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ADVANCED WASTE FORMS RESEARCH AND DEVELOPMENT

COMPREHENSIVE PROGRESS REPORT

MASTER

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1.0 Introduction (G. J. McCarthy)

This report covers research and lab-scale development activities for the period July through December 1976. Completion of the report has been delayed in order that the characterization studies on the new supercalcine formulation SPC-2 might be included. Thus, sections 2.0 and 4.0 describe progress through December 30, while section 3.0 covers work through mid-March. This will be the last report of its type. In December, we were requested to provide brief monthly reports rather than these elaborate and detailed progress reports at less frequent intervals. In addition to the monthly reports, we will prepare topical reports as coherent parts of our research are prepared for publication. After approval by ERDA, those persons currently receiving our progress reports will also be receiving preprints of these articles. We anticipate that articles on cesium fixation and on ruthenium fixation will be available within the next 6 - 9 months.

For an overview of progress during the six month period, the reader is referred to the Penn State Contributions to the PNL Quarterly Reports. These are included as an Appendix to this report.

2.0 Cesium Fixation in Aluminosilicates (S.A. Gallagher)

The current objectives in research on cesium aluminosilicates are the investigation of phase relations in the appropriate (for supercalcine) portion of the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system and the development of methods of preparing pure single phases of CsAlSiO_4 and $\text{CsAlSi}_2\text{O}_6$ (pollucite) for further study. The former is being approached through a study of isothermal sections of the diagram at 1000, 1200, and 1400°C along with an examination of various compositions along the $\text{CsAlSiO}_4-\text{SiO}_2$ join for solid solution ranges. Some hydrothermal synthesis and flux growth experiments have been performed, and gels were employed in attempts to prepare pure single phases.

2.1 Isothermal Sections

As has been mentioned in previous reports, the greatest interest in the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system lies in that portion of the diagram which is rich in alumina and silica. This is because an excess of both alumina and silica will be added to the waste to form pollucite ($\text{CsAlSi}_2\text{O}_6$) in supercalcine. Further background information on the phase diagram is given in an earlier report*.

Isothermal sections consist of a series of tie lines which connect two phases that are in equilibrium (i.e. are compatible) at a particular temperature. Tie lines consist of straight lines which cannot cross one another. With sub-solidus isothermal sections, it is possible to specify the final products of crystallization for a given composition, although the path of crystallization cannot be followed. The tie lines form a set of triangles such that any composition within a particular triangle will consist of either the three phases represented by the apexes of that triangle, or in the case of solid solutions, two phases -- the solid solution phase and the phase represented by the opposite apex.

To determine the existence of a tie line, a mixture with the composition corresponding to a midpoint of the proposed tie line was prepared and fired in a sealed tube at the temperature of interest until equilibrium had been reached. It will be assumed that equilibrium has been reached when a steady-state phase assemblage is observed, i.e., when the x-ray diffractograms of the fired material and the same material after refiring at the same temperature have the same phases present and have the same relative intensities for corresponding peaks.

Two sets of tie lines have been proposed for this system and are shown in Figure 1. In alternative I, the compatible phases would be

- A. $\text{CsAlSiO}_4(1:1:2)-\text{Al}_2\text{O}_3$
- B. $\text{CsAlSi}_2\text{O}_6(1:1:4)-\text{Al}_2\text{O}_3$
- C. $\text{CsAlSi}_2\text{O}_6(1:1:4)-\text{Mullite } (3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$
- D. $\text{CsAlSi}_3\text{O}_8(1:1:6)-\text{Mullite}$
- E. $\text{CsAlSi}_5\text{O}_{12}(1:1:10)-\text{Mullite}$

In alternative II, they would be

- A. $\text{CsAlSiO}_4(1:1:2)-\text{Al}_2\text{O}_3$
- B. $\text{CsAlSi}_2\text{O}_6(1:1:4)-\text{Al}_2\text{O}_3$
- C. $\text{CsAlSi}_5\text{O}_{12}(1:1:10)-\text{Al}_2\text{O}_3$

This set of tie lines was proposed with the omission of the feldspar stoichiometry phase (1:1:6) which has been reported by Russian scientists but has not yet been observed under any conditions in our studies.

Mixtures corresponding to the midpoints of each of these tie lines were prepared from an analysed sample of CsAlSiO_4 with a molar ratio of 1.06 Cs_2O : 1.00 Al_2O_3 : 2.15 SiO_2 and amorphous Al_2O_3 and SiO_2 . The alumina was prepared by firing $\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ at 800°C overnight. The silica was prepared by firing Ludox (a colloidal suspension of silica) at 600°C overnight.

* Quarterly Report, C00-2510-6, August 1975.

Figure 1. Alternative Compatibility Relations in a portion of the system $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$

These mixtures were ground, pelletized, and sealed in 5 mm Pt tubes. Three tubes were made from each mixture - one each for firing at 1000°C, 1200°C, and 1400°C. Weights of the sealed tubes were recorded before and after each firing to determine whether or not the tubes had leaked. None of the tubes had leaked. However, if leaks had been found, it would have meant that one or more of the starting materials (most likely Cs) was volatilized and new mixtures would have been prepared before continuing the firings. The tubes were kept in the furnaces from one to four weeks before removal for x-ray diffraction analysis. After the diffractograms were recorded, the material was reground, repelletized and then fired at the same temperature for another long period of time. This process is continued until a steady-state assemblage is observed. In some cases, this has yet to be achieved even after months of heat treatment.

The temperature range of 1000 - 1200°C is used for supercalcine crystallization and sintering and is therefore the reason for choosing these temperatures. However, at these temperatures, reaction times for everything except pollucite crystallization are quite long. The increase in temperature to 1400°C should help to speed up the reaction.

Table 1 shows the results of the x-ray diffraction analysis after heating the tie line midpoint compositions at each of the three temperatures. Note that A and B are the same for both proposed sets of tie lines and are given only once. The phases are listed in order of decreasing intensity in the x-ray diffractograms.

After 7 weeks at 1000°C, the six proposed tie line mixtures with the exception of A ($\text{CsAlSiO}_4-\text{Al}_2\text{O}_3$) were only weakly crystallized and showed broad low intensity peaks in the diffractograms. All of the mixtures still contained some of the CsAlSiO_4 starting material. Equilibrium had not been reached in any case except possibly A ($\text{CsAlSiO}_4-\text{Al}_2\text{O}_3$) which was well crystallized.

After heating at 1200°C for approximately three months, A and B have reached equilibrium. This confirms the existence of the proposed tie lines between $\text{CsAlSiO}_4-\text{Al}_2\text{O}_3$ (A) and between $\text{CsAlSi}_2\text{O}_6-\text{Al}_2\text{O}_3$ (B). Note that C, D, E, and F all contain the same phases but in varying amounts. It appeared that the CsAlSiO_4 was first converted to $\text{CsAlSi}_2\text{O}_6$ which then slowly converts to $\text{CsAlSi}_5\text{O}_{12}$. In each case, the diffractograms showed well crystallized phases and none of the starting material except in A where it was one of the proposed phases. However, a steady-state phase assemblage has not been obtained in C, D, E, or F.

Table 1

X-RAY DIFFRACTION ANALYSES CORRESPONDING TO THE ISOTHERMAL SECTIONS
OF A PORTION OF THE $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ DIAGRAM

Tie-line Midpoint	X-Ray Phase Assemblage
1000°C/7 weeks	
A	$\text{CsAlSiO}_4 + \text{Al}_2\text{O}_3$
B	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6 + \text{Al}_2\text{O}_3$
C	$\text{CsAlSi}_2\text{O}_6 + \text{CsAlSiO}_4 + \text{SiO}_2$
D	$\text{CsAlSi}_2\text{O}_6 + \text{CsAlSiO}_4 + \text{SiO}_2$
E	$\text{SiO}_2 + \text{CsAlSi}_2\text{O}_6 + \text{Al}_2\text{O}_3 + \text{CsAlSiO}_4$
F	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CsAlSi}_2\text{O}_6 + \text{CsAlSiO}_4$
1200°C/3 months	
A	$\text{CsAlSiO}_4 + \text{Al}_2\text{O}_3$
B	$\text{CsAlSi}_2\text{O}_6 + \text{Al}_2\text{O}_3$
C	$\text{CsAlSi}_2\text{O}_6 + \text{Al}_2\text{O}_3 + \text{CsAlSi}_5\text{O}_{12} + \text{SiO}_2$
D	$\text{CsAlSi}_2\text{O}_6 + \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CsAlSi}_5\text{O}_{12}$
E	$\text{SiO}_2 + \text{CsAlSi}_5 + \text{CsAlSi}_2\text{O}_6 + \text{Al}_2\text{O}_3$
F	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CsAlSi}_2\text{O}_6 + \text{CsAlSi}_5\text{O}_{12}$
1400°C/10 days	
A	$\text{CsAlSiO}_4 + \text{Al}_2\text{O}_3 + \text{CsAlSi}_2\text{O}_6$
B	$\text{CsAlSi}_2\text{O}_6 + \text{Al}_2\text{O}_3$
C	$\text{CsAlSi}_2\text{O}_6 + \text{Al}_2\text{O}_3 + \text{CsAlSi}_5\text{O}_{12}$
D	$\text{CsAlSi}_2\text{O}_6 + \text{CsAlSi}_5\text{O}_{12} + \text{Al}_2\text{O}_3 + \text{SiO}_2$
E	$\text{CsAlSi}_5\text{O}_{12} + \text{Al}_2\text{O}_3 + \text{SiO}_2$
F	$\text{Al}_2\text{O}_3 + \text{CsAlSi}_5\text{O}_{12} + \text{SiO}_2$

Only ten days at 1400°C produced well crystallized phases for each of the proposed tie line mixtures. It required three months to achieve good crystallinity at 1200°C, and after seven weeks at 1000°C, only poorly crystallized material was produced. This illustrates the fact that shorter reaction times are possible at 1400°C. Even so, a steady-state phase assemblage has not been reached for any of the tie line mixtures. Again, only A contained some of the starting material CsAlSiO_4 , which is expected in this case.

These results indicate the need for even further heating if equilibrium is going to be achieved with this "dry" method. When "dry" or ceramic techniques fail to give equilibrium in phase equilibria investigations, several other procedures can be tried. The reactions may be carried out under hydrothermal conditions. "Mineralizers" or fluxes can be added to the mixtures. More reactive starting mixtures can be prepared from gel precursors. These procedures can be used separately or in combination. They have all had notable success in other silicate phase equilibria studies where achieving equilibrium is a problem. Each has been utilized in our studies.

2.2 Sealed Tube Runs along the CsAlSiO_4 - SiO_2 Join

A number of compositions along the CsAlSiO_4 (1:1:2)- SiO_2 join of varying molar ratios has been studied in an effort to test for possible solid solution behavior of the phases which exist along this join. The three phases which definitely exist are CsAlSiO_4 (1:1:2), $\text{CsAlSi}_2\text{O}_6$ (1:1:4-Pollucite), and $\text{CsAlSi}_5\text{O}_{12}$ (1:1:10). Another phase which may or may not exist is $\text{CsAlSi}_3\text{O}_8$ (1:1:6).

Figure 2 shows these compositions and the other compositions lying between these points which have been studied. These mixtures were prepared by the "dry" method described above, and the reaction products were analysed in the same manner.

In order to better visualize these molar ratios, they can be converted to a mole percent of the aluminosilicate phases. This conversion is also given in Figure 2. After heating these samples in sealed Pt tubes at 1200°C for 1.5-3 months, x-ray diffractograms were made. The results of the analysis of these diffractograms are given in Table 2. The phases are again listed in decreasing order of intensity in the diffractograms. Figure 3 summarizes what has been learned so far about this join at 1200°C.

Except for the 1:1:12 sample, where some starting material (CsAlSiO_4) still remained, the samples appeared to have reached equilibrium. The data indicated that any solid solution of pollucite ($\text{CsAlSi}_2\text{O}_6$) in CsAlSiO_4 would be less than 10 percent. Compositions below 10% pollucite in CsAlSiO_4 will have to be prepared to determine whether or not any solid solution does exist.

Solid solution of CsAlSiO_4 in $\text{CsAlSi}_2\text{O}_6$ appears to exist up to at least 30% CsAlSiO_4 content. More compositions will have to be studied in order to better define the solid solution boundary. The amount of $\text{CsAlSi}_5\text{O}_{12}$ solid solubility in $\text{CsAlSi}_2\text{O}_6$ must be small, if anything, because the 1:1:4.2 assemblage is clearly two phase. Equilibrium was apparently not reached in the $\text{CsAlSi}_5\text{O}_{12}$ - SiO_2 region, so this region was left blank in Figure 3. Work continues on this 1200°C join.

2.3 Reactions under Hydrothermal Conditions

Barrer and McCallum* have carried out hydrothermal crystallizations of cesium aluminosilicate gels for $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-n\text{SiO}_2$ where $1 < n < 10$ in the temperature range of 160-450°C. Further investigations of this system are being carried out in our laboratory using sealed Pt tubes inside stellite bombs at temperatures up to 800°C and 1 kbar water pressure.

* J. Chem. Soc. 4029 (1953).

Figure 2. Compositions studied along the CsAlSiO_4 - SiO_2 join and their conversion to mole percents.

TABLE 2

X-RAY DIFFRACTION ANALYSIS OF THE RUNS ON THE CsAlSiO_4 - SiO_2 JOIN

MOLAR RATIO	X-RAY PHASE ASSEMBLAGE
1:1:2.2	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6$
1:1:2.5	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6$
1:1:3	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6$ (equal intensity)
1:1:3.4	$\text{CsAlSi}_2\text{O}_6$
1:1:4	$\text{CsAlSi}_2\text{O}_6$
1:1:4.2	$\text{CsAlSi}_2\text{O}_6 + \text{CsAlSi}_5\text{O}_{12}$
1:1:5	$\text{CsAlSi}_2\text{O}_6 + \text{CsAlSi}_5\text{O}_{12}$
1:1:6	$\text{CsAlSi}_2\text{O}_6 + \text{CsAlSi}_5\text{O}_{12}$
1:1:10	$\text{CsAlSi}_5\text{O}_{12}$
1:1:12	SiO_2 (tridymite) + $\text{CsAlSi}_2\text{O}_6 + \text{CsAlSiO}_4$

Figure 3. Partial representation of the 1200°C phase relations on the join CsAlSiO_4 - SiO_2 . The wavy boundaries indicate uncertainty in the solid solution phase boundaries.

Desiccated gels, powders prepared by the "wet" method, and powders prepared by the combination of a gel and dried powders were used as starting mixtures. The gels were prepared from analysed solutions of CsNO_3 , $\text{Al}(\text{NO}_3)_3$, and Ludox. The procedure for preparing the gels is as follows:

1. Pipette proper amount of Ludox into a beaker
2. Acidify with HNO_3 to pH=5
3. Pipette proper amount of $\text{Al}(\text{NO}_3)_3$ into the beaker
4. Pipette proper amount of CsNO_3 into the beaker
5. Neutralize with NH_4OH to pH=7
6. Allow to gel and then dry at 70°C overnight
7. Heat at 600°C overnight for denitration and dessication.

The "wet" method, which utilizes co-crystallized nitrates and Ludox, has been described elsewhere*. Other powders were prepared from the appropriate amount of a desiccated gel and amorphous alumina and silica powders.

After preparation, the powders were placed in Pt tubes along with 0.05 cc of distilled water, and the tubes were sealed. The sealed capsules were placed inside the bombs, pressurized, and then heated for several days. The starting compositions, temperatures, and x-ray phase assemblage of the products are summarized in Table 3.

With the exception of pollucite ($\text{CsAlSi}_2\text{O}_6$) from the 1:1:4 molar ratio and $\text{CsAlSi}_5\text{O}_{12}$ from the 1:1:10 molar ratio, the desired phases were generally not formed. The products obtained from the gels plus powders mixtures for the tie lines E and F still contain some amorphous material and have thus not reached their equilibrium crystalline assemblage.

The products of the hydrothermal synthesis of the gels were first dried at 600°C overnight and then annealed in sealed Pt tubes at 1200°C for several days. X-ray diffractograms showed that the phase assemblages remained unchanged after this heat treatment.

Although the desired products were generally not formed, this combination of both temperature and pressure produced well crystallized material in only 4-5 days compared to 3 months at 1200°C. Pollucite was present in all the phase assemblages except one. Therefore, it appears that pollucite formation is favored under hydrothermal conditions. This would not be surprising since naturally occurring pollucite contains some water, and there was water present in the Pt tube during synthesis. The proper combination of variables such as starting materials, temperature, pressure, etc. have not been found to form all of the desired products.

* Annual Report, COO-2510-5, June 1975.

TABLE 3

HYDROTHERMAL REACTIONS DATA

Molar Ratio of $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ in Starting Material	Temperature (°C)	Pressure (psf)	X-Ray Phase Assemblage of Products
<u>gel preparations</u>			
1:1:2	300	13,000	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6$
1:1:2	400	11,000	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6$
1:1:4	625	10,000	$\text{CsAlSi}_2\text{O}_6$
1:1:6	760	11,000	$\text{CsAlSi}_2\text{O}_6$
1:1:10	795	11,500	$\text{CsAlSi}_5\text{O}_{12}$
<u>wet preparations</u>			
1:1:2	710	11,000	$\text{CsAlSi}_2\text{O}_6$
1:1:4	425	17,000	$\text{CsAlSi}_2\text{O}_6$
1:1:8	415	16,000	$\text{CsAlSi}_2\text{O}_6 + \text{Quartz}$
1:1:12	400	14,000	$\text{CsAlSi}_2\text{O}_6 + \text{Quartz}$
1:1:20	410	13,000	$\text{CsAlSi}_2\text{O}_6 + \text{Quartz}$
<u>gel + $\text{Al}_2\text{O}_3 + \text{SiO}_2$ preparations</u>			
1:1:10-Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) (Tie line E)	790	9,000	$\text{CsAlSi}_2\text{O}_6 + \text{Mullite} + \text{Al}_2\text{O}_3 +$ amorphous phase
1:1:10- Al_2O_3 (Tie line F)	790	7,600	$\text{CsAlSi}_2\text{O}_6 + \text{Mullite} + \text{Al}_2\text{O}_3 +$ amorphous phase

In the case of the tie lines, some of the starting material remained unreacted under the particular conditions that were chosen. Further investigations using hydrothermal synthesis are planned, especially in the study of the tie lines.

TABLE 4

ATTEMPTS AT FLUX GROWTH OF CsAlSiO_4 USING CsF AND CsCl

Temperature (°C)	X-Ray Phase Assemblage for	
	$\text{CsF} + \text{Al}_2\text{Si}_2\text{O}_7(\text{gel})$	$\text{CsCl} + \text{Al}_2\text{Si}_2\text{O}_7(\text{gel})$
650	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6$	CsCl
750	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6$	amorphous phase
850	$\text{CsAlSiO}_4 + \text{CsAlSi}_2\text{O}_6$	amorphous phase

TABLE 5

X-RAY DIFFRACTION ANALYSIS FOR GEL SYNTHESIS OF CESIUM ALUMINOSILICATES

Molar-Ratio	600°C	950°C	1050°C	1200°C
1:1:2	amorphous phase	vw $\text{CsAlSi}_2\text{O}_6$ vw CsAlSiO_4 amorphous phase	CsAlSiO_4 $\text{CsAlSi}_2\text{O}_6$	CsAlSiO_4 $\text{CsAlSi}_2\text{O}_6$
1:1:4	amorphous phase	$\text{CsAlSi}_2\text{O}_6$ amorphous phase	$\text{CsAlSi}_2\text{O}_6$ amorphous phase	$\text{CsAlSi}_2\text{O}_6$ vw $\text{CsAlSi}_5\text{O}_{12}$
1:1:6	amorphous phase	amorphous phase	vw $\text{CsAlSi}_2\text{O}_6$ amorphous phase	$\text{CsAlSi}_2\text{O}_6$ $\text{CsAlSi}_5\text{O}_{12}$
1:1:10	amorphous phase	vw $\text{CsAlSi}_5\text{O}_{12}$ amorphous phase	w $\text{CsAlSi}_5\text{O}_{12}$ amorphous phase	$\text{CsAlSi}_5\text{O}_{12}$ amorphous phase

w = weak

vw = very weak

2.4 Flux Growth of CsAlSiO_4

A crystal structure has not yet been determined for CsAlSiO_4 . Barrer*, Solov'eva**, and Langlet*** have each proposed a different unit cell, but all attempts at precise indexing of our CsAlSiO_4 d-spacing data on one of these cells have failed. X-ray powder data and indexing trials are given in an earlier report.****

The next step in trying to determine the crystal structure of CsAlSiO_4 will require the growth of single crystals. These crystals should be at least 50-100 μm in diameter. One method which has been investigated was the use of fluxes to aid in crystal growth.

R.S. Roth at the National Bureau of Standards suggested the use of CsF as a flux since he had been able to grow single crystals of potassium aluminosilicates using KF as a flux. Cesium chloride was also chosen as a flux. Both compounds have melting points between 600°C and 700°C and are readily soluble in water. Therefore, they should melt at a low enough temperature to prevent excessive loss of cesium and any excess flux remaining after firing could be washed away with water.

A gel of alumina and silica in the ratio of 1:2 was prepared by a method similar to that described in the previous section. Appropriate amounts of the gel were added to CsF and CsCl (150% of the Cs required to form 1:1:2 was used). These mixtures were ground, pelletized, and placed in Pt tubes with one end sealed. The other end was then loosely crimped shut. Separate pellets were heated at 650, 750 and 850°C overnight. X-ray diffractograms were made of the products. The phase assemblages are given in Table 4. Cesium fluoride reacted with the alumina-silica gel to form both CsAlSiO_4 and $\text{CsAlSi}_2\text{O}_6$ at all three temperatures. Apparently, the CsCl did not react with the gel at any of these temperatures. At 750 and 850°C it may have volatilized leaving only the alumina-silica gel (which does not crystallize into $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ at these low temperatures). Although these temperatures are above the melting points of both CsF and CsCl, the usual effects of melting were not apparent in any of the samples. Work is continuing with other starting materials and experimental conditions.

2.5 Gel Preparation of Cesium Aluminosilicates

Gels were prepared in the molar ratios of 1:1:2, 1:1:4, 1:1:6, and 1:1:10 $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ from analysed solutions of Ludox, $\text{Al}(\text{NO}_3)_3$, and CsNO_3 by the procedure described in the section on hydrothermal synthesis. Pellets made from the dried gels were then fired at 600°C, 950°C, 1050°C, and 1200°C. The results of the X-ray diffraction analysis of the products are summarized in Table 5.

No crystallization took place at 600°C, and all the phases were amorphous. A temperature of 1200°C or higher was required to completely crystallize these samples. For the 1:1:2 molar ratio both CsAlSiO_4 and $\text{CsAlSi}_2\text{O}_6$ were observed. In the 1:1:4 molar ratio sample, there was a trace of $\text{CsAlSi}_5\text{O}_{12}$ along with the stoichiometric phase $\text{CsAlSi}_2\text{O}_6$. Both $\text{CsAlSi}_2\text{O}_6$ and $\text{CsAlSi}_5\text{O}_{12}$ were present after heating the 1:1:6 mixture. The 1:1:10 mixture was apparently not fully crystallized even at 1200°C since it still contained some amorphous material.

* Barrer, R.N. and McCallum, N., J. Chem. Soc. 4029 (1953).

** Solov'eva, T.V. et al, Russ. J. Inorg. Chem. 15 (7) 909 (1970).

*** Langlet, G., Synthesis and Crystallographic Study of Compounds of the System $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, Univ. of Paris, 1969.

**** Second Quarterly Report, C00-2510-8, December 1975.

2.6 Summary of Progress and Future Plans

As early as 1905, Day and Allen* began studying the phase relationships of the Na aluminosilicates. Studies of the K aluminosilicates were begun in 1922 by Morey and Bowen**. Since then many other important rock forming minerals have been studied. Yet in 1976, the phase relationships in the Cs aluminosilicate system have not been determined even though pollucite, a naturally occurring mineral, is the major source of Cs in the world.

Based on the results obtained to date in our study of the cesium aluminosilicates, it appears that the only phase whose formation is kinetically favored is pollucite. All other phases in this system have required lengthy heating times for formation and have often occurred along with pollucite or other phases. Perhaps, when faced with difficulties such as these, others who had chosen to study Cs aluminosilicates became discouraged and abandoned their work. However, today the fixation of Cs in radioactive waste is a major problem, and this work must be completed.

A brief summary of progress and future plans follows.

- . Several compatibility lines (tie lines) have been established on the phase diagram.
- . The existence of a solid solution range in pollucite at 1200°C has been established but precise determination of its limits still needs more work. Measurement of the cell parameter as a function of composition will be determined.
- . Attempts to grow single crystals of CsAlSiO_4 suitable for single crystal x-ray diffraction have been unsuccessful to date, but work continues with other starting materials and experimental conditions.
- . Pollucite formation is favored by hydrothermal conditions. Other desired aluminosilicate phases have, so far, not formed. Further investigations using other starting materials, temperatures, pressures, etc. will be continued.
- . Use of desiccated gels to prepare pure phases has yielded only limited success. Efforts will continue.

Another area which has not yet been investigated is the possible solid solution of Nepheline, $\text{NaAlSi}_3\text{O}_8$, and $\text{RbAlSi}_3\text{O}_8$ in $\text{CsAlSi}_2\text{O}_6$ (pollucite). When pure pollucite has been prepared this work will also be started.

* Day, A.L., and Allen, E. T., 1905, The isomorphism and thermal properties of the feldspars: Carnegie Inst. Washington Pub., 31.

** Morey, G. W., and Bowen, M.L., 1922, The melting of potash feldspar: Am. Jour. Sci., 5th ser., N. 4, p. 1-21.

3.0 Supercalcine Development: Low Sodium Wastes

3.1 Compatibility Studies (G. J. McCarthy and D. E. Pfoertsch)

Compatibility studies continue to be the basis of supercalcine crystalline phase formation modeling. The studies described below are concerned with the crystal chemical roles of Na (in low concentrations), Ce, molybdate and phosphate in the increasingly more complex supercalcine formulations currently being developed.

CS-84-87. Sodium containing silicate apatite structure phases are described in section 4.1 of this report. When present in wastes (such as PW-7) in small concentrations, will Na crystallize as one of these A_{ss} phases or in pollucite?

Nitrate solutions, Ludox and phosphoric acid were mixed in proportions appropriate for the following phase pairs:

After drying the solutions and calcining, the usual 1050 and 1200°C/6 hr. firings were carried out.

A close comparison of the pollucite cell parameters in 84 and 85 indicated that the Na was crystallizing in pollucite in 85 as formulated. Run 86 is formulated such that P and A_{ss} would have to compete for the Na. The 1/4 Na can crystallize in either phase, leaving the other in a defect model. The X-ray analysis showed that Na crystallized in pollucite. The A_{ss} reflections were broader than usual, a result of its defect state. Extra reflections of $NdPO_4$ were also observed. This was the first indication of a fact confirmed during several other of our activities described later, namely that lowering the Ca concentration of A_{ss} prevents crystallization of $[PO_4]$ in A_{ss} . It formed monazite structure $NdPO_4$ instead.

Based on these runs, Na will continue to be assigned to crystallize in $(Cs,Na)AlSi_2O_6$ in PW-7-based supercalcine formulations.

CS-87-90. Occasionally, an unambiguous identification of the scheelite structure solid solution phase [S_{ss}] in the diffractograms of certain complex compatibility studies and in some supercalcine formulations has been difficult. The main reason has been a near overlap of most or all of the strong S_{ss} reflections with those of A_{ss} . However, the possibilities that the molybdate was being incorporated in, or reacting with, A_{ss} or that it was slowly reacting with the excess (Al+Si) added routinely in supercalcine formulations could not be ruled out. These four runs were designed to test the compatibility of a Ca-RE-phosphate-silicate A_{ss} with pure $AE MoO_4$ both with and without an excess of (Al+Si). The heat treatments were 1050 and 1200°C for 4 and 18 hrs. and two weeks. The stoichiometries were

The runs established the following:

- S_{ss} and A_{ss} coexist unchanged (i.e. are compatible) during the two weeks of firing at 1050°C and during the 18 hr. firing at 1200°C. When the S_{ss} is $SrMoO_4$, after two weeks at 1200°C the S_{ss} reflections are reduced in intensity and a few very weak reflections of a Sr aluminosilicate appear. It appears that at this higher firing temperature the Sr in S_{ss} very slowly reacts with the excess (Al+Si). This means that a corresponding amount of Mo oxide is lost to volatilization.
- When Sr is present, it is distributed between the A_{ss} and S_{ss} phases. This was readily apparent since the S_{ss} phase had a smaller unit cell size than pure $SrMoO_4$. The distribution is temperature dependent, with the S_{ss} becoming more Sr rich with increasing crystallization temperature.

One effect of the additions of excess (Al+Si) was to displace the phosphate substitution from A_{ss} and replace it with silicate (and aluminate?). A small amount of free $NdPO_4$ was observed in the diffractograms.

These results reinforce earlier data indicating the compatibility of A_{ss} and S_{ss} . The fact that very long firings at 1200°C could result in the volatilization of considerable molybdenum is not of serious concern because typical supercalcine crystallization temperatures are lower than 1150°C and shorter than 6 hrs. Note that the mechanism described here could be the reason that traces of Mo were volatilized in the severe thermal stability tests on supercalcine 76-3 described in section 3.4. Once again it has been observed that Sr has a strong affinity to combine with (Al+Si) and form aluminosilicates. In later supercalcine formulations we will minimize Sr additions in favor of Ca for Mo fixation as S_{ss} .

CS-91 + 95. The supercalcine formulation (SPC-2) used in the August, 1976 engineering scale spray calciner run at PNL (see Section 3.2) was based on a phase formation model thoroughly tested by compatibility studies. However, there were several small differences between the model and the observed phase formation. One reason was the use by PNL of a less expensive commercial "rare earth mix" which is not a good simulation of the fission product distribution of RE's. It was too rich in Ce and did not contain the substantial amounts of Gd required for PW-7. Another reason was the small reduction in alkaline earth additives from that in the model. It was therefore decided to make a series of compatibility studies using the exact compositions of SPC-2 to verify the correct identification and the compatibility of this modified assemblage of phases.

CS-91 used the millimolar ratios of the ions which, according to the model, were to have yielded $A_{ss} + S_{ss}$:

161 Ce	150 Ca	27 Ba
94 La	100 $[PO_4]$	95 Mo
102 Nd*	47 Sr	204 Si

The actual x-ray phase assemblage after crystallization at 1100°C for 6 hrs was $A_{ss} + F_{ss} + M_{ss} + S_{ss}$. The F_{ss} cell parameter was 5.42Å, nearly that of pure CeO_2 . The monazite structure phase $[M_{ss}]$ had cell parameters close to those of pure $LaPO_4$, confirming that the larger RE's prefer this phase while the smaller RE ions prefer to form in A_{ss} . In SPC-2 crystallized at the same temperature, the M_{ss} phase was also rich in $LaPO_4$. The S_{ss} phase had a unit cell midway between $SrMoO_4$ and $BaMoO_4$, whereas SPC-2 had a distinctly smaller cell, presumably due to substitution of the smaller Ca ion on the alkaline earth (AE) site. In this run, Ca may be tied-up in A_{ss} and possibly in F_{ss} in part. A 24hr crystallization firing at 1100°C gave identical products. Crystallization at 1200°C for 6 and 24 hrs produced the same phase assemblage, except that $CeO_2 [F_{ss}]$ was growing weaker, due presumably to reduction of Ce to the 3+ valence combined with its incorporation in A_{ss} (which was more intense in the diffractograms). This observation is consistent with the fact that long high temperature firing, or firing in nitrogen atmospheres, of SPC-2 promotes reduction of Ce^{4+} and crystallization in A_{ss} . Heat treatment at 900°C for 2 weeks of the 1100°C product yielded no changes in the phase assemblage.

In CS-92, excess (Al+Si) was added to the formulation of CS-91 to simulate the real conditions in supercalcines where an excess of (Al+Si) is added to insure Cs fixation as pollucite even in high-Cs transients in the waste stream. The phase assemblage in all firings was the same with the addition of a small amount of the cristobalite phase of SiO_2 from the excess of that material added. Free cristobalite is not observed in the more complex supercalcine mixes, so the excess silica must substitute in one of the established phases. Pollucite is a good candidate since this phase has been repeatedly found to exhibit a wide stoichiometry range.

* 102 Nd is a valid crystal chemical stand-in for 19Pr + 61Nd + 11Sm + 7Gd + 2Y + 2 others.

The millimolar ratios of the ions in CS-93 were

161 Ce	100 [PO ₄]	51 Cs
94 La	47 Sr	10 Rb
102 Nd	27 Ba	10 Na
150 Ca	95 Mo	148 Al
		539 Si.

The addition of the alkalis and the appropriate (Al+Si) should result in the addition of pollucite to the phase assemblage of CS-92. The phase assemblage for the 1100 and 1200°C firings for 6 and 24 hrs and after treatment of the 1100°C product for 2 weeks at 800°C was as expected:

Again the amount of F_{ss} decreased and A_{ss} increased in the 1200°C firings due to incorporation of Ce in A_{ss} . The S_{ss} unit cell was now essentially identical in size to the smaller S_{ss} cell observed in crystallized SPC-2, which suggested that with the addition of Cs, some of the Ca was released from some other phase to substitute in S_{ss} .

CS-94 and 95 added first 106 Zr and then 100 Fe + 12 Cr + 5 Ni. The role of Zr was readily confirmed. The tetragonal-ZrO₂ phase [T_{ss}] appeared with moderate intensity in the diffractograms and the unit cell of F_{ss} shrank from 5.42 to the value observed in SPC-2, 5.37Å, due to incorporation of Zr in F_{ss} . The weak (Fe₂O₃)_{ss} reflections became obvious when Fe and Cr were added to the formulation. With CS-91 + CS-95 we have produced a laboratory scale simulation* in stopwise fashion of the supercalcine formulation, SPC-2. Our identification of the phases in the very complex diffractograms of crystallized SPC-2 have been confirmed. The effective compatibility of the seven phase assemblage under long term crystallization firings and at the highest HLM storage temperature has also been confirmed.

Comparison of a 16° 2θ portion of the diffractograms of CS-95 and SPC-2 crystallized under the same conditions is shown in Figure 4. It is important to note the higher degree of crystallinity (sharper and stronger reflections) of SPC-2, especially in P, F_{ss} and S_{ss} . The chemical mixing obtained from spray calcining of liquid batches results in a more reactive and more easily crystallized supercalcine powder.

3.2 Supercalcine Formulation SPC-2 (76-3)

A second engineering-scale supercalcine run was performed in the summer of 1976. It was based on a PW-7-type waste and had the Penn State identifying number 76-3 and the PNL number SPC-2. The PNL notation is adopted for the balance of this report.

3.2.1 Phase Formation Model (G.J. McCarthy). In our progress report C00-2510-11, June 11, 1976, p. 26, we listed the formulation and the proposed phase formation for the upcoming PNL engineering-scale tests. In July, we completed a new series of lab-scale supercalcine simulations in which the alkaline earth (Ca,Sr) additions in this formulation were reduced by factors of one-quarter and one-third. The alkali volatilization behavior, as indicated in the "silica tube test", actually decreased somewhat in both cases. A careful study of the crystalline phase formation, combined with the insights from the more recent compatibility studies described in the previous section, provided an explanation for the improvement. The phosphate in PW-7 had been assigned to the A_{ss} phase to crystallize as Ca₃RE₇[SiO₄]₆[PO₄]₂. Although this phase is readily synthesized pure, it is somewhat unstable in the presence of the aluminosilicates in the complete supercalcine

* The trace of Ru in SPC-2 was not included in these CS runs.

Figure 4 X-ray diffractogram tracings of compatibility run CS-95 and supercalcine SPC-2 after identical firings of 1125°C for 2.5 hrs in air. Reflections in CS-95 have been deconvoluted for clarity. The A_{ss} reflections are hatched and the M_{ss} reflections are cross-hatched. Note the sharper and more intense reflections in SPC-2, indicating greater crystallinity.

mix. Some of the Ca prefers to react with the aluminosilicate, which leaves the phosphate free to form monazite structure $\text{REPO}_4[\text{M}_{\text{ss}}]$. In the light of these insights, a modified formulation was substituted for the PNL demonstration. It was identical to that listed in Table 5 of the June 11, 1976 report except that the total alkaline earth additive was reduced by one-third. The new phase formation model became:

100 RE 100 $[\text{PO}_4]$ }	100 $\text{REPO}_4 [\text{M}_{\text{ss}}]$
257 RE (64 Ca) (193 Si) }	32 $\text{Ca}_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2$
106 Zr	106 tetragonal- $\text{ZrO}_2 [\text{T}_{\text{ss}}]$
95 Mo (95 AE) }	95 $\text{AEMoO}_4[\text{S}_{\text{ss}}]$ AE = Ca, Sr, Ba
27 Sr 27 Ba }	in S_{ss}
6 Ru	6 RuO_2
54 Cs 10 Rb 10 Na (148 Al) (256 Si) }	74 $(\text{Cs}, \text{Rb}, \text{Na})\text{AlSi}_2\text{O}_6 [\text{P}]$
100 Fe 12 Cr 5 Ni 2 Cd }	$(\text{Fe}, \text{Cr})_2\text{O}_3 + \text{Ni}(\text{Fe}, \text{Cr})_2\text{O}_4 [\text{SP}_{\text{ss}}]$ in A_{ss}

Only 10% of the Ru concentration of PW-7 was added for economic reasons. As is our established practice, twice the (Al+Si) required for alkali fixation was added. The Ce in PW-7 was included with the other nine rare earth (RE) elements. Our experience had been that when Ce was present in its usual fission product concentration, 14 mole % of the total rare earths in PW-7, it behaved as a trivalent RE and crystallized in A_{ss} . However, for reasons of economy, the waste simulant used in the PNL demonstration had a less expensive "RE mix" and did not include the substantial Gd concentration of PW-7. Thus, although the total RE concentration was appropriate to PW-7, the distribution of RE's was three times too rich in Ce and far too poor in Gd. This discrepancy caused a single inconsequential variation in the crystalline phase assemblage from the model when SPC-2 was crystallized in air. Most of the Ce took a tetravalent crystal chemical role in the product. When it was crystallized in a nitrogen atmosphere, the reducing conditions caused Ce to behave as a typical RE^{3+} and the phase formation occurred exactly according to the model.

The molar and oxides concentration of SPC-2 is listed in Table 6.

Table 6

Composition of Supercalcine SPC-2

Ion	Molarity	Oxide	g Oxide per liter of Calcined SPC-2	Weight Percent Oxide	
<u>from the modified PW-7 waste:</u>					
Ce	0.161	CeO ₂	27.7	16.3	(12.7) ^a
Zr	0.106	ZrO ₂	13.0	7.6	(5.9)
RE ^b	0.102 ^b	RE ₂ O ₃	17.1	10.0	(7.8)
Fe	0.100	Fe ₂ O ₃	8.0	4.7	(3.7)
[PO ₄]	0.100	P ₂ O ₅	7.1	4.2	(3.2)
Mo	0.095	MoO ₃	13.7	8.0	(6.3)
La	0.094	La ₂ O ₃	15.3	9.0	(7.0)
Cs	0.054	Cs ₂ O	7.6	4.5	(3.5)
Sr	0.027	SrO	2.8	1.6	(1.3)
Ba	0.027	BaO	4.1	2.4	(1.9)
Cr	0.012	Cr ₂ O ₃	0.9	0.5	(0.4)
Rb	0.010	Rb ₂ O	0.9	0.5	(0.4)
Na	0.010	Na ₂ O	0.3	0.2	(0.1)
Ru ^c	0.006	RuO ₂	0.8	0.5	(0.4)
Ni	0.005	NiO	0.4	0.2	(0.2)
Cd	0.002	CdO	0.3	0.2	(0.1)
<u>supercalcine additives:</u>					
Si	0.539	SiO ₂	32.4	19.1	(14.8)
Ca	0.150	CaO	8.4	4.9	(3.8)
Al	0.148	Al ₂ O ₃	7.5	4.4	(3.4)
Sr	0.020	SrO	2.1	1.2	(1.0)
			170.4 g oxides	100.0%	
(70.5% waste loading)					
<u>other waste constituents^d:</u>					
U(Pu,Np)	0.1195	U ₃ O ₈	33.6		(15.5)
Ru ^c	0.053	RuO ₂	7.1		(3.2)
Pd	0.032	PdO	3.9		(1.8)
Te	0.012	TeO ₂	1.9		(0.9)
Rh	0.010	Rh ₂ O ₃	1.3		(0.6)
Ag	0.002	AgO	0.3		(0.1)
			218.5 g oxides		(100.0%)
(76.9% waste loading)					

^a value in parentheses is the wt% of the oxide after addition of the appropriate amounts of U, Ru, Pd, Te, Rh, Ag.

^b RE=0.061 Nd + 0.019 Pr + 0.011 Sm + 0.007 Gd + 0.003 Y (Note: 0.002 RE is a stand-in for Am+Cm)

^c Ru concentration in the spray supercalcine SPC-2 was 10% of the actual PW-7 value of 0.059 M. The addition of the remaining 0.053 M was made after calcination.

^d These constituents were not included in the large batch of SPC-2 because of their expense or radioactivity. None require fixation additives. The only PW-7 constituent not included above is Ie.

3.2.2 Crystallization, Consolidation and Leachability of SPC-2 (G.J. McCarthy, M.T. Davidson and D.E. Pfoertsch). Crystallization of the spray supercalcline SPC-2 as-received from PNI begins at about 950°C. Heat treatment in air at 1050°C for as little as 30 min. is adequate to crystallize all of the phases that can be observed by x-ray diffraction. These phases and their nominal compositions are:

A portion of a diffractogram demonstrating the crystallization of these seven phases is given in the lower part of Figure 4 and the upper part of Figure 5. Two other phases in the phase formation model were expected to be present below the detection level of the x-ray method. The presence of the ferrimagnetic $Mi(Fe,Cr)_2O_4$ phase in crystallized SPC-2 was confirmed by the action of a hand magnet on the powder. The presence of a Ru phase, presumably RuO_2 , was ascertained indirectly during the Ru volatilization studies described below (sections 3.3 and 3.4).

The fluorite structure solid solution phase [F_{ss}] was not specified in the phase formation model, but formed because of the large excess of Ce, as discussed above. If the crystallization is carried out in a nitrogen atmosphere, the F_{ss} phase disappears and the A_{ss} and T_{ss} phases are stronger in relative intensity. This is clearly illustrated in the top two diffractograms of Figure 5.

In order to gather some data relevant to processing conditions for supercalcline formulations similar to SPC-2, a series of firings were carried out in which temperatures were varied from 800 to 1200°C and time from 10 min to 16 hours. Weight lost during firing and pellet diameter shrinkage were recorded. These data are summarized in Table 7. Some of the generalizations to be drawn from the data include:

- Residual volatiles (H_2O , NO_x , CO_2). It is reasonable to assume that there is no significant oxides (Ca_2O , MoO_3 , etc.) volatilization during 800°C firings (with the possible exception of RuO_2). The 800°C weight losses indicate that spray supercalcline SPC-2 has about 12wt% residual volatiles.
- Oxides volatilization. There is apparently a small, but measurable, loss of volatile oxides, probably alkali oxides, from the high surface area powders of "as received" SPC-2 at temperatures as low as 1050°C. At 1200°C, these losses are significant. When surface areas are reduced by pelletizing SPC-2, weight losses do not exceed the 12% level of residual volatiles until 1200°C. The "silica tube tests" on SPC-2 pellets indicated a small, but real, alkali volatilization beginning at about 1150°C. For this reason, 1125°C was chosen as the routine crystallization temperature for pelletized SPC-2.
- Consolidation. The maximum diameter shrinkage in the 0.5 in pellets, was 24-25%. This shrinkage could be obtained after 8 hrs at 1000°C, 2 hrs at 1050 or 20 min at 1125°C. In each case, crystallization of all phases was observed. From the processing standpoint, it appears that a 0.5-2 hr. pass through a tunnel kiln in which the maximum temperature reaches ~1125°C should be adequate to crystallize and consolidate pellets of SPC-2.

Another concern was relatively long term thermal stability at the highest waste storage temperatures. A -400 mesh powder of pressed (73,500 psi) and fired (1125°C, 2.5 hrs) SPC-2 showed the following weight losses:

1st day: 0.5%

14 days: 0.6%

When the SPC-2 was pre-fired (900°C, 2 hrs) to remove most of the residual volatiles, the weight losses became:

1st day: 0.05%

14 days: 0.17%

The results from the second case suggest that much of the small weight losses observed in the first were due to traces of residual volatiles that were still not driven off during the 1125°C-2.5 hr firing. Again, it should be noted that silicate apatites (A_{ss}) are known to retain (OH) on their halide sites at temperatures as high as 1100°C.

Figure 5. Portions of the diffractograms of SPC-2 crystallized in air and in nitrogen atmospheres, and of SPC-2 plus uranium crystallized in air. Each specimen was fired at 1125°C for 2.5 hrs. Reflections of the F_{ss} phases are hatched. The arrows in the middle tracing indicate that F_{ss} reflections are not present. Note the more intense A_{ss} reflections in this tracing due to incorporation of Ce in A_{ss} . When the appropriate amount of U is added to SPC-2, F_{ss} becomes the dominant phase in the diffractogram and A_{ss} is not formed.

Table 7

Crystallization/Consolidation Firings of 76-3 (SPC-2)

Pretreatment	T(°C)	t(hrs)	Wt Loss (%)	Pellet Diameter Shrinkage (%)
None "as received" powder	800	2	12.0	-
	1050	2	13.0	-
	1200	2	16.4	-
		4	17.0	-
None "as received" 0.5 in. pellets (73,500 psi)	800	2	11.6	6.6
	900	2	10.5	10.2
		8	10.2	9.8
	1000	2	11.6	23.0
		16	11.9	24.2
	1050	2	11.2	24.0
		8	10.9	24.8
	1100	2	11.2	24.4
		8	10.9	25.2
	1150	2	11.6	23.4
		8	11.8	23.6
	1200	2	13.6	23.5
		8	14.4	24.3
	1125	10 min	9.7	19.4
		20 min	9.1	23.7
		30 min	9.5	24.1
		45 min	9.5	22.8
		60 min	10.2	23.6
3 days at 800°C 0.5 in. pellets (73,500 psi)	1100	2	1.1	23.4
	1150	2	1.5	23.4
	1200	2	2.4	20.5
2 hrs. at 900°C 0.5 in. pellets (73,000 psi)	1125	10 min	0.6	15.5
		20 min	0.9	17.4
		30 min	1.0	21.3
		45 min	1.0	22.6
		60 min	1.2	22.5

Hot Pressed SPC-2. Several hot pressing preparations are scheduled for each supercalcline formulation for two reasons: first, to obtain dense super calcline specimens for properties (leachability, thermal conductivity, etc.) measurements, and second, to have some estimate of potential product improvements in case hot pressing is to be considered further for HLW solidification.

SPC-2 was vacuum hot pressed at about 1000, 1100 and 1200°C and 3000 psi. Time at T_{max} was about 10 min. The 1000°C disc was lighter in color than the others (brown vs. black). The 1200°C disc had large pores in its interior which suggested the presence of gas there during processing. Measured densities (all $\pm 0.04 \text{ g/cm}^3$) were:

<u>SPC-2:</u>	1000°C	3.67		
	1100°C	4.12	<u>SPC-1:</u>	1100°C 3.73.
	1200°C	3.81		

Apparently, 1100°C gives the most dense specimens for both SPC-1 and SPC-2. The lower density of the 1200°C specimen can be attributed to the pores.

X-ray characterization of the products showed poor crystallization at 1000, moderate to good at 1100 and very good at 1200°C. The near surface areas of the 1100 and especially the 1200°C pellets, which were also nearest to the graphite punch and die, showed far less F_{ss} and more A_{ss} than the interior regions. The Ce^{4+} in F_{ss} is reduced to Ce^{3+} which then reacts with available silica and is incorporated in A_{ss} . This same effect is observed during crystallization in nitrogen and the diffractogram was very similar to the middle tracing in Figure 5. The pore-rich region of the 1200°C specimen may be a result of the formation of CO from the reaction of oxygen released by the $CeO_2 + Ce_2O_3$ reduction with the graphite tooling.

Soxhlet leachability was obtained for SPC-2 crystallized and consolidated in several ways. The data are given in Table 8. The 72 hr values for cold pressed and fired SPC-2 are comparable to those observed in the best HLW glass while those for hot pressed SPC-2 (1100°C) are slightly better. We have no explanation for the substantial differences in weight losses for two samplings of the same batch of 1200°C hot pressed SPC-2, except that this is not uncommon in the Soxhlet test. More extensive and comprehensive leachability evaluation of SPC-2 is underway at PNL.

3.2.3 Supercalcine SPC-2 Plus Uranium (G. J. McCarthy and D. E. Pfoertsch) The PW-7 series of wastes have comparatively high U concentrations. If the correct amount of U and the other PW-7 constituents had been included in SPC-2 (0.1195M, includes extra U as a stand-in for Mp and Pu), U as U_3O_8 would constitute 15.5 wt % of the product (See Table 6). We added the appropriate amount of a uranyl nitrate solution to dried SPC-2 powder to form a slurry that was next calcined and fired (as pellets) at 1000 - 1200°C for 2 1/2 hrs. The order of relative intensity of the crystalline phases in the diffractograms of the 1125°C firings of SPC-2 with and without U is:

<u>SPC-2</u>	<u>SPC-2 + U</u>
S- F_{ss} (5.37Å)	VS- F_{ss} (5.39Å)
S- A_{ss}	M- T_{ss}
M- T_{ss}	M- M_{ss}
M-P	M-P
M- S_{ss}	M- S_{ss}
MN- M_{ss}	M-(Fe_2O_3) $_{ss}$
VM-(Fe_2O_3) $_{ss}$	Amorphous Halo

This difference is clearly illustrated in the top and bottom tracings of Figure 5. The U oxide was incorporated in F_{ss} as expected. The striking difference is the absence of the A_{ss} phase. Our explanation is that a U- F_{ss} has a stronger RE^{3+} affinity than does a silicate A_{ss} . The amorphous phase could be the released SiO_2 in a non-crystalline form. Note that M_{ss} is present, so apparently RE^{3+} prefers to form M_{ss} with the available $[PO_4]$ rather than F_{ss} . We must be careful, however, in generalizing the U crystal chemical role from SPC-2, because as explained above, this formulation was prepared at PNL with three times the PW-7 ratio of Ce and with a corresponding reduction in RE^{3+} . The Ce would almost certainly prefer substitution as Ce^{4+} in F_{ss} to form $(U,Ce,Zr)O_{2+x}$.

Table 8

Soxhlet Leachability of SPC-2 Specimens

Specimen Preparation	% Wt Lost in X days (cumulative)		Cumulative IAEA Leachability*
One gram fragments			
Using SPC-2 "as received"	0.09	3	
Using prefired (900°C) SPC-2	0.07	3	
Pressed (73,500 psi) and fired (1125°C):			
"as received"	1.48	3	2 x 10 ⁻⁵
	1.45		
	3.30	7	2 x 10 ⁻⁵
prefired	0.89	3	1 x 10 ⁻⁵
	0.86		
	2.17	7	2 x 10 ⁻⁵
Not pressed (3000 psi)			
1000°C	3.53	3	6 x 10 ⁻⁵
1100°C	0.72	3	
	3.35	.28	
	4.63	.35	
	5.99	.42	
1200°C - sample 1	1.04	3	
	1.48	.28	
	1.52	.35	
	2.11	.48	
1200°C - sample 2	0.72	3	
	3.71	.28	
	6.26	.35	
	7.21	.42	
			9 x 10 ⁻⁶

* surface area of $200 \text{ cm}^2\text{g}^{-1}$

The RE^{3+} species may still be more stable in an A_{ss} . This question was resolved with compatibility studies described below.

There was a striking difference between the appearances of fired pellets of SPC-2 and (SPC-2+U). The latter were black and, after the 1125 and especially the 1200°C firings, were moderately deformed. A small amount of melting may have occurred. If the RE's did not form A_{ss} as formulated, then the CaO and SiO_2 added to form the A_{ss} with RE (~15 wt% of SPC-2) could have combined with "free" Fe_2O_3 and other oxides to form a melt in these higher temperature firings. The phase diagram of the system $\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ has a 1192°C eutectic near the high silica apex and a 1204°C near the " Fe_2O_3 " apex.

The partial melting, or high level sintering, appears to have enhanced the SPC-2 consolidation. The 72 hr Soxhlet leachability of two samples of the 1125°C/2-1/2 hr (SPC-2+U) pellets showed a small improvement over the SPC-2 values:

	SPC-2	SPC-2+U
Prefired(900°C/2 hr), then	0.89%	0.73%
Fired 1125°C/2 1/2 hrs	0.86%	0.76%

Of course, this could be simply a reflection of the dilution of leachable species by adding U. The leachate was clear and showed no signs of U^{4+} oxidation and subsequent leaching.

The effects of the addition to SPC-2 of the amount of U appropriate for PW-7 on crystalline phase formation were described above. Addition of U prevented the crystallization of A_{ss} by (presumably) taking the RE^{3+} into Ce-U-rich F_{ss} . As we noted, this behavior might not be typical of all PW-7 based supercalcine formulations because the RE concentrations in the simulated waste were far too rich in Ce and poor in RE^{3+} . A series of compatibility runs cleared up the basic question, but introduced some new complexities into interpretation of phase formation.

First, it was shown that crystallizing a composition of Ce+U+mixed RE^{3+} oxides equal to that used in SPC-2 did give a single phase F_{ss} diffractogram ($a_0 = 5.43\text{\AA}$). When the appropriate amount of Zr was added to the mix, the F_{ss} cell decreased in size to 5.38-5.39 $\text{\AA}$ and a small amount of an unknown second phase appeared. The same phase occurred in many other compatibility studies and is being called, for the time being, "phase y". Its reflections do not match any of the U- or U-RE-oxides in the Powder Diffraction File, although it has a few coincidences with U_3O_8 polymorphs. Several scouting runs in the U-Ce-RE-O system are in progress with the aim of narrowing down the composition of this phase.

Next the compatibility of $Ca_2RE_8[SiO_4]_6O_2$ (using the PW-7 ratios of RE^{3+}) with UO_{2+x} , ($UO_{2+x}+CeO_2$) and ($UO_{2+x}+CeO_2+ZrO_2$) was tested. The basic question was answered; an A_{ss} phase plus an F_{ss} phase rich in UO_{2+x} are compatible during crystallization firings of from 2.5 to 24 hrs at 1050 - 1200°C. However, it is likely that a small amount of the RE^{3+} is incorporated in F_{ss} rather than A_{ss} . And again, phase "y" is observed in all products. The results obtained here will be incorporated into the crystalline phase modeling in SPC-3.

3.2.4 A More Complete SPC-2 Formulation (G.J. McCarthy and M. T. Davidson). One of our objectives this year is to check on the crystal chemical roles of Pd, Rh and Te in current supercalcine formulations. We are preparing as complete a supercalcine batch as is possible without including radioactive* elements. To get the batch as homogeneous as possible, we use liquid additives to dried SPC-2 spray supercalcine. The SPC-2 is treated at 900°C for 2 hours to remove the ~12 wt% of residual nitrates and water in the "as received" powder. The recipe for a kilogram of the complete SPC-2 is

765.6 g	900°C fired SPC-2
590 ml	Uranyl nitrate (1 M)
740 ml	Ruthenium nitrate (ROC/RIC)
10 ml	Silver nitrate (1 M)
345 ml	Palladium Nitrate (ROC/RIC)
48 ml	Rhodium nitrate (ROC/RIC)
8.83 g	TeO ₂ .

The Ru, Pd and Rh nitrates are calculated for the concentrations supplied by Research Organic/Research Inorganic Chemicals Co. (ROC/RIC). We tried $(NH_4)_2TeO_4$ as a soluble Te source, but were unable to obtain sufficient dissolution to produce a reliable standard solution. The powders and solutions are mixed to the consistency of a slurry and slowly dried, followed by a 600°C calcining. X-ray diffraction will be used to check for any changes in crystalline phase assemblage. However, it is likely that the phases of all but U will be below the level of detection, so the SEM will be important for phase analysis of the lesser constituents. Volatilization behavior of Ru and Te during crystallization will be characterized.

* Te is not included; U is a stand-in for Np and Pu; RE's are stand-ins for Pm, Am and Cm.

Eventually, studies on the role of Tc in supercalclines will have to be carried out. The crystal chemistry of Tc in complex oxides prepared at high temperatures is not well known. We have no confidence therefore, that Mn, Mo or Re would be a valid crystal chemical stand-in. It could also have volatilization characteristics quite different from any of these.

3.2.5 X-Ray Characterization of Disc Pelletized and Coated Supercalcines (G. J. McCarthy and C. A. Smith). Spray Supercalcine 76-3 (SPC-2) has been successfully disc pelletized by A. A. Garrett of PNL. He has also recently found that the addition of a small amount of clay of the montmorillonite type to Supercalcine 76-3 produces considerable improvements the pelletizing process. From the thermal stability standpoint, the clay addition could further reduce Cs volatilization during crystallization from its already low levels. It was shown in earlier reports* that montmorillonite type clays have a very high Cs affinity at typical crystallization-consolidation temperatures. The possible effects of clay additions on Cs volatilization will be evaluated in the coming months.

X-ray diffractograms were obtained for PNL-prepared specimens of disc pelletized 76-3 fired at 1110°C for 30 hrs. and (76-3 + 6 wt% clay) which had been fired at 975, 1050 and 1140°C. In each specimen, the usual assemblage of 76-3 solid solution phases was observed. The assemblage for the pure 76-3 was the following:

The phases are listed in order of decreasing relative intensity in the diffractogram. The presence of SP_{ss} was confirmed by the action of a magnet on powder ground from the pellets. The cubic cell parameter of F_{ss} and the 2θ position of the (112) reflection of S_{ss} are given in parentheses. The usefulness of these numbers in making comparisons between firings was explained above in section 3.2.2.

There were no significant differences between the crystalline phase assemblages of the disc pelletized supercalcine fired at PNL and cold pressed pellets prepared and fired in our laboratory at about the same temperature. A somewhat larger cell parameter for F_{ss} in disc pellets (5.35Å vs. 5.37Å) was one minor difference, but this could be simply the result of a slightly different firing atmosphere between the two sites which could have affected the Ce valence in F_{ss} .

Almost the same assemblage of phases was observed in the products of each firing of (76-3+5% clay) disc pellets. Only one additional phase was detected, and its amount along with the size of the S_{ss} cell, varied with firing temperature:

975°C: S_{ss} (28.4°)	MW** - $SrAl_2Si_2O_8$
1050°C: S_{ss} (28.3°)	W - $SrAl_2Si_2O_8$
1140°C: S_{ss} (28.2°)	VW - $SrAl_2Si_2O_8$

The extra reflections provided a good match to the powder pattern of the anorthite structure phase of $SrAl_2Si_2O_8$. The decrease in the 2θ angle of the strongest reflection of S_{ss} (the (112)) is an indication of the substitution of a large ion into the cell of S_{ss} . It appears that at lower crystallization temperatures, some Sr reacts with the clay to form the $SrAl_2Si_2O_8$ phase. This leaves S_{ss} , $(Ca,Sr,Ba)MoO_4$, somewhat depleted in Sr, and makes its cell smaller than that of the S_{ss} phase crystallized without clay additions. With higher firing temperatures, the S_{ss} phase retains more of this Sr, and the amount of Sr available to react with the clay is less. The only harmful consequence likely to result from this Sr exchange would be incomplete Mo-fixation as S_{ss} in lower temperature firings of supercalcine-clay composites. We will look for any differences in Mo-fixation during "flowing atmosphere tests" (see section 3.3) of the thermal stability of these pellets to be made in the near future.

Coated Supercalcine 75-2. Disc pelletized cores of our first engineering-scale batch of supercalcine, formulation number 75-2***, were prepared by A. A. Garrett of PNL and forwarded to M. F. Browning of Battelle, Columbus Laboratories (BCL) earlier this year. The following specimens of this type were submitted

* COO-2510-6, August 1975, pp. 13-16.
COO-2510-8, December 1975, pp. 14-21.

** MW = medium-weak, W = weak, VW = very weak.

*** See reports COO-2510-8, 10 and 11, December 1975 - June 1976, for details.

to us for x-ray phase analysis by J. M. Rusin of PNL.

Supercalcine 75-2 (SPC-1) coated with pyrolytic carbon (PyC). Normal air-atmosphere crystallization of 75-2 yields products whose diffractograms show reflections of a very strong A_{ss} phase, a pollucite (P) phase with moderately intense reflections and weak reflections of S_{ss} , F_{ss} , T_{ss} , and SP_{ss} . The diffractogram of the 75-2 pellets coated at BCL with PyC showed the usual sharp reflections of A_{ss} and P. Notably, the S_{ss} reflections were absent, which indicated that either this phase was present below the level of detection by the x-ray method or it had been modified during the production of the PyC coatings. Several other moderate to weak reflections gave a good match to two carbide phases, Mo_2C and the solid solution phase $(Sr,Ba)C_2$. The reflections of these two phases plus A_{ss} and P, accounted for all reflections in the diffractograms.

The PyC coatings are developed in a fluidized bed apparatus from a mixture of hydrocarbons and hydrogen. Possibly, the $(Sr,Ba)MoO_4(S_{ss})$ phase was reduced to the metals, and these, in turn, reacted with the hydrocarbon to form the metal carbides. According to Hanson*, Mo_2C and $(Sr,Ba)C_2$ are the most stable, room temperature carbides of these metals. The tetragonal cell parameters of the dicarbide phase are far closer to those of SrC_2 than to BaC_2 , as would be required by the far greater concentration of Sr than Ba in 75-2. The next step in the characterization of these coatings would be to look for the Mo_2C and $(Sr,Ba)C_2$ phases by SEN/characteristic x-ray energy analyses.

Supercalcine 75-2 coated with PyC and Al_2O_3 . The phase assemblage identified from the ground pellets included A_{ss} , P, $\alpha-Al_2O_3$ and reflections assigned to the proposed carbides which were even stronger than observed in the previous PyC-only coated specimen.

Aluminum chloride was used as the source of Al in this run. The bed temperature was 1100°C. When aluminum ethylate is substituted for the chloride, a lower temperature can be used. A second sample of coated pellets prepared from the ethylate at 500°C were also studied. The phase assemblage was almost identical to that of the high temperature coated pellets, except that the $\alpha-Al_2O_3$ reflections were less intense. It was a surprise to see several reflections which fit the $\alpha-Al_2O_3$ pattern, because " α " is not the stable phase at this preparation temperature.

Comments. During a recent meeting at PNL it was noted by Messrs. Garrett and Browning that the disc pellets of our first supercalcine formulation were somewhat porous. This allowed penetration of the pellet interiors by the vapor species and the apparent reactions just described. More recent improvements in pelletizing techniques and supercalcine formulations have led to denser, better consolidated products. In these cores, the vapor-supercalcine reactions may be minimized. We will continue to characterize the coated pellets for crystalline phase formation as they become available. If necessary, we will design experiments to evaluate the effects of any interactions on the overall stability of the supercalcine cores at storage temperatures.

* M. Hanson, Constitution of Binary Alloys, (Second Ed.) McGraw-Hill, 1958.

3.3 Thermal Stability of Supercalcine 76-3 (R. G. Johnston)

One of the major aims of supercalcine development is to minimize volatilization of metal oxides during the crystallization-consolidation firings and during subsequent processing steps such as coatings production. If a standard waste calcine equivalent to 76-3 without the additives were heated for several hours at 1050-1150°C, it would lose to volatilization most or all of its Cs, Rb, Na, Mo, Ru, Cd and perhaps Cr. This volatilization is greatly suppressed in supercalcine through the crystallization of these elements in refractory phases. An exception is Ru, where it was found that candidate refractory phases were not compatible with the Cs fixation phase pollucite. With respect to the thermal stability of 76-3, we were encouraged by the lack of staining of the support bricks during the many crystallization firings described above. This staining has been a qualitative indication of significant metal oxides volatilization in unsuccessful formulations. When it was noted by our standard silica tube test that some Cs and Ru volatilization had occurred in 76-3 during an 1150°C/2 hour firing, we decided to expand the scope of our thermal stability characterization to include a new, more severe test. The work described in this section is still qualitative in that it simply identifies the species being volatilized during crystallization-consolidation firings while giving only the roughest estimate of the amount lost. Quantitative thermal stability characterization of 76-3 is being performed at PKL.

3.3.1 The Effects of Flow Rate and Atmosphere on Thermal Stability. Most "ceramic" materials are treated as "condensed" phases over their entire service ranges. The equilibrium vapor pressures of the constituent metals and oxides in a typical ceramic are very small over this service temperature-pressure range, causing no change in the bulk composition with time. Many of the phases in 76-3 behave as good condensed phases at typical crystallization temperatures. These are A_{ss} , T_{ss} , F_{ss} , SP_{ss} , Fe_2O_3 , and H_{ss} . In the other three, pollucite, S_{ss} , and RuO_2 , there are component oxides or oxidation products that have significant equilibrium vapor pressures which can result in materials transport and composition change during heat treatment. If the phases are being heated in a rapidly flowing atmosphere, they will try unsuccessfully to establish the equilibrium vapor pressures in this atmosphere and will thus rapidly volatilize the high vapor pressure species. In our experiments we will be treating a variety of specimens in a flowing atmosphere. Flow rates will be measured in space velocity, cm^3 gas/ cm^3 -sec. We will also modify the composition of the atmosphere and test this effect on the volatilization of those phases which are sensitive to the oxygen partial pressure.

As yet, no process for supercalcine crystallization-consolidation has been designed or selected. Our tests of the thermal stability of this early supercalcine formulation under both "stagnant" atmosphere conditions (the silica tube test), and atmospheres with high flow rates will be useful both in conceptual designs for processes and in further optimization of supercalcine formulations.

Flowing gas experiments were conducted in open-ended silica tubes, with a metered flow rate (roughly 1 standard cubic foot per hour -- 1 SCFH) and a bubbler attached to the exit hose. Although the gas volume moved was small, the space velocity in the 8mm I. D. tubes was very high. Once the pellets shrank due to sintering, they experienced a space velocity of 144,000/hr. This space velocity is comparable to that seen in automotive exhaust catalyst systems. The pellets saw even larger space velocities prior to their shrinkage.

In order to simulate processing temperatures along a profile similar to what the waste might encounter in one type of crystallization furnace, a tunnel kiln, the temperature of the samples was increased from the insertion value of 600°C to 1125°C over a period of 1-1.5 hours, and maintained there for 2-2.5 hours. At the end of this time, the sample tubes were withdrawn from the furnace. When possible, weight losses of the samples were measured on a Mettler microgram balance. A schematic and typical temperature profile of the

Figure 6. X-ray emission spectra of:

- (a) Frosted tube, RCS-47B (supercalcine 76-3, RuO_2 doped, flowing air).
- (b) Black deposit, RCS-47B
- (c) Frosted tube, RCS-47C (flowing N_2)
- (d) Smokey tube, RCS 47C.

Si results from the glass tube.

tube furnace used in these experiments may be found on page 25 of Report C00-2510-8, December 12, 1975.

Tests were run using Supercalcine 76-3 doped to 1.75 RuO_2 concentration (76-3Ru), prefired Supercalcine 76-3 (prefired 20 hours at 800°C to remove residual volatiles), and disc-pelletized 76-3 fired at 1110°C at PNL. The first tests, designated RCS-47A, B, and C, were qualitative tests on pellets of RuO_2 -doped 76-3 (76-3Ru) fired at 1100°C under flowing oxygen, air, and nitrogen respectively. After firing, black stains and white frosting were observed on the inside of the silica glass near the furnace edge where the temperature was 800-950°C.

The stained and frosted tubes which resulted from these experiments were cut and examined for characteristic x-ray emissions under a scanning electron microscope. Frosted segments of the glass tubes yielded the characteristic emissions of Mo, Cs, and Ru. In the oxygen run (RCS-47A), Mo and Cs predominated in the frosted area, with a very small amount of Ru also present. The results were similar for the air run (RCS-47B), although much more Ru was seen. This difference was a result of the varied character of the RuO_2 deposits. In the oxygen run, a well-defined band of RuO_2 was seen, with no spreading at the edges. In the air run, a similar amount of deposition was observed, but the edges of the band were diffused and poorly defined. This diffuse RuO_2 deposition extended well into the frosted area. In the nitrogen run (RCS-47C), only Mo and Cs were observed.

The black, metallic-appearing stained areas contained Ru, lesser amounts of Cs and Mo, and in the case of the pure oxygen run, Cr. Only a small, smoky ring was observed in the nitrogen experiment. Ru was present, but very weak, in this ring. Comparisons of the x-ray emission spectra of these runs may be seen in Figure 6. Rubidium is another potential volatile species, but it could not be detected in any of the spectra because

Figure 7.

- (a) Schematic of silica tube WT-8 (SPC-2, prefired 8 hr, 1110°C; fired 600°C < T < 1115°C, 1 hr; 1115°C, 2.5 hr; ~1 SCFH flowing air). Scanning, major components of stains and SEM examination area are indicated.
- (b) Blow-up of x-ray emission spectra of WT-8, showing major and minor components of stained tube.
- (c) X-ray emission spectra of WT-8; blow-up of Cs peaks area.

its L α lines are masked by the Si peak and its K α lines lie at an energy not attainable on our instrument.

Another experiment (WT-10), using prefired 76-3, was performed in flowing nitrogen under the typical firing conditions mentioned above. Some light frosting due to Cs was observed, as well as a very light RuO₂ stain. No yellow staining was observed. This run is awaiting SEM analysis. Its weight loss was 1.9%.

These experiments show that a nitrogen atmosphere in the processor will virtually eliminate RuO₂ loss. RuO₂ was present only in trace amounts, both in the x-ray emission spectra and on the inner surface of the silica tubes. The nitrogen atmosphere also appeared to reduce MoO₃ loss visually (reduction of the yellow deposit compared to air experiments to be described below), but the spectra of RCS-47C did not confirm this. The change of atmosphere appears to have little effect on the amount of Cs frosting observed. The differences in tube frosting arising from prefired 76-3 processed in air versus nitrogen were minimal.

Two experiments tested disc-pelletized SPC-2 which had been processed at 1110°C at PNL under "stagnant" air conditions for retention of potentially volatile oxides. SPC-2 which had been fired in a kyanite crucible for 30 hours was fired for an additional 18 hours in our flowing air system at 1125°C (run WT-3). The sample was subjected to an airflow of ~1 SCFH for 8 hours of this time. Noticeable, but not heavy, RuO₂ loss was noted as a result of this test. Frosting due to Cs, and a yellow stain were also observed. The results seen here demonstrate that significant Ru remained in the supercalcine even after the 30 hour 1110°C firing given the pellets at PNL.

Disc-pelletized SPC-2 which had been fired for 8 hours on an inconel tray at 1110°C at PNL was also examined. A 1.21 gram sample of this material was fired at 1125°C for 2.5 hours under an airflow of ~1 SCFH (run WT-8). The stains which resulted from this treatment were similar to those seen in run WT-3 above, although they were much heavier. An SEM x-ray emission analysis of a stained section of the tube from this run and a schematic of the tube itself are reproduced in Figure 7. As can be seen in the figure, Cs and Mo were predominant in the stain, with traces of Cd and Cr also present. The yellow color presumably results from MoO₃, with traces of a Cr phase adding to the effect. This experiment showed a weight loss of 1.2%. Significant RuO₂ deposits occurred further downstream in the glass tube, and in the tygon air line. The severity of the observed staining indicates that a large percentage of the potentially volatile oxides were retained in the pellets during the original firing.

Calcine 76-3

Supercalcine 75-2, (2 hr, 900°C prefire)

Supercalcine 76-3, (20 hr, 800°C prefire)

Supercalcine 76-3, Second Firing

Boat Center

Supercalcine 76-3, Third Firing, Fragmented Pellets

Supercalcine 76-3, Flowing Nitrogen (20 hr, 800°C prefire)

SPC-2 (30 hr PNL Firing)

/// = Frosting \\\ = Black Coating ≡, . = Yellow Coating

Figure 8. Sketches of tubes resulting from several flowing gas experiments

A further series of experiments treated Calcine 76-3 (Supercalcine 76-3 less additives, no prefiring -- Run WT-9), Supercalcine 75-2 (prefired 2 hours at 900°C -- Run WT-4), and our prefired Supercalcine 76-3 (Run WT-5) to identical firing and airflow conditions. As expected, 76-3 showed the best results. For Calcine 76-3, extremely heavy Cs frosting and yellow Mo coatings were observed, as well as a moderate RuO₂ stain (most of the RuO₂ deposition occurred in the tygon gas line downstream in this case). Supercalcine 75-2 yielded Cs frosting over a similar portion of the tube (from the sample to the furnace edge), but to a lesser degree. A slight yellow MoO₃ stain was observed as well. No RuO₂ was included in 75-2, so no comparison can be made in this case. The tube containing 76-3 showed no discernable yellow stain, light Cs frosting near the furnace edge and the sample boat's position, and a very heavy RuO₂ stain. Weight losses from the samples of 75-2 and 76-3 (0.98 and 0.85 gm initially) were both 1.3%. A sample of the Calcine 76-3 showed a weight loss of 5.3%.

This series of runs indicates the superior thermal stability of 76-3. It retains Cs and Mo considerably more effectively than did 75-2, which was found to have adequate thermal stability both at PNL and Battelle Columbus. Although the test is not quantitative, the large reduction in both the area of and the severity of the Cs frosting and MoO₃ coating says that the increase in fixation effectiveness is large.

The sample of 76-3 used above in run WT-5 was refired twice in order to further examine the rate of volatilization of the samples in flowing air. In these cases the samples were simply inserted at 1115°C and fired for 2.5 hours at a flow rate of ~1 SCFH. Very slight staining and frosting were observed after the first firing (WT-6), in which the pellets from WT-5 were simply fired again. The observed weight loss was 0.1%. For the second firing (WT-7), the pellets were fragmented and reweighed prior to insertion into the furnace. A heavier Cs frosting and a faint yellow stain were seen in this case. In both runs the black staining attributed to RuO₂ was barely discernable. The weight loss for the third firing was 1.1%, which is a clear demonstration of the effect of surface area on volatilization rate. This weight loss was an order of magnitude higher at the same temperature, time and airflow after the pellets had been fragmented.

These runs indicate the relative volatilization rates of RuO₂, Cs₂O and MoO₃ from 76-3. RuO₂ appears to have nearly vanished during the first heating, while evidence of Cs₂O loss persisted and MoO₃ staining reappeared when the pellets were fragmented. The sharp dip in weight loss in the second firing coupled with the rise in the third after fragmentation of the pellets suggests that the loss of Cs and Mo occurs primarily near the surface of the pellet. Volatilization of RuO₂ apparently occurs throughout the pellet. A schematic representation of the tubes resulting from the experiments discussed above showing the staining which occurred in each may be seen in Figure 8.

The problem of RuO₂ loss is not nearly so severe as these results seem to indicate at first glance. Processing of the waste could be designed so that the space velocity is held at a low value. Such a system would subject the waste to conditions similar to those seen by the batch of SPC-2 fired on an Inconel tray at 1110°C for 8 hours at PNL. This waste, upon refiring in flowing air, showed considerable RuO₂ loss, indicating that much RuO₂ had been retained during the original firings.

Stagnant air tests of 76-3 run as described earlier showed very little Cs frosting and RuO₂ deposition. These tests indicate that RuO₂ and Cs loss should be very low under stagnant air conditions. If the processing and coatings steps are performed under a nitrogen atmosphere, RuO₂ volatilization will be virtually eliminated.

The extreme sensitivity of the silica tube test is illustrated by the SEM x-ray emission spectra of a tube which contained 76-3 fired at 1150°C for 2 hours after having its temperature slowly raised over a period of ~1.5 hours from 600°C. Although a light frosting was present, no x-ray emission peaks from Cs, or anything else, were observed. Another example is WT-6, with its 0.1% weight loss and light, but easily discernible, frosting and coatings.

We have conclusively demonstrated the superiority of Supercalcine 76-3 to earlier formulations. We have also determined that processing in a nitrogen atmosphere effectively eliminates RuO₂ volatilization, and examined the species volatilized from the waste form qualitatively by the various forms of the silica tube test. We shall continue to use air flow tests in silica tubes to examine waste stability under severe conditions, both for the silicate supercalcines and any new formulations. We intend to examine these wastes under varying airflow and space velocity conditions in order to more accurately estimate the loss rate of volatiles from supercalcine processing. Nitrogen atmosphere tests will also be continued.

3.4 Ruthenium Fixation (R. G. Johnston)

In Annual Report C00-2510-11 (June 11, 1976), we discussed the reasons why the very promising Ru fixation phase SrRuO_3 was dropped from consideration. Since then we have examined the behavior of RuO_2 in supercalcine to determine what losses might be expected at typical processing temperatures and times if, as now seems desirable, we simply leave it alone.

As noted in the above-mentioned report, RuO_2 proved to be compatible with all of the phases in the supercalcine mix (simulated 75-2). The results of these experiments are summarized in Table 9. In two hour firings at 1200°C on open fire bricks, an assemblage of simulated waste phases (RCS-41) lost 2.4% of its weight. Under no circumstances can we assume that this loss is all RuO_2 , as structural and adsorbed water will also be driven off at this temperature, adding to any observed weight loss. Also, other species such as Cs_2O have a finite vapor pressure at processing temperatures, adding to any observed weight loss.

A number of experiments were run to examine what portion of the observed weight losses can be attributed to RuO_2 . Batches of Supercalcines 75-2 and 76-3 were prefired at 900°C for 2 hours. A portion of this material was doped with powdered RuO_2 to the appropriate proportions (5.5 wt % for 75-2 and 4.5 wt % for 76-3). Four samples (~500 mg each) of each doped and undoped supercalcine were fired in capped platinum cups at 1125°C (a likely supercalcine processing temperature), and were carefully weighed after 1, 2 and 4 hours at this temperature. The results of these experiments are summarized below.

	Average Weight Loss (Weight Percent)			
	1 hr	2 hr	4 hr	Total
Supercalcine 75-2	0.76% (0.02)	0.19% (0.03)	0.31% (0.09)	1.25% (0.12)
75-2 + 5.5 wt % RuO_2	1.89% (0.10)	0.75% (0.12)	0.35% (0.03)	2.99% (0.24)
Supercalcine 76-3	0.88% (0.04)	0.14% (0.01)	0.18% (0.03)	1.19% (0.05)
76-3 + 4.5 wt % RuO_2	0.91% (0.06)	0.24% (0.04)	0.77% (0.06)	1.92% (0.15)

(standard deviations shown in parentheses)

These results give an indication of what increase in weight loss can be expected when present supercalcine formulations are brought to full RuO_2 concentration. As can be seen, 76-3 shows superior thermal stability to 75-2 when both are doped to full RuO_2 concentration. Doped 75-2 showed a loss of ~33% of its RuO_2 when fired for 4 hours at ~1125°C. Fully doped 76-3 lost only ~18% of its RuO_2 (percentage adjusted to correct for the initial RuO_2 concentration - 10% of full strength - contained in undoped 76-3). Note that in doped 75-2, the majority of the extra weight loss due to RuO_2 occurs in the first two hours of firing, whereas 76-3 showed its greatest weight loss in the second two hours of firing. In the first two hours of processing, doped 76-3 lost only 3% of the RuO_2 it contained, while 75-2 lost ~31% of its RuO_2 .

An interesting phenomenon was noted in these samples. Undoped pellets of 75-2 showed an 11% shrinkage due to sintering, while 76-3 shrank by 20%. When full dopings of RuO_2 were added, the shrinkage of 76-3 was unchanged, but the 75-2 pellets showed 20% shrinkage after 4 hours of firing. Most of this additional shrinkage occurred in the second two hours of firing. The entire shrinkage of all of the 76-3 pellets occurred during the first hour of firing. Apparently RuO_2 acts as a sintering agent in the waste, yielding a denser, less porous product and reducing the loss of volatiles.

Clearly, these experiments do not tell the whole story. The tests detailed in Section 3.4.1 illustrate this fact. The array of vapor species over the waste at processing temperatures is complex, and varies as crystallization of the supercalcine approaches completion. More sophisticated experiments like those described in Section 3. . . in both stagnant and flowing gas are being conducted now. Data from these experiments will allow a better determination of the rate of RuO_2 loss, and will show whether it will be completely lost from supercalcine formulations under accident conditions.

We still believe that leaving RuO_2 alone in supercalcine is the best approach. We have not determined as yet if the volatility of RuO_2 in supercalcine at processing temperatures is any less than its volatility when fired alone. As mentioned in the above section, maintaining a nitrogen atmosphere during crystallization-consolidation firings appears to virtually eliminate RuO_2 loss. This approach should be given serious consideration when designing conceptual supercalcine processing schemes.

Table 9

Ruthenium Compatability Studies and Results

Run #	Reaction	Firing Time	Temp (°C)	wt. Loss (%)	X-ray Phase Assemblage
RCS 36	$\text{RuO}_2 + \text{S}_{ss} + 1/2\text{A}_{ss} \rightarrow \text{RuO}_2 + \text{S}_{ss} + 1/2\text{A}_{ss}$	2 hr	1050	1.2	$\text{S-A}_{ss} + \text{M-S}_{ss} + \text{M-RuO}_2$
36A	" "	2 hr	1200	4.3	core- $\text{S-A}_{ss} + \text{M-S}_{ss} + \text{M-RuO}_2$ outer surface- $\text{S-A}_{ss} + \text{M-S}_{ss} + \text{VM-RuO}_2$
RCS 37	$\text{P}_{ss} + \text{RuO}_2 \rightarrow \text{P}_{ss} + \text{RuO}_2$	2 hr	1050	3.8	$\text{VS-RuO}_2 + \text{M-P}_{ss}$
37A	" "	2 hr	1200	15.1	$\text{S-RuO}_2 + \text{S-P}_{ss}$
RCS 38	$\text{RuO}_2 + \text{FeO}_{1.5} \rightarrow \text{RuO}_2 + \text{FeO}_{1.5}$	2 hr	1050	3.6	$\text{VS-RuO}_2 + \text{M-FeO}_{1.5}$
38A	" "	2 hr	1200	10.1	$\text{S-RuO}_2 + \text{M-FeO}_{1.5}$
RCS 39	$\text{RuO}_2 + 1/2\text{A}_{ss} \rightarrow \text{RuO}_2 + 1/2\text{A}_{ss}$	2 hr	1200	1.6	$\text{S-A}_{ss} + \text{M-RuO}_2$
39A	" "	2 hr	1050	1.0	" "
RCS 40	$\text{RuO}_2 + \text{S}_{ss} \rightarrow \text{RuO}_2 + \text{S}_{ss}$	2 hr	1200	*	$\text{VS-S}_{ss} + \text{VS-RuO}_2$
40A	" "	2 hr	1050	1.1	" "
RCS 41	$\text{RuO}_2 + \text{P}_{ss} + 2\text{S}_{ss} + 1/2\text{A}_{ss} + \text{FeO}_{1.5} + \text{ZrO}_2$ $\rightarrow \text{RuO}_2 + \text{P}_{ss} + 2\text{S}_{ss} + 1/2\text{A}_{ss} + \text{FeO}_{1.5} + \text{ZrO}_2$	2 hr	1200	2.4	$\text{M-A}_{ss} + \text{M-S}_{ss} + \text{M-P}_{ss} + \text{M-ZrO}_2 + \text{M-RuO}_2 + \text{VM-FeO}_{1.5}$
41A	" "	2 hr	1050	1.3	" " "

* Pellet dropped and broken, no wt. loss.

4.0 Supercalcine Development: High-Sodium Wastes

In Section 7 of our Annual Report* we described the first steps taken toward developing a supercalcine formulation for high-sodium wastes such as the AGNS formulation PW-7a. Nepheline ($\text{NaAlSi}_3\text{O}_8$) was chosen as the most promising candidate for Na fixation. It can be crystallized readily at moderate temperatures (900-1100°C). It should have reasonable leaching resistance and good thermal stability during crystallization. During studies of the compatibility of nepheline with other established supercalcine phases, two problem areas requiring crystal chemical surveys were encountered. They involved phases containing two of the more abundant constituents of PW-7a, the rare earths and Mo. The next two subsections will consider the range of Na substitutions in RE-silicate apatite phases and the existence and stability of sodalite structure phases with a wide variety of possible substitutions. The third section will describe several compatibility studies among what could be the major phases of a high-Na supercalcine.

4.1 Crystal Chemistry of Sodium in Rare Earth Silicate Apatites (G.J. McCarthy and D.E. Pfoertsch)

In our last report, under the discussion of compatibility runs that included nepheline (Ne) and the rare earth silicate apatite structure solid solution (A_{ss}), we suggested that some Na, or perhaps even Ne itself, was soluble in A_{ss} . The only available literature reports of Na substitution in silicate apatites are those of Ito** and Felsche*** on $\text{NaRE}_9[\text{SiO}_4]_6\text{O}_2$ phases. Solid solution models with greater Na substitution can be postulated if either defects in the apatites halide sites (the "O₂" sites in the case of oxyapatites) or charge balancing cation substitutions, or both, are included. Thirty different Na- A_{ss} possibilities have been tested under preparation conditions selected for their relevance to supercalcine processing and to establishing the existence of the phase. Solutions of Na, RE and Al nitrates, H_3PO_4 and LUDOX-AS were boiled-down, calcined at 600°C, pelletized and fired at the following temperatures and times

800°C	2 hours	1050°C	6 hours, 4, 8 and 12 days
950°C	6 hours		

From earlier observations, 800°C was selected as the lowest temperature at which significant crystallization might occur in high-sodium supercalcine. The other two temperatures would be typical 6 hour crystallization temperatures. Temperatures were kept below 1100°C to minimize the possibility of Na volatilization. The longer term firings were included as checks on the attainment of a steady state phase assemblage for each of the compositions. Samples were contained in platinum cups supported in depressions carved into high alumina-silica firebrick. A cover fashioned out of this firebrick was placed over the assemblage of specimens to protect the furnace from Na oxide vapors. This cover also serves as a qualitative indicator of Na volatilization since the area just above the sample will be stained white (or other color depending on the cation composition in the proposed phase) if appreciable Na volatilization has occurred during firing. Crystalline phases were identified by X-ray powder diffraction. The presence of the standard array of hexagonal apatite structure reflections in the diffractograms was taken as evidence of the existence of an A_{ss} phase at this composition. The thirty solid solution models tested are listed in Table 10. With the exception of the first 9 models, Nd has been used as the crystal chemical stand-in for all RE³⁺.

* COO-2510-11, June 11, 1976

** J. Ito, Am. Mineralog. 53 890 (1968).

*** J. Felsche, J. Solid State Chem. 5 266 (1972).

Table 10

Models for Sodium Substitution in A_{55}

Number	Solid Solution Model	Apatite Phase - Pure in Diffractogram?
1	$\text{NaNd}_9 [\text{SiO}_4]_6 \text{O}_2$	yes: 800°/2h. <u>only</u>
2	$\text{NaGd}_9 [\text{SiO}_4]_6 \text{O}_2$	yes: 800°/2h. <u>only</u>
3	$\text{NaY}_9 [\text{SiO}_4]_6 \text{O}_2$	no
4	$\text{Na}_2\text{Nd}_8 [\text{SiO}_4]_6 \text{O}$	no: 800°/2h., 950°/6h., 1050°/6h./4, 8d. yes: 1050°/12d. <u>only</u>
5	$\text{Na}_2\text{Gd}_8 [\text{SiO}_4]_6 \text{O}$	no
6	$\text{Na}_2\text{Y}_8 [\text{SiO}_4]_6 \text{O}$	no
7	$\text{Na}_3\text{Nd}_7 [\text{SiO}_4]_6$	no: 800°/2h., 950°/6h., 1050°/6h. yes: 1050°/4, 8, 12 d.
8	$\text{Na}_3\text{Gd}_7 [\text{SiO}_4]_6$	no: 800°/2h., 950°/6h., 1050°/6h. yes: 1050°/4, 8, 12 d.
9	$\text{Na}_3\text{Y}_7 [\text{SiO}_4]_6$	no
10	$\text{Na}_2\text{Nd}_8 [\text{SiO}_4]_4 [\text{PO}_4]_2 \text{O}_2$	no
11	$\text{Na}_3\text{Nd}_7 [\text{SiO}_4]_4 [\text{PO}_4]_2 \text{O}$	no
12	$\text{Na}_4\text{Nd}_6 [\text{SiO}_4]_4 [\text{PO}_4]_2$	no
13	$\text{NaNd}_8\text{Al} [\text{SiO}_4]_6 \text{O}_2$	no
14	$\text{Na}_2\text{Nd}_6\text{Al}_2 [\text{SiO}_4]_6 \text{O}$	yes: 800°/2h., 950°/6h. no: 1050°/6h./4, 8, 12d.
15	$\text{Na}_3\text{Nd}_4\text{Al}_3 [\text{SiO}_4]_6$	yes: 800°/2h., 950°/6h. no: 1050°/6h./4, 8, 12d.
16	$\text{Na}_2\text{Nd}_6\text{Al}_2 [\text{SiO}_4]_4 [\text{PO}_4]_2 \text{O}_2$	no
17	$\text{Na}_3\text{Nd}_4\text{Al}_3 [\text{SiO}_4]_4 [\text{PO}_4] \text{O}$	no
18	$\text{Na}_4\text{Nd}_2\text{Al}_4 [\text{SiO}_4]_4 [\text{PO}_4]$	no
19	$\text{CaNa}_{1.5}\text{Nd}_6\text{Al}_{1.5} [\text{SiO}_4]_6 \text{O}$	yes: all firings
20	$\text{CaNa}_{2.5}\text{Nd}_4\text{Al}_{2.5} [\text{SiO}_4]_6$	yes: 800°h. <u>only</u>
21	$\text{CaNaNd}_8 [\text{SiO}_4]_5 [\text{PO}_4] \text{O}_2$	yes: 800°/2h. <u>only</u>
22	$\text{CaNaNd}_7\text{Al} [\text{SiO}_4]_5 [\text{PO}_4] \text{O}_2$	yes: 800°/2h. <u>only</u>
23	$\text{CaNa}_2\text{Nd}_5\text{Al}_2 [\text{SiO}_4]_5 [\text{PO}_4] \text{O}$	yes: 800°/2h. <u>only</u>

24	$\text{CaNa}_3\text{Nd}_3\text{Al}_3 [\text{SiO}_4]_5[\text{PO}_4]$	no
25	$\text{CaNa}_4\text{NdAl}_4 [\text{SiO}_4]_4[\text{PO}_4]_2$	no
26	$\text{CaNa}_2\text{Nd}_7 [\text{SiO}_4]_5[\text{PO}_4]_0$	no
27	$\text{CaNa}_3\text{Nd}_6 [\text{SiO}_4]_5[\text{PO}_4]$	no
28	$\text{Ca}_2\text{NaNd}_7 [\text{SiO}_4]_6\text{O}$	yes: all firings
29	$\text{Ca}_2\text{Na}_2\text{Nd}_6 [\text{SiO}_4]_6$	yes: 800°/2h., 950°/6h. no: 1050°/8h./4, 8, 12d.
30	$\text{Ca}_2\text{Na}_3\text{Nd}_5 [\text{SiO}_4]_4[\text{PO}_4]_2$	no

"h." = hours, "d." = days at the firing temperature

Runs 1 + 3. Based on the previous preparations of phases of this stoichiometry by Ito and Felsche, it was assumed that these would be the easiest to prepare. However, only in the brief 800°C firings of the Nd and Gd models did we observe a pure apatite pattern in the diffractograms. Thus, the A_{ss} phase forms metastably only at lower temperatures. Higher temperature firings of these two bulk compositions gave multiphase assemblages in which A_{ss} reflections predominated. Some of the additional phases included the sesquioxides ($\text{A-Nd}_2\text{O}_3$, $\text{C-Gd}_2\text{O}_3$) and a previously unobserved phase which was identified later as " NaNdO_4 " reported first by Chichagov et al.* None of the proposed Y phases (runs 3,6,9) formed under our experimental conditions and, moreover, A_{ss} was not one of the major phases in any of their diffractograms.

Neither Ito or Felsche reported difficulties in preparing these Na phases. Of course, they did not use our supercalcine-oriented experimental procedure. This inconsistency is both interesting and relevant and we hope to have time to look into the preparations of these A_{ss} by other techniques in the coming months.

Runs 4 + 9. Both Ito and Felsche favor an "oxyapatite" model (i.e. O_2 on the halide sites, e.g. $\text{Nd}_{9.33}[\text{SiO}_4]_6\text{O}_2$) as the most stable RE silicate apatite stoichiometry. They are skeptical about the existence of phases with one (eg. $\text{Nd}_{8.67}[\text{SiO}_4]_6\text{O}$) or two (eg. $\text{Nd}_8[\text{SiO}_4]_6\text{O}_2$) oxygen defects per formula unit. Runs 4 through 9 were designed to test whether phases with coupled Na for Nd substitution and oxygen defects could be synthesized under our experimental conditions. Runs 4, 7 and 8 did give pure A_{ss} phases, but only after several days of firing at 1050°C. The sesquioxides were the major impurity phase in the lower temperature and shorter duration firings. It was interesting to note that the Na- A_{ss} phases appear to be more stable for the defect A_{ss} models than for the pure oxyapatites. We conclude that although the Nd and Gd models in runs 4-9 do crystallize in the apatite structure, the approach to equilibrium is so slow that they could not reach this state during the brief supercalcine crystallization heat treatments.

Runs 10 + 12. By changing the oxygen concentration on the halide site, three different combinations of Na-Nd substitutions are possible in the five silicate to one phosphate apatite phase. Most of the reflections in the diffractograms were due to an apatite phase, but with each of the firings of all of the three models there were one or more prominent extra reflections due to NdPO_4 .

* A. V. Chichagov et al, Soviet Phys. Cryst. (Eng. Trans.) 14 95 (1969).

Runs 13 + 15. One of the reasons for undertaking this survey was to check for possible solid solution of nepheline, NaAlSiO_4 , in silicate A_{ss} 's. These three models consider 1Na/1Al coupled substitutions for 2Nd with charge compensation provided by vacancies in the halide site. In the brief 800°C firing, the $\text{NaNd}_8\text{Al}[\text{SiO}_4]_6\text{O}_2$ model has an almost phase-pure apatite pattern. With longer and higher temperature firings, reflections of $\text{Nd}_2\text{Si}_2\text{O}_7$ appear. The diffractograms of runs 14 and 15 show phase-pure A_{ss} in the 800 and 950°C firings, but at 1050°C, very weak extra reflections of NdAlO_3 and NaAlSiO_4 appear.

Runs 16 + 18. When one $[\text{PO}_4]$ group is substituted for a $[\text{SiO}_4]$ group in the 14-16 models, it is possible to substitute an extra Na/Al for Nd. However, for each of the firings of each model, there were prominent reflections of NdPO_4 in the diffractograms.

Runs 19,20. In these two models, one Ca is added to the equimolar Na/Al for Nd substitutions. As was the case of runs 4 and 14, the model with one-half oxygen occupancy on the halide site, $\text{CaNa}_{1.5}\text{Nd}_8\text{Al}_{1.5}[\text{SiO}_4]_6\text{O}$, showed the pure apatite pattern of reflections in the diffractograms.

Runs 21 + 27. In the various firings of each of these phosphate - silicate - A_{ss} models, the phase NdPO_4 was observed in the products. The 800°C firing of 21 and 22 did give a pure A_{ss} pattern, but this phase was apparently metastable, since higher temperature firings gave only multiphase assemblages.

Runs 28 + 30. Here the number of Ca ions in the model was increased to two per formula unit. The model in run 28 gave a pure A_{ss} phase for all firings. The 800 and 950°C firings of the $\text{Ca}_2\text{Na}_2\text{Nd}_6[\text{SiO}_4]_6$ model gave phase-pure apatite patterns, but the 1050°C firings had one extra reflection which could not be assigned to any known phase of the component oxides. It is possible that the A_{ss} phase is ordered and thereby gives extra (superlattice) reflections in the diffractograms. There are two large cation sites in apatite, six seven-fold and four nine-fold sites. This is another problem which would make an interesting study in the future.

The phosphate model of run 30 is like all of the other phosphate models in that NdPO_4 is observed as an additional phase.

Conclusions and Implications for Supercalcine Design. Several general observations can be abstracted from the thirty A_{ss} models studied.

- The sodium substituted models with one-half occupancy on the halide site seem to be the most stable (e.g. $\text{Na}_2\text{Nd}_8[\text{SiO}_4]_6\text{O}$ and $\text{Na}_2\text{Nd}_6\text{Al}_2[\text{SiO}_4]_6\text{O}$).
- Considerable Na and Al can be substituted for the RE in the silicate models. The crystal chemical role of Al in this structure type is open to question because Al^{3+} can substitute both on the tetrahedral ($[\text{SiO}_4]$) and larger cation sites. However, the models were carefully selected to give Al no choice but to substitute on the 7- or 9-fold sites. Work on these Al phases is novel since there has been only one previous report of Al substitution in the larger cation sites in phosphate apatites and no report of its substitution in silicate apatites.
- Sodium substitution for RE seems to destabilize the phosphate-silicate apatite models and cause REPO_4 to form as a separate phase. Thus, in dirty supercalcine formulations we will assign the $[\text{PO}_4]$ to the formation of a monazite structure solid solution $[\text{M}_{ss}]$ phase, REPO_4 .
- Concurrent substitution of Ca with the Na (and Al) for RE seems to promote the stabilization of silicate apatite phases. This observation has been made in a number of our apatite crystal chemical studies. We will continue to add some Ca to dirty supercalcine formulations to promote rapid crystallization of A_{ss} phases.

With the experience gained from these runs our next step, according to the usual supercalcine development procedure, would be to try to prepare several of the most promising models using the actual rare earth distributions in PW-7a and typical supercalcine crystallization conditions. The compatibility of these phases with other supercalcine phases would be tested next. However, since the development of high sodium supercalcine formulations is our highest priority at this time, it would be desirable to skip these time consuming steps, at least for the time being. An examination of the changes in supercalcine formulations which would result from a "fine-tuning" of the A_{ss} composition indicates that these changes would involve only small variations in the silica additive. For example, it might be found that a model intermediate between runs 19 and 20 is the most stable A_{ss} in high Na supercalcines. Using round numbers for the Na, $[PO_4]$ and RE millimolar concentrations in PW-7a, the phase formation model and additives would then be

340 RE	60 $CaNa_2Al_2RE_4(SiO_4)_6O_{0.5}$	60 Ca 120 Al 360 Si
100 $[PO_4]$	100 $REPO_4$	
600 Na	480 $NaAlSiO_4$	480 Al 480 Si
required additives		60 Ca 600 Al 840 Si.

If we propose instead that Na crystallize only in nepheline, and use our standard Ca-RE-silicate A_{ss} stoichiometry, the models and additives would be

340 RE	30 $Ca_2RE_8(SiO_4)_6O_2$	60 Ca 180 Si
100 $[PO_4]$	100 $REPO_4$	
600 Na	600 $NaAlSiO_4$	600 Al 600 Si
required additives		60 Ca 600 Al 780 Si.

In either case, the Ca and Al additives are the same and the Si differs by only 60 millimoles. Of course, different A_{ss} models would give different variations in required additives in the comparison just described. However, all of these variations should be within the range of excess Al plus Si routinely added to supercalcine formulations to insure fixation of alkalis. Thus, we will proceed to complex compatibility studies and supercalcine formulations design without further work on Na-substituted A_{ss} .

4.2 Sodalite Structure Phases (G.J. McCarthy and M.T. Davidson)

Sodalite is a mineral with nominal composition $Na_8Al_6Si_6O_{24}Cl_2$ or, written differently, $Na_2[NaAlSiO_4]_6Cl_2$. A phase with the sodalite structure was first encountered in our work during compatibility studies between $SrMoO_4(S_{ss})$ and $NaAlSiO_4$ (nepheline, Ne)*. It was observed that these two phases reacted partially at supercalcine crystallization temperatures to form $Sr_2[NaAlSiO_4]_6(MoO_4)_2^{**}$. Since the sodalite structure phases will be forming in dirty supercalcines, it was necessary to perform a crystal chemical survey of the substitution of HLW cations into this structure type.

* Annual Report, COO-2510-11, pp. 29,30.

** For the remainder of this section, the $NaAlSiO_4$ portion of the sodalite phase formulae will be written as Ne = nepheline. Thus, the formula for this phase becomes $Sr_2[Ne]_6(MoO_4)_2$.

The methodology was similar to that used in the sodium-apatite studies just described. Solutions of nitrates and MoO_3 were dried and the resulting powder was calcined at 600°C for one hour. Pellets of each batch were fired at 950 and 1050°C for six hours in covered firebricks. Stains on the bricks were indications of oxides volatilization.

Table 11 lists the stoichiometries of the sodalite structure solid solution (So_{ss}) models tested, the phase formation observed after each firing and whether any staining of the firebrick was noted. A discussion of the rationale for each model and the results follows.

Run 1. The mineral "nosean", a member of the sodalite group, has the idealized formula $\text{Na}_2[\text{Ne}]_6\text{SO}_4$. As we suggested in the Annual Report (p. 30), if the Na_2MoO_4 analog of this phase could be readily crystallized under supercalcine preparation conditions, and if the thermal stability of this analog were adequate, it would then be possible to eliminate Mo-fixation additives. Unfortunately, the results of this run indicate that such a phase has only begun to form after firing at 950°C for 6 hrs. and that it dissociates into its Ne and Na_2MoO_4 components at 1050°C . Some staining of the brick was observed at the higher temperature, which is indicative of the limited thermal stability of Na_2MoO_4 . This phase is also water soluble, so it cannot be allowed to form in supercalcine.

Run 2,3. These models tested whether CsNaMoO_4 and Cs_2MoO_4 would combine with Ne to form a So_{ss} phase. The fact that Cs attacks the Ne and forms pollucite instead is yet additional proof of the great stability of this Cs fixation phase. This has been demonstrated many times over the last eighteen months of our research.

Run 4 + 6. The mineral "hauyne" another member of the sodalite group, has the idealized formula $\text{Ca}_2[\text{Ne}]_6(\text{SO}_4)_2$. These three runs were designed to test the stability of molybdate hauyne analogs of Ca, Sr and Ba under supercalcine preparation conditions. When crystallized at 950°C , the Ca- So_{ss} is only partially formed, but since the remainder of the molybdate is still fixed in the scheelite structure CaMoO_4 phase, this is an acceptable occurrence in supercalcine. The higher crystallization temperature of 1050°C produced a pure So_{ss} phase. The Sr- So_{ss} phase appears to be somewhat less stable than the Ca phase. It was not fully formed from SrMoO_4 and Ne after 6 hrs. at 1050°C . A phase-pure Sr- So_{ss} was obtained after a 6 hr - 1200°C firing. The Ba- So_{ss} phase begins to form at 950°C , but at 1050°C some of the Ba combines with some of the alumina and silica in Ne to form the Ba-feldspar structure phase, celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$). The pure Ba- So_{ss} is the least stable among the alkaline earth- So_{ss} models, if indeed it can be formed at all.

We project that when Ba constitutes only 15-25% of the total alkaline earth content available to form So_{ss} , it will crystallize in the So_{ss} . This question will be investigated in the coming months.

Runs 7 + 9. The question addressed here was whether one of the six Na's in each of the proposed alkaline earth-molybdate So_{ss} phases could be replaced by Cs. This would have provided a different crystal chemical role for Cs in dirty supercalcine. However, as we found in runs 2 and 3, the Cs reacts with the appropriate amount of Al and Si to form pollucite instead.

Runs 10 + 12. There is a small amount of chromium in MLM. In clean supercalcines it crystallizes as Cr^{3+} in the $(\text{Fe}_2\text{O}_3)_{\text{ss}}$ and/or SP_{ss} phases. However, the presence of a large excess of alkali in the high Na wastes could favor the crystallization of chromates where the Cr would be hexavalent. One likely crystal chemical role for chromate is in the So_{ss} phase. These three runs were designed to test the stability of alkaline earth-chromate- So_{ss} phases under supercalcine crystallization conditions.

The Ca model crystallized readily into a phase-pure So_{ss} . However, the presence of stains on the firebrick covering the pellets indicated some level of oxides volatilization. The green color is characteristic of Cr^{3+} , although the vapor species of Cr probably had a higher valence when it left the sample. The Sr model was not fully formed at 950°C , but was a phase-pure So_{ss} at 1050°C . Again, there was evidence of volatilization of Cr and probably some Na. The Ba model showed no sign of forming a So_{ss} phase, even when

Table 11

Sodalite Structure Solid Solution Models

Number	Sodalite	Crystalline Phase Formation*	Stains**
1	$\text{Na}_2[\text{Ne}]_6\text{MoO}_4$	950 $\text{Ne}+\text{Na}_2\text{MoO}_4+\text{So}_{\text{ss}}$ 1050 $\text{Ne}+\text{Na}_2\text{MoO}_4$	None Pale white
2	$\text{CsNa}[\text{Ne}]_6\text{MoO}_4$	950 $\text{P}+\text{Ne}+\text{Na}_2\text{MoO}_4$ 1050 $\text{P}+\text{Ne}+\text{Na}_2\text{MoO}_4$	None Pale white
3	$\text{Cs}_2[\text{Ne}]_6\text{MoO}_4$	950 same assemblage as 2 1050	None Pale white
4	$\text{Ca}_2[\text{Ne}]_6(\text{MoO}_4)_2$	950 $\text{So}_{\text{ss}}+\text{CaMoO}_4+\text{Ne}$ 1050 So_{ss}	None None
5	$\text{Sr}_2[\text{Ne}]_6(\text{MoO}_4)_2$	950 $\text{So}_{\text{ss}}+\text{SrMoO}_4+\text{Ne}$ 1050 $\text{So}_{\text{ss}}+\text{SrMoO}_4+\text{Ne}$	None None
6	$\text{Ba}_2[\text{Ne}]_6(\text{MoO}_4)_2$	950 $\text{BaMoO}_4+\text{Ne}+\text{So}_{\text{ss}}$ 1050 $\text{BaAl}_2\text{Si}_2\text{O}_8+\text{BaMoO}_4$	None Pale white
7	$\text{CsCa}_2\text{Na}_5[\text{AlSiO}_4]_6(\text{MoO}_4)_2$	950 $\text{So}_{\text{ss}}+\text{P}+\text{CaMoO}_4+\text{Ne}$ 1050 $\text{So}_{\text{ss}}+\text{P}+\text{CaMoO}_4$	None Pale white
8	$\text{CsSr}_2\text{Na}_5[\text{AlSiO}_4]_6(\text{MoO}_4)_2$	950 $\text{So}_{\text{ss}}+\text{SrMoO}_4+\text{P}+\text{Ne}$ 1050 $\text{So}_{\text{ss}}+\text{SrMoO}_4+\text{P}+\text{Ne}$	None Pale white
9	$\text{CsBa}_2\text{Na}_5[\text{AlSiO}_4]_6(\text{MoO}_4)_2$	950 $\text{BaMoO}_4+\text{P}+\text{Ne}$ 1050 $\text{BaAl}_2\text{Si}_2\text{O}_8+\text{P}+\text{BaMoO}_4$	None Pale white
10	$\text{Ca}_2[\text{Ne}]_6(\text{CrO}_4)_2$	950 So_{ss} 1050 So_{ss}	Light brown Green
11	$\text{Sr}_2[\text{Ne}]_6(\text{CrO}_4)_2$	950 $\text{So}_{\text{ss}}+\text{Ne}+\text{SrCrO}_4$ 1050 So_{ss}	Light brown Green
12	$\text{Ba}_2[\text{Ne}]_6(\text{CrO}_4)_2$	950 BaCrO_4+Ne 1050 BaCrO_4+Ne	Light brown Green
13	$\text{Na}_2[\text{Ne}]_6\text{CrO}_4$	950 $\text{So}_{\text{ss}}+\text{Ne}$ 1050 $\text{So}_{\text{ss}}+\text{Ne}$	Light green Green
14	$\text{CsNa}[\text{Ne}]_6\text{CrO}_4$	950 $\text{So}_{\text{ss}}+\text{P}+\text{Ne}$ 1050 $\text{So}_{\text{ss}}+\text{P}+\text{Ne}$	Light green Green
15	$\text{Cs}_2[\text{Ne}]_6\text{CrO}_4$	950 $\text{P}+\text{Ne}+\text{x}$ 1050 $\text{P}+\text{Ne}+\text{x}$	Light green Green

* After firing for 6 hrs. at the indicated temperature; phases listed in the order of decreasing intensity in the diffractograms; Ne = nepheline ($\text{NaAlSi}_3\text{O}_8$), So_{ss} = sodalite structure solid solution phase, P = pollucite ($\text{CsAlSi}_2\text{O}_6$).

** Stains on the firebrick covers over the pellet specimens are indicative of oxides volatilization.

the firing temperature was raised to 1200°C. It is interesting that the stability of BaCrO_4 was great enough to prevent Ba from attacking the Ne to form celsian, whereas the stability of BaMoO_4 was not sufficient for this purpose. In other words, BaCrO_4 is compatible with NaAlSiO_4 at 1050°C while BaMoO_4 is not.

Runs 13 + 15. Run 13 is a check on whether the chromate analog of nosean is stable under supercalcine crystallization conditions. The phase assemblages of the products of both firings consisted of the So_{ss} phase with extra Ne. This result alone suggests that some Na_2CrO_4 is volatilized during crystallization, and the suggestion is confirmed by the observation of heavy stains on the covering firebrick. It is interesting to note that the chromate phase $\text{Na}_2[\text{Ne}]_5\text{CrO}_4$ is more readily formed than the molybdate $\text{Na}_2[\text{Ne}]_6\text{MoO}_4$.

Conclusions and Application to Supercalcine Design. Several general observations can be abstracted from these runs.

- . Both Ca and Sr form stable molybdate and chromate So_{ss} phases. The Ca phases are more readily formed than the Sr phases.
- . Cs does not substitute in the So_{ss} structure. It forms pollucite with Al and Si from the Ne.
- . Ba does not form either a chromate or a molybdate So_{ss} phase when it is the only alkaline earth. It is possible that it can be stabilized in the So_{ss} structure when it is only 10-30% of the alkaline earth constituents.
- . The all-Na chromate- So_{ss} appears to be more stable than the corresponding molybdate- So_{ss} . However, some Cr oxide volatilization is observed during the crystallization of the former. Sodium volatilization was observed for both phases during crystallization at 1000°C.

We propose that the ability to rapidly synthesize a So_{ss} phase from Ne and a given salt is related to the structure ("lattice") energy of the salt. In the case of the sodium salts, we predict that the structure energy of Na_2MoO_4 is greater than Na_2CrO_4 . Thus, the latter can be broken into its components more readily to be incorporated with Ne to form the So_{ss} phase. Similarly, CaCrO_4 would have a lower structure energy than CaMoO_4 because the former combines with Ne to form So_{ss} at a lower synthesis temperature. We have often commented on the high stability of SrMoO_4 ; that of CaMoO_4 should be lower since it formed a So_{ss} phase at 1050°C while SrMoO_4 did not. The situation with the Ba and Cs phases is not so simple. In this crystal chemical study, we have been actually dealing with either five or six oxide component systems in which literally dozens of binary and ternary oxide phase are possible. The combination of Ba and Cs with alumina and silica yields the most stable phases in these systems.

In our development of dirty supercalcine formulations we will continue to adjust compositions so that equimolar (Ca+Sr+Ba) is available to fix Mo in So_{ss} , and we will propose the crystallization of So_{ss} from the reaction of Ne with this So_{ss} . Meanwhile, we will check, through compatibility studies, whether Ba can be substituted in So_{ss} , and whether Cr prefers to crystallize as chromate in So_{ss} or as "chromite" in $(\text{Fe}_2\text{O}_3)_{\text{ss}} + \text{SP}_{\text{ss}}$. The latter question is of some importance since crystallization of So_{ss} could require alkaline earth additives while the other phases would not.

4.3 Compatibility Studies (G.J. McCarthy and D.E. Pfoertsch)

In the Annual Report (pp. 28-32) we described the first group of compatibility studies for high sodium wastes. The waste formulation used in designing the molar ratios of those runs was the MSF composition, PW-8a. With the uncertain future of waste solidification at Nuclear Fuel Services in mind, we have based all recent compatibility studies on the AGNS composition PW-7a. Table 12 lists the important constituents of PW-7a and the molar ratios which will be used in compatibility studies. The significant differences from PW-8a are the lower Na and much lower Fe concentrations.

Table 12
Major Constituents of PW-7a

Constituent	M in PW-7a	Mole%	Approximate Molar Ratios*
Na	0.590	37.2	6 Na
RE ³⁺	0.304	19.2	3 RE ³⁺
Zr	0.106	6.7	1 Zr
Mo	0.095	6.0	1 Mo
Cs	0.054	3.4	1 Cs+Rb
Ce	0.051	3.2	1 Ce
Fe	0.100	6.3	1 Fe
[PO ₄]*	0.100 **	6.3	1 [PO ₄]
Sr	0.027	1.7	0.5 Sr+Ba
Ba	0.027	1.7	
Cr	0.012	0.8	
Rb	0.010	0.6	
U	0.110	6.9	1 U
	1.586	100.0	

* for use in high-Na compatibility studies

In the first group of compatibility studies described in that Annual Report, we found that the following phase assemblages were compatible:

The composition of the apatite structure solid solution, A_{ss} , is not specified in this listing because there appeared to be evidence that Ne was reacting with the RE silicate A_{ss} to form a Na-Al-RE-silicate A_{ss} . Several of the Na- A_{ss} runs described in section 4.1 demonstrated that this can indeed happen. The A_{ss} stoichiometry also included the substitution of $[\text{PO}_4]$ for some of the $[\text{SiO}_4]$. The results described in section 4.1 also suggest that REPO_4 would crystallize separately from A_{ss} in high Na stoichiometries. Yet, a careful reexamination of the diffractograms of the appropriate runs (CS-156-158) did not reveal any REPO_4 reflections. One additional point should be made about that earlier group of runs. In CS-157, the compatibility of " $\text{Na}_2[\text{Ne}]_6\text{MoO}_4$ " and $\text{Ca}_3\text{Nd}_7[\text{SiO}_4]_5[\text{PO}_4]\text{O}_2$ was being tested. The resulting phase assemblage did consist of $(\text{So}_{ss} + \text{A}_{ss})$. But, we know now, from the results described in section 4.2, that the So_{ss} phase must have crystallized with some or all of the Ca designated for A_{ss} substituted for Na in it. The pure Na- So_{ss} does not form under supercalcine crystallization conditions.

** It was later learned that the actual $[\text{PO}_4]$ concentration in PW-7a is 0.236M. The data in Table 12 were derived from p. 19 of BAML-1893 which listed the $[\text{PO}_4]$ concentration as 0.100 M. The availability of this extra phosphate in PW-7a means that a smaller quantity of additives will be needed to fix the RE, since an extra 0.136 M RE will react with $[\text{PO}_4]$ to form M_{ss} .

The first two runs to be described below will extend the compatibility studies to include more of the ions in PW-7a in their possible supercalcine phases. In these runs, the second most abundant "constituent", the trivalent RE³⁺ group, is crystallizing in a silicate-A_{ss} phase. Supercalcine formulations that have the RE's in this crystal chemical role will henceforth be classified as having the "Nepheline-Apatite Model" to distinguish them from a second type of high-Na supercalcine model which has been under investigation in the last few months.

During several recent supercalcine crystallization and compatibility studies, we have noted the coexistence of CsAlSi₂O₆[P] and REPO₄[M_{ss}] in the same phase assemblage. This observation implies that the two phases are compatible, i.e. that the RE is fixed in a sufficiently stable phase so that it does not attack pollucite and impede its Cs fixation function. To check whether REPO₄ and pollucite were compatible once formed, we fired a mixture of NdPO₄ and CsAlSi₂O₆ at 1050 and 1200°C for 6 and 48 hrs. The two phases remained unchanged, and thus were compatible under all of the firing conditions. This result led us to initiate a second group of compatibility studies aimed at exploring the feasibility of another class of supercalcine formulations based on a "Nepheline-Monazite Model". The experimental procedure was the same as that described in the previous two sections except that the firing temperatures were 1050 and 1200°C for 6 hrs. A description of the rationale and results of each compatibility study follows.

CS-159. 10NaAlSiO₄+Ca₂RE₈[SiO₄]₆O₂+Ca₂[Ne]₆(MoO₄)₂+2CsAlSi₂O₆. Except for the Cs, the molar ratios of the phases are approximately those derived from a supercalcine formulation based on MLW PW-7a (see Table 12). The Cs concentration is doubled to insure that the pollucite reflections will be observable in the x-ray diffractograms.

The proposed phase assemblage was observed in each of the diffractograms. A 950°C firing was added. Even at this relatively low temperature, each of the four proposed phases was well crystallized. The relative intensity of Ne decreased in the 1050°C firing compared to the 950°C. This is another indicator that either Ne is substituting in A_{ss}, or it is being incorporated in So_{ss}. The former behavior was demonstrated as being possible in section 4.1. The latter substitution would be allowed if we find that a smaller amount of the "salt" (here CaMoO₄) may be able to react with Ne to form sodalite structure phases with the general formula Ca_{2-x}[Ne]₆(MoO₄)_{2-x}. If x were 1 or even less, then 6 or more of the "excess" Ne formula units in the proposed phase assemblage could have been incorporated in So_{ss}. However, there was no major change in the cubic unit cell parameter of So_{ss} in the 1050°C firing in which the amount of free Ne was lower. In the 1200°C firing, free Ne was absent and pollucite was depleted. There were heavy stains on the firebrick covers. Both of these results indicate that some Cs, and probably Na, were volatilized from the sample. There was, however, no staining of the firebricks in the 950 and 1050°C firings.

CS-160. 10NaAlSiO₄+Ca₂RE₈[SiO₄]₆O₂+Ca₂[Ne]₆(MoO₄)₂+2CsAlSi₂O₆+2ZrO₂+CeO₂+2REPO₄. This phase assemblage accounts for all of the major constituents in Table 12 except U. In the products of the 950 and 1050°C firings, the phase assemblage was the same: A_{ss}+So_{ss}+F_{ss}{5.40A}+T_{ss}+P+Ne+M_{ss}+Fe₂O₃. As expected, the (2ZrO₂+CeO₂) combined to form an (F_{ss}+T_{ss}) phase assemblage. Thus, the predicted crystalline phase formation model is correct. There was no staining of the firebricks in either firings.

There was a major change in phase assemblage for the 1200°C firing. Pollucite was depleted again, and (F_{ss}+T_{ss}) had combined to form a single phase F_{ss} with a cell parameter of 5.22Å. Such a small F_{ss} cell can only be obtained when some REO_{1.5} has been incorporated in the CeO₂-ZrO₂ solid solution*. This means that some of the RE is not fixed in A_{ss}. This may also be interfering with the complete fixation of Cs in pollucite. It is apparent that further "fine-tuning" of the stoichiometries of the proposed phases and the required additives will be necessary if supercalcine crystallization temperatures as high as 1200°C will be required. However, we are encouraged by the high thermal stability of the current formulations in the 950-

* See Report C00-2510-9, pp 4,5.

1050°C range. If adequate consolidation of disc pelletized "cores" can be obtained in the 900-1050°C crystallization temperature range, then supercalcine formulations based on the current nepheline-apatite phase formation models may be satisfactory enough to proceed to an engineering scale demonstration of a dirty supercalcine in the near future.

CS-161. $6\text{NaAlSiO}_4 + 3\text{REPO}_4$. Sodium and the rare earths are the two most abundant constituents of PW-7a. This run is a test of the compatibility of the Na and RE phases, nepheline and monazite. These phases are compatible at both firing temperatures and will be the two most important phases in the nepheline-monazite model supercalcine formulations.

CS-162. $6\text{NaAlSiO}_4 + \text{CsAlSi}_2\text{O}_6 + 3\text{REPO}_4$. We had shown that all binary combinations of these three phases were compatible. This run confirmed that the three are themselves compatible under supercalcine crystallization conditions.

CS-163. $6\text{NaAlSiO}_4 + \text{CsAlSi}_2\text{O}_6 + 3\text{REPO}_4 + \text{CaMoO}_4$. It was expected that some of the Ne would combine with CaMoO_4 to form So_{ss} . The diffractograms of the products of both firings showed sharp and intense reflections of $(\text{P} + \text{M}_{ss} + \text{So}_{ss})$, with only a trace of Ne. We have been giving the formula of So_{ss} as $\text{Ca}_2[\text{Ne}]_6(\text{MoO}_4)_2$, based on our own synthesis work and on the mineralogic literature. The results of this run suggest that as little as one mole of CaMoO_4 may combine with 6Ne to form So_{ss} , or in other words, a So_{ss} phase with a formula $\text{Ca}[\text{Ne}]_6\text{MoO}_4$ might be stable. We are investigating this possibility now.

A check of Table 12 shows that in the runs through CS-163, a crystal chemical role in a compatible assemblage of crystalline phases has been assigned for the following major constituents of PW-7a:

Also, earlier results suggest that Rb should crystallize in P and that Ba and Cr may substitute in So_{ss} .

The other major constituents to be considered are Ce, Fe and U, and compatibility studies are currently being formulated to elucidate their crystal chemical roles in a nepheline-monazite model supercalcine. However, because of an upcoming major meeting at PNL on progress in development of the multibarrier waste forms, these necessary CS-runs were postponed temporarily in favor of scouting tests of several high sodium supercalcine formulations. The phase formation modeling was based only on the CS runs completed to date, plus insights from our successful "clean" supercalcine formulations. The simulated waste included all of the constituents in Table 12 plus Ni, Ca, and Ag. Many of the key phases specified in the models were observed in the diffractograms (e.g. P, So_{ss} , A_{ss} , M_{ss}) but unexpected reflections were also observed. We will postpone the discussion of these results until the CS-runs necessary to interpret the crystalline phase formation have been completed. However, we should note that the results were very encouraging from the thermal stability standpoint. The alkalis, Cs, Rb and Na, appeared to be well-stabilized in the aluminosilicate phases, since only very minor staining of the firebricks and frosting of the silica tubes were produced by crystallization firings of up to two hours at 1100°C.

APPENDIX

Penn State Contribution to the PNL Quarterly for July - September, 1976

SUPERCALCINE (G.J. McCarthy, The Pennsylvania State University).

The nature of the Penn State participation in the Alternative Waste Form Program and the supercalcine concept have been described in previous reports. Current objectives of the Supercalcine Task include, 1) refinement of existing formulations for PH-4b and PH-7 wastes, 2) development of formulations for the high Ra wastes PH-7a and -8a, 3) determination of crystalline phase behavior of Ce, Ru, Zr, Pd, Rh and the actinides in supercalcine 4) consideration of the effects of radiation and transmutation on supercalcine stability.

Characterization of Supercalcine 76-3 (SPC-2). (G.J. McCarthy, M.T. Davidson, D.E. Proertsch and R.G. Johnston)

The engineering scale spray calcination of this formulation is described elsewhere in this report. The simulated HLW was a simplified PH-7 without the very expensive elements (Pd,Rh), the radioactive elements (Tc, U, Pu, Np, Am, Cm, Po) and Te. The Ru concentration was only 10% of its value in PH-7. The additives required for formation of the crystalline phases specified by the phase formation model were nitrate solutions of Ca, Sr and Al and a colloidal suspension of SiO₂. Waste oxides loading was 21 wt.-%.

Crystalline Phase Formation Model. Based on many compatibility studies and on laboratory simulations of supercalcines, the phase formation model specified for 76-3 (SPC-2) was

Crystallization and X-Ray Phase Analysis. After spray calcination, the product is very fine powder which is x-ray amorphous. It must be fired at

temperatures from 1000-1200°C in order to give both crystallization of the specified phases and sintering into the desired shapes. Firing tests lasting from two to eight hours at temperatures from 800-1250°C have been performed on the "as received" powder and on 1/2 in. diameter pellets cold pressed at 74,000 psi. The shrinkage in pellet diameter was recorded as a measure of the degree of sintering. X-ray powder diffractometers were used for phase identification.

Good crystallization and sintering were obtained with firing temperatures as low as 1050°C for two hours. The crystalline phase assemblage and shrinkage in pellet diameter (24.1%) remained constant for all firings between 1050 and 1250°C.

Each of the phases specified in the phase formation model was identified in the firing products. The reflections of A_{SS}, N_{SS}, T_{SS}, S_{SS}, P, and (Fe,Cr)₂O₄ were distinct in the x-ray diffractograms, but the amounts of RuO₂ and Sp_{SS} were below the level of detection. The identification of RuO₂ is described later. The ferrimagnetic Sp_{SS} was clearly identified by the action of a hand magnet on the product.

One additional phase was also in the product. It was a fluorite structure solid solution [F_{SS}] phase with the approximate composition (Ca_{0.6}Zr_{0.2}Th_{0.2})₁₀ as estimated from its cubic cell parameter. The phase formation model had called for Ce to be fixed in A_{SS}. However, the amount of Ce contained in the less expensive "rare earth mixes" used in engineering scale processing tests at PNL exceeded by a factor of three the actual Ce concentration of PH-7. As we demonstrated earlier this year,* only a limited amount of Ce can be accommodated in A_{SS}. Thus, in 76-3, the excess Ce reacts with part of the free ZrO₂ to form the F_{SS} phase.

Thermal Stability. Data on this property are both preliminary and qualitative. The lack of staining of the firebricks used in all of the crystallization tests (800-1250°C) is one qualitative indication that there is no major waste oxides volatilization. The silica tube test for Cs volatilization indicated a very small amount of Cs loss at 1150°C after 2 hrs., but little or none after 2 hrs. at 1100°C. Pure pollucite (CsAlSi₂O₆) shows a corresponding behavior. There was a light deposit of a black substance near the cooler end of the silica glass tubes after both firings. We have previously found that this indicates the presence of Ru and its volatilization, at least in part, during crystallization. However, we found that this Ru volatilization deposit can be virtually eliminated by crystallization of 76-3 in a nitrogen rather than an air atmosphere.

* Quarterly Progress Report, January - March 1976.

Supercalcine For High Sodium Wastes. (G.J. McCarthy, D.E. Pfoertsch, and M.T. Davidson).

Crystalline phase formation in supercalcines designed for high Na wastes (PW-7a, PW-8a) will be quite different from that just described for the low Na PW-7 waste. Two of the major differences will be the crystallization of a sodalite structure solid solution (S_{ss}) and an A_{ss} with significant Na substitution. Fifty-four possible solid solution models for these two phases have been studied with the following results.

- The molybdate nosean variety of S_{ss} is $AE_2[NaAlSiO_4]_6(MoO_4)_2$, where $AE=Ca, Sr$. The Ca phase is by far more stable. It crystallizes completely at 800°C in a few hours, whereas the Sr phase is still not fully reacted after 6 hrs. at 1200°C. Thus, Ca would be a better additive to promote S_{ss} crystallization.
- There is also a chromate nosean variety of S_{ss} $AE_2[NaAlSiO_4]_6(CrO_4)_2$ in which Ca again appears to form a more stable phase than Sr. Compatibility tests will be needed to find whether Cr would crystallize in this phase or in the Fe_2O_3 and Sp_{ss} phases.
- Cs cannot be substituted for any of the Na in the various S_{ss} phases. It reacts with Al and Si instead to form pollucite.
- Na and coupled Na-Al substitutions are possible in silicate A_{ss} . Simple Na-RE-silicates have been crystallized in the apatite structure, but only after lengthy firings at 1050°C. Some solid solution models containing Na, Ca, RE and Al crystallized in apatite structures after only brief firings in the 800-1000°C range suitable for high Na supercalcines. Some examples are $Na_2Al_2Mg_6[SiO_4]_6O$, $Na_{1.5}Al_{1.5}CaNd_6[SiO_4]_6O$ and $Ca_2Na_2AC_6[SiO_4]_6$.
- Phosphate appears to be incompatible with Na substitutions in A_{ss} . $REPO_4$ [M_{ss}] impurity phases were noted in the firing products of all phosphate containing solid solution models. Thus, specify $[PO_4]$ in M_{ss} rather than A_{ss} in the high Na supercalcines.

Penn State Contribution to the PNL Quarterly for October-December, 1976

SUPERCALCINE (G. J. McCarthy, The Pennsylvania State University)

The nature of the Penn State participation in the Alternative Waste Forms Program and the supercalcine concept have been described in previous reports. Current objectives of the Supercalcine Task include, 1) refinement of existing formulations for PW-4b and PW-7 wastes, 2) development of formulations for the high Na waste PW-7a, 3) determination of crystalline phase behavior of Ca, Ru, Fe, Pd, Rh and the actinides in supercalcine 4) consideration of the effects of radiation and transmutation on supercalcine stability.

Characterization of Supercalcine 76-3 (SPC-2). (G. J. McCarthy, M. T. Davidson, D. E. Pfoertsch and R. G. Johnston)

Crystalline phase formation in SPC-2 fired in air was described in our July-September Quarterly Report contribution. The phases identified by x-ray diffraction or other means were A_{ss} , F_{ss} , S_{ss} , T_{ss} , P , M_{ss} , $(Fe_2O_3)_{ss}$, SP_{ss} , and RuO_2 . We have observed full crystallization under processing conditions as minimal as 10 min at 1125°C or 2 hrs at 1000°C. Consolidation of the SPC-2, as measured by pellet diameter shrinkage, was as effective with the latter treatment as with any of the 1000-1200°C, 2-16 hr firings. This evidence for good crystallization and consolidation with relatively brief and lower temperature heat treatment will be important input concerning the core crystallization - consolidation requirements into the process design for the multibarrier waste form.

A. A. Garrett of PNL finds that small additions of a nonmorillonite-type clay (5 wt%) to SPC-2 improve the pelletizing process. In samples supplied by him, we find that the clay has little effect on the crystalline phase formation. The clay does appear to deplete somewhat the Sr concentration of S_{ss} , forming with it a small amount of an aluminosilicate phase tentatively identified as the anorthite structure polymorph of $SrAl_2Si_2O_8$. We are currently studying the effects of several levels of clay additions to SPC-2 on the leachability, Cs volatility and pressed-pellet consolidation.

Scanning electron microscope (SEM) characterization of cold pressed (72,500 psi) and fired (1125°C, 2 1/2 hrs.) SPC-2 is in progress. To date, A_{ss} , P , SP_{ss} , and S_{ss} crystals have been identified in the specimens. Quantitative measurements of porosity on various specimens give values between 4 and 7 volume %.

Soxhlet leachability has been measured on these cold-pressed and fired specimens. SPC-2 as-received contained about 10 wt% of H_2O , MO_x , CO_2 . Several specimens were prepared from SPC-2 which had been pre-fired at 900°C for 2 hrs in order to remove most of these volatiles. The weight losses in a 72 hr test were 1.4% (2×10^{-5}) for the as-received SPC-2 and 0.88% (1×10^{-5}) for the pre-fired SPC-2. These data indicate an approximately three-fold decrease in leachability compared to the earlier supercalclene demonstration SPC-1.

X-Ray Characterization of Coated Cores of 75-2 (SPC-1). (G. J. McCarthy and E. A. Seitch)

Disc pelletized cores of the first engineering-scale batch of supercalclene, formulation number 75-2, were prepared by A. A. Garrett of PML and forwarded to M. F. Browning of SCL earlier this year. The following specimens of this type were studied by x-ray powder diffraction in order to identify the crystalline phases present at this stage of the processing of the multibarrier waste form.

Supercalclene 75-2 (SPC-1) coated with pyrolytic carbon (PyC). Normal air-atmosphere crystallization of 75-2 yields products whose diffractograms show reflections of a very strong A_{ss} phase, a pollucite (P) phase with moderately intense reflections, and weak reflections of S_{ss} , F_{ss} , Y_{ss} , and SP_{ss} . The diffractogram of the 75-2 pellets coated at BCL with PyC showed the usual sharp reflections of A_{ss} and P. Notably, the S_{ss} reflections were absent, which indicated that either this phase was present below the level of detection by the x-ray method or it had been modified during the production of the PyC coating. Several other moderate to weak reflections gave a good match to two carbide phases, Mo_2C and the solid solution phase $(Sr,Ba)C_2$. The reflections of these two phases plus A_{ss} and P, accounted for all reflections in the diffractograms.

The PyC coatings are developed in a fluidized bed apparatus from a mixture of hydrocarbons and hydrogen. Possibly, the $(Sr,Ba)MoO_4[S_{ss}]$ phase was reduced to the metals, and these, in turn, reacted with the hydrocarbon to form the metal carbides. According to Hanson,** Mo_2C and $(Sr,Ba)C_2$ are the most stable room

temperature carbides of these metals. The tetragonal cell parameters of the dicarbide phase are far closer to those of SrC_2 than to BaC_2 , as would be required by the far greater concentration of Sr than Ba in 75-2. The next step in the characterization of these coatings would be to look for the Mo_2C and $(Sr,Ba)C_2$ phases by metallography or SEM/characteristic x-ray energy analyses.

Supercalclene 75-2 coated with PyC and Al_2O_3 . The phase assemblage identified from the ground pellets included A_{ss} , P, $\alpha-Al_2O_3$ and reflections assigned to the proposed carbides which were even stronger than observed in the previous PyC-only coated specimen.

Aluminum chloride was used as the source of Al in this run. The bed temperature was 1100°C. When aluminum ethylate is substituted for the chloride, a lower temperature can be used. A second sample of coated pellets prepared from the ethylate at 500°C were also studied. The phase assemblage was almost identical to that of the high temperature coated pellets, except that the $\alpha-Al_2O_3$ reflections were less intense. It was a surprise to see several reflections which fit the $\alpha-Al_2O_3$ pattern, because " α " is not the stable phase at this preparation temperature.

Supercalclene Formulations for High-Sodium Wastes. (G. J. McCarthy and D. E. Froelisch).

Nepheline [Ne], $NaAlSi_3O_8$, has been selected as the fixator phase. Two types of phase formation models are being developed for PM-7a-based supercalclenes. The models differ chiefly by the crystal chemical role of the Rare Earths (RE's). In the first model, the RE's crystallize in an apatite structure solid solution [A_{ss}] phase and in the second, they crystallize in a monazite [M_{ss}] phase.

Compatibility of many of the phases of the nepheline-apatite model has been demonstrated:

PM-7a Ion	Crystalline Phase
Na, No, Sr	$NaAlSi_3O_8$ and $(Ca,Sr)_2[NaAlSi_3O_8]_6(MoO_4)_2$ [Ne] [SO _{ss}]
Cs(Rb)	$CsAlSi_2O_6$ [P]
RE(La,Ce,Pr,Md,Pu,Sm,Eu,Gd,Y) [PO ₄]	$Ca_2RE_8[SiO_4]_6O_2$ and $REPO_4$ [A _{ss}] [M _{ss}]

* IAEA leachability units in g/cm²/day; the usual value of 200 cm²/g for surface area was used.

** G. J. McCarthy, Nucl. Technology, Jan 1977.

*** M. Hanson, Constitution of Binary Alloys, 2nd Edition, McGraw-Hill, New York (1958).

Zr,Fe

(Zr,...)O₂ Fe₂O₃
[T_{ss}]

Little or no alkali volatilization was observed during crystallization of these phase assemblages at 950 and 1050°C. Other compatibility studies involving Ce, U, Ba and Cr are in progress.

In a second phase formation model also being evaluated, the RE's are crystallized completely in REPO₄[M_{ss}]. Here, phosphoric acid replaces some of the silica as a supercalcine additive.

Progress was made on understanding the crystal chemistry of the sodalite structure solid solutions [So_{ss}], the monazite structure solid solution [M_{ss}] and high-sodium A_{ss} phases.

Te in Supercalcine. A literature survey yielded information on several potential phases for Te crystallization in supercalcine. Attempts were made to synthesize these as pure phases. Many of the promising compounds or solid solution phases either did not form under typical supercalcine crystallization conditions, or they lost Te during firing. The compound Ca₃TeO₆ is a very stable, refractory Te phase. Unfortunately, it appears that Ca₃TeO₆ is not compatible with pollucite. We will soon be looking into partial (TeO₄) substitution for (NbO₄) in So_{ss}.