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ANNUAL REPORT

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1.0 Introduction and Highlights (G. J. McCarthy)

This Annual Report will describe work accomplished during the last six months, with brief reviews of important results obtained during the last year included where appropriate. Two additional reports were completed during this last report period. The first discussed the crystal chemical role of the rare earths in HLW calcine, glass and supercalcine*. The second was a technical progress report on supercalcine development which was also submitted for publication**.

Brief highlights of the research to be described in this report are as follows.

- . Thermogravimetric analysis on cesium aluminosilicates was performed by S. A. Gallagher during her three month stay at PNL. Pollucite, $\text{CsAlSi}_2\text{O}_6$, appears to have more than adequate thermal stability for Cs fixation in supercalcine.
- . In spite of earlier promising, but preliminary, results, SrRuO_3 is not suitable as a Ru fixation phase. Strontium oxide has a greater affinity to form aluminosilicates than to form SrRuO_3 . This means that it can prevent complete Cs fixation as pollucite during the supercalcine crystallization firing. The possibility of leaving Ru as RuO_2 during supercalcine crystallization is being assessed.
- . The apatite solid solution [A_{ss}] phases used in supercalcine phase formation models have been easily prepared as pure phases. Use of Ca instead of Sr as an alkaline earth additive yields a more stable A_{ss} phase. The partial substitution of phosphate for silicate in supercalcine A_{ss} has been confirmed.
- . "Pyrex" glass can be used, if necessary, as a consolidation aide for supercalcine. Weight ratios have been optimized for two firing temperatures in terms of soxhlet leachability. However, this is not the preferred approach to supercalcine consolidation.
- . The phase formation models developed for PW-4b-type wastes were routinely applied to PW-7, in spite of several significant composition differences in the latter. Uranium oxide remains as a fluorite structure oxide after supercalcine crystallization, but it does seem to have incorporated either or both CeO_2 or ZrO_2 . Characterization of this F_{ss} phase will require further study.

A simplified PW-7-type formulation will be used in a second engineering scale evaluation of supercalcine in the near future.

- . Work was initiated on the application of supercalcine concepts to the high Na, "dirty", wastes PW-7a and PW-8a. Nepheline, $\text{NaAlSi}_3\text{O}_8$, looks like the best candidate for Na fixation. Extensive modifications to the phase formation models will be necessary because of the high Na concentration. Based on observations during several complex compatibility studies, it appears that good overall thermal stability at as high as 1200°C might be attainable for nepheline based supercalcine formulations.
- . A thorough literature review of the oxide crystal chemistry of Te has been completed.

Appended to this report are drafts of two recent contributions from this project to PNL's Quarterly Progress Reports on the Waste Fixation Program. These should be consulted for a further overview of our recent progress. Appendix C is a compilation of x-ray powder diffraction data (obtained with other support) for selected A_{ss} and F_{ss} phases. This original data should be valuable to those engaged in crystalline phase characterization of high level waste solids.

* G. J. McCarthy, "Crystal Chemistry of the Rare Earths in Solidified High Level Nuclear Wastes" Presented at the 12th Rare Earth Research Conf., Vail Colorado, July 21, 1976 [C00-2510-9].

** G. J. McCarthy, "High Level Waste Ceramics; Materials Considerations, Process Simulations and Product Characterization", Presented at the Am. Nucl. Soc. Annual Meeting, Toronto, June 16, 1976 and submitted to Nuclear Technology [C00-2510-10].

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

One of the major problems in fixation of cesium in supercalcine is its high volatility at waste processing temperatures. Therefore, the thermal stability of the two cesium aluminosilicates which were being considered as phases for the fixation of cesium in supercalcine was studied during the last report period.

2.1 Sample Preparation

The samples that were tested were CsAlSiO_4 , $\text{CsAlSi}_2\text{O}_6$ (Pollucite), and $(\text{Cs}_{.74}\text{Na}_{.13}\text{K}_{.13})\text{AlSi}_2\text{O}_6$. The third is a pollucite with some Na and K substituted for part of the Cs to simulate the alkali concentration (K for Rb) expected in a PW-7 type waste. CsAlSiO_4 was prepared as described in the last report.* Pollucite was prepared from the appropriate amounts of a 1M CsNO_3 solution, a montmorillonite-type clay (Gelwhite L), and a 1M aluminum nitrate solution**. Gelwhite L is described further in the last report*. The mixture was dried and denitrated for 2 hr at 600°C. It was then heated at 800°C for 2 hrs. and at 1050°C for 6 hrs. to complete the crystallization. This sample was washed in distilled water to remove excess Cs and soluble forms of minor impurities in the clay, and was then fired at 1200°C for 2 hr. The $(\text{Cs}_{.74}\text{Na}_{.13}\text{K}_{.13})\text{AlSi}_2\text{O}_6$ was prepared from a 1M CsNO_3 solution, a 1M Na nitrate solution, a 1M K nitrate solution, Gelwhite L, and a 1M Al nitrate solution by a method similar to that used for pollucite.

2.2 Thermal Stability Studies

The amount of weight lost on firing CsAlSiO_4 and pollucite at 1050, 1200 and 1400°C in air were obtained. The test specimens were in the form of 1/2 in. diameter pellets weighing approximately one gram. It was supported in a platinum lined refractory crucible. A large SiC muffle furnace was used. Phase analysis of the fired product was by x-ray powder diffraction.

The data for CsAlSiO_4 were described in the last report*. Weight losses for pollucite after a 24 hr firing were:

1050°C	0.4%
1200°C	2.8%
1400°C	8.3%

The pollucite weight losses were somewhat lower than those for CsAlSiO_4 fired at the same temperature. More importantly, the CsAlSiO_4 products were found to contain considerable $\text{CsAlSi}_2\text{O}_6$, which is indicative of substantial Cs losses, whereas the product obtained from firing pollucite was pure pollucite according to the x-ray analyses.

S. A. Gallagher spent the first three months of 1976 at PNL in the laboratory of W. J. Gray. Financial assistance was provided by The Northwest College and University Association for Science (NORCUS). The objective of this stay was to continue thermal stability characterization of the aluminosilicates and supercalcine using the PNL thermogravimetric analyses facilities.

The thermogravimetric analysis was performed in a SiC tube furnace at a temperature of 1200°C.

* COO-2510-8, December 12, 1975, pp 9-10.

** Gelwhite L has somewhat less than the required 1Al/2Si ratio.

Figure 1. TGA of Cesium Aluminosilicates.

One gram pellets 1/2" in diameter were suspended from a milligram balance on a small Pt dish into the alumina tube inside the furnace. A downward air flow of $1 \text{ ft}^3 \text{ hr}^{-1}$ was maintained during each run. The weight loss was recorded continuously as a function of time, and the vapor species were collected on a Pt coated cold finger for analysis by x-ray fluorescence and atomic absorption spectrometry. The results are shown in Figure 1.

The weight losses for each sample were not significantly different and are all below 1% for 24 hrs. The bar graphs show the relative amounts of the metallic elements in the vapor species collected on the cold finger for the major constituents in each sample. All the samples contained some Na and K since the clays which were used in their preparation contained small amounts of Na and K. No alumina or silica was found in any of the material collected on the cold finger. In each case, it is the alkali elements which vaporize. Cesium is the predominant element in the vapor species, constituting 70-80 wt% of the total. The sample containing known amounts of Na and K lost more Na and less Cs, but more Na and less Cs were present in the original sample. It could indicate that Na is less strongly bound than Cs in the pollucite structure.

If the observed weight loss is due only to alkali volatilization, then the percentage of the original Cs present in the samples that would be volatilized is 0.6% for CsAlSiO_4 , 1.5% for pollucite, and 7.3% for $(\text{Cs}_{.74}\text{Na}_{.13}\text{K}_{.13})\text{AlSi}_2\text{O}_6$ in 24 hrs. Since both natural pollucite and clays contain water and $(\text{OH})^-$ groups, these percentages could be even lower if any water or $(\text{OH})^-$ groups incorporated into the test specimens had been lost along with the vapor species which were actually collected. This problem will be addressed in the future.

A great deal of time was spent looking for the cause of the substantial discrepancies in the weight losses recorded for the two techniques, i.e., weight loss of a pellet fired in a large furnace and the TGA. Samples size and surface area were approximately equal for both methods. Therefore, such things as temperature at the sample surface and air flow rate were investigated as possible sources of the discrepancy. In work now being carried out by W. J. Gray, it looks as though a steep temperature gradient near the sample may prove to be the cause of the differences in weight loss for the two methods.

In spite of an apparently slightly greater Cs volatilization in the TGA work, pollucite is still the best candidate for a Cs fixation phase in supercalcine. It is more readily synthesized than CsAlSiO_4 and can be readily crystallized in the whole waste with the addition of aluminum nitrate and a soluble form of silica. CsAlSiO_4 is thermally unstable and decomposes into an assemblage containing pollucite when heated. Pollucite has a very small weight loss at typical waste processing temperatures and times (for example, much less than 1% at 1150°C for two hours). It has also been reported by Isaacson and Brownell* that pollucite has a very low water leaching rate.

Work carried out since returning to Penn State consisted of sealed Pt tube runs for the investigation of the isothermal sections of the phase diagram $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$. Results to date show that reaction times of even several weeks at 1200°C are not sufficient to produce a steady state phase assemblage when using dry powders made into pellets as starting materials. Alternative starting materials may produce a more rapid approach to equilibrium. Results also suggest that the compound $\text{CsAlSi}_5\text{O}_{12}$ (1:1:10) reported by Ito** is an equilibrium phase but that $\text{CsAlSi}_3\text{O}_8$ (1:1:6) reported by Borutskaya*** cannot be formed under these synthesis conditions.

* Isaacson and Brownell, Ultimate Storage of Radioactive Wastes in Terrestrial Environment, Report No. ARH-SA-126, August 1972.

** Ito, Am. Min. 61 170-1 (1976).

*** Borutskaya, Dokl. Akad. Nauk SSSR 222 (4) 924-7 (1975).

3.0 Ruthenium Fixation

3.1 Review of Candidate Phases for Ruthenium Fixation (R.G. Johnston)

We have continued the investigation of the suitability of the perovskite phases SrRuO_3 and CaRuO_3 for the fixation of Ru in a thermally stable phase in supercalcine. These perovskite structure oxides, as explained in a previous report, fit the criteria of easy formation and good thermal stability at expected supercalcine processing temperatures in the range of 1050°C - 1200°C . The refractory perovskites are also typically leach resistant.

The phase SrRuO_3 was chosen for more extensive evaluation over the other perovskite phases CaRuO_3 , BaRuO_3 and LaRuO_3 . It exhibited superior thermal stability to CaRuO_3 and BaRuO_3 . LaRuO_3 possesses even greater thermal stability than SrRuO_3 , but will not form in supercalcine due to the overwhelming preference of the rare earths for the apatite structure phase, as noted in previous reports.

The thermal decomposition data are given in Figure 2. Section (a) of this Figure is data obtained by Gandhi et al.* of Ford Motor Co. These data were obtained from research on Ru-containing oxides for use as NO_x catalysts in automotive exhaust systems. The measurements were performed on high surface area powders in a high velocity stream of 97.5% N_2 , 2.5% O_2 gas flowing at a space velocity of 100,000/hr. (cm^3 gas at NTP per cm^3 catalyst bed volume per hour). These are not the conditions expected during supercalcine crystallization, but this data does serve to rank the thermal stability of candidate phases.

The data in parts (b) and (c) were obtained from firings of varying lengths on pressed pellets of oxide in SiC muffle furnaces in "stagnant air", i.e., where convection is the only gasflow mechanism. All measurements were converted to %Ru loss per hour to correspond to Gandhi's data. Note that the variance of gasflow and active surface area conditions produce striking differences in Ru loss figures at a given temperature. More will be said about this in a following section.

As can be seen from Figure 2, with the above mentioned exception of LaRuO_3 , SrRuO_3 possesses the best stability of the candidate oxides for Ru fixation.

3.2 Compatibility Studies (R.G. Johnston and M.T. Davidson)

A key requirement for a fixation phase in supercalcine is compatibility with the other supercalcine phases during the short crystallization firings (1000 - 1200°C) and indefinitely at waste storage temperatures ($T < 800^\circ\text{C}$). Preliminary studies detailed in Report COO-2510-8 indicated that SrRuO_3 probably would coexist with the other phases in supercalcine, and would form, if RuO_2 could be kept intimately mixed with it long enough. A more detailed examination of the compatibility question has been carried since then.

Data from the ruthenium compatibility study (RCS) runs are compiled in Table 1. For these runs, unless otherwise mentioned, preformed oxide phases (e.g., $\text{CsAlSi}_2\text{O}_6$, SrMoO_4) were intimately mixed in the appropriate amounts, pressed into 1/4 inch cylindrical pellets at 100,000 psi and fired in both covered and uncovered Pt cups. A detailed discussion of the key runs follows:

RCS 18 Series: This series of runs examined the compatibility of SrRuO_3 with the simulated PM-4b pollucite composition ($\text{Cs}_{0.84}\text{K}_{0.16}\text{AlSi}_2\text{O}_6$ where K is a stand-in for Rb). One to one molar mixtures of these oxides were fired at 800, 1050, 1150, and 1200°C for varying times. Rather large weight losses were

*Gandhi, Stephen and Shelef, Mat. Res. Bull., 10, 873 (1975).

Figure 2. Thermal Stability of Ru containing Phases

- a) Ru loss rate as a function of temperature, on high surface area powders under flowing 25% O_2 in N_2 at 100,000 /hr. (from Gandhi, et.al)
- b) Ru loss rate as a function of temperature, on pelletized oxides in stagnant air. c) Ru loss rate as a function of temperature for pellets of RuO_2 in stagnant air.

Table 1

Ruthenium Compatibility Studies and Results

Run #	Reaction	Firing time	Temp(°C)	Wt. Loss (%)	X-ray Phase Assemblage
RCS 18	$SR+P_{ss} \rightarrow SR+P_{ss}$	6 hr	1050	16.0	$VS-SR+S-P_{ss}+W-Sr_2Al_2SiO_7+VW-RuO_2+VW-SrSiO_3$
18A	" "	2.8 hr	1050	10.0	" "
18B	" "	12 days	800	6.2	$VS-SR+VS-P_{ss}+W-RuO_2+VW-Sr_2Al_2SiO_7$
18C	" "	2 hr	1200	25.0	$S-P_{ss}+S-RuO_2+M-Sr_2Al_2SiO_7+VW-SrSiO_3$
18D	" "	2 hr	1150	5.3	$VS-SrRuO_3+S-P_{ss}+W-RuO_2+M-Sr_2Al_2SiO_7$
RCS 19	$SR+S_{ss} \rightarrow SR+S_{ss}$	6 hr	1050	<1	$VS-S_{ss}+VS-SR$
RCS 20	$SR+A_{ss} \rightarrow SR+A_{ss}$	6 hr	1050	2.1	$M-SR+VS-A_{ss}$
20A	$4SR+A_{ss} \rightarrow 4SR+A_{ss}$	2.8 hr	1050	1.0	$VS-SR+M-A_{ss}$
20B	$SR+1/2A_{ss} \rightarrow SR+1/2A_{ss}$	2 hr	1200	2.6	$M-SR+S-A_{ss}$
RCS 21	$SR+S_{ss}+P_{ss} \rightarrow SR+S_{ss}+P_{ss}$	6 hr	1050	9.0	$S-SR+S-S_{ss}+S-P_{ss}+W-RuO_2+M-Sr_2Al_2SiO_7+VW-SrSiO_3$
21A	" "	2.8 hr	1050	4.7	$S-SR+S-S_{ss}+S-P_{ss}+W-RuO_2+VW-Sr_2Al_2SiO_7$
RCS 22	$SR+P_{ss}+A_{ss}+S_{ss} \rightarrow SR+P_{ss}+A_{ss}+S_{ss}$	6 hr	1050	4.4	$S-A_{ss}+M-S_{ss}+M-P_{ss}+W-RuO_2+VW-Sr_2Al_2SiO_7$
22A	" "	2.8 hr	1050	2.3	" "
RCS 23	$SR+Fe_2O_3 \rightarrow SR+Fe_2O_3$	2 hr	1050	1.4	$VS-SR+M-SrFe_{12}O_{19}$
23A	" "	2 hr	1200	3.1	$VS-SR+M-SrFe_{12}O_{19}$
RCS 24	$SR+2S_{ss}+P_{ss}+1/2A_{ss}+FeO_{1.5} \rightarrow SR+2S_{ss}+P_{ss}+1/2A_{ss}+FeO_{1.5}$	2 hr	1050	1.7	$S-A_{ss}+S-S_{ss}+W-P_{ss}+W-SR+VW-Sr_2Al_2SiO_7$
24A	" "	2 hr	1200	5.6	$S-A_{ss}+S-S_{ss}+W-P_{ss}+VW-SR+VW-Sr_2Al_2SiO_7$
RCS 25	$SR+ZrO_2 \rightarrow SR+ZrO_2$	2 hr	1050	1.8	$VS-SR+S-ZrO_2$
25A	" "	2 hr	1200	13.0	$S-SR+S-SrZrO_3+M-ZrO_2+M-SrZr_{1-x}Ru_xO_3(?)$
RCS 26	$SR+2S_{ss}+P_{ss}+1/2A_{ss}+FeO_{1.5}+ZrO_2 \rightarrow SR+2S_{ss}+P_{ss}+1/2A_{ss}+FeO_{1.5}+ZrO_2$	2 hr	1050	1.8	$M-A_{ss}+M-S_{ss}+W-ZrO_2+W-P_{ss}+VW-SrRuO_3+VW-RuO_2$
26A	" "	2 hr	1200	4.5	$S-S_{ss}+M-A_{ss}+W-ZrO_2+W-P_{ss}+VWRuO_2$
26B	" "	12 days	800	3.0	$S-A_{ss}+M-S_{ss}+M-SR+M-ZrO_2+M-P_{ss}+W-FeO_{1.5}$
26C	" "	10.5 days	840	3.4	$S-A_{ss}+M-S_{ss}+M-ZrO_2+M-SR+M-P_{ss}+W-FeO_{1.5}$

RCS 31	$CR+2S_{ss}+1/2A_{ss}+FeO_{1.5}+2ZrO_2+P_{ss}$ $+CR+2S_{ss}+P_{ss}+1/2A_{ss}+FeO_{1.5}+2ZrO_2$	12 days	800	1.9	$S-A_{ss}+M-S_{ss}+M-ZrO_2+W-P_{ss}+W-CR+W-FeO_{1.5}$
31A	"	2 hr	1050	1.9	$M-A_{ss}+M-S_{ss}+M-ZrO_2+W-P_{ss}+W-RuO_2+VW-CR$
31B	"	2 hr	1200	7.2	$M-A_{ss}+M-S_{ss}+W-RuO_2+W-ZrO_2$
RCS 32	$P_{ss}+CR+P_{ss}+CR$	12 days	800	7.2	$VS-P+S-CR+W-RuO_2+VW-Ca_2Al_2SiO_7$
32A	"	2 hr	1050	7.0	$VS-P+S-CR+W-RuO_2+W-Ca_2Al_2SiO_7$
32B	"	2 hr	1200	28.0	$S-P+S-RuO_2+VW-Ca_2Al_2SiO_7$
RCS 33	$P+SR+P+SR$	12 days	800	7.4	$VS-P+VS-SR$
33A	"	2 hr	1050	10.0	$VS-P+VS-SR+VW-SrSiO_3$
33B	"	2 hr	1200	31.0	$S-P+M-SR+W-SrSiO_3$
RCS 34	$P+CR+P+CR$	12 days	800	8.9	$VS-CR+S-P$
34A	"	2 hr	1050	9.6	$VS-P+VS-CR$
34B	"	2 hr	1200	33.0	$VS-P+M-CR+W-\alpha-CaSiO_3+W-Ca_2Al_2SiO_7$
RCS 35	$SR+1/2A_{ss}+2S_{ss}+2ArO_2$ $+SR+1/2A_{ss}+2S_{ss}+2ZrO_2$	2 hr	1050	2.0	$VS-A_{ss}+VS-S_{ss}+S-SR+M-ZrO_2$
35A	"	2 hr	1200	6.5	$VS-A_{ss}+VS-S_{ss}+S-SrZrO_2+M-ZrO_2$

X-ray intensities: VS=Very Strong, S=Strong, M=Medium, W=Weak, VW=Very Weak

Abbreviations: CR=CaRuO₃; SR=SrRuO₃; A_{ss}=Ca₂Nd₈[SiO₄]₆O₂; S_{ss}=(Sr_{0.75}Ba_{0.25})MoO₄; P_{ss}=(Cs_{0.84}K_{0.16})AlSi₂O₆; P=CsAlSi₂O₆

observed, particularly at 1200°C where a 25.8% weight loss was noted. A "worst case" weight loss indicates that about half of the Ru and Cs present could have been lost.

In the diffractograms of the 1200°C test, no SrRuO_3 is seen, but RuO_2 , pollucite, and phases which turned out to be $\text{Sr}_2\text{Al}_2\text{SiO}_7$ (strontium gehlenite) and SrSiO_3 are plainly seen. These additional phases were also seen in the 800°C, 12 day run, but to a much lesser degree.

Apparently both Cs and Ru are being lost, as RuO_2 is visible in the diffractograms. To test which loss is predominate, a silica tube test was conducted. In this test, a pellet of RCS18 was fired near the sealed end of a silica glass tube, the open cold end of which (outside the furnace) was plugged with polyester fiber. Indirect evidence from this test (frothing of the tube by $\text{CsO}_{0.5}$ vs. RuO_2 deposition) suggests that the majority of the weight loss in this case is due to Cs volatilization. The losses are easily differentiated, with RuO_2 forming its typical black ring near the furnace edge. The frosting observed was much greater than that seen when a similar amount of pollucite of the same composition was given the same treatment by itself. Note that the weight loss in this case is much less than that of any other tests above 1000°C.

These results show that SrRuO_3 and pollucite can attack one another and thereby allow the volatilization of both Cs and Ru species. Left behind is strontium gehlenite and SrSiO_3 in roughly equimolar amounts, and such pollucite as remains after the SrO released from SrRuO_3 is exhausted. The large proportion of RuO_2 seen in the diffractograms indicates that thermal decomposition of SrRuO_3 plays only a small role in the results seen here. The reaction rate is definitely temperature dependent, and probably is not complete after 2 hours at 1200°C. A possible equation for this reaction is:

It should be noted that gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) is found in nature to show stoichiometry variation of the form $\text{Ca}_2\text{Al}(\text{Al},\text{Si})_2\text{O}_7$, with appropriate charge balancing. Such variation in the stoichiometry of $\text{Sr}_2\text{Al}_2\text{SiO}_7$ could explain why neither $\text{AlO}_{1.5}$ nor SiO_2 are seen in the diffractograms.

RCS 19: This run tested the compatibility of SrRuO_3 with the scheelite solid solution ($\text{Sr}_{0.75}\text{Ba}_{0.25}\text{MoO}_4$). As expected, these phases were perfectly compatible, showing very small weight loss. This single experiment, a long firing at 1050°C, was judged to show sufficient compatibility.

RCS 20 Series: This series tested the compatibility of the apatite solid solution (represented by $\text{Ca}_2\text{Nd}_8[\text{SiO}_4]_6\text{O}_2$) and SrRuO_3 . Weight losses were small, in the range of 1 - 2.7%, and no additional phases were observed. The majority of this weight loss was probably water adsorbed on, or incorporated in, A_{55} , as indicated by a fortunate mixing error. In runs at 1050°C, a mix containing 4 SrRuO_3 to 1 A_{55} lost half as much weight as a mix fired twice as long and containing a 1:1 SrRuO_3 - A_{55} ratio. The question of water in A_{55} is now being examined. These phases are judged to be compatible.

* At several points in this discussion, a "worst case" weight loss will be mentioned. Such a weight loss is based on the weight percent of $\text{CsO}_{0.5}$ and RuO_2 present in the run. These are potential resultants from the breakdown of pollucite and SrRuO_3 , and are volatile in air at the reaction temperatures. The "worst case" weight loss requires $\text{CsO}_{0.5}$ and RuO_2 to be the only species being volatilized, and transforms the recorded weight loss to a percentage of the initial amounts of these species calculated to be present. We must recognize that residual volatiles are present in the various supercalcine phases, and in supercalcine itself. The proportion of such volatiles present in the material volatilized from a given experiment will have a strong effect on the true proportion of Cs and Ru lost from the run, particularly if the recorded weight loss is small. The question of residual volatiles in these species is now under examination.

RCS 23 Series: For the moment, descriptions of RCS 21, 22, and 24 will be skipped so that the results of two other two-phase compatibilities may be discussed. In RCS 23 and 23A, the compatibility of SrRuO_3 and Fe_2O_3 were examined. Both experiments yielded $\text{SrRuO}_3 + \text{SrFe}_{12}\text{O}_{19}$, an analog of magnetoplumbite. This reaction could consume at maximum 17% of the available SrRuO_3 in this run (which possesses twice the Fe_2O_3 with respect to SrRuO_3 as is seen in supercalcine). At 1200°C in 2 hours, according to the observed weight losses, this reaction is roughly half-way to completion. No residual RuO_2 or Fe_2O_3 were observed, although quantities present were probably insufficient for detection by x-ray diffraction.

RCS 25 Series: As noted in Report COO-2510-B, when only enough SrO is present to react with either RuO_2 or ZrO_2 , SrO preferentially reacts with RuO_2 at 1050°C . However, some SrZrO_3 will also form. A two hour compatibility test conducted at 1050°C showed little or no reaction of ZrO_2 with SrRuO_3 , and very small weight losses. However, at 1200°C they do interact, resulting in the phase assemblage shown in Table 1. About 37% of the available RuO_2^* is lost by volatilization. These results indicate that SrO has a greater affinity for RuO_2 at and below 1050°C , but a greater affinity for ZrO_2 at 1200°C .

RCS 21, 22 and 24 Series: In these compatibility runs, S_{ss} , $\text{S}_{\text{ss}} + \text{A}_{\text{ss}}$, and $2\text{S}_{\text{ss}} + 1/2 \text{A}_{\text{ss}} + \text{Fe}_2\text{O}_3$ (to approximate a true supercalcine mix) respectively were added to $\text{SrRuO}_3 + \text{pollucite}$. These runs showed no changes other than those observed in RCS 18. S_{ss} , A_{ss} , and Fe_2O_3 apparently do not inhibit nor promote the $\text{SrRuO}_3 - \text{pollucite}$ interaction. No Fe_2O_3 was observed in RCS 24, but its diffraction peaks were weak to begin with. No $\text{SrFe}_{12}\text{O}_{19}$ was observed in this run, nor was any RuO_2 . The absence of $\text{SrFe}_{12}\text{O}_{19}$ indicates that the $\text{SrRuO}_3 - \text{pollucite}$ reaction predominates, as $\text{FeO}_{1.5}$ was seen in RCS 26. RuO_2 may have been present in amounts less than required for x-ray detection. Worst case weight losses were about 80% of those seen in RCS 18 for RCS 21, 22, and 24.

RCS 26 Series: Here we have taken RCS 24 and added the percentage of ZrO_2 appropriate to the supercalcine mixes. (The formulation used in this run is based on Supercalcine 76-2, see Section 6.3). A number of tests were conducted, including very long runs at 800° and 840°C , temperatures in the range of the centerline storage temperatures along the waste canisters axis. The weight losses observed at 1050° and 1200°C were comparable to those in previous runs on a "percent of volatiles lost" basis. After 2 hours at 1200°C , SrRuO_3 is no longer detectable by x-ray diffraction. P_{ss} weakens visibly in the diffractograms. No extraneous phases are observed, although indications are that weight loss is here also a result of the pollucite - SrRuO_3 interaction. RuO_2 and $\text{Sr}_2\text{Al}_2\text{SiO}_7$ are probably present below the limits of x-ray detection. In the 800°C runs, both pollucite and SrRuO_3 weaken visibly.

RCS 31 Series: This group of runs is RCS 26 with CaRuO_3 substituted for SrRuO_3 . The weight losses observed are comparable to those seen in RCS 26 at 800°C and 1050°C . At 1200°C the weight loss is roughly 75% greater. The phase assemblages seen are also comparable to those shown in RCS 26 at 800 and 1050°C , although RuO_2 is barely visible in 31A. At 1200°C the resemblance ends, with pollucite, SrRuO_3 , and Fe_2O_3 disappearing. Of the weak residue peaks, only RuO_2 can be identified with certainty. As expected, CaRuO_3 is less stable in supercalcine.

RCS 32 Series: This series and the two following were designed to help pin down exactly what was happening in the pollucite - SrRuO_3 compatibility tests. In RCS 32, P_{ss} was mixed with CaRuO_3 and fired as shown in Table 1. The behavior followed that of RCS 18 very closely, producing Ca-analog's to the phase assemblages seen in RCS 18. CaSiO_3 was not seen. The weight losses were comparable to those in RCS 18, but somewhat higher.

RCS 33 and 34 Series: Pollucite can exhibit stoichiometry variation, as has been noted previously. K and Na can be substituted for Cs. Such substitution will occur in supercalcine. Such substitutions were incorporated in the P_{ss} used in RCS 18 and 32. How, then, does an unsubstituted pollucite,

* "Worst case" weight loss.

$\text{CsAlSi}_2\text{O}_6 = \text{P}$, interact with SrRuO_3 ? RCS 33 and 34, mixes of SrRuO_3 and CaRuO_3 with $\text{CsAlSi}_2\text{O}_6$ respectively, were designed to answer this question. With these runs comparisons could be made with RCS 18 and 32.

Distinct differences were observed between RCS 18 and 32, containing $(\text{Cs,K})\text{AlSi}_2\text{O}_6$, and RCS 33 and 34, containing $\text{CsAlSi}_2\text{O}_6$. For all firings, the weight losses of RCS 33 and 34 were roughly 15% higher than those seen in RCS 18 and 32. The only 800 or 1050°C run whose diffractograms showed phases other than pollucite and SrRuO_3 was RCS 33A, which possessed small amounts of SrSiO_3 . Additional phases were seen in all 800 and 1050°C firings of RCS 18 and 32. At 1200°C, SrSiO_3 was prominent in RCS 33, rather than both SrSiO_3 and gehlenite as in RCS 18. In RCS 34B (1200°C), $\alpha\text{-CaSiO}_3$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ were present.

Two notable differences were observed between the RCS 18 and 32 series and the RCS 33 and 34 series. First, SrRuO_3 and CaRuO_3 did not vanish for RCS 33 and 34 at 1200°C as they had for RCS 18 and 32. These phases are still present in medium strength in the diffractograms. Secondly, no free RuO_2 is observed in any of the diffractograms from RCS 33 and 34. It was present in all of the RCS 18 and 32 series diffractograms. This fact, together with the higher weight loss, may be taken to indicate that a layer volatilization of Ru oxides has taken place. The evidence indicates that $\text{CsAlSi}_2\text{O}_6$ still interacts destructively with SrRuO_3 , but not as rapidly as does $(\text{Cs}_{0.84}\text{K}_{0.16})\text{AlSi}_2\text{O}_6$. In the case of RCS 33 and 34 the reaction rate between pollucite and Sr or CaRuO_3 is probably comparable to the rate of Ru oxide loss, as is indicated by the absence of RuO_2 from their diffractograms.

RCS 35 Series: This series is RCS 26 less Fe_2O_3 and P_{ss} . As expected from the results of RCS 25, the phase assemblage is compatible at 1050°C, but not at 1200°C. At 1200°C, SrRuO_3 is replaced by SrZrO_3 and some Ru oxides are lost. RuO_2 was not visible in the diffractograms of this series.

Discussion

Also noteworthy are the partial results of RCS 44 and 45. In these tests pellets containing Supercalcine 75-2 (uncrystallized and crystallized, respectively) and 7 atomic% Ru (with respect to the other waste ions) in the form of SrRuO_3 were fired at 1150°C for 2 hours in silica tubes as described for RCS 18D. With tube frosting and RuO_2 coating as a very rough guide, equivalent amounts of Cs and Ru species appear to have been volatilized. Weight losses seen in RCS 45 were roughly 0.7%. The striking difference between this and the weight losses of the muffle furnace runs is probably due to the difference in convective airflow between the two systems.

Although SrRuO_3 is very temperature stable by itself, and appeared to be compatible with other phases in supercalcine in preliminary compatibility studies, more recent examinations have shown some flaws in this phase's utility. At the highest crystallization temperatures it has proven to be incompatible with the realistic supercalcine phases $(\text{Cs}_{0.84}\text{K}_{0.16})\text{AlSi}_2\text{O}_6$, Fe_2O_3 , and ZrO_2 . The compatibility tests described above show that the over-riding problem is interaction with the pollucite solid solution. The data given show that Fe_2O_3 , ZrO_2 , RuO_2 , Al-Si-O, and MoO_3 all form phases with SrO. The relative stability of these phases or, in other words, the "affinity" of SrO for these oxides can be presented schematically.

NbO_3 has the greatest SrO affinity and this is quite important to Mo fixation in S_{55} . SrO next goes after any available aluminosilicate and can therefore decompose pollucite. The data shows that SrO affinity for Fe_2O_3 , ZrO_2 , and RuO_2 varies with temperature. At 1050°C for instance, the phase $\text{SrRu}_{0.5}\text{Fe}_{0.5}\text{O}_3$ forms quite easily as shown by Fibb, et al.^{*}, and our own experiments. Neither RuO_2 or Fe_2O_3 get preferential treatment from SrO at this temperature.

3.3 Discussion of Ruthenium Fixation in Supercalcine (G.J. McCarthy and R.G. Johnston)

It should be clear to the reader who has followed the laboriously documented compatibility studies in the preceding section that, in spite of being the best candidate, SrRuO_3 cannot be used as a Ru fixation phase in supercalcine. Cesium fixation is a far more important problem, and it has been shown that $\text{CsAlSi}_2\text{O}_6$ and SrRuO_3 are not compatible at typical supercalcine crystallization temperatures. The Sr has a stronger affinity for alumina-silica than does Cs . Yet, an interesting observation was contained in those same runs which were demonstrating the inapplicability of SrRuO_3 . The Sr may have reacted with pollucite, but it left RuO_2 behind. In other words, a significant portion of the Ru present in any given sample had not been lost to volatilization. The question arises, how great a problem would Ru volatilization during crystallization of supercalcine be if it were simply left alone? Workers at PNL have found that very little Ru is volatilized during calcining. In a supercalcine formulation, this Ru should be present as RuO_2 after calcining and could remain in this form during crystallization, if it were compatible with each of the established supercalcine phases. Reference to Figure 2(c) indicates that a pure RuO_2 pellet loses about 5% of its Ru in an hour at 1200°C . Would a supercalcine pellet containing only 5 wt% RuO_2 not lose an even smaller percentage of its total Ru during a short 1200°C crystallization and/or coatings production step?

During the latter part of this last report period we began to address these questions. Using the same procedures described in the previous section, we tested the compatibility of RuO_2 with individual examples and combinations of the supercalcine phases, A_{55} , P , S_{55} , T_{55} , Fe_2O_3 and with supercalcine 75-2. Ruthenium dioxide was compatible with all of them as had been expected from the frequent observation of unreacted RuO_2 in the RCS runs. Weight losses were recorded, and, for the most part, these were encouragingly small. At this time, we have not been able to separate the weight losses due to Ru volatilization from those due to residual volatiles in the various supercalcine phases and in supercalcine itself. Efforts will be made in this direction during the coming months. However, silica tube tests at 1150°C on various RuO_2 - crystalline phase - supercalcine composites do show a dark haze in the cooler parts of the tube, which is indicative of some Ru volatilization.

Our current assessment of the Ru problem is that it appears to be best to leave Ru alone in supercalcine formulations, and to expect at least a small amount of Ru loss during crystallization if no other steps are taken to decrease Ru volatilization. In the coming months, we will be determining the magnitude of this Ru loss, studying the vaporization processes in the Ru-O system and checking for simple techniques which might reduce or eliminate Ru volatilization during supercalcine crystallization.

^{*} Gibb, et al., J. Solid State Chem., 14, 193-202 (1975).

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

Only a few compatibility studies on PW-4b-based waste were carried out during the last report period since the crystalline phase formation models were largely understood by that time. Two important questions addressed in this series of runs were the crystal chemical role of Ce in supercalcine and the effect on crystalline phase formation of the deliberate excesses of (Al + Si) added to insure Cs fixation as pollucite. The results of these CS runs confirmed the insights derived from the crystal chemical studies described in section 5.2, namely that the Ce in H&W can be incorporated into the A_{ss} phase along with the other RE's as long as sufficient silica is available. Up until then we had expected Ce to remain tetravalent in CeO_2 -based phases (F_{ss}), and indeed it did, except when large excesses of SiO_2 above that required for (P + A_{ss}) formation were added. Runs CS-81 and 81a clearly illustrate this effect. The phase formation model was:

CS-81a: identical model except for the addition of a three-fold excess of Al nitrate plus Ludox above that required for pollucite formation. This simulates the three fold excess added to supercalcine 75-2.

The phase assemblage in CS-81 was $A_{ss} + S_{ss} + F_{ss} + P$ plus very small amounts of T_{ss} and $\alpha\text{-Fe}_2\text{O}_3$. With the addition of excess alumina and silica the A_{ss} x-ray reflections grew in relative intensity, the F_{ss} phase all but disappeared and the T_{ss} reflections' intensity increased substantially. This is a clear manifestation of the variable role of Ce. When only the stoichiometric amount of SiO_2 is available, CeO_2 reacts with ZrO_2 to form the Ce-rich $(\text{Ce,Zr})O_2[F_{ss}]$ and Zr-rich $(\text{Zr,Ce})O_2[T_{ss}]$ phases. Here the Ce is tetravalent. When excess SiO_2 is available, the Ce becomes trivalent and is incorporated in A_{ss} , thereby increasing the proportion of A_{ss} . This liberates the Zr from F_{ss} and thus increases the relative amount of T_{ss} . Based on these compatibility runs, the basic crystalline phase formation model in supercalcine was modified to include Ce with the other RE in A_{ss} formation and thereby leave ZrO_2 to form T_{ss} . This will be reflected in the "Model B" and "Model C" supercalcine runs to be described in section 6.2 below.

In another series of CS-runs the question of substitution of some of the available Fe for additive Al in "ferric pollucite", $\text{Cs}(\text{Al}_{1-x}\text{Fe}_x)\text{Si}_2\text{O}_6$, was considered. It was first demonstrated that pure Fe-pollucite, $\text{CsFeSi}_2\text{O}_6$, could be readily formed from Cs and Fe nitrates plus Ludox. However the compatibility run of $(\text{CsFeSi}_2\text{O}_6 + \text{AlO}_{1.5})$ vs. $(\text{CsAlSi}_2\text{O}_6 + \text{FeO}_{1.5})$ showed clearly that the aluminosilicate was more stable. We will therefore continue to add Al nitrate in order to obtain the most effective Cs fixation as pollucite.

5.0 Apatite Crystal Chemistry in Supercalcine

Because the rare earths (RE) are the most abundant "constituent" of "clean" HLW's, the apatite structure phase into which the RE's crystallize is the most abundant phase in supercalcine. A major portion of our time during this report period was devoted to a number of apatite crystal chemical studies relevant to supercalcine crystallization.

5.1 Silicate Apatites (G. J. McCarthy and C. A. Smith)

A phase with the apatite structure has been unequivocally identified by x-ray diffraction as the major crystalline component of supercalcine. The best confirmation of a proper x-ray identification in a complex mixture is to prepare the pure phase of the proposed stoichiometry, confirm that a single phase has been formed by indexing all of its reflections and match its diffractogram to the appropriate set of reflections in the supercalcine diffractograms. Therefore, using experimental procedures similar to those for preparing supercalcine, the following silicate apatite structure phases containing alkaline earths and rare earths were synthesized:

The Nd was chosen as a stand-in for the RE in PW-4b, as is our established practice. The Gd phases were included in order to confirm the existence of the A_{ss} phase in Gd-rich PW-7-based wastes. All four phases were readily formed at 1100 to 1200°C in a few hours. Higher temperature firings (1400°C) were used to obtain sharper reflections for the complete x-ray analysis. Every reflection observed for each phase could be indexed on the hexagonal unit cell of the apatite structure. Complete indexed x-ray powder data* and computer least squares refined cell parameters are given in Appendix C.

In earlier reports we have discussed the various silicate apatite stoichiometries which have been proposed over the last decade or so. We elaborated on this somewhat in the preprint of the 12th Rare Earth Conference paper**. We should reiterate here also that the actual stoichiometry of the A_{ss} phase in supercalcine is still in question. The x-ray powder patterns of A_{ss} and $\text{Sr}_2\text{Nd}_8[\text{SiO}_4]_6\text{O}_2$ are very similar, but this does not prove that the A_{ss} in supercalcine 75-2 has that composition and stoichiometry. In fact, there is a wide range of stoichiometry for apatite phases consisting of AE, RE and silica, as is shown in Figure 3. The AE:RE ratio could vary from 6:4 to 2:8, if all of the literature reports used to prepare the figure are correct. In the coming months we will put some effort into identifying the actual apatite model forming in supercalcine both through continued crystal chemical study and through quantitative electron probe elemental analyses of individual A_{ss} crystals.

5.2 Cerium in A_{ss} (G. J. McCarthy, C. A. Smith and M. T. Davidson).

We first became suspicious of the proposed role of Ce in supercalcine when characterizing 75-2. The reflections of the F_{ss} phase were weaker than expected if Ce were all assigned to F_{ss} . We then showed through selected compatibility runs that the excess silica was combining with Ce in A_{ss} (see section 4.0).

* Partial support for obtaining this data was provided by the Joint Committee on Powder Diffraction Standards.

** G. J. McCarthy, "Crystal Chemistry of the Rare Earths in Solidified High Level Nuclear Wastes", Proc. 12th Rare Earth Conf., Vail Colorado, July 21, 1976 (in press).

Figure 3. Phases reported in the system $\text{AEO}-\text{RE}_2\text{O}_3-\text{SiO}_2$. Apatite structure phases have been reported in the "wedge-shaped" hatched region.

It was next necessary to go back one more step and make a brief crystal chemical study of Ce in A_{55} which was designed to answer the questions: how much Ce can be incorporated in A_{55} ?; what is the valence of Ce in A_{55} , 3+ or 4+?

The stoichiometries selected for study conformed to the following models:

where $x = 1, 2, 3, 4$

AE = Ca, Sr

The Ca compounds with $x = 1, 2$, and 3 readily formed an A_{55} phase but the phase with $x = 4$, $\text{Ca}_6\text{Ce}_4[\text{SiO}_4]_6$, could only be converted to an apatite structure phase by repeated firings at 1400°C . The first firing gave a white product which was identified by x-ray diffraction as $\text{CeO}_2 + \text{CaSiO}_3$ (pseudo-wollastonite). After several more days of firing the pellet became grey-black and gave a pure apatite pattern. It was obvious that the key step in forming the A_{55} was partial or complete reduction of Ce^{4+} to Ce^{3+} . The end member ($x = 4$) $\text{Ca}_6\text{Ce}_4[\text{SiO}_4]_6$ is an example of a phase at the most AE rich "tip" of the A_{55} "wedge" in Figure 3. This is only the second report of an apatite phase with stoichiometry *.

* The first was by A. G. Cockbain and G. V. Smith, Mineralog. Mag. 36 4-1 (1967).

For AE = Sr, only the phase with $x = 1$, $\text{Sr}_3(\text{Nd}_6\text{Ce})[\text{SiO}_4]_6\text{O}_{2-y}$, could be synthesized. All of the other products had major SrSiO_3 in the phase assemblages. The product for $x = 4$ was white and gave a sharp $\text{CeO}_2 + \text{SrSiO}_3$ pattern. This demonstrates that equilibrium in the reaction

is to the right. The contrast between the syntheses of the Ca and Sr versions of the $x = 4$ model is illustrated in Figure 4. Both were fired for the same time at 1400°C. In the Ca case, some or all of the Ce^{4+} was reduced to Ce^{3+} and the apatite formed, but in the Sr case, the combination of $\text{SrSiO}_3 + \text{CeO}_2$ was more stable.

Although it was not critical to supercalcine development, we did perform one test designed to gain insight into the valence of Ce and the corresponding oxygen concentration on the halide site. A specimen of the $x = 3$ model of the Ca- A_{ss} , $\text{Ca}_5(\text{Nd}_2\text{Ce}_3)[\text{SiO}_4]_6\text{O}_{2-x/2}\square_{x/2}$, was fired in pure oxygen and in hydrogen at 900°C with the idea that the oxygen treatment would stabilize more Ce^{4+} , and the hydrogen treatment more Ce^{3+} . Precision cell parameters were obtained for each product in order to look for the unit cell modifications which would accompany major changes in Ce valence (and thus ionic radius). The cell parameters were

	$\frac{a}{\text{\AA}}$	$\frac{c}{\text{\AA}}$	Volume
Oxygen firing	9.495(3)	6.980(2)	545.0(3)
As prepared in air	9.500(3)	6.982(2)	545.7(3)
Hydrogen firing	9.494(3)	6.978(2)	545.4(3)

The slight variations fall within the error of the measurements. There were no significant color changes among the specimens. It seems that the hydrogen did not reduce the specimen beyond that obtained in air. Thus, at this point, we propose that the valence of Ce is very close to 3+ and thus the halide sites in A_{ss} are essentially vacant. Direct confirmation of this hypothesis would require TGA in controlled atmospheres and perhaps higher temperatures. The analysis, however, is beyond the scope of this program.

In order to apply these results to supercalcine phase formation, it should be noted that the RE(Nd) to Ce ratio in PW-4b is about 3 to 1 in PW-4b and about 6 to 1 in PW-7. Thus, if Sr is used as the AE additive in supercalcine formulations, not all of the Ce can be incorporated into the $\text{Sr-}A_{ss}$ phase and some free CeO_2 (F_{ss}) will also be observed. However, if Ca is the AE additive, then a more stable A_{ss} phase will be formed which can incorporate all of the Ce. This explains beautifully why most, but not all, of the Ce in 75-2 was incorporated into the $\text{Sr-}A_{ss}$. A minor CeO_2 -rich F_{ss} was still observed in crystallized 75-2. However, it should be noted that the partial $[\text{PO}_4]$ for $[\text{SiO}_4]$ substitution in HLW A_{ss} may allow increased Ce^{3+} stabilization in $\text{Sr-}A_{ss}$. Wamaker* has reported synthesizing $\text{Sr}_{4.5}\text{Ce}_{4.5}[\text{SiO}_4]_{4.5}[\text{PO}_4]_{1.5}$, which has more Ce stabilization than we found in the pure silicate A_{ss} .

As a result of this work, in all subsequent supercalcine formulations Ca has been specified as the AE additive and Ce has been included with the other RE's (see sections 6.2 and 6.3).

5.3 Phosphate in A_{ss} (G.J. McCarthy and D.E. Pfoertsch)

PW-4b and especially PW-7 contain significant concentrations of phosphate which occurs in the HLW stream from decomposition of a fuel reprocessing chemical. We have assumed since the first

* W. Wamaker et al. Philips Res. Repts. 26 373 (1971).

Figure 4. Portions of the X-ray Diffractograms of the products from $\text{Ca}_5\text{Ce}_4[\text{SiO}_4]_6$ and " $\text{Sr}_5\text{Ce}_4[\text{SiO}_4]_6$ " syntheses.

introduction of the A_{55} phase that $[\text{PO}_4]$ tetrahedra would readily substitute for the $[\text{SiO}_4]$ tetrahedra in the apatite structure, with accompanying charge balancing cation substitutions. There was ample crystal chemical evidence to support this assumption*. Several syntheses of pure phases were carried out in order to demonstrate the existence of the phosphate-silicate made from PH-4b and PH-7 HLW's and to provide pure phases to PNL for radiation damage testing.

Table 2 lists the phases whose syntheses were attempted. As usual, the mixtures started as solutions, were dried and calcined and then fired at 1050 and 1200°C for 2 to 6 hours. In a few cases where the reactions looked incomplete the firing temperature was raised to 1450°C.

* Much of the work on phosphate-silicate apatite solid solutions was done by W. Wanmaker et al. Philips Res. Repts. 26 373 (1971) and J. Solid State Chem. 3 452 (1971).

Table 2
Phosphate and Phosphate-Silicate Apatites

Proposed Phase	Product(s) Identified by X-Ray Diffraction
$\text{Ca}_8\text{Nd}_2(\text{PO}_4)_6\text{O}_2$	<u>1050°C</u> : $\text{NdPO}_4 + \text{Ca}_3(\text{PO}_4)_2$ <u>1450°C</u> : $\text{Ca}_3\text{Nd}(\text{PO}_4)_3 + \text{glass (melted)}$
$\text{Ca}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$	<u>1050°C</u> : $\text{GdPO}_4 + \text{Ca}_3(\text{PO}_4)_2$ <u>1450°C</u> : $\text{Ca}_3\text{Gd}(\text{PO}_4)_3 + \text{glass (melted)}$
$\text{Sr}_8\text{Nd}_2(\text{PO}_4)_6\text{O}_2$	$\text{A}_{\text{ss}} + \text{minor Sr}_3(\text{PO}_4)_2$
$\text{Sr}_8\text{Gd}_2(\text{PO}_4)_6\text{O}_2$	$\text{A}_{\text{ss}} + \text{minor Sr}_3(\text{PO}_4)_2$
$\text{Ca}_3\text{Nd}_7(\text{SiO}_4)_5(\text{PO}_4)\text{O}_2$	pure apatite*
$\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)\text{O}_2$	pure apatite*
$\text{Sr}_3\text{Nd}_7(\text{SiO}_4)_5(\text{PO}_4)\text{O}_2$	$\text{A}_{\text{ss}} + \text{SrSiO}_3 + \text{Sr}_3(\text{PO}_4)_2 + \text{Sr}_3\text{Nd}(\text{PO}_4)_3 + \text{NdPO}_4(?)$
$\text{Sr}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)\text{O}_2$	apatite plus minor GdPO_4
$\text{Ca}_{3.5}(\text{Nd}_{3.25}\text{Gd}_{3.25})(\text{SiO}_4)_{4.5}(\text{PO}_4)_{1.5}\text{O}_2$	pure apatite*
$\text{Sr}_{3.5}(\text{Nd}_{3.25}\text{Gd}_{3.25})(\text{SiO}_4)_{4.5}(\text{PO}_4)_{1.5}\text{O}_2$	$\text{A}_{\text{ss}} + \text{SrSiO}_3 + \text{Sr}_3\text{Nd}(\text{PO}_4)_3$

* See Appendix C for complete x-ray powder data and computer least-squares refined cell parameters of this phase.

Before preparing phosphate-silicate solid solutions we first attempted to prepare the pure phosphate end members. As noted in the previous section, the Nd phase was a stand-in for the RE phase in PM-4b and the Gd phase was included because of the high Gd composition in PM-7.

The mixtures of Ca, RE and P oxides reacted to form NdPO_4 (monazite) + $\text{Ca}_3(\text{PO}_4)_2$ (whitlockite) instead of an apatite at both 1050 and 1200°C. Since these phases showed no sign of reacting, even after repeated firings, we raised the temperatures to 1450°C. The specimens melted and partially crystallized on cooling into a glass plus a phase with a body centered cubic x-ray powder pattern and a cell parameter near 9.9Å. The patterns could not be matched with anything in the JCPDS Powder Diffraction File. After some literature searching, the unknown was unambiguously identified as one of a class of $\text{AE}_3\text{RE}(\text{PO}_4)_3$ phases having the eulytite structure*.

When Sr was selected as the RE in the phosphate end member, the preparations each gave an almost pure apatite product. However, with the presence in the products of $\text{Sr}_3(\text{PO}_4)_2$ as a minor phase, even after repeated firings, we doubt that the Sr-phosphate- A_{ss} has the structure model chosen.

One useful insight from these four preparations is the greater ease at crystallizing the pure phosphate- A_{ss} when Sr was the AE. This may explain the rather puzzling observation that A_{ss} in supercalcine seemed to have incorporated some Sr even though sufficient Ca was available. Crystal

* First reported by G. Engel, Zeit. fur Anorg. u. Allgem. Chem. **387**, 22 (1972). Engel was unable to prepare phases with $\text{AE}=\text{Ca}$ so our synthesis of $\text{Ca}_3\text{RE}(\text{PO}_4)_3$ phases is original work.

chemical studies (eg. sections 5.1 and 5.2) have indicated that Ca-silicate- A_{ss} is more stable than Sr-silicate- A_{ss} . However, with the addition of $[PO_4]$ to the A_{ss} structure, there may be an increased stabilization of Sr in the AC sites. The next set of preparations indicated that the situation is somewhat more complex.

The $RE/[PO_4]$ ratio in PW-4b is close to 7/1. The next group of A_{ss} preparations in Table 4 was chosen to approximate this ratio. With the substitution of one $[PO_4]$ for $[SiO_4]$ in $AE_2RE_8[SiO_4]_6O_2$, the AE/RE ratio must be modified to maintain charge balance. The AE=Ca phases readily crystallized in the apatite structure, whereas the AE-Sr mixtures did not yield phase pure products. The RE=Gd mixture came closer to forming an apatite than the RE=Md mixture.

The $RE/[PO_4]$ ratio in PW-7 is about 7/2, which is approximated by the 6.5/1.5 ratio selected for the last two stoichiometries in Table 4. The use of both Nd and Gd as RE more closely simulates the RE distribution in PW-7. Again, the Ca- A_{ss} was easily synthesized but the Sr- A_{ss} could not be prepared as a pure phase.

In supercalcine 75-2, the only AE additive was Sr. The results just described imply that there should be considerable difficulty in crystallizing a Sr-silicate-phosphate A_{ss} , at least for the stoichiometries selected. Yet, a major A_{ss} phase was observed in diffractograms of 75-2 fired at temperatures as low as 850°C for two hours. None of the extra phases listed in Table 4 were observed in fired 75-2. This is further evidence that crystal chemical and compositional studies on the A_{ss} phase should continue, especially those aimed at better defining the stoichiometry and the roles of impurity ion substitutions.

6.0 Supercalcine Development (G. J. McCarthy and D. E. Pfoertsch)

A combination preprint and technical progress report on supercalcine development was recently issued*. The data and discussion contained therein will not be repeated here. The preprint (referred to below as "C00-2510-10") should be considered as an integral part of this Annual Report.

6.1 Consolidation of Supercalcine 75-2.

Consolidation of 75-2 by cold pressing and firing, both with and without sintering aides, was discussed in the last major report.** This work was continued during the early part of this year, but was phased-out when we learned of the significant progress in the adaptation of the disc pelletizer to supercalcine consolidation. Results of the work up to that time will be discussed.

A significant improvement in leaching resistance was obtained when a lead borosilicate (PBS) glass frit was added to 75-2 as a consolidation aide*. We felt that the use of a Corning Code 7740 ("Pyrex") glass frit would offer two advantages over this PBS frit. First, the 7740 has greater leaching resistance, so the composite should have a lower bulk leachability. Second, the 7740 softens at a much higher temperature, so higher crystallization temperatures should be possible before pellet deformation due to the softening of the glass begins.

As received spray supercalcine 75-2 was heated loose at 900°C for 2 hours in order to drive off most of the residual volatiles (H_2O , MO_x , CO_2). It was then mixed in a "shaker-mill" with selected amounts of a -200 mesh 7740 frit. One-half inch pellets of these mixtures, pressed at 25,000 psi, were placed in Pt boats and heated for one hour at 1100°C and 1200°C. Specimens with more than 14 wt% 7740 showed signs of partial melting at 1100°C. Those with more than 10 wt% 7740 were partially melted at 1200°C. The three day weight loss in a soxhlet leachability test on pure 75-2 fired at 1100°C was about 3.8 wt%. Figure 5 demonstrates how this leachability is markedly decreased with additions of increasing amount of 7740 frit, due primarily to the improved consolidation. The amount of frit added did not seem to make much difference when the firing temperature was 1200°C.

One reason that we will not emphasize this approach to supercalcine consolidation is that the addition of a glass reduces the level of thermodynamic stability built into the crystalline phase assemblage, i.e. the glass and the crystals are not thermodynamically compatible. One result of this incompatibility is that the glass can react with the crystalline phases and thereby eliminate the atomic-level fixation which is the "cornerstone" of the supercalcine concept. This effect is clearly demonstrated in Figure 6. A composite consisting of 90 wt% 75-2 plus 10 wt% 7740 (fired initially at 1100°C for one hour) was heated at 900, 1100 and 1200°C for three weeks. Weight losses were recorded at one to three day intervals. The losses at 900°C are relatively small, but even at the end of 21 days they seem to be steadily increasing. Losses at 1100°C are high during the first week of firing, but they level-off and show a more gradual increase during the next two weeks. At 1200°C, the loss rate is quite substantial at about one third of a percent per day.

The x-ray diffractograms of the products of these three week firings show a range of glass - supercalcine reaction varying from very little at 900°C to almost complete at 1200°C. Even after one hour at 1200°C, the intensities of the 75-2 reflections have been reduced to half of their 1200°C - no frit values. At the end of three weeks at 1200°C, only weak reflections of the phases less soluble in silicate glasses ($CeO_2[F_{SS}]$, $ZrO_2[T_{SS}]$ and S_{SS}), plus a remnant of the A_{SS} and P phases, remain. Although HLW storage temperatures in the 1100-1200°C range are not anticipated, these results highlight a potential problem in using glass frit consolidation aides with supercalcine.

The microstructure of the 90 wt% supercalcine 75-2/10 wt% 7740 composite fired at 1100°C for one hour was studied by scanning electron microscopy. In figure 7A we note the relatively porous nature

* G. J. McCarthy, "High Level Waste Ceramics: Materials Considerations, Process Simulation and Product Characterization", C00-2510-10. Presented at the ANS Annual Meeting, June 1976 and submitted to Nuclear Technology.

** C00-2510-8, December 1975, pp 47-53.

Figure 5. Variation of the 72 hr. Soxhlet leachability for supercalcine 75-2 to which Corning code 7740 frit had been added before a one hour firing at the designated temperature. (Each data point is averaged from 2-4 measurements).

Figure 6. Thermal Stability of a 75-2/7740 composite during three weeks of heat treatment at the designated temperature.

of the product. Most of the porosity varies in size from about 5 to 50 μm and is closed. Even at this magnification one can observe large crystals in a fine-grained crystalline matrix. An enlarged photomicrograph of the regions having these large crystals (Figure 7b) revealed that they were associated with the 7740 glass. Energy dispersive elemental analysis of these crystals, e.g., at point A, showed that the major constituents were RE's and Si. Shoulders on the Si peak also indicated the presence of P and Sr in this phase. This elemental composition is typical of the A_{SS} phase. At point B, the energy spectrum showed only Si and a small amount of Al. Pyrex (7740) is 81% SiO_2 , 13% B_2O_3 *, 4% Na_2O * and 2% Al_2O_3 . The elemental analysis*, plus the general vitreous appearance, suggest that this grey phase is the 7740 glass. Apparently the glass acted as a flux which enhanced the crystal growth rate of A_{SS} . In the fine grained matrix both A_{SS} and pollucite [P] crystals were identified. Potassium as well as Cs were detected in the crystals of P. At the time this work was terminated, no individual crystallites of T_{SS} or S_{SS} had been located.

* Na and B could not be detected with the particular attachment used in these analyses.

** C00-2510-8.

A

B

Figure 7. Photomicrographs of a composite of 90% supercalcine 75-2 and 10% 7740 after firing for one hour at 1100°C. See text for discussion.

6.2 Supercalcine Formulations Based on HLW PM-7.

In our last major report^{*} we described successful supercalcine formulations for PM-4b based HLW. More recent work has been oriented to PM-7 based HLW. The chief differences in the latter are significantly greater RE, $[PO_4]$, U and Fe concentrations plus a small amount of Na. Table 3 gives the compositions of two simplified PM-7 waste formulations in use at Penn State. Uranium was left out of PSUN-5 because, in the x-ray diffraction analysis of supercalcine products, the relatively high concentration of the intensely scattering UO_{2+x} phase would "swamp-out" the reflections of minor crystalline phases. However, after these phases had been identified, the U was added (PSUN-5a) and its effects on the phase assemblage and relevant properties were determined.

Table 4 is the current supercalcine phase formation model ("Model C"). It incorporates many of the observations and conclusions from the crystal chemical and compatibility studies performed over the last year. In Model C, all of the rare earths, including Ce, are to be crystallized in a Ca-silicate-phosphate- A_{ss} , Mo is fixed in the S_{ss} phase using the Ba and Sr available in PM-7 plus additional Sr and the alkalis Cs, Na and Rb(K as a stand-in) are fixed in pollucite. The elements Zr, Fe, Ni, Cr, and U in those runs where it is added, are left alone to form simple oxides (T_{ss} , SP_{ss} and F_{ss}). The small amount of Cd is assigned to A_{ss} .

Sixteen supercalcine formulations using the phase formation model in Table 5 were evaluated. The parameters under investigation included:

- The amounts of excess (Al+Si) necessary to fix Cs in pollucite, and the effects, if any, on the crystalline phase formation.
- The effects of excesses in AE(Ca+Sr) concentration above that specified in the phase formation model.
- The effects, if any, of U on the crystalline phase formation.

An error was made in preparing the first batch of PSUN-5a which, after its source was found, proved to be informative. A ten-fold excess of Na and K nitrates was added to the waste simulation. The supercalcine batches made from this waste showed obvious signs of waste volatilization (stained reaction bricks, frosted silica tubes) during the 1050 - 1200°C crystallization firings. Elemental analysis of the bricks showed that Cs, K, Cr, Fe and U were chiefly responsible for the stains. When the runs were repeated without the error in Na and K concentration, the extensive volatilization ceased. This error demonstrated the very undesirable effects of unfixed alkalis.**

It was found, again in these runs, that at least twice the amount of (Al+Si) necessary for Cs fixation as pollucite was required to prevent Cs volatilization in our lab scale simulations of calcination and crystallization firings. If the alkaline earth additions (Ca and Sr) were increased to 1.5 or more of the amount required in the phase formation model, signs of Cs volatilization reappeared even when twice the (Al+Si) for P formation was also present. It is apparent that the AE's, and especially Sr, are attacking the P phase (see section 3 for a further discussion of Sr effects on pollucite). It is also possible that the current phase model is calling for more AE than is being used in the A_{ss} crystallization. Two steps are being taken to determine if this is the case. First, we will lower the AE additions in a new series of lab-scale supercalcine formulations and record the effects on the phase

^{*} C00-2510-8.

^{**} Na volatilization was not detectable with the technique used.

Table 1

Simplified PW-7-Based Wastes

Component	Molarity in PW-7	Mole Percent PSUW-5	Mole Percent PSUW-5a
RE*	0.153	16.9	15.0
Gd	0.153	16.9	15.0
Ce	0.051	5.9	5.0
Zr	0.106	11.7	10.3
U	0.1195	-	11.5
Fe	0.100	11.0	9.8
[PO ₄]	0.100	11.0	9.8
Mo	0.095	10.5	9.3
Cs	0.051	5.6	5.3
Sr	0.027	3.0	2.6
Ba	0.027	3.0	2.6
Cr	0.012	1.3	1.1
Na	0.010	1.1	1.0
Rb(K)	0.010	1.1	1.0
Ni	0.005	0.6	0.5
Cd	0.002	0.2	0.2

* La, Pr, Nd, Pm, Sm, Eu, Y plus stand-in for Am and Cm. Ce not included with RE because role in either A_{ss} or $UO_{2+x}-CeO_2[F_{ss}]$ is possible.

formation, especially on Mo fixation in S_{ss} . Second, when we obtain samples of the new PIL supercalcline run (76-2; see section 6.3), we will perform quantitative elemental analysis on the A_{ss} phase with a sophisticated electron microprobe which was recently put into operation on campus*.

The crystalline phase formation, as characterized by x-ray diffraction, was in good agreement with phase formation model C. When the large excesses of (Sr+Ca) were added without corresponding excesses in the (Al+Si) additions, the pollucite reflections grew weaker. At the same time, the cell parameters of the S_{ss} phase were smaller, a sure indicator of major incorporation of Ca in (Sr,Ba)MoO₄. Strontium aluminosilicate reflections were stronger than usual (see C00-2510-10). It appears that the "unused" Ca replaced some Sr in S_{ss} and the Sr reacted with (Al+Si) to form aluminosilicates. This is a further indication of the need for more analysis of the A_{ss} stoichiometry in supercalcline so that alkaline earth additions may be minimized.

* More detailed compositional analysis was not performed on the A_{ss} crystals in Figure 7B because of the likelihood of 7740-"flux" interactions, which could invalidate any extrapolations to "non-fluxed" A_{ss} phases.

Table 4
Supercalcine Phase Formation Model C
(Based on PSUM-5a)

mM* in PSUM-5a	Proposed Phase Formation	Required Additives (mM)
350 {RE+Ce} 98 [PO ₄]	$39.6 \text{ Ca}_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2 \left. \vphantom{\text{Ca}_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2} \right\} A_{ss}$ $16.3 \text{ Ca}_8\text{RE}_2[\text{PO}_4]_6\text{O}_2$	210 Ca 238 Si
115 U } 103 Zr }	in $(\text{U,Zr})\text{O}_{2+x}[\text{F}_{ss}] + (\text{Zr,U})\text{O}_{2+x}[\text{T}_{ss}]$	- -
98 Fe } 11 Cr } 5 Ni }	in $(\text{Fe,Cr})_2\text{O}_3 + \text{SP}_{ss}$	- - -
93 Mo	93 $(\text{Sr,Ba})\text{MoO}_4[\text{S}_{ss}]$	93 Sr
53 Cs } 10 Rb(K) } 10 Na }	73 $(\text{Cs}_{0.72}\text{K}_{0.14}\text{Na}_{0.14})\text{AlSi}_2\text{O}_6$ Pollucite	73 Al 146 Si
26 Sr } 26 Ba }	in S_{ss}	-52 Sr
2 Cd	in A_{ss}	-2 Ca
1000 mM of PSUM-5a requires:		208 Ca 41 Sr 73 Al 384 Si

* millimoles

In those formulations where U phase formation was considered, an F_{ss} phase with cell parameters ranging from 5.37 to 5.40 Å (depending on firing temperature and time) had the most intense reflections in the diffractograms. Since the T_{ss} phase was either missing or had very weak reflections, we assume that some or most of the ZrO_2 was incorporated into this F_{ss} . It is also possible that some or all of the Ce had a greater affinity for this F_{ss} phase than for A_{ss} . Either or both of these substitutions could account for the lower cell parameter observed for F_{ss} than is typical of pure UO_{2+x} (5.44-5.48 Å). It is apparent that a study of the fluorite structure phases in the appropriate compositional region of U-Ce-Zr-O in air at 1000-1200°C would be very useful in supercalcine phase formation modeling, especially in the high-U PM-7 based wastes.

Table 5

New Supercalcine Formulation for Engineering Scale Tests

nM PH-7	Proposed Phase Formation	Required Additives
357 RE 100 PO ₄	$40.5 \text{ Ca}_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2 \left. \vphantom{\begin{matrix} 40.5 \\ 16.7 \end{matrix}} \right\} \text{A}_{ss}$ $16.7 \text{ Ca}_8\text{RE}_2[\text{PO}_4]_6\text{O}_2$	214 Ca 243 Si
106 Zr	in T _{ss}	-
95 Mo	95 [Sr,Ba]MoO ₄ [S _{ss}]	95 Sr
54 Cs 10 Rb(K) 10 Na	$74 (\text{Cs}_{0.72}\text{K}_{0.14}\text{Na}_{0.14})\text{AlSi}_2\text{O}_6[\text{P}]$	74 Al 148 Si
100 Fe 12 Cr 5 Ni	in SP _{ss} + oxides	- - -
27 Sr 27 Ba	in S _{ss}	-54 Sr
2 Ag 2 Cd	in A _{ss}	-4 Ca
907 nM		210 Ca 41 Sr 74 Al 391 Si

Supercalcine Formulation 76-2:

per liter of PSUN-5 add   0.210 L. of 1M Ca(NO₃)₂
                                          0.041 L. of 1M Sr(NO₃)₂
                                          0.148 L. of 1M Al(NO₃)₃

Includes twice the (Al+Si)
 required for (Cs+K+Na) fixation   0.539 L. of 1M LUDOX-A5

Waste loading: 68%   Fission Product Loading: 44%

6.3 Supercalcine Preparation at PNL

A second engineering scale spray calciner demonstration of supercalcine has been scheduled for PNL in the summer of 1976. The waste simulation will include all RE's, Zr, Mo, Cs, Fe, [PO₄], K (for Rb), Na, Sr, Ba, Cr, Ni, Ag and Cd in the concentrations found in PH-7. Table 5 gives the details of the phase formation model and the exact formulation. Waste loading is about 68%. It would have been somewhat higher if some of the other constituents of PH-7 which do not require fixation additives* had been included.

* U, Pd, Rh (and perhaps Ru - see section 3.3).

7.0 Development of Supercalcine for High Sodium Wastes (G.J. McCarthy, M. T. Davidson and D. E. Pfoertsch)

Up to this time the emphasis in supercalcine development has been oriented toward "clean" wastes such as PW-4b and PW-7. It was assumed that if supercalcine concepts were to be applied at all it would be in later reprocessing plants where the requirement of maintaining "clean" wastes would be built into the design of the plant. After the recent successful engineering-scale demonstration of the supercalcine concept with an PW-4b-based waste simulation and the scheduling of a PW-7-based run, we were asked to also include the high sodium "dirty" wastes in our development program.

High Na commercial wastes are generated by two means, neutralization of the acid PUREX waste with NaOH and mixing the intermediate level waste stream with the high level wastes. The former step was taken with the wastes in storage at the Nuclear Fuel Services (NFS) plant at West Lake N.Y., and the latter procedure is projected for the AGNS plant in Barnwell, S.C. Waste formulation PW-8a is typical of the NFS MLLW and is 1.2M in Na, 0.9M in Fe and 0.897M in all other ionic species.* PW-7a, the waste formulation projected for AGNS, is 0.59M in Na, 0.1M in Fe and 1.05M in all other ionic species. This means that PW-8a is 40 mole% Na and PW-7a is 34 mole% Na. Obviously, major modifications of supercalcine formulations will be necessary to adequately fix all of this highly volatile (above ~700°C) and highly soluble Na.

7.1 Sodium Aluminosilicate Scouting Runs.

Probably the only class of Na-containing oxides which have reasonable thermal stability (in the 1000 - 1200°C range) and leaching resistance are the aluminosilicates. Three Na aluminosilicates are known

NaAlSiO_4	{ Nepheline (stable to 1254°C) Carnegieite (1254 to 1526°C m.p.)
$\text{NaAlSi}_2\text{O}_6$	jadeite (high pressure phase, cannot be synthesized at one atmosphere)
$\text{NaAlSi}_3\text{O}_8$	albite feldspar (m.p. 1118°C)

It appeared that from this selection only nepheline (abbreviated "Ne") would be suitable. Albite has too low a melting point and, from earlier experience with crystallization of high SiO_2 gels, we knew that a batch made by the usual drying-calcining techniques could not be crystallized

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* excluding, H, OH, NO_3 which will be lost during calcining.

over the temperature-time range of interest. The obvious first step is to see how easy it will be to crystallize Ne and, since PW-8a is also 30 mole% Fe, to check on its compatibility with Fe_2O_3 . A mixture of the appropriate amounts of Na, Fe and Al nitrates plus Ludox (SiO_2 sol)* was dried, calcined at 600°C for 2 hours and fired at 900, 1050 and 1200°C for 2 hours. The product phase assemblage in all three cases was well crystallized $\text{NaAlSi}_3\text{O}_8$ plus $\alpha\text{-Fe}_2\text{O}_3$. There was no sign of melting. Thus, $\text{NaAlSi}_3\text{O}_8$ and Fe_2O_3 could be the two major phases in a PW-8a-based supercalcine formulation.

Although jadeite, $\text{NaAlSi}_2\text{O}_6$, cannot be synthesized at atmospheric pressure, its Fe analog aegirine, $\text{NaFeSi}_2\text{O}_6$, is easily synthesized. It might be possible that a solid solution of $\text{NaFeSi}_2\text{O}_6$ with the composition "NaAlSi₂O₆" could be synthesized by solid state methods if the temperature were kept low enough.** However, a mixture of components which would give $\text{Na}(\text{Fe}_{0.75}\text{Al}_{0.25})\text{Si}_2\text{O}_6$ melted even at 900°C .

In PW-8a there is approximately one Cs for every 20 Na. The next question addressed was whether $\text{NaAlSi}_3\text{O}_8$ would allow the ~5% replacement of Cs for Na. The crystallization product of this mixture was Ne plus a small amount of pollucite (P), $\text{CsAlSi}_2\text{O}_6$. The x-ray reflections were shifted to lower angles, a sign of some Cs solubility. But, the presence of free P showed that the Cs solubility in Ne was considerably less than 5 mole%.

All of these results were promising. Nepheline is a common rock forming mineral with reasonably low water solubility. Like most network silicates (including pollucite), it dissolves in strong mineral acids (e.g. HCl), so it would not be suitable for geological storage where unusually low pH solutions might be expected. However, most storage sites being considered would have slightly alkaline conditions if water were present. The other very important consideration is the low Na vapor pressure of nepheline expected at supercalcine crystallization temperatures. The next logical step in this quick evaluation is to check the compatibility of Ne with other important supercalcine phases such as S_{ss} , A_{ss} , T_{ss} etc.

7.2 Compatibility Studies Involving Nepheline

The experimental procedure was the same as described in previous reports. Nitrate solutions, NaNO_3 and a Ludox suspension were the starting materials. After a boil down with stirring the mixtures were calcined at 600°C for 2 hours, pelletized and fired at 950, 1050 and 1200°C for two hours.

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* We also established that Ne could be formed from a mixture of NaNO_3 and kaolinite clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) at 900°C and above.

** The $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ phase diagram indicates that the m.p. of aegirine (1310°C) is lowered by "NaAlSi₂O₆" additions (D.K. Bailey and J.F. Schairer, *J. Petrol.* 1, 130 (1966)).

Any sign of staining of the support bricks due to volatilization of alkalis was noted. Phases were identified by x-ray powder diffraction.

The compatibility of nepheline with individual and mixed phases observed in the products of "clean" HLW formulations are described below.

CS-150: $5\text{NaAlSi}_2\text{O}_6(\text{Ne}) + \text{CsAlSiO}_6(\text{P})$. All firings gave the same phase assemblage, Ne+P. The Ne had a slightly larger unit cell, and the P has a slightly smaller unit cell, than are observed in the pure phases. This confirms a small level of solubility of Cs in $\text{NaAlSi}_2\text{O}_6$ and Na solubility in $\text{CsAlSi}_2\text{O}_6$. The extent of solid solubility of these phases will be determined by S. A. Gallagher during the coming year. Thus, it is clearly established that Cs saturated nepheline is compatible with a Na saturated pollucite.

CS-151: $5\text{NaAlSiO}_4 + \text{CsAlSi}_2\text{O}_6 + 1/2\text{Ca}_3\text{Nd}_7[\text{SiO}_4]_5[\text{PO}_4]_2(\text{A}_{55})$. The compatibility of the apatite solid solution phase, the host for the rare earths and phosphate, was tested next. The diffractograms of all firings showed major A_{55} and P and only a small amount of Ne. The unavoidable conclusion is that some of the nepheline was incorporated in A_{55} , i.e. Na has another crystal chemical role in A_{55} . The only well established silicate A_{55} known to contain Na is $\text{NaRE}_{10}[\text{SiO}_4]_6\text{O}_2^*$ but work has recently appeared on phosphate A_{55} 's with as much Na as $\text{Na}_3\text{RE}_3\text{AE}_4[\text{PO}_4]_6\text{F}_2^{**}$. We also demonstrated in earlier reports that some $[\text{AlO}_4]$ can be substituted for $[\text{SiO}_4]$ in A_{55} . It is not surprising then that considerable $\text{Na}_2[\text{AlO}_4][\text{SiO}_4]$ (Ne written with two formula units) is soluble in A_{55} . The question of Na in apatites is critical to designing high-Na supercalcine formulations and will thus occupy a good deal of our time in the months to come.

This question is also important at the other end of the "Na Spectrum". A clear role for Na in A_{55} would establish another site for Na fixation in the basically "clean" formulations. The Na in PW-7 is 0.01M out of a total of 1.15M. This small amount is readily substituted into pollucite, $(\text{Cs},\text{Na})\text{AlSi}_2\text{O}_6$. Perhaps 0.02 or 0.03M Na would also be incorporated in P. If much more Na is present in the HLW, an additional fixation phase will have to be found. The formation of an apatite having the hypothetical formula $\text{Na}_3\text{CaRE}_6[\text{SiO}_4]_5[\text{PO}_4]$ in supercalcine would mean that in PW-7, where the total RE concentration is 0.36M, half that amount of Na (0.18M) could be crystallized in the A_{55} phase along with the RE, $[\text{PO}_4]$ and additive Ca and $[\text{SiO}_4]$. This would mean that current supercalcine phase formation models could be applied to HLW formulations containing up to ca. 0.2M Na. Thus, the crystal chemical and compatibility study of high Na apatites is very important to Na fixation in both "clean" and "dirty" HLW.

CS-152: $5\text{NaAlSiO}_4 + \text{CsAlSi}_2\text{O}_6 + 2\text{SrMoO}_4[\text{S}_{55}]$. A new phase, never before encountered in our studies, was observed in each of the firings of this assemblage of oxides. No nepheline was present in the products. Most of the SrMoO_4 had reacted with the Ne to form a cubic sodalite^{***} structure phase $\text{Sr}_2\text{Na}_6[\text{AlSiO}_4]_6(\text{MoO}_4)_2$ (or $6\text{NaAlSiO}_4 \cdot 2\text{SrMoO}_4$). Since there was one formula unit too little of Ne in the starting mixture, excess SrMoO_4 was also observed. Pollucite was compatible with both phases.

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

** I. Mayer et al, J. Solid State Chem. 11 33 (1974).

*** Sodalite is $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$ (or $6\text{NaAlSiO}_4 \cdot 2\text{NaCl}$).

A phase of this structure type has also been observed by workers at the Hahn-Meitner Institute* as one of the crystallized phases in their glass-ceramic waste forms. They call this phase Mo-nosean because of its analogy to the mineral nosean, $\text{Na}_8[\text{AlSiO}_4]_6(\text{SO}_4)$ (or $6\text{NaAlSiO}_4 \cdot \text{Na}_2\text{SO}_4$). The phase observed in CS-152 differs from this in that it has 2SrMoO_4 rather than Na_2SO_4 in the formula. Nevertheless, we shall call phases with CaMoO_4 or SrMoO_4 in the formula "Mo-nosean" (abbreviated "MoNo") in order to conform with the HMI precedent.

The crystallization of this structure type has several important implications for supercalcine development. First, since $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{MoO}_4)$ should also exist, it should then be possible to fix Mo without adding Sr by simply utilizing the large amount of Na already in the "dirty" wastes. Second, many other substitutions are known in this structure type, so it could become a host for some of the minor HLW constituents. For example, R. R. Neurgaonkar of our laboratory has shown that (SO_4) , (TeO_4) and (CrO_4) can substitute on the (MoO_4) sites.** Of course, Cl, Br and I readily substitute on these sites. These halides along with $[\text{SO}_4]$ are often troublesome trace constituents in HLW. Finally, this sodalite structure phase has the potential of being the first iodine fixation phase developed for supercalcine.

Clearly, a thorough crystal chemical and compatibility study of the sodalite structure type is also important to "dirty" waste supercalcine development and work has been initiated on this task.

CS-153: $5\text{NaAlSiO}_4 + \text{CsAlSi}_2\text{O}_6 + 2(\text{Zr}_{0.9}\text{Ca}_{0.1})\text{O}_{1.9}[\text{T}_{55}]$. After the RE's, Zr is the next most abundant constituent. In complex supercalcine formulations the tetragonal ZrO_2 phase is observed instead of the equilibrium monoclinic pure ZrO_2 phase. We have assumed that some of the Ca additive is stabilizing the T_{55} phase, so we have included a small amount of Ca in this mixture. The products of each firing contained He + P and monoclinic ZrO_2 , along with a significant amount of a poorly crystallized unknown phase. This was not a known Ca zirconate or silicate or zircon. The problem is probably with the Ca addition. Since the unknown phase did not occur in CS-155 (below) it is apparently not going to be stable in more complex phase assemblages.

CS-154: $5\text{NaAlSiO}_4 + \text{CsAlSi}_2\text{O}_6 + 2\text{Fe}_2\text{O}_3$. All products gave the same phase assemblage: $\text{P} + \text{He} + \alpha\text{-Fe}_2\text{O}_3$. Iron oxide is compatible with the P+He phases.

CS-155: $5\text{NaAlSiO}_4 + \text{CsAlSi}_2\text{O}_6 + 2\text{Fe}_2\text{O}_3 + 2\text{SrMoO}_4 + 2\text{ZrO}_2$. This is a combination of all of the phases in the first four runs. An 800°C firing was added. In all four firings the phase assemblage is $\text{A}_{55} + \text{MoNo} + \text{S}_{55} + \text{T}_{55} + \text{Fe}_2\text{O}_3 + \text{P}$. The degree of crystallinity starts as moderate and becomes high by 1050°C . With this run, eight (actually seventeen if the RE are considered separately) of the most abundant constituents of PW-8a have been crystallized, Na, Fe, RE, Zr, Mo, $[\text{PO}_4]$, Cs, Sr. The phase formation model needs to be modified to include the MoNo instead of He + S_{55} .

Three more compatibility runs were carried out, but in these the role of Mo in a sodalite structure phase was specified and the ratios of six major components, Na, Fe, RE, Mo, $[\text{PO}_4]$ and Cs were selected to correspond to the ratios in PW-8a. Table 6 gives the composition of a simplified PW-8a waste which will be used in formulations in the coming months. Since good crystallization was occurring at such low temperatures, an 800°C firing was added. Covered reaction crucibles were used and after each firing they were checked for any signs of Na and/or Cs volatilization.

* A. K. Dē et al. Am. Ceram. Soc. Bull. 55, 500 (1976).

** R. R. Neurgaonkar and F. A. Hummel, Nat. Res. Bull. 11 61 (1976).

Table 6
Composition of PSUM-8
(Based on HLN PM-8a)

Constituent	Molarity in PM-8a	Mole Percent
Na	1.200	43.89
Fe	0.901	32.96
RE (incl. Ce)	0.204	7.46
Zr	0.106	3.88
Mo	0.095	3.47
Cs+Rb	0.064	2.34
[PO ₄]	0.050	1.83
Cr	0.040	1.46
Sr	0.027	0.99
Ba	0.027	0.99
Ni	0.020	0.73
	2.734*	100.0

* The full PM-8a is 2.997M so this simulation contains 91.2% of the constituents in PM-8a.

CS-156: $6 \text{ NaAlSiO}_4 + 1/7 \text{ Ca}_3\text{Nd}_7[\text{SiO}_4]_5[\text{PO}_4]\text{O}_2$. The Na to RE ratio is close to that in PM-8a. The products of all of the firings, 800, 900, 1050 and 1200°C for 6 hours, gave well crystallized $A_{ss} + \text{Ne}$. There were no major shifts in the positions of the A_{ss} reflections compared to pure $\text{Ca}_3\text{Nd}_7[\text{SiO}_4]_5[\text{PO}_4]\text{O}_2$ (see Appendix C) which would have been a clear sign of substantial Ne incorporation in A_{ss} . However, due to the close similarity of the ionic radii of Na, Ca and Nd, little expansion or contraction of the unit cell may be occurring. This question will require further careful analysis. From this run we can conclude only that Ne is compatible with a Na-saturated A_{ss} .

CS-157: $3 \text{ Na}_8[\text{AlSiO}_4]_6(\text{MoO}_4) + \text{Ca}_3\text{Nd}_7[\text{SiO}_4]_5[\text{PO}_4]\text{O}_2$. We will call the sodalite structure phase, $6 \text{ NaAlSiO}_4 \cdot \text{Na}_2\text{MoO}_4$, Mo-sodalite ("MoSo") to distinguish it from $6 \text{ NaAlSiO}_4 \cdot 2 \text{ SrMoO}_4$ ("MoNo"). As noted above, the existence of a MoSo could offer the possibility of Mo-Fixation without addition of an alkaline earth (Ca or Sr). The compatibility of this hypothetical MoSo was tested with A_{ss} . The product in all four firings from 800 to 1200°C was $A_{ss} + \text{MoSo}$ plus a small amount of Ne. The presence of Ne in the phase assemblages was another clue that some Na was substituting in A_{ss} , leaving Ca to substitute in MoSo. The net result of this exchange would be a small amount of free NaAlSiO_4 . Again, we see the inadequacy of current A_{ss} stoichiometries in high Na formulations.

CS-158: $18 \text{ NaAlSiO}_4 + 3 \text{ Na}_8[\text{AlSiO}_4]_6(\text{MoO}_4) + \text{Ca}_3\text{Nd}_7[\text{SiO}_4]_5[\text{PO}_4]\text{O}_2$. The proportions of Na, RE and Mo approximate those in PM-8a. Again all four firings from 800 to 1200°C gave the same crystalline phase assemblage, $A_{ss} + \text{MoSo} + \text{Ne}$. The three proposed structure types are thus compatible, even though the Na content of A_{ss} is still not known.

Two points are notable. The first is the low crystallization temperature. The level of crystallinity at 800°C is equivalent to that obtained after firings of 100-200°C higher in "clean" HLM formulations. The second is that the high alumina-silica crucibles and covers showed no trace of Na or Cs volatilization even in the 1200°C - 6 hour firing. This means that we seem to be already well on the way to designing a suitably thermally stable crystalline phase assemblage for the high Na wastes. We have no data yet on the leachability of these new phase assemblages.

8.0 Review of Literature Relevant to Tellurium Fixation in Supercalcine

8.1 Introduction (G.J. McCarthy)

Tellurium is only a minor constituent in HLW (1.5 mole% in PW-4b, 1.0% in PW-7 and 0.4% of PW-8a). However, it is classified as a "troublesome" constituent because some or all of its oxides have been shown to volatilize from calcine and glass HLW solids (1). The next steps in supercalcine development are an assessment of the Te volatility in supercalcine and, if necessary, a study of Te fixation in sufficiently refractory phases.

There are two mechanisms by which Te could be fixed in supercalcine. In the first, the small amount of Te could be incorporated in existing phases. For example, it might crystallize with Mo in the tetrahedral sites in S_{ss} to form the phase " $Sr(Mo_{0.85}Te_{0.15})O_4$ " or with Si and P in A_{ss} in a phase like " $Ca_4RE_6[SiO_4]_{4.5}[PO_4][TeO_4]_{0.5}O_2$ ". If Te is not being stabilized in any of the existing supercalcine phases, then it will be necessary to develop a specific Te-fixation phase, check its compatibilities etc., as has already been done for Cs and Mo fixation.

In order to proceed with studies of both of these fixation mechanisms it was first necessary to survey the literature for data on the oxide crystal chemistry of Te-containing phases which might be stable at supercalcine crystallization temperatures (1000 - 1200°C). The following is a list of a number of group classes of phases containing Te, along with whatever preparation, crystal chemical, water solubility and thermal stability information was available in the published reports.

8.2 Literature Review (D.E. Pfoertsch)

Rare Earth Tellurates and Tellurites

RE_2TeO_6 (RE = Ce, Dy, Gd, La, Nd, Pr, Sm): This series of RE tellurates was prepared by passing Te vapor over RE oxides in a hydrogen current. The synthesis temperatures varied from 1000° - 1100°C. Only the tellurates of La, Nd, Pr and Sm proved to be stable in air when heated to 1000°. This was thought to be due to partial decomposition and formation of a protective metal oxide film at the surface. All but the tellurate of Ce dissolve completely in HNO_3 to yield the RE nitrates and tellurous acid (2).

$RE_2Te_4O_{11}$: Compounds of this type are stable at room temperature; however, when heated at 700°C or above, oxidation of Te^{4+} to Te^{6+} takes place, with the rate of oxidation increasing as the RE content increases. Single crystals were prepared by slow cooling from melts of the composition 85 mole% TeO_2 and 15 mole% $REO_{1.5}$. Melt temperatures were varied from 850° - 1000°. Tightly covered Pt. crucibles were used. These compounds belong in the monoclinic system with the crystals in the form of platelets with extended basal pinocoidal faces.

$RE_2Te_3O_9$: These compounds comprise the normal RE tellurites prepared by precipitation from a tellurous acid solution and firing the gelatinous precipitate at 800°C in nitrogen. Three structural groups were found, depending upon the size of the RE-ion:

- La and Nd tellurites
- Sm, Eu, Gd, Dy, Ho, Er and Y tellurites
- Tm, Yb and Lu tellurites

At the melting temperatures (>950°C) oxidation and volatilization of TeO_2 were rapid with no crucible material (including Pt) able to contain the melts (4).

$RE_4Te_3O_{12}$: Compositions of this type were prepared at 800°C. $Dy_4Te_3O_{12}$ was found to be cubic but with a limited stability range; when heated to 850°C the cubic phase broke down. There is some indication that excess RE oxide may stabilize the cubic phase over a larger temperature range (e.g. with RE_2TeO_5) (5).

$\text{RE}_3\text{M}_2\text{Li}_3\text{O}_{12}$ ($\text{M} = \text{Te}, \text{W}$): An extended series of RE tellurate garnets was prepared from stoichiometric amounts of carbonates, hydroxides and oxides slowly heated to 700°C to oxidize TeO_2 , then reground and fired at 850°C for 10 hours. No significant loss of Li or Te was recorded. The RE tellurate garnet lattice constants were larger than for $\text{RE}_3\text{Al}_5\text{O}_{12}$ garnets and smaller than for $\text{RE}_3\text{Fe}_5\text{O}_{12}$ (6). Te was found to occupy the 6-coordinated sites with the RE's occupying the 8-coordinated sites (7).

Three additional RE tellurates were also found: LaCaLiTeO_6 (orthorhombic), LaKMgTeO_6 (perovskite) and LaPbLiTeO_6 (rhombohedral) (8).

Te⁶⁺-Containing Garnets

$\text{A}_3\text{Te}_2\text{B}_3\text{O}_{12}$ ($\text{A} = \text{Bi}, \text{Ca}, \text{Cd}, \text{Na}$; $\text{B} = \text{Al}, \text{Fe}, \text{Gd}, \text{Ga}, \text{Li}, \text{Zn}, \text{Co}$). $\text{Na}_3\text{Te}_2\text{Al}_3\text{O}_{12}$ and $\text{Na}_3\text{Te}_2\text{Ga}_3\text{O}_{12}$ were prepared by firing oxides and carbonates at 700°C for 12 and 20 hours respectively. $\text{Ca}_3\text{Te}_2\text{Zn}_3\text{O}_{12}$ and $\text{Ca}_3\text{Te}_2\text{ZnCo}_2\text{O}_{12}$ were prepared by firing at 1050°C for 1 hour. $\text{Cd}_3\text{Te}_2\text{Zn}_3\text{O}_{12}$ and $\text{Cd}_3\text{Te}_2\text{Zn}_2\text{CoO}_{12}$ formed at 900°C, 1 hour (9). Te^{6+} forms a stable octahedral complex with $[\text{TeO}_6]^{6-}$. Te occupies the 6-coordinated sites, Bi, Na, Ca the 8-coordinated sites, and Fe, Ga, Al, Li, Zn the 4-coordinated sites (10,11).

Fluorite Related Structure Tellurium Compounds

MTe_3O_8 ($\text{M} = \text{Ti}, \text{Sn}, \text{Hf}, \text{Zr}$): All compounds in this group are isostructural and cubic and have the space group $\text{Ia}\bar{3}$. Ti is in octahedral coordination with Te surrounded as in paratellurite TeO_2 ; the cations form an ordered fcc subcell. The Te polyhedron in SnTe_3O_8 has been reported as a distorted trigonal bipyramid (12).

Tri-Rutile Tellurium Compounds

A_2TeO_6 ($\text{A} = \text{Al}, \text{Cr}, \text{Fe}, \text{Ga}$): Compounds of this type were formed from stoichiometric amounts of the constituent oxides and fired at 650° - 700°C (11). Al_2TeO_6 was also prepared by heating $\text{Al}_2\text{Te}_3\text{O}_9$ with O to yield TeO_2 and Al_2TeO_6 (13). X-ray data and lattice constants are available.

Perovskite Structure Tellurium Compounds

A_3TeO_6 ($\text{A} = \text{Ba}, \text{Ca}, \text{Mg}, \text{Pb}, \text{Sr}$): Ca_3TeO_6 was formed by reacting TeO_2 with excess CaO or CaCO_3 . This compound shows ordered (cryolite) and disordered forms, both with Te in pseudo-octahedral coordination (14,15). Lattice constants and additional x-ray data are available (16,17,18).

A_2BTeO_6 ($\text{A} = \text{Ba}, \text{Ca}, \text{Cd}, \text{Na}, \text{Pb}, \text{Sr}$; $\text{B} = \text{Ca}, \text{Cd}, \text{Mg}, \text{Co}, \text{Ni}, \text{Zn}, \text{Mn}, \text{Pb}, \text{Zr}, \text{Sr}$): Most of these compounds were formed by slow heating to 700°C and then at 1050° - 1360°C (19). The sub-type A_2MgTeO_6 ($\text{A} = \text{Ba}, \text{Pb}, \text{Sr}$) was prepared from stoichiometric amounts of the constituent oxides and fired slowly to 700°C during which time TeO_2 was oxidized to TeO_3 . The compounds were then reground and fired for 20 hours at 850°C for the PbO-containing compound and 20 hours at 1050°C for Sr and Ba-containing specimens (20). $\text{Sr}_2\text{NiTeO}_6$, $\text{Sr}_2\text{ZnTeO}_6$, $\text{Na}_2\text{ZrTeO}_6$ and $\text{Sr}_2\text{CoTeO}_6$ were found to be orthorhombic (21). $\text{Ba}_2\text{NiTeO}_6$ is a hexagonal perovskite with two formula units per primitive cell in a rhombohedral setting (22). Additional data on ferroelectric characteristics and lattice constants is available (23).

$\text{A}_2\text{B}_2\text{TeO}_9$ ($\text{A} = \text{Ba}, \text{Sr}$; $\text{B} = \text{Na}, \text{Li}$): Lattice constants are available (24).

$\text{A}_3\text{B}_2\text{TeO}_9$ ($\text{A} = \text{Ba}, \text{Sr}$; $\text{B} = \text{Fe}$): These compounds were prepared by firing at 450°C for 24 hours, then at 800°C several times and at 900°C for 20 hours several times with grinding and crushing between each firing stage. $\text{Ba}_3\text{TeFe}_2\text{O}_9$ is a hexagonal perovskite and $\text{Sr}_3\text{TeFe}_2\text{O}_9$ is cubic (25).

Tellurite Compounds

MTeO_3 ($\text{M} = \text{Ba}, \text{Ca}, \text{Cd}, \text{Mn}, \text{Sr}$): BaTeO_3 was prepared from melts. It is monoclinic with pyramidal TeO_3 groups and Ba in a distorted 9-coordination with the O atoms. TeO_3 polyhedra are not linked with one another but with BaO_9 polyhedra along common corners and edges. BaO_9 are linked by common edges only (26).

CaTeO_3 can be prepared by reacting TeO_2 with excess CaO or CaCO_3 and firing from $500^\circ - 780^\circ\text{C}$. The melting point has been reported as 870° (27) and 1045°C (28). CaTeO_3 has two crystalline modifications and is oxidized by air at high temperatures (29). Cd- and MnTeO_3 are stable up to $\sim 850^\circ\text{C}$ only. SrTeO_3 can be fired from $650^\circ - 1000^\circ\text{C}$ (m.p. 1030°C) but goes through several structural transitions (30,31).

$\text{M}_2\text{TeO}_3 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Li}, n = 0$; $\text{M} = \text{Na}, \text{Cs}, n = 5$; $\text{M} = \text{K}, \text{Rb}, n = 3$): It has been reported that these compounds can be heated in air to 1000°C without decomposition occurring. The melting points vary from $640 - 780^\circ\text{C}$. At $500^\circ - 550^\circ\text{C}$ Te^{4+} is oxidized to Te^{6+} and the process is reversed above 800°C (32).

MTe_2O_5 ($\text{M} = \text{Ba}, \text{Ca}, \text{Cd}, \text{Mg}, \text{Mn}, \text{Ni}, \text{Sr}$): Most of these compounds have low melting points ($690^\circ - 870^\circ\text{C}$) (33,34). $\text{Ca-}, \text{Cd-},$ and SrTe_2O_5 when cooled from melts form a mica-like tellurite. MTe_2O_5 is orthorhombic and melts incongruently at $\sim 850^\circ\text{C}$ (35).

$\text{M}_2\text{Te}_3\text{O}_8$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Ni}$): $\text{Mg}_2\text{Te}_3\text{O}_8$ is monoclinic and melts at 870°C ; it is isostructural with $\text{Zn}_2\text{Te}_3\text{O}_8$ (36,37). $\text{Ni}_2\text{Te}_3\text{O}_8$ is monoclinic with Te in a distorted trigonal bipyramid (38).

$\text{M}_2\text{Te}_3\text{O}_9$ ($\text{M} = \text{Al}, \text{In}, \text{Cr}, \text{Pr}$): All these compounds with the exception of Pr tellurite are isostructural. $\text{In}_2\text{Te}_3\text{O}_9$ was found to be orthorhombic (39). $\text{Pr}_2\text{Te}_3\text{O}_9$ can be fired to 1000°C (40).

$\text{M}_4\text{Te}_3\text{O}_{13}$ ($\text{M} = \text{Co}, \text{Mg}$): Mg- tellurite is unstable and Co- tellurite melts at $\sim 850^\circ\text{C}$.

$\text{MTe}_6\text{O}_{13}$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Co}$): These compounds are characterized by low melting points ($\sim 790^\circ\text{C}$).

Other Tellurium Compounds

$\text{Ca}_3\text{TeO}_6 \cdot \text{UO}_2^{++}$: This uranyl activated phosphor is reported to be highly refractory and can be fired up to 1300°C (41).

Te_2MoO_7 and $\text{TeMo}_4\text{O}_{13}$: Both compounds have low melting points, 551° and 748°C , and the former forms a dark yellow glass (42,43).

ZnTeO_3 : In this compound Te occurs in " TeO_3 trigonal bipyramids, reflecting the covalent nature and with one-sided bonding typical of Te^{4+} ." (44).

$\text{Ca}_2\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{TeO}_4)_2$: Cubic sodalite structure; $(\text{Te}^{6+}\text{O}_4)$ tetrahedra are located in voids in the aluminosilicate network. This compound must be prepared in sealed Pt capsules due to Te volatilization at 1150°C (45).

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APPENDIX A

Penn State Contribution to PNL Quarterly Report for January-March 1976.

The Materials Research Laboratory at Pennsylvania State University, University Park, Pa., is operating under a subcontract to investigate advanced solidified waste forms, e.g., forms other than melt-formed glasses or glass-ceramics. The overall objective is to develop a waste form in which all of the radioactive atoms will be isolated in thermally and chemically stable crystalline phases. If adequately consolidated, this waste form might stand alone; but it is also being considered as the innermost, or atomic level, barrier in a multiple layer optimum waste form which would include other layers of glass, ceramic or metal matrices, impervious coatings, etc. Because this waste form utilizes the existing calcining processes with a compositionally modified waste liquid it has been termed "supercalcine". Near term objectives are 1) to determine which are the best crystalline phases for Cs, Rb and Sr fixation, 2) to develop "supercalcine" formulations containing all major commercial waste atoms and 3) to demonstrate supercalcine processing on an engineering scale at PNL and develop means of consolidating the crystallized product.

Emphasis during the last quarter was on learning more about the rare earth silicate-phosphate apatite structure phase which is the dominant species in crystallized supercalcine and on consolidation methods for the PW-4b-based spray supercalcine prepared at PNL. The first steps have been taken toward development of supercalcine formulations for PW-7-based wastes.

Supercalcine Crystal Chemistry (G. J. McCarthy, C. A. Smith, H. T. Davidson, D. E. Pfoertsch)

To date, identification of the structures and approximate compositions of the phases in crystallized supercalcine has been accomplished through careful studies of x-ray diffractograms. Compositional - microstructural analyses by Scanning Electron Microscopy which will add further chemical information are in progress. The best confirmation of a proper x-ray identification in a complex mixture is to prepare the pure phase of the proposed stoichiometry, confirm that a single phase has been formed and match its diffractogram to a set of reflections in the supercalcine diffractograms.

These steps have been carried out from the beginning of this project, but were given special emphasis during the last quarter. The following stoichiometries were selected to approximate the proposed the compositions of phases identified in crystallized supercalcine and described in the preceding quarterly report.*

Each of these stoichiometries gave well-crystallized single phases of the specified structure type when prepared according to the same calcining and firing schedules as supercalcine. The comparison of diffractograms of these phases to those of crystallized supercalcine confirmed the phase assignments made earlier. Unit cell parameters and complete x-ray powder data have been determined for each phase and are available from the author.

When simple waste calcine is fired, the dominant crystalline phase is a fluorite structure solid solution (F_{ss}) obviously rich in CeO_2 . It was puzzling that when only 30wt% of additives are combined with the wastes to produce supercalcine the F_{ss} phase is weak or absent in the diffractograms of the crystallized product. Compatibility studies confirmed that CeO_2 does not react with any of the well established phases in supercalcine. The explanation may be in the excess SiO_2 which is included in every supercalcine formulation to insure Cs fixation as $\text{CsAlSi}_2\text{O}_6$. Perhaps the Ce was reacting with this SiO_2 to form an apatite structure phase which would be incorporated in solid solution with the "tailor-made" apatite phase.

A series of silicate apatite models including various proportions of Ce, Sr and Nd were tested. It was found that if Ce were the alkaline earth then Ce could completely replace Nd in the model $\text{Ca}_{2-x}\text{Nd}_{8-2x}\text{Ce}_x[\text{SiO}_4]_6\text{O}_{2-x}\square\frac{x}{2}$ ***

* October-December, 1975.

** The A_{ss} and P compositions expected from PW-7 based supercalcine formulations; K is a stand-in for Rb. All other phases are based on PW-4b waste.

*** The products were black, indicating some amount of reduction of Ce^{4+} to Ce^{3+} —this model assumes complete reduction to Ce^{3+} . Experiments designed to establish the actual valence of Ce in these phases are in progress.

i.e. x can have any value from 0 to 4. When Sr replaces Ca, less Ce can replace Nd. For $x = 2$ or more, other phases (e.g. SrSiO_3 , CeO_2) are formed in addition to an unknown apatite stoichiometry. However, $\text{Sr}_2\text{Nd}_6\text{Ce}(\text{SiO}_4)_6\text{O}_2$ gives the approximate Ce/RE ratio in PH-4b and both excess Sr and SiO_2 were added in supercalcine 75-2. Therefore, these crystal chemical results imply that future supercalcine formulations should specify Ce in the A_{55} rather than an F_{55} phase. This has also been demonstrated in several of the compatibility studies described below.

In all of our phase formation models we have assumed, based on ample literature data, that the phosphate present in the wastes will substitute for the $[\text{SiO}_4]$ groups in A_{55} . The correctness of this assumption was confirmed through preparation of a number of A_{55} phases containing either Sr or Ca with the rare earth and phosphate concentrations found in PH-4b and PH-7 wastes. Two of these compositions were listed in the A_{55} group at the beginning of this section.

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

Sixteen complex assemblages of oxides were studied to gain further insight into the phase formation in crystallized supercalcine, especially where excess Al and Si have been added. Highlights of the results follow.

- The role of Ce described in the previous section was confirmed through a series of increasingly more complex assemblages of constituent oxides to which excess SiO_2 had been added. The Ce acts as a typical RE^{3+} and, combined with the required proportion of the excess SiO_2 , substitutes into the A_{55} phase.
- The compatibility of the tetragonal phase of ZrO_2 (T_{55}), probably containing some CeO_2 or CaO in solid solution, with other supercalcine phases was confirmed.
- It had been repeatedly noted that the reflections of the S_{55} phase $(\text{Sr,Ba,Ca})\text{MoO}_4$ grow weaker in diffractograms of supercalcine with extended firing above 1100°C . Several runs indicated that this may be due in part to replacement of some Sr by Ca in S_{55} . It appears that the Sr has a stronger tendency to form aluminosilicates. The x-ray intensity of CaMoO_4 is less than an equimolar amount of SrMoO_4 .

Supercalcine Development (G. J. McCarthy and D. E. Pfoertsch)

Consolidation. The engineering scale preparation of a fine powder spray supercalcine (using a simplified PH-4b waste) at PNL has been demonstrated.

The next step in establishing the feasibility and desirability of including supercalcine as the first barrier of a multi-barrier ("Russian Doll") alternative waste form is consolidation of the powder into coarse grains or pellets. These waste particles can then be given inert impervious coatings by one of the processes being developed by W. J. Gray et al* at PNL. In addition to the atomic scale isolation of dangerous nuclides, supercalcine will be superior to standard calcine in these coatings processes because of its almost negligible waste volatilization at the high coatings processing temperatures.

Pellet formation using a disc pelletizer is being studied at PNL with very promising results. We are utilizing simple cold pressing for pellet forming followed by firing at 1100 - 1200°C for crystallization-sintering. Recently, we found that adding small amounts (2-12wt%) of Corning code 7740 ("Pyrex") glass frit to the supercalcine gave much improved consolidation and very good leaching resistance and thermal stability. A typical set of processing conditions and properties follows.

90% Spray Supercalcine 75-2 (60% waste loading)
10% 7740 frit, -200 mesh

pressed into 1/2 in. pellets at 25,000 psi

fired at 1100°C for 1 hr.

soxhlet leachability:

% weight loss after 1 day: 0.41
3 days: 0.34, 1.1, 0.55

thermal stability (-200 mesh powder)

% weight lost after 1 day at 1200°C : 1.5%
2 days at 1200°C : 3.2%
3 weeks at 1200°C : 6.2%
3 weeks at 1050°C : 4.3%
3 weeks at 900°C : 1.2%

The soxhlet weight loss values are comparable to those observed for the better glass waste forms which have only half this level of waste loading. The weight losses* of the powdered product are higher than desired but still quite reasonable when it is considered that the oxides of Cs, Mn, Rb, and K** make up ~18 wt% of the product oxide components. It should be noted that previously formed pellets showed no detectible weight losses during one hour's firing

* We have reason to believe that some of these losses may be due to slow release of H_2O previously incorporated in the A_{55} phase as (OH) on the halide site.

** Gray, BNWL-1932, finds that these are the most readily volatilizable species.

at 1050°C. This indicates that supercalcine pellets could have coatings applied at this temperature without fear of significant waste volatilization.

As we have previously reported, hot pressing is the optimum consolidation technique for oxide powders such as supercalcine. To see how much improvement could be obtained with this method, we had pure supercalcine 75-2 vacuum hot pressed at the same crystallization temperature we had used in air firings. The conditions were 15 min. at 1100°C and 3000 psi in a 2 in. graphite reactor. The product was very hard and dense and could be polished to a mirror finish. It had a 3 day soxhlet weight loss of 0.49% even though the level of waste loading was 57%. If hot pressing can be developed for remote operation under high flux conditions, it will be the process of choice for supercalcine consolidation.

PW-7 Based Formulations. PW-7 differs from PW-4b in having significantly higher RE^{3+} (Gd), Fe, (PO_4) and U concentrations plus a small amount of Na. Since we feel that the crystal chemical roles of these constituents are substantially (though not completely) understood, our current supercalcine phase formation models were also applied to this waste formulation*. The x-ray diffractograms of the crystallized product were consistent with the phase formation model and showed only a few weak unidentified reflections. According to the model, Gd and (PO_4) were incorporated in A_{ss} , Na in pollucite, U in an F_{ss} phase and Fe remained as the oxide. Evidence of Cs and other waste species volatilization at 1100°C (stained bricks, frosted silica tubes) was absent for the formulation where twice the (Al+Si) required for pollucite $[(Cs,K,Na)AlSi_2O_6]$ formation was added. Experience has indicated that in actual spray calciner preparation, where the complex oxide mixtures will have far greater homogeneity, this level of excess (Al+Si) will not be necessary.

When the alkaline earth (Ca and Sr) additive concentration was increased by a factor of 1.25 above that called for in the phase formation model, there was evidence of some Cs volatilization during the crystallization heat treatment. Apparently the Sr or Ca ties-up some Al and/or Si and prevents full crystallization of pollucite. This sensitivity to excesses of either waste constituents or additives is not desirable. We currently suspect that the A_{ss} model used may be calling for too much additive Ca, so we will continue to concentrate our crystal chemical and compatibility studies on this important supercalcine phase.

* Only Ru, Te, Ag and the radioactive species were not included in our simulated waste.

APPENDIX B

Penn State Contribution to PNL Quarterly Report for April-June 1976

Supercalcine (G. J. McCarthy)

The Materials Research Laboratory at the Pennsylvania State University, University Park, PA, is participating in this program through an investigation of crystalline ceramic waste forms which are potential advanced options to melt-formed HMW glass or glass-ceramics.

The objective is to develop a waste form in which all of the radioactive atoms will be isolated in thermally and chemically stable crystalline phases. Because this waste form uses the existing calcining processes with a compositionally modified waste liquid it has been termed "supercalcine." Although supercalcine could be considered alone as an improved calcine product, current emphasis is on its use as high stability "cores" in the multibarrier waste form.

Short term objectives are 1) to determine which are the best crystalline phases for cesium, ruthenium and tellurium fixation, 2) to develop supercalcine formulations containing all non-radioactive commercial waste atoms and 3) to demonstrate supercalcine processing on an engineering scale at PNL and develop means of consolidating the crystallized product.

Emphasis during the last quarter was on further critical examination of Cs and Ru fixation phases for supercalcine and on initiation of work on developing supercalcine formulations for high-βa wastes such as PW-7a and PW-8a. A technical progress report on supercalcine development was prepared and issued during the quarter.

Crystalline phases for Cs and Ru fixation (S. A. Gallagher, R. G. Johnston and G. J. McCarthy)

A Cs fixation phase must prevent Cs volatilization during supercalcine crystallization firings. Thermogravimetric analysis on cesium aluminosilicates was performed by S. A. Gallagher during her three month stay at PNL. Pollucite, $CsAlSi_2O_6$, appears to have more than adequate thermal stability for Cs fixation in supercalcine.

* G. J. McCarthy, "High Level Waste Ceramics; Materials Considerations, Process Simulations and Product Characterization", Presented at the Am. Nucl. Soc. Annual Meeting, Toronto, June 16, 1976 and submitted to Nuclear Technology [COO-2510-10].

Based on thermal stability characterization of HLW calcine and glass products, it appeared that Ru volatilization during supercalcine crystallization was going to be a major problem. We thus set the development of a Ru fixation phase as one of the first objectives in supercalcine studies. After an extensive survey of candidate phases and solid solutions, SrRuO_3 was chosen as the best possibility. However, in spite of earlier promising, but preliminary, results, SrRuO_3 is not suitable as a Ru fixation phase. Strontium oxide has a greater affinity to form aluminosilicates than to form SrRuO_3 . This means that it can prevent complete Cs fixation as pollucite during the supercalcine crystallization firing. The possibility of leaving Ru as RuO_2 during supercalcine crystallization is being assessed, since residual RuO_2 was observed routinely in most phase assemblages after firings of up to three hours at 1200°C .

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

With the very promising results from the cold engineering scale demonstration of a supercalcine formulation based on PN-4b*, we have been asked to investigate the application of supercalcine concepts to the high Na, "dirty", wastes PN-7a and PN-8a. Nepheline, $\text{NaAlSi}_3\text{O}_8$, looks like the best candidate for Na fixation. Extensive modifications to the phase formation models will be necessary because of the high Na concentration. For example, in the presence of high nepheline concentrations, the scheelite structure phase, SrWO_4 , reacts to form a cubic sodalite structure phase, $\text{Sr}_2\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{WO}_4)_2$ (or $6\text{NaAlSi}_3\text{O}_8 \cdot 2\text{SrWO}_4$). This type of phase has also been observed as one of the products in the devitrified glass-ceramic HLW product under investigation at the Hahn-Meitner Institute**. The rare earths still crystallize in an apatite structure phase, but this phase appears to have a substantial Na concentration.

Based on observations during several complex compatibility studies, it appears that good overall thermal stability at as high as 1200°C might be attainable for nepheline based supercalcine formulations.

* G. J. McCarthy, Quarterly Progress Reports, October-December, 1975 and January-March, 1976.

** A. K. D6 et al. Am. Ceram. Soc. Bull. 55, 500 (1976).

Role of Te in Supercalcine (D. E. Pfoertsch and G. J. McCarthy)

An extensive literature search for relevant oxide crystal chemistry of Te has been completed. At high temperatures, Te is usually hexavalent and almost always in sixfold coordination by oxygen. No information was found on the potential solid solubility of Te in apatite or scheelite structure oxide phases. A study of this possibility has been initiated.

APPENDIX C

X-Ray Powder Data for Selected A_{55} and F_{59} Phases

$$a_0 = 9.532(2) \text{ \AA}$$

$$c_0 = 7.021(2) \text{ \AA}$$

dA	hkl	hkl
4.13	20	200
3.95	20	111
3.51	18	002
3.23	30	102
3.120	30	210
2.851	100	211
2.876	45	112
2.752	25	300
2.674	2	202
2.332	2	212
2.290	8	310
2.254	10	221, 103
2.177	3	311
2.166	3	302
2.101	10	113
2.065	8	400
2.036	1	203
1.97A	25	222
1.918	14	312
1.893	5	320
1.873	30	213
1.829	16	321
1.802	18	410
1.779	20	402
1.755	10	004
1.667	1	322
1.6490	2	500, 114
1.6152	2	204
1.6027	1	412
1.5600	4	420
1.5487	8	331, 403
1.5300	8	214
1.4940	10	502
1.4812	6	510, 304
1.4722	6	323
1.4490	8	511, 332
1.4275	1	413
1.3469	1	115
1.3332	3	404, 431+
1.3144	3	333
1.2986	5	521, 423

$$a_0 = 9.421(2) \text{ \AA}$$

$$c_0 = 6.888(2) \text{ \AA}$$

dA	hkl	hkl
4.08	20	200
3.89	25	111
3.44	16	002
3.17	30	102
3.08	30	210
2.814	100	211
2.730	40	112
2.720	30	300
2.265	9	310
2.228	6	221
2.150	2	311
2.134	4	302
2.065	12	113
2.040	8	400
1.944	25	222
1.891	14	312
1.871	6	320
1.842	35	213
1.806	17	321
1.781	20	410
1.755	30	402, 303
1.722	12	411, 004
1.587	4	501, 204
1.5418	5	420
1.5308	8	331
1.5046	8	421, 214
1.4746	12	502
1.4549	8	304
1.4507	12	323
1.4332	5	511
1.4286	8	332
1.3162	5	431, 404
1.2960	4	333
1.2835	6	521
1.2647	8	602
1.2578	8	215
1.2441	5	510
1.2377	10	414
1.2352	6	515

$$a_0 = 9.579(3) \text{ \AA}$$

$$c_0 = 7.111(3) \text{ \AA}$$

dA	hkl	hkl
4.79	4	110
4.15	25	200
3.98	20	111
3.56	12	002
3.27	30	102
3.137	40	210
2.862	100	211, 112
2.766	30	300
2.700	3	202
2.301	6	310
2.270	4	221
2.186	6	311, 302
2.125	8	113
2.074	5	400
2.058	2	203
1.986	25	401, 222
1.972	14	312
1.903	6	320
1.891	25	213
1.839	14	321
1.811	20	410
1.792	20	402
1.778	10	004
1.634	2	204
1.5678	4	420
1.5583	6	403, 331
1.5469	8	214
1.5039	8	502
1.4955	6	304
1.4900	2	510
1.4841	6	323
1.4574	8	511, 332
1.3242	2	335
1.3068	3	425, 521
1.2992	2	324
1.2953	8	216
1.2687	2	602
1.2668	10	414, 610+

$$a_0 = 9.463(4) \text{ \AA}$$

$$c_0 = 6.971(3) \text{ \AA}$$

dA	hkl	hkl
4.73	5	110
4.10	25	200
3.91	18	111
3.49	14	002
3.21	35	102
3.096	35	210
2.830	100	211
2.807	55	112
2.731	30	300
2.655	4	202
2.272	5	310
2.238	4	221, 103
2.161	2	311
2.151	6	302
2.086	10	113
2.049	4	400
1.958	25	222
1.904	16	312
1.881	6	320
1.859	30	213
1.816	14	321
1.789	20	410
1.769	25	303, 402
1.745	12	004
1.732	2	411
1.6547	3	322
1.6372	2	500, 114
1.6058	8	204
1.5491	5	420
1.5376	8	331, 403
1.5189	9	214
1.5119	3	421
1.4832	12	502
1.4706	8	510, 304
1.4616	8	323
1.4386	8	511, 332
1.3275	3	404
1.3228	3	451
1.2892	3	521, 423
1.2781	3	324
1.2716	8	602, 215

APPENDIX C

(continued)

$a_0 = 9.499(3) \text{ \AA}$

$c_0 = 6.974(2) \text{ \AA}$

dA	1/I ₁	hkl
4.11	20	200
3.93	20	111
3.30	25	002
3.22	25	102
3.11	25	210
2.841	100	211
2.816	35	112
2.742	20	300
2.324	4	212
2.281	8	310
2.246	4	221, 103
2.160	2	311
2.158	3	302
2.094	10	113
2.057	6	400
2.028	2	203
1.965	16	222
1.911	10	312
1.887	5	320
1.856	30	213
1.822	14	321
1.796	14	410
1.774	18	303, 402
1.749	8	004
1.739	1	411
1.662	2	223, 320
1.643	2	500, 114
1.609	1	204
1.597	2	412
1.577	4	313
1.547	6	314, 321
1.524	6	215, 311
1.469	8	502
1.476	3	510, 501
1.467	6	323
1.414	6	511, 302

$a_0 = 9.408(3) \text{ \AA}$

$c_0 = 6.891(2) \text{ \AA}$

dA	1/I ₁	hkl
4.08	20	200
3.69	25	111
3.45	20	002
3.17	30	102
3.08	30	210
2.812	100	211
2.880	40	112
2.716	25	300
2.631	2	202
2.296	4	212
2.260	7	310
2.226	5	221
2.147	5	311
2.133	4	302
2.064	8	113
2.037	2	400
2.001	6	203
1.943	20	222
1.890	10	312
1.869	5	320
1.841	30	213
1.805	14	321
1.778	14	410
1.754	20	303, 402
1.722	10	004, 411
1.640	2	200
1.529	1	311
1.503	1	214, 121
1.473	8	502
1.453	5	510
1.435	5	501
1.450	5	323
1.431	5	511
1.427	5	502

$a_0 = 9.444(3) \text{ \AA}$

$c_0 = 6.927(2) \text{ \AA}$

dA	1/I ₁	hkl
4.09	20	200
3.90	20	111
3.46	25	002
3.19	30	102
3.09	25	210
2.823	100	211
2.792	35	112
2.726	20	300
2.643	3	202
2.306	4	212
2.268	8	310
2.235	4	221
2.156	3	311
2.142	2	302
2.074	10	113
2.045	6	400
2.011	2	203
1.951	16	222
1.898	10	312
1.876	5	320
1.850	30	213
1.812	16	321
1.785	14	410
1.761	18	303, 402
1.730	10	004, 411
1.646	4	420
1.533	6	311, 403
1.510	6	214, 421
1.479	8	502
1.462	4	304
1.456	6	323
1.437	5	511
1.433	5	332

$a_0 = 5.349(2) \text{ \AA}$

dA	1/I ₁	hkl
3.09	100	111
2.675	35	200
1.892	60	220
1.614	50	311
1.544	12	222
1.337	10	400
1.228	20	331
1.197	14	420
1.0921	18	422
1.0296	16	511

$a_0 = 5.458(1) \text{ \AA}$

dA	1/I ₁	hkl
3.15	100	111
2.729	30	200
1.930	55	220
1.6455	45	311
1.5755	10	222
1.3645	8	400
1.2323	18	331
1.2206	12	420
1.1142	14	422
1.0505	12	511

$a_0 = 5.369(1) \text{ \AA}$

dA	1/I ₁	hkl
3.100	100	111
2.685	25	200
1.898	45	220
1.619	35	311
1.550	10	222
1.342	6	400
1.232	12	331
1.2005	8	420
1.0960	8	422
1.0334	10	511