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RADIATION EFFECTS IN SYNROC-D

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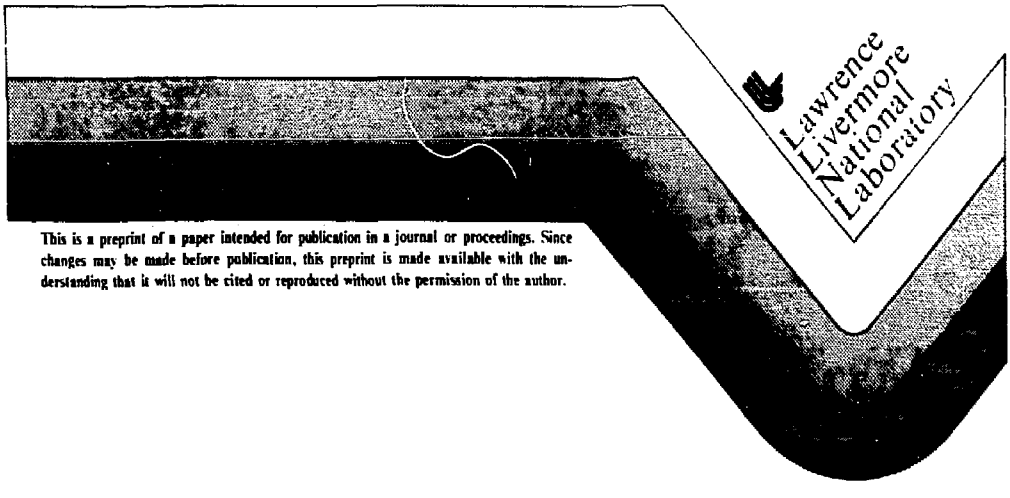

Abstract

This paper describes SYNROC-D and the irradiation it will be subjected to over the first million years of storage. This will include about 8×10^{24} alpha decays per m^3 and a total ionization dose of about 1×10^{11} rads. Methods of simulating the radiation effects are discussed. Previous work by others is reviewed and compared on a dpa basis. ^{238}Pu doping experiments to simulate internal alpha decay are described, and the progress is discussed. It is concluded that dose rate effects on swelling and metamictization of perovskite and zirconolite are small over a wide range of dose rate, and that swelling and metamictization in these minerals does not anneal significantly over geological time periods.

Radiation Effects in SYNROC-D*

I. Introduction

The management of high level nuclear wastes from the reprocessing of nuclear reactor fuel elements is an important technological challenge. Ringwood[1-3] has proposed to isolate the waste radionuclides as dilute solid solutions in the constituent minerals of a synthetic rock, called SYNROC. The particular assemblage of phases proposed for U.S. defense wastes (generated from the production of plutonium for nuclear weapons) has been labeled SYNROC-D. One of the most significant questions bearing on the use of any solid nuclear waste form is whether the radioactive decay of the reactor wastes will significantly decrease the waste form's ability to contain them. This paper presents the background information necessary for understanding radiation effects in SYNROC-D, discusses methods of simulating these effects, reviews the data from previous work, and describes our own actinide doping project and the progress to date.

II. Properties of Interest

There are four conceivable mechanisms by which radionuclides could be removed from a monolith of solid waste: dissolution or leaching, volatilization, particulate dispersion, and melting followed by liquid flow. For a ceramic waste form, particularly one designed for defense waste, which has a relatively low thermal output, melting need not be considered. Volatilization might be of concern in fire accidents during processing, temporary storage, or transportation. Particulates might be of concern

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in impact accidents. Once the waste is placed in a geological repository, only leaching is important. Combining an understanding of these mechanisms with a consideration of radiation effects observed in other, similar materials, one concludes that the most important properties which should be examined for radiation effects are the following: leaching rate, volume changes, and fracturing. In addition, some consideration should probably be given to stored energy (from the accumulation of lattice defects, the so-called Wigner effect), volatility, and thermal conductivity.

The Department of Energy has established a Materials Characterization Center (MCC) at Battelle Pacific Northwest Laboratories. One of its responsibilities is to develop standard testing methods for nuclear waste forms. In the most recent draft[4] of the standard method MCC-6, for preparation and characterization of actinide-doped waste forms, it is stated that several MCC procedures are under development that will be applicable for testing alpha-decay effects in radioactive waste forms, including such properties as leaching behavior, density, microstructure, and tensile strength.

III. Description of SYNROC-D and its Phases

The original composition of SYNROC was called SYNROC-A, and consisted of the minerals hollandite, perovskite, zirconolite, Ba-feldspar, kalsilite, and leucite. To reduce cesium leachability, Ringwood proposed a second composition, called SYNROC-B, which contained only the first three of the minerals listed[3], such that cesium would go into the hollandite phase. SYNROC-C is the same as SYNROC-B, except that it contains about 10-20 weight percent of calcined simulated high level wastes from the reprocessing of commercial nuclear fuel.[5]

The defense nuclear wastes stored at the Savannah River Plant and those to be generated in the future are composed of fission products and actinides in predominately non-radioactive material.[6] SYNROC-D is a composition specially designed to immobilize these wastes.[7,8] In forming SYNROC-D, the scheme will be to remove most of the inert, soluble salts and concentrate the rest of the material by evaporation and calcining. Non-radioactive mineral-formers will be added and mixed with the waste prior to calcination. The resulting mixture will be hot-pressed or sintered to form a polycrystalline assemblage. Although minor changes may yet be made, SYNROC-D currently consists of zirconolite, perovskite, two spinel phases (hercynitic and ulvospinels), and nepheline. Some glassy phase may currently be present as well, but efforts are underway to produce completely crystalline material. The maximum grain size is 1 to 5 micrometre, with the spinel grains generally larger than those of perovskite and zirconolite. The quadrivalent actinides are expected to dissolve primarily in the zirconolite. The trivalent actinides, as well as the rare earths and strontium, are expected to enter the perovskite.

Zirconolite is a relatively uncommon titanate mineral. In its pure, undamaged state, it has the chemical formula $CaZrTi_2O_7$ and a monoclinic crystal structure. Natural zirconolite has been found to include Nb, Ta, Th, U, Fe, Mn, Mg, Y, and rare earths in its crystal structure.[9] When uranium is substituted for all the zirconium, pyrochlore ($CaUTi_2O_7$) is formed, having a cubic structure.

Perovskite, $CaTiO_3$, has an orthorhombic crystal structure and is much more common in nature than zirconolite.[10] In natural specimens, the rare earths and alkalis commonly replace calcium, while small-sized cations such as niobium and tantalum replace titanium.

Nepheline, $(Na,K)AlSiO_4$, is an important natural rock-forming mineral having a hexagonal crystal structure. Natural samples generally contain some calcium.[11,12]

The spinels are a common mineral group having the general formula AB_2O_4, where A is Mg, Fe^{+2}, Zn, Mn^{+2}, or Ni, and B is Al, Fe^{+3}, Mn^{+3} or Cr. The structure is isometric.[11]

As can be seen, SYNROC-D is composed of a variety of mineral phases, each having a unique structure. This makes it important to perform radiation effects experiments on the actual polyphase material. Single phase studies, while helpful in interpreting the behavior of the polyphase material, cannot measure effects due to differential swelling or interphase grain boundaries, for example.

IV. Processes Resulting from Radioactive Decay in High Level Waste Forms

High level nuclear waste forms in general will be subject to damage primarily from alpha recoil nuclei, alpha, beta, and gamma radiation, and to a minor extent from neutrons and fission fragments. The beta and gamma radiation come mainly from the fission products. The actinides are the main source of the alpha radiation. The beta and gamma radiation mainly produce ionization, which is spread out along the paths of the beta particles and the Compton or photoelectrons which result from gamma-ray interactions. Some direct atomic displacements are also produced by this radiation. Most of the direct atomic displacements result from recoiling alpha-emitting nuclei, and to a lesser extent from alpha particles themselves. The alpha particles produce more concentrated ionization, and finally stop in the material, resulting in trapped helium. Nuclei of both actinides and fission products undergo transmutation when they decay, altering the chemical composition of the waste form.

V. Spatial Distribution of Radiation Effects in SYNROC-D

In high level defense waste, during the first 10^6 years, the decay of plutonium isotopes, particularly ^{238}Pu, will produce most of the alpha-recoil nuclei, and hence, most of the atomic displacements. Smaller contributions will come from ^{241}Am and the curium isotopes. Under the oxidation-reduction conditions present during SYNROC-D manufacture, it is not known at this time whether plutonium will be in the +3 or the +4 oxidation state, and hence, whether it will preferentially go into the perovskite or the zirconolite phases, respectively. However, it is expected to partition between these two phases. The direct atomic displacements will therefore be concentrated in them, since the ranges of the recoil nuclei (less than 0.1 micrometre) will be less than the grain size (about 1 micrometre). The displacements due to alpha particles, the ionization dose, and the helium atom implantation will be more or less uniformly distributed throughout the SYNROC-D phases, since the ranges of alpha, beta, and gamma radiation exceed the grain size. Transmutation products will generally remain in the phases in which their parent nuclei were initially dissolved.

As mentioned above, of the five phases in SYNROC-D, only perovskite and zirconolite will experience significant alpha-recoil damage. The nepheline and the two spinel phases will be damaged only by alpha-particles in the bulk. Since the alpha-recoils have a range of about 50 nm and the actinide phases constitute only 33 volume percent of SYNROC-D, the fraction of the inert phases receiving alpha-recoil damage will be less than 7 percent, assuming a one-micrometre grain size. The average

damage in this 7% of the volume will be about one-sixth that experienced by the actinide phases. Thus the damage in the inert phases due to alpha-recoils is less than 10% of the alpha particle damage and can be ignored.

VI. Temporal Distribution of Irradiation

The principal fission products in high level defense waste[6] are ^{137}Cs and ^{90}Sr, having half-lives[12] of 30.17 and 28.82 years, respectively. About half of the one-million-year ionization dose in SYNROC-D will be delivered by the fission products in the first 1000 years, and will amount to about 5×10^{10} rads. An approximately equal amount of ionization dose will be delivered by the alpha particles from decay of the actinides. The principal actinides in defense waste, and their half-lives[12] are as follows: ^{238}Pu - 87.74 years, ^{239}Pu - 2.41×10^4 years, ^{241}Pu - 14.4 years, ^{241}Am - 433 years, and ^{240}Pu - 6.57×10^3 years. The ionization dose arising from actinide decay, as well as most of the atomic displacements, will therefore be produced over a somewhat longer timescale than the fission product ionization. The total concentration of alpha decays in SYNROC-D in one million years is expected to be about 8×10^{24} alpha-decays per m^3, based upon Savannah River composite waste without aluminum removal,[14] a specific alpha activity[6] of 4.6×10^{-3} curie/gram of Fe_2O_3, a 23 weight % Fe_2O_3 loading in SYNROC-D, and a SYNROC-D density of 4 Mg/m^3.

VII. Temperature History

After production, it is planned that SYNROC-D would be sealed in canisters and placed in a geological repository. The temperature of the waste would be determined by a balance between its heat output and the

conductance of the medium in which it was placed. It is thus dependent on such parameters as the waste loading in SYNROC-D, the dimensions of the canister, and the thermal conductivities of the SYNROC-D, the canister material, the geologic material, and any gases present in gaps. Although these parameters are not completely specified at present, approximate calculations indicate that the centerline temperature of a SYNROC-D filled canister will not exceed 200°C, and could be considerably less.

VIII. Methods of Simulating SYNROC-D Radiation Effects

As mentioned above, SYNROC-D will undergo displacement damage, ionization, and internal transmutations with rather non-uniform temporal and spatial distributions. In order to reach some conclusions in a timely manner, it is necessary to accelerate the damage process, so that periods of, say, a million years, can be simulated in a few months.

In the past, several methods have been used for radiation effects simulation. All of them offer advantages and disadvantages, and it is necessary to have a fundamental understanding of radiation effects to compare their results. A few of the more common methods are external bombardment using gamma rays, electrons, light ions, heavy ions, or neutrons, and internal bombardment using short half-life actinide doping to bring about internal alpha decay, and uranium, boron, or lithium doping coupled with neutron irradiation to induce internal fission or (n, alpha) reactions. In addition, transmutations have been simulated by doping and irradiating with a high fluence of thermal neutrons to induce capture reactions, which are followed by beta decay.

It is generally agreed that short half-life actinide doping is the best way to simulate damage due to alpha decay of actinides. It should

produce the same type of damage with the same spatial distribution, but accelerated in time by several orders of magnitude. This approach has been taken in the past with other high level waste forms, and is the basis for the standard test procedures ISO/DIS 6962 and MCC-6.

Ionization doses to the levels expected in defense waste can be delivered to bulk samples either by electron or gamma ray bombardment. Gamma irradiation is easier experimentally, and is capable of treating larger samples without problems of temperature control.

Transmutation is difficult to simulate. Weber et al[15] have doped waste glasses with stable ^{133}Cs, neutron-irradiated to produce capture to ^{134}Cs, and annealed to remove neutron damage. The ^{134}Cs then decays to ^{134}Ba with a 2.1 year half-life. This simulates the decay of ^{137}Cs to ^{137}Ba in the actual waste, which proceeds with a 30.17 - year half-life. Changes in density and leach rates are measured at intervals of 6 to 12 months. This approach may be more appropriate for glass waste forms than for SYNROC-D, because the unavoidable neutron damage is uniformly distributed, which is closer to the actual case for glass than for a polyphase material.

IX. Review of Radiation Effects Research by Others on SYNROC and its Phases.

There are a number of experimental studies of radiation effects on SYNROC phases as well as a few observations on SYNROC-based waste forms. These include fast neutron irradiations,[16-18] ion bombardment,[19] electron irradiation,[20] doping with alpha-emitters[21,22] thermal neutron irradiation of U-doped samples to produce fission-fragment damage,[23] and studies of natural specimens containing uranium and thorium.[10,24,25]

Unlike metals, for which the experimental basis and theory of radiation effects are well-developed, non-metallic inorganic solids have received relatively little attention. With the exception of the alkali halides and a few simple oxides there is virtually no basic information on production thresholds and defect configurations in these materials. Thus, any comparison of diverse radiation sources will necessarily be crude.

The first step in comparing radiation damage from different sources is straightforward: the determination of the primary recoil spectrum resulting from the exposure. For neutrons, this requires a knowledge of interaction cross-sections and kinematics. A number of codes using standard cross-section files have been developed for this purpose. For charged particle irradiations both electronic and nuclear stopping powers are required, since, as the particle slows, its energy is partitioned between recoiling atoms and electrons. Again a number of codes are available for this purpose.

The next step involves the partitioning of the energy of the primary recoil between surrounding atoms in the lattice and electrons, through several generations of recoils. That portion of the energy which has been used to produce atomic displacements at the end of this process is termed the damage energy, E_D. In multi-element systems the theory of this process is not well-developed. Even simple models of the displacement process in binary systems[26] reveal a marked dependence on recoil energy when thresholds for the two elements differ by a factor of two, or mass ratios are greater than four.

Since present theory does not enable us to make exact calculations of damage energy for multi-element materials, we must make a simplifying assumption at this point. We have chosen to calculate damage energy for each primary recoil by assuming it stopped in a monatomic solid made up of the same chemical element as the recoil atom itself. In the few cases studied,[27] this approximation is as good or better than assuming all recoils stop in a medium which has an atomic number reflecting some weighted average of the atomic numbers of all the chemical species present in the solid. Also, it offers the advantage of using Robinson's[28] analytical formula for Lindhard[29] partitioning.

The total damage energy deposited per unit volume thus becomes our basis for comparison of various irradiation experiments. It is customary, however, to make comparisons on a dpa (displacements per atom) basis. For metals a standard definition has been adopted[30] based on the Kinchin-Pease[31] model. The number of displacements, $\langle n \rangle$, is given by

$$\langle n \rangle = .8E_D/2E_0 \qquad (1)$$

where E_0 is the displacement threshold. We have used this definition with E_0=25eV to make comparisons even though, in fact, the actual number of dispaced atoms may be significantly different.

The results for the various sources of damage are given in Table 1. For the alpha-recoil nucleus, 3 MeV Ar^+, and fission fragments the MIX[32] code was used with Lindhard[29] stopping theory and, for the alpha-particle, with stopping given by Ziegler.[33] A Mott scattering code[34] was used for electrons.

For the HIFAR reactor the spectrum given by Reeve and Woolfrey[17] was used above .183 MeV, and our estimate was used for lower energy neutrons. The code of Logan and Russell,[35] as modified by Kinney, was used to determine the damage energy cross-section from the 1978 ENDL[36] files. This resulted in a value 16% higher than that obtained by Reeve and Woolfrey. The result given for the reactor work of Wittels and Sherrill[16] is simply an educated guess, since they gave no spectral information.

Considering all sources of error; namely dosimetry, crosssections, stopping powers and the simple approximations used, the comparisons can only be expected to be good to within a factor of 2. We note that the number of displacements obtained here for the alpha-recoil nucleus is about 2/3 that obtained by many authors. This is the result of considering electronic losses for all recoils, not just those of the original alpha-recoil itself.

The property change measurements reported for the various experiments generally included measurements of volume expansion and/or x-ray lattice parameter changes. In some cases only x-ray line intensities were measured, and in a few cases TEM examination was reported. The volume change of a sample at high doses depends sensitively on the microstructure; i.e. grain size, porosity; minor phases, etc., and is not a valid parameter for comparison of different samples. For example cold-pressed and sintered samples of SYNROC-B swelled three times as much as hot-pressed samples of the same composition[37] during neutron irradiation. From the results of two actinide doping experiments,[21,22] it appears that volume changes measured by XRD are only in agreement with macroscopic measurements up to about 2% swelling. We have there-

fore chosen the damage energy for 1% swelling as a comparison parameter characteristic of changes in the lattice, independent of microstructure. Since data were not necessarily available for exactly 1% swelling, linear interpolation or extrapolation of doses was used. Available results are presented in Table 2 and Figure 1 for zirconolite and perovskite. Data on Ba-hollandite is also included,even though this phase is not a component of SYNROC-D, because it is of interest for commercial waste forms. For each sample the radiation exposures listed were converted to dpa. Also listed are dpa equivalent values of alpha decays/m^3, and ionization doses. For the reactor irradiations, ionization doses are based on estimates of gamma ray fluxes. For hollandite the equivalent alpha dose is only for damage from the alpha-particle. The final column lists damage rates in dpa/yr.

As can be seen from Table 2 and Figure 1, the dpa levels for 1% swelling in perovskite and zirconolite are comparable to each other and are about half that found for hollandite. For perovskite and zirconolite the dpa required for 1% swelling for all the irradiations is within a factor of six, even though the experiments span a range of 10^{11} in dose rate! This would indicate that the initial radiation response of SYNROC phases is not dose-rate dependent.

Since the 10^6-year doses expected in SYNROC-D will exceed those required for 1% swelling, we would like to have an additional comparison at higher doses, using a parameter again characteristic of the mineral, and not dependent on its microstructure. Since both perovskite and zirconolite can be found in nature in a metamict state, the radiation exposure required to eliminate x-ray lines in either powder pattern or

Laue measurements is well-defined and provides a good measure of the amount of disordering produced by irradiation. Although more precise x-ray and TEM methods reveal an underlying crystallinity[10,23] at this point, at doses an order of magnitude larger we expect samples to become TEM amorphous in the absence of concurrent annealing.[10,21,38,39]

The results are given in Table 3 and Figure 2. In cases where the exact exposure for x-ray metamictrization was not determined, we have given the highest measured exposure at which x-ray lines still appeared and/or the lowest exposure at which the samples were observed to be metamict. In the case of the Kaiserstuhl zirconolites, the value shown in Table 3 is an estimate by Sinclair and Ringwood of the exposure required to eliminate the high-2θ lines. In addition to the natural samples analyzed by Sinclair and Ringwood[10] from isotopic dating by Oversby and Ringwood[40], we have also included two examples of metamict perovskite minerals.[24,25] For these samples alpha-doses were estimated by Oversby[41] based on the most probable ages. For the 3 MeV Ar^+ irradiations of Cartz and Karioris[19] the maximum sample dimensions were about equal to the range of the Ar ions. Since a distribution of particle sizes was used, we have estimated dpa from Table 1, using values for the first third of the range.

For zirconolite the doses required to produce an x-ray metamict structure by internal alpha decay in natural and in doped specimens are within a factor of two, even though the displacement rates span 10^9 in magnitude. The results of 3 MeV Ar^+ irradiations at a rate 3-4 orders of magnitude higher than that in doped samples are also within our uncertainty of a factor of two. Dose rate effects are clearly not important at low temperatures and doses of 2-3 x 10^{25} alphas/m^3, cor-

responding to expected million-year doses in SYNROC-D.

While the bounds for the dose required to cause perovskite to become x-ray metamict are not as narrow as those for zirconolite, we expect it to occur at less than 1 dpa. Again dose rate effects do not appear to be important. As in Table 2, the equivalent hollandite doses are for alpha particle damage only.

Since except for the fission fragment work, the observed swelling and metamictization correlate well when compared on a dpa basis, but do not correlate when compared on an ionization dose basis, we can conclude that ionization effects do not contribute significantly to these property changes. This is based primarily on the results from electron irradiations of Sethi[20] for which the ratio of ionization to displacement damage is two to four orders of magnitude larger than that for the other experiments. On a dpa basis, fission fragments are a factor of 50 more effective than the other radiation sources, a conclusion already reached by Vance.[23] Damage tracks (ionization-produced displacements) are expected to appear in minerals[42] at ionization densities in excess of 10-20 MeV/mg/cm^2. Alpha particles (>1 MeV) and 3 MeV Ar^+ produce maximum densities of 2 and 8 MeV/mg/cm^2, while for fission fragments the density is above 10 MeV/mg/cm^2 over 80% of the range. As a result, the dense ionization caused by fission fragments leads to additional displacements. As can be seen in Table 3, 3-MeV Ar^+ produce metamictization in Ba-Hollandite at (perhaps) an order of magnitude lower dpa level than reactor neutrons. This suggests that the threshold for track production in Ba-Hollandite may be less than 8 MeV/mg/cm^2.

For the loadings given in section VI we expect displacement damage in 10^6 years of 0.3 dpa in perovskite and zirconolite and .03 dpa in

nepheline and the two spinels. From the results indicated in Tables 2 and 3, we expect both the actinide-containing phases to be x-ray metamict, or nearly so, and to expand 2-3%. From the results of reactor irradiations[43] and fission fragment damage[23] on spinels, we would not expect any significant changes at .03 dpa. Nepheline, on the other hand, might be expected to show significant changes at this level, due to the higher susceptibility of complex silicates[44,45] to radiation damage and ionization effects.

The most important conclusion to be drawn from this comparison is that dose rate effects are not important for zirconolite and perovskite irradiated by internal alpha decay, thus justifying the use of accelerated testing in evaluating radiation effects in SYNROC-D. The reason for this appears to be that the temperature required for annealing the displacement damage in these minerals is well above room temperature, as well as the ambient temperatures experienced by the natural samples during most of their lives. This is supported by the observations of Cartz and Karioris,[19] who found that temperatures above 600°C were required to anneal ion damage in times of a few hours in perovskite. It is also consistent with the annealing studies of Sinclair and Ringwood[10] on natural zirconolites and perovskites, in which temperatures from 400 to 1200°C were used.

X. Lawrence Livermore National Laboratory SYNROC-D Radiation Effects Experimental Plan

Since Lawrence Livermore National Laboratory is the lead laboratory for SYNROC-D development, we decided to do as close a simulation of expected radiation effects on this material as is possible, given the time frame for decision-making on waste selection. Accordingly we

have chosen to dope SYNROC-D to 10 wt. % of ^{238}Pu. This will produce a dose of 4 X 10^{24} alphas per m^3 in about 200 days. Depending on programmatic requirements, samples could be stored for a longer period to achieve a higher dose. We chose ^{238}Pu rather than ^{244}Cm partly because, as noted above, the plutonium isotopes will be the principal source of alpha recoil damage in defense waste, and it is not clear that curium and plutonium will partition in the same way between zirconolite and perovskite under the redox conditions present during SYNROC-D manufacture.

In order to measure the radiation effects, we would like to compare samples which have undergone internal alpha decay to control samples which have not. Because of the programmatic need to produce this high damage level in a few months, the plutonium loading is fairly high. Accordingly, we decided to make the control samples with 10 wt. % ^{239}Pu, in order to preserve the same chemical composition. The control samples will therefore be subject to some alpha decay damage. However, with the isotopic purities we plan to use, the control samples will have dose rates about a factor of 200 less than that of the ^{238}Pu - containing samples.

In addition to the internal alpha decay, we want to simulate the ionization dose which the waste will receive, since ionization may produce important effects. It is desirable to deliver this dose early in the life of the experimental samples, and to preserve the ratio of ionization dose to alpha decay concentration. By irradiating both ^{238}Pu - containing samples and controls, it is possible to examine both independent and synergistic effects of ionization dose. We plan to deliver the dose using spent fuel from the HFIR reactor at Oak Ridge National Labora-

tory. Fuel elements are cycled through this reactor every 23 days, and are burned at high flux until they are self-poisoned. While they are cooling in water storage, samples may be placed inside them for gamma irradiation. The dose for one 23-day period is 2.65×10^{10} rads. We plan to irradiate both ^{238}Pu-containing and control samples for 1, 2, and 3 periods.

Most of the samples will be stored at room temperature during alpha decay. A few, however, will be stored at 200°C to determine whether there is a temperature effect. We are not simulating transmutations at present.

On the basis of cost, availability of the necessary facilities, and proximity to the main SYNROC-D development effort, we have chosen to carry out the plutonium doping and most of the sample characterization and testing at the General Electric Co. Vallecitos Nuclear Center in Pleasanton, CA, a short distance from LLNL. A large alpha cell with metallographic facilities is available there, and G.E. has considerable experience in handling and characterizing radioactive ceramic materials and in encapsulating them for shipment. Accordingly, we have entered into a contract with G.E., which became effective on January 23, 1981

Solutions of the plutonium isotopes in nitric acid will be prepared in the Plutonium Technology Facility at LLNL. The SYNROC-D pellets, approximately 10 grams in size, will be hot-pressed in graphite dies by G.E., using powders and Pu solutions supplied by LLNL. Ceramography and scanning electron microscopy will be carried out by G.E., and x-ray diffraction will be performed at LLNL. Leaching will follow the standard method MCC-1, Matrix A, which consists of 7-day, 90°C static leach testing in deionized water. Sample densities will be

measured by flotation in thallium malonate-formate solutions, coupled with liquid density measurement, using a Mettler-Paar Liquid Density Meter. Macroscopic swelling will be measured by dilatometry. Plutonium isotope concentrations in the samples will be evaluated by gamma ray spectrometry.

With these experiments, we plan to simulate both the alpha decay and ionization effects which would occur in the first million years of defense waste storage, and determine the changes in structure, leaching, and density which result. The expected temperature range will be bracketed to evaluate any temperature effects.

XI. Experimental progress up to September 30, 1981

During Fiscal Year 1981, we have obtained and checked out all the necessary equipment, and have hot-pressed 20 SYNROC-D pellets. In order to simulate plutonium doping, we have made pellets with U and Ce, respectively, at high enough concentrations to simulate 10 wt. % Pu. These elements are in the +4 and +3 oxidation states, respectively, and have larger ionic radii than the corresponding Pu ions. The pellets had nearly 100% of theoretical maximum density, and were crack-free. We were able to diamond saw the pellets into 1 mm - thick wafers. X-ray diffractometry indicated the presence of the expected SYNROC-D phases, with no significant amounts of additional phases present. Scanning electron microscopy showed no voids and typical 1 to 5 micrometre grain size. Although the grain size was too small for quantitative energy-dispersive x-ray analysis, it was possible to observe that considerable U was present in the zirconolite grains, and considerable Ce went into the perovskite grains. It therefore appears that Pu can be dissolved in SYNROC-D at concentrations up to 10 wt %. Accordingly, we

are moving the equipment into the hot cell to begin experiments with plutonium.

Because of the small grain size, we expect to be limited in our ability to make quantitative measurements of plutonium distribution. One approach may be to perform high temperature treatments to encourage grain growth, followed by energy dispersive x-ray analysis.

XII. Conclusions

In the first million years, SYNROC-D will be subject to a total alpha decay concentration of about 8×10^{24} alpha decays per m^3 and a total ionization dose of about 1×10^{11} rads. Considering the expected spatial and temporal distributions, the best way to simulate the radiation effects appears to be ^{238}Pu doping with external gamma irradiation. Experiments with U and Ce indicate that Pu can be dissolved in SYNROC-D to a concentration of 10 wt %, which will produce one-million-year-equivalent alpha decay in 400 days. Comparison of radiation effects measurements performed on SYNROC phases by others indicates that this acceleration of the irradiation will not seriously affect the results.

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Figure Captions

Figure 1 - Comparison of Displacements per Atom (dpa) Required to Produce 1% Increase in Volume in SYNROC Minerals for Different Types of Irradiation (α means internal alpha decay; n means neutron irradiation. References are given in Table 2.)

Figure 2 - Comparison of Displacements per Atom (dpa) in SYNROC Minerals Required to Eliminate Powder or Laue Pattern, Producing X-Ray Metamict State, for Different Types of Irradiation (α means internal alpha decay, n means neutron irradiation, ff means internal fission fragment irradiation, Ar^+ means argon ion bombardment, and e means electron bombardment. References are given in Table 3.)

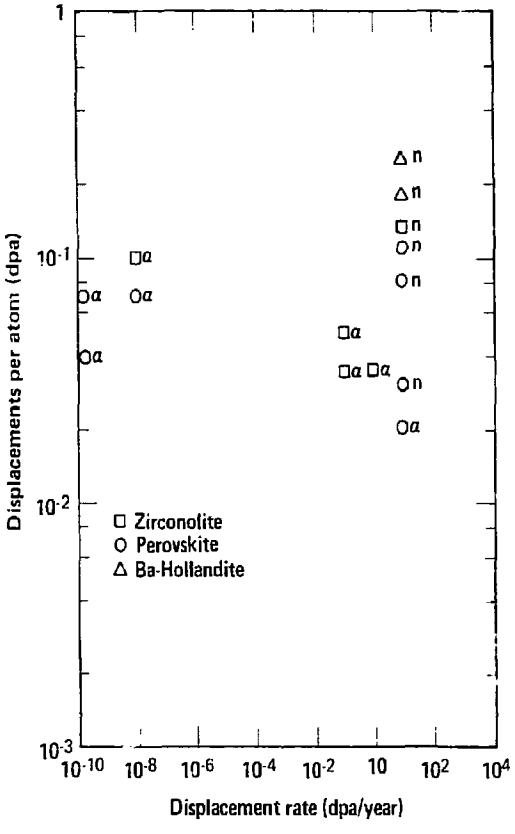
1
10^{-1}
10^{-2}
10^{-3}
Displacements per atom (dpa)
□ Zirconolite
○ Perovskite
△ Ba-Hollandite
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
10
10^{2}
10^{4}
Displacement rate (dpa/year)

FIG. 1

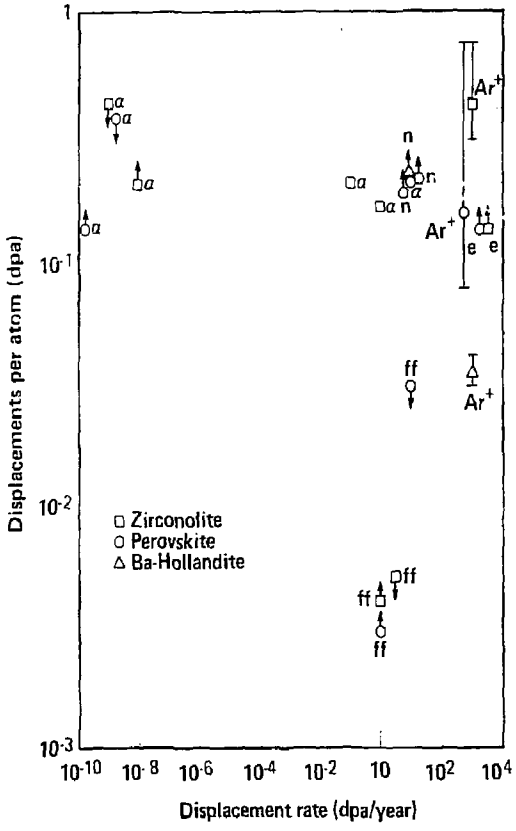
1
10^{-1}
10^{-2}
10^{-3}
Displacements per atom (dpa)
10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10 10^{2} 10^{4}
Displacement rate (dpa/year)
□ Zirconolite
○ Perovskite
△ Ba-Hollandite
α
n
Ar+
e
ff

FIG. 2

TABLE 1

Results of Displacement Calculations for SYNROC Phases

Type of Irradiation		Displacement Damage
^{238}Pu alpha-decay		980 displacements/recoil 120 displacements/alpha
HIFAR Reactor	Fast Neutrons	3.2 dpa/10^{25} n/m^2 (E>1 MeV)
BSR Reactor	Fast Neutrons	1 dpa/10^{25} n/m^2 (E>.05 MeV)
3 MeV Ar^+	Average Over Range	2.7 dpa/10^{20} ions/m^2
1 MeV e^-	First Third of Range Thin sample At Damage Peak	1.5 3 dpa/$10^{27}e^-/m^2$ 6.0
^{235}U fission	(full fragment mass distribution taken into account)	8 x 10^4 displacements/fission

TABLE 2

Exposure Required to Produce One Percent Increase in Volume

Damage Source	Ref	Sample	Interpolated Exposure	dpa	Equivalent alphas/m^3	Ionization dose MGy	dpa/yr
Zirconolite							
Reactor Neutrons	18	$CaZrTi_2O_7$	4.0×10^{23} n/m^2 (E>1 MeV)	.13	10.6×10^{24}	10.6×10^{24}	10^{1}
^{nat}U + Th alpha-decay	10	Kaiserstuhl Zirconolites	8.2×10^{24} alphas/m^3	.10	8.2×10^{24}	1.5×10^{3}	10^{-8}
^{238}Pu alpha-decay	21	Cubic $CaPuTi_2O_7$	2.7×10^{24} alphas/m^3	.034	2.7×10^{24}	500	10^{0}
^{238}Pu alpha-decay	21	$Ca(Pu_{.2}Zr_{.8})Ti_2O_7$	2.7×10^{24} alphas/m^3	.034	2.7×10^{24}	500	10^{-1}
^{244}Cm alpha-decay	22	$CaZrTi_2O_7$ + 3 w/o ^{244}Cm	4.0×10^{24} alphas/m^3	.049	4.0×10^{24}	800	10^{-1}

TABLE 2 (cont.)

Exposure Required to Produce One Percent Increase in Volume

Damage Source	Ref	Sample	Interpolated Exposure	dpa	Equivalent alphas/m^3	Ionization dose MGy	dpa/yr
Perovskite							
Reactor Neutrons	17	$CaTiO_3$	2.5×10^{23} n/m^2 (E>1 MeV)	.08	6.6×10^{24}	10^4	10^1
Reactor Neutrons	18	$CaTiO_3$	3.5×10^{23} n/m^2 (E>1 MeV)	.11	9.3×10^{24}	1.5×10^4	10^1
Reactor Neutrons	16	$BaTiO_3$	2.5×10^{23} n/m^2 (E>.05 MeV)	.03	2.1×10^{24}	10^4	10^1
^{nat}U + Th alpha-decay	10	Loparite	3.4×10^{24} alphas/m^3	.04	3.4×10^{24}	700	10^{-10}
^{nat}U + Th alpha-decay	10	Baikal + Jacupiranga Perovskites	5.7×10^{24} alphas/m^3	.07	5.7×10^{24}	10^3	10^{-10}-10^{-8}
^{244}Cm alpha-decay	46	$^{244}CmAlO_3$	1.6×10^{24} alphas/m^3	.02	1.6×10^{24}	350	10^1
Ba-Hollandite							
Reactor Neutrons	17	$BaAl_2Ti_6O_{16}$	5.6×10^{23} n/m^2	.18	1.5×10^{26}	2×10^4	10^1
Reactor Neutrons	18	$BaAl_2Ti_6O_{16}$	7.7×10^{23} n/m^2	.25	2.1×10^{26}	3×10^4	10^1

TABLE 3

Exposure Required to Eliminate Powder or Laue Pattern (X-ray Metamict)

Damage Source	Ref	Sample	Exposure	Calculated dpa	Displacement Equivalent	Ionization dose MGy	dpa/yr
Zirconolite							
^{nat}U + Th alpha	10	Kaiserstuhl Zirconolite	$>1.6\times10^{25}$ alphas/m^3	>.20	$>1.6\times10^{25}$	$>3\times10^{3}$	10^{-8}
^{nat}U + Th alpha	10	Jacupiranga Zirconolite	$<3.4\times10^{25}$ alphas/m^3	<.42	$<3.4\times10^{25}$	$<7\times10^{3}$	10^{-9}
^{238}Pu alpha	21	$CaPuTi_2O_7$	1.3×10^{25} alphas/m^3	.16	1.3×10^{25}	2.5×10^{3}	10^{0}
^{244}Cm alpha	46	$CaZrTiO_2O_7$ 3w/o ^{244}Cm	1.6×10^{25} alphas/m^3	.20	1.6×10^{25}	3×10^{3}	10^{-1}
3 MeV Ar^+	19	$CaZrTiO_2O_7$	$2\text{-}6\times10^{19}$ ions/m^2	.3-.8	$3\text{-}7\times10^{25}$	10^{3}-3×10^{3}	10^{3}
^{235}U fission	23	$CaZrTiO_2O_7$	$4.5\text{-}6\times10^{21}$ f/m^3	.004-.005	$3.3\text{-}4.5\times10^{23}$	45-500	10^{0}-10^{1}
1 MeV electron	20	$CaZrTi^2O_7$	$>4\times10^{25}$ e-/m^2	>.13	$>1.1\times10^{25}$	$>10^{6}$	10^{3}-10^{4}

TABLE 3 (cont.)

Exposure Required to Eliminate Powder or Laue Pattern (X-ray Metamict)

Damage Source	Ref	Sample	Exposure	Calculated dpa	Displacement Equivalent	Ionization dose MGy	dpa/yr
Perovskite							
Reactor Neutrons	17	$CaTiO_3$	$>6.5\times10^{23}$ n/m^2 (E>1 MeV)	>.21	$>1.7\times10^{25}$	$>2.5\times10^{4}$	10^{1}
Reactor Neutrons	16	$BaTiO_3$	$>1.8\times10^{24}$ n/m^2 (E>.15 MeV)	>.18	$>1.5\times10^{25}$	$>5\times10^{4}$	10^{1}
^{nat}U + Th alpha	10	Baikal Perovskite	$>1.1\times10^{25}$ alphas/m^3	>.13	$>1.1\times10^{25}$	$>2.5\times10^{3}$	10^{-10}
^{nat}Th alpha	24	Irinite	$<1.3\times10^{26}$ alphas/m^3	<1.6	$<1.3\times10^{26}$	$<3\times10^{4}$	10^{-8}
^{nat}U + Th alpha	25	Loparite	$<3.0\times10^{25}$ alphas/m^3	<.37	$<3.0\times10^{25}$	$<7\times10^{3}$	10^{-9}
^{244}Cm alpha	46	$CmAlO_3$	1.6×10^{25} alphas/m^3	.20	1.6×10^{25}	3.5×10^{3}	10^{1}
3 MeV Ar^+	19	$CaTiO_3$	10^{19}-10^{20} ions/m^2	.1-1.	10^{25}-10^{26}	5×10^{2}-5×10^{3}	10^{3}
^{235}U fission	23	$CaTiO_3$	3×10^{21}-3×10^{22} f/m^3	.003-.03	$2\text{-}20\times10^{23}$	30-300	10^{0}-10^{1}
1 MeV e^-	20	$CaTiO_3$	$>4\times10^{25}$ e^-/m^2	>.13	$>1.1\times10^{25}$	$>10^{6}$	10^{3}-10^{4}
Ba-Hollandite							
Reactor Nuetrons	17	$BaAl_2Ti_6O_{16}$	$>6.5\times10^{23}$ n/m^2 (E>1 MeV)	>.21	$>1.7\times10^{26}$	$>2.5\times10^{4}$	10^{1}
3 MeV Ar^+	19	$BaAl_2Ti_6O_6$	$2\text{-}3\times10^{18}$ ions/m^2	.03-.04	$3\text{-}4\times10^{25}$	10^{2}-1.5×10^{2}	10^{3}