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EFFECT OF RADIATION ON SPINEL CERAMICS FOR PERMANENT CONTAINERS FOR NUCLEAR WASTE TRANSPORTATION AND STORAGE*

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ABSTRACT

NUCON Systems, Inc., NY (Nucon) has proposed an alternative waste management technology and developed ceramic material formulations from inexpensive spinel ($MgAl_2O_4$) refractory powder (no inorganic additives) in order to fabricate ceramic containers for the transportation and permanent storage of nuclear waste. Nucon has contracted with the Brookhaven National Laboratory (BNL) Department of Advanced Technology (DAT) to develop a test methodology and provide evaluation of the effects of radiation on these materials.

The Gamma Irradiation Facility (GIF) of BNL was used to irradiate samples. The radiation resistance of three spinel compositions (B1, B2, and C2) and two physical forms (slip cast bars and extruded rods) were tested. The spinel compositions differ only in particle and crystal size distributions and suppliers. Compressive strengths of unirradiated baseline samples were compared to those of samples irradiated to total gamma doses of $1x10^8$, $5x10^8$, and $1x10^9$ rad. Other physical evaluations included water absorption, bulk and geometric density, apparent specific gravity, and apparent porosity.

This presentation discusses the first results of the application of the BNL–Nucon's test methodology. The paper is a continuation of the series of presentations on the "ceramic container" project made at the Waste Management Technology Section of the American Ceramic Society Annual Meetings of 1995, 1998, and 1999 [1, 2, and 3].

INTRODUCTION

Existing technologies for dealing with high level nuclear wastes involve mixing them with and/or immobilizing them in inert and attenuating materials, such as concrete, metal, boron silicate glass and special ceramics. Such technologies have their limitations, including high costs and increased associated hazards. Because of their hazardous nature, all the associated waste treatment practices, including the mixing and forming processes, are very expensive, especially the hot isostatic pressing of ceramic waste forms. The very act of mixing almost invariably results in a significant increase in the volume of waste and thus leads to higher storage and disposal costs. While in storage and, particularly after disposal, the stabilized waste form may be subjected to environmental insults, including those of chemical, water, thermal, biological and radioactive nature.

These can cause degradation and ultimately lead to contamination of the filling

and surrounding materials. One proposed solution is to use stainless steel containers for the transportation and temporary storage of untreated nuclear waste and products. Such containers are very expensive but, more importantly, even they are not totally immune to leaking after dozens of years, particularly in the region of the closure welds. Thus it is now generally accepted that current technological methods do not represent the ultimate solution to the permanent and inexpensive isolation and storage of high-level nuclear waste and products.

The "ceramic container" project promises to be a breakthrough in the existing waste management technology paradigm because ceramic container assembly minimizes the need for initial treatment and excludes waste immobilization processes. At the same time, it provides an acceptable, stable isolating structure in which nuclear waste products can be safely transported, stored and permanently disposed.

Cost-effective technologies for the production of large thick-walled ceramic vessels and their lids and seamlessly closing of ceramic containers have been developed and patented [4, 5, and 6]. The first ceramic vessel is a major component in an onion-like container assembly that employs additional vessels and interim layers made of other materials to provide the necessary radiation attenuation and protection from outside mechanical impacts. The ceramic vessel itself is the innermost component, into which the nuclear waste is loaded before the vessel is seamlessly closed. The complete container assembly constitutes a stable mechanical barrier that provides complete separation of radioactive materials from the normal environment.

In order to develop such a ceramic vessel, Dr. Rokhvarger has developed an innovative ceramic formulation based on a readily available and inexpensive refractory alumina-magnesia spinel ($MgAl_2O_4$). The unique properties and advantages of this spinel, a material which is extremely stable over geological time periods under all practically possible chemical, water, biological, thermal and radiation corrosion impacts, have been discussed in several articles by specialists at the U.S. Department of Energy and reviewed in [3]. The same reference, [3], discussed the major features of Nucon's technology, such as employing extrusion and slip-casting forming methods to make possible the cost-effective industrial production of large thick-walled container vessels and their lids.

Three key physical parameters, compressive strength, gas impermeability and radiation resistance, must be optimized if the newly developed spinel ceramics are to find application in the proposed ceramic containers. It is essential that the spinel ceramics meet the regulatory requirements with regard to these three parameters if the total ceramic container concept is to become feasible and workable. The present program was conceived to demonstrate that the newly developed spinel ceramics meet at least the radiation stability requirements being practically nonporous and high dense material.

REGULATORY RADIATION REQUIREMENTS

Candidate materials for all waste container applications (including storage of spent fuel and disposal of low- and high-level wastes) are subject to assessment of performance, including stability under high radiation conditions. The basic U.S. federal requirements for packaging, storage and transportation of all radioactive wastes (including spent nuclear fuel) are contained in several parts of the Code of Federal Regulations. However, these documents themselves are generally not prescriptive of actual materials properties. Guidance on interpretation of the regulations with regard to

specific material property requirements is usually contained in related documents such as regulatory guides and branch technical positions. A review of the latter revealed only one specific radiation resistance requirement for containers - that high integrity containers be able to withstand "10^8 rad or greater if necessary" [7]. There is no specification of energy spectrum or flux, but the original goal of 10^8 rad is based on being approximately equivalent to the total dose acquired over 300 years by a waste form loaded to a Cs-137 or Sr-90 concentration of 10Ci/ft^3. Cumulative doses of the gamma radiation calculated for the storage applications of various high-level nuclear wastes typically exceeding 10^8rad should not significantly exceed 10^9rad for the first 1000 years of waste exposures when 95% - 99% of gamma radiation and 100% of alpha and beta radiation have to be emitted.

With regard to the radiation energy spectrum, Cs-137 emits gamma rays with energy of approximately 662 keV; Sr-90 is a pure beta emitter. In reality, the spectrum seen by a container, especially one containing spent fuel after ten or more years of the exposure in a water pool, will be very broad and would mostly include gamma and beta rays. However, we suppose, for low- and high-level waste containment, the tests can be performed in a "gamma irradiator or equivalent" [7]. If a Co-60 radiation source is used, it will emit gamma rays with energies of 1.17 MeV and 1.33 MeV. When dealing with dense materials such as steels, concrete, and ceramics, small differences in gamma energy levels are not considered important.

CERAMICS SAMPLING

Ceramic samples were prepared and preliminary tested at the Center for Ceramic Research, Rutgers University, NJ by Dr. Rokhvarger and two his associates from Nucon Systems, Inc. Three spinel formulations, designated B1, B2 and C2, were investigated. The B1 and B2 samples were in the form of slip cast rectangular beams, measuring nominally 8mm x 16mm x 50 and 150mm long. The C2 samples were in the form of extruded rods, nominally 9mm diameter x 50mm and 130mm long. The samples were weighed and measured at the outset of the program then loaded into a Pyrex jar of internal diameter 70mm (2.75 inch) for exposure to gamma radiation. Sample irradiation took place in the BNL Gamma Irradiation Facility (GIF), which uses Co-60 sources. Co-60 is a beta/gamma emitter with strong gamma lines at 1.3325 MeV and 1.1732 MeV and beta at 0.318 MeV. In order to minimize the time to dose, all ceramic samples were irradiated using a dose rate of ~1×10^6rad/h. The highest dose achieved was 1×10^9rad, equivalent to about 1000 years exposure as a spent fuel container.

All irradiation were done under GIF ambient conditions, i.e., the samples were open to air, at a constant temperature of ~7°C, the approximate temperature of the coolant water in the GIF. Due to size constraints in the irradiation zone and the number of samples required for testing, only 50mm long samples were irradiated for each composition.

SAMPLE EXAMINATION

Pre- and post-irradiation tests included visual observations, measurements of sample mass, sample dimensions, compressive strength, and specific gravity, as described below. Dye-penetrant tests were conducted in accordance with ASTM E 165 [8] to

determine cracks or flaws visible to the unaided eye. Sample dimensions were measured to ± 0.0001mm and sample mass to ±0.001g.

Sample densification was determined in accordance with ASTM C 373 [9]. These values were derived from the masses of dry samples and of water-impregnated samples. The latter samples were impregnated by boiling in water for 5 h, followed by weighing, first suspended in water, then after dabbing briefly with a damp towel such that a "saturated" weight is obtained. Weights were compared to the original "dry" sample weight. The 50mm long bar and rod samples were found to weigh slightly less than the 50g minimum sample size recommended in [9], leading to increased statistical uncertainty in these measurements. This error was countered in two ways. First, the number of specimens for each group (dose/formulation) was increased beyond the recommended 5 to 8. Second, comparison of results from the longer 150mm samples allowed an assessment of the effect of size on the statistical uncertainty.

Because of the nondestructive nature of the density measurement, samples were subsequently dried then used for compression testing in accordance with ASTM C 773 [10]. This procedure specifies cylindrical specimens with a length-to-diameter ratio of approximately 2.0, with sample strength not to exceed 80% of the testing machine load capacity. Samples were cut to appropriate size using an Isomet low speed diamond wafering saw. Bar samples were squared and clamped three at a time, with their large flat surfaces abutting to form a 24mm x16mm x 50mm blocks. Rod samples, which were slightly bowed, required the fabrication of a special jig to ensure that the cuts were normal to the length of the sample. A split holder was made such that 5 samples could be cut at once while squaring each sample individually. Compression testing was done using an Instron 5582 load frame. In each case a minimum of ten specimens was tested for each set of parameters investigated (spinel formulation and exposure condition).

The complete sample matrix is summarized in Tables 1 and 2. Table 1 presents the radiation exposure matrix and lists the number samples (of length 50mm) and the doses received for each of the three formulations to be investigated. B1 and B2 samples were pulled from the GIF after total doses of $1x10^8$, $5x10^8$ and $1x10^9$ rad were accumulated. C2 samples were similarly sampled at $1x10^8$ and $5x10^8$ rad, but were removed slightly premature of $1x10^9$ rad due to closure activities in the GIF. The highest dose for these samples was $9.9x10^8$ rad.

Table 1. Radiation Exposure Matrix

Sample	Nominal sample dimensions (mm)	# of samples exposed to $1x10^8$ rad	# of samples exposed to $5x10^8$ rad	# of samples exposed to $1x10^9$ rad
Rod (C2)	∅8 x 50	8	8	8
Beam (B1)	7 x 14 x 50	8	8	8
Beam (B2)	7 x 14 x 50	8	8	8

Table 2 outlines the density and compression test matrix. Density tests were performed on all 50mm-long specimens. In addition, tests were performed on 5 150mm-long unirradiated B1 and B2 bar specimens and 10 150mm-long unirradiated C2 rod samples. Compression tests were performed using specimens cut from the 50mm samples used in the density tests. The rod samples yielded 2 compression test specimens while the each beam sample yielded 6 smaller compression test specimens.

Table 2. Test Matrix

Sample	Test type (Nominal specimen dimensions, mm)	# of unirradiated specimens	# of specimens exposed to $1x10^8$ rad	# of specimens exposed to $5x10^8$ rad	# of specimens exposed to $1x10^9$ rad
Rod (C2)	Density (Ø8 x 50) (Ø8 x 150)	8 5	8 -	8 -	8 -
	Compression (Ø8 x 16)	10	10	10	10
Beam (B1)	Density (7 x 14 x 50) (7 x 14 x 150)	8 5	8 -	8 -	8 -
	Compression (7 x 7 x 14)	10	10	10	10
Beam (B2)	Density (7 x 14 x 50) (7 x 14 x 150)	8 5	8 -	8 -	8 -
	Compression (7 x 7 x 14)	10	10	10	10

DISCUSSION OF THE TEST RESULTS

Sample Observations. On removal from the irradiation source, all the B1/B2 samples were noticeably discolored to a medium brown color. The highest dose ($1x10^9$ rad) produced only a slightly darker color than the lowest ($1x10^8$ rad). This phenomenon results as electrons are displaced, forming 'color centers' within the material. This interaction is very unstable, however, and in all cases the color faded rapidly (within 48 h) to a light ivory color. Within a few days samples were only slightly tinted compared to unirradiated samples. Thermal annealing is known to accelerate return to a normal color. The C2 samples were irradiated after completion of the B1/B2 irradiations. As with B1/B2 samples, all the C2 samples discolored to a medium brown color, again with little difference between minimum and maximum dose. However, this color persisted much longer than it did with the B1/B2 samples. A possible reason for this is significantly

Table 3. Measured Geometric Sample Densities (g/cm^3) for B1, B2 and C2 Samples (Mean ± 2σ)

	B1		B2		C2	
	Pre-Radiation	Post-Radiation	Pre-Radiation	Post-Radiation	Pre-Radiation	Post-Radiation
1×10^8 Rad	3.36±0.01	3.37±0.01	3.31±0.02	3.32±0.02	3.40±0.03	3.41±0.02
5×10^8 Rad	3.39±0.03	3.41±0.02	3.29±0.03	3.30±0.03	3.37±0.03	3.39±0.03
1×10^9 Rad	3.39±0.04	3.39±0.03	3.31±0.02	3.32±0.01	3.38±0.03	3.38±0.04
Unirradiated	3.38±0.02		3.31±0.01		3.39±0.01	

Table 4. Mean Water Absorption (%), Apparent Porosity (%), Apparent Specific Gravity (g/cm^3), and Bulk Density (g/cm^3) of B1, B2, and C2 Samples (Mean ± 2σ)

Radiation dose / Sample Characteristics		1×10^8 Rad	5×10^8 Rad	1×10^9 Rad	Unirradiated	
					L=50mm	L=150mm
B1	Water Absorption (%)	0.01±0.00	0.01±0.01	0.01±0.00	0.00±0.00	0.02±0.00
	Apparent Porosity (%)	0.02±0.01	0.03±0.02	0.02±0.01	0.01±0.01	0.07±0.01
	Apparent Specific Gravity (g/cm^3)	3.43±0.00	3.47±0.02	3.45±0.02	3.46±0.03	3.44±0.01
	Bulk Density (g/cm^3)	3.43±0.00	3.48±0.02	3.44±0.02	3.46±0.03	3.43±0.01
B2	Water Absorption (%)	0.18±0.05	0.17±0.04	0.10±0.04	0.16±0.04	0.07±0.04
	Apparent Porosity (%)	0.60±0.15	0.60±0.15	0.34±0.13	0.53±0.13	0.25±0.13
	Apparent Specific Gravity (g/cm^3)	3.43±0.00	3.43±0.00	3.43±0.00	3.44±0.00	3.44±0.00
	Bulk Density (g/cm^3)	3.41±0.01	3.41±0.00	3.42±0.01	3.42±0.01	3.43±0.01
C2	Water Absorption (%)	0.04±0.01	0.04±0.01	0.02±0.01	0.03±0.01	0.06±0.01
	App. Porosity (%)	0.15±0.03	0.14±0.04	0.08±0.04	0.11±0.03	0.19±0.03
	Apparent Specific Gravity (g/cm^3)	3.39±0.01	3.39±0.02	3.38±0.02	3.39±0.02	3.37±0.00
	Bulk Density (g/cm^3)	3.39±0.01	3.38±0.02	3.38±0.02	3.39±0.02	3.37±0.00

smaller particle size of C2 composition where particles are in the range of 0.5–3.9μm and 50% of the grains are less 1.5μm

Density Measurements. Geometric densities were calculated by dividing the sample weight by the measured volume. The as-received mean densities of the B1, B2 and C2 samples were 3.38 ± 0.02, 3.31 ± 0.01, and 3.39 ± 0.01 g/cm^3, respectively. These data are shown in Table 3, along with measurements made on irradiated samples immediately on their removal from the GIF. Based on these data there appear to be no consistent changes, either in sample dimensions or mass, due to absorbed radiation. The slight changes noted in mass could be attributed to the fact that samples were not prepared (cleaned, dried) prior to measurement.

Sample bulk densities, apparent specific gravity, water absorption, and apparent porosity, derived from the ASTM C 373 testing, are shown in Table 4. These data were slightly higher than measured geometric density values, probably due to errors in the volume measurements, which do not take into account irregularities in shape and surface texture of the samples. The data show the B2 samples have the highest water absorption and apparent porosity, and B1 the lowest. These results also correlate with the surface textures of the materials, with C2 the roughest and B1 the smoothest. Surface texture may be a source of error, especially for measurement of saturated weight, because the sample is dabbed with a damp towel in an attempt to dry the surface without drawing pore water from the sample. All samples should be ultimately gas impenetrable. Again, no statistical significant changes were evident following irradiation.

Compressive Strength Measurement. Sample compressive strengths were measured for unirradiated and irradiated samples in accordance with ASTM C 773 [10]. Samples with a nominal height to axial cross section ratio of 2.0 were tested, as described previously. Steel contact blocks (1.50" x 1.50" x 0.73") and cushion pads (1.0" x 1.0" x 0.030") were fabricated, for compliance with Procedure A of ASTM C773. Furthermore, compressive strength test specimens were checked on an optical comparator to ensure conformance with Section 8.1 of the ASTM C773, that sample ends were enough plane, parallel and perpendicular to the axis of the specimen. As Table 5 showed, for 2σ level of confidence and even for 3σ level of confidence we could not determine a change in compressive strength of the ceramic samples as a result of the sample irradiation. It should be noticed that compressive strength of C2 samples closes to theoretical, which is a separate and significant achievement of the developed ceramic technology.

Table 5. Compressive Strengths in MPa of B1, B2 and C2 Samples (Mean ± 2σ)

	B1	B2	C2
1 x 10^8 Rad	437 ± 62	359 ± 35	740 ± 41
5 x 10^8 Rad	395 ± 23	530 ± 81	728 ± 28
1 x 10^9 Rad	468 ± 59	449 ± 31	754 ± 32
Unirradiated	435 ± 35	561 ± 51	781 ± 49

CONCLUSIONS

It is developed an alternative waste management technology for the permanent containerization of nuclear and hazardous waste, featuring a patented cost-effective technology of the production and sealing of thick-walled ceramic containers. Samples of newly-developed, highly dense (gas impenetrable), high strength spinel ceramics were exposed to gamma radiation for doses up to 10^9rad, in order to simulate the radiation impacts of nuclear wastes during their permanent disposal in completely sealed ceramic vessel of the container package.

It was shown that irradiation to $1x10^9$rad produced no statistically significant effects on the physical properties of the spinel samples. Sample geometric and bulk densities, apparent specific gravity, water absorption and apparent porosity were in line with preliminary data supplied by Nucon specialists. The spinel material and refractory products from it are well known to be extremely resistant to combining chemical, water, and thermal or biological impacts. Now it is shown that commercial products from this material would also retain their mechanical integrity under radiation during a millennium-long time period. Thus, this new advanced and cost-effective technology for producing gas tight and high strength thick-walled ceramic products from the originally developed spinel ceramic formulation appears to be appropriate for use in multi-purpose containers intended for the safe transportation and geological time-period storage/disposal of nuclear and hazardous wastes.

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