U.S. DEPARTMENT OF
ENERGY

PNNL-23706

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pseudo-Glassification Material for G-Demption, LLC

AM Casella
EC Buck
RO Gates
BJ Riley

September 2014

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

PNNL-23706

Pseudo-Glassification Material for G-Demption, LLC

AM Casella
EC Buck
RO Gates
BJ Riley

September 2014

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

G-Demption, LLC has requested that PPNL provide design input for a "pseudo-glassification" process associated with their proposed technology for generating gamma irradiation stations from used nuclear fuel. The irradiation design currently consists of an aluminum enclosure designed to allow for proper encapsulation of and heat flow from a used fuel rod while minimally impacting the streaming of gamma rays from the fuel. In order to make their design more robust, G-Demption is investigating the benefits of backfilling this aluminum enclosure with a setting material once the used fuel rod is properly placed. This process has been initially referred to as "pseudo-glassification", and strives not to impact heat transport or gamma streaming from the used fuel rod while providing increased fuel rod protection and fission gas retention. PNNL has compiled an internal material evaluation and discussion for the "pseudo-glassification" process in this report.

Contents

Figures

Tables

1.0 Discussion of Candidate Materials (Survey of Materials)

PNNL has experience with four broad categories of materials for consideration in the "pseudo-glassification" process. These materials include (1) glass, (2) resin/epoxy/paste, (3) cement/grout/clays/specialty ceramics, and (4) metals/alloys/salts. Each of these materials has benefits and drawbacks for use in the proposed process. Glasses and Ceramics are currently viewed as optimal materials for immobilization or encapsulation of highly radioactive slurries generated from the reprocessing of nuclear fuels, but they generally require processing to occur at elevated temperatures and often have high-Z materials such as lead incorporated within them. Certain specialty ceramics have been developed that can be machined allowing for the possibility of manufactured components that could be used in encapsulating a fuel rod. Resins, epoxies and pastes have the advantage of being economical and easy to use, but they are generally composed of organics that are not resistant to radiation damage. Cements and grouts are heavy and more time and energy intensive, but some have been engineered to address concerns analogous to those posed by the G-Demption system. A low melting point eutectic metal alloy system that could be melted and poured into and around the fuel rod could be considered. In addition, alternatives to an aluminum enclosure should be evaluated, alloy families such as zircaloy, stainless steel, and Inconel may provide better overall performance and safety. These additional materials could not only be used to augment the structural integrity of the system but also to tailor the dose to the levels approved by the Food and Drug Administration (FDA) for food irradiation, see Table 1.

Table 1: Process, Foods, Dosage Approved for Irradiation by the FDA (FDA, 2014)

Process / Product	Dose (kGy) (1Gy = 100 rad)	Purpose
Wheat, Wheat Flour	0.2-0.5	Insect Disinfestation
White Potatoes	0.05-0.15	Sprout Inhibition
Pork	0.3-1.0	Control Trichinella Spiralis
Herbs, Spices, Seasoning	≤30	Microbial Control
Poultry, Fresh or Frozen	≤3	Microbial Control
Meat, Uncooked and Chilled	≤4.5	Microbial Control
Meat, Uncooked and Frozen	≤7.0	Microbial Control

1.1 Glasses

A wide variety of glasses have been designed for various uses and any number of additional glasses can be engineered to suit the needs of novel endeavors. However, the cost and time associated with design, fabrication, and testing of optimally designed glasses is beyond the bounds of the current level of effort desired by G-Demption. Instead, it is a synopsis of the current state of existing glass technology that is of use for immediate design consideration.

Table 2 provides a list of glasses that melt at fairly low temperatures for consideration in the "pseudo-glassification" process. Each of these glasses has some component fraction of high-Z materials that are undesirable for the current objective. However, if it is decided that a glass is a preferred material for use, then those glasses in the table with minimal gamma interference can be considered as a starting point for design or for more extensive investigation of possible glasses for use. Each of these glasses has a melting point below the melting point of the G-Demption aluminum encapsulation device (660°C). However, the glass melting points are a significant fraction of the aluminum melting point, which implies that if one of these glasses were to be used, additional engineering would be needed for process optimization. For instance, it may be necessary to first let the glass harden around a used fuel rod that has first been placed within a thin sleeve of material with a higher melting point and then placed within the aluminum encapsulation. If the glass does not wet the surface of the material used for the sleeve, the sleeve could be removed prior to insertion of the glass encapsulated rod into the aluminum encapsulation.

Table 2: Compositions (in mol%) of candidate glasses

Ref.	Al_2O_3	B_2O_3	Bi_2O_3	CaO	Er_2O_3	GeO_2	Li_2O	Na_2O	Nd_2O_3	P_2O_5	PbO	TeO_2	TiO_2	ZnO	Melting Point (°C)
[1]	-	18.51	-	-	-	-	-	-	-	-	57.74	-	-	23.75	541
[2]	-	12.00	-	-	-	-	10.00	-	1.00	12.00	-	65.00	-	-	540
[3]	-	14.96	-	-	0.29	-	-	24.93	-	-	-	59.83	-	-	522
[3]	-	14.95	-	-	0.31	-	-	19.94	-	-	-	64.80	-	-	553
[3]	-	14.96	-	-	0.30	4.99	-	19.94	-	-	-	59.82	-	-	541
[3]	-	14.95	-	-	0.31	6.98	-	17.94	-	-	-	59.81	-	-	533
[3]	-	14.95	-	-	0.31	4.98	-	17.94	-	-	-	61.81	-	-	534
[3]	4.98	14.95	-	-	0.31	4.98	-	14.95	-	-	-	59.81	-	-	520
[3]	9.97	14.95	-	-	0.32	4.98	-	9.97	-	-	-	59.81	-	-	551
[4]	-	55.00	45.00	-	-	-	-	-	-	-	-	-	-	-	590
[4]	-	45.00	55.00	-	-	-	-	-	-	-	-	-	-	-	584
[4]	-	40.00	60.00	-	-	-	-	-	-	-	-	-	-	-	577
[5]	-	33.16	-	-	-	-	2.21	-	-	-	39.19	-	-	25.45	580
[5]	-	32.43	-	-	-	-	4.34	-	-	-	38.36	-	-	24.87	588
[5]	-	31.00	-	-	-	-	8.40	-	-	-	36.71	-	-	23.90	500
[6]	-	60.00	-	25.00	-	-	-	-	-	-	-	-	-	15.00	550
[6]	-	60.00	-	25.00	-	-	-	-	-	-	-	-	2.50	12.50	555
[6]	-	60.00	-	25.00	-	-	-	-	-	-	-	-	5.00	10.00	558
[6]	-	60.00	-	25.00	-	-	-	-	-	-	-	-	7.50	7.50	554
[6]	-	60.00	-	25.00	-	-	-	-	-	-	-	-	10.00	5.00	558
[6]	-	60.00	-	25.00	-	-	-	-	-	-	-	-	12.50	2.50	558
[6]	-	60.00	-	25.00	-	-	-	-	-	-	-	-	15.00	-	558

[1] (Jinn-Shing et al. 1990), [2](Rao et al. 2000), [3](Hocde et al. 2004), [4](Cheng et al. 2006), [5](Zivanovic et al. 2000), [6](Gabr et al. 2007)

1.2 Resins, Epoxies, and Pastes

For disambiguation, a resin is a material that forms a polymer when subject to a heating (thermosetting) process. Epoxies are resins in which a copolymer (hardener) is used to increase material strength. A paste is a mixture of solid and liquid, that when dried, hardens to form an adhesive.

As with glasses, there are many different resins, epoxies, and pastes currently available. The primary concern with these materials is that they tend to break down when subjected to strong radiation fields. Previous studies have shown that different resins have varying degrees of radiation hardness. It is difficult to express the susceptibility of a material to radiation damage with one consistent metric. In general, damage threshold levels indicate nominal fluence at which a component can be expected to fail due to radiation effects. This failure can be caused, for instance, by loss of transparency for optical components or the embrittlement of elastomeric compounds used for gaskets and seals. A generic comparison of radiation resistance has been generated and is listed in Table 3 for an array of plastics/resins/epoxies.

Table 3: Relative radiation resistance of general resin and epoxy materials (Vandergriff, 1990)

Relative Radiation Resistance	Resin Materials
High	Glass-fiber phenolics, asbestos-filled phenolics, certain epoxy systems, polyurethane, polystyrene, mineral-filled polyester, mineral-filled silicones, furane-type resins, polyvinyl carbazole
Moderate	Polyethylene, melamine-formaldehyde resins, urea-formaldehyde resins, aniline-formaldehyde resins, urfilled phenolic resins, silicone resins
Poor	Methyl methacrylate, unfilled polyesters, cellulosic, polyamides, teflon

Although relative radiation resistance of several materials is useful in narrowing down the search, it does not give an indication of actual material performance in gamma fields for the intended purpose. A glimpse of radiation hardness based on evaluated performance is available for select compounds as shown in Table 4 (Vandergriff, 1990). In Table 4, the measure of radiation is a generic “damage threshold” in terms of RAD. To further understand the performance of the materials listed in Table 4 and other materials to be considered, the damage threshold can be more explicitly characterized. For instance, the acetal resin Delrin is listed as having a damage threshold of approximately 6×10^5 RAD. This damage threshold was measured explicitly as a degradation of tensile strength and elongation. More specifically, Delrin has been demonstrated to have a 20% decrease in tensile strength at 3×10^6 RAD, a 20% loss of elongation at 1×10^6 RAD, a 50% decrease in tensile strength at 8×10^6 RAD and a 50% loss of elongation at 2×10^6 RAD. The damage thresholds listed in Table 4 are approximate and generic. It is not apparent what the direct impact of these values are on the performance of each listed material as a pseudo-glassification material. However, they do indicate the relative resistance of each material to gamma irradiation. Once the localized dose rate for a given used fuel rod is determined from burnup and decay conditions, the time that the material can be expected to maintain its integrity can be estimated from the values presented in Table 4. Once a candidate material is selected, a more thorough investigation of the expected effects of radiation on its performance can be performed.

Table 4: A more specific characterization of material radiation resistance (Vandergriff, 1990)

Material	Description	Radiation Damage Threshold (RAD)
Borosilicate Glass	Glass	10^7
Aluminum/Aluminum alloys	Metal/alloy	5×10^{13}
Delrin	Acetal resin	6×10^5
Lustran/Royalite	Acrylonitrile-Buradiene-Styrene (ABS)	10^7
Diallyl Phthalate	Glass-filled polyester	$10^9 – 10^{10}$
Novalac/glycidyl amine	Epoxy resins cured with aliphatic amines or acid anhydrides	$2\times10^8 – 4\times10^9$
Duralon	Asbestos containing furane-based resin	3×10^8

One option for the use of a paste would be to fill the space between the used fuel rod and the aluminum encapsulation structure with a boron nitride powder and water. This process could be performed at room temperature, fill the gaps nicely, and, once dried, be compact enough to prevent the fuel rod from moving. Boron nitride is also known to be fairly resistant to gamma irradiation.

1.3 Cements, Grouts, Clays, and Specialty Ceramics

One intriguing characteristic that is currently studied regarding cements, grouts, and clays is the incorporation of constituents that act to sequester mobile compounds released from the object that they enclose. The zeolite mineral, clinoptilolite, would provide a significant barrier to any cesium, and possibly strontium, release. Clay minerals, such as smectites, would be easily available and provide a barrier to many of the elements including strontium, cesium, and probably carbon. Technetium is known to be present within the used fuel in the form of nano-particles. Clay backfill will provide a significant barrier to the transport of such particles. Manganese oxide inclusions will reduce plutonium and americium to an insoluble species that will strongly sorb. Neptunium and uranium transport will be attenuated by a mixture of clays and metal oxides. Iodine can be sequestered by including 400-1000 ppm silver dispersed into the clay and zeolite. Silver-mordenite (zeolite) has been used in gas flow systems to trap iodine; however, such high levels of silver are unnecessary. The actual concentration of iodine in the fuel as well as all other fission products is in the ppm range; hence, chemical means for precipitating them do not require large concentrations of trapping agents. Any released iodine will react with Ag to form AgI, a relatively insoluble compound. A synopsis of known inclusions for retarding transport of radioisotopes of concern is as follows:

- **Plutonium**. Important isotopes with respect to release include ^{239}Pu, ^{242}Pu, and ^{238}Pu. Plutonium is only sparingly soluble and sorbs strongly to oxide mineral surfaces (generally less strongly to silicates) (Lu et al. 2003; EPA 1999; EPA 2004). The introduction of manganese oxides or iron oxides would severely limit any Pu migration.

- **Americium**. Americium is sparingly soluble but sorbs strongly to mineral surfaces, including colloids (Degueldre et al. 1994). Americium exhibits large K_d values often in the range of 1,000 to >100,000 mL/g, depending on the pH. However, the concentrations of dissolved americium may be controlled by precipitation in many environments (EPA 2004). Therefore, high reported sorption measurements may reflect precipitation reactions.

- **Neptunium**. The NpO_2^+ ion may be soluble under anticipated repository conditions and will be less likely to participate in colloid formation than the other actinides. The sorption properties of Np(V) have a strong dependence on pH (EPA 2004; Bradbury and Baeyens, 2005, Figure A4 (c and d), pg. 889). Retention or sorption of neptunium in alteration products has been observed under high pH conditions (Ménard et al. 1998; Lu et al. 2000; McNamara et al. 2005); however, because these high pH regimes (i.e., >pH 9) are not anticipated to occur in the waste package environment, this high pH data has not been used in the model.

- **Cesium**. Few stable cesium complexes will exist in groundwater. Cs^+ ion exchange will occur with Na^+ or Ca^{2+} in montmorillonite (Atun et al. 1996) and in uranyl silicates, such as boltwoodite (Burns, 1999) and uranophane (Douglas et al., 2002). The degree of sorption/desorption will depend on the availability of clays and the concentration of other ions that will compete for adsorption sites; however, within the low ionic strengths anticipated in the repository environment, this is not considered to be an important process. Cesium will only sorb weakly onto iron oxides (Torstenfeld et al. 1982).

- **Strontium**. The Sr^{2+} species will sorb to clays (Torstenfelt et al., 1982; Missana et al, 2008).

- **Iodine**. Iodine is considered highly mobile in a nuclear fuel. Dispersed nano-particles of silver (400-1000 ppm) in the clay backfill will enable iodine to precipitate if it is released. The quantity of these agents need not be high because the actual concentration of the fission product is small (EPA 2004).

- **Uranium**. Uranium (^{235}U, ^{233}U, and ^{238}U) is the most abundant radioactive element in fuel. It can be effectively sorbed with a combination of clay and iron oxides. The sorption edge for uranium on hematite is near pH 5.5 (Missana et al., 2003; Pabalan et al., 1997; Bradbury et al., 2005).

- **Tin**. Tin is stable in its tetravalent form, Sn(IV), where $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ are the dominant hydrolytic species. ^{126}Sn is the long-lived isotope that has been considered in some dose estimates although it is unlikely to play a role in the engineered SNF irradiation system. Sn(IV) sorbs strongly to smectite clay (Bradbury and Baeyens, 2005).

The pH and ionic strength (particularly concentrations of Na^+, Ca^{2+}, and K^+) primarily control the behavior of the mineral surfaces, particularly clays and zeolites (as is demonstrated in Figure 1). It is essential to control the composition of any backfill materials. For instance, sulfur can cause excessive corrosion or reduce the impact of the silver particles for sequestering iodine. Hence, very pure sources for the clay, iron, and zeolite materials are needed. For minerals in which the sorption mechanism is primarily by ion exchange (e.g., clay minerals), ionic strength impacts sorption of alkali metals on clay minerals (especially at their edges), because cations compete with radionuclides for exchange sites (Atun et al. 1996). Given the small expected water content and the large amount of added materials containing these ions, the local ionic strength might be high, limiting sorption in some instances.

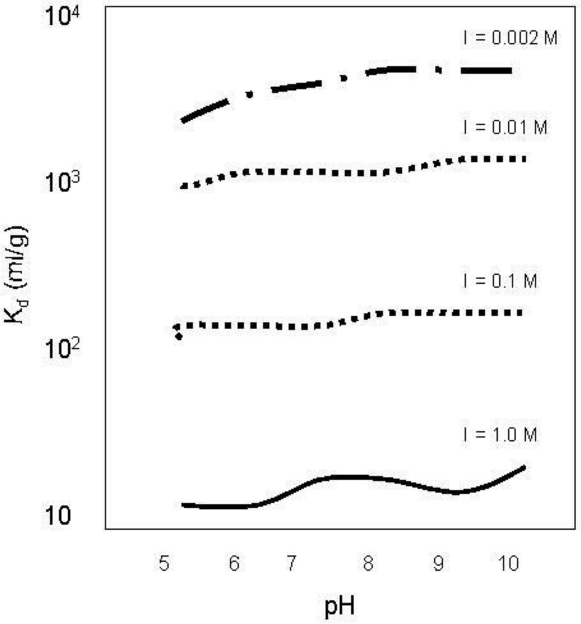

Figure 1. Schematic plot adapted from data reported for cesium sorption on montmorillonite with pH and NaCl concentration (Serne and Relyea 1982).

Macor® supplied by Corning is a machinable glass ceramic composed of approximately 55% fluorophlogopite mica and 45% borosilicate glass. Macor® is not dimensionally affected by irradiation. Small pieces are used with high tolerances of one micrometer as comparators to measure irradiation-induced dimensional changes in other materials. Macor® can be machined with high speed steel and carbide tools to very tight tolerances up to 0.0005 inches. It has a continuous use temperature of 800 °C and a peak temperature of 1000 °C. Its coefficient of thermal expansion (Figure 2) matches most metals and sealing glasses. It has high density and zero porosity. Macor® can be joined or sealed both to itself and to other metals. Metalizing using metal inks or sputtering can be done to solder. Brazing is possible to itself and various metals and the sealing glass will form a vacuum tight seal. Fabrication in full 12-ft fuel rod lengths would likely be unreasonably expensive, however, sections could be machined and a sealed sleeve fabricated inside the metal capsule. Given its dimensional stability under irradiation and compatibility with metals over a wide temperature range, it could be used to form a sealed inner ceramic canister that effectively double-encapsulates the fuel rod. The thermal conductivity of Macor® is presented in Figure 3 for design considerations concerning thermal transport (Corning, 2014).

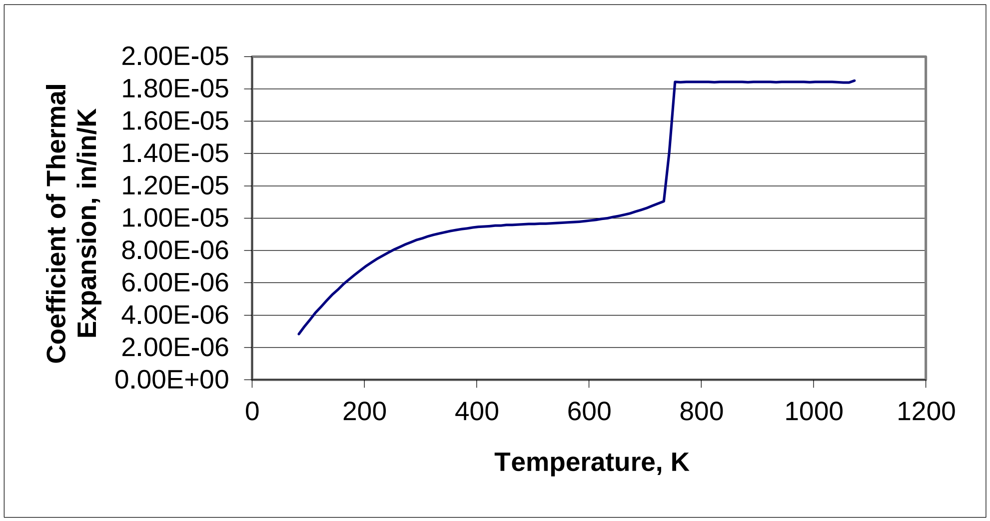

Figure 2: Macor® Coefficient of Thermal Expansion, Derived from Corning Thermal Data (Corning, 2014)

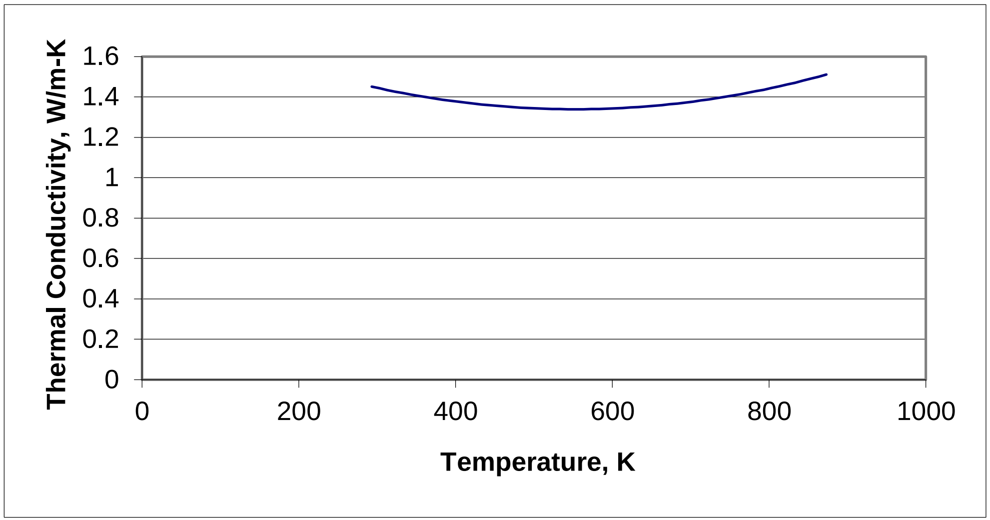

Figure 3: Macor® Thermal Conductivity, Derived from Corning Thermal Data (Corning, 2014)

1.4 Metals, alloys, and salts

Another possibility is to backfill the apparatus with a eutectic system that melts at a low temperature and is solid at the operating temperature of the apparatus. Lead-Bismuth is a popular eutectic system that melts around 128 °C. It could be poured as a low-viscosity liquid into the apparatus at ~250 °C and allowed to cool to a solid. Of course, this material would be a large attenuator, but there may be a more suitable eutectic out there. Another beneficial attribute of such a eutectic material is that after it is used, it could be recovered by heating it up and pouring it out. Wood's metal is a common solder that is ~50% bismuth, ~25% lead, ~12.5% tin, and ~12.5% cadmium and melts at ~70 °C. Field's metal is ~32.5% Bi, ~51% In, and ~16.5% Sn and it melts at ~60 °C. Rose metal is ~50% bismuth, ~25% lead, and ~25% tin and melts around 94 °C and it does not contract on cooling.

Unfortunately, the very low melting eutectic systems include heavy metals that act to attenuate gamma rays, which is a disadvantage for the current application, but may be used selectively to tailor the dose levels to meet regulatory requirements. An in-depth survey of alloy systems may generate an optimal solution for pseudo-glassification of the rod in the G-demption encapsulation device. However, there are many considerations that may not be satisfactorily discussed in the available literature. These considerations include: 1) the alloy melting point, 2) the alloy strength, 3) the propensity of the material to wet the surface of the ziraloy cladding of the irradiated fuel rod and the aluminum encapsulation device, 4) a low tendency to interact with zircaloy or aluminum, 5) a low tendency to expand or contract during solidification/melting or during heating or cooling, 6) it might not be cost-prohibitive to use, and 7) it would likely have a limit on the maximum fraction of high-*Z* materials. Below is a cursory survey of potential metals and alloys (Hansen 1958).

The general strategy in an initial survey of potential alloys is a direct effect of the physical restrictions placed on the system. Primarily, in order to be used as a pseudo-glassification material as initially defined, the alloy must flow at a temperature that is significantly lower than the melting point of the materials that it comes into contact with. As aluminum has a melting point of around 660 °C and zirconium has a melting point of 1855°C, a good starting point for the material search is to find an aluminum alloy that has a lower melting point than aluminum. The upside of this strategy is that, in many cases, a eutectic can be formed that has a lower melting point than each of the pure constituents and an aluminum alloy is very likely to wet aluminum. The downside is that the material is likely to interact with the aluminum. After aluminum alloys are assessed, metals with lower melting points than aluminum are surveyed for possible matches. These metals are typically those that alloy with aluminum to form the lower-melting point materials. Materials such as gold and silver have been dismissed from this survey due to high costs. High-Z materials have also been dismissed from this survey.

- Aluminum-bearing alloys
    - Al-Ca: Aluminum forms a eutectic with calcium that melts at 545 °C at a calcium atomic percent of 65%.
    - Al-Cu: Aluminum forms a eutectic with copper that melts at 548 °C at a copper atomic percent of 17.3%
    - Al-Ga: Aluminum and gallium mixtures have lower melting points than pure aluminum. These melting points decrease with increasing quantities of gallium and approach the melting point of gallium (29.8 °C) as the gallium atomic percent approaches 100%.
    - Al-Ge: Aluminum and germanium for a eutectic that melts at 424 °C at a germanium atomic percent of 30.3%
    - Al-Li: Aluminum and lithium mixtures have lower melting points than aluminum at high lithium concentrations ~ 70% by atom.
    - Al-Mg: Aluminum and magnesium mixtures (37.4–70% Mg) melt at 450–437 °C, respectively.
    - Al-Sn: Aluminum and tin mixtures (75–100% Sn) melt at ~500–232 °C, respectively.

  - Al-Zn: Aluminum and zinc mixtures have lower melting points than aluminum. A minimum melting point of 382 °C occurs at a zinc atomic weight percent of 88.7%.

- Non-aluminum metals and alloys

  - Na: Pure sodium melts at around 98 °C and is not soluble in aluminum. Sodium is reactive with water, so moisture and humidity are a concern when it is used.

  - Na-Rb: Sodium and rubidium mixtures have very low melting points with a minimum of -5 °C occurring at a rubidium atomic percent of 75.5%.

  - Na-Se: Sodium and selenium mixtures have a wide range of melting points. At selenium concentrations above 70 atomic%, the melting point is below 300 °C.

  - Na-Sb: Sodium and antimony mixtures have higher melting points than pure sodium. However, if it is deemed that an optimal melting point for the alloy to be used by slightly higher than that of pure sodium, small quantities of antimony can be added. A mixture of sodium with 5 atomic% antimony has a melting point of around 400 °C.

  - Na-Sn: Sodium and tin form mixtures with a variety of melting points. At tin concentrations above 80 atomic%, the melting point is <300 °C.

  - Sn: Pure tin has a melting point of ~232 °C. Sn forms a eutectic (melting point 228.3 °C) with Al at a composition of 97.8 atomic% Sn. The solubility of Al in the eutectic at the eutectic temperature is 0.05 mass%.

  - Sn-Zn: Tin and zinc mixtures have melting points < 419.4 °C. A eutectic with a melting point of 198 °C is formed at a tin concentration of 85 atomic%.

In addition to metals and alloys, salt mixtures can be formed that have relatively low melting points. Fluoride salts such as FLiBe (Li_2BeF_4; M.P. ~ 460 °C) and FLiNaK (mole percent LiF(46.5)-NaF(11.5)-KF(42); M.P.= 454 °C) have been used as coolants in molten salt reactors (Holcomb et al. 2009, Williams 2006). Williams (Williams 2006) includes information on several more molten salt systems. One general issue with these salts is that they tend to be fairly corrosive to the materials of construction of the system in which they are used. Alternatively, mixtures of nitrate salts for heat storage have reportedly been engineered to have melting points below 80 °C (US Patent 7,828,990 2010).

2.0 Discussion of Material Properties and Logistics of Filling the G-Demption Apparatus

While the choice of using aluminum as the material of construction for the G-Demption encapsulation device initially makes sense from financial and thermal transport perspectives, it can be quite constricting in the consideration of materials, structural integrity, and processes used to meet the objectives of the pseudo-glassification process. The previous section provided a survey of materials that exhibit some properties that are amenable to the optimal function as pseudo-glassification materials in the current manifestation of the of the G-Demption encapsulation device. This section provides a discussion of design considerations for implementation of the actual pseudo-glassification process.

The first consideration involves the overall thermal transport of the system. Aluminum is an excellent conductor of heat, but this property is not fully exploited unless the aluminum is actually in contact with the heat source (in this case, the used fuel rod.) With this concept in mind, one topic of concern arises from the fact that, in the current design, the used fuel rod will be placed within a pre-fabricated aluminum encapsulation device of set dimensions. This means that the material to be used for the pseudo-glassification process must be able to flow into the space between the rod and the aluminum encapsulation device, wet the surface of both the rod and the aluminum, and maintain contact with all surfaces during and after solidification. These criteria are nearly impossible to meet as, in general, materials tend to incur dimensional variation during phase changes. There are several alternative design considerations to alleviate this difficulty:

1. The material to be used can be a low-melting material that remains a liquid throughout the operation of the irradiation device. This option offers some significant opportunities for optimizing thermal transport, but does little to provide mechanical shock resistance or an enhanced transport barrier for radionuclide retention. If the concern regarding mechanical shock could be allayed by the design of the main encapsulation structure, then the liquid of choice for maintaining thermal transport efficiency could be as simple as water.

2. The material could be introduced as a pourable solid (such as micro-beads, micro-spheres, or a non-clumping powder) that would flow much like a liquid and be “packable” by vibration. If the material has decent thermal transport properties, this will allow for better heat transport via conduction that is available from air, even though the material contains small gaps. This option would provide a more robust protection from mechanical shock that a liquid and may also provide a more substantial barrier to radionuclide transport.

3. A material that undergoes minimal contraction during solidification could be used. If loss of contact from the rodlet or aluminum is realized, it may be minimized and some contact may remain. As long as the material does not recede from the rodlet (forming a potential transport pathway), it may prove to be a substantial transport barrier and may also provide significant protection from mechanical shock. Depending on any modified design of the encapsulation device, compression could be applied externally in order to force continual contact during solidification.

4. A material could be selected that undergoes slight expansion during solidification. This could be optimal as long as expansion is not so great as to cause physical damage to the encapsulation device.

5. A material that is added as two components that undergo a chemical or physical reaction could result in a continuous bond between the rod and the aluminum. Using a resin, epoxy, or paste discussed in the previous section may achieve this objective.

6. The design of the apparatus could be modified to incorporate the pseudo-glassification material during fabrication/setup. In this scenario, the irradiated rod would first be placed into a mold filled with the material of choice in such a way that the material encapsulated the rod and remains in intimate contact. The aluminum outer casing could then be pressed or molded around it. This would allow for materials with higher melting points to be considered.

3.0 Conclusions

The analysis presented in this report does not single out any one specific recommended material, but rather presents a basis of materials and considerations from which more informed engineering decisions can be made regarding the proposed “pseudo-glassification” process. The determination of the appropriate material will accompany a careful consideration of the scenarios in which the pseudo-glassification material is expected to serve its intended role. For instance, if structural support in the event of off-normal highly-energetic events (terrorist attacks, earthquakes, fires) are being considered, then material properties such as the propensity of the selected glass, ceramic, cement, resin, etc. to crack is a primary concern. If such an event is sufficiently impactful as to crack the aluminum encapsulation along with the pseudo-glassification material, it will likely crack the fuel and cladding as well. In this case, radionuclide release will not likely be greatly impeded by the presence of the pseudo-glassification material. A categorization of the cracking phenomena is important, however, as there is a significant difference between the formation of hairline cracks and shattering of the pseudo-glassification material. If the fuel and pseudo-glassification material is cracked and radionuclide release occurs, then zeolite-containing cements that exhibit properties of sorbing important radionuclides offer some promise and should be considered for further investigation.

The choice of the material is difficult to pin down as it changes with modified processes. A significant effort was put forth in this report to find recommended materials that would be compatible with the existing G-Demption design. However, the list of materials to be considered could be greatly increased if the material of construction for the encapsulation device were to be adjusted. Zirconium and Stainless Steel Alloys commonly used in the nuclear industry should be considered to increase the overall strength and integrity of the structural components of this system. These materials have higher melting points than aluminum and can accordingly withstand the temperatures necessary for use of glasses, metals, and alloys that have higher melting points. The standards and codes for the construction and operation of irradiation facilities, particularly those surrounding accident and seismic scenarios and the safety of the public and environment, may be easier to satisfy and less costly overall when using high strength structural materials such as stainless steel. Zirconium has high strength and ductility and is corrosion resistant and biocompatible and therefore can be used in irradiators handling medical devices and food for human consumption. Use of these materials may also facilitate regulatory review and approval by the NRC which mandates that commercial irradiators use proper design for source integrity, safety systems, and facility design criteria to ensure the NRC limit for exposure to the public from a licensed facility will be no greater than 100 millirem per year.

While it is not easy to generate a single recommended material that addresses all concerns, it is hoped that the materials and considerations in this report aid in the design of the G-Demption device. If a design change that has minimal impact on the fabrication and operation of the apparatus is the primary consideration, then a flowable solid, paste, epoxy, or resin may be the most efficient and economical choice. In the case of the flowable solid (non-clumping powder), the solid could be poured into the G-Demption encapsulation device like sand and then subjected to vibration in order to effect a hard packing. In any of these cases, however, the retrieval of the irradiated rod from the device would be difficult. If design changes involving a greater impact on the fabrication and operation of the device can be considered, then perhaps metals, alloys, salts, glasses, and modifications to the materials of construction (as well as the construction process) can provide more robust solutions. Due to the limited scope of this project, it is difficult for us to provide a more solid recommendation, but we feel that an expanded study could provide insight into more optimal materials and associated fabrication/operation protocols.

4.0 References

Atun, G.; Bilgin, B.; and Mardinli, A. 1996. "Sorption of Cesium on Montmorillonite and Effects of Salt Concentration." *Journal of Radioanalytical and Nuclear Chemistry, 211,* (2), 435-442.

Bradbury, M.H. and Baeyens, B. 2005. "Modeling the Sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on Montmorillonite: Linear Free Energy Relationships and Estimates of Surface Binding Constants for Some Selected Heavy Metals and Actinides." *Geochimica et Cosmoschimica Acta, 69,* (4), 875-892.

Burns P.C. 1999. "Cs Boltwoodite Obtained by Ion Exchange from Single Crystals: Implications for Radionuclide Release in a Nuclear Repository." *Journal of Nuclear Materials, 265,* 218-223.

Cheng, Y. ; H. Xiao, W. Guo, and W. Guo, "Structure and crystallization kinetics of Bi_2O_3-B_2O_3 glasses," *Thermochimica Acta*, **444**(2), 173-178 (2006).

Corning,http://www.corning.com/specialtymaterials/advanced_optics/specialty_glass_ceramics/products/macor/index.aspx, accessed September, 2014.

Degueldre, C.; Ulrich, H.J.; Silby, H. 1994. "Sorption of ^{241}Am onto Montmorillonite, Illite and Hematite Colloids." *Radiochimica Acta, 65,* (1994), 173-179.

Douglas, M.; Clark, S.B.; Utsunomiya, S.; and Ewing, R.C. 2002. "Cesium and Strontium Incorporation into Uranophane, $[Ca(UO_2)(SiO_3OH)]_2 \bullet 5H_2O]$." *Journal of Nuclear Science and Technology, Supplement 3,* 504-507.

EPA (U.S. Environmental Protection Agency) 1999. *Understanding Variation in Partition Coefficient, Kd, Values*. EPA 402-R-99-004A&B Two volumes. Washington, D.C.

EPA 2004. "Review of Geochemistry and Available K_d Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium." Volume III of *Understanding the Variation in Partition Coefficient, K_d, Values.* EPA 402-R-04-002C. Washington, D.C.

FDA,http://www.fda.gov/Food/GuidanceRegulation/GuidanceDocumentsRegulatoryInformation/IngredientsAdditivesGRASPackaging/ucm110730.htm, Accessed September, 2014.

Gabr, M.; K.A.-A. Ali, and A.G.E.-D. Mostafa, "Infrared analysis and physical properties studies of B_2O_3-CaO-ZnO-TiO_2 glass system," *Turkish Journal of Physics*, **31**(1), 31-39 (2007).

Hansen, M. ; *Constitution of Binary Alloys, 2nd Ed.*, Metallurgy and Metallurgical Engineering Series, McGraw-Hill, New York, 1958.

Hocde, S.; S. Jiang, X. Peng, N. Peyghambarian, T. Luo, and M. Morrell, "Er^{3+} doped boro-tellurite glasses for 1.5 μm broadband amplification," *Optical Materials*, **25**(2), 149-156 (2004).

Holcomb, DE et al. *An Analysis of Testing Requirements for Fluoride Salt-Cooled High Temperature Reactor Components.* Technical Report ORNL/TM-2009/297, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2009.

Jinn-Shing, L.; P. Jaw-Chay, and H. Ching-Wang, "A study of nucleation and devitrification kinetics of a low-melting-point solder-glass system PbO-ZnO-B_2O_3 by differential thermal analysis," *Thermochimica Acta*, **161**(1), 29-36 (1990).

K. U. Vandergriff, *Designing Equipment for Use in Gamma Radiation Environments*, ORNL/TM-11175, May 1990.

Lu, N.; Conca, J.; Parker, G.R.; Leonard, P.A.; Moore, B.; Strietelmeier, B.; and Triay, I.R. 2000. *Adsorption of Actinides onto Colloids as a Function of Time, Temperature, Ionic Strength, and Colloid Concentration, Waste Form Colloids Report for Yucca Mountain Program (Colloid Data Summary from 1999 to 2000 Research)*. LA-UR-00-5121. Los Alamos, New Mexico.

Lu, N.; Reimus, P.W.; Parker, G.R.; Conca, J.L.; and Triay, I.R. 2003. "Sorption Kinetics and Impact of Temperature, Ionic Strength and Colloid Concentration on the Adsorption of Plutonium-239 by Inorganic Colloids." *Radiochimica Acta, 91*, 713-720.

McNamara, B.; Hanson, B.; Buck, E.; Soderquist, C. 2005. "Corrosion of Commercial Spent Nuclear Fuel. 2. Radiochemical Analyses of Metastudtite and Leachates." *Radiochimica Acta, 93,* (2005), 169-175.

Ménard, O.; Advocat, T.; Ambrosi, J.P.; and Michard, A. 1998. "Behavior of Actinides (Th, U, Np and Pu) and Rare Earths (La, Ce and Nd) During Aqueous Leaching of a Nuclear Waste Glass Under Geological Disposal Conditions." *Applied Geochemistry, 13*, 105-126.

Missana, T.; García-Gutiérrez, M.; and Fernndez, V. 2003. "Uranium (VI) Sorption on Colloidal Magnetite Under Anoxic Environment: Experimental Study and Surface Complexation Modelling." *Geochimica et Cosmochimica Acta, 67,* (14), 2543-2550.

Missana, T.; Garcia-Gutierrez, M.; Alonso, U. 2008. “Sorption of strontium onto illite/smectite mixed clays,” Physics and Chemistry of the Earth, Parts A/B/C, 33, S156-S162.

Pabalan, R.T. and Turner, D.R. 1997. “Uranium(6+) Sorption on Montmorillonite: Experimental and Surface Complexation Modeling Study.” *Aquatic Geochemistry, 2*, 203-226.

Rao, T.V.R. ; R.R. Reddy, Y.N. Ahammed, M. Parandamaiah, N.S. Hussain, S. Buddhudu and K. Purandar, “Luminescence properties of Nd^{3+}:TeO_2-B_2O_3-P_2O_5-Li_2O glass,” *Infrared Physics and Technology*, **41**(4), 247-258 (2000).

Serne, R.J. and Relyea, J.F. 1982. *The Status of Radionuclide Sorption-Desorption Studies Performed by the WRIT Program.* PNL-3997. Richland, Washington: Pacific Norwest Laboratory.
ACC: NNA.19900416.0121.

Torstenfelt, B.; Andersson, K.; and Allard, B. 1982. “Sorption of Strontium and Cesium on Rocks and Minerals.” *Chemical Geology, 36*, 128-137.

US Patent 7,828,990. “Low-melting point heat transfer fluid” J.G. Cordaro and R.W. Bradshaw. 2010.

Williams, DF. *Assessment of Candidate Molten Salt Coolants for the NGNP/NGI Heat-Transfer Loop.* Technical Report ORNL/TM-2006/69, Oak Ridge National Laboratory, Oak Ridge, Tennessee. 2006.

Zivanovic, V.D. ; N.S. Blagojevic, S.R. Grujic, L.C. Karanovic, and B.R. Bozovic, “The devitrification of PbO-B_2O_3-ZnO glass doped with Li_2O,” *Journal of the Serbian Chemical Society*, **65**(12), 891-898 (2000).

Distribution

No. of
Copies

1 U.S. Department of Energy
Office of Science and Technical Information
P.O. Box 62
Oak Ridge, TN 37831 (PDF)

1 G-Demption, LLC
Russell@G-Demption.com
Russell Goff (PDF)

No. of
Copies

1 Local Distribution
Pacific Northwest National Laboratory

Andrew M. Casella	(PDF)
Edgar C. Buck	(PDF)
Robert O. Gates	(PDF)
Brian J. Riley	(PDF)
Gary E. Spanner	(PDF)

Pacific Northwest
NATIONAL LABORATORY

U.S. DEPARTMENT OF
ENERGY

Proudly Operated by **Battelle** *Since 1965*

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)
www.pnnl.gov