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ADVANCED WASTE FORMS RESEARCH AND DEVELOPMENT

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1.0 Introduction

This report describes our activities during the last two months.

A significant portion of our time was spent reviewing the literature on the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (Langlet thesis, section 2.1.1), on the use of clays and zeolites for Cs-fixation of aqueous wastes (section 2.3) and on silicate-phosphate apatite structure crystal chemistry (section 2.4.1).

The results from the latest group of compatibility studies (CS-runs, section 2.4.2) have been used to modify our first demonstration supercalcine formulation so that it is more in line with the actual crystalline phase formation. Supercalcine formation 75-2 is described in section 2.5.

We will be presenting a summary of our work at several sites in West Germany in August in a lecture entitled "Crystalline Ceramic Nuclear Waste Forms". An outline of this lecture may be gleaned from the slides which are reproduced in Appendix A. Many of these slides were also used in our presentations at the American Ceramic Society Annual Meeting in May 1975.

2.0 Supercalcine Development

2.1 Cesium Fixation

Part of our effort since the last report was devoted to a review of what is perhaps the most comprehensive study of Cs aluminosilicates for Cs fixation made to date, the Langlet thesis* of 1969. The following section describes his results and comments on those areas relevant to Cs fixation in aluminosilicates found to be lacking in his thesis. The second section below (2.1.2) reports on the first stages of the $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system study.

2.1.1 Langlet Thesis (S. A. Gallagher)

In his thesis Synthesis and Crystallographic Study of Compounds of the System $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, Gerard Langlet used the following as his criteria for the development of a cesium compound capable of incorporating radioactive ^{137}Cs :

1. Low solubility in H_2O and the usual solvents
2. High fusion or decomposition temperature
3. A considerable cesium content
4. High density
5. Good structural stability as a function of composition
6. Good structural stability against ^{137}Cs disintegration

Table I of his thesis lists those compounds which were prepared and studied as well as the starting materials which were used. All reactions were performed in the solid state at high temperature in air using platinum crucibles. The study of the ternary system $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ was based upon the preparation, structural properties and behavior of the compounds as a function of temperature. Two compounds were found to exist in this system - CsAlSiO_4 and $\text{CsAlSi}_2\text{O}_6$ (pollucite).

Langlet reported the preparation of pure CsAlSiO_4 by solid state reaction of CsNO_3 with kaolinite in the range of 500°C to 1000°C . From his study of the reaction by differential thermal analysis (DTA), he proposed the following mechanism for the reaction.

*Langlet never published his results in the open literature and thus we became aware of it only through a reference in another paper. Our review of this thesis was greatly facilitated by an English translation supplied by Ray Isaacson of ARHCO.

1. Dehydration of kaolinite and filling of pores with melted alkaline salt.
2. Decomposition of alkaline salt and incorporation of the oxide into the aluminosilicate matrix.

Langlet indexed this compound which he reported quantitatively as CsAlSiO_4 on an orthorhombic cell with lattice parameters of $a_0 = 9.34\text{\AA}$, $b_0 = 9.86\text{\AA}$, and $c_0 = 8.96\text{\AA}$. He also reported that the 200 and the 002 as well as the 022 and the 202 diffraction lines begin to approach each other above 100°C while the 022 line decreases in intensity with respect to the 202 line. His thesis stated that at 500°C only one line remained of the group 220, 022, and 202. Having reported the appearance of pollucite at 1150°C , and the appearance of $\alpha\text{-Al}_2\text{O}_3$ at 1500°C , the chemical formula which he proposed for this decomposition is as follows:

Langlet further reported that CsAlSiO_4 has a cubic structure ($a_0 = 9.37\text{\AA}$) at 1130°C .

Barrer and McCallum¹ also reported the hydrothermal preparation of CsAlSiO_4 from a gel consisting of CsOH , $\text{Al}(\text{OH})_3$, and silica gel in the temperature range 160°C to 450°C in an autoclave. Above 300°C pollucite was formed. These authors reported a cubic lattice with $a_0 = 13.27\text{\AA}$. No compositional analysis was reported.

Solov'eva, Vydrik and Moroz² reported the preparation of pure CsAlSiO_4 in the range 800°C to 1500°C from starting materials of Cs_2CO_3 , $\text{Al}(\text{OH})_3$, and silicic acid gel. The composition of the sample corresponded to theoretical composition of CsAlSiO_4 . A hexagonal cell with $a_0 = 16.31\text{\AA}$ and $c_0 = 9.15\text{\AA}$ was reported. A large number of reflections could be indexed on a cubic lattice where $a_0 = 9.42\text{\AA}$, indicating a pseudocubic structure.

¹J. Chem. Soc. 4029-35 (1953).

²Russ. J. Inorg. Chem. 15(7) 909-11 (1970).

There have been three different structures proposed for CsAlSiO_4 with no explanation for these differences. If this phase decomposes to form pollucite with the loss of Cs_2O as a vapor and the production of free Al_2O_3 , it is possible that the structure of CsAlSiO_4 varies as the composition varies. A careful study of the structure in relationship to the stoichiometry must be performed. The cesium loss should be monitored as a function of temperature, and x-ray diffractograms should be taken after each heat treatment. If the basic hypothesis (structure varies with composition) holds, the x-ray diffractograms will show different structures for different ranges of stoichiometries.

Langlet also reported the preparation of $\text{CsAlSi}_2\text{O}_6$ (pollucite) starting with CsNO_3 , kaolinite, and silica. The following table summarizes the results of the x-ray diffractograms³:

Up to 415°C	kaolinite + CsNO_3
415 - 480°C	kaolinite
480 - 820°C	no distinct diffraction pattern
820 - 1100°C	CsAlSiO_4 with progressive appearance of $\text{CsAlSi}_2\text{O}_6$
above 1200°C	$\text{CsAlSi}_2\text{O}_6$ alone

He therefore proposed the following chemical formula for the preparation of pollucite:

Retention of cesium is reported to be dependent on the alumina content and is summarized below⁴:

- With 10% Al_2O_3 - 55-65% of initial Cs is retained
- With 15% Al_2O_3 - more than 90% of the initial Cs is retained even with 50% Cs_2O at the beginning
- With 20% Al_2O_3 - retention remains good to 40% of the initial Cs_2O and then becomes poor.

³Langlet, pp. 89.

⁴Langlet, pp. 92.

He concluded from this that for the best retention of cesium, the limit of Cs_2O content is 40% and that of Al_2O_3 is 15%. Weight loss data for various compositions is given in Table 17 of Langlet's thesis. The results of the leach tests are given in Table 18 of his thesis.

Langlet reported that the lattice parameter of pollucite fluctuates between 13.68 and 13.77 Å depending on the cesium content. Here, however, no phase transformations were observed to 1500°C. The two extremes in composition are reported as $1\text{Cs}_2\text{O}-1\text{Al}_2\text{O}_3-4\text{SiO}_2$ (40.8% Cs) and $0.895\text{Cs}_2\text{O}-0.35\text{Al}_2\text{O}_3-4\text{SiO}_2$ (36.5% Cs). All studies show that pollucite is cubic with Al^{3+} and Si^{4+} ions distributed statistically. Langlet showed that pollucite has a low expansion coefficient and could therefore withstand thermal shock at high temperatures.

Langlet further studied the effect of the disintegration of ^{137}Cs into ^{137}Ba (stable) on the structure of pollucite. He indicates that the pollucite structure should be able to retain its integrity at least for one half life period (~30 years).

It is evident that pollucite as well as CsAlSiO_4 varies in composition. A complete study of the composition vs. the pollucite lattice parameter a_0 still remains to be done. Isothermal sections of the phase diagram $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ would be well worth investigation since this would require the mapping of structural fields for both CsAlSiO_4 and pollucite in relation to composition for different temperatures. The study will require the preparation and compositional analysis of samples of varying stoichiometries. The thermal stability and leachability of these samples can then be studied as a function of their composition. This work has been initiated as described in the next section.

2.1.2. Phase Relations in a Portion of the System $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (S. A. Gallagher)

The next phase of research to be undertaken concerning the fixation of cesium in radioactive waste will be a study of the isothermal sections of the phase diagram $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ in the temperature range of 1000-1250°C. Three compounds have been reported to exist between cesium, aluminum, and silicon- CsAlSiO_4^1 , $\text{CsAlSi}_2\text{O}_6^2$ (pollucite), and $\text{CsAlSi}_3\text{O}_8^3$ - with ratios of 1:1:2, 1:1:4 and 1:1:6 of $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, respectively. Figure 1 shows the compounds which are reported to exist for this system. Because the high

Figure 1. Phase in the system $\text{Cs}_2\text{O}-\text{Al}_2\text{O}_3 - \text{SiO}_2$.

○ Literature reference only.

● Literature reference confirmed by our laboratory preparation.

1. J. Chem. Soc., 2475-85 (1968).
2. Russ. J. Inorg. Chem., 13(3), 215-8 (1968).
3. Comp. Rend. Acad. Sci. USSR 258-61 (1931).
4. Inorg. Mat., 1(8), 1301-11 (1965).
5. Russ. J. Inorg. Chem., 11(5), 626-9 (1966).
6. C. R. Acad. Sci. Paris 259, 3769-70 (1964).
7. Siberian Chem. J., 55-61 (1967).

Figure 2. Proposed Area of Study.

volatility of cesium and the hygroscopic nature of many $\text{Cs}_2\text{O-SiO}_2$ and $\text{Cs}_2\text{O-Al}_2\text{O}_3$ phases precludes these from interest in Cs fixation, a smaller more restricted area of the diagram has been selected for the actual study (Figure 2). This is the area which will be of the greatest interest in the fixation of Cs since it deals with an area rich in alumina and silica and should contain the most stable compositions. The homogeneity ranges and phase relations of the various $\text{Cs}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ phases will be mapped at several temperatures using CsAlSiO_4 as a starting material to which SiO_2 and Al_2O_3 will be added.

Before this investigation can begin, a large batch of well characterized CsAlSiO_4 must be prepared. In order to find the best method of preparing CsAlSiO_4 , a number of reactions were studied. The starting materials as well as the expected products of these reactions are listed in Table 1. The results of the x-ray diffraction analyses performed on the actual products which were obtained using these starting materials after 800, 950, and 1025°C heatings for 18 hours are shown in Table 2. The products which were formed agree generally with those which were predicted based on previous literature reports.

Table 1
Preparation Methods for CsAlSiO₄

Method	Starting Materials	Expected Product Based on Literature Reports	
1	Cs ₂ CO ₃ + kaolinite	CsAlSiO ₄	
2	Cs ₂ CO ₃ + metakaolin	CsAlSiO ₄	
3	Cs ₂ CO ₃ + Al(NO ₃) ₃ ·9H ₂ O + Ludox	CsAlSiO ₄	Pollucite
4	Cs ₂ CO ₃ + Al(OH) ₃ ·nH ₂ O (unfired) + silicic acid gel (unfired)	CsAlSiO ₄	
5	Cs ₂ CO ₃ + alumina (Al(OH) ₃ ·nH ₂ O decomposed) + silicic acid gel (unfired)	CsAlSiO ₄	Pollucite
6	Cs ₂ CO ₃ + alumina (Al(NO ₃) ₃ ·9H ₂ O decomposed) + silicic acid gel (unfired)	CsAlSiO ₄	Pollucite
7	Cs ₂ CO ₃ + alumina (Al(OH) ₃ ·nH ₂ O decomposed) + silica (Ludox decomposed)	CsAlSiO ₄	Pollucite
8	Cs ₂ CO ₃ + alumina (Al(NO ₃) ₃ ·9H ₂ O decomposed) + silica (Ludox decomposed)	CsAlSiO ₄	Pollucite
9 ⁸	Cs ₂ CO ₃ + alumina (Al(OH) ₃ ·nH ₂ O decomposed) + silica (silicic acid decomposed)	CsAlSiO ₄	Pollucite
10	Cs ₂ CO ₃ + alumina (Al(NO ₃) ₃ ·9H ₂ O decomposed) + (silicic acid decomposed)	CsAlSiO ₄	Pollucite

⁸ Russ. J. Inorg. Chem. 15(7), 909-11 (1970).

Table 2
Results of X-ray Diffraction Analysis

Method	800°C	950°C	1025°C
1	CsAlSiO ₄	CsAlSiO ₄	-
2	CsAlSiO ₄	CsAlSiO ₄ (sharp peaks)	-
3	unknown phase	CsAlSiO ₄ Pollucite	-
4	amorphous	amorphous	amorphous
5	amorphous	amorphous	CsAlSiO ₄ + Pollucite
6	amorphous	CsAlSiO ₄ (sharp peaks)	CsAlSiO ₄ + Pollucite
7	amorphous	amorphous	amorphous
8	-	amorphous	amorphous
9	amorphous	amorphous	amorphous
10	-	amorphous	amorphous

Good crystallinity, ease of formation, and purity are the characteristics required for the CsAlSiO₄ which must be prepared. Therefore, the best method for obtaining this product with the desired characteristics is method 2 - Cs₂CO₃ + metakaolin. Preparation of CsAlSiO₄ by this method is now underway.

2.2 Ruthenium Fixation (R. G. Johnston)

A number of ternary compounds, all of the perovskite or related structure, are under continuing investigation for the fixation of Ru in a thermally stable phase in supercalcine. Phases currently being studied are SrRuO_3 (previously reported), CaRuO_3 , PbRuO_3 , and BaRuO_3 , their solid solution with structurally analogous phases and related compounds in their respective systems.

SrRuO_3 has been tested for stability at 1200°C and 1400°C (see Table 3 for data on these experiments). At 1185°C, a 24-hour firing yielded only SrRuO_3 , with a negligible weight loss. A much longer firing at 1200°C and a firing at 1400°C yielded $\text{SrRuO}_3 + \text{Sr}_2\text{RuO}_4 +$ an unknown phase, with considerable weight loss. The appearance of Sr_2RuO_4 is a result of the loss to volatilization of one RuO_2 per 2SrRuO_3 . Intermediate length firings are now being conducted at 1200°C to determine the time interval in which SrRuO_3 begins to break down noticeably at this temperature.

Stoichiometric CaRuO_3 and PbRuO_3 have been formed as other candidate phases. CaRuO_3 possesses the GdFeO_3 structure, and is closely analogous to NdFeO_3 . PbRuO_3 may also be written as $\text{Pb}_2\text{Ru}_2\text{O}_6$ ¹, as it is a defect pyrochlore¹. This phase formed easily at temperatures lower than those previously used in this study. Lead volatility is also a problem in the formation of this phase, hence the lower preparation temperatures. The thermal stability of these phases is now under investigation. The solid solubility of CaRuO_3 and NdFeO_3 in each other is also being closely examined. Attempts have been made to form the phase BaRuO_3 , but these have as yet only yielded BaRuO_3 - the major phase - plus an as yet unidentified second phase which persists at all firing temperatures. The weight losses in these cases are only 1-2% over what would be expected from the loss of CO_2 in the initial reaction.

The solid solubilities of some of the phases $\text{Sm}_2\text{Ru}_2\text{O}_7$ - $\text{Sm}_2\text{Zr}_2\text{O}_7$ (RW42) and NdFeO_3 - SrRuO_3 (RW40), which were noted in the previous report, have been closely examined by x-ray diffraction. The unit cell parameters in RW42 - 1,2,3 show no changes from those of the pure starting materials, showing con-

¹Van Loan, Ceramic Bulletin, 51 (3), 231 (1972).

clusively that no solid solution of $\text{Sm}_2\text{Ru}_2\text{O}_7$ in $\text{Sm}_2\text{Zr}_2\text{O}_7$ or vice versa exist. In RW40 - 1,2,3, the unit cell parameters do differ significantly, indicating the existence of solid solution of SrRuO_3 in NdFeO_3 . The unit cell parameters obtained by a least squares computer refinement of their x-ray powder data are as follows:

$$\begin{aligned} \text{Sm}_2\text{Zr}_2\text{O}_7, a_0 &= 10.597 \text{ \AA}; \quad \text{Sm}_2\text{Zr}_2\text{O}_7 \text{ in RW42 - 1,2,3, } a_0 = 10.597 \text{ \AA} \\ \text{Sm}_2\text{Ru}_2\text{O}_7, a_0 &= 10.286 \text{ \AA}; \quad \text{Sm}_2\text{Ru}_2\text{O}_7 \text{ in RW42 - 1,2, } a_0 = 10.286 \text{ \AA} \end{aligned}$$

NdFeO_3	5.455(4) \AA	5.587(2) \AA	7.76(1) \AA
RW40-1, $\text{NdFeO}_3(\text{ss})$	5.48 (1) \AA	5.597(6) \AA	7.75(1) \AA
RW40-2, $\text{NdFeO}_3(\text{ss})$	5.479(9) \AA	5.598(5) \AA	7.75(1) \AA
RW40-3, $\text{NdFeO}_3(\text{ss})$	5.48 (1) \AA	5.598(5) \AA	7.75(1) \AA

The extent of the solid solution of SrRuO_3 in NdFeO_3 is as yet unanswered. Unreacted SrRuO_3 is seen in the diffractograms of RW40 - 1,2,3, but whether there is any solid solution of NdFeO_3 in SrRuO_3 remains unanswered due to the close proximity of the major SrRuO_3 diffraction peaks to those of NdFeO_3 . Since Nd has been found to form apatite structure phases in the presence of SiO_2 instead of NdFeO_3 (P_{ss}) the question of SrRuO_3 solubility in NdFeO_3 is no longer relevant to supercalcine development.

Table 3

Ruthenium Fixation Studies and Results

Run No.	Starting Composition	Firing Temperature, °C	Firing Duration (hr.)	Weight Loss, %	X-ray Phase Analysis
SR6-3A	SrRuO_3	1185	24.33	1.49	SrRuO_3
-3B	"	1200	414.0	19.96	$\text{SrRuO}_3 + \text{Sr}_2\text{RuO}_4 + \text{unknown phase}$
-3C	"	1400	47.8	11.38	$\text{SrRuO}_3 + \text{Sr}_2\text{RuO}_4 + \text{unknown phase}$
PR1-1	$\text{PbO (yellow)} + \text{RuO}_2$	790	20.0	$< 1^\dagger$	PbRuO_3
CR1-1	$\text{CaCO}_3 + \text{RuO}_2$	1050	21.0	20.06*	CaRuO_3
-2	CaRuO_3 (CR1-1)	1075	23.5	< 1	CaRuO_3
BR1-1/1A**	$\text{BaCO}_3 + \text{RuO}_2$	910, 1040	4.0, 65.0	14.32*	$\text{BaRuO}_3 + \text{unknown phase(s)}$
-2	BR1-1/1A	1225	17.0	< 1	$\text{BaRuO}_3 + \text{unknown phase(s)}$
-3	BR2	1210	31.0	< 1	$\text{BaRuO}_3 + \text{unknown phase(s)}$
BR2-1	$\text{BaCO}_3 + \text{RuO}_2$	1050	21.0	14.61%*	$\text{BaRuO}_3 + \text{unknown phase(s)}$
-2	BR2-1	1075	23.5	$< 1\%$	$\text{BaRuO}_3 + \text{unknown phase(s)}$

* 95% or more of this loss is CO_2

** No intermediate regrinding between heatings 1 and 1A

† This run showed a very slight ($< 1\%$) weight gain

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

During the last two months we have been reviewing the literature on Cs fixation with clays and other aluminosilicates and continuing to investigate Cs aluminosilicate formation this time using dehydroxylated (i.e., heat treated) clays.

The literature review was drawn chiefly from the Review-Bibliography of Brownell *et al*¹ which was largely devoted to Cs fixation, and from IAEA Technical Report No. 136.² Almost all of the previous work was concerned with ion exchange fixation of Cs in aqueous wastes by clays, zeolites and natural soils. The montmorillonite-bentonite group of clays and vermiculite were found to have the greatest Cs exchange capacity. This is a rather well-known phenomenon in areas like water treatment and soil science. The work of G. S. Barney of ARHCO was also reviewed in ref. 1. He forms well crystallized pollucite at 80-100°C in a very alkaline (pH > 10) solution from a mixture of CsOH and bentonite. L. L. Ames, Jr., of PNL has performed similar studies at higher temperatures. Both workers point out the importance of high pH which breaks down the clay structure to an Al-Si-gel before forming pollucite.

At this time we cannot say how relevant these aqueous ion exchange and hydrothermal syntheses results will be to supercalcine development. We have no plans at this time to modify the pH of the very acid commercial waste liquid before adding an (alumina + silica) source. However, we should note that montmorillonite and bentonite have proven to be the most effective of the clays studied to date for Cs fixation, both in the hydroxylated form as described in our last report and the heat treated form described below. For this reason we are obtaining samples of the common commercial montmorillonites and bentonites from the major U.S. distributors. These will be used in a comparison study of their ability to form well crystallized pollucite in CAS, CS and supercalcine formulations at moderate temperatures (950-1050°C).

¹L. E. Brownell, C. H. Kindle and T. L. Theis, ARH-2731 Rev., December 1973.

²"The Use of Local Minerals in the Treatment of Radioactive Wastes", IAEA, Vienna 1972. (copy kindly supplied by H. Godbee of H-ORNL).

Both primary references note that the zeolite clinoptilolite $((x)_5\text{Al}_6\text{Si}_{30}\text{O}_{72}, x = \text{Na, K, Ca, Mg, Al})^*$ has exceptional ion exchange capacity for aqueous Cs. Most of this work was performed by L. L. Ames Jr., of PNL. We will also evaluate this mineral as a Cs fixation agent in supercalcine as soon as a sample can be obtained.

Table 5 lists the starting compositions and results of our latest series of CAS runs. The experimental procedures were described in the last report (COO-2510-5).

We found no really pronounced differences in the ability of the natural vs the dehydroxylated (heat treated at 800°C for 6 hrs) clays to form well crystallized CsAlSiO_4 or $\text{CsAlSi}_2\text{O}_6$ (pollucite) at a given temperature. Thus, at this point we are planning to use the natural clays, dried to remove adsorbed and interlayer (but not structural) water. All of our reading and experience to date point to the choice of pollucite rather than CsAlSiO_4 as the desirable Cs aluminosilicate. Montmorillonite and bentonite are the best (alumina + silica) sources for pollucite formation.

Also included in Table 5 are three runs which use a corresponding amount of aluminum nitrate + LUDOX instead of a clay as the (alumina + silica) source. It is interesting to note that CAS-21 and 22 were x-ray amorphous even after 6 hours of firing at 1050°C. Supercalcine formulation 75-1 described in the last report used this same (alumina + silica) source instead of a clay. The results given in Table 5 imply that using montmorillonite or bentonite instead would give better crystallized pollucite. This hypothesis will be tested in the coming months.

A silica tube test for Cs fixation was performed on each CAS run to date. A pellet of each batch dried at 130°C was placed inside a silica tube sealed at one end. The tube was then placed inside a furnace heated to 600°C and left for one hour. The furnace was then turned up to 1050°C (it takes ~45 min to reach this temperature) and left there for an additional hour. The tubes were examined for evidence (frothing and devitrification) of Cs volatilization. Kaolinite, halloysite and pyrophyllite did not fix Cs completely even when added to CsNO_3 in twice the required stoichiometric amount. As little as 1.5 times the stoichiometric amount of montmorillonite or bentonite required for pollucite formation gave perfectly clear glass after

*Composition of a natural specimen described by W. S. Wise et al, Am. Mineral. 54, 887 (1969).

Table 5

Cs Aluminosilicates for Cs Fixation

Run	Composition	Phases* in X-Ray Diffractogram			
		700	800	900	1050
CAS - 7	$2\text{CsNO}_3 + \text{Al}_2\text{Si}_2\text{O}_7$ [Kaolinite- Δ]	A	A	A	S-O
CAS - 9	$2\text{CsNO}_3 + 1.5\text{Al}_2\text{Si}_2\text{O}_7$ [Kaolinite- Δ]	A	A	A	S-C
CAS - 9	$2\text{CsNO}_3 + \text{Al}_2\text{Si}_2\text{O}_7$ [Halloysite- Δ]	A	A	A	S-O
CAS - 10	$2\text{CsNO}_3 + 1.5\text{Al}_2\text{Si}_2\text{O}_7$ [Halloysite- Δ]	A	A	A	M-C
CAS - 11	$\text{CsNO}_3 + \text{AlSi}_2\text{O}_{5.5}$ [Pyrophyllite- Δ]	M-P _y (Δ)	M-P _y (Δ)	M-C+M-P _y (Δ)	M-C + M-P _y (Δ)
CAS - 12	$\text{CsNO}_3 + 1.5\text{AlSi}_2\text{O}_{5.5}$ [Pyrophyllite- Δ]	M-P _y (Δ)	M-P _y (Δ)	S-P _y (Δ)+W-C	W-C + W-P _y (Δ)
CAS - 13	$\text{CsNO}_3 + 2.0\text{AlSi}_2\text{O}_{5.5}$ [Pyrophyllite- Δ]	S-P _y (Δ)	S-P _y (Δ)	M-P _y (Δ)	W-P _y (Δ)
CAS - 14	$\text{CsNO}_3 + (x)\text{AlSi}_2\text{O}_{5.5}$ [Montmorillonite- Δ]	A	W-Q	W-P	S-P
CAS - 15	$\text{CsNO}_3 + 1.5(x)\text{AlSi}_2\text{O}_{5.5}$ [Montmorillonite- Δ]	A	W-Q	W-P	S-P
CAS - 16	$\text{CsNO}_3 + 2.0(x)\text{AlSi}_2\text{O}_{5.5}$ [Montmorillonite- Δ]	W-Q	W-Q	W-Q	S-P+W-Q
CAS - 17	$\text{CsNO}_3 + (x)\text{AlSi}_2\text{O}_{5.5}$ [Bentonite- Δ]	A	W-Q	W-P+W-C	S-P
CAS - 18	$\text{CsNO}_3 + 1.5(x)\text{AlSi}_2\text{O}_{5.5}$ [Bentonite- Δ]	A	W-Q	W-P+W-Q	S-P+W-Q
CAS - 19	$\text{CsNO}_3 + 2.0(x)\text{AlSi}_2\text{O}_{5.5}$ [Bentonite- Δ]	W-Q	W-Q+W-Mt(Δ)	W-Q+W-Mt(Δ)	S-P+W-Q
CAS - 20	$\text{CsNO}_3 + \text{Al}(\text{NO}_3)_3 + 2\text{SiO}_2$ [LUDOX]	A	A	A	S-P
CAS - 21	$\text{CsNO}_3 + 1.5\text{Al}(\text{NO}_3)_3 + 3.0\text{SiO}_2$ [LUDOX]	A	A	A	A
CAS - 22	$\text{CsNO}_3 + 2.0\text{Al}(\text{NO}_3)_3 + 4\text{SiO}_2$ [LUDOX]	A	A	A	A

S = strong, M = medium, W = weak

A = amorphous, C = "cubic", $\text{Cs}_{1-x}\text{AlSiO}_4$, O = "orthorhombic" CsAlSiO_4 P = pollucite, Py(Δ) = reflections of fired pyrophyllite, Mt(Δ) = reflections of fired montmorillonite.

the firing which implied complete Cs fixation. It is interesting to note that 1.5 times the required amount of Al nitrate + LUDOX was not enough for complete Cs fixation, but twice the required amount was. This is another recommendation for using these last two clays in future supercalcine formulations.

2.4 Compatibility Studies

In the last report we described the appearance of an apatite structure phase (A_{ss}) in fired supercalcine formulations whenever SiO_2 had been added. We have since found that this A_{ss} phase will form in any formulation containing both rare earths (RE) and SiO_2 . This is an important finding since RE's are the most abundant components of nuclear waste PW-4b and (alumina + silica) will be added in supercalcine formulations for Cs fixation. It will be shown below that $NdO_{1.5}$ competes favorably with Cs_2O to form A_{ss} instead of pollucite when (alumina + silica) are present. Thus, in future supercalcine formulations it will be necessary to add excess SiO_2 to allow the RE to form A_{ss} and leave (alumina + silica) free to fix Cs in an aluminosilicate. However, it will first be necessary to know the approximate composition of the A_{ss} phase which will form in supercalcine since nearly one-third of the species in nuclear wastes have been shown to form phases of the apatite structure type. In fact, the apatite structure ranks with perovskite and spinel in having such wide ranging ionic substitutions. In order to know what range of compositions is possible in nuclear waste + additives formulations it was necessary to thoroughly review the literature on apatite structure phases and the results of this review are given below. We will then describe the results of the latest group of compatibility studies (CS-runs), many of which involved these apatite phases.

2.4.1. Literature on Apatite Structure Phases (G. J. McCarthy)

The natural apatite minerals are predominantly phosphates (e.g., $Ca_{10}[PO_4]_6F_2$) but we will limit this discussion to the special silicate and phosphate-silicate apatites relevant to supercalcine phase formation. All of the important work on these latter phases has been reported only in the last ten years.

The structural formula of the apatite structure type is

We will be interested in $A, B = Ca, Sr, Ba, RE, Na, K$, $X = Si$ or P and $Y = Oxygen$.

* The Roman Numerals give the coordinations of the ions.

Ito¹ made the first comprehensive study of silicate apatites. Some of the relevant aspects of his work are summarized below.

- Boron and phosphorous readily substitute for silicon in the tetrahedral sites. Since there is P_2O_5 in PW-4b we will look for mixed phosphate-silicates in crystallized supercalcine. To date we have not noted A_{ss} phases in crystallized waste glasses from PNL even though all the appropriate components (Ca, Sr, RE, Si, P, B) are available in the glass. A_{ss} phases have been observed in Hahn-Meitner crystallized glasses.
- Silicate apatites lose (OH) water below 1100°C even though phosphates can retain it at higher temperatures.
- Li and Na are readily substituted in the 7- and 9-fold sites, but K can substitute only to a limited extent. This seems to rule out a role for the much larger Cs ion in this structure type.
- He proposes that there are 26 oxygens in every oxyapatite phase. For example, a Sr⁺-Nd-silicate apatite phase would be $Sr_2Si_8[SiO_4]_6O_2$ rather than the defect form $\square Sr_3Nd_6[SiO_4]_6 \square_2$ proposed by Grisafe and Hummel² and noted in our last report.
- There is complete solid solution between $Ca_2RE_8[SiO_4]_6O_2$ and $Ca_8RE_2[PO_4]_6O_2$.

Rare earths alone, without alkalis or alkaline earths can form apatite structure silicates. Some time ago we³ prepared Nd, Sm and Eu silicates, found the apatite space group ($P6_3/m$) and, from chemical analyses, suggested a formula of $RE_4(SiO_4)_3$ for these phases. Grisafe and Hummel² realized that

¹ J. Ito, Am. Mineral. 53, 890 (1968).

² D. A. Grisafe and F. A. Hummel, Am. Mineral. 55, 1131 (1970).

³ G. J. McCarthy, W. B. White and R. Roy, J. Inorg. Nucl. Chem. 29, 253 (1967).

these were apatites and proposed the doubled formula with extensive defects:

Felsche⁴, who later surveyed all of these rare earth silicates, favored the 26 oxygen per unit cell formula for these phases $\text{RE}_{9.33} \square_{0.67} [\text{SiO}_4]_6 \text{O}_2$ originally proposed by Kuzmin and Belov⁵. Felsche reported almost exactly the same cell parameters for $\text{Sm}_{9.33} [\text{SiO}_4]_6 \text{O}_2$ as we had in 1967, and when his paper appeared we found that our chemical analysis of "samarium silicate" fit this formula much better than it did $\text{Sm}_8 [\text{SiO}_4]_6$. This question of the correct formula for RE silicate and alkaline earth (AE)-RE silicates will be important when we come to designing supercalcline formulations to include the A_{ss} phase.

Felsche⁴ synthesized a complete series of $\text{NaRe}_9 [\text{SiO}_4]_6 \text{O}_2$ (RE = La to Lu, Y) phases. This suggests another crystal chemical role for small amounts of Na in nuclear wastes converted into supercalcline.

Wanmaker et al.⁶ confirm the existence of silicate-phosphate apatites containing both AE and RE elements and give three solid solution formulae:

Note that the last two formula contain 25 and 24 oxygens per unit cell respectively. Schwarz⁷ has also reported phases of this type but, as noted

⁴J. Felsche, J. Solid State Chem. 5, 266 (1972).

⁵E. A. Kuzmin and N. V. Belov, Dokl. Akad. Nauk SSSR, 65, 88 (1965).

⁶W. L. Wanmaker, J. W. ter Vrugt and J. G. Verlijsdonk, J. Solid State Chem. 3, 452 (1971).

⁷H. Schwarz, Inorg. Nucl. Chem. Letters 3, 231 (1967).

above, there is still some question about whether these exist. Because of its importance to supercalcine formulations, we will look into this question ourselves in the coming months.

Finally, from a survey of a dozen or so other papers we found many more minor substitutions possible in this structure type. These can be summarized as follows:

This will give some idea of the very large number of potential crystal chemical substitutions possible in the actual phase formed in crystallized supercalcine. Note also that small amounts of halides (F, Cl) which might appear in the waste liquid can be accommodated in the Y-site of apatite. The question of (OH) retention in the Y-site during moderate temperature (900-1050°C) crystallization will also have to be considered.

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

The background to this area of our work and its importance to supercalcine development were described in detail in the last report (COO-2510-5).

The reactions being tested and the results of twenty-six CS runs are given in Table 5. A brief discussion of each run follows.

CS-25. This was a very critical run with respect to the information it gave on crystalline phase formation in supercalcine formulations which use (alumina + silica). additions to fix CS in pollucite. It demonstrates that $CsAlSi_2O_6$ and $NdO_{1.5}$ are not compatible phases at typical supercalcine crystallization temperatures. $NdO_{1.5}$ is a stand-in for the total RE^{3+} oxides which constitute ~23 wt% of PW-4b oxides. If (alumina + silica) are to be added for CS fixation then additional SiO_2 will have to be added to "passify" the $REO_{1.5}$ by allowing it to form an A_{ss} phase. This conclusion is obvious from the x-ray phase assemblage. The Nd to Si ratio was 1 to 2. In pure $RE-A_{ss}$ according to the Felsche stoichiometry, for every 9.33 Nd only 6 Si are required, leaving 12.67 Si available still to form Cs aluminosilicates. Note that the Si-poor aluminosilicate " $CsAlSiO_4$ "

Table 5
Compatibility Studies and Results

Run Number	Reactions	X-ray Phase Assemblage* After Firing at T(°C) for 6 Hrs.	Comments
Cs-25	$\text{CsO}_{0.5} + \text{AlO}_{1.5} + 2\text{SiO}_2 + \text{NdO}_{1.5} \xrightarrow{I} \text{CsAlSi}_2\text{O}_6 + \text{NdO}_{1.5}$	1050°: M-A _{ss} + M-CsAlSiO ₄ (C) + W-CsAlSi ₂ O ₆ 1200°: M-A _{ss} + M-CsAlSi ₂ O ₆ + M-CsAlSiO ₄ (C)	Apatite structure phase formed Cs-aluminosilicates both Cs-deficient
Cs-26	$\text{CsO}_{0.5} + \text{AlO}_{1.5} + 2\text{SiO}_2 + \text{FeO}_{1.5} \xrightarrow{I} \text{CsAlSi}_2\text{O}_6 + \text{FeO}_{1.5}$ (or $\text{CsFeSi}_2\text{O}_6 + \text{AlO}_{1.5}$)	1050+1200°: S-CsAlSi ₂ O ₆ + M-FeO _{1.5} + W-CsAlSiO ₄ (C)	Reaction confirmed
Cs-27	$\text{CsO}_{0.5} + \text{AlO}_{1.5} + 2\text{SiO}_2 + \text{BaO} + \text{ZrO}_2 \xrightarrow{I} \text{CsAlSi}_2\text{O}_6 + \text{BaZrO}_3$	1050+1200°: S-CsAlSi ₂ O ₆ + S-BaZrO ₃	Reaction confirmed
Cs-28	$2\text{SrO} + 2\text{NdO}_3 + \text{NiO} \xrightarrow{I} \text{Sr}_2\text{NiMoO}_6 + \text{MoO}_3$ $\xrightarrow{II} 2\text{SrMoO}_4 + \text{NiO}$	1050+1200°: S-SrMoO ₄ + H-NiO	Reaction 2 confirmed
Cs-29	$2\text{SrO} + 2\text{NdO}_3 + \text{NiO} + 2\text{FeO}_{1.5} \xrightarrow{I} 2\text{SrMoO}_4 + \text{NiFe}_2\text{O}_4$	1050+1200°: S-SrMoO ₄ + H-NiFe ₂ O ₄	Reaction confirmed
Cs-30	$\text{CsO}_{0.5} + \text{AlO}_{1.5} + 2\text{SiO}_2 + \text{CaO} + \text{MoO}_3 \xrightarrow{I} \text{CsAlSi}_2\text{O}_6 + \text{CaMoO}_4$	1050+1200°: S-CsAlSi ₂ O ₆ + S-CaMoO ₄	Reaction confirmed
Cs-31	$\text{CsO}_{0.5} + \text{AlO}_{1.5} + 2\text{SiO}_2 + \text{CaO} + \text{ZrO}_2 \xrightarrow{I} \text{CsAlSi}_2\text{O}_6 + \text{CaZrO}_3$	1050°: S-CsAlSi ₂ O ₆ + M-F _{ss} (5.12) + W-CsAlSiO ₄ (C) + W-X 1200°: S-CsAlSi ₂ O ₆ + M-F _{ss} (5.12) + W-X	Reaction favored CaO in SS with CsAlSi ₂ O ₆ ?
Cs-32	$\text{CsO}_{0.5} + \text{AlO}_{1.5} + 2\text{SiO}_2 + \text{CaO} \xrightarrow{I} \text{CsAlSi}_2\text{O}_6 + \text{CaO}$	1050+1200°: S-CsAlSi ₂ O ₆ + M-CsAlSiO ₄ (?)	No free CaO Reaction Favored

Run Number	Reactions	X-ray Phase Assemblage After Firing at T(°C) For 6 Hrs.	Comments
CS-33	$UO_2 + SrO + MoO_3 + 2CaO_2 \xrightarrow{1} (2Ce,U)O_{2+x} + SrMoO_4$	1050+1200°: S-F _{ss} (5.42) + M-SrMoO ₄	Reaction confirmed
CS-34	$UO_2 + BaO + MoO_3 + 2CeO_2 \xrightarrow{1} BaUO_4 + 2CeO_2 + MoO_3$ $\xrightarrow{2} BaMoO_4 + (2Ce,U)O_{2+x}$	1050+1200°: S-F _{ss} (5.42) + M-BaMoO ₄	Reaction B confirmed
CS-35	$UO_2 + SrO + ZrO_2 + 2CeO_2 \xrightarrow{1} (2Ce,U)O_{2+x} + SrZrO_3$	1050°: S-F _{ss} (5.40) + W-SrZrO ₃ + M-X 1200°: S-F _{ss} (5.35) + W-SrZrO ₃ + S-X	Reaction not pseudobinary
CS-36	$UO_2 + BaO + ZrO_2 + 2CeO_2 \xrightarrow{1} (2Ce,U)O_{2+x} + BaZrO_3$	1050+1200°: S-F _{ss} (5.35) + S-BaUO ₄ + M-BaZrO ₃	BaUO ₄ more stable than BaZrO ₃ in the presence of CeO ₂
CS-37	$3CaO_{0.5} + 3AlO_{1.5} + 6SiO_2 + 6NdO_{1.5} + 3SrO + 3MoO_3 \xrightarrow{1} 3CsAlSi_2O_6 + 3SrMoO_4 + 6NdO_{1.5}$	1050°: M-A _{ss} + M-SrMoO ₄ + W-CsAlSi ₂ O ₆ 1200°: S-A _{ss} + M-SrMoO ₄ + W-X	1050°C: A _{ss} + S + CsAlSi ₂ O ₆ possibly compatible 1200°C: Cs + some MoO ₃ (?) lost
CS-38	same as CS-37 except 3CaO for 3SrO	1050°: M-A _{ss} + W-CsAlSi ₂ O ₆ + W-CaMoO ₄ 1200°: S-A _{ss} + W-CsAlSi ₂ O ₆ + W-CaMoO ₄ (?) + W-X	Same as above - smaller A _{ss} cell indicates Ca present in A _{ss} phase
CS-39	$3CaO_{0.5} + 3AlO_{1.5} + 6SiO_2 + 6NdO_{1.5} + 6FeO_{1.5} + 3SrO + 3MoO_3 \xrightarrow{1} 3CsAlSi_2O_6 + 6NdFeO_3 + 3SrMoO_4$	1050°: M-NdFeO ₃ + M-CsAlSi ₂ O ₆ + M-SrMoO ₄ + W-A _{ss} + W-Fe ₂ O ₃ 1200°: S-A _{ss} + M-SrMoO ₄ + W-Fe ₂ O ₃	1050°C: proposed reaction favored - A _{ss} beginning to form 1200°C: A _{ss} favored; Ca lost

Run Number	Reactions	X-ray Phase Assemblage After Firing at T(°C) for 6 Hrs.	Comments
CS-40	same as CS-39 except 3CaO for 3SrO	1050+1200°: M-A _{ss} +W-Fe ₂ O ₃ +W-CaAlSi ₂ O ₆	Ca favors A _{ss} formation for Nd vs NdFeO ₃ ; some CaAlSi ₂ O ₆ residual at each temperature
CS-41	same as CS-37 except add 8CeO ₂	1050°: M-CeO ₂ +M-A _{ss} +W-SrMoO ₄ +W-CaAlSi ₂ O ₆ 1200°: S-CeO ₂ +M-A _{ss} +W-SrMoO ₄	Same result as CS-37 with CeO ₂ admixed
CS-42	3SrO+6NdO _{1.5} +6SiO ₂ $\frac{1}{2}$ Sr ₃ Nd ₆ [SiO ₄] ₆	1050+1200°: S-A _{ss} +VW-X	Cell parameters close to Ito's Sr ₂ Nd ₈ [SiO ₄] ₆ O ₂
CS-43	3SrO+6NdO _{1.5} +6SiO ₂ +CeO ₂ $\frac{1}{2}$ CeSr ₃ Nd ₆ [SiO ₄] ₆ O ₂	1050+1200°: S-A _{ss}	Reaction confirmed
CS-44	CeO _{0.5} +3SrO+6NdO _{1.5} +6SiO ₂ $\frac{1}{2}$ CeSr ₃ Nd ₆ [SiO ₄] ₆ O _{0.5}	600°: B-A _{ss} 1050+1200°: S-A _{ss} +VW-X	Cs stain on brick. Diffractogram identical to CS-42
CS-45	3CaO+6NdO _{1.5} +6SiO ₂ $\frac{1}{2}$ Ca ₃ Nd ₆ [SiO ₄] ₆	1050+1200°: S-A _{ss}	Cell parameter close to Ito's Ca ₂ Nd ₈ [SiO ₄] ₆ O ₂
CS-46	3CaO+6NdO _{1.5} +6SiO ₂ +CeO ₂ $\frac{1}{2}$ CeCa ₃ Nd ₆ [SiO ₄] ₆ O ₂	1050+1200°: S-A _{ss}	Reaction confirmed
CS-47	CeO _{0.5} +3CaO+6NdO _{1.5} +6SiO ₂ $\frac{1}{2}$ CeCa ₃ Nd ₆ [SiO ₄] ₆ O _{0.5}	1050+1200°: S-A _{ss}	Cs stain on brick. Diffractogram identical to CS-45

Run Number	Reactions	X-ray Phase Assemblage After Firing at T(°C) for 6 Hrs.	Comments
CS-42a	$8\text{Nd}_{0.5} + 6\text{SiO}_2 \rightarrow \text{Nd}_8[\text{SiO}_4]_6$	1050+1200*: S-A _{ss} +W-NdO _{1.5} +VW-X	Cell parameters of A _{ss} phase closer to Felsche's ^{ss} Nd _{9.33} [SiO ₄] ₆ O ₂
CS-42b	$2\text{SrO} + 8\text{NdO}_{1.5} + 6\text{SiO}_2 \rightarrow \text{Sr}_2\text{Nd}_8[\text{SiO}_4]_6\text{O}_2$	1050+1200*: S-A _{ss}	Diffractograms almost identical to CS-42; confirms Ito's stoichiometry for the Sr-Nd-A _{ss} prepared at 1050-1200°C
CS-45a	$2\text{CaO} + 8\text{NdO}_{1.5} + 6\text{SiO}_2 \rightarrow \text{Ca}_2\text{Nd}_8[\text{SiO}_4]_6\text{O}_2$	1050+1200*: S-A _{ss}	confirms Ito's stoichiometry

*A_{ss} = Apatite structure solid solution; CsAlSiO₄ (C) = pseudocubic Cs-deficient phase of "CsAlSiO₄";

F_{ss} = Fluorite structure solid solution; X = reflections due to unidentified phase or phases.

Intensity of reflections of the phase in the diffractogram: S = strong, M = medium, W = weak.

is one of the resultant phases along with $\text{CsAlSi}_2\text{O}_6$. Weight loss and observation of the sample brick showed clearly that some of the CS was volatilized.

The results of this run also explain why a 2.5 excess of (alumina + silica) over the stoichiometric amount is required for supercalcine formulation 75-1. Clearly, the $\text{AlO}_{1.5}$ excess is not required; it is only excess SiO_2 which must be added to "passify" the $\text{REO}_{1.5}$. Several supercalcine formulations using only the excess SiO_2 will be tested in the coming month. Questions still arise as to what is the actual composition of A_{ss} formed from the total waste plus additives. These questions will be addressed in runs described below and in others now in progress.

CS-26. This run demonstrates that $\text{FeO}_{1.5}$ is compatible with $\text{CsAlSi}_2\text{O}_6$ and that the Al-pollucite is more stable than its Fe-analog ($\text{CsFeSi}_2\text{O}_6$).

CS-27. In CS-21 we tested the compatibility of $\text{CsAlSi}_2\text{O}_6$ + SrZrO_3 and found that SrZrO_3 was not stable enough to prevent SrO from interfering with $\text{CsAlSi}_2\text{O}_6$ formation. In CS-27 we see that BaZrO_3 is a stable enough phase and coexists with $\text{CsAlSi}_2\text{O}_6$ at 1050 and 1200°C.

Because of the considerable stability of BaZrO_3 and the preference of BaO to form BaZrO_3 rather than BaMoO_4 (CS-6) we will assign the Ba in future supercalcine formulations to BaZrO_3 formation.

CS-28,29. These are follow-up runs to CS-17 and 18 which were testing the possibility of Mo in 6-coordination in the perovskite structure phase, $\text{Sr}_2\text{NiMoO}_6$. In CS-28 we see that 2SrMoO_4 + NiO is a more stable phase assemblage than $\text{Sr}_2\text{NiMoO}_6$. In CS-29, the affinity of NiO for Fe_2O_3 to form the spinel phase is once again demonstrated. Thus, in the presence of Fe (which is, of course, the case in PW-4b), Ni will form NiFe_2O_4 rather than " $\text{Sr}_2\text{NiMoO}_6$."

CS-30. In CS-4 we saw that SrMoO_4 + $\text{CsAlSi}_2\text{O}_6$ are compatible. Since we are thinking of replacing Sr with Ca as a supercalcine additive, is CaMoO_4 also compatible with pollucite? CS-30 demonstrates that they are compatible.

CS-31,32. From these two runs it appears that CaZrO_3 is not as stable a phase as CaMoO_4 and CaO is available to interfere with pollucite formation. Free CaO in CS-32 is even more of a problem. The reaction brick showed signs of Cs volatilization in both runs. As was the case with Sr additions, we will have to be sure that there are no substantial excesses of Ca in supercalcine formulations.

CS-34,35,36. These are continuations of CS-15 and 16 and each is concerned with determining the crystal chemical role of U in waste + additive formulations. In CS-34, UO_x shows a preference for forming a F_{ss} with CeO_2 when MoO_3 is also present to tie-up BaO as BaMoO_4 . Note that without the MoO_3 , BaUO_4 would be formed (CS-16).

In CS-35 the proposed reaction is too simple a model for the actual behavior. Some SrZrO_3 is formed but the cell parameters of F_{ss} , $5.40\text{\AA}$ and $5.35\text{\AA}$, indicate that a substantial fraction of the original ZrO_2 is in solid solution with CeO_2 . If UO_2 were the only other F_{ss} component with CeO_2 then the cell parameter would expand from $5.41\text{\AA}$ rather than contract. Again, in CS-36, some of the ZrO_2 that would have been used to form BaZrO_3 is in solid solution with CeO_2 leaving BaO free to form BaUO_4 . The results to date imply that in an alkaline earth poor environment UO_{2+x} will be found in solid solution with CeO_2 , while in the presence of excess Sr or Ba complex Sr uranates or BaUO_4 are formed. Several more runs with even more complex mixtures of PW-4b + additive (especially SiO_2 ; USiO_4 stability?) constituents will be needed to deduce the actual role of UO_{2+x} in supercalcine.

CS-37 $\rightarrow$ CS-41. In this series of runs we are testing the stability of A_{ss} compared to $\text{CsAlSi}_2\text{O}_6$ and other phases known to be quite stable in crystallized waste (SrMoO_4 , NdFeO_3 etc).

In CS-37 and 38 the affinity of $\text{NdO}_{1.5}$ for SiO_2 is again demonstrated. The diffractogram indicates that the A_{ss} phase has some alkaline earth in solid solution and is not simply pure $\text{Nd}_{9.33}[\text{SiO}_4]_6\text{O}_{24}^*$. This leaves some MoO_3 "unfixed" and vulnerable

*From the positions and splittings of certain reflections; see CS-42 a,b below.

to volatilization. Not all of the AE oxide is tied-up in A_{ss} since some $SrMoO_4$ and $CaMoO_4$ respectively are noted in the diffractograms. With part of the available SiO_2 used in A_{ss} formation some of the Cs that would have been fixed in $CsAlSi_2O_6$ must have been lost. Weight losses and examination of the reaction bricks confirmed this.

No Al-containing phase was noted in any of the diffractograms of these and similar runs. If Cs is lost then excess Al must be available. It could be present as poorly crystallized oxide (we always check for γ and α - Al_2O_3). One interesting possibility is that $[AlO_4]$ partially replaces $[SiO_4]$ in A_{ss} . We will be looking into this in the next quarter.

$NdO_{1.5}$ has shown a strong tendency to form $NdFeO_3$ in the presence of $FeO_{1.5}$. Will $FeO_{1.5}$ "passify" $NdO_{1.5}$ and prevent the A_{ss} formation which interferes with Cs fixation? In the 1050°C firing of CS-39 it almost appears to be working. $NdFeO_3$ is a prominent phase and A_{ss} is just beginning to form. $NdFeO_3$ must be close to A_{ss} ($Sr_2Nd_8[SiO_4]_6O_2$?) in stability. However, after the 1200°C firing, the Nd is all in A_{ss} and free $FeO_{1.5}$ is observed. The formulation of CS-40 is identical except that Ca is used as the AE in place of Sr. Here there is no question of A_{ss} vs $NdFeO_3$ stability at 1050°C. Apparently the Ca- A_{ss} is more stable than the Sr- A_{ss} . This is an important observation for supercalcline design since the AE are added for MoO_3 fixation as $AEMoO_4$. In order to know what quantities of AE's to add we must know the crystal chemical preferences of each.

In CS-41 we are checking on whether CeO_2 would tie up $NdO_{1.5}$ in a F_{ss} instead of A_{ss} . The results indicate that it will not. The F_{ss} cell parameter is that of pure CeO_2 .

CS-42 + CS-47. Each of these runs was designed to learn more about the composition, x-ray powder data and ionic substitutions of the A_{ss} phases.

In CS-42 and 45, we used the Grisafe and Hummel* stoichiometry for a AE-RE-silicate apatite but the results fit better with the Ito* stoichiometry.

* See section 2.4.1 for the background and references to this discussion.

Can Ce be incorporated in A_{ss} ? Runs CS-43 and 46 demonstrate that it can. This substitution has never been reported in any of the silicate-apatite literature reports.

The limited K^+ solubility in A_{ss} observed by Ito made it unlikely that the much larger Cs^+ could be contained in A_{ss} as CS-44 and CS-47 suggest. As expected, all of the Cs was volatilized and the diffractograms were identical to, but indicated better crystallinity than, CS-42 and 45. We attribute the improved crystallinity to the presence of Cs as a "mineralizer" during initial A_{ss} crystallization.

Runs CS-42a, 42b and 45a are designed according to Felsche's and Ito's stoichiometries for A_{ss} 's. Pure A_{ss} phases were obtained and the hexagonal cell parameters corresponded closely with those reported by Felsche for $Nd_{9.33}[SiO_4]_6O_2$ and Ito for $AE_2Nd_8[SiO_4]_6O_2$. Long term firing to check for steady state phase assemblages were still in progress at the time this report was prepared.

The well crystallized pure phases will be used to obtain x-ray powder data not currently available. In particular, the positions of several reflections as well as the unit cell parameters will be useful because they can be used to distinguish a pure RE silicate apatite from an AE-RE-silicate apatite.

We will use the Ito stoichiometry with 26 O's per unit cell in future CS-runs and in the supercalcine formulation described in the next section. We should note that Grisafe and Hummel used considerably higher temperatures and longer firing times (typically 1350°C for 2 days) than we will. Their defect stoichiometries, $\square_2RE_8[SiO_4]_6\square_2$ and $\square AE_3RE_6[SiO_4]_6\square_2$, may apply to A_{ss} phases prepared under these conditions.

2.5 Supercalcine Formulation 75-2 (G. J. McCarthy)

A new set of phase formation hypotheses has been assembled based on the compatibility studies completed to date. Table 6 lists these along with the crystal chemical bookkeeping needed to give the total base formulation.

Our new supercalcine formulation based on this base formulation, but with twice the (Al + Si) needed for Cs fixation as pollucite, is labeled 75-2:

Supercalcine Formulation 75-2

For every liter of PSUW-4* add

0.220 M Sr nitrate

0.196 M Al nitrate

0.581 M SiO₂ (as LUDOX)

This formulation and others based on it will be tested in the coming months with the objective of optimizing the concentration and form of the (Al + Si) additions and replacing some or all of the Sr additive with Ca.

* See Table 7, p. 39, Annual Report, C00-2510-5.

NOTE: errors in column 4 of Table 7 of that report:

change 110.0g Nd(NO₃)₃·6H₂O to 71.2g

change 1.1g Y₂O₃ to 1.4g

Table 6

Phase Formation Hypotheses in #75-1

Meq in PSUW-4	Phase Formation	Additives
265 RE^{3+} 39 PO_4	$31.5 \text{ Sr}_2\text{RE}_8[\text{SiO}_4]_6\text{O}_2$ $6.5 \text{ Sr}_8\text{RE}_2[\text{PO}_4]_6\text{O}_2$	$+ 63 \text{ Sr}$ $+ 52 \text{ Sr}$ $+189 \text{ Si}$
164 Zr 42 Ba 99 Ce	$42\text{BaZrO}_3 + \text{F}_{ss}$	
147 Mo	147 SrMoO_4	+147 Sr
42 Sr		- 42 Sr
83 Cs 15 K	$98(\text{Cs}_{0.85}\text{K}_{0.15})\text{AlSi}_2\text{O}_6$	$+ 98 \text{ Al}$ $+196 \text{ Si}$
77 Fe 8 Ni 19 Cr	$\text{NiFe}_2\text{O}_4 + \text{oxides}$	
1000 meq		$+220 \text{ meq Sr}$ $+ 98 \text{ meq Al}$ $+385 \text{ meq Si}$

Appendix

Crystalline Ceramic Nuclear Waste Forms

Presented At

Kernforschungszentrum Karlsruhe, August 19, 1975

Hahn-Meitner-Institut für Kernforschung, Berlin, August 20, 1975

Slide 1:

CRYSTALLINE CERAMIC NUCLEAR
WASTE FORMS

Dr. G. J. McCarthy
Pennsylvania State University

- PART I: Crystalline Phase Formation on Firing
a Typical Nuclear Waste Calcine.
- PART II: A Ceramic - Nuclear Waste Composite
Prepared by Hot Pressing.
- PART III: Fixation of Nuclear Wastes in a
Crystalline Waste Form ("Supercalcine")

Slide 2:

NUCLEAR WASTE FORMS
"SOLIDIFICATION"

Slide 3:

Crystalline Phases Formed in Fired Waste PW-4b

- PW-4b "boil down" calcine supplied by BPNL;
heated 500-1350°C:
500- 800°C: essentially x-ray amorphous
poorly crystallized F_{ss}
800-1000°C: beginning of crystallization
1000-1350°C: all "steady-state" phases formed.
- F_{ss} obvious but unambiguous identification of other
phases difficult.
- Study of simpler combinations of PW-4b components
necessary.

Slide 4:

Waste Formulation Studied

- "Simplified" PW-4b with chemical stand-ins.
In order of abundance:
 RE^{3+} , Fe, Mo, Zr, Ce, Cs, Ni, Sr, Ba, U
- Note: half of Fe is a stand-in for Ru
some of Mo is a stand-in for Tc
most of Ni is a stand-in for Pd
some of U is a stand-in for TU
Nd will be used as a stand-in for RE^{3+} .

Slide 5:

Experimental

- Volumetric Mixing - nitrates and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.
- Solutions dried; product "calcined" 500°C - 2 hrs.
- Pelletized and fired 1050 - 6 and 48 hrs.
1350 - 6 hrs.
- X-ray powder diffraction phase analysis.

Slide 6:

SELECTED RUNS

1050 - 6 hrs.

Composition	X-ray Phase Analysis
(A) Nd + Ce	F_{ss} (11.03)
(B) Nd + Ce + Mo	F_{ss} (5.49) + $Nd_2Mo_3O_{12}$
(C) Nd + Ce + Mo + Fe + Zr	$Nd_2Mo_3O_{12}$ + F_{ss} (5.39) + F_{ss} (5.28) + Fe_2O_3
(D) (C) + Sr	F_{ss} (5.30) + S_{ss} + P_{ss} (3.88)
(E) (D) + Ni	F_{ss} (5.32) + S_{ss} + P_{ss} (3.88) + Sp_{ss}
(F) (E) + U	F_{ss} (B-5.32) + S_{ss} + P_{ss} (3.88) + Sp_{ss}
(G) (F) + Cs	F_{ss} (5.38) + F_{ss} (5.34) + S_{ss} + P_{ss} (3.91) + Sp_{ss}

F = fluorite; S = scheelite; P = perovskite; Sp = spinel.

Slide 7:

Crystalline Phases in Fired Waste

- F_{ss} : $(Ce, Nd, Zr, U \dots)O_{2+x}$
 $(Zr \dots)O_{2+x}$
- Sp_{ss} : $(Ni, Fe)(Fe, Cr)_2O_4$
- S_{ss} : $(Sr, Ba, Nd^{3+}, Cs(?))MoO_{4+x}$
- P_{ss} : $(Nd, Sr, Ba \dots)(Fe, Zr, Cr, Ni(?), Mo(?))O_{3+x}$
- No major role for Cs in any phase.
- All of the above should have fair-to-good thermal stability and leaching resistance.

PART II

Slide 8:

Waste: PW-4b Calcine

- Essentially X-ray amorphous
- Major Components are oxides of
 - RE^{3+} (Nd, La, Pr, Sm)
 - Zr
 - Mo(Tc)
 - Ce
 - Cs
 - Ru
 - Fe
 - Ni(Pd)
- Other components, oxides of
 - Sr
 - Ba
 - U
 - Cr
 - Te
 - Rb
 - Co
 - P
 - Ag
 - Cd
 - (Plus others in trace quantity)
- Prepared by spray drying at BPNL; UO_2 added later.

Slide 9:

Matrix: α -quartz

- Low water solubility
- Low reactivity with waste
- Thermodynamic stability (as α or β) over the temperature range of interest; transformation to other polymorphs is sluggish at higher temperatures.

Consolidation Aids

- Lead borosilicate glass: low melting range and viscosity at hot pressing temperatures; moderate leaching resistance.
- "Pyrex" (Corning 7740) high leaching resistance but viscosity too high at temperature range of interest.

Slide 10: Hot Pressing Apparatus

Slide 11: Graphite "punch" and "dies"; 1 inch and 2 inch samples

Slide 12:

Composition and Sample Characterization of Selected Runs

Run No.	Formulation (wt%)	Hot Pressing ^a Temperature (°C)	H ^b	S.G. ^c	Leachability (72 Hr., % weight loss)	Porosity and Average Size (S/D)
HP-41	30 PW-4b 60 Quartz 7 PHS	1200	>>SS	3.1	1.1	0.72 - 1.7µ
HP-43	"	1100	>SS	3.1	1.6	1.22 - 1.6µ
HP-49	"	1000	<SS	3.0	2.7	4.92 - 1.7µ
HP-51	25 PW-4b 67.5 Quartz 7.5 PHS	1200	>>SS	3.0	0.92	-
HP-55	20 PW-4b 72 Quartz 8 PHS	1200	>>SS	3.0	0.81	-

^a pressure = 3000 psi, time at temperature = 10 min. in each case.

^b Hardness relative to a stainless steel (SS) point.

^c Specific Gravity.

Slide 13:

X-Ray Phase Analysis of HP-41

VS- Quartz (+W-Cristobalite)

S- Fluorite Structure Solid Solution ($a_0 = 5.40\text{\AA}$)
(Ce, RE, $^{3+}$ Zr, U ...) O_{2+x}

S- Scheelite structure solid solution
(Sr, Pb, Ba, RE $^{3+}$...) MoO_4

W- Spinel structure solid solution
(Ni, Co ...) (Fe, Cr ...) $2O_4$

W- RuO_2

W- Fluorite Structure Solid Solution ($a_0 = 5.31\text{\AA}$)
(Zr, Cr ...) O_{2+x}

Slide 14:

Microstructure of Sample HP-41 (see Report C00-2510-4)

Slide 15:

Soxhlet leach test apparatus

Slide 16: Leachability of HP-41

- Nine determinations of 72 hr. % weight losses
Penn State: 1.1, 1.1, 1.2, 1.0, 1.3, 1.2
BPNL : 1.0, 1.4, 1.4
- Leachability results on other materials

Pyrex glass 0.55%	Silica glass 0.19%
"Bottle glass" 4.2%	α - Al_2O_3 0.08%
Kyanite 0.72%	Waste Glass (40% PW-4b) 0.83%
Waste glass (33% PW-4b) 0.44%	Waste Glass (26% PW-4b) 0.57%
- 6-9% of Cs present in HP-41 was leached out in 3 days.
- HP-41 lost 1.9wt% after 10 days leaching; ~17% of Cs was leached out of HP-41.

Slide 17: Thermal Stability of Sample HP-41 at 800°C, 900°C and 1050°C
(see Report C00-2510-4)

Slide 18: Recommendations

- Determine engineering feasibility
- Optimize matrix: aluminosilicates for Cs fixation; Other refractory oxides; Other glass consolidation aides
- Optimize waste/matrix ratios to fit desired properties (leachability, heat generation etc)
- Optimize processing conditions and reactor
- Use "supercalcine" instead of calcine

PART III

Slide 19: Development of Supercalcine

- Crystalline phases formed in fired waste. **PART I:**
- Desirable phases for "fixation" of problem species (Cs, Ru, Te...).
- Compatibility studies - "Crystal chemical affinities" of waste and additive species.
- Supercalcine formulations - consolidation and characterization.

Slide 20: Cs Fixation: Phases Studied

• Perovskite Type

• Scheelite Type

* Structure type not known; probably related to scheelite type

- Oxide Chemistry of Cs surveyed: many other phases but very few stable to 1000°C and water insoluble.

Cs FIXATION: Aluminosilicates

- Two types of Cs Aluminosilicates are known:
"CsAlSiO₄": wide range of stoichiometry and least two distinct phases: near-stoichiometric is orthorhombic (Fr.) or hexagonal (Russ.); Cs-deficient phase is pseudo-cubic.
- "CsAlSi₂O₆" (Pollucite): Well established structure; stoichiometry range likely; Cs not exchangeable; good thermal stability.
- Phase Equilibrium and Crystal Chemistry
Investigation of portions of the Cs₂O - Al₂O₃ - SiO₂ system are in progress.
- Alumina + silica from clays, zeolites, micas and Al nitrate + silica sol.

Slide 22: Ru Fixation

- RuO_2 , unstable at high temperatures in oxidizing atmosphere; stable refractory phase to fix Ru needed

• Phases Studied

Slide 23:

Compatibility Studies

Examples

Slide 24: Supercalcine Formulations

1. List waste composition in milliequivalents (millimoles) of cations.
2. Propose crystalline phase formation for each cation based on crystal chemical insight, fixation studies, compatibility studies and previous supercalcine runs.

Use additives if the cations necessary to form the phases are not available in the waste.
3. Sum the waste and additives = supercalcine formulation.

Slide 25: Illustrative Example

Waste (meq)	Proposed Phase Formation	Bookkeeping
110 Cs	110 CsNbO ₃	+ 110 Nb
180 Mo	180 (Sr,Ba)MoO ₄	+ 180 Sr
80 Fe	80 NdFeO ₃	-
260 Nd	80 NdFeO ₃	-
100 Ce	(Ce ₁₀₀ Nd ₁₈₀ Zr ₁₇₀)O _{2-x}	-
170 Zr		-
50 Sr	(Sr,Ba)MoO ₄	- 50 Sr
50 Ba		- 50 Sr
1000 meq.	required additives per equivalent of waste:	80 meq Sr 110 meq Nb

Slide 26: Experimental

- Supercalcine formulation boiled-down, dried, fired at 500°C-2 hrs., ground and pelletized.
- Fired at 1050°C, 2, 6 and 24 hrs.
1200°C, 6 hrs.
- Weight loss recorded, x-ray phase assemblage determined.
- Silica glass tube experiment - Cs volatilization
- (Consolidation and leach testing)
- (Fluidized bed and spray calcining at BPNL)

Slide 27: Evidence of Cs volatilization on the high-silica support brick after firing at 1050°C

Slide 28: Evidence of Cs volatilization from pellet placed inside a silica glass tube and heated for 2 hours at 1050°C.

Slide 29:

Crystalline Ceramic Nuclear Waste Form
Conceptual Flow Sheet