatures. The products of CS-12 are similar except that the reaction is even less complete than in CS-11.

The results indicate that the unusual tetravalent iron perovskites, SrFeO_3 and BaFeO_3 , will not be formed in nuclear waste calcine or supercalcine because of the availability of large excesses of trivalent rare earths compared to Sr, Ba and Fe, which stabilize instead the trivalent oxidation state in the Fe.

CS-13, 14. The phase $\text{Nd}_2\text{Mo}_3\text{O}_{12}$ was observed in many of our early phase formation runs but never occurred in the presence of Sr and Ba because scheelite structure SrMoO_4 and BaMoO_4 were formed instead. These two runs were included to give a definitive demonstration that BaO and SrO have a greater MoO_3 affinity than $\text{NdO}_{1.5}$. This was confirmed in both cases since the scheelite structure phase formed and the $\text{NdO}_{1.5}$ was observed uncombined.

CS-15, 16. Although U is not a major component of PW-4b, its phase formation in the complex supercalcine formulations is of importance, both for its own sake and because Pu should behave similarly. A number of CS runs will be aimed at learning more about the crystal chemical affinities of U.

UO_2 is isostructural with CeO_2 and forms extensive solid solutions with it. Ce is sometimes used as a stand-in for U because of the similarity of their oxides. When Sr or Ba are used as supercalcine additives and therefore present in large excesses compared to U, will it form any of the known Sr and Ba uranites and uranates instead of going into solid solution with CeO_2 ?

* J-C Joubert etal, J. Solid State Chem. 2 343 (1970).

CS-15 gave a complex phase assemblage in which pure CeO_2 was the only unambiguously identified phase. No single Sr-U-O phase was identified but a mixture of these is likely, indicating incomplete reaction.

It is now becoming widely recognized in crystal chemistry that in ternary phases, when one of the cations is very large, a greater valence will be stabilized in the polyvalent second cation. The stabilization of Fe^{4+} by Ba and Sr has already been noted. In CS-16 Ba is the large cation which stabilizes U^{6+} in BaUO_4 leaving CeO_2 a pure phase. This is then one possibility for a U phase in a crystalline waste form. Other runs will be needed to show whether this phase will form from $\text{BaO} + \text{UO}_2$ in the presence of MoO_3 and ZrO_2 .

CS-17, 18. In our phase formation and supercalcine studies we have often noted perovskite structure (Pss) solid solution phases with cell parameters in the $4.00 - 4.20\text{\AA}$ range. We have speculated that $(\text{Ba,Sr})_2\text{NiMoO}_6$ might be a major component of these solid solutions. CS-17 and 18 were designed to find out whether the pure phases will form at typical supercalcine processing temperatures.

In CS-17, $\text{Sr}_2\text{NiMoO}_6$ formed readily at $1050 + 1200^\circ\text{C}$, but the presence of a few extra weak reflections implied incomplete reaction or more complex phase relations. In CS-18, Ba is probably too large for the A-site in this perovskite phase so $(\text{BaMoO}_4 + \text{NiO})$ was a more stable phase assemblage under our reaction conditions.

We will soon determine whether Ni prefers to form this phase or the previously observed NiFe_2O_4 spinel structure phase.

CS-19. In CS-3 we learned that SrO has a greater MoO_3 affinity than Cs_2O and that the phase assemblage $(\text{SrMoO}_4 + \text{CsAlSiO}_4)$ was compatible at supercalcine crystallization temperatures. Does this also apply to $(\text{SrMoO}_4 + \text{CsAlSi}_2\text{O}_6)$?

The alumina-silica source used to form $\text{CsAlSi}_2\text{O}_6$ was aluminum nitrate plus a silica sol (LUDOX). After the solutions are dried and calcined pellets pressed from the powders are heated in Pt foil cups contained in high silica refractory bricks. When Cs is a component in any run we use a fresh brick and carefully note its appearance. A white "stain" in the vicinity of the pellet indicates Cs volatilization from the pellet and reaction with the brick.

The diffractograms of CS-19 showed well crystallized pollucite ($\text{CsAlSi}_2\text{O}_6$) plus SrMoO_4 at both temperatures, confirming the proposed reaction and demonstrating the compatibility of the two phases. There was no stain observed on the brick, which implied that Cs was adequately "fixed" by this alumina - silica source in a sufficiently refractory phase. The results of this run and of several promising supercalcine runs based on it led to the preparation of supercalcine formulation 75-1 described in Section 2.5.

CS-20, 21. In several of our recent supercalcine formulations we have added an appropriate amount of Sr to PW-4b to form SrZrO_3 with the available ZrO_2 . This was in addition to the Sr added to form SrMoO_4 with MoO_3 . However, as noted above, there are some well known Sr silicates and aluminosilicates. Will the Sr react with ZrO_2 completely or will it compete with Cs for alumina-silica in supercalcine formulations?

In CS-20, where kaolinite was used as the alumina-silica source, the reaction took place as suggested. However, a stain on the brick indicated that some Cs was lost during the firings. Even more Cs was lost during the firings of CS-21 and the complex X-ray diffractograms indicated incomplete reaction. It appears that ZrO_2 has an only slightly greater SrO affinity than alumina-silica.

CS-22, 23, 24. These runs were aimed at learning more about what could happen to the Cs fixation ability of clays if Sr were present in substantial excess in supercalcine formulations. The phase formation results are complex and the interpretation is necessarily incomplete due to lack of reference data on Sr silicates and aluminosilicates. To summarize, Sr and Cs appear to have about the same affinity for the alumina-silicas. Both Cs and Sr aluminosilicates are formed. The Sr analog to gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) was identified unambiguously and one or more Sr silicates are good possibilities in the products. The loss of Cs during firing was evident from the stains on the brick and those losses were greatest in the case of kaolinite (CS-22). These runs demonstrate that the amount of Sr additions to waste in supercalcine formulations must be carefully evaluated and controlled since large transient excesses could interfere with Cs fixation in aluminosilicates. Alternatively, substantial excesses of alumina-silica additives should be used to assure that there will always be sufficient amounts for Cs fixation.

2.5. Supercalcine Formulations (G. J. McCarthy and D. E. Pfoertsch)

Nineteen possible supercalcine formulations have been evaluated since the last report and several of the most recent look very promising indeed. The experimental procedures used were the same as those described in the previous two reports (C00-2510-1 p21ff, C00-2510-3, p5ff). The first group of twelve runs used the ten component simplified version of PW-4b (PSUW-1, Nd, Mo, Zr, Ce, Cs, Fe, Ni, Ba, Sr, Cr) described in the earlier report (C00-2510-1, p 18) and the last seven used a similar formulation (PO_4 and K for Rb have been added) which will be described in Section 3.0.

The process for designing a supercalcine formulation based on proposed phase formation for each waste and additive cation has also been described in detail in the two reports listed above and will not be repeated here. Table 6 lists the phase formation hypotheses, the required additives and the observed X-ray phase assemblage for the 1050°C -6 hour firing for each of the supercalcine runs.

The major problem to date in supercalcine development has been finding the right group of additives to react with Cs preferentially to form a sufficiently refractory phase so that no Cs is volatilized during firing at $1050 - 1200^\circ\text{C}$. At this time, a run is considered to be successful if it shows no volatilization on firing of any waste species during the silica tube test described in the last report. Several of the formulations described below passed this first screening test. Important observations or conclusions from each group of runs follow.

SW-12, 13. The phase $(\text{Cs},\text{La})\text{MoO}_4$ was shown in section 2.1 to be a promising phase for Cs fixation at temperatures near 1000°C . These two runs were designed to test whether this phase would form in the complex supercalcine mixture. The Cs and Mo were available in the waste and the required La was added. Sr (in 12) and Sr+Fe (in 13) were also added.

The desired phase did not form and the Cs was not fixed. The phases formed were all similar to those described in earlier reports.

CS - 14, 15, 16, 17. In our initial review of complex oxides of Cs (C00-2510-1, Appendix 1) we found that several niobates of Cs had high melting points. In a personal communications from Sandia (Dr. J. K. Johnstone) we also heard of enhanced Cs fixation when niobate resins were used instead of titanates in the Sandia Solidification Process. In these four runs Nb was added for Cs fixation and Sr and Fe levels were varied to check for their effect on phase formation and Cs fixation. The Cs niobate proposed was $\text{Cs}_2\text{Nb}_4\text{O}_{11}$

Table 6
Supercalcine Studies and Results

Run	Proposed Phase Formation	Additives (in meq) to 1000 meq of PSUW-1 or 4	X-Ray Phase Assemblage (1050°C, 6 hour firing)
SW-12	(Cs,Ls)MoO ₄ (Ba,Sr)MoO ₄ (Ce,Nd)O _{2-x} Ni(Fe,Cr)O ₃ SrZrO ₃ NiO	81 La 92 Sr	S-Pss(5.49)+M-Pss(4.07)+W-Pss(3.88)+M-Pss(4.00)+W-Sss
SW-13	same as 12 except all Nd as NdFeO ₃ and all Ni as NiFe ₂ O ₄	81 La 92 Sr 211 Fe	S-Pss(3.93)+M-Pss(5.44)+M-Pss(4.08)+W-Sss
SW-14	same as 12 except Co in Co ₂ Nb ₄ O ₁₁ and Zr in (Ce,Zr)O ₂	162 Nb 93 Sr	S-Pss(5.40)+S-Pss(5.33)+M-Pss(3.98)+M-Pss
SW-15	same as 14 except Zr in SrZrO ₃	162 Nb 254 Sr	S-Pss(5.43)+M-Pss(4.00)+W-Sss+M-Pss(5.35)
SW-16	same as 15 except Nd as NdFeO ₃ and Ni as NiFe ₂ O ₄	162 Nb 254 Sr 211 Fe	M-Pss(3.91)+M-Pss(5.43)+M-Sss+W-Pss(4.05)+ W-Pss(3.99)+W-NiFe ₂ O ₄
SW-17	same as 16 except 4-fold excess of Nb added	648 Nb 254 Sr 211 Fe	S-Pss(3.98)+M-Pss(5.42)+M-Pss(5.27)+W-NdNiO ₄ +W-Sss
SW-18	Ce ₂ Si ₂ O ₇ (Ba,Sr)MoO ₄ (Ce,Nd)O _{2-x} (Ca,Zr)O ₂ Ni(Fe,Cr)O ₃ NiO (12-fold excess of SiO ₂ -quartz)	972 Si 93 Sr	M-Quartz+M-A ₈₈ +M-Pss(5.36)+W-X
SW-19	same as 18 except 48-fold excess of SiO ₂ -quartz	3888 Si	VS-Quartz+W-Cristobalite+M-Pss(5.39)+M-A ₈₈ +W-X
SW-20	CeAlSiO ₄ (Ba,Sr)MoO ₄ (Ce,Nd)O _{2-x} Ni(Fe,Cr)O ₃ SrZrO ₃ NiO	41 Al ₂ Si ₂ O ₅ (OH) ₄ Kaolinite 254 Sr	M-Pss(5.43)+M-Pss(4.08)+M-A ₈₈ +W-Sss(?)

Run	Proposed Phase Formation	Additives (in meq) to 1000 meq of PSUV-1 or 4	X-Ray Phase Assemblage (1050°C, 6 hour firing)
SW-21	same as 20 except 3-fold excess of kaolinite used	$172\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_6$ 256 Sr	$\text{M-Fes}(5.38)+\text{M-A}_{\text{ss}}+\text{W-Sr}_2\text{Al}_2\text{SiO}_7+\text{W-Pes}(3.92)$
SW-22	same as 20 except Ca in $\text{CaAlSi}_2\text{O}_6$	81 Al 162 Si 256 Sr	$\text{M-Fes}(5.41)+\text{M-A}_{\text{ss}}+\text{M-Pes}(4.09)+\text{W-Pes}(3.88)$
SW-23	same as 22 except 3-fold excess of (Al+2Si)	263 Al 486 Si 234 Sr	$\text{M-A}_{\text{ss}}+\text{M-Pes}(5.41)+\text{M-Pes}(5.18)+\text{W-CaAlSi}_2\text{O}_6+\text{W-Sr}_2\text{Al}_2\text{SiO}_7$
SW-24	(PSUV-4 Waste used in SW-24-30) $(\text{Ca,K})\text{AlSi}_2\text{O}_6$ $\text{Nd}(\text{Fe,Cr})\text{O}_3$ $(\text{Ca,Nd})\text{O}_{2-x}$ NiFe_2O_4 SrZrO_3 $(\text{Nd,Y})\text{PO}_4$ $(\text{Ba,Sr})\text{MoO}_4$ (78% waste loading)	98 Al 196 Si 227 Sr	$\text{S-A}_{\text{ss}}+\text{M-Pes}(5.25)+\text{W-CaAlSi}_2\text{O}_6+\text{W-Pes}(4.09)+\text{W-Ssa}(?)$ +W-X
SW-25	same as 24 except 2-fold excess of (Al+2Si) (71% waste loading)	196 Al 392 Si 227 Sr	$\text{S-A}_{\text{ss}}+\text{W-CaAlSi}_2\text{O}_6+\text{M-Pes}(5.15)+\text{W-Ssa}(?)+\text{W-Pes}(4.14)$ +W-Pes(5.40)+W-X
SW-26	same as 24 except 3-fold excess of (Al+2Si) (65% waste loading)	294 Al 588 Si 227 Sr	$\text{M-A}_{\text{ss}}+\text{M-Pes}(5.40)+\text{W-CaAlSi}_2\text{O}_6(?) + \text{Ssa}(?) + \text{W-CaAlSiO}_6(\text{C})?$ +W-X
SW-27	same as 24 except 4-fold excess of (Al+2Si) (58% waste loading)	392 Al 768 Si 227 Sr	$\text{M-A}_{\text{ss}}+\text{M-Pes}(5.36)+\text{M-Pes}(5.18)+\text{W-Ssa}(?)$
SW-28	same as 26 except partial replacement of Sr additive by Ca (67% waste loading)	294 Al 588 Si 108 Ca 119 Sr	$\text{S-A}_{\text{ss}}+\text{M-Pes}(5.17)+\text{W-Ssa}(?) + \text{Pes}(5.39)+\text{W-X}$
SW-29	same as 26 except replacement of Sr additive by Ca (69% waste loading)	294 Al 588 Si 227 Ca	$\text{S-A}_{\text{ss}}+\text{M-Pes}(5.16)+\text{W-X}$
SW-30	same as 26 except less Sr additive used (71% waste loading)	294 Al 588 Si 61 Sr	$\text{M-Ssa}+\text{W-X}$ (poorly crystallized phase assemblage) or $\text{H}-(\text{Nd}_2\text{Si}_2\text{O}_7)\text{ss}?$

a Intensity of reflection of phases in X-ray diffractogram: S = strong, M = medium, W = weak, VW = very weak. To crystalline phase shorthand, add A_{ss} = aperiodic structure solid solution, B = broad reflection.

(mp 1153°C), although one is actually only checking the effect of Nb additions on Cs fixation and other stoichiometries could have been chosen equally well.

The weight losses on firing and silica tube tests for each of these runs indicated that Cs was not fixed by the additives used. There did seem to be a small improvement with increased Fe additions but not enough to merit further work along this line. The X-ray phase assemblages were well crystallized and rich in Pss phases, especially in SW-17 where the Nb was in excess. Apparently the Nb prefers to form the perovskite structure phase rather than to react selectively with Cs.

SW-18, 19. The silica tube test shows the great affinity of SiO_2 for Cs. These two runs were designed to see if simple additions of quartz to the waste liquid would affect Cs volatilization. Some Sr was also added for Mo fixation as SrMoO_4 . We appreciated that these formulations were for informational purposes only since Cs silicates, if formed, would not be sufficiently leach resistant. The weight losses and silica tube tests indicated that Cs volatilization was significantly reduced but not eliminated in both cases.

The X-ray diffractograms showed free quartz as expected as well as the familiar fluorite structure solid solution phases. However, a completely new (to this study) phase was noted in each of the diffractograms. By considering the positions and intensities of the reflections it was identified as having the apatite structure type similar to that of a samarium silicate we studied some years ago.* After further study the best match of the data was found to be with a group of alkaline earth-rare earth silicates first reported by two of our colleagues at Penn State.** The stoichiometric analogy of this phase to apatite is not obvious and requires defects ($\square$) on two of the crystallographic sites:

It is likely that when this type of phase is prepared from a complex waste formulation other substitutions take place and some or all of the defect sites are filled. Since there are coupled defects on both cation and anion sites the latter is especially likely. For this reason we have introduced another phase shorthand notation, A_{ss} = apatite structure solid solution,

* G. J. McCarthy, et al, J. Inorg. Nucl Chem. 29 253 (1967).

** D. A. Grisafe and F. A. Hummel, Am. Mineralog. 55 1131 (1970).

rather than reporting a unique composition and stoichiometry.

This A_{ss} phase is apparently very stable, since it occurred in almost every supercalcine run in which SiO_2 was used as an additive (see below). Nothing is known of its compatibility with Cs aluminosilicates and little is known about the cations (especially Cs) which may be substituted in solid solution with it. For these reasons a considerable portion of our time in the coming months will be devoted to a crystal chemical and compatibility study of this solid solution phase. This work will have importance beyond supercalcine development. At the recent Ceramic Society Conference (Washington, DC, May 6, 7, 1975) the Hahn-Meitner group reported that an alkaline earth-rare earth silicate was one of the major phases to crystallize from commercial nuclear waste glasses. Although they did not know its structure type, compositional analogy suggests that this is very similar to or the same as the apatite structure phase just described.

SW-20,21. These two runs were designed to test the ability of kaolinite to fix Cs in a refractory aluminosilicate phase. Sr was also added for MoO_3 fixation. The CAS runs described above had not yet been performed so it was not known that kaolinite was only moderately effective for Cs fixation. Weight losses and the silica tube test confirmed that kaolinite additions would not work. The silicate apatite phase was observed in each phase assemblage after firing along with the Sr-gehlenite phase, $Sr_2Al_2SiO_7$. No $CsAlSiO_4$ was observed.

SW-22,23. These runs corresponded to 20 and 21 except that pollucite, $CsAlSi_2O_6$, was the proposed Cs fixation phase. The Al was added as $Al(NO_3)_3$ and the Si as LUDOX-AS, an ammonia stabilized colloidal suspension of SiO_2 made by duPont.

The usual screening tests showed that SW-23 was the most promising formulation to date. Very little clouding of the silica tube was noted after a $1050^\circ C$ - 2 hour firing and pollucite was identified in the product crystalline phase assemblage.

We have purposely not elaborated on each phase assemblage in the SW-runs, but we will take time here to look at SW-22 and 23 as illustrations of the level of interpretation possible from the data. The phases formed in SW-22 and the probable major chemical constituents were:

M-F _{ss} (5.41)	close to pure CeO_2
M-A _{ss}	$Sr_3Nd_6Si_6O_{24}$
M-P _{ss} (4.09)	$(Ba,Sr)ZrO_3$ ($\sim Sr_2MoNiO_6$)
W-P _{ss} (3.88)	$Nd(Fe,Cr)O_3$

Other phases such as some CsAlSiO_4 may be present, but at or below the detection limit of x-ray powder diffraction (~ 5 wt%) or they could be poorly crystallized. Note that S_{ss} (SrMoO_4) is not reported. Its two key reflections coincide with strong reflections in A_{ss} so we cannot report its presence unambiguously in this and subsequent runs. The crystal chemical role of Mo when Al-Si additives are used is now a puzzle which can only be solved with well chosen compatibility and phase formation runs.

SW-23 differs from 22 only in having 3 times the (Al + 2Si) necessary for pollucite formation from Cs. Yet the phase assemblage is quite different:

SrZrO_3 does not occur here because Sr is tied-up in the A_{ss} and gehlenite phases. The ZrO_2 released forms the smaller cell F_{ss} typical of $(\text{Ce,Zr})\text{O}_2$.

SW-24, 25, 26, 27. With the apparent success of SW-23 at Cs fixation in mind, this series of runs was designed to further evaluate formulations similar to SW-23 but with different levels of Al (as $\text{Al}(\text{NO}_3)_3$) + Si (as LUDOX) additives. The slightly different PSUW-4 waste (see below) was used instead of PSUW-1. In each case Sr was added for Mo fixation as SrMoO_4 and for SrZrO_3^* formation. SW-24, which had only the stoichiometric addition of (Al + 2Si), showed signs of Cs loss on firing in the silica tube test. The brick in the vicinity of the pellets was stained, which is also indicative of Cs loss. This is understandable since some of the Si was tied-up in the A_{ss} phase and thus not all of the Cs could be fixed as $\text{CsAlSi}_2\text{O}_6$. Some of the stronger pollucite reflections were just distinct enough to be observed.

The weight losses and silica tube test showed that Cs was fixed during firing at 1050°C in CS-25 to 27. Weight losses on pellets which had been heated to 950°C were all less than 0.5%. After further firing at 1050° for

* At this time it was not known whether Sr additives had a greater affinity for MoO_3 or ZrO_2 , so enough Sr was added to form both phases. Run CS-5 later demonstrated the SrO-MoO_3 affinity.

up to 6 hours the high silica brick showed no signs of Cs volatilization. The pellets used in silica tube tests had been heated only to 600°C where little or no Cs is lost to volatilization. Of course, the appearance of A_{ss} as a major phase in these runs means that much of the proposed phase formation does not apply. In future runs using these additives we will have to design around this apparently very stable phase. More phase formation work will be needed in order to identify all of the crystalline phases.

SW-28,29. In these runs Ca was substituted in part and in full for Sr in SW-26. The tests showed the same good Cs fixation as in 26. The phase assemblages were similar except that the A_{ss} unit cell was smaller due to substitution of the smaller Ca^{2+} for Sr^{2+} .

SW-30. This run utilized the results of run CS-5 above which showed that SrO would react with MoO_3 in preference to ZrO_2 . Thus, Sr additions were for $SrMoO_4$ formation only which required only one-quarter as much Sr additive as in SW-26. Cs fixation was not affected. Phase formation was quite different from SW-26 since no A_{ss} was formed. Several of the broad reflections could be due to $SrMoO_4(S_{ss})$ but unfortunately these also coincided with some of the strong reflections of $Nd_2Si_2O_7$ so that unambiguous identification was not possible. It appears that lower Sr (or Ca) additions prevent formation of the A_{ss} phase which may or may not be desirable. This lead will be explored in the coming months.

3.0 Waste PSUW-4 and Supercalcine Formulation 75-1.

3.1 Waste Formulation PSUW-4 (G. J. McCarthy and M. T. Davidson)

Agreement has been reached with PNL on a simplified PW-4b type of formulation to be used in initial engineering scale processing and evaluation of supercalcine formulations. This waste formulation, PSUW-4, is described in Table 7.

In order to further understand baseline crystalline phase formation in fired wastes we have given the calcine from this new waste formulation the same series of heat treatments as previously described for PW-4b. These were 1050 and 1200°C for 6 hrs. and 1400°C for 24 and 48 hrs. A portion of the diffractogram of the 1050°C - 6 hrs. firing is given in Figure 4. All of the observed reflections have been indexed on three of the solid solution phases described in C00-2510-2. The reflections were sharp enough and numerous enough to perform rough unit cell parameter computer refinements. The unit cells of the three phases are:

F_{ss} (Fluorite structure solid solution-cubic)	$a_o = 5.39\text{\AA}$
P_{ss} (Perovskite structure solid solution-pseudocubic)	$a_o = 3.89\text{\AA}$
S_{ss} (Scheelite structure solid solution-tetragonal)	$a_o = 5.49\text{\AA}$ $c_o = 12.54\text{\AA}$

The scheelite structure phase has a cell size close to midway between $SrMoO_4$ ($a_o = 5.39$, $c_o = 12.02\text{\AA}$) and $BaMoO_4$ ($a_o = 5.58$, $c_o = 12.82\text{\AA}$). Its composition is probably then $(Ba_{0.5}, Sr_{0.5})MoO_4$. The perovskite structure phase is well enough crystallized that the slight orthorhombic distortion characteristic of $NdFeO_3$ and $NdCrO_3$ is clearly observed (e.g. note the 3 P_{ss} reflections near 32° 2θ instead of one in Figure 4). Its composition is thus probably $Nd(Fe_{0.8}, Cr_{0.2})O_3$.

Table 8 is a continuation of the "crystal chemical bookkeeping" used in the preceeding discussion and in supercalcine "proposed phase formation" listings. Of the proposed phases only $REPO_4$, which would have the monazite structure, and NiO are not observed. These are present in such small amounts that they may be below the detection limit of X-ray diffraction. The major phase in the diffractogram shown in Figure 4 is F_{ss} with a cell parameter of 5.39Å. Does there exist then a fluorite structure phase at the composition $(Ce_{0.2}, RE_{0.5}, Zr_{0.3})O_{1.75}$? On this question rests the validity of the analysis in Table 8 and the depth of our understanding of phase formation in fired wastes. Fortunately,

Table 7

Waste Formulation PSUW-4

Atom	Molarity in PW-4b	Atomic %	Formulation for One Litre of PSUW-4
RE ³⁺ (Nd)	0.1647	25.1	110.0g Nd(NO ₃) ₃ ·6H ₂ O
Y	0.0064	1.0	1.1g Y ₂ O ₃
Zr	0.106	16.4	28.3g ZrO(NO ₃) ₂ ·2H ₂ O
Mo	0.095	14.7	13.7g MoO ₃
Ce(U)	0.064	9.9	27.8g Ce(NO ₃) ₃ ·6H ₂ O
Cs	0.054	8.3	10.5g CsNO ₃
Fe	0.050	7.7	20.2g Fe(NO ₃) ₃ ·9H ₂ O
Sr	0.027	4.2	5.7g Sr(NO ₃) ₂
Ba	0.027	4.2	7.1g Ba(NO ₃) ₂
Cr	0.012	1.9	4.8g Cr(NO ₃) ₃ ·9H ₂ O
K(Rb)	0.010	1.5	1.0g KNO ₃
Ni	0.005	0.8	1.5g Ni(NO ₃) ₂ ·6H ₂ O
PO ₄	0.025	3.9	2.9g NH ₄ H ₂ PO ₄
H	1.0		63.7 ml conc. HNO ₃

NOTE: Ru not included; Fe not stand-in for Ru
 Pd not included; Ni not stand-in for Pd
 Tc not included; Mo not stand-in for Tc
 Rh, Ag, Cd, Te not included.
 Ce + Nd + Y selected to correspond to "RE Mix" + "Didymium"
 in use at PNL. Fission product rare earths have less La
 and Ce and more Nd.

Figure 4: Diffractogram (CuK α radiation, 2°2 θ /min) of Waste Formulation PSUW-4 Fired at 1050°C for 6 hours.

Table 8

Crystal Chemical Bookkeeping for Fired PSUW-4

<u>Meq in PSUW-4</u>	<u>Proposed Phase Formation</u>
260 RE ³⁺	62 RE(Fe _{0.8} ,Cr _{0.2}) ₃ O ₃ 25 REPO ₄ in 343(Ce _{0.2} ,RE _{0.5} Zr _{0.3}) ₀ 1.75
106 Zr	in 343(Ce _{0.2} ,RE _{0.5} ,Zr _{0.3}) ₀ 1.75
95 Mo	54(Ba _{0.5} ,Sr _{0.5})MoO ₄ 41 MoO ₃ volatilizes
64 Ce	in 343(Ce _{0.2} ,RE _{0.5} ,Zr _{0.3}) ₀ 1.75
54 Cs	volatilizes
50 Fe	in 62 RE(Fe _{0.8} ,Cr _{0.2}) ₃ O ₃
27 Sr } 27 Ba }	54(Ba _{0.5} ,Sr _{0.5})MoO ₄
12 Cr	in 62 RE(Fe _{0.8} ,Cr _{0.2}) ₃ O ₃
10 K	volatilizes
5 Ni	5 NiO
25 PO ₄	25 REPO ₄

with the aid of an unsupported graduate student; we have been slowly accumulating data on phase formation and cell parameters in the system $\text{CeO}_2 - \text{NdO}_{1.5} - \text{ZrO}_2$. The composition $20\text{CeO}_2 - 50\text{NdO}_{1.5} - 20\text{ZrO}_2$ falls in the cubic fluorite structure solid solution region at 1050°C but phase separates into two cubic solid solutions at 1400°C . In exact correspondence with the reference phase diagram there are two fluorite structure phases in PSUW-4 fired at 1400°C , Fss(5.40) and Fss(5.35). This is a very clear example of the value of and need for crystal chemistry and phase equilibria studies on the simpler nuclear waste oxide systems.

Phase formation at $1200^\circ\text{C} - 6$ hrs. is identical to that at 1050°C . At $1400^\circ\text{C} - 24$ hrs., the Fss phase has split into two phases as just described and the Sss phase appears also to be splitting into a Ba-rich phase and Sr-rich phase. Solid solution behavior in $\text{BaMoO}_4 - \text{SrMoO}_4$ has never been studied so it is not known whether there is complete miscibility between these two scheelite structure phases at steady state conditions. A scheelite structure phase has also been observed in crystallized PW-4b borosilicate glasses, so a study of this system would have relevance to all nuclear waste forms.

The only other phase previously observed in fired PW-4b calcine is the spinel structure solid solution rich in NiFe_2O_4 . When we first described it (C00-2510-2) we noted that it was only observed where Ni had been used as a stand-in for Pd and thus was a much more abundant constituent. In PSUW-4 Ni is not added as a stand-in for Pd, so the absence of a Sp_{ss} is consistent with our earlier discussion of this phase.

3.2 Supercalcine Formulation 75-1 (G. J. McCarthy)

Based on the results of the SW-23 through 30 runs described above, a preliminary supercalcine formulation, #75-1, has been prepared for submission to PNL. Briefly, the formulation uses 2.5 times the Al (as $\text{Al}(\text{NO}_3)_3$) + 2Si (as LUDOX-AS) necessary for pollucite formation with Cs. The Sr added is about 1.5 times that necessary for SrMoO_4 formation. This formulation has about 70% waste loading. The specific formulation 75-1 is

per liter of PSUW-4 (Table 7):

0.145 Moles of Sr [145 ml $1\text{M}\text{Sr}(\text{NO}_3)_2$]
 0.245 Moles of Al [245 ml $1\text{M}\text{Al}(\text{NO}_3)_3$]
 0.490 Moles of Si [490 ml of 1M LUDOX]

Supercalcine 75-1 prepared by spray and fluidized bed calcination at PNL will then be evaluated for consolidation (with and without bonding aids) thermal stability, leachability, etc both at PNL and Penn State.

4.0 X-Ray Phase Analysis of PNL "Glass Sintered" Waste Form (G. J. McCarthy and C. A. Smith)

A sample of this type of waste form marked #140-2 was submitted by W. A. Ross of PNL for a thorough study of crystalline phase formation. The product was made from a mixture of #75-10 frit (47% SiO_2 , 16% B_2O_3 , 15% ZnO , 7.5% CaO , 6% Na_2O , 6% K_2O , 2% MgO) and waste formulation PW-4b-2 calcine and had been fired at 875°C for 2 hours.

The product showed relatively good crystallization in spite of the rather low firing temperature and short time. This could be due largely to the familiar "mineralizing" effect of the alkalis Na and K in the frit and calcine. There was also a broad maximum in the diffractograms characteristic of the presence of noncrystalline phases (glass and amorphous oxides).

All of the major crystalline phases were identified. Three were familiar from our pure calcine firing studies and a fourth was a phase not previously reported in waste forms characterization studies. The approximate probable compositions of the four major phases were:

1. F_{ss} (5.35) $(\text{Ce,Zr})\text{O}_2$ - fluorite structure
2. $S_{ss} \begin{cases} a_o = 5.26\text{\AA} \\ c_o = 11.94\text{\AA} \end{cases}$ $(\text{Sr,Ca,RE,Na})\text{MoO}_4$ - scheelite structure
3. Sp_{ss} $a_o = 8.36\text{\AA}$ $(\text{Ni,Zn,Mg,Co})(\text{Fe,Cr})_2\text{O}_4$ - spinel structure
4. REBSiO_5 . This phase occurs in nature as the mineral stillwellite $(\text{La,Ce})\text{BSiO}_5$.

The tetragonal unit cell of the scheelite phase was intermediate in size between SrMoO_4 ($a_o = 5.39$, $c_o = 12.02\text{\AA}$) and CaMoO_4 ($a_o = 5.23$, $c_o = 11.43\text{\AA}$). The $(\text{RE,Na})\text{MoO}_4$ phases also have a tetragonal scheelite structure (for $\text{RE} = \text{La}$, $a_o = 5.34$, $c_o = 11.74\text{\AA}$) so it is likely that some $(\text{RE} + \text{Na})$ is also incorporated in the scheelite phase.

These four phases account for ~90 wt% of the crystalline phase assemblage. A number of weak unindexed reflections are also observed. Zircon (ZrSiO_4) could account for some of them, but we cannot identify this phase unambiguously. Phases which might have been expected but were not present include willemite (Zn_2SiO_4), Na_2MoO_4 , $P_{ss}(\text{Sr,Ca})\text{ZrO}_3$, $P_{ss}(\text{NdFeO}_3)$ and the silicate apatite structure phases such as $(\text{Sr,Ca})_3\text{RE}_6\text{Si}_6\text{O}_{24}$.