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RADIATION AND TRANSMUTATION EFFECTS
RELEVANT TO
SOLID NUCLEAR WASTE FORMS

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Rockwell International

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ABSTRACT

Radiation effects in insulating solids are discussed in a general way as an introduction to the quite sparse published work on radiation effects in candidate nuclear waste forms other than glasses.

Likely effects of transmutation in crystals and the chemical mitigation strategy are discussed.

It seems probable that radiation effects in solidified HLW will not be serious if the actinides can be wholly incorporated in such radiation-resistant phases as monazite or uraninite.

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1.0 INTRODUCTION

Self-irradiation and transmutation effects in solidified nuclear waste forms could be of considerable significance. The general idea that radiation effects will be deleterious is based on the well-known lattice disruption and dimensional changes, and the increased rate of etching ("fission track" development) in some radiation-damaged solids, both crystalline and vitreous. Radiolysis effects might also be expected to be damaging because of the very reactive nature of radiation-induced free radicals. However, such generalities are of little value in evaluating quantitatively the actual radiation effects on the properties of a particular waste form, and the quantitative effect on the waste package system.

Over the last 30-odd years, there has been a great deal of work on fundamental radiation effects in all types of solids. In the present report, such radiation-effects research in nonmetallic inorganic solids will be reviewed in a general way. Since it seems unlikely that solid waste forms will be metallic (an electrolytically made metallic form was, however, proposed recently⁽¹⁾) apart from the use of metals as encapsulants or canisters, there will be little discussion of radiation effects in metals.

Information on radiation effects in candidate solid nuclear waste forms is quite sparse but will be briefly discussed. Attention will be drawn to crystalline phases known to have substantial radiation resistance. There have been some recent reviews along these lines,⁽²⁻⁴⁾ but the emphases in the present work will be somewhat different.

Transmutation effects might also cause difficulties in nonmetallic waste forms. When a nuclide radioactively decays, the daughter ion may be chemically different to the parent. Thus although the parent nuclide may fit into the waste form at the atomic level, the daughter ion may not so fit and the waste form would then be rendered further from thermodynamic equilibrium. This effect will be discussed in more detail in Section 6, but the bulk of this report will be concerned with radiation effects.

TABLE 1
CHEMISTRIES OF HIGH-LEVEL NUCLEAR WASTES
FROM REPROCESSING

Component	Mole Percent			
	PW-4b	PW-7	PW-7a	PW-8a
Rare earths	26.4	30.9	20.5	6.7
Zr	13.2	9.2	6.1	3.5
Mo	12.2	8.2	5.5	3.2
Ru	7.6	5.1	3.4	2.0
Cs	7.0	4.7	3.1	1.8
Fe	6.4	8.7	5.8	30.0
Pd	4.1	2.8	1.8	1.1
Sr	3.5	2.3	1.6	0.9
Ba	3.5	2.3	1.6	0.9
[PO ₄]	3.2	8.7	5.8	1.7
U	1.4	9.6	6.3	3.7
Rb	1.3	0.9	0.6	0.3
Na	--	0.9	34.0	40.0
Am+Cm+Pu	0.2	0.2	0.2	0.1
Others	9.8	5.5	3.7	4.1

PW is U.S. Energy Research and Development Administration shorthand for Purex process wastes. PW-4b and PW-7 are "clean" HLW's. (Clean is equivalent to low sodium.)

PW-7a and PW-8a are "dirty." (Dirty is equivalent to high sodium.)

PW-7 contains an excess of gadolinium used as a neutron absorber plus more iron, [PO₄], uranium, and some sodium.

PW-8a is typical of HLW in storage at Nuclear Fuel Services, West Valley, New York.

Data from Reference 7.

The important radioactive decay particles in nuclear wastes are α -particles, α -recoil nuclei, β - and γ -rays, neutrons, and fragments from spontaneous fission. The chemical compositions of HLW from reprocessing are shown in Table 1. The content of long-lived radioactive nuclides in fission products is indicated in Table 2. The time evolution of the α , β , and neutron productions in the (reprocessed) waste from 1 tonne of heavy metal fuel has been given by Roberts et al.⁽⁵⁾ (See Figure 1). Whereas β - and γ -rays reputedly (see below) produce essentially only ionization effects (electron-hole pairs), α -rays and, more importantly, α -recoil nuclei produce significant numbers of atomic displacements (Table 3). Based on calculations such as those shown in Table 2 and those of Roberts et al.,⁽⁵⁾ Malow and Andresen⁽⁶⁾ have calculated the time evolution of the number of atomic displacements from α , β , and fission events in a reference waste form (20% of 6-year-old waste oxides from commercial reprocessing, in borosilicate glass) and also give the time evolution of the number of α -events $\cdot \text{cm}^{-3}$ in the reference waste form (see Figure 2). Using the data of References 5 and 6, we calculated the α - and β -doses for 10^3 and 10^6 years for wastes of various ages (see Table 4).

The above calculations however, refer only to atomic displacements calculated by the basic methods of Kinchin and Pease⁽⁹⁾ and self-annealing and displacements due to ionization effects (radiolysis) are ignored. However, for fission-fragment irradiated zircon, zirconia, α -alumina, and U_3O_8 it can be deduced⁽¹¹⁻¹⁴⁾ that each fission event produced $\sim 10^6$ - 10^7 displaced atoms, a value much higher than those given in Table 3. Very recently, Hobbs and co-workers⁽¹⁵⁻¹⁷⁾ have rendered quartz amorphous by electron irradiation, and have attributed the effects to radiolysis, not classical atom displacement. Though it is suggested⁽¹⁶⁾ that the β/γ self-irradiation of silicate-based solid waste media could produce comparable effects to α -recoil events, quantitative justification of the proposal is presently lacking — particularly as the radiolysis experiments are influenced by the quantities of H_2O in the quartz and are carried out at very high electron-beam current densities. Effects of purely ionizing radiation have also been studied in vitreous silica and density changes have been observed; again radiolysis effects would seem to be responsible.⁽¹⁸⁻¹⁹⁾

TABLE 2

YIELDS OF STABLE (OR LONG-LIVED)* FISSION PRODUCTS FROM THERMAL FISSION OF ^{235}U

(Z) Element	A_R	% Yield [†]	Radioactive (%)	$t_{1/2}$ Year	(Z) Element	A_R	% Yield [†]	Radioactive (%)	$t_{1/2}$ Year
(34) Selenium	79	0.4	11	$\sim 6 \times 10^4$	(50) Tin	126	0.1	37	1×10^5
(35) Bromine		0.3	-	S	(51) Antimony	125	0.1	30	2.7
(36) Krypton		3.8			(52) Tellurium		2.5	-	S
(37) Rubidium		1.3	-	S	(53) Iodine	129	1.0	83	1.6×10^7
(38) Strontium	90	6.2	60	29	(54) Xenon		20		
(39) Yttrium		4.8	-	S	(55) Cesium	134 135 137	20	5 15 44	2 3×10^6 30
(40) Zirconium	93	36.9	20	1.5×10^6	(56) Barium		6.7	-	S
(41) Niobium		<0.1	-		(57) Lanthanum		6.6	-	S
(42) Molybdenum		25.1	-	S	(58) Cerium	144	12.3	2	0.8
(43) Technetium	99	6.1	100	2×10^5	(59) Praseodymium		5.9	-	S
(44) Ruthenium	106	9.3	5	1.0	(60) Neodymium		20.5	-	S
(45) Rhodium		4.9	-	S	(61) Promethium	147	2.3	100	2.6
(46) Palladium	107	1.4	15	7×10^6	(62) Samarium	151	1.9	5	90
(47) Silver		0.2	-	S	(63) Europium	154 155	0.2	~ 28 2	85 49
(48) Cadmium		0.1	-	S	(64) Gadolinium		<0.1	-	S
(49) Indium		<0.1	-	S					

* $t_{1/2} > 0.5$ year[†]% Yield is the number of atoms per 100 fissions A_R = atomic weight of radioactive isotope

S = stable

Data from Reference 8

a. Alpha Dose to Wastes

b. Neutron Dose to Wastes

c. Beta Dose to Wastes

Figure 1. Alpha, Neutron, and Beta Doses to Wastes
(see Reference 5)

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TABLE 3
ATOMIC DISPLACEMENTS DUE TO DIFFERENT RADIATIONS

Radiation	Number of Displacements	Maximum* Displacements	Principal Energy Transfer Mechanism	Reference
α -particle (E = 6 MeV)	~100	2×10^5	Ionization except at very end of trajectory	5
Associated α -recoil (E = 0.1 MeV)	~2000	4×10^3	Displacement/ionization	5
>0.5 MeV β^- average = 1.5 MeV	<0.1	6×10^4	Ionization	5
2 MeV γ	<<0.1	8×10^4	Ionization	5
46.5 MeV Ni^{6+}	8×10^3	2×10^6	Ionization	5,10
$^{10}\text{B}(n,\alpha)^7\text{Li} + 2.8 \text{ MeV}$	800	1×10^5	As for α -particle	5,6
$^{235}\text{U}(n,f)^{141}\text{Ba} + 168 \text{ MeV}$	1×10^3 (5) 5×10^3 (10) $\sim 10^5$ (6)	7×10^6	Ionization	5,6,10
Fast neutron	200	$4 \times 10^4/\text{MeV}$	Ionization	5

* (Incorrectly) assuming (a) all energy used for bond-breaking and (b) displacement energy = 25 e.v.

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Figure 2. Time Evolution of α , β , and Spontaneous Fission Dose in a Reference Borosilicate-Glass Containing 20 Weight Percent of 6-Year-Old Reprocessing Waste Oxides (After Reference 6)

TABLE 4
RADIATION DOSES IN NUCLEAR WASTE FORMS
(Commercial Waste - 20 waste oxides in borosilicate glass)

Dose	age of waste (yr)		
	1	10	50
cumulative dose (cm^{-3}) after 10^3 years			
α dose	2.0×10^{18}	1.7×10^{18}	1.3×10^{18}
β dose	1.9×10^{20}	1.3×10^{20}	1.0×10^{20}
cumulative dose (cm^{-3}) after 10^6 years			
α dose	3.0×10^{19}	3.0×10^{19}	2.9×10^{19}
β dose	3.1×10^{20}	2.5×10^{20}	2.2×10^{20}

These values were calculated from the results of References 5 and 6. Values for defense wastes will be 10^2 less in each case, but precise values will depend on the actual composition of the waste form.

To make laboratory studies which relate to the radiation response of a solidified waste form for many years after solidification, it is clearly necessary to use accelerated testing. For α -recoil damage, this can be done most directly by incorporating short-lived α -emitters such as ^{236}Pu , ^{238}Pu , or ^{244}Cm in the waste form. However, a whole range of other possible irradiation techniques exists: fast neutrons, fast-neutron fission of ^{235}U or ^{238}U , slow-neutron fission of ^{235}U , slow-neutron reactions on ^{10}B or ^6Li , accelerated ions or "external" α -sources. Each of these methods has obvious advantages and disadvantages (Table 5). In Section 5, the most appropriate tests for the radwaste problems will be discussed.

TABLE 5
VARIOUS KINDS OF ATOM DISPLACEMENT-PRODUCING TECHNIQUES

Type	Approximate Neutron cross-section (barns)	Natural Isotopic Abundance (%)	Range
(1) $^{10}\text{B}(n,\alpha)^7\text{Li} + 2.8 \text{ MeV}$	4000 (slow)	19.8	$\sim 2 \mu\text{m}$
(2) $^6\text{Li}(n,\alpha)^3\text{H} + 4.8 \text{ MeV}$	900 (slow)	7.5	$\sim 5 \mu\text{m}$
(3) $\text{U}(n,f)\text{f}^1 + 170 \text{ MeV}$	600 (slow) ^{235}U 300 (fast) ^{235}U ~ 0.5 (fast) ^{238}U	0.7 (^{235}U) 99.3 (^{238}U)	$\sim 10 \mu\text{m}$
(4) Fast neutrons ($\geq 1 \text{ MeV}$)	~ 3		$\sim 1 \text{ cm}$
(5) Accelerated ions (H^+ , D^+ , T^+ , He^+ , Kr^+ , etc.)	--		$\sim 10 \mu\text{m}$ (highly dependent on mass & energy)
(6) "External" α -sources (^{210}Po , ^{244}Cm)	--		$\sim 10 \mu\text{m}$
(7) Spontaneous fission sources (^{252}Cf)	--		$\sim 10 \mu\text{m}$

Comments

- (1) B may be difficult to disperse or dissolve in radwaste phases — unless dispersed at $< 1 \mu\text{m}$, self-absorption of ^7Li , α is a problem. However, B may substitute for Al.
- (2) Same as (1), unless phase of interest contains alkali metals or, possibly, alkaline earth oxides.
- (3) Even if insoluble, U can be dispersed at $\sim 2 \mu\text{m}$ scale in ceramic phases so self-absorption problem relatively unimportant.
- (4) Wide energy spectrum and different atomic masses and scattering cross-sections makes detailed calculations difficult.
- (5) Unless using very light, very energetic ions, only a thin layer of target is irradiated -- so substrate epitaxy complications ensue. Damage profile non-uniform even in irradiated layer -- leads to characterization difficulties. Also very difficult to avoid sample heating effects, with consequent annealing phenomena.
- (6) As for (5), very thin and depth-dependent damage profiles. Intrinsic dose limit, because only α -emitting atoms within $\sim 10 \mu\text{m}$ of the surface of the source can provide α -particles which may emerge from the source.
- (7) As for (6), fission flux $\sim 3\%$ of α -flux.

2.0 RADIATION EFFECTS IN SOLIDS: GENERAL DISCUSSION

2.1 IONIZATION EFFECTS

All crystalline solids contain lattice defects such as solid solution impurities, second-phase material, grain boundaries, coherent precipitates, surfaces, voids, vacancies, dislocations, etc. These defects perturb the nominally periodic charge distribution, and the lattice can be regarded as the sum of a periodic charge distribution plus a set of impurity charges located at the various lattice imperfections. (These impurity charges are largely screened out by the conduction electrons in metals.) When electron-hole pairs are created by ionizing radiation in non-metals, electrons can be trapped by positive impurity charges and vice-versa for holes. If the localized impurity charge in a non-metal can only bind one electron or hole, a hydrogen atom model will describe the gross features of the impurity and electron (hole) system, but if more than one electron (hole) can be bound, the gross description will be that of a He, ... atom. All these systems constitute color centers (bound excitons in a semiconductor) though, of course, if their principal allowed transitions do not lie in the optically-visible region (1.8-3.0 e.v.), no actual coloration will be observed.

The formation and bleaching kinetics of these defect systems can be followed with various spectroscopic techniques. An important point is that (neglecting radiolysis effects) the number of these defects saturates with ionization dose, the limiting feature being the number of lattice imperfections in the solid.

Another effect of ionizing radiation is radiolysis of organic molecules, water, anions and (light) alkali halides: this effect is essentially radio-decomposition of the molecules by the formation of an (unstable) highly-excited state of the particular molecule. The radiolysis of water has been widely studied; the various radiolytic products formed are H^+ , OH^- , O_2^{2-} , H^0 , O^- , H_2O_2 , etc. These free radicals or atomic/molecular species are highly reactive and might be expected to produce gas buildup or uncontrolled chemical reactions on the solid nuclear waste form. However, in each radiolysis event, a free radical is accompanied by other radicals or electrons which, in a solid, will have a very strong tendency

to recombine rather than react with the solid. As mentioned earlier, ionization may cause atomic displacements by solid-phase radiolysis in silicates.

2.2 DISPLACEMENT EFFECTS

To move an atom in a solid from its regular site, ≈ 25 e.v. has to be imparted to the atom so that all the bonds to its neighbors are broken. Obviously, energy transfer from the radiation field to the nuclei critically depends on the mass of the bombarding particles. The approximate atomic displacement capabilities of various kinds of radiations were indicated in Table 4.

The most detailed studies of atomic displacement damage have been made in simple solids, notably the lighter alkali and silver halides. In the former, as mentioned earlier, displacements giving rise to anion vacancies (F-centers when an electron is trapped) and, of course, associated anion interstitials, can be created by purely ionizing radiation. In the latter, the main phenomenon is the interconversion of Ag^{2+} , Ag^+ , and Ag^0 . The alkaline earth oxides have also been studied in a fair amount of detail, using fast-electron and neutron irradiations.

Fast-neutron effects have been widely studied in covalent SiO_2 , graphite and diamond (for a review of the early work, see Reference 20).

The basic conclusions, derived from optical and electron paramagnetic resonance spectroscopy, X-ray diffraction, and dilatometry, are that at low doses and using not-too-massive particles, the Frenkel defect predominates. The vacancy may exist in a variety of charge states. In non-monatomic solids, it is the anion lattice, rather than the cation lattice, which is prone to displacements. Because of the extreme sensitivity in certain cases of electron paramagnetic resonance, a variety of surface radicals can be identified in irradiated powders, especially when different atmospheres are provided.

At higher radiation doses (and irradiation temperatures) the point defects aggregate into multi-atomic defects and condense to form dislocation loops; X-ray patterns become diffuse (strictly speaking, for point defects, diffuse scattering

builds up near reciprocal lattice positions at the expense of the Bragg scattering) and easily-measurable dimensional changes may occur. In general, irradiation of a crystalline material leads to a volume expansion or density decrease since an interstitial tends to expand the lattice more than the complementary vacancy contracts it. Such dimensional changes (which may however, be positive or negative) are also observed in glasses and "devitrification" of "amorphous" thin films may occur.

Generally speaking, only small dimensional changes occur in metals but radiation creep via the induced vacancies is important for load-bearing alloys. Radiation also enhances corrosion and may change order-disorder kinetics appreciably in alloys. Since optical and microwave spectroscopies are not viable for the study of defects in irradiated metals, basic studies have generally relied on low temperature ($\sim 4^{\circ}\text{K}$) irradiation and have mostly utilized studies of electrical resistivity.

Note that the above discussion is geared to point defects; for very heavy, energetic bombarding particles there will be an enhanced probability of relatively large groups of ions being more or less simultaneously displaced so that new phases with the same compositions as the parent solid could, in principle, form. Such a concept is inherent in the well-known "thermal spike" mechanism of radiation damage in solids, though it must be said that except possibly for fission fragment irradiation, there is very little evidence for such microphase formation. One possibility is the fission-fragment induced phase transformation in ZrO_2 ,⁽¹³⁾ although a recent discussion of this system did not favor the "thermal spike" mechanism.⁽¹⁵⁾

Quite a large, basically non-overlapping, literature exists on metamict minerals such as zircon which suffer radiation damage in nature due to incorporation of radioactive α -emitters (U, Th, and daughters) in their structures (or because they are geologically emplaced next to such radioactive-element-bearing materials). These studies are, by and large, much more phenomenological than the aforementioned radiation studies on synthetic structures because the natural minerals are structurally more complex (see References 21-23 for reviews).

2.3 STRUCTURAL SENSITIVITY TO RADIATION

The sensitivity of refractory crystalline materials to radiation varies widely although there is general agreement that anisotropy of the structure is a key feature.^(12,24) "Open" structures, with "holes" or "channels," should allow location of displaced atoms in metastable interstitial sites, rather than favor interstitial-vacancy recombination,⁽²⁵⁾ though it was earlier argued that such a condition would not be sufficient for metamictization.⁽⁹⁾ A further condition must be met; namely, the T_x ⁽²⁶⁾ or rapid crystallization temperature must be well above room temperature, i.e., formation in principle of a non-crystalline solid is not enough; it must also be retained at the temperature of observation. Several authors have also commented^(20,24) that covalent rather than ionic bonding promotes radiation sensitivity. Of course, high bond strength is related to T_x .

2.4 RADIATION-INDUCED PROPERTY CHANGES RELEVANT TO RADWASTE SCIENCES

For radioactive waste management, characterization of structural changes in the waste form as a result of self-irradiation damage is of interest, but more information is required. Over 10^6 years the density change of a HLW glass and, presumably, a (well) tailored ceramic form would be of the order of 1%, from accelerated ^{244}Cm doping tests.^(27,28) However, by far the most important properties of the glass or ceramic waste form are those of general reactivity and "solubility" or "leachability" in various possible groundwaters. Little definitive evidence on these questions exists, apart from the obvious fact that the very existence of very old metamict minerals in a variety of mineralogical environments establishes that the absolute "solubility" or "leachability" is not very large.

Haaker and Ewing⁽²³⁾ have argued that alteration of minerals is "enhanced" by metamictization but gave no quantitative data. Mumpton and Roy⁽¹⁶⁾ tabulated the analyses of the products of a large number of hydrothermally-treated metamict zircons and showed that only in a few cases, was a small excess of ZrO_2 present, possibly arising because the " SiO_2 " in the amorphous ZrSiO_4 was more easily available to attack by hydrothermal solutions. Most metamict zircons remained reasonably stoichiometric. Irradiated diamond etches (in molten KNO_3) more rapidly after

fast neutron damage,⁽²⁹⁾ and the entire science of fission track etching in minerals, such as mica⁽³⁰⁾ depends on the higher solubility of the damaged region.⁽³¹⁾ However, this "development" can only be brought about by very specific, corrosive etchants which selectively attack the damaged region. Fission tracks can, of course, also be "developed" in glasses⁽³²⁾ showing that radiation effects in waste forms are in no way confined to crystalline materials. From crystal chemical considerations, radiation damage should be no more drastic in increasing "solubility" or "leachability" than non-crystalline solid formation (by means other than irradiation), but experiments are necessary to examine this proposition. For relatively isodesmic phases such as zircon or monazite where all the bond strengths are very high, the crystalline — noncrystalline transformation should make relatively little difference to solubility, since the weakest bonds (where attack occurs) are essentially unaffected.

3.0 WORK ON RADIATION STUDIES IN CANDIDATE NUCLEAR WASTE FORMS

3.1 COMMERCIAL HLW

In prototype HLW glasses which were self-irradiated by ^{244}Cm incorporation, corresponding to α -doses which would occur after $\sim 10^5$ years post-solidification storage in a "reference" glassy waste form, ⁽⁵⁾ no significant changes were observed in leach rate, density, etc. Again, no significant deterioration effects were observed in waste glasses subjected to the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction at a total dose equivalent to $\sim 10^5$ years of storage after solidification. ⁽⁶⁾ Other studies in the U.K. support these results. ⁽³³⁾

Using fast fission of ^{235}U and (separately) accelerated Ni^{6+} ions in doses equivalent to $>10^6$ years of post-solidification self-irradiation, measurements of stored energy were made ⁽¹¹⁾ and no impairment of durability was observed. However, no leach tests were made and there was local heating of the specimen in the Ni^{6+} -irradiation experiments which would have promoted annealing behavior.

HLW glasses which had been crystallized to a ceramic were studied by the ^{244}Cm irradiation technique, using a dose equivalent to $\sim 10^3$ years of irradiation, and again no deleterious effects were evident, although amorphization of certain of the devitrification phases was observed. ⁽²⁷⁾

For crystalline ceramic waste forms, information is very sparse, though the "PSU supercalcine-ceramic" ^(7,34,35) showed no great changes of leach resistance on doping with ^{244}Cm such that equivalent doses of $\sim 10^3$ years storage were sustained. ⁽²⁸⁾ However, the apatite phase was rendered amorphous. Although γ -irradiation of the (non-doped) supercalcine-ceramic is reported to have had some effect on its leaching behavior, ⁽³⁶⁾ this would presumably have been due to radiolysis of the leaching solution, certainly not displacement damage in the ceramic.

It seems that one can safely conclude that no major decrease in the durability of either glass or PSU-ceramic candidate commercial HLW forms will occur after 10^5

or 10^3 years of self-irradiation, respectively, but experiments are clearly necessary to extend these times by some orders of magnitude, in both these and new materials.

Several candidate crystalline radiophases were irradiated with doses of $\sim 10^{15}$ fission fragments $\cdot \text{cm}^{-3}$.⁽³⁷⁾ It was deduced, however, that fission fragment irradiation is probably not a good simulator of α -recoil damage, but that the technique has merit insofar as many candidate phases can be rendered X-ray amorphous, so that limiting leach rate and density changes on metamictization can be evaluated.

3.2 DEFENSE HLW

Since defense wastes have low radioactive loadings, ~ 100 times lower than commercial wastes, it would be expected that radiation effects in non-partitioned defense wastes would be minor. This could well be the case, but since the actual chemistries of the defense wastes are completely different to those of commercial wastes -- the waste forms could be chemically very different also, unless dilution into borosilicate glass was used for both defense and commercial waste (the present "reference" process).

Essentially the only published information available is that on simulated Savannah River sludge diluted $\sim 1:3$ with borosilicate glass and in which the α -emission was produced by incorporation of ^{238}Pu or ^{244}Cm .⁽³⁸⁾ Only very small density changes were observed after $\sim 10^6$ years equivalent self-irradiation, and no significant leaching behavior changes were observed although some microcracking did take place. In the present work, a hot-pressed simulated Savannah River sludge-based ceramic showed no microcracking when doped with ~ 1 wt % ^{235}U and irradiated for 1, 3, and 10 hours in a neutron flux of 5×10^{12} n/cm².s (fast) + 1×10^{13} n/cm².s (thermal). This, however, was not surprising since the ranges of the fission fragments were considerably in excess of the grain size ($\sim 2 \mu\text{m}$) of the material. The fast neutron doses and fission fragment doses per hour were $\sim 2 \times 10^{16}$ n/cm² and $\sim 1.5 \times 10^{15}$ fissions $\cdot \text{cm}^{-3}$. The unirradiated ceramic consisted of spinel, hematite, plagioclase, and $(\text{Na,Ca})\text{U}_2\text{O}_7$ as far as X-ray diffraction was concerned. The uranate phase was rendered amorphous after a 1-hour

irradiation, and the spinel and plagioclase phases became nearly amorphous after 10 hour irradiation; the hematite phase was unaffected. However, as mentioned earlier, fission fragment irradiation has dubious value as a simulation of α -recoil effects.

4.0 LIKELY RADIATION EFFECTS ON SOLIDIFIED NUCLEAR WASTE FORMS

The radiation doses of $\sim 10^{20} \alpha \cdot \text{cm}^{-3} + \sim 10^{13} - 10^{14} \text{ fissions} \cdot \text{cm}^{-3} + \beta^-$ and γ -irradiation experienced in a solidified commercial HLW after 10^6 years would certainly have undesirable effects on a poorly designed crystalline waste form. For instance, such a dose would render zircon amorphous and increase its specific volume by $\sim 16\%$ (see References 14,21, for example). Here we view the reduction of radiation effects in solidified commercial HLW as a design problem in which the goal is to ensure that substantially all the α - and fission-fragment emitters are concentrated in radiation-insensitive phases.

The most radiation-insensitive phase known presently is almost certainly the fluorite-structured $(\text{U,Ln,An})\text{O}_{2\pm x}$. This material is known to be structurally resistant to the above radiation doses,^(12,39) with a lattice expansion of $\leq 1\%$, and its leaching behavior appears to be satisfactory and insensitive to α -damage,⁽⁴⁰⁾ as long as reducing conditions are maintained. (Reducing conditions are desirable for many other elements in radwaste also, such as Tc, Ru, Mo, etc.). Monazite, though it displays unexpected sensitivity to fission fragment irradiation,⁽³⁷⁾ should also be quite resistant to the above radiation dose.^(41,42)

Thus, from the point of view of radiation sensitivity, the ceramic formulations of McCarthy^(7,34,35) in which monazite replaces the radiation-sensitive apatite⁽²⁸⁾ should be eminently satisfactory. The titanate-ceramics (Synroc)^(43,44) seem less satisfactory notwithstanding the deliberately low (10%) waste loading factor. Though the radiation doses would be somewhat lower than the above, in 10^6 years of self-irradiation the perovskite and zirconolite phases, which for α -recoil radiation appear to be approximately as sensitive as zircon,^(42,45,46) will be well on the way to being amorphous.⁽⁴⁴⁾ Although it has been argued that amorphism, per se, will not disastrously decrease leach resistance, there have been counter-arguments in this regard.⁽²³⁾ Experimental data obtained in the laboratory on this question are still virtually non-existent, so judgment cannot really be made at this time.

However, it seems that differential expansion effects will be large, bearing in mind that in titanate ceramics^(43,44) the hollandite phase (not an α -emitter host) will be substantially unaffected, if near-amorphism of the perovskite and zirconolite leads to a density decrease (and therefore volume expansion) comparable to that attendant^(20,45,57) upon the amorphization of zircon (~16%), quartz (~14%), or diamond (~45%). Somewhat unexpectedly, however, in a neutron-irradiated synthetic multiphase preparation ("Synroc B") in which the hollandite, perovskite, and zirconolite was irradiated, there was virtually no microcracking, while in single phase hollandite and perovskite preparations irradiated to the same dose (equivalent to $\sim 10^4$ years of exposure) cracking was fairly extensive.⁽⁴⁸⁾

These examples, however, are only for particular ceramic formulations. The main point is that it should be possible by proper design, to make ceramic (or glass) formulations for commercial HLW in which the radiation damage problems are only second-order effects. Obviously, if the commercial HLW is aged before solidification, radiation effects can be further reduced (see Table 4).

5.0 RADIATION SIMULATION METHODS FOR SOLID WASTE FORMS

The various ways of producing radiation damage in solids have been mentioned. We have seen that solid HLW forms will experience a variety of radiation effects. As mentioned previously, although calculations⁽⁵⁾ indicated that the density of atomic displacements produced by α -decay in waste forms would exceed that produced by fission fragment irradiation by about four orders of magnitude, these calculations neglect self-annealing and ionization effects in the fission fragment case. Indeed it seems likely from recent work⁽³⁷⁾ that for some phases, fission fragment irradiation effects would be at least comparable to α -recoil effects (e.g., monazite); other phases, not containing α -emitting or fissionable ions, would receive fission fragment doses from adjacent phases (containing fissionable ions) but virtually no α -recoil dose (e.g., hollandite); in yet others, the α -recoil effects would dominate the fission phenomena (UO_{2+x}). In some cases, α -particle damage might be more important than α -recoil damage (UO_{2+x} ; Reference 39).

For structural studies, it is suggested that wastes should be doped with α -emitters. If further experiments suggest that solid-phase radiolysis effects⁽¹⁵⁻¹⁷⁾ are significant, then extended ^{60}Co γ -irradiations could be employed; doses in the order of $10^{12}R$ are required, however.⁽⁴⁾

For (radiation effects on) leaching studies, however, if the specific radioactivity of the sample is much higher than that of the form simulated (to produce adequate structural damage) then leaching effects produced by radiolysis of the solvent by the sample will be greatly exaggerated. Here it is suggested that structural damage be produced by a means that leaves the sample only minimally radioactive (by "external" irradiation).

6.0 TRANSMUTATION EFFECTS

Table 2 shows the fission products derived from U-based reactor fuel, and Table 6 shows the key elements for which transmutation problems will arise when the nuclides are solidified. The transmutation problem in a solid waste form derives from the fact that when a nuclide undergoes radioactive decay, the newly-formed atom may be a chemically different species, having a different ionic size and, possibly, valence. Thus, if the nuclide is chemically incorporated in a solid form before transmutation, it may not fit into the lattice after transmutation has occurred.

TABLE 6
RELATIVELY ABUNDANT FISSION PRODUCT ELEMENTS
FOR WHICH A VALENCE CHANGE WILL OCCUR IN A
SOLID WASTE FORM AND WHICH HAVE $t_{1/2} < 10^5$ YEARS

Element	Stable Daughter	$t_{1/2}$ (year)
Cs	Ba	30
Sr	Zr	29
Kr*	Rb	11

*Will not exist in general waste stream

In typical nuclear reprocessing wastes, the most significant transmutations are $^{137}_{55}\text{Cs} + \beta^- \rightarrow ^{137}_{56}\text{Ba}^{2+}$ ($t_{1/2} = 30$ years) and $^{90}_{38}\text{Sr}^{2+} + \beta^- \rightarrow ^{90}_{39}\text{Y}^{3+}$ ($t_{1/2} = 29$ years) $\beta^- \rightarrow ^{90}_{40}\text{Zr}^{4+}$ ($t_{1/2} = 64$ h). For the latter decay series, the amount of Y^{3+} relative to Zr^{4+} is negligible.

In both the $\text{Cs}^+ \rightarrow \text{Ba}^{2+}$ and $\text{Sr}^{2+} \rightarrow \text{Zr}^{4+}$ transmutations the ionic size differences are 20-40%. This alone poses problems, but there are several structures in which the ionic radius tolerance factor is substantial; for example, the XII-fold site in perovskite has been known for many years to tolerate a 40% size change.

A mechanism for charge compensation is another matter, and both crystalline and non-crystalline phases (insulators) share the same problem which must be resolved by corresponding changes in other cations or anions. (No transmutation problem due to valence changes occurs in a metal; "electrical neutrality" does not apply. However, a metal containing appreciable Cs or Sr would be very reactive with water.) For insulating crystals it seems clear that some proportion ($\approx 1\%$) of transmutation could be accommodated but that disproportionation or "decomposition" would take place after a certain proportion of the ions had become transmuted. If this process took place at a sufficiently low temperature (preventing appreciable atomic diffusion) the lattice strains around the transmuted (now misfitting) ions would cause smearing-out of the X-ray diffraction pattern much in the same way as does radiation damage cold-work or glass formation. The transmutation-induced departure from thermodynamic equilibrium would increase as transmutation continued, and it would be a question of kinetics when phase decomposition would occur.

Two lines of experimentation are possible to study the possible effects of transmutation on solid waste forms. These are: (1) fundamental transmutation studies using radioactive or neutron-induced transmutation, and (2) chemical studies of phase stabilities when transmutation is simulated, with emphasis for the problem of nuclear waste disposal on mitigation of phase disproportionation or decomposition.

6.1 FUNDAMENTAL TRANSMUTATION STUDIES

Virtually no relevant studies have actually been performed, though one⁽⁴⁹⁾ is in progress. To study transmutation effects on the structures of crystals, diffraction studies are vital. Although isolated (transmuted) cation studies in solids can be made with techniques such as γ angular correlation, Mössbauer, optical, and paramagnetic resonance spectroscopies, this information does not directly relate to the "collective" state of the solid and its phase constitution. Ten percent of transmutation of a major element in the phase of interest should be sought as a minimum in fundamental studies. In such studies, both radioactive and

neutron-induced transmutation would seem worth pursuing. The advantages of (reactor) neutron-induced transmutation are that the desired sample can be prepared using stable isotopes so that there are no constraints on sample preparation, either in terms of material volume or of preparation time. The disadvantages are the long irradiation times required to produce an adequate degree of transmutation and possible radiation damage complications from fast neutron fluxes.

Other considerations are as follows:

- 1) Parent and daughter must not be variable-valence transition metals or actinides (see below);
- 2) After neutron capture, transmutation must take place in a reasonable time and via β^- , β^+ , or electron-capture, not by fission or evolution of massive particles which would introduce additional radiation damage;
- 3) No other nuclei, including the daughter of the compound nucleus, must undergo any significant transmutation.

Even with quite a high thermal neutron flux, say 10^{14} n/cm²·s, for 10% transmutation the product of the isotope abundance and the particular absorption cross-section must exceed 30 barns, if irradiation times are not to exceed one year.

The most favorable cases appear to be $^{133}_{55}\text{Cs}^+ + {}^1_0\text{n} \rightarrow ^{134}_{55}\text{Cs}^+ \xrightarrow{\beta^-}$
 $^{134}_{56}\text{Ba}^{2+}$ and $^{174}_{72}\text{Hf}^{4+} + {}^1_0\text{n} \rightarrow ^{175}_{72}\text{Hf}^{4+} \xrightarrow{\epsilon} ^{175}_{71}\text{Lu}^{3+}$. However, the induced radioactivities would be formidable for ~10% transmutation, the specific activities of possible host compounds being on the order of 100 Ci/gm on withdrawal from the reactor and the principal half-lives being 2.0 and 0.2 years, respectively, for the two cases above.

These levels of activity will surely tax X-ray diffraction apparatus, even with large amounts of shielding to reduce the radioactive background. Electron diffraction would be a preferred technique, especially as the absolute activity of an electron diffraction sample would be quite low (for general discussions of problems of diffraction on radioactive samples (see References 50 and 51).

6.2 CHEMICAL MITIGATION STUDIES

Here the approach is to select multiple-cation solids for transmutation resistance, the idea being to select structures which can accommodate parent and daughter in the same site and which contain cations which can change valence to compensate for the transmutation-induced valence change.

For example, with the $\text{Cs}^+ \rightarrow \text{Ba}^{2+}$ transmutation we would seek a mineral phase solid solution of the type

This approach to mitigation of the transmutation problem has been explored in some detail.⁽⁵²⁾ Though simple in concept, it has not been found very easy to apply the strategy; so far, perovskite looks promising to deal with the $\text{Cs} \rightarrow \text{Ba}$ transmutation, but no system for the $\text{Sr}^{2+} \rightarrow \text{Zr}^{4+}$ transmutation has been found. Other possible solid phase hosts have also been discussed and it was also pointed out that the transmutation problem will not disappear in an amorphous waste form.⁽⁵²⁾

6.3 THE TRANSMUTATION PROBLEM IN SPECIFIC RADWASTE FORMULATIONS

Dilution is an obvious means of easing the transmutation problem. Defense wastes are already very dilute in radionuclides so no important problems of phase instabilities due to transmutation are anticipated. However, formulations for reprocessing waste could have difficulties. The Ringwood^(43,44) formulation is designed to be a dilute solution of radwaste in three major phases, Ba-hollandite, zirconolite, and perovskite, so further dilution of the radwaste by the Ba, Ca, Zr, Al, and Ti oxides composing the "solvent" could be achieved. Within limits, also, the mixture could be diluted by just the problem elements, viz., Cs and Sr.

On the other hand, the McCarthy^(7,34,35) formulations were found in the present work not to be amenable to dilution by the tailoring additives, Ca, Sr, Al, and Si oxides insofar as additions of any combinations of excess Al_2O_3 and

SiO_2 (added as SiO_2 sol and aluminum nitrate solution to the starting mixture) upset the phase assemblage. Nor could the formulation tolerate dilution with pollucite (again added in the form of stoichiometric mixtures of Cs, Al, and Si oxides via SiO_2 sol and metal nitrate solutions). In both cases, the pollucite and scheelite phases (for Cs and Sr,Mo, respectively) were "lost," as far as X-ray diffraction was concerned. For Al_2O_3 and SiO_2 additives, some extra X-ray reflections were observed but for the "pollucite" addition, there were no extra reflections observed. No great increase in Cs volatility was observed on firing, both from gravimetric work and from the observations that, on firing at 1100 or 1200°C, the X-ray diffraction patterns of air-fired materials were very similar to those of materials fired in welded platinum capsules.

7.0 CONCLUSIONS AND FINAL REMARKS

In the light of existing data on refractory phases, radiation and transmutation effects should have little significance in ceramic forms for defense wastes, because of the high degree of dilution of the critical radioactive ions in these wastes.

For reprocessing wastes, the more dilute and the older the waste, the less will be the problems with radiation and transmutation, but for radiation at least there appear to be crystalline materials such as monazite and uraninite which are quite radiation-resistant. Here the design problem is to ensure all the α -emitters enter the uraninite and/or monazite phases. However, the possibilities that β -emission could cause appreciable radiation damage need examination.

For Cs- and Sr-bearing phases in reprocessing wastes it will not be easy to design for transmutation resistance in conjunction with thermal stability, leach resistance. However, the chemical mitigation approach⁽⁵²⁾ might apply in a metastable sense if transition metal ions are present in the Cs- and Sr-containing phases. Even if future work produces appropriate transmutation-resistant phases for Cs and Sr individually, this would produce of itself little stimulus for partitioning nuclear waste streams unless the regulatory situation necessitates transport of wastes.

The main driving force for partitioning Cs and Sr from reprocessing wastes is that the ^{137}Cs and ^{90}Sr can be made up into quite soluble forms such as $^{137}\text{CsCl}$ and $^{90}\text{SrF}_2$ (and leaving a Na-rich solution which can be evaporated to dryness, leaving an essentially nonradioactive salt cake), as is done for the defense wastes at the Hanford site; these materials need only be encapsulated onsite in an appropriate container for ~500 years, since at the end of this period, the ^{137}Cs and ^{90}Sr have virtually completely decayed to stable elements. The remaining fission products and actinides from the original (aged) waste streams will have minimal γ -heat production so the appropriate waste form should be correspondingly easier to design. Nevertheless, this would add considerably to the cost of the operation.

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QUARTERLY PROGRESS REPORT
OCTOBER 1, 1979 THROUGH DECEMBER 31, 1979

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1.0 PROJECT DESCRIPTION AND OBJECTIVES

A multitask program is being carried out for the development and characterization of Tailored Ceramics as a waste form for the geologic storage of radioactive wastes. The feasibility of producing the waste form safely and reliably under large-scale remote operating conditions is being assessed, and the long-term stability of the ceramic form is being evaluated vis-a-vis borosilicate glass.

Tailored Ceramics are crystalline assemblages made by high-temperature and pressure consolidation of a nuclear waste with selected additives. The specific crystalline phase assemblages produced by the waste tailoring process closely approximate those found in natural minerals which have persisted for geologic ages. These consolidated ceramic forms provide a total volume reduction for the waste and are extremely hard, dense materials with low surface areas and potential for high leach resistance.

The program involves basic studies at the Pennsylvania State University's Materials Research Laboratory, applied research at Rockwell International's Science Center, process and remote fabrication technology development at Rockwell International's Energy Systems Group, and engineering development support at Rockwell's Hanford Operations. This integrated effort is directed toward advancing Tailored Ceramic technology to the state where it provides a viable alternative waste form for use at the SRP and other installations.

2.0 SUMMARY AND HIGHLIGHTS

2.1 TAILORED CERAMIC WASTE FORM DEVELOPMENT AND CHARACTERIZATION

Generic and Fundamental Studies (Task 2) are underway on (1) crystalline phases for Savannah River Plant (SRP) sludges, and phases for iodine and fluoride fixation, (2) cement matrices for Tailored Ceramic phases, (3) mechanism and kinetics of dissolution of pollucite, Sr-feldspar, and nepheline, and (4) fundamental transmutation effects. Simulated SRP sludge yielded spinel and, depending on additives, α - Al_2O_3 , UO_2 , cristobalite, and mullite. Nd monazite appears to be compatible with a variety of high silica and high alumina cements. $\text{CsFeSi}_2\text{O}_6$ appears promising as resistant to the ^{137}Cs to ^{137}Ba transmutation.

Formulation and Consolidation Studies (Task 3) have established an initial tailoring formula based on alumina, yielding a four-phase crystalline assemblage: corundum, spinel, magnetoplumbite, and uraninite. Hard, dense hot-pressed ceramic pellets have been prepared in the laboratory, and host phase identification for various species of concern is underway.

The initial Radiation and Transmutation Effects (Task 4) effort has included the establishment of a program plan and key contacts with other researchers in the field, the initiation of a detailed literature review of the radiation damage field as applied to nuclear waste forms, and a start on formulating the program's first radiation damage experiments. Task 5 Geologic Strata Compatibility studies had not been initiated during the quarter.

2.2 TAILORED CERAMIC PROCESS AND EQUIPMENT DEVELOPMENT

Under Engineered Containment (Task 6), current technology is under review and assessment, and a report library has been established.

Under Process Evaluation and Definition (Task 7), the unit operations needed to carry out steps in the Tailored Ceramic process are under evaluation. Hot pressing, hot isostatic pressing, and calcination are the operations of immediate interest in conjunction with the processing concept in which the alumina in the waste is retained to serve as a tailoring ingredient in forming a consolidated Tailored Ceramic waste form.

3.0 TECHNICAL PROGRESS

3.1 TAILORED CERAMIC WASTE FORM DEVELOPMENT AND CHARACTERIZATION

3.1.1 Generic and Fundamental Studies

Task 2, "Generic and Fundamental Studies," is devoted to the development and characterization of new materials capable of either containing the desired radionuclide as an essential part of the crystal structure (the high-loading option) or taking some quantity of the radionuclide into stable solid solution (the low-loading option).

3.1.1.1 Optimum Phases for Tailored Ceramics

This aspect of the work is with the crystalline phases that can be formed from a Savannah River Plant (SRP) sludge and with new crystalline waste forms specifically designed for the radionuclides in other high-level wastes.

Work has been started on phases for strontium, cesium, iodine, and rare earth elements. In each case, the approach is to first identify crystalline hosts that will accept the radionuclide(s) in question, then address questions of thermal stability during synthesis and processing, and then investigate mutual compatibility of phases that must coexist in the final ceramic product.

3.1.1.1.1 Crystalline Phases from Fired Simulated Savannah River Sludge

Since these materials are rich in aluminum and iron, there appears to be a very good possibility of forming ceramics directly by firing the sludge. Ceramic bodies were made by drying solutions or slurries at $\sim 120^{\circ}\text{C}$, calcination at 600°C , grinding, pelletizing using a pressure of $\sim 3 \times 10^4$ psi, and firing at $900\text{--}1200^{\circ}\text{C}$. On firing a simulated sludge

at 900-1200°C, a spinel of undetermined constitution was the dominant phase, but many other unidentified X-ray lines were observed.

Use of silica, alone and with other additives, was then studied for tailoring of the SRP sludge. A mixture of nitrate solutions (of cation composition similar to the previous simulation) plus Ludox (colloidal SiO_2) was made. X-ray data similar to those for the additive-free simulation were obtained with ceramics fired at 1000-1200°C.

The effect of fairly large quantities of tailored additions to the nitrate-based simulation was studied, the additions being (1) 60 mole % SiO_2 , (2) 280 mole % Al^{3+} + 60 mole % SiO_2 , and (3) 60 mole % PO_4^{3-} . The SiO_2 and H_3PO_4 additions (1 and 3 above) produced melting on subsequent firing at 1200°C. The mechanical properties of pellets made with all of these additives were poor, while those of the addition-free material seemed satisfactory.

Addition of sodium, a potentially damaging additive from a leaching standpoint, was explored, as was that of calcium. The additions to the nitrate-base simulation were (1) 60 mole % Na^+ , (2) 60 mole % Ca^{2+} , and (3) 60 mole % Na^+ + 60 mole % Ca^{2+} . As found by McCarthy for commercial wastes, sodium additions improved the mechanical properties. Calcium addition produced somewhat less of an improvement, but the addition (3) produced a poorly crystallized and mechanically weak "ceramic" even on firing at 1200°C. Spinel was a dominant phase in (1) and (2) but was absent in (3). No nepheline or sodium silicate phases were observed.

A second nitrate + Ludox mixture was made up with enhanced uranium and strontium concentrations to try to clarify the phases bearing these elements. The hydroxides were precipitated with excess NH_4OH and then calcined and fired as usual. The effect of 10 mole % additions of calcium or aluminum was trivial as far as X-ray diffraction was concerned, but the addition of 10 mole % SiO_2 was to promote the formation of UO_{2+x} as against a presumed uranate phase.

Spinel was observed in most cases. High SiO_2 led to an amorphous phase and cristobalite formation. High Al led to $\alpha\text{-Al}_2\text{O}_3$ formation, while high Al plus Si led to formation of $\text{Al}_6\text{Si}_2\text{O}_{13}$ (mullite). With high PO_4^{-3} additions, no phase identifications were obtained.

The spinel was not noticeably suppressed by (so is, therefore, presumably compatible with) Al_2O_3 and SiO_2 additions. Moreover, as there was a large fraction of unreacted (albeit crystallized) Al_2O_3 and SiO_2 , there appears to be no impediment to the formation of Sr-feldspar and pollucite to tie up ^{90}Sr , ^{134}Cs , and ^{137}Cs .

As expected, firing in a reducing atmosphere promoted the formation of the UO_{2+x} phase rather than U_3O_8 or the presumed uranate phase. However, the chemical details of why adding SiO_2 to the second nitrate simulation promoted UO_{2+x} as against the uranate phase are not clear.

3.1.1.1.2 Iodine Fixation

A candidate crystalline host for ^{129}I is boracite. The mineral boracite is $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$. However, there are many isostructural compounds in which magnesium is replaced by other intermediate-size cations and chlorine is replaced by bromine or iodine. The halogen in the boracite structure is encapsulated within a three-dimensional framework of boron-oxygen polyhedra, suggesting that this structure may be useful for immobilizing iodine. So far, synthesis of an iodine boracite has not been successful.

Fe-I-boracite crystals, grown elsewhere by chemical transport techniques, were unaffected by a γ -dose of $\sim 10^9\text{R}$, but decomposed on heating in air at 900°C , $\alpha\text{-Fe}_2\text{O}_3$ being the major decomposition product detected by X-ray diffraction. Some evidence was obtained that Fe-I-boracite is unstable on prolonged heating at 300°C . If substantiated, this result severely jeopardizes Fe-I-boracite as a candidate iodine

fixer. Although iodine would be processed separately from the main nuclear waste, an iodine fixer would be buried in the same repository as high-level waste, and thus it would experience near-field temperatures of $\geq 100^{\circ}\text{C}$, even though β , γ -heating in the iodine fixer itself would be negligible because of the long half life of ^{129}I .

3.1.1.1.3 Fluoride Fixation; Thorex Wastes

McCarthy showed that fluoride-bearing phases could not be accommodated in "supercalcine" Tailored Ceramic phases based on PW-4b and PW-7 high-level nuclear wastes. It was shown that $\text{Ca}_5(\text{PO}_4)_3\text{F}$ was thermally stable up to $\sim 1000^{\circ}\text{C}$, although chemical analysis showed the F content to be only about 50% of the theoretical value. After heating at 1200°C , the F content was only about 1.5% of the theoretical value, but the X-ray patterns were apparently virtually unchanged. In the present work, heating the fluorapatite phase at 1350°C caused complete decomposition to $\alpha\text{-Ca}_3(\text{PO}_4)_2$.

$\text{Sr}_2\text{FeO}_3\text{F}$ is reportedly stable at temperatures of up to 1200°C . Well crystallized $\text{Sr}_2\text{FeO}_3\text{F}$ was produced by drying, calcination, and firing mixed nitrate and NH_4F solutions. A firing temperature of $\sim 900^{\circ}\text{C}$ seemed to be optimum, although phase-pure material was not obtained. However, heat treatment for 1 week at 1050°C produced complete decomposition into SrFe_2O_4 plus unknown phases.

3.1.1.2 Tailored Ceramic Composites

Commercial and modified cements are being considered as matrices or bases for ceramic waste forms. To test their suitability, samples were prepared for controlled curing and leaching experiments. Individual Tailored Ceramic waste form phases are being examined to delineate their behavior in cement matrices more precisely. An alumina based cement (Secar 71) and two silicate cements (Class C and Class H) were chosen.

NdPO_4 is a monazite structure compound (where neodymium is a model rare earth and a stand-in for the actinides) which is the first Tailored Ceramic phase being tested for compatibility in cement compounds.

Samples were prepared with cement as-received and modified as follows:

- 1) NdPO_4 plus 20 wt % of the cement
- 2) Compositionally adjusted with amorphous SiO_2
- 3) Addition of SiO_2 and NdPO_4 .

Addition of SiO_2 was intended to approximate tobermorite for the silicate cements and feldspar + Al_2O_3 for the aluminate cement.

Each cement formulation was cast to permit sampling at intervals during isothermal curing (60°C). Accelerated hydrothermal leach testing, and characterization of the solids by X-ray diffraction and SEM, were performed on samples taken after 28 and 56 days. Interpretation of the data from X-ray diffraction is underway.

Hydrothermal leaching was conducted for 28 days at 200°C and 30.4 MPa overpressure on subsamples of approximately 0.05 gm (total solids) sealed in noble metal tubes with 0.5 gm deionized water. Solutions were analyzed by atomic emission. Solids remaining after leaching were studied by X-ray diffraction and scanning electron microscopy. Refinement of these studies is continuing.

For all cement composites analyzed, and the presence of NdPO_4 did not appear to alter the hydration products of the cement. Grains of the NdPO_4 remained tightly bonded in the cement, even through leaching, and no alteration of the structure or chemistry of the monazite structure compound was detected. Some of the desired phases were achieved with the compositionally adjusted cements. Experiments on samples cured longer than 28 days should be conclusive.

No neodymium was detected in any of the leachates. The amounts of phosphorus detected were less than that available from the starting cements. Accelerated leaching of NdPO_4 in deionized water under the same conditions has been undertaken to determine its proclivity to release phosphorus without the complicating presence of the cements.

3.1.1.3 Dissolution of Tailored Ceramics

A three-pronged investigation of the stability, dissolution, leaching, and dissolution mechanisms of the crystalline phases which are candidate components for Tailored Ceramics is underway, including (1) measurement of the dissolution of these materials at low temperatures including a study of the dissolution mechanism, (2) measurement of the dissolution and possible breakdown of the solid phases at hydrothermal temperatures, and (3) an investigation of the surface chemistry and surface reaction layers of the leached solid phases utilizing sputter-induced optical spectroscopy as the primary characterization tool.

3.1.1.3.1 Low-Temperature Dissolution of Pollucite

Pollucite (ideal formula $\text{CsAlSi}_2\text{O}_6$) is still one of the leading crystalline hosts for the immobilization of ^{137}Cs . Natural pollucite ground to -45 to -60 mesh was used for the initial experiments. In water at 25°C and at neutral pH, the uptake of cesium into solution resulted in concentrations after 14 days on the order of 0.05 to 0.3 ppm--about at the threshold of the analytical methods. Accordingly, dissolution experiments at low pH where dissolution rates are expected to be much higher were undertaken, with the idea to gradually increase pH and then extrapolate the dissolution rates into the neutral pH range. Under highly acid conditions, cesium, aluminum, and silicon all appear in solution apparently governed by parabolic (dissolution kinetics) rate laws.

3.1.1.3.2 Other Dissolution-Related Studies

Strontium feldspar is being considered as a possible host for ^{90}Sr in a ceramic waste form. As it is not known to occur naturally, it must be synthesized. Several methods for synthesis are being tried to determine the optimum one.

Some literature survey and other preliminary work has been done with a view to determining the stability and alkali extraction from the nepheline (ideally NaAlSiO_4 , usually $\sim\text{Na}_{0.75}\text{K}_{0.25}\text{AlSiO}_4$) phase.

3.1.1.3.3 High-Temperature, High-Pressure Dissolution Apparatus

To simulate conditions in an open system environment, candidate crystalline materials will be leached in a flowthrough system at controlled pressures and temperatures (Figure 3.1). Water from a reservoir is pumped by a pneumatic pump into the system at a predetermined pressure. It is circulated by a metering piston pump through the reaction vessel which is heated in a furnace. Effluent from the reaction vessel may be sampled before or after the quench chamber. Solid samples may be retrieved from reaction vessel and quench chamber at the end of a run.

Several modifications were made to the equipment to extend the period between repairs and to facilitate the repairs. Also, a modification was made to improve the high-temperature sampling.

3.1.1.3.4 Surface Chemistry

Another aspect of the dissolution work is to determine how the surface chemistry of Tailored Ceramics influences dissolution processes. Sufficiently surface sensitive techniques such as sputter-induced photon spectrometry (SIPS), ion scattering spectrometry (ISS), and Auger electron spectrometry (AES) are used to determine changes in surface composition

Figure 3.1. Circulating hydrothermal apparatus from H.L. Barnes, C.W. Burnham and W.F. Downs (1978) "Experimental Evaluation of Geochemical Conditions in Geothermal Energy Systems," Final Report on National Science Foundation Grant No. AER-08473.

due to ion-exchange and/or readsorption (complexing) with solubilized species. Initial work has been undertaken using polished faces of natural monazite single crystals.

3.1.1.4 Fundamental Transmutation Effects

Combined radiation and transmutation effects may be deleterious to crystalline material under a certain combination of circumstances. The experimental design to investigate this is for first examining recognizable crystal structure effects through transmutations induced in synthetic crystalline materials. Since neutron-induced transmutations are easier to introduce in the short term than radioactive decay-induced transmutation, this program will examine the potentials of transmutation effects through the former, using Tailored Ceramic crystalline structures.

The following have been chosen as suitable for this study: Cs $\rightarrow$ Ba, Sr $\rightarrow$ Y, Tc $\rightarrow$ Ru, In $\rightarrow$ Sn, Lu $\rightarrow$ Hf, Hf $\rightarrow$ Lu, Rb $\rightarrow$ Sr, and Hf $\rightarrow$ Ta. Of these, depending upon the ready availability of enriched stable isotopes, the Tc $\rightarrow$ Ru and Hf $\rightarrow$ Lu transmutations will be examined initially. Some detailed calculations on these isotopes have been completed. The problems associated with performing X-ray diffraction studies on radioactive materials are being examined using the results of these calculations. A typical set of calculated results for the transmutation experiment,

shows that it is possible to achieve about 12% conversion of the ^{174}Hf in 25 days' irradiation. This would amount to about 2.5% of total conversion of all Hf $\rightarrow$ Lu in the crystalline matrix. Another isotope of this element ^{181}Hf is available with an artificial enrichment of 95%. This isotope undergoes the following neutron transmutation induced changes:

A 100-day irradiation of a crystalline matrix containing ^{181}Hf results in about 3.5% change in the total hafnium. Allowing adequate decay time following irradiation, this can be converted to tantalum in the crystal matrix.

A special glove box facility with a furnace is being set up to incorporate ^{99}Tc in crystalline ceramics. Pending arrival of some of the materials, radiation effects of similar materials are being examined using a fission product spectrum source (a reactor in a shutdown mode) and a combined neutron, gamma, and electron flux of a research reactor.

$\text{CsAlSi}_2\text{O}_6$ (pollucite) has been put forward as a promising Cs fixer, because it is refractory and has a high leach resistance. However, the $\text{Cs} \rightarrow \text{Ba}$ transmutations could degrade the crystal integrity in a few years. Barium has low solubility in $\text{CsAlSi}_2\text{O}_6$. It seems possible, however, that the isomorphous compound $\text{CsFeSi}_2\text{O}_6$ might have host potential since the $\text{Cs}^+ \rightarrow \text{Ba}^{2+}$ transmutation could be accommodated by a $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ transformation. One-day Soxhlet tests on $\text{CsFeSi}_2\text{O}_6$ showed ~5 wt % loss for a preparation fired for 6 hr at 1100°C and ~1 wt % loss for preparations fired (1) 25 hr at 1100°C , (2) 16 hr at 1330°C , and (3) 28 hr at 1400°C . Further losses of ~1 wt % per day were obtained for (2) and (3) after subsequent 3-day Soxhlet tests. These values are far too high to be acceptable.

The preparation (3) was found to be phase-pure by X-ray diffraction, and an uncompact sample of $\text{CsFeSi}_2\text{O}_6$ powder remained single phase after a DTA run to a maximum temperature of 1470°C was carried out. These results show that the thermal stability of $\text{CsFeSi}_2\text{O}_6$ is satisfactory. A heat treatment of 10 hr in N_2 at 1000°C did not cause an observable departure from phase purity.

Mn, Ni, and Co analogs of pollucite were prepared, although not as yet in phase-pure form. Assuming, as found for $\text{CsFeSi}_2\text{O}_6$, that the

lattice parameters were insensitive to the starting stoichiometry, the parameters of the Mn, Fe, Co, and Ni pollucites were found as 13.76, 13.85, 13.69, 13.68 (all ± 0.02) Å, respectively.

A natural pollucite (Smithsonian Institute, Sample 135267) was found to display no evidence for either Fe^{2+} or Fe^{3+} in solid solution. Heating for 1/2 hr in air at 600°C was sufficient to render the initially clear crystal completely opaque. This result was presumably due to dehydration, by analogy with similar known phenomena in beryl and cordierite which occur on heating at $\sim 800^\circ\text{C}$. The associated change in the lattice parameter was $< 0.3\%$ after heating to 600°C , and no further change in the parameter ensued on heating at temperatures to 1200°C .

No effects on the X-ray patterns of $\text{CsAlSi}_2\text{O}_6$ and $\text{CsFeSi}_2\text{O}_6$ were observed after a small dose of γ -irradiation (10^9 R). Samples are presently being neutron-irradiated to a dose of $\sim 2 \times 10^{18}$ nvt (fast) and further samples, either mechanically mixed with U_3O_8 or with the U dispersed as an X-ray amorphous phase, have been prepared for fission-fragment irradiation.

A crystalline material that will accommodate ^{90}Sr and its decay products is being designed. The host must satisfy the usual requirements of a nuclear waste form plus the two criteria of being able to accommodate the decrease in ionic radius upon decay of radioactive $^{90}\text{Sr}^{+2}$ (1.26 Å) to radioactive $^{90}\text{Y}^{+3}$ (1.02 Å) to stable $^{90}\text{Zr}^{+4}$ (0.84 Å), and being able to accommodate the change in valence states as shown above through some charge compensation mechanism.

One possible way to do this is to incorporate Sr into a crystalline solution phase that can also dissolve appreciable amounts of Y and Zr. The first attempt was to try to incorporate SrO into crystalline solution with ZrO_2 . SrO was found to be insoluble (less than 1 mole percent) in ZrO_2 forming a two-phase mix of SrZrO_3 and ZrO_2 at all compositions investigated.

The second attempt sought to determine the limits of crystalline solubility of SrO , Y_2O_3 , and ZrO_2 in the rare earth (RE) oxides La_2O_3 , CeO_2 , Nd_2O_3 , Gd_2O_3 , and Y_2O_3 . Again, however, SrO was found to have negligible solubility forming a two-phase mixture of RE_2O_3 and an unknown $\text{SrO-RE}_2\text{O}_3$ compound of low symmetry. These unknown compounds have been synthesized and are being characterized by powder diffraction techniques.

The third attempt at finding a suitable host for ^{90}Sr fixation was to try to incorporate Sr into a synthetic garnet of the approximate composition $\text{SrCa}_2\text{Fe}_2\text{Si}_3\text{O}_{12}$. Experimental work has commenced and is now underway.

Monazite appears to be very resistant to metamictization from dissolved α -emitters, but after a critical radiation dose monazite might be rendered semi-amorphous and then not recrystallize as recognizable monazite when annealed.

Ce and La monazites, doped with up to 5 mole percent natural U, are presently being irradiated with neutrons. U-doped huttonite and zircon, produced by the usual calcination/firing technique, are being similarly irradiated.

Nine natural monazites from various sources were annealed at 950 and 1100°C and in most cases an X-ray volume contraction of ~1%, together with sharpening of the diffraction lines, was observed. If this result can be associated with α -recoil damage, rather than chemical zoning effects, monazite is clearly not completely immune to radiation damage.

Zirconolite ($\text{CaZrTi}_2\text{O}_7$), doped with U, has been prepared for fission-fragment irradiation. Numerical calculations have been made of the α -recoil damage which would be measured by the TRU-bearing phases in high-level waste. As an indication, if zircon incorporated all the TRU ions (hypothetically), it would be rendered amorphous (with a density decrease of ~16%) after $\sim 10^4$ years.

3.1.2 Formulation and Consolidation Studies

Efforts have been focused on developing a suitable crystalline phase assemblage for simulated Savannah River Plant (SRP) defense waste which will provide a high quality Tailored Ceramic with a minimum of additives. In the initial efforts, a number of samples representing the range of compositions for simulated waste called out in the July 5, 1979, SRL letter from J. A. Kelley to D. L. McIntosh in both untailored and tailored* forms have been made up, hot pressed, and analyzed for phase and microstructural content. The information obtained from these runs has been used to design phase compatibility studies, direct the development of new tailoring schemes, and to orient geochemical stability studies.

With aluminum and iron being the bulk cations in the SRP waste, these elements have to a great extent controlled the properties of the hot-pressed ceramics. Tailored waste samples with the Al/Fe ratio ranging from 0.14 to 22.3 have thus far been examined. Results show that at the lower extreme of Al/Fe, crystalline spinel determines the ceramic properties, while α -alumina (sapphire) dominates at the other extreme. The characterization results from these samples have shown the high Al composition to provide the most promising physical and chemical characteristics for a Tailored Ceramic waste form.

The hot-pressed pellets formed (see Figure 3.2) from the high Al tailored waste composition ($\text{Al}_2\text{O}_3 = 65$ to 85 mole percent of calcine) are extremely hard with a density greater than 93% that of theoretical. The crystalline grains are small (2000-10,000 Å) and show a very high degree of crystalline microstructural isolation. Figure 3.3 shows a bright field transmission micrograph of a hot-pressed sample made up

*That is, with selected additions to produce a ceramic with the desired phase assemblage.

Figure 3.2. One inch diameter hot-pressed multiphase ceramic, HASR1
Mole percent composition (Calcine)

Fe_3O_3	3.8%
Al_2O_3	84.8
MnO_2	5.7
U_3O_8	0.17
CaO	0.68
NiO	1.1
Na_2O	3.60
Cs_2O	0.009

Pressing T&P: 1400°C , 3820 PSI
Calculated Density: 3.7833 G/CC
Archimedes Density: 3.826 G/CC
% Theoretical Density: >93%

Figure 3.3. Bright field transmission micrograph of high alumina composition simulated SRP waste, sample HASR1.

U = Uraninite

C = Corundum

S = Spinel

↑ = Magnetoplumbite

from Kelley's high Al (without Al removal) composition and without the addition of Ion Siv IE95. The micrograph illustrates the dense, polyphase nature of the ceramic. The four constituent phases present are (Fe,Mg)-spinel (hercynite) labelled S, α -alumina (sapphire) labelled C, UO_2 uraninite labelled U, and magnetoplumbite shown with arrows. No continuous intergranular glassy phase is present and each phase is microstructurally isolated from others of the same type. SIMS analysis of this sample showed Cs to be retained during hot pressing and STEM analysis indicated that it is primarily located in the magnetoplumbite structure. Work is continuing with a number of high Al compositions to optimize hot-pressing parameters and to determine the effects of adding ranges of trace elements and Ion Siv IE95.

To establish the basic phase compatibility relationships controlling the ceramic formation, studies have been initiated on the $\text{CaO-Fe}_2\text{O}_3\text{-Nd}_2\text{O}_3$ and $\text{CaO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ phase diagrams. Preliminary leach testing experiments at 90°C in distilled water have been started on samples of hot-pressed high Al waste.

3.1.3 Radiation and Transmutation Effects

This task was initiated to study the effects of nuclear decay radiation and transmutations on Tailored Ceramic waste forms now under development. The objective is to carry out a series of irradiation experiments that simulate radiation and transmutation effects in proposed Tailored Ceramic materials on an accelerated time scale. The results will be used to assess the durability of Tailored Ceramics in isolating nuclear waste nuclides from the environment over a geologic time scale.

Results of the initial program effort included the establishment of a program plan and key contacts with other researchers in the field, the initiation of a detailed literature review of the radiation damage field as applied to nuclear waste forms, and a start on formulating the program's first radiation damage experiments.

A literature review on radiation and chemical effects on nuclear waste forms was initiated during the report period. The objective of this background research is to establish a firm foundation for planning the experimental program and the interpretation of the results. The literature review emphasizes the simulation of radiation effects in high-level nuclear waste forms; radiation effects on covalent (plus some ionic) metal oxides which are basic constituents of proposed Tailored Ceramic waste oxide compositions; the formation and properties of the metamict state; and the effects of alpha particles on naturally occurring minerals. A draft report entitled "The Simulation of Radiation Effects in High-Level Nuclear Waste Forms" is in preparation. This review covers work on glass as well as crystalline waste forms. A second draft report reviewing radiation damage effects in naturally occurring minerals has been initiated.

Work has begun on formulating the program's first radiation damage experiments. It appears at present that these experiments will be reactor neutron irradiations of doped Tailored Ceramic crystalline phases, with the dopants consisting of one or more isotopes with large thermal-energy neutron cross sections. The major effects these experiments will simulate include alpha-decay and recoil nucleus damage and transmutation damage. The phases to be investigated, and the dopants and doping procedures to be used, will depend in large measure on those phases selected under the Task 2 and Task 3 program efforts to host key waste radionuclides. Attractive choices at present include ^6Li doping of a spinel phase and ^{10}B interstitial doping in monazite.

A spent thermoelectric generator with a ^{90}Sr heat source has been located with the cooperation of the Department of Energy. The ^{90}Sr is incorporated in the crystalline phase $^{90}\text{SrTiO}_3$, a form of the mineral phase perovskite. This mineral is similar to some crystalline phases proposed in Tailored Ceramics formulations. About 35% of the ^{90}Sr in the source has decayed to the stable nuclide ^{90}Zr in the 20 years since

this source was manufactured. The source thus appears to provide an ideal opportunity to study transmutation damage in a single-phase crystalline material. Means to acquire this source are now being pursued.

3.1.4 Geologic Strata Compatibility

This task had not been initiated during the quarter being reported.

3.2 PROCESS AND EQUIPMENT DEVELOPMENT

3.2.1 Engineered Containment

The results of the trade study currently in progress will be used to guide the development of the process(es) for consolidation of Tailored Ceramics and the loading of canisters with the dense ceramic bodies. The process will be constrained to mate with the SRL process flow diagram and to utilize both the waste materials separation processes and the final clean canister handling process.

Investigations of current technology have begun with the review and assessment of published reports. In conjunction with this review, a file has been established for the collection and cross-referencing of pertinent report data.

A trade study whose thrusts are to identify the critical process parameters involved in the production and the containment of consolidated Tailored Ceramic waste forms, and to optimize the canister size, weight, heat load, and matrix material selection combinations has been initiated.

3.2.2 Process Evaluation and Definition

Process flow diagrams of increasing complexity will be prepared for promising process sequences leading to the issuance of a report at the

end of the fiscal year. Order of magnitude cost estimates will be prepared on the more promising process sequences. In all cases, these sequences will utilize the existing SRL front-end waste removal and stream separation process steps.

Calcination studies of waste compositions containing aluminates will be performed to evaluate the feasibility of producing a calcine which can be consolidated at an acceptable temperature to form a dense Tailored Ceramic body.

Waste technology reports have been assessed for their applicability to the Tailored Ceramic process. Information on the specific wastes to be immobilized is undergoing evaluation. The need for the removal of aluminum from the waste is in question, with the thought that its ceramic end products, Al_2O_3 and Al-spinels, are very stable ceramic species and are quite acceptable as final chemical forms. One critical parameter in these considerations is the minimum satisfactory consolidation (sintering) temperature at which a dense closed-pore ceramic containing possible high amount of Al_2O_3 either as corundum or in a spinel can be formed from the waste calcine.

Preliminary flow diagrams and material balances are being developed for processes in which the alumina is not removed from the waste. These sequences involve the use of the existing SRL plan for removing the supernate and the sludge fractions from the waste tanks, an additive "tailoring" step, a calcination step, and a calcine densification step (such as extrusion or cold pressing) to form a body which is hot pressed (either uniaxially or isostatically). The logistics of the sizes and the numbers of pressings, and of process lines, are being examined in the Task 6 trade study.

In the considerations of the "alumina-in" process sequence, it is evident that a highly sinterable alumina must be produced in the calcination step in order that the final hot pressing be possible at tractable temperatures (1200°C , as a nominal maximum). Accordingly a test study of the calcination process step has been initiated using guidance from Task 3.

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