


APPENDIX E

FCT DOCUMENT COVER SHEET ¹

Name/Title of Deliverable/Milestone/Revision No. Joint Workplan on Filler Investigations for DPCs (Milestone M4SF-18SN010305022)

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This deliverable was prepared in accordance with Sandia National Laboratories
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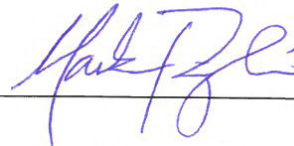
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Joint Workplan on Filler Investigations for DPCs

Fuel Cycle Research & Development

Prepared for the
U.S. Department of Energy
Office of Spent Fuel and Waste Science and Technology
by
Sandia National Laboratories
Albuquerque, New Mexico
December, 2017
SFWD-SFWST-2018-000481 Rev. 0



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Revision History

Version	Description
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Abbreviations

2D	2-dimensional
3D	3-dimensional
AECL	Atomic Energy of Canada, Ltd.
BWR	Boiling water reactor
CAC	Calcium aluminate cement
CANDU	Canadian commercial reactor designator
CPAC	Calcium phosphate aluminate cement
CPC	Calcium phosphate cement
CSAC	Calcium sulfoaluminate cement
DFC	Damage fuel canister
DOE	Department of Energy (U.S.)
DPC	Dual-purpose canister
EBS	Engineered barrier system
FTIR	Fourier transform infra-red (analytical method)
GDSA	Generic disposal system analysis
HA	Hydroxyapatite
MgPC	Magnesium phosphate cement
MIT	Massachusetts Institute of Technology
MKP	Magnesium potassium phosphate
MPC	Multi-purpose canister (vendor designation equivalent to DPC)
ONDRAF/NIRAS	Belgian nuclear waste management program
OPC	Ordinary Portland cement
PA	Performance assessment
PWR	Pressurized water reactor
R&D	Research & development
SEM/EDS	Scanning electron microscopy/energy-dispersive spectroscopy
SNF	Spent nuclear fuel
SNL	Sandia National Laboratories
TSC	Transport-storage canister
UDB	Unified Data Base
UFD	Used Fuel Disposition (R&D campaign)
UNF-ST&DARDS	Used Nuclear Fuel-Storage, Transportation & Disposal Analysis Resource and Data System
XRD	X-ray diffraction
YMP	Yucca Mountain Project

Title: Joint Workplan on Filler Investigations for DPCs

Milestone: M4SF-18SN010305022

Work Packages: SF-18SN01030502 and SF-18OR01030501

Deliverable description: Perform literature review and market research to identify specific filler material sources and equipment options. Review filler performance requirements from previous work in the U.S. and internationally. Produce a workplan with input from, and agreement with ORNL to demonstrate filler emplacement in scale-models representing DPCs.

1. Introduction

Previous work on fillers for dual-purpose canisters (DPCs) includes:

- Swedish program (Oversby and Werme 1995)
- Massachusetts Institute of Technology (MIT) concept development (Forsberg 2000, 2002; Forsberg et al. 2001)
- Yucca Mountain Project (YMP) studies including demonstration testing (Cogar 1996a; Wallin 1996; Massari 1999)
- Atomic Energy of Canada Ltd. (AECL) demonstration (Forsberg 1997)
- Filler studies by the Belgian program (ONDRAF/NIRAS 2001)
- Filler selection analysis for the Spanish program (Puig et al. 2008a)
- DPC fillers study for the Used Fuel Disposition (UFD) campaign (Jubin et al. 2014)

This work follows on these previous studies, most of which evaluated the use of granular solids (MIT, Belgium, YMP, AECL, UFD) or molten metal fillers (YMP, UFD). Use of cementitious fillers was also examined by UFD in the context of spent fuel transportation.

This workplan addresses filler attributes (i.e., possible requirements), assumptions needed for analysis, selection of filler materials, testing needs, and a long-range perspective on R&D activities leading to filler demonstration and a safety basis for implementation.

A key assumption for this work is that access to DPC internal void volume is limited to the original vent/drain ports, or new ports created in similar fashion (e.g., by drilling through the canister shell). Cutting canister lids off, or other modifications to expose the fuel assemblies, are considered out of scope for this workplan. This is primarily because filling of open canisters (prior to installing lids) has already been studied and demonstrated at full scale. The AECL waste package development program demonstrated filling of v fuel with silicate particles and fine sand (Forsberg 1997), while the YMP demonstrated filling of a pressurized water reactor (PWR) fuel assembly with steel shot (Cogar 1996a). Whereas these demonstrations used dry particulate fillers, emplacement of liquid fillers with similarly exposed fuel would likely present no additional problems. If the DPC lids are cut off it is likely that virtually any filler material could be emplaced. Some questions would remain, for example, emplacement of dry particulate fillers could require either that the lids are cut off in a dry facility. As discussed later in this plan, the possibility of emplacing dry particulate material through small ports will be investigated.

This workplan therefore focuses on fillers that can be emplaced as liquids which then solidify. Two major approaches are identified: 1) molten metal fillers introduced at higher temperature, and

2) liquids such as resins or cement slurries that solidify at much lower temperature. It is anticipated that much of the effort to investigate molten metal fillers will be performed by Oak Ridge National Laboratory (ORNL), and that low-temperature fluids or slurries will be mostly investigated by Sandia National Laboratories (SNL) at least in the first part of the program (filler properties characterization). Scaled emplacement testing or demonstration will be performed later, and may be a joint effort.

1.1 DPC Construction Details

Canister shells are generally made from stainless steel sheet (typically grade 304L) of 0.5" or 0.625" thickness, which is cold-rolled and welded to form cylinders. A base plate is welded on the bottom, and fixtures are installed for handling the canister during fabrication.

A fuel basket is fabricated and lowered into the shell, and permanently attached. The basket provides structural support, heat transfer, and criticality control for the fuel (Greene et al. 2013). There are two general types of baskets:

- Tube-and-plate type with a square, longitudinal, metal fuel tube holding each fuel assembly (Figure 1). The tubes are held in place by transverse spacer plates, which are held in position by support rods that run the length of the basket. Fuel tubes are typically thin-walled stainless steel, and spacer plates may be stainless, aluminum, or plated steel (to reduce cost but prevent exposure of steel to the fuel pool). Many spacer plates are typically used (Figure 2) and they may be of different materials within the same basket, e.g., aluminum plates may be used as thermal shunts, and steel plates for strength.
- Egg-crate type baskets use longitudinal plates in a rectilinear array, forming square cells to receive fuel assemblies (Figures 1 and 3). The longitudinal plates may be stainless or aluminum-B₄C composite such as Metamic[®] (Figure 4). The egg-crate baskets are rigid and self-supporting once the plates are attached together to form a grid.

Neutron absorbing materials are added, and flux trap geometry is maintained for some fuel basket designs, between each pair of adjacent fuel assemblies. Recent DPC designs rely more on neutron absorbing plates and less on flux trap geometry, which gives a more compact basket that increases the fuel capacity. The neutron absorbing material is generally ceramic B₄C in particle form, which is hot-rolled with aluminum to form sheet (e.g., Boral[®]) that can be cut and formed. Sheets of aluminum-based neutron absorbing material are typically attached to the walls of the basket cells by thin cover sheets of stainless steel that are tack-welded in place, but the welds are intermittent and do not seal the aluminum from moisture if it exists in the canister environment. The Metamic HT[®] basket (Figure 4) is a departure from this type in which the egg-crate structure is fabricated almost entirely from aluminum-B₄C composite.

The empty, open canister is placed into a shielded transfer cask, open at the top, which is then submerged in the fuel pool. Fuel assemblies are loaded one at a time. The shield plug is then placed on the top, and the transfer cask with DPC is hoisted from the pool. The shield plug is welded, and the canister is dewatered. This is accomplished using a drain tube (runs to the bottom of the fuel cavity) and a top vent. Bulk water is removed by suction or applied gas pressure, and final dewatering is performed by circulating dry inert gas as the canister heats up from fuel heating. Every basket design has features that allow water to drain from the fuel toward the drain tube. These take the form of limber holes (Figure 2) or standoffs between the basket and the base plate. Similar provisions are made to allow gas and water vapor movement during final dewatering. After

dewatering, the drain and vent ports are covered and welded. During all of these operations radiation protection is provided by the transfer cask and the shield plug.

The remaining steps in DPC deployment for fuel storage and transportation are discussed in other sources (Greene et al. 2013; Raddatz & Waters 1996; EPRI 2009).

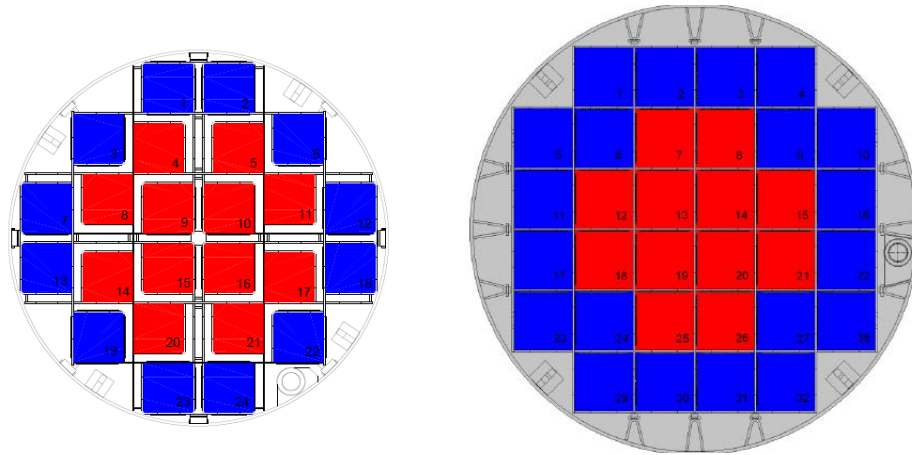


Figure 1. Basket arrangements for a fuel tube design (MPC-24, left) and an egg-crate design (MPC-32, right) (from Greene et al. 2013).

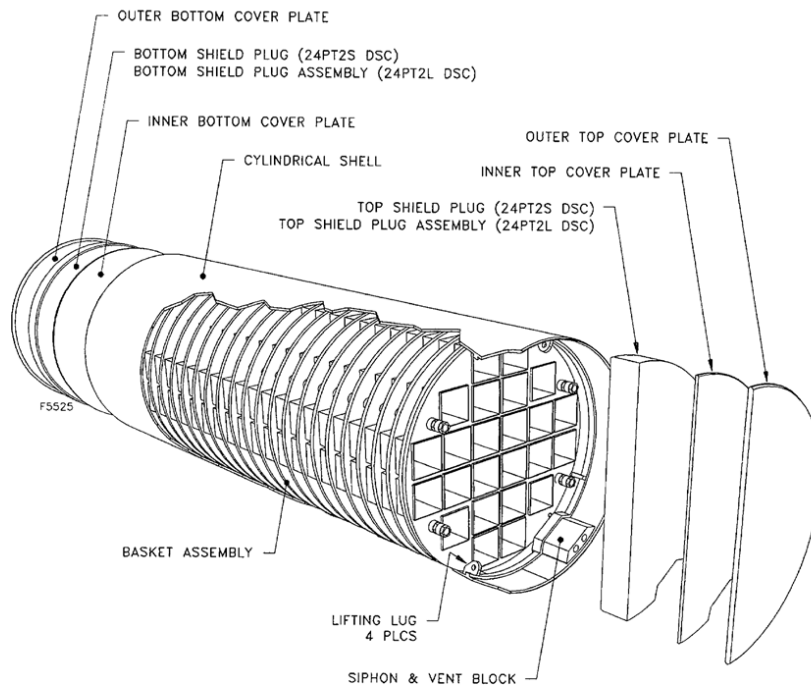


Figure 2. Cutaway of NUHOMS® 24-PT2 basket, shell, and lids (from Greene et al. 2013).

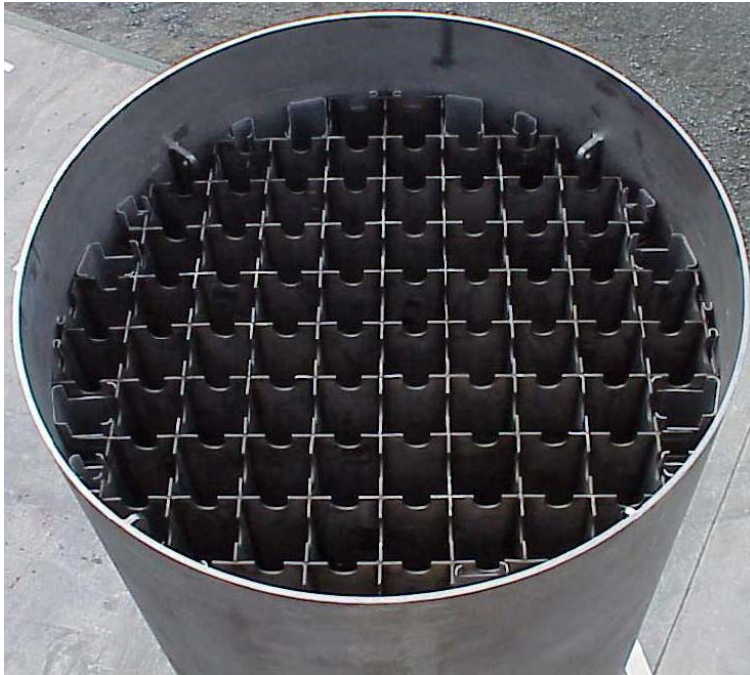


Figure 3. Top view of MPC-68 shell and basket (from Greene et al. 2013).



Figure 4. Metamic HT[®] basket for MPC-89 canister (from Greene et al. 2013).

2. Filler Performance Criteria

Desirable attributes for filler materials and the methods used for emplacement are developed here (Table 1) starting from a previous study (Maheras et al. 2012). These attributes are not hard and fast requirements because tradeoffs are possible, so they may be prioritized or adjusted for specific fillers. For example, the capacity to incorporate neutron absorbers may be needed only for materials that contain significant fractions of hydrogen or other neutron moderating elements.

The attributes in Table 1 are compared to other previous studies (Oversby and Werme 1995; Puig et al. 2008a) in the following paragraphs.

An early study for the Swedish disposal R&D program (Oversby and Werme 1995; summarized by Jubin et al. 2014) suggested a three-tiered approach to filler attributes: 1) those that ensure void filling and long-term stability, 2) other desirable properties, and 3) undesirable properties. The fill material should be placed in the canister in a way that does not damage the fuel and results in a residual void volume of less than 40% of the original void volume (with small-scale intergranular porosity). Virtually the entire DPC volume should be filled, with less than 10% volume compaction after emplacement, since a relatively small region can achieve criticality when flooded with water, with degraded components. These void volume and compaction limits are derived from original (preliminary) criticality simulations of packages containing 12 fresh (un-irradiated) BWR fuel assemblies, attributed to Risenmark (1993). As pointed out by Puig et al. (2008a) initial fuel enrichment is higher at present than the 3.6% used in these original calculations.

The Swedish effort further proposed that filler material should have solubility less than 100 mg/L at 50°C in pure water and in the water of the anticipated repository environment (Jubin et al. 2014). Desirable properties were also identified (in no particular order):

- Chemical compatibility with the disposal system
- Homogeneous properties and consistency between batches
- Well-understood long-term durability
- Favorable rheological properties for emplacement in the canister
- The material contains a neutron-absorbing material or has the capacity to incorporate one
- Potential to attenuate radionuclides released from spent fuel
- Potential to suppress the generation of hydrogen
- Reasonable cost (in the context of system cost)
- Low density to limit total canister weight

And undesirable properties were also identified, including:

- Limited availability
- Potential to enhance corrosion of the canister, fuel cladding, or the fuel itself
- Generates gas when altered (as by radiolysis) or reacted with water or other substances
- Contains water
- Affinity for absorbing air (which could interfere with liquid flow completely filling a canister, but would also be integral to a filler strategy that relies on foam)

Table 1. Desired attributes for filler materials (adapted from Maheras et al. 2012).

Criticality Avoidance	<ul style="list-style-type: none"> • Provide moderator displacement • Neutron absorption capability if needed • Minimize neutron moderation • Provide isotopic dilution of fissile radionuclides • Capacity to fill greater than 60% of the canister free volume (e.g., complete filling with less than 40% porosity) • Fill material does not compact by more than 10% of its initial volume
Heat Transfer Properties	<ul style="list-style-type: none"> • Promote heat transfer from the fuel during handling and after disposal
Stability Properties	<ul style="list-style-type: none"> • Thermal stability and expansivity • Chemical stability (e.g., low solubility, low reactivity) • Radiation stability • Chemically compatible with cladding, fuel, neutron absorbers, fuel baskets, and other materials within canister • Limited gas generation (radiolytic, or on contact with ground water)
Homogeneity and Rheological Properties	<ul style="list-style-type: none"> • Homogeneous and consistent batches • Good rheological properties (e.g., setting time, viscosity) to ensure proper filling • Wetting behavior for fuel and canister materials
Remediation	<ul style="list-style-type: none"> • Allows for safe recovery of fuel from a canister (e.g., after unsuccessful filling)
Material Availability and Cost	<ul style="list-style-type: none"> • Low to moderate cost • Material available in required purity
Weight and Radiation Shielding	<ul style="list-style-type: none"> • Fill material doesn't add excessively to canister weight • Good radiation shielding properties
Operational Considerations	<ul style="list-style-type: none"> • Easy to emplace • Able to place in the canister without damaging fuel or canister (flow characteristics and pressure) • Fill material does not adversely react to canister handling and emplacement in the repository

Puig et al. (2008a) reviewed filler material choices for spent fuel waste packages, identifying five categories of selection criteria: 1) criticality avoidance, 2) general desirable properties, 3) general undesirable properties, 4) performance improvement features, and attributes not directly related to repository performance but potentially important. The fillers discussion reiterated the 60% free

volume filling requirement discussed above, and the 10% maximum settlement criterion which was based on a calculation that criticality could result from a 40-cm high unfilled region (attributed to Agrenius 1993). They identified a fuel cladding temperature limit of 350°C.

Thermal, radiation, and chemical stability criteria were similar to those listed above (Table 1). Criteria for disassembly and fuel retrieval (from a filled canister) were included. The presence of air in the filler was associated with formation of nitric acid by radiolysis, possibly contributing to stress corrosion cracking. The Spanish waste program is considering the use of clay-based buffers, so compatibility with buffer function (low hydraulic conductivity, diffusion resistance) was also identified as a filler attribute. Sorption capacity of fillers for released radionuclides, mechanical strength to maintain configuration, chemical durability (especially natural analogs), control of hydrogen generation, radiation shielding, low weight, and low cost were also identified.

Finally, filler studies for the Yucca Mountain Project (Cogar 1996a; Wallin 1996; and Massari 1999) considered a range of materials but focused on solid particulates (steel shot, glass or ceramic beads possibly containing depleted uranium) that could be loaded before final closure of the canister. This included a full-scale, single-assembly demonstration of loading steel shot. Requirements identified at that time included the capability "...of unloading a damaged waste package after the occurrence of a design basis event" (Massari et al. 1999). Probabilistic treatment of postclosure criticality was also described such that the probability and consequences of waste package criticality must be sufficiently low that the total system performance of the repository is not impacted (in accordance with 10CFR60). DPC direct disposal at Yucca Mountain (with and without fillers) has been considered previously (BSC 2003; Kessler et al. 2008) and important aspects of postclosure criticality that might apply have been identified (Hardin et al. 2015).

Filler criteria are discussed below (Section 5) in the context of selection materials for testing.

3. Assumptions

Assumptions of various types were documented previously for investigation of feasibility of direct disposal of DPCs (Hardin and Howard 2013). This section reviews that list for the purpose of identifying any constraints on, or conflicts with, potential filler strategies.

3.1 Assumptions from Previous Direct Disposal Analysis

DPC Characteristics

- a) DPCs contain commercial UNF. Average burnup for existing UNF in dry storage is nominally 40 GW-d/MT, with a reasonable-bound value of 60 GW-d/MT for future DPCs. These values may be used in generalized analyses to evaluate DPC disposal feasibility (more reactor-site specific or canister-specific bounding values may be available as discussed in Section 2).

Discussion: These values (from Carter et al. 2012) provide representative and bounding values (5% enrichment and 60 GW-d/MTU burnup) for criticality, thermal, and radiolysis studies with fillers. Filler emplacement may not be sensitive to burnup, but these studies will depend on burnup and cooling time.

- b) The capacity of DPCs is typically 32 PWR assemblies or 68 BWR assemblies. Larger DPCs are available (Greene et al. 2013) from NAC International (Magnastor[®] 37/87 system, nominally 37-PWR or 87-BWR), Holtec International (MPC-37/89, nominally 37-PWR or 89-BWR), and Transnuclear (NUHOMS[®] 37 series).

Discussion: The 37-PWR (89-BWR) is current and represents the type of DPCs for which fillers could be most beneficial.

- c) Storage-only canisters can be included in the evaluations.

Discussion: Storage-only canister based systems include the MSB (24-PWR, Energy Solutions) and the NUHOMS[®] 24PS, -24PL, -24PHBS, -24PHBL, -52B and -07P (Transnuclear). These canisters currently exist at the Idaho National Laboratory, and at the Calvert Cliffs, Surry, Oconee, Arkansas Nuclear One, Palisades, Davis-Besse, Point Beach, Susquehanna, and H.B. Robinson nuclear power plants. These are sealed canisters, not to be confused with non-canistered cask systems of any type that have bolted closures. Fillers might be implemented at power plant sites and used to modify “non-transportable” (i.e., storage-only) canisters (with provision for amended licensing).

Potential DPC Modifications

- d) Liquid fillers can be introduced through the existing drain tube, or new vents, ports, or drain tubes can be installed.

Discussion: This assumption is intended to remove uncertainty in filler selection, as to whether there would be adequate rate of filler flow through the existing drain tube. The assumption may be unnecessary, because a liquid suitable for penetrating DPC void spaces (low viscosity, self-leveling, delayed setting time) might not produce much restriction in the filling tube.

Disposal Concepts

- e) Surface decay storage of DPCs and storage-only canisters for up to 100 years (out-of-reactor) can be assumed in disposal feasibility evaluations. Further, heat generation is assumed to be that typical for 50-year old fuel.

Discussion: Up to 100 years of decay storage can be assumed for thermal analysis of filled canisters. The envelope of 50 to 100 years allows specification of cases for thermal analysis that depend on limited heat output as well as minimal heat output.

- f) Underground handling and transport of DPCs will be shielded.

Discussion: Shielded transporters and handling equipment are available so that fillers will not be relied upon entirely for worker shielding.

Criticality Analysis

- g) Analysis of postclosure criticality will include full burnup credit (i.e., actinides and fission products), and assembly-specific or cask-specific characteristics.

Discussion: Past studies have identified situations where burnup credit and detailed modeling (principal isotopes, BSC 2003; more complete isotopics, EPRI 2008) is needed in DPC disposal analysis. Burnup credit analysis may allow some DPCs to be disposed of directly without fillers for criticality control.

- h) Consequence analysis may also be used to include or exclude postclosure criticality.

Discussion: Whereas postclosure criticality consequence analysis has been proposed (DOE 2003, Section 3.7) and the impact on radionuclide inventory may be negligible (Rechard et al. 1996), the applicability to DPC direct disposal is constrained if criticality is to be an *unlikely event*. Alternatively, the use of consequence analysis is limited if regulatory guidance such as that at 60.131(h) pertains: "...criticality is not possible unless at least two unlikely, independent, and concurrent or sequential changes have occurred..." Hence, fillers should be designed such that postclosure criticality is *very unlikely* or at least *unlikely* in the regulatory sense.

Surface Facilities

- i) DPCs will be sealed at the power plants or at a centralized storage facility and fuel will not be removed at the repository. However, opening and subsequent re-sealing of de-watering ports may be permitted.

Discussion: Opening and re-sealing of de-watering ports, in order to pump in filler material, is the primary approach, but not the only approach to be pursued in this plan.

- j) Any necessary DPC inspection can be done remotely in a hot cell, and detected non-conformances can be corrected or mitigated by re-packaging.

Discussion: It may further be assumed that DPC inspections would likely be performed to confirm filler installation (and that the ease of inspection could be a factor in filler selection).

Finally, we note that logistical performance of a SNF management system in the U.S. is beyond the scope of this R&D plan, except for aspects of filler implementation that are directly affected by material selection.

3.2 DPCs Targeted for Filler R&D

The preliminary objective for DPC fillers would be to provide criticality control by means of moderator displacement, with the possibility of added neutron absorption, over repository performance time frames. Criticality analysis of degraded DPCs flooded with groundwater has been performed for 556 as-loaded DPCs that reside at 23 decommissioned and operating reactor sites (Liljenfeldt et al. 2016). Two simplified configurations were used to assess DPC reactivity after flooding in a repository:

- Complete loss of neutron absorbing components (and replacement by water in the model) due to unspecified chemical degradation and transport processes, and flooding with fresh water. Aluminum-based neutron absorbing materials are expected to corrode on exposure to groundwater, and not to perform their function over any postclosure timeframe.
- Complete loss of the internal basket structure (including neutron absorbers) with elimination of assembly-to-assembly spacing, and flooding with fresh water.

Both configurations were analyzed for most DPCs, however, only the second configuration was used for DPCs with plated carbon steel structural components. DPCs were analyzed using as-loaded SNF inventory, including both PWR and BWR fuel types, and 13 design variants with capacity for 24 and 37 PWR assemblies, and 68 BWR assemblies. The criterion for subcriticality ($k_{eff} < 0.98$) was applied up to 13,000 years from loading. The reader is referred to the published results of these criticality analysis, which include responses to both fresh and saline groundwater compositions (Liljenfeldt et al. 2016; Hardin et al. 2015). The results show that a majority of the BWR DPCs would remain subcritical when flooded with fresh water, although the analyses did not include modern designs with baskets holding 87 or 89 BWR assemblies.

PWR DPCs can be divided into two broad categories, those with flux traps and those without. A majority of the PWR DPCs analyzed with flux trap designs would remain subcritical, while those without flux traps would not. The analysis did not include modern PWR DPCs with egg-crate baskets constructed mostly from aluminum-based neutron absorbing material (Metamic HT[®]) which are expected to be more susceptible to criticality as loss of neutron absorbing components would amount to loss of the internal basket structure as well. In summary, filler implementation for postclosure criticality control would be targeted to PWR DPCs without flux traps, including modern designs with heavy use of aluminum-based materials for the basket structure.

3.3 Spent Fuel Condition at Disposal

Fuel cladding integrity may be important for filler radiolysis calculations since the higher energy and shorter range of alpha emanation (compared with gamma) ensures more radiolytic activity per disintegration.

A previous cladding integrity analysis (BSC 2005) concluded that less than 2% of the fuel, including all of the stainless-steel clad fuel, received at the repository is failed (perforated) upon receipt at the repository. All failed fuel was assumed to axially split upon waste package failure in an oxidative environment. For analysis of fillers this assessment is conservative, if the stainless steel fuel is re-packaged instead.

In the recent GC-859 survey (EIA 2012) which describes spent fuel status through June 2013, approximately 2% of the ~245,000 discharged assemblies were reported as failed, with known damaged fuel packaged in damage fuel containers (DFCs). The extent of damage for much of this

fuel (especially that which is not packaged in DFCs) is not explicitly known. DFCs typically use very fine mesh screen at the top and bottom, which may prevent filler penetration of the void spaces within. Additional investigation may be needed to ensure proper filling of the DPCs that contain failed assemblies in DFCs.

4. Scoping Analysis of Canister Environment for Filler Performance

Cement or polymer filler material loaded canisters will immediately encounter gamma and neutron radiation, and elevated temperature. As the system heats up (assuming filler is at ambient temperature or cooled, before loading) pressure will build up from thermal expansion, evaporation of moisture, and cement expansion on cure (if it occurs, and apart from thermal expansion). Pressure would be relieved at the vent, and the rate of venting would depend on the permeable flow characteristics of the curing filler. For scoping discussions in this R&D plan the fuel temperature limit is assumed to be 150°C, which will require some thermal aging of DPCs, although higher limits may be possible.

Molten-metal fillers would be heated externally, and the DPCs would be pre-heated to above the filler melting temperature, before loading. This temperature would be approximately 200°C, or somewhat higher if needed to ensure filler flow properties and complete filling. Such a temperature is within the temperature limits for the canister and the fuel (NRC 2003). Note that if the entire canister is heated, the fuel temperature will increase further from decay heating. However, previous calculations have shown that the temperature differential between fuel and canister wall (when the fuel is the only source of heating) is much less than 100 C° (DOE 2008).

Subsequent cooling will cause thermal contraction, with materials exhibiting different expansivity. For example, the difference in linear thermal expansion coefficients for a filler that is mostly tin, and stainless steel, is on the order of 10^{-5} C^{-1} , which will induce a small amount of void space on cooling ($150 \text{ C}^{\circ} \times 10^{-5} \times 3 = 0.45\%$). If the filler bonds to the fuel and basket surfaces on freezing, then thermal contraction will also induce small tensile loads that would be at least partially relieved by creep.

4.1 Thermal History

To investigate short-term temperature rise for cement fillers that could be sensitive to temperature during cure, a numerical case was implemented in FLAC (Itasca 2011). The model is a 2D cross-section through a fuel rod and surrounding cement, with adiabatic boundaries. Thermal properties were extracted from literature (UO₂, Zircaloy properties from IAEA 2008) or assumed in the case of cement (conductivity 1.5 W/m-K, specific heat 1,300 J/kg-K, density $1.97 \times 10^3 \text{ kg/m}^3$). Heat generation was assigned to fuel rods such that a 21-PWR waste package with 17×17 assemblies would have total output of 10 kW. Heat of reaction in the cement was set to 10 kW/m³ for the duration of the simulation. Initial temperature of the fuel was 150°C, while the cement was introduced at 25°C. These inputs are subject to review and modification (for example, the heat output of a DPC at disposal could be as high as 18 kW) to conform to existing performance analyses.

The simulation shows that temperature rise is not limited by conductivity (short distances are involved), and that temperature in the cement rises by about 0.0013 K/sec (Figures 5 through 7). Thus, a 25 C° temperature rise would occur in about 5 hours, dominated by heat capacity.

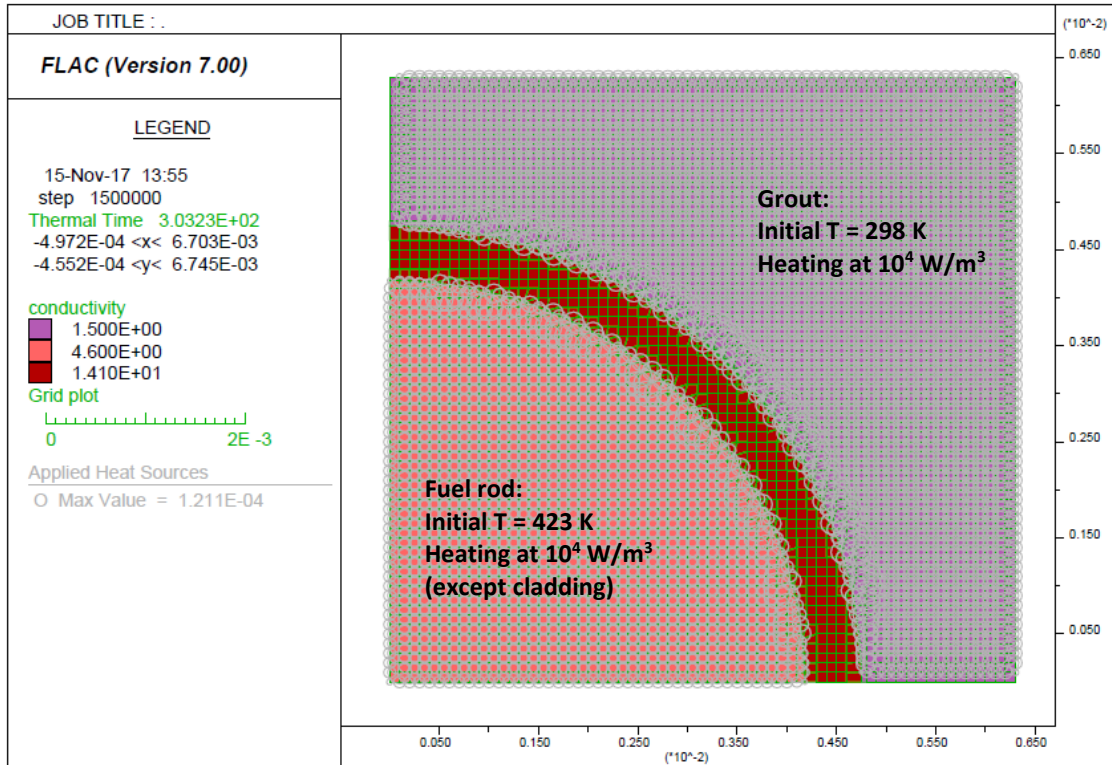


Figure 5. Fuel rod-scale adiabatic model for short-term temperature history.

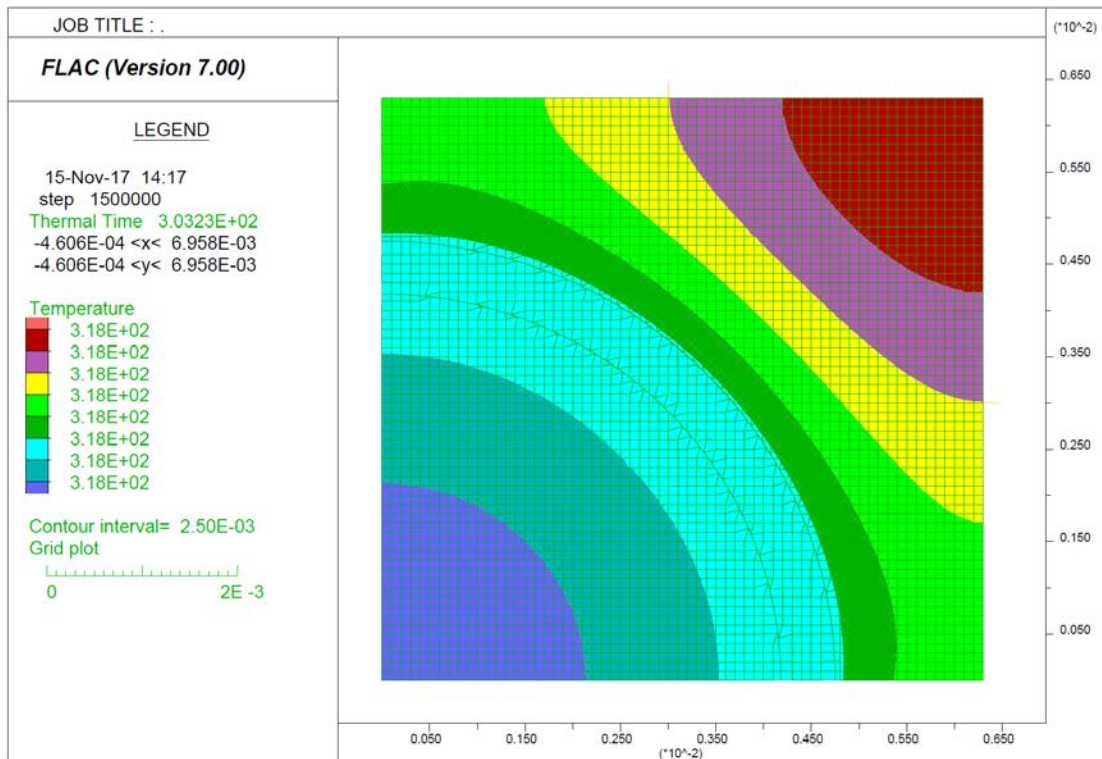


Figure 6. Rod-scale temperature calculation showing equilibration at 300 seconds.

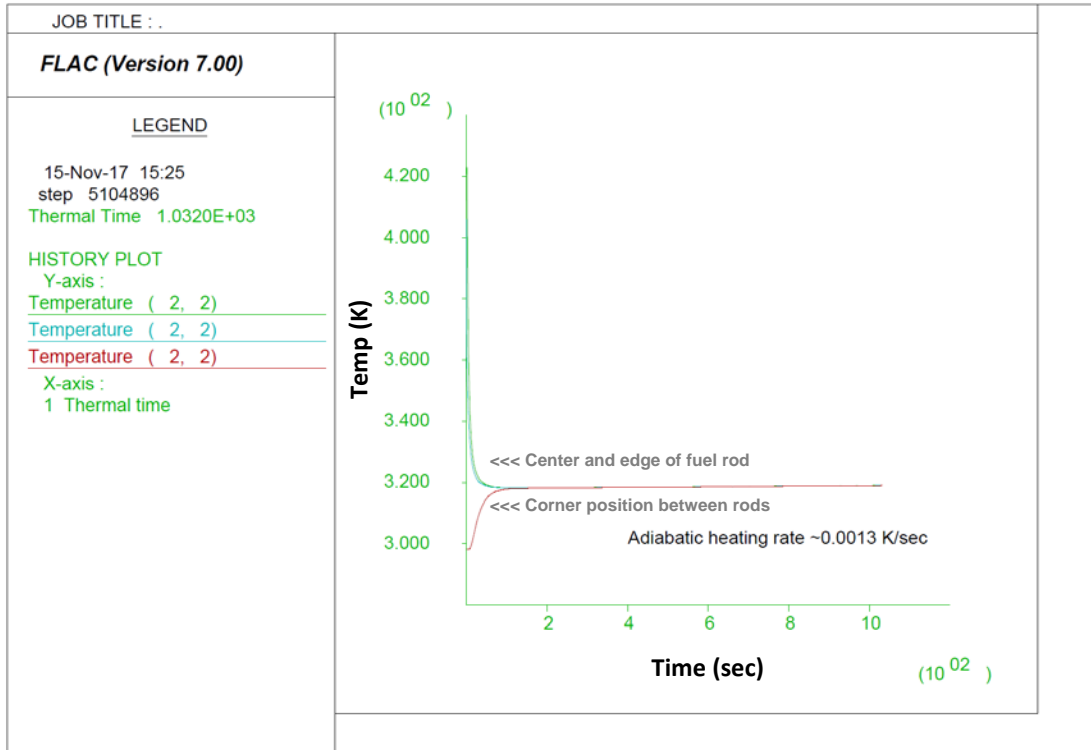


Figure 7. Temperature histories for outer edge of cladding, and corner position between rods.

To investigate longer-term temperature rise, and the effect of thermal conductivity, additional simulations are needed for an entire canister. For example, a PWR assembly of 264 fuel rods infused with filler is calculated to have effective thermal conductivity of 2.67 W/m-K. This value can be used for most of the assemblies in a DPC, while the maximum discretization can be reserved for one or more assemblies near the middle for investigation of peak temperature. The canister external temperature can be assigned any value that is readily achievable in storage, or in the disposal environment.

When the filler is stabilized and initial off-gassing is judged to be complete, the loaded DPC would be re-sealed. From this point until canister breach hundreds to many thousands of years later, the internal environment would be closed. Changes would then be limited to cooling effects, and chemical reactions augmented by radiolysis.

4.2 Canister Pressure Limit

Previous waste package design work used nuclear containment boundary requirements for pressure vessels (DOE 2008; ASME BPVC Section III - *Rules for Construction of Nuclear Facility Components, Division I- Metallic Components, Subsection NB Class 1 Components*). Components designed to these specifications can serve as part of the fluid-retaining pressure boundary of a reactor coolant system. It is typically used for reactor pressure vessels and piping, generally with a safety factor of 1.5 to yield, and 3.5 to ultimate tensile strength. Of course, this approach is scoping only because it does not take into account the stress condition at the canister ends, particularly at the end welds.

Using best-available public information on DPC construction (Greene et al. 2013) shell thicknesses and diameters (overall) for typical DPCs are given in Table 2.

Table 2. Shell thicknesses and diameters for typical canisters.

Vendor	Canister Type	Shell Thickness (in)	Overall Diameter (in)
Holtec	MPC-24/ MPC-32/MPC-68	0.5	68.5
	MPC-37/MPC-89	0.5	75.5
NAC	MPC (CY style)	0.625	70.64
	UMS [®] TSCs	0.625	67.1
	Magnastor [®]	0.5	71
Transnuclear	NUHOMS [®] 24-PWR versions	0.625	67.19
	24-PTH, 32-PWR and 37-PWR versions	0.5	67.19
	32-PTH versions	0.63	69.75
FuelSolutions	VSC 24 PWR	1.0	62.5
	W74 64-BWR	0.625	66

The ratio of diameter to $2\times$ wall thickness describes the effect of internal pressure on hoop stresses, and this ratio is approximately 70 for DPCs. With yield stress of 215 MPa (www.asm.matweb.com) and a safety factor of 1.5 to yield, the maximum internal pressure would be 2 MPa. Ultimate tensile strength (test specimens) is reported at 505 MPa, so there is margin for additional loading. Further, the maximum elongation at rupture is 70%, which would not be achieved in a waste package setting, but would ensure that a canister shell in yield would readily expand against the disposal overpack imparting additional strength, possibly without canister breach. Note that this discussion does not account for residual stress (DPC shells are cold-rolled and welded without stress relief), nor does it account for end effects particularly shears and moments produced at the top and bottom welds, or metallurgical damage to the DPC during storage. However, it does show that SS304 grades (universal in DPC shell construction) can maintain containment integrity, inside a more robust overpack, in response to internal pressure on the order of 1 MPa or greater. This pressure is much less than the H₂ pressure needed to sequester hydrogen by reducing oxidized iron (Grundfelt and Crawford 2014) and by extension, by reducing other species present.

DPCs are designed and analyzed to withstand stresses due to pressurization with He following loading. Design pressures vary with canister type. However, larger canisters with higher heat output have higher pressures to improve heat transfer. Maximum canister pressure is calculated based on stresses incurred during off-normal and accident conditions. Using best-available public information on DPC construction, typical design and maximum canister pressures are shown in Table 3. *Additional modeling of DPC pressurization response is needed to support modeling of thermomechanical loading and internal gas generation. This should include thermodynamic modeling of H₂ equilibria with substances present in the canister in significant quantities.*

Table 3. Internal pressure values used in licensing of some DPCs.

Vendor	Canister Type	SNF capacity	Design Pressure (psig)	Max. Pressure (psig)
BNFL	W74	64-BWR	10	30
	VSC	24-PWR	0	1.5
Holtec	HI-STORM 100®	24-PWR/32-PWR/68-BWR	100	200
	HI-STAR 100®	24-PWR/32-PWR/68-BWR/80-BWR	100	125
NAC	MPC	26-36	0	18
	UMS	24-PWR/56-BWR	0	15
	MAGNASTOR®	37-PWR/87-BWR	110	250

4.3 Gas Generation from Radiolysis and Alpha Production

The radiation dose to filler materials can be estimated for scoping purposes, using the 400 Gy/hr gamma dose rate calculated for PWR fuel assemblies with 45 GW-day/MTU burnup and 20-year age out-of-reactor (R. Cumberland, verbal communication). Assuming this gamma flux originates entirely from fission products with 30-yr half-life, the total dose can be estimated by integrating the exponential decay equation

$$\frac{\partial N}{\partial t} = -\lambda N_0 e^{-\lambda t}$$

over many half lives. The result calculated for fillers installed in DPCs containing fuel with 50-year age, shows that the total dose to filler materials is on the order of 50 MGy. This precludes the use of many organic polymers as shown in the gamma tolerance table (Table 4).

Table 4. Gamma radiation dose tolerance for organic polymers.

Polymer	Tolerance (kGy)	Comments
Thermoplastics		
Aromatic Polyamide (Nylons)/Polyimide	10,000	High heat/strength grade.
Polyimides	10,000	
Polystyrene	10,000	All styrenes are stabilized by benzene ring structure.
Polysulfone	10,000	Amber color before irradiation.
Polyurethane	10,000	Excellent clarity and chemical resistance to stress-cracking. Drying is essential.
Thermosets		
Allyl Diglycol Carbonate (Polyester)	5,000-10,000	All thermosets as a class are highly resistant.
Phenolics	50,000	
Polyesters	100,000	

Excerpted from: http://www.nordion.com/wp-content/uploads/2014/10/GT_Gamma-Compatible_Materials.pdf

In a gas-filled canister penetrating gamma and neutron radiation from the fuel interacts with the basket and the canister, but not the filler (e.g., helium gas) which absorbs negligible amounts of radiation. In a canister with solid filler, significant energy would be absorbed. The principal effect is that chemical bonds are broken by gamma energy, forming reactive chemical species and

hydrogen gas. The flux of neutrons produced by spontaneous fission and (α,n) events decreases in the first few hundred years from decay of ^{238}Pu , ^{241}Pu and ^{241}Am , ^{242}Cm and ^{244}Cm (Hsue et al. 1979). Whereas this discussion focuses on the production of hydrogen from gamma radiolysis of water during the first few hundred years, neutrons from (α,n) reactions could also be relatively important especially over very long time frames.

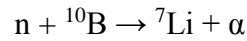
The potential for radiolytic production of H_2 is high, as shown by the following scoping calculation. If the initial H_2O inventory in a filled canister is 1 m^3 , exposed to a gamma dose of 50 MGy, roughly 2,600 moles of H_2 could be produced:

$$\begin{aligned} N_{\text{H}_2} &= \text{Dose per Unit Mass} \times \text{H}_2\text{O Mass} \times G_{\text{H}_2} \\ &= 50 \times 10^6 \text{ J/kg} \times 10^3 \text{ kg H}_2\text{O} \times 3 \times 10^{16} \text{ molecules H}_2/\text{J} \div N_{\text{Avogadro}} \\ &= 2.5 \times 10^3 \text{ moles H}_2 \end{aligned}$$

Where the value for G_{H_2} is taken from experiments at saturated aqueous conditions, near-neutral pH, and 25°C reported by Elliott et al. (1990, Figure 1). The same dose could also produce a similar quantity of gaseous O_2 , although oxygen radicals are often assumed to form H_2O_2 .

For an internal pressure of 1 MPa, 10% of the total DPC interstitial volume of 6 m^3 at pressure would represent about 250 moles of gas, which is an order of magnitude less than the potential H_2 production. Thus, there is the potential for damaging H_2 gas pressure depending on the availability of moisture and the efficiency of radiolysis.

Another possible source of gas generation is the neutron capture reaction



where the α particle becomes a helium atom after redox reaction in the solid matrix. *Model calculations of radiolysis, including gamma and neutron doses inside the canister, are needed to estimate the rate of radiolysis, particularly of H_2O producing H_2 gas, H_2O_2 , and other products, using literature G values. Neutron capture by ${}^{10}\text{B}$ needs to be included in the gas generation calculation.*

Strategies for reducing H_2 gas generation include minimizing moisture availability, recombination, permeation, and getters. The cement could be approximately 10 to 50% water by weight initially, because existing recipes for similar mixes contain this much, and added water is needed to achieve self-leveling flow properties and retarded set in the cement slurry. Hence the amount of water present in a DPC will be on the order of 1 m^3 . Only a small amount of the initial water is likely to be taken up as bound water in phosphate or aluminate mineral structures, with much of it creating micro-pores between and around insoluble grains. Some of this water could be removed by venting and self-heating after cure, before the DPC is resealed. *This will depend on the permeability and curing rate of the cement, and the maximum temperature, and will be a focus of laboratory testing.*

A recombination strategy could work by using catalysts to react stoichiometric proportions of H_2 and O_2 gases (Hariprakash et al. 2001) similar to the catalytic plugs used in sealed lead-acid batteries. The rate of gas production by electrolysis during battery charging is readily calculated and comparable to the rate from radiolysis in DPCs containing water. Other catalysts are available for converting H_2O_2 to water and oxygen gas (granular MnO_2 or TiO_2) although this reaction may occur fast enough in response to gamma radiation (McDonell 1954) or in the presence of stainless steel (Russo et al. 2013) without added solid catalysts. Hence, recombination strategies could be viable and would not necessarily need to last more than a few hundred years during which the

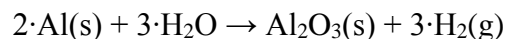
gamma flux is greatest. *A recombination strategy based on readily available and long-lasting catalysts should be investigated, including efficiency, longevity, and a method for testing recombination in the laboratory.*

Hydrogen permeation refers to slow flow of hydrogen into and through solid materials. It occurs by splitting of H₂ and migration of monatomic H into the surface of a metallic solid, with internal storage, and recombination as H₂ on the downgradient surface. The process can be measured but is slow, possibly 1 to 2 orders of magnitude slower than needed to disperse radiolytic hydrogen generated in a few hundred years. *Survey of literature on applicable permeation measurements, and calculation of leakoff rate from a DPC, are needed.*

Getters in gaseous systems are solid materials such as Ti or Mg metals that absorb H₂ or other gases without significant change in solid volume. With treatments such as activation by heating, materials such as Mg can be made to take up on the order of 5% H₂ by weight. For the 2,600 moles of H₂ estimated above, approximately 100 kg of Mg (or more) would be needed. Getters such as Mg and Ti foils that work in vacuum systems would need to be formulated to work in a moisture environment. Organic getters are also used, but would be subject to radiolytic breakdown. *The availability of novel getters that absorb H₂ in moisture environments should be further examined.*

The foregoing discussion focuses on gamma radiolysis of water, but there is also a possibility for direct exposure of UO₂ to the filler moisture environment, with alpha radiolysis. Previous studies have assumed that a small fraction of spent fuel rods have defective cladding (see assumptions). Such an initial condition is difficult to avoid in analysis because direct detection of defective cladding in irradiated fuel assemblies would be prohibitive. Hence alpha radiolysis must be assumed in the vicinity of some of the fuel. *An approach to estimate alpha radiolysis activity should be developed using current spent fuel postclosure degradation models, and used to better understand the chemical environment in affected regions.*

Finally, for DPCs containing plates of aluminum-based material as neutron absorbing material (mainly Boral[®] or Metamic[®]) the reaction of aluminum and water could produce approximately 30 kmoles of H₂ represented stoichiometrically by the reaction:



giving an estimate for the amount of H₂ produced (assume 52 plates for a 32-PWR assembly canister):

$$\begin{aligned} N_{\text{H}_2} &= (\# \text{ plates})(\text{area} \times \text{thickness})(\text{Al density}/\text{MW}) \times (1.5 \text{ mol H}_2/\text{mol Al}) \\ &= 52 \times (0.2 \text{ m} \times 4 \text{ m}) \times 0.006 \text{ m} \times (3,000 \text{ kg/m}^3 / 0.023 \text{ kg/mol Al}) \times 1.5 \\ &= 5 \times 10^4 \text{ mol H}_2 \end{aligned}$$

Note that if neutron absorber plates do not degrade significantly prior to canister breach from other causes, then gas production from Al corrosion will not be important. Similarly, stainless steel corrosion could yield on the order of 1 mole/yr of H₂ for 100 nm/yr corrosion rate, depending on availability of moisture or oxidants (H₂O or H₂O₂). *Further thermodynamic and kinetic analysis is needed for the multiple processes that would compete for residual moisture in cement fillers (e.g., corrosion of Boral[®] and other metallic materials vs. bound and adsorbed water in cement).*

4.4 Thermal Expansion/Contraction

Linear thermal expansion of 304 stainless steel ($17.3 \times 10^{-6} \text{ C}^{-1}$) is greater than for cement and concrete (10^{-5} C^{-1} as an analog for filler cement), so the shell would not be stressed during cement curing and temperature increase. However, after some years of heating and final cure of the cement, gradual contraction of the shell could induce tensile stress on the order of 180 MPa, as shown by the following scoping calculation:

$$\epsilon = \Delta T \times (\alpha_{\text{SS304}} - \alpha_{\text{Filler}}) = 125 \text{ C}^\circ \times (17.3 \times 10^{-6} \text{ C}^{-1} - 10^{-5} \text{ C}^{-1}) \approx 0.09\% \text{ tensile strain}$$

acting in stainless steel with Young's modulus of 200 GPa. This assumes no inelastic deformation of the filler, and no void space between the filler and the internal surfaces of the canister. The calculated tensile strain would be developed very gradually, and is less than the yield strength of the canister shell (but does not include possible pressurization from radiolytic gas generation). *Thermal expansivity during cure and eventual cooldown needs to be measured for filler materials.*

5. Filler Material Selection

This section reviews available fillers and makes preliminary selections for testing, in two groups: slurry cements (typically water based), and low-temperature molten materials (e.g., molten metals). In addition, a preliminary investigation of dry particulate fillers is described.

The selection produces lists of candidate materials in each group, for laboratory and possibly scale-model testing. Selection criteria are identified, and advantages and disadvantages are indicated qualitatively. This selection process can be revisited at any time, for example if undesirable attributes are discovered for certain materials, or additional materials become available.

5.1 Previous Studies

Maheras et al. (2012) reviewed filler material analyses done initially by the U.S. Department of Energy (DOE; Fish et al. 1982; Forsberg 1997, 2000; Forsberg et al. 1995; Pope et al. 1996; Wynhoff et al. 1982), Allied-General Nuclear Services (Anderson 1981), the Canadian Nuclear Fuel Waste Management Program (Johnson et al. 1994; Shelson 1983; Teper 1987a,b), the Belgian waste management program (Bennett and Gens 2008), Spain (Puig et al. 2008a,b), Sweden (Oversby and Werme 1995; Puig et al. 2008a,b), and more filler studies done later by the U.S. DOE Yucca Mountain Project (Arthur 2000; Cogar 1996a,b; Mobasheran 1999; Montierth 2000; Moscalu et al. 2000; Radulescu 2001; Wallin 1996). Fillers considered by these programs include oxides/silicates, injected metal alloys, organic binders, sands, air/gases, glass, graphite, boron carbide, cements, glass beads, bauxite, depleted uranium compounds, metallic shot, zeolites, phosphate minerals, and clays. Although a wide variety of filler materials has been identified, there is only sparse information available about injection or emplacement of the materials into fuel canisters (Maheras et al. 2012).

A range of water-based slurry cements is developed below that represents previous work on such cements, and adds some new compositions. Past work has emphasized dry particulate fillers, for example Oversby and Werme (1995) considered glass beads, lead shot, copper spheres, sand, olivine, hematite, magnetite, crushed rock, bentonite clay, other clays, and concrete. Of these, glass beads were identified as the leading type because they can be made to contain one or more burnable poisons and have a number of other positive features including the ability to manufacture beads with homogeneous properties. Copper spheres were also identified because copper would already be present in the Swedish engineered barrier system. Magnetite was also identified because it is likely to be present in the host rock.

5.2 Filler Selection for Testing

The discussion below focuses on fillers that can be injected into DPCs as slurries or molten metals, to form a monolith after curing or cooling. We avoid dry powders, grains, and beads (Teper 1987a,b) which might be difficult to inject into interstices, and typically do not react together to form a monolith. (Scoping investigation of dry particulate filler performance is discussed below.)

Criteria for qualitative comparison of cement or molten metal alternatives include the following:

- **Injectability** – The ease of handling, mixing, pumping, and emplacement of filler material. Candidate fillers must be injected through one or more ports with inner diameters of roughly 10 to 20 mm. The ease of maintaining filling rate and temperature conditions to control solidification. Pumpable so that ~6,000 liters can be pumped into a canister and flow into all interstices, before setting as a monolithic pour.

- **Void Filling** – Self-leveling, and readily penetrates DPC interstices with apertures as small as ~1 mm. While filling small voids, it also acts as a carrier and binder for boron carbide powder, or other chemically inert particulate.
- **Long-Term Chemical Stability** – Forms a long-lasting solid with expected longevity of thousands of years in groundwater, and natural analog evidence. Filler has low permeability to groundwater after package breach, which can slow its degradation. Filler may delay degradation of basket components such as neutron absorber plates, by limiting moisture availability.
- **Retrievability/Recoverability** – Can be removed from filled canisters for safety reasons, or to recover economic value in spent fuel. Retrievability may be a second-order concern, because if entire waste packages can be retrieved then they can generally be processed by various methods to separate spent fuel constituents.
- **Material Compatibility** – Chemically inert or reacts very slowly with DPC internal components, especially Zircaloy cladding and aluminum-based neutron absorber or structural materials. Stable to groundwater and chloride brine (permits use in a salt repository) after set and during aging at temperature. Controllable shrinking/expanding behavior during initial set and subsequent gradual cooling (limits stresses and maintains low permeability). Filler readily bonds to metal surfaces of the fuel and canister internals (promotes void filling and durability).
- **Moderator Displacement** – Capability to eliminate water and other neutron moderators from the canister.
- **Gas Generation** – Gas generation by chemical reactions or as a result of radiolysis, is limited or can be controlled so as to avoid initiating canister rupture. Resists radiolysis from gamma and neutron radiation. Filler has low water content (to control porosity and to limit radiolytic gas generation).
- **Solidification Temperature** – The conditions of emplacement, particularly temperature, are consistent with maintaining the integrity of both the filler and the spent fuel. Solidifies in a temperature environment of ~150°C (a nominal temperature for spent fuel rods after some aging). Controllable heat of fusion or reaction (e.g., on the order of roughly 10 W per liter, during set) to limit contribution to the peak temperature. Thermal conductivity before and after set is sufficient to dissipate heat of fusion and waste heat, so the filled canister temperature stabilizes at an acceptable and predictable level.
- **Toxicity** – Filler material does not include large amounts of constituents that are known toxins (e.g., regulated metals).
- **Radionuclide Sequestration** – Certain chemical affinities may exist between fillers or their weathering products, and long-lived radionuclides important to repository performance assessment (PA). Examples include actinides and phosphates, and iodine and bismuth solids.
- **Material Cost** – Filler material cost is reasonable (e.g., commensurate with selection of filling vs. other approaches to fuel preparation such as re-packaging).

5.2.1 Slurry Cements

Because the DPC filler must physically stabilize the fuel elements, stabilizers, and neutron poisons in place to prevent criticality for at least several thousand years, the DPC filler must be made of a material that can maintain structural integrity for several thousand years, possibly in contact with groundwater. Consideration of high-solids cements is motivated by geologic and archaeological observations that certain materials are stable in nature and that natural analogues exist. For example, pozzolanic cements used by the Romans still maintain structural integrity today. The ancient Greeks also used pozzolanic cements hundreds of years before that. A DPC filled with cement might therefore be expected to maintain some structural integrity for a few thousand years. Analogous arguments could not be made for DPCs filled with recently developed man-made materials such as organic polymers.

The term slurry cements identifies formulations that contain relatively insoluble solid constituents such as silica, alumina, etc., in significant amounts, but which can serve as pumpable grout. Some constituents of slurries may be soluble (e.g., CaO) but not all, as would be the case if liquids were mixed to form insoluble precipitate. Such chemical solution grouts (or ultrafine, low-solids slurries) have special properties such as rapid setting, adhesion, expansivity, and light weight, and they may be used where more conventional slurry cements have not performed.

Ordinary Portland Cement

Milestone (2006) reviewed radionuclide immobilization in cements and emphasized their inexpensiveness, availability, ease of preparation and “ability to penetrate complex waste forms”. Moreover, cements are radiation-stable and, because of their alterable composition, provide operational flexibility.

Ordinary Portland cement (OPC) is a sintered mixture of calcium silicates, gypsum, and minor fillers. OPC has also been blended with fly ash, blast furnace slag, and volcanic ash (pozzolans). Two obstacles to using OPC are the high temperatures caused by its exothermic reaction with water, and high pH (> 12) in the water in contact with the cement. Including blast furnace slag and fly ash decreases the temperature swing, and attendant thermal stresses, and lowers the pH slightly. The high pH of OPC fluids would be detrimental to DPC performance because it would favor corrosion of aluminum metal in the Boral[®] neutron absorber, and because most of the radionuclides in the fuel sorb sparingly and are highly soluble under high pH conditions. Little radionuclide retardation would occur in an OPC filler once fuel elements were exposed to water.

Predicting the long-term stability of OPC is problematic because it is a metastable mixture of phases that transform to more thermodynamically stable assemblages through largely uncertain kinetic pathways. Carbonation, the formation of calcite and a reduction in solution pH, occurs rapidly and predictably near and on OPC surfaces, but the long-term reaction of calcium silicates in OPC is less clear.

Chemically Bonded Phosphate Cements

Chemically bonded ceramics have ionic or covalent bonds instead of hydrogen bonding and van der Waals bonds that are active in Portland cement (Wagh 2004). So-called ceramic cements are ceramic because of chemical bonding, and cements because they are mixed and set at low temperature. Phosphate ceramics are inorganic, nontoxic, have neutral pH, and are insoluble (at near-neutral pH). They are made from low-cost naturally occurring materials, and they are self-bonding, i.e., a second layer will bond to the previous one. Encapsulation of radioactive waste in

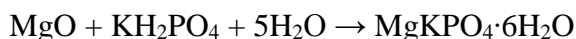
the U.S. and other countries is a major application of chemically bonded phosphate cement (Wagh 2004).

Phosphate cements are typically grouped with acid-base cements, because they involve reaction of a soluble source of metal cations (e.g., MgO or ZnO) and an acidic phosphate salt. Calcium is quite soluble as CaO leading to very fast reaction times, so Ca-phosphate formulations rely on other Ca compounds such as phosphates, aluminates, or carbonates. The following discussion focuses on cements that have been previously studied (and which in some cases are commercially available). These include phosphate cements with Mg and Ca, and Ca-aluminate-phosphate cement, all of which are considered chemically bonded. It also included Ca-aluminate and Ca-sulfoaluminate cements, which are considered hydraulic cements.

Aluminum phosphate cements are not included in the following discussion because they are not amenable to slurry emplacement and control of final porosity. They exhibit resistance to water only after being heated to 150°C or greater, which converts unstable hydrous phases to crystalline berlinite (AlPO₄). The conversion liberates water and creates porosity (Wagh 2004, Section 11). To control final bonded porosity and strength, the particulate alumina must be initially graded or compacted to limit void space, before wetting with concentrated phosphoric acid. The amount of berlinite in converted cement is evidently relatively small, serving to coat particles of unreacted alumina (Wagh 2004).

Mg-Phosphate Cements

Mg-phosphate cements (MgPCs) are less exothermic than OPC and result in lower pH (4 to 8). Ceramicrete[®] is a Mg-phosphate cement developed at Argonne National Laboratories (Singh et al. 1997) for stabilizing waste streams (Covill et al. 2011; Stefanko et al. 2011). The Ceramicrete synthesis reaction is:



Not all of the particulate MgO is reacted once the cement sets (~ 2 hours). The only clear natural analogue for Mg-phosphate cements comes from ancient middens where the mineral struvite is found. These cements develop high strength, are resistant to temperature swings and road salt, and maintain bond strength better than other construction materials (Wagh 2004, Section 9.3). They tend to cure more slowly than other chemically bonded cement types and can therefore be used more readily in large monolithic pours.

Calcium Aluminate Cement

Calcium aluminate cement (CAC) is typically formulated from fused limestone and bauxite, ground to fineness. The manner and temperature of kilning distinguish various commercial products. CAC may contain some silica, but calcium aluminates generally take the place of the calcium silicates in OPC. It may be mixed with OPC to accelerate strength while maintaining self-leveling, and to provide resistance to heat and chemical attack. CAC is considered to be a hydraulic cement and not chemically bonded (Wagh 2004). Calcium and alumina are combined to form Ca-aluminate hydrate as the bonding phase. CSACs have exceptional early strength development and durability.

Calcium Sulfoaluminate Cement

Ca-sulphoaluminate cement (CSAC) is a variant of CAC that includes sulfate from a source such as gypsum, that promotes the growth of crystalline ettringite. CSAC provides similar advantages

to CAC with the addition of sulfate resistance. Whereas ettringite is stable, the presence of abundant sulfate in the canister environment could promote microbial activity (e.g., *Desulfovibrio sp.*) and/or the formation of corrosive H₂S. This comparison may not be relevant to filler performance, however, it is considered as a complicating factor in the discussion below. CSAC is also considered to be a hydraulic cement and not chemically bonded, although it derives chemical stability from ettringite.

Calcium Aluminate-Phosphate Cement

Calcium aluminate-phosphate cement (CAPC) has been formulated for use as wellbore cement, by mixing CAC and sodium polyphosphate. Other formulations use concentrated phosphoric acid (Wagh 2004, Section 15). After reaction the primary phases are hydroxyapatite (Ca₅(PO₄)₃(OH)₂), boehmite (AlOOH), hydrogarnet (Ca₃Al₂(SiO₄)_x(OH)_{4(3 - x)}), and the zeolite analcime (NaAlSi₂O₆·H₂O).

Hydroxyapatite is stable in sedimentary rock formations (natural analogs), sorbs and sequesters radionuclides (e.g. Moore and Rigali 2015; Rigali et al. 2016) and is a component in sealants for geothermal wells (Sugama 2007). Other naturally occurring secondary Ca-phosphate minerals include monetite and brushite. Natural analogue support for the use of calcium phosphate cements comes from buried vertebrate bones and teeth made of apatite which can remain intact for thousands of years. A complicating factor is that bones and teeth contain organic matter in addition to calcium phosphate, but pure calcium phosphate would be used to fill DPCs. Dental enamel has a lower organic content and is more resistant, and is probably a better analog than bone. Higher calcium phosphate content increases the likelihood of fracture.

Water and acidic conditions (pH < 5) *in situ* can sharply decrease the persistence of calcium phosphate, which could be useful because a mildly acidic solution (pH 4) could be used to dissolve and flush calcium phosphate from canisters for intact fuel retrieval. Acidic conditions are not expected to prevail in filled DPCs because: 1) natural waters require particular conditions such as abundance of reduced sulfur, to become acidic, and 2) the contents of DPCs will be selected so as not support acid-generating reactions.

CAPC is used in geothermal wells at high temperature (Sugama 2007). Thermalock[®] is a CAPC product sold by Haliburton, which is CO₂ and acid resistant. Citric acid is used as a retarder and the material can be foamed using surfactants, though foaming can cause connected, open bubbles, and possibly an undesirable increase in hydraulic permeability. Post-setting cracking in wellbore applications is prevented by the addition of milled carbon microfibers (up to 14 wt %). In practice, Thermalock[®] is reported to achieve (Sugama 2007):

- Pumpability for at least 3 hours (followed by set).
- Compressive strength > 3.5 MPa (500 psi) at 24 hour-curing time.
- Water permeability < 10⁻⁴ Darcy.
- Bond strength to steel casing > 0.35 MPa (50 psi).
- Fracture toughness > 0.008 MN/m^{3/2} at 24 hour-curing time.
- Cost < \$15/bag (42.7 kg).
- Slurry density of foamed cement < 1.3 g/cm³.

The service life of Thermalock[®] cement in a corrosive geothermal environment is estimated to be ~20 years (Sugama 2007). Its persistence in more benign chemical environments must be verified.

Calcium Phosphate Cements

Calcium phosphate cements have been developed for medical/dental repair of bones and teeth (e.g. Meffert et al. 1992; Ong and Chan 2000). A potentially important aspect of dental cements described in the literature is short setting time which would need to be retarded by complexing calcium ions or by dilution with water. The large number of published recipes, the simplicity of the final hydroxyapatite composition, and its similarity to natural analogs make an attractive alternative to CAPC although additional testing will be needed to formulate a self-leveling grout.

The foregoing categories of cements are listed in Table 5, which provides compositional information for published examples, and reported types of testing performed.

Table 5. Information on published and commercially available phosphate cements.

Material	Type/Composition	Source/Contact	Testing Performed	Reference(s)
Mg-K-PO₄ Cements (MgPC)				
Ceramicrete	MgKPO ₄ binder (moles): MgO 1 KH ₂ PO ₄ 1 H ₂ O 5	Dileep Singh/ANL (630/252-2785)		
Modified Ceramicrete ANL Mix 071510	MgKPO ₄ cement mixture (grams): SR3.10 Binder 17.4 Class C fly ash 20.8 Sand 48.4 Boric acid powder 0.9 Water 12.5	Dileep Singh/ANL (630/252-2785)	Tested in adjunct to SRNL study: Expansion Peak temperature Working time static/dynamic (ASTM D-6103) Flow cone/viscosity (ASTM C-939) Compressive strength (ASTM C-942 or D-5873)	Stefanko et al. (2011)
Bindan SR3.10 Binder	MgKPO ₄ cement binder	Tom Lally/Bindan (630/734-0277)	Used as ingredient for SRNL studies; see Mix 34	http://bindancorp.com/bindan-technology/
Bindan Mono-Grouts	Combining binder, fly ash, and aggregate types	Tom Lally/Bindan (630/734-0277)	Tested in SRNL study: Expansion Working time static/dynamic (ASTM D-6103) Compressive strength (ASTM C-942 or D-5873) Adiabatic calorimetry (temperature rise)	http://bindancorp.com/bindan-technology/ Stefanko et al. (2011) used Class F fly ash to prevent separation
SRNL Reactor-P Grout Recommended Mix 34	Grout mixture (% w/w): SR3.10 binder 14.0 Class F fly ash 19.3 KIM 301 water-proofing 1.0 ASTM C33 masonry sand 54.3 Chilled water (10°C) 12.3 Boric acid retarder (as needed) Other set retarder (e.g. Grace Daratard 17) (as needed)	Christine Langton/SRNL	Tested in SRNL study: Expansion Working time static/dynamic (ASTM D-6103) Flow cone/viscosity (ASTM C-939) Compressive strength (ASTM C-942 or D-5873) Adiabatic calorimetry (temperature rise)	Stefanko et al. (2011) found MKP binder to be slightly expansive (decreased with boric acid)
Ca-Aluminate Cements (CAC)				
CAC cement binder (not mixed w/ aggregate)	Limestone (CaO < 40% w/w) Bauxite (Al ₂ O ₃ > 37% w/w) (SiO ₂ < 6% w/w) (Fe ₂ O ₃ < 18.5% w./w) (no added silica)	Royal White Cement 8316 East Freeway. Houston, TX 77029 866-923-6368	Autoclave expansion Wet density Thermal expansion Compressive strength Tensile strength Dielectric constant Dielectric strength Resistivity Thermal conductivity	www.royalwhitecement.com

Material	Type/Composition	Source/Contact	Testing Performed	Reference(s)
Sauereisen Electrical Potting Cement No. 76	Single-component hydraulic CAC (casting/molding; moisture required for cure)	160 Gamma Dr. Pittsburgh, PA 15238 412-963-0303	Autoclave expansion Wet density Thermal expansion Compressive strength Tensile strength Dielectric constant Dielectric strength Resistivity Thermal conductivity	www.sauereisen.com
Ca-Sulphoaluminate Cements (CSAC)				
CSAC cement binder (not mixed w/ aggregate)	Limestone (CaO < 42.5% w/w) Bauxite (Al ₂ O ₃ > 34% w/w) (SiO ₂ < 10% w/w) (Fe ₂ O ₃ < 2.5%) (no added gypsum or silica)	Royal White Cement 8316 East Freeway. Houston, TX 77029 1-866-923-6368	Compressive strength vs. time Other ?	www.royalwhitecement.com
Ca-Aluminate Phosphate Cements (CAPC)				
Waste encapsulation cement R&D	CAC cement mixed with NH ₄ H ₂ PO ₄ fertilizer solution	Brookhaven	XRD (crystalline HA)	Sugama & Carciello (1991)
Thermalock Cement	Calcium aluminate cement (30–60%) Fly ash (30–60%) Sodium polyphosphate (1–5%) Crystalline silica, quartz (1–5%)	Haliburton	Various	http://www.halliburton.com/en-US/ps/cementing/materials-chemicals-additives/cement-blends/thermalock-cement.page
Ca-Phosphate Cements (CPC)				
Soil stabilization by chemical grouting	NH ₄ H ₂ PO ₄ and (NH ₄) ₂ HPO ₄ solutions mixed to desired pH (4 to 8), combined with either Ca(NO ₃) ₂ or Ca(CH ₃ COO) ₂ solution, repeated over a range of concentrations, and mixed with a clean sand fraction.	University research project	pH Compressive strength vs. time	Akiyama and Kawasaki (1991) achieved set; found strength to be ~0.1 MPa.
Dental cements	Various acid-base cement formulations, typically forming hydroxyapatite, and using fillers such as silica.	Various vendors and published research	Various including setting time, strength, and resistance to leaching.	Wilson and Nicholson (2007) Zhang et al. (2011)

Comparison of Cement Slurry Fillers

Qualitative comparison of the cement types discussed above is provided in Table 6. Differences among the candidate types include:

Injectability

- All cement types identified are injectable if mixed with enough water (which degrades other properties such as porosity and radiolytic gas generation).
- CPC probably requires development of a slurry with self-leveling properties and pumpability (the other types have already been developed as grouts).
- Differences in porosity may result from differences in the amount of water needed for injectability.

Void Filling

- All cement types rely on water as a vehicle and will wet the canister and fuel surfaces.

Long-Term Chemical Stability

- Chemical stability of CAPC and CPC may be superior because of Ca-phosphate bonds.
- Long-term chemical stability of OPC based formulations may be limited as there are few, if any, natural analogs of the same composition (compared with phosphate minerals).
- Stability of MgPCs has been extensively tested in nuclear waste encapsulation applications (Ceramicrete; Singh et al. 1997; Covill et al. 2011).

Retrievability/Recoverability

- Ca-phosphate and Mg-phosphate bonds can be dissolved with a dilute acid such as HCl.
- Dissolution of Ca-aluminate bonds and solubilization of the products has not yet been tested.
- Similar acidic conditions can attack OPC formulations but may leave insoluble residues.

Material Compatibility

- Material interactions will be examined in the manner of Milestone (2006).
- Material compatibility questions with OPC and CSAC involve the microbial utilization of sulfate.
- Material compatibility questions with CAC and CSAC involve the possible addition of alkaline salts to activate the alumina (cements containing phosphate have circum-neutral pH and may exhibit additional buffering).
- Ca-aluminate and Ca- or Mg-phosphate formulations should not attack stainless steel or Zircaloy if the pH is circum-neutral both before and after set.
- Bonding to metallic surfaces and to previously poured cement, and controlled expansion/shrinkage, have been established for the commercial binder products (Table 5).

Moderator Displacement

- Water content will be challenging for all cement slurry formulations, such that capacity to stabilize a neutron absorbing filler (e.g., B₄C) is required.

Gas Generation

- The presence of water and any organic constituents of cements may require measures to control radiolytic gas accumulation (which could build up gas pressure).

Solidification Temperature

- Solidification temperature has been studied for CAPC borehole cement (Wagh 2004) but needs to be evaluated for other formulations to assure that adequate set can be obtained following the temperature-time trajectory anticipated for fillers.

Toxicity

- Toxicity is low for all cement types considered.

Radionuclide Sequestration

- Actinides (U, Pu) are readily immobilized by phosphate in groundwater environments.

Material Cost

- Material cost could be low for OPC-based formulations, but greater for chemically-bonded cements requiring more expensive components.

Given the similarity of the cement types and their availability, representative compositions from each subgroup of cements identified in Table 5 will be selected for testing, screening, and demonstration as discussed in Sections 6 and 7. Preliminary recipes are noted in Table 6.

Table 6. Comparison of slurry cement options on selection criteria.

Material	Injectability	Void Filling	Long-Term Chemical Stability	Retrievability/Recoverability ^E	Material Compatibility	Moderator Displacement	Gas Generation	Solidification Temperature	Toxicity	Radionuclide Sequestration	Material Cost	Recipe Guidelines (w/w % of solids)	Potential Source
Generic OPC			–	?	–	–		?			+	For comparison only.	
Magnesium phosphate cement (MgPC)				+		–		?			+	(based on Mix 34 from Table 2) SR3.10 binder 20 Class F fly ash (reactive) 20 Fine silica sand 60 Water (sufficient; nom. 15 g/100 g) Retarder ^A (as needed)	Bindan Corp. (binder) Oak Brook, IL 630/734-0277
Calcium aluminate cement (CAC)			?	?	?	–		?			?	CAC binder (RWC 40) 10 to 100% Fly ash Type C (inert) 10 to 30% Fine silica sand (inert) 10 to 40% Water (sufficient) Retarder ^A (as needed)	Royal White Cement Co. (binder) Houston, TX 713/676-0000
Calcium sulfoaluminate cement (CSAC)			?	?	?	–		?			?	CSAC binder (RWC) 10 to 100% Fly ash (Type C, inert) 0 to 30% Fine silica sand (inert) 0 to 30% Water 20 to 50% Retarder ^A (as needed)	
Calcium aluminate phosphate cement (CAPC)			?	+		–					+	Haliburton ThermoLock [®] (mix as provided)	Halliburton Corp. (mixed cement product) Houston, TX /871-4000
												Deep/Geothermal Cement Alternative ^B Calcined alumina 96.8% Aluminum hydroxide 2.2% 45% H ₃ PO ₄ solution 48.4 mL per 100 g dry	
Calcium phosphate cement (CPC)	?		+	+		–		?			+	Geothermal CAPC Alternative ^B Monocalcium aluminate (CaAl ₂ O ₄) 24% Sodium polyphosphate (Na ₅ P ₃ O ₁₀) 40% Fly ash (Type C, inert) 36% Water (sufficient)	Bindan Corp. (binder compounds) Oak Brook, IL 630/734-0277
												Binder (TTCP 73%, DCPA 27%) ^C 10 to 100% Fly ash Type C (inert) 10 to 30% Fine silica sand (inert) 10 to 40% Water (sufficient) Retarder ^A (as needed)	

Notes:
^A Boric or citric acid in dry form. ^B Wagh 2004, Table 15-2. ^C Wagh 2004, Section 13.4; TTCP is Ca₄(PO₄)₂O and DCPA is CaHPO₄, mixed in stoichiometrically for hydroxyapatite Ca₅(PO₄)₃·OH.
^D This is a qualitative table and the entries are approximate: “+” signifies desirable attributes, “–” signifies undesirable, and no-entry signifies neither.

5.2.2 Low-Melting Point Metal Alloys

Candidate metallic materials with natural analogue evidence of long-term stability include Bronze Age (~5,000 BC) and Iron Age (~1,300 BC) artifacts. Materials suitable for tools and weapons, have strength and thermal properties that may not be amenable to DPC fillers. However, there are a large number of low-melting temperature metals and alloys available, as suggested by the list in Table 7.

While various types of glass are abundant in the geologic record and relatively stable, only two low-melting point glasses are included in Table 7.

Available Alloys and Sources

Metal/metal-alloy pours should have the following characteristics (e.g., Johnson et al. 1994):

- Possess no major defects, e.g. shrinkage voids.
- React minimally with DPC steels and cladding.
- Have low casting temperature to reduce thermal stresses.
- Wet steel and cladding surfaces to aid void filling.

Eutectic composition is desirable because the liquid-solid transition occurs at a discrete temperature, avoiding a “pasty” temperature band within which the mixture is neither uniformly liquid or solid. Defined melting-solidification temperature also occurs with pure metals. Even with eutectic compositions, a transition occurs whereby the mixture remains both partially liquid and solid, as the latent heat of fusion dissipates (cooling), or is provided externally (melting). Molten metals may exhibit substantial (a few percent) volume increase on solidification.

Metals

Low-melting point metals that can be used as fillers include tin, lead, bismuth, cadmium, and zinc. Melting points for tin, lead, bismuth, and cadmium are below 350°C. Zinc has a melting point of 419°C. Lead and cadmium are regulated materials and in particular lead is toxic, very heavy, and can cause embrittlement of other metal components. In addition, zinc has the potential to interact with fuel cladding. However, for this intended filler application potential cladding interactions may not be critical.

Metal Alloys

Low-melting point eutectics can be formed by combining the above metals in proper ratios. For example, the Sn₆₃Pb₃₇ alloy, a solder used in electronics, has a melting point of 183°C. A lead-free or cadmium-free eutectic, e.g., Sn_{95.6}Ag_{3.5}Cu_{0.9} with a melting point of 217°C or Sn₉₁Zn₉ with a melting point of 199°C, should also be investigated.

Glasses

Glasses are known for their excellent chemical stability and can be a promising candidate as DPC fillers. Borosilicate glass is used extensively in vitrification of high level waste and it has been shown that fission product particulates are immobilized in glass matrix. However, common glasses have very high melting points (>1000°C), i.e., much higher than some canister components such as aluminum. Recently, low-melting point glasses have been formed with melting temperatures in the approximate range 220 to 400°C. For example, Vaneectect[®] with melting point less than 300°C or solder glass with melting point less than 400°C could be viable candidates.

Table 7. Candidate molten metal/metal alloy filler characteristics.

Label ^A	Composition	Melting Point (°C) ^B	Ref.
Pure Metals			
Tin	Sn 100%	232	1
Bismuth	Bi 100%	271	
Cadmium	Cd 100%	321	
Lead	Pb 100%	327	
Zinc	Zn 100%	419	
Alloys			
Low 117 [®]	Sn 8.3% Pb 22.6% Bi 44.7% Cd 5.3% In 19.1%	47	2
Low 136 [®]	Sn 12% Pb 18% Bi 49% In 21%	58	
Bend	Sn 13.3% Pb 26.7% Bi 50% Cd 10%	70	
Woods	Sn 12.5% Pb 25% Bi 50% Cd 12.5%	70 – 76	
Safe	Sn 11.3% Pb 37.7% Bi 42.5% Cd 8.5%	71 – 88	
Mellottes	Sn 15.5% Pb 32% Bi 52.5%	95	
Rose	Sn 25% Pb 25% Bi 50%	95 – 115	
Matrix [®]	Sn 14.5% Pb 28.5% Bi 48% Sb 9%	103 – 227	
Base	Pb 44.5% Bi 55.5%	124	
Pb36A	Sn 62% Pb 36% Ag 2%	179	
Pb37A	Sn 63% Pb 37%	183	
PB40A	Sn 60% Pb 40%	183 – 191	
Sn10A	Sn 10% Pb 90%	275 – 302	
Sn03A	Sn 3% Pb 97%	314 – 320	
Pb94B	Sn 5% Pb 93.5% Ag 1.5%	296 – 301	
Alloys (lead/cadmium free)			
Tru [®]	Sn 42% Bi 58%	138	2
Cast [®]	Sn 60% Bi 40%	138 – 170	
KappAloy9 [®]	Sn 91% Zn 9%	198	1
Tin foil	Sn 92% Zn 8%	199	
Indalloy [®]	Sn 95.6% Ag 3.5% Cu 0.9%	217	
Sn96A	Sn 96.3% Ag 3.7%	221	3
AG40B	Zn 96% 4% Al	381-387	1
Glasses			
Solder glass	PbO-B ₂ O ₃	320-380	4
Glasses (lead free)			
Vaneetect [®]	VO-Ag	220-300	5

^A ANSI/J-STD-006 or other. ^B A single value signifies eutectic composition.

References:

¹ <http://www.matweb.com>

² www.belmontmetals.com/product/eutectic-alloys

³ www.ami.ac.uk/courses/topics/0128_sm/index.html

⁴ www.telux-glas.de/content/en/downloads/solder-glass.pdf

⁵ phys.org/news/2012-11-300c-low-melting-glass-hermetic-gold-tin.html

Comparison of Molten Fillers and Recommendation for Testing

Qualitative comparison of the metal alloy types discussed above is provided in Table 8. This comparison is based on the following assumptions:

- Molten metals/metal alloys are expected to exhibit injectability and void filling performance as long as the canisters and fuel surfaces are wetted by the melt. Glasses may be more viscous and sticky (hence their description in the literature as sealants).
- For molten metal/metal alloy fillers long term chemical stability in the intact canisters is plausible, but remains to be tested for repository conditions after package breach and exposure to groundwater.
- Material compatibility may be questionable for metallic fillers due to possibility of galvanic reactions; on the other hand metallic fillers may galvanically protect the fuel or waste package. Also, telluric currents in the disposal environment may be important.
- Glass is electrically non-conductive (which limits heating options).
- Metals will likely not produce gas after solidification and prior to package breach (when gas pressure is important to canister integrity). However, off-gassing of glass from aging and radiation dose may be possible
- Pure metals and typical glasses have higher solidification temperatures than metal alloys, particularly eutectic compositions.
- Metals, alloys and glasses are particularly toxic if they contain Pb or Cd, although not all candidates contain these elements.
- Material cost will be higher if the filler contains much Sn or Ag. Cost of Vaneetect[®] glass is unknown.
- Some compaction following solidification is likely for metal-based fillers.
- Handling is uncertain due to heating requirements.

Molten metals/metal alloys require development of handling and heating capabilities to avoid premature solidification during filling.

Given the similarity of the molten metal types and their availability, representative compositions from each subgroup identified in Table 7 will be selected for investigation as discussed in Section 6.2.

Table 8. Comparison of molten metal/metal alloy and glass options on selection criteria.

Material	Injectability	Void Filling	Long-Term Chemical Stability	Retrievability/Recoverability	Material Compatibility	Water Content	Gas Generation	Solidification Temperature	Toxicity	Radionuclide Sequestration	Material Cost	Recipe Guidelines (w/w %)	Potential Source
Pure Metals (Sn, Bi, Cd, Pb, Z)			+	?	?	+	+	-		?			
Metal Alloys			+	?	?	+	+		-	?	-	Sn based alloys: Sn: 3-60% Pb: 15-95% Cd, Bi: as needed Pb based alloys: Pb 44.5% Bi 55.5%	Belmont Metals Inc. 330 Belmont Avenue Brooklyn, NY 11207
Metal Alloys (Pb- and Cd-free)			?	?	?	+	+			?	-	Sn based alloys: Sn: 40-95% Zn, Bi, Ag, Cu: as needed Zn based alloys; Zn: >90% Al: as needed	
Glasses (e.g., solder glass)	?	?	+	?	?	+	?	-	-	?	?	PbO-B ₂ O ₃	TELUX Spezialglas GmbH Weißwasser, Germany
Glasses (lead free)	?	?	?	?	?	+	?			?	?	VO	Hitachi Chemical Co., Ltd.
<p>“+” signifies desirable attributes, “-“ signifies undesirable, and no-entry signifies neither.</p> <p>Notes:</p> <ol style="list-style-type: none"> 1. This is a qualitative table that lumps together filler materials without distinguishing their differences, so the entries are approximate. For example, material costs for the pure metals shown vary widely and are shown as neither desirable nor undesirable, whereas material costs for metal alloys are shown as undesirable due to the market prices of Sn and Bi which are needed for most low melting temperature alloys. 2. Injectability and void filling could be desirable attributes for metal/metal alloys, depending on wettability as discussed in the text. 3. Retrievability/recoverability is uncertain due to the possibility that remnants of the filler would essentially solder or seal fuel into the basket. 4. Solidification temperature is shown as undesirable, or neither, because of the burden of dealing with higher temperature (compared to cement fillers). 5. Toxicity is shown as undesirable for material categories likely to include Pb, and neither for others. 													

5.3 Dry Particulate Fillers

Dry particulate fillers offer the advantages of low temperature emplacement and low cost, without the complication of residual water in the canister when it is sealed. Their function would primarily be to provide criticality control by moderator exclusion and by incorporating neutron poisons (other functions have been identified such as radionuclide sequestration). The interstitial volume of particulate fillers would allow significant water in a flooded canister, at least before the particles degrade in contact with groundwater, hence the capability to include neutron poisons. Dry particles should have the capability to include neutron absorbers such as boron (e.g., in glass beads) or depleted uranium (DU; in purpose-made solid spherical particles).

To fill DPCs through ports and without cutting the lids off, the particles must flow. For best results the particles should be uniform, spherical, hard, and smooth (Cogar 1996a). To use the existing drain and vent ports, or new ports drilled into the canister sides, the particles must essentially behave as a self-leveling fluid. An alternative is to drill a separate port through the lid over each fuel assembly and fill each fuel cell by particles under the impetus of gravity alone; this alternative is currently out-of-scope for this workplan.

6. Testing and Analysis Needs

Testing will be conducted in phases to narrow the alternatives, combined with further definition of requirements and modeling of filler performance. Laboratory testing will be conducted first to support analysis and design of demonstration tests. Testing and demonstration of two approaches (low-temperature cement fillers, and high-temperature molten metal/metal alloy/glass fillers) will proceed in parallel unless and until there are indications that one or the other is infeasible. Each approach will start with multiple candidate materials, and will use carefully selected tests to down-select for further testing. This workplan will culminate in demonstration of filler emplacement in one or more physical models, with numerical simulation support. More than one such demonstration may be conducted with different filler materials. Ultimately this work is conceptual, and future decisions to implement a particular type of filler will be part of a design process that relies (at least in part) on the results produced here.

The following description of phased testing is presented separately for cements, including chemically bonded cements, and for molten metal/metal alloy/glass fillers. Laboratory testing during the first phases will support investigation of the following general areas, in approximate order of priority:

- **Injectability** – Void filling efficacy, and conditions of emplacement including temperature, heat generation and dissipation, and control of setting.
- **Durability and material compatibility** – Long-term chemical stability and resistance to degradation before package breach (aging and radiolysis) and after breach (exposure to groundwater and the disposal environment).
- **Gas generation** – Radiolysis and radiogenic helium production before waste package breach, and methods for mitigating the effect from gas accumulation on internal pressure.
- **Postclosure performance** – Efficacy of criticality control, and effects from radionuclide complexation and sorption, after waste package breach.
- **Retrievability and recoverability** – Feasibility of removing solidified filler from canisters, for retrieval of spent fuel.

Some of these areas may not apply to some filler materials, for example, gas generation may not occur prior to package breach, for metal/metal alloy fillers. Also, for areas such as injectability, options for testing may be skewed toward physical model studies rather than benchtop laboratory testing. These differences will be reflected in the specific tests proposed.

Toxicity and material cost will be evaluated using technical literature and other sources. Other aspects may also be evaluated without resort to testing, if sufficient information is already available. In general, easier test methods (safety, cost, duration) will be applied before more complex methods.

The following sections describe testing and analysis that will be performed prior to selecting candidate materials for physical model studies (i.e., scale demonstration, described in Section 7).

6.1 Testing for Cement Slurry Materials

Injectability Testing

Injectability testing will primarily involve quantifying cement viscosity, separation, setting time, physical properties, and entrained particle distribution for various cement recipes. Starting with the recipes described in Table 6, proportions (especially water content) will be adjusted to optimize these properties (e.g., Wang et al. 2013; Yue and Bing 2013).

Following the testing approach reported by Stefanko et al. (2011) for Mg-phosphate cements, an initial set of measurements will include the following tests performed repeatedly in Phase 1, focused on refining or modifying the recipes shown in Table 6. The following measurements can be conducted quickly on a large number of samples as needed:

- Flow cone/viscosity (ASTM C-939 *Standard Test Method for Flow of Grout for Preplaced-Aggregate Concrete – Flow Cone Method*) – Time of flow through a calibrated funnel, repeated at intervals after mixing indicates pumpability and self-leveling, and their duration.
- Working time, static and dynamic (ASTM C-143 *Standard Method of Test for Slump of Hydraulic Cement Concrete* or ASTM D-6103 *Standard Test Method for Flow Consistency of Controlled Low Strength Material*) – Simple tests performed at intervals after mixing to provide separate indication of pumpability and setting time.
- Separation, measured by allowing curing cement to rest in a graduated cylinder, and measuring the volume of liquid that separates over 2 hours (Wagh 2004, Section 15.2.4).
- Direct measurement of shrinkage/expansion during set and cure (Wagh 2004, Section 15.4.3). Measurements of expansivity of the cement during curing, and of the solidified filler material (at temperature) are needed to interpret final filled configuration (e.g., presence of gaps).
- Compressive strength (ASTM C-942 *Standard Test Method for Compressive Strength of Grouts for Preplaced-Aggregate Concrete in the Laboratory*) – Measurement after cure, on cubes cast in molds or sawn from larger samples. Strength (e.g., 28-day) indicates the extent of chemical bonding and consequent durability.
- Bulk density of cured samples using standard measurements of volume and weight.
- pH measurements of uncured slurry and cured material (pulverized, slurried in water) using pH paper.
- Major ion analysis of solutions separated (by settling and/or filtration) from uncured cements, by ion chromatography and atomic absorption or mass spectrometry. Samples will be acquired during the above activities, stabilized, stored, and analyzed later depending on which are most promising.

Detailed test planning will include numbers of variations (starting with varying water content around the nominal or medial recipe for each cement type from Table 6, to adjust viscosity and setting time) and numbers of replicates.

Testing will continue in Phase 2 using refined or modified cement compositions:

- Viscosity measurements made by rheometer or consistometer, wherein the mixture is mechanically stressed between moving plates or cylinders.
- Contact angle measurement with an optical goniometer, between uncured cements and stainless steel, aluminum, and zirconium alloy surfaces.
- Heat evolution from cement setting, measured using thermocouples in an insulated vessel (a total heat of reaction since rate of cure may be sensitive to temperature). Thermal analysis using measured cement setting enthalpies will be used to predict and optimize setting times (phosphate cement compositions) under the actual thermal regime of DPCs.
- Moisture content from thermal-gravimetric analysis (TGA).
- Porosity (grain density) measurement on cured, dried, and crushed samples using helium pycnometry.
- Gas permeability of just-cured samples (Wagh 2004, Section 15.2.5) using an approach such as ASTM C 204 (*Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus*). Permeability can be used to infer pore structure, and as a parameter in analysis of dewatering filled DPCs by heating and venting to atmosphere.
- Sectioning of cured samples to visually estimate variability in the distribution of entrained particles.
- Thermal properties of uncured and cured material, heat of fusion calorimetry. Thermal analysis will use uncured and cured heat dissipation properties and setting enthalpy to model the actual thermal regime during filling.

Detailed test planning will include variations and replicates for this test series as well. This series will likely include some recipes with additional ingredients such as plasticizers and retarders. With such variations portions of the previous test series (e.g., working time, separation, shrinkage, compressive strength) will be repeated.

Durability and Material Compatibility Testing

Durability testing requires mapping out all the potential long-term reactions between phosphate cement and the DPC internals and fuel, testing cement leachability, and building natural analogue evidence for long-term durability (phase identification). The testing described here will be performed in Phase 2 except as noted, using selected cement recipes:

- Leach testing of selected cements (with parallel analysis of long-term chemical reactivity and natural analogue evidences). Preliminary leach testing (ASTM C-1220-10 *Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste*) will involve static leaching of solid coupons for 28 days in deionized water at 90°C. This test may be extended in duration, and a fluid phase repeatedly analyzed for comparison to reaction path analysis. The test will also be repeated selectively in an autoclave at higher temperature and pressure to accelerate aging and alteration.
- Leach testing of solid coupons similar to that described above, but in simulated NaCl brine.

- If sample integrity is maintained during static leaching, selected physical properties (density, porosity, compressive strength) will be measured for comparison to unleached samples.

Retrievability and Recoverability Testing

Phosphate cements can be dissolved in dilute solutions of acids such as HCl (Higuchi et al. 1986). This test will be performed in Phase 2, and will consist of exposing intact samples of cured cement to acidic solutions (pH ~4) until the material is reduced to its insoluble grains including B₄C, alumina, silica, etc. Coupons of cladding alloys will be included in the test. A further leaching step with a basic solution (pH ~10) may be used to further solubilize the mixture. The pH 4 to 10 range is probably safe for zirconium alloy cladding (Fraker 1989) but more acid or alkaline conditions could also be used if necessary, with little or no cladding damage.

Gas Generation Testing

The test consists of irradiating a cement sample that is encapsulated in a metallic tube and ported to an analyzer for H₂, O₂, H₂O₂ and other gases. An isotopic gamma source will be used (e.g., <https://neutrons.ornl.gov/hfir/gamma-irradiation>) and the sample will be flushed with inert gas during exposure. The results will be compared to a control without irradiation. The test will be repeated with different cement compositions, including some with catalysts such as entrained MnO₂ particles. Pre- and post-test examination of irradiated samples (e.g., FTIR, compressive strength) would evaluate breakage of chemical bonds. Leach testing of the type described above for Phase 2, will be repeated with irradiated solid samples. This test will be done in Phase 3, following on predictive calculations of gamma dose to the filler material, radiolytic species production, and resulting chemical reactions.

A similar test may be done using a reactor-based neutron source, such as the High-Flux Isotope Reactor at ORNL.

Postclosure Performance Testing

Based on cement degradation observed from durability and gas generation testing, a solid phase composition will be selected for batch sorption testing with surrogate radionuclide species (e.g., long-lived iodide and cesium ions, or uranyl). The solids will be ground to fineness and rinsed prior to testing. The liquid phase will be sampled at intervals for mass spectrographic and chromatographic analysis. The test will follow predictive calculations of speciation, complexation, and sorption, in Phase 3.

6.2 Testing and Analysis for Molten Metal/Metal Alloy and Glass Materials

There has been relatively limited experimental work conducted on the filling of fuel storage containers with molten materials (Jubin et al. 2014). Near-term activities identified in the 2014 report included: 1) assess the availability (e.g., cost) of filler materials and compatibility with the fuel, and materials of canister and basket construction; and 2) perform a demonstration of the proposed filling operation at a limited scale. The activities described below will fulfill that recommendation. The format of presentation is similar to Section 6.1, but the technical questions are different.

Injectability Testing

Injectability testing prior to scaled demonstrations will primarily involve quantifying molten filler material properties before and after solidification including viscosity, cooling behavior, wetting

properties, homogeneity, thermal properties during initial cooling and after set, density and other relevant physical and thermal properties.

An initial set of measurements will include the following tests performed in Phase 1, focused on selecting one or more promising molten filler materials (metals, metal alloys, and glasses) for demonstration testing:

- Viscosity measurements whereby the molten filler flow behavior is examined over a range of temperatures. Adaptation of standard viscometric methods may be needed.
- Observation of cooling behavior (e.g., over a range of cooling rates) in the laboratory to verify compositional uniformity, void filling, wetting of DPC surfaces while molten, and bonding to DPC surfaces during cooling.
- Bulk density measurements using standard measurements of volume and weight.
- Shrinkage/expansion measurements, for example, solidification in a length of steel pipe. Measurements of expansivity of the melt during cooling and solidification, and of the solidified filler material (at temperature) are needed to interpret final filled configuration (e.g., presence of gaps).
- Porosity and compositional uniformity observations by destructive testing on solidified filler material.

A more complicated set of measurements will be performed in Phase 2 using filler compositions selected based on previous testing:

- Thermal properties of molten material, heat of fusion calorimetry, and thermal properties of set material. Thermal analysis will use molten filler heat dissipation properties and setting enthalpies to model the actual thermal regime during filling.
- Non-destructive measurements of filler material in molten and solid states to estimate electrical resistivity and magnetic permeability (induction heating parameters).

Durability and Material Compatibility Testing

The testing described here will be performed in Phase 2 using selected molten filler materials identified above. Durability testing will involve leach testing of metal alloys using solid coupons in deionized water. The test will also be repeated selectively in an autoclave at higher temperature and pressure to accelerate aging and alteration. Durability of irradiated samples will also be tested in Phase 3. Leaching degradation products will be characterized using instrumental analyses such as microprobe (SEM/EDS) and x-ray diffraction (XRD) methods. Chemical reactivity analysis will consist of reaction path calculations to assess the postclosure potential for significant changes in composition from interaction with water, and with materials present in the DPC (e.g., fuel cladding and basket materials). Similar reaction path calculations will assess the potential for production of high and low pH groundwaters, and their interactions with filler materials.

Retrievability and Recoverability Testing

This test will consist of remelting and draining filler material from purpose-designed containers with materials and geometry representative of DPC internals, to evaluate the ease of retrieving fuel in relatively intact condition. The test will be performed in Phase 2 to support filler down-selection.

Gas Generation Testing

The test consists of irradiating metal/metal alloy samples, and glass samples, that are contained in a sealed tube and ported to an analyzer for H₂, O₂, H₂O₂ and other gases. An isotopic gamma source will be used (e.g., <https://neutrons.ornl.gov/hfir/gamma-irradiation>) and the sample will be flushed with inert gas during exposure. This test will be performed on only a limited number of samples, without replicates, because gas generation is not expected. It will be performed in conjunction with similar irradiation testing of cements (Section 6.1) in Phase 3, following predictive calculations of gamma dose to the filler materials.

A similar test may be done using a reactor-based neutron source, such as the High-Flux Isotope Reactor at ORNL.

Postclosure Performance Testing

Based on degradation observed from testing described above, a solid phase composition will be selected for batch sorption testing with surrogate radionuclide species (e.g., long-lived iodide and cesium ions, uranyl). The solids will be prepared from processed filler material. The liquid phase will be sampled at intervals for mass spectrographic and chromatographic analysis. The test will follow predictive calculations of speciation, complexation, and sorption, in Phase 3.

6.3 Testing for Dry Particulate Filler Materials

Studies in Canada and the U.S. involved demonstration of dry particulate filler emplacement, although for different reasons. The AECL program emphasized fillers that could mechanically support pressure loads on the canisters, including silica sand, coarse and fine glass beads, steel shot, and bauxite grains. Glass beads and silica sand compared favorably to other materials on the basis of handling and density characteristics determined in the laboratory (Teper 1987a; Johnson et al. 1994). Filling, sealing, and pressure loading of full-scale test canisters containing dummy fuel assemblies was then performed (Teper 1987b; Teper and Reid 1989). The U.S. program tested steel shot (Cogar et al. 1996a) which could serve to impede flow and radionuclide transport from breached waste packages in an unsaturated repository, and provide moderator exclusion for criticality control.

As stated by Jubin et al. (2014) for solid, spherical dry particulate filler material, tests similar to those conducted by the AECL (Teper and Reid 1989; Forsberg 1997) are needed to demonstrate void filling for moderator displacement effect. Also, they recommended that the tests look at glass beads and glass beads containing DU for neutron absorption and attenuation of actinide transport. Desired data would include packing density as a function of particle size and size distribution, identification of major voids, particle segregation, and the effectiveness of vibration.

Pouring dry shot into fuel cells has been demonstrated already for a mockup PWR fuel assembly (Cogar et al. 1996a) and repetition of that work is not proposed here. Rather, we plan to investigate the flow behavior of ideally selected particles (uniform spherical glass beads, or ceramic beads, in sorted size ranges, of the types used for grit-blasting, with vibration). If these materials can be shown to flow as needed for filler emplacement through a limited number of ports, the work can be extended to more dense compositions and graded particle size distributions. This activity will investigate the self-leveling behavior of ideally selected particles such as hollow glass beads, and solid beads of glass or ceramic.

We note that particles can also be slurried in a fluid such as water and pumped in, and the fluid removed subsequently, e.g., by evaporation. This method could leave substantial residual water,

and the potential for particle bridging during emplacement could significantly increase the void-filling uncertainty. Accordingly, we propose that work on particle slurries be deferred to a future time when more is known about filling DPCs with slurry cement.

7. Analysis and Simulation

This section discusses successive numerical and physical simulations needed to support development and demonstration of DPC fillers. Numerical simulations will be developed alongside laboratory testing, bench-scale “unit-cell” physical models, and larger scale demonstration models.

7.1 Supporting Analysis

7.1.1 Supporting Analysis for Cement Slurry Fillers

The following technical analyses are planned to start in Phase 1 and run throughout the R&D program as needed to answer key design questions and support simulation and physical model testing.

Thermochemical Analysis of Cement Composition and Cure

Thermodynamic modeling will be used to support robust understanding of cement and pore water compositions. It will evaluate the solid phases that form when water is added to phosphate-type cements, to mixes of phosphate and other cement types, and to mixes containing silica or fly ash (pozzolan), as listed in Table 5. The same modeling tools will be used to evaluate setting temperature effects. Many cement phases are hydrous, and their stability may depend on the temperature at which they form. The modeling approach will also be used to evaluate cement leaching into simulated dilute groundwater. Reaction path calculations track mineral alteration and dissolution, and leachate composition, as functions of the volume of water interacting with the contents of a waste package, at equilibrium conditions and ambient temperature. A thermodynamic database of relevant species will be assembled for this analysis. Such data are widely available for OPC phases, although pure mineral data are frequently substituted as analogues for the poorly crystalline cement phases that actually form. Limited data on phosphate cement phases are also available in the literature (Wagh 2004).

Further thermodynamic and kinetic analysis is needed for the multiple processes that would compete for residual moisture in cement fillers. This analysis will effectively be a pre-test calculation for possible experiments to measure the corrosion rate of aluminum (i.e., Boral[®]), and the extraction of moisture from cured filler materials, both as functions of temperature and relative humidity in a closed container. The results will be used to estimate the extent of aluminum-based material corrosion in the sealed canister for thousands of years.

Postclosure Leaching Analysis

Chemical reactivity analysis will include a series of reaction path calculations to assess the postclosure potential for significant changes in composition from aging and radiolysis, such as pH shifts and gas generation, caused by interactions between the DPC internals, fuel, and cement prior to waste package breach. Similar reaction path calculations will assess the potential for production of high and low pH groundwaters, and their interactions with cement.

Leaching analysis will also be extended in collaboration with the generic disposal system analysis (GDSA) task, to account for the influence of the partially intact canister and overpack, and the availability of water. To incorporate filler leaching into PA models, an advanced submodel for the engineered barrier system (EBS) is needed. With limited water available to attack the filler material, and low solubility of chemically bonded filler materials, durability will potentially be much greater than for lab studies in which samples of filler materials are leached directly *in vitro*.

Natural Analogues

Natural analogue evidences for aluminate and phosphate mineral persistence in the geologic, anthropologic, and medical literature will be collected in parallel. Dental enamel is a promising analogue for crystalline hydroxyapatite, as would result in cements containing calcium and phosphate. Other phosphate minerals such as struvite and berlinite also have natural analogues.

DPC Shell Pressure Rating

Additional mechanical analysis of DPC pressurization is needed to estimate that capacity of canisters to withstand internal gas generation. This information will be used in conjunction with radiolysis modeling and test results (Section 6) to evaluate the importance of gas generation, particularly for cement-based fillers containing water.

Fate of Hydrogen Gas in Sealed Canisters

A survey of literature on applicable H₂ gas permeation measurements in stainless steels, and calculation of leakoff rate from a DPC, will be performed. The availability of novel getters that absorb H₂ in moisture environments will be further examined.

A recombination strategy based on readily available and long-lasting catalysts should be investigated, including efficiency of catalysts, longevity, and a method for testing recombination in the laboratory.

7.1.2 Supporting Analysis for Metal/Metal Alloy and Glass Fillers

Literature review and a technology survey is needed to further determine characteristics of fillers. This analysis would focus on previous applications (e.g., whether monolithic pours can be readily achieved), state of knowledge of physical properties (e.g., melt properties), special considerations (e.g., safety of molten materials, toxicity), and material cost.

7.2 Numerical Simulation

7.2.1 Phase 1 Numerical Simulation

Criticality

Scoping criticality analysis will be performed to examine filler effectiveness in preventing criticality over a repository performance period, for all potential filler materials. Criticality analysis is an important step to determine whether a filler material will be considered for further numerical and physical simulations. Criticality analysis should consider filler durability, and any changes chemical composition or physical state over geological time (i.e., >10,000 years). Criticality analysis that are intended to be used for licensing of DPC direct disposal will need to be validated using a set of criticality experiments applicable to DPCs with fillers. Criticality analysis will be performed using as-loaded canister configurations. The Used Nuclear Fuel-Storage, Transportation & Disposal Analysis Resource and Data System (UNF-ST&DARDS) (Liljenfeldt et al. 2016) is being developed as a foundation resource for the DOE Office of Nuclear Energy. It has been demonstrated to streamline computational analysis capabilities for the time-dependent characterization of SNF and related systems, and has been used for as-loaded canister-specific criticality analyses. UNF-ST&DARDS incorporates the Unified Database (UDB), a comprehensive, controlled, domestic SNF system database that is integrated with nuclear analysis capabilities to support various objectives related to SNF management and the fuel cycle analyses.

Thermal

Thermal analysis in 3D is needed to determine temperature distribution within the DPCs during and after pouring. For cement fillers, these calculations will estimate the time-temperature trajectory for curing in different parts of the canister, while for molten metal/metal alloy fillers the distribution of temperature will help determine the solidification time and the requirements for a heating system. Thermal simulations are a starting point for multi-physics simulations coupling flow and detailed descriptions of filler material rheology, to be performed later.

For molten metal/metal alloy fillers thermal analysis will support material down-selection. UNF-ST&DARDS thermal models will be used for scoping calculations. The thermal analysis capability of UNF-ST&DARDS models will be supplemented by use of COBRA-SFS, a submodel that provides pin-level resolution of temperatures within a canister.

Flow

Flow simulation is needed initially to evaluate injectability and void filling, and to establish a platform that can be used later to evaluate conditions that could cause material damage during filling due (i.e., pressure effects, erosion, overheating). Flow simulation using massively parallel simulation codes such as PFLOTRAN will help determine the needed volume of filler material and permissible flow rates.

Filler Dose Analysis

A radiation dose analysis of emplaced filler materials will be performed to understand the potential for radiation damage as a function of position within the canister, and as input to radiolysis calculations. Dose levels will be used in scoping radiolysis analysis to estimate long term production of gases and potentially corrosive aqueous species.

7.2.2 Phase 2 Numerical Simulation

Coupled Thermal-Flow

Flow simulation coupled with heat transfer, accounting for filler material enthalpies, is needed to simulate filling for both cement-based and molten metal/metal alloy fillers. Applications include filling rate (limited by temperature-dependent curing rate of cements) and preventing premature solidification of metallic fillers during the filling process.

Radiolysis

Model calculations of radiolysis, including gamma and neutron doses inside the canister, are needed to estimate the rate of radiolysis, particularly of H₂O producing H₂ gas, H₂O₂, and other products, using literature G values. Neutron capture by ¹⁰B needs to be included in the gas generation calculation.

Pre-Test Predictions

Predictive simulations will be performed for bench-scale unit-cell studies (Section 7.3.2). Test observations will be matched to predicted responses, and compared in test documentation.

7.2.3 Phase 3 Numerical Simulation

Coupled Thermal-Flow

For cement fillers, multiphase non-isothermal simulation (e.g., PFLOTRAN) will evaluate the feasibility of moisture removal by self-heating of the canister after cure, with the vents open.

Whereas cement fillers may have low permeability, vapor flow may be possible at a temperature on the order of 200°C (corresponding to water vapor pressure less than the canister pressure rating).

Coupled Thermal-Flow-Mechanical

Coupling to mechanical response is planned to evaluate the potential for canister component failure due to pressure gradients during filling and imposed loading during solidification (i.e., expansion) of fillers. The approach is applicable to both cement and molten metallic fillers.

Pre-Test Predictions

Predictive simulations will be performed for separate-effects unit-cell studies (Section 7.3.3). Test observations will be matched to predicted responses, and compared in test documentation.

Postclosure Performance Assessment

By this time in the multi-year R&D program enough will be known about filler behavior that the postclosure response before and after waste package breach and exposure to groundwater can be simulated in a manner suitable for incorporation in PA models. These models will be generic, and developed by the GDSA task that is led by SNL for the DOE Office of Spent Fuel and Waste Science and Technology.

7.2.4 Phase 4 Numerical Simulation

Pre-Test Predictions

Predictive simulations will be performed for the scale demonstration test (Section 7.3.4). Test observations will be matched to predicted responses, and compared in final R&D project documentation.

7.3 Physical Model Simulation

Physical simulation activities will include: 1) simple bench-scale “unit-cell” injectability testing to screen proposed filler materials; 2) “separate-effects” testing to determine the filler behavior in response to variations in composition or filling conditions; and 3) integrated scale mock-up DPC filling demonstration. Characterization of the proposed filler materials (Section 6) prior to bench-scale testing is important for successful progression of the overall R&D program.

7.3.1 Phase 1 Physical Model Studies

Laboratory testing will be performed in Phase 1 as described in Sections 6.1 and 6.2 (Injectability Testing). Physical model testing for cement fillers will commence in Phase 2 (Section 7.3.2).

Molten Metal/Metal Alloy Filler Phase 1 Activities

A unit-cell model (test bed) will be fabricated or acquired, at appropriate scale and using representative materials such as stainless steel, for investigation of metal/metal alloy fillers. Initial filling experiments will be performed using fluids or slurries (e.g., ambient temperature, high-solids or “sticky” mixtures) that can be readily removed to preserve the cell for further testing.

Molten metal alloys require heating and special handling prior to pouring. In addition, DPCs would be pre-heated to prevent solidification until after filling is complete. The overall heating system is crucial to the filling process. A heating system, e.g., induction heating, will maintain the required temperature of the unit cell and the filler material during filling operations. Phase 1 will focus on the design and development of a molten metal handling and heating system, including induction

coil size, frequency, penetration depth, power and current requirements, heating efficiency, and cooling requirements. The goal is to prepare to test emplacement characteristics of metal/metal alloy fillers and identify challenges during filling, in follow-on Phase 2.

7.3.2 Phase 2 Physical Model Studies

Cement Filler Unit-Cell Testing

A simple unit-cell configuration will be constructed from inexpensive materials such as acrylic plastic, to test emplacement characteristics of cement-based fillers (that do not require heating). The unit cell may not resemble a DPC or a fuel assembly in size or configuration, but it will be designed to produce flow conditions that challenge the injectability conclusions drawn from filler property studies in Phase 1 (Section 6.1) and numerical simulation. Data collection will be limited to simple methods such as destructive examination for voids, moisture content, and uniformity of composition and physical properties. This activity, combined with laboratory testing in Phase 2 (Section 6.1) will be used to support selection of filler materials for testing in subsequent phases.

Molten Metal/Metal Alloy Filler Unit-Cell Testing

Testing will be performed to develop and demonstrate injection of molten fillers. Again, the unit cell may not resemble a DPC or a fuel assembly in size or configuration, but it will be produce flow conditions that challenge the injectability conclusions drawn from previous studies (Section 6.2) and numerical simulation. Data collection will be limited to simple methods such as destructive examination for voids, uniformity of composition, and physical properties. This activity, combined with laboratory testing in Phases 1 and 2 (Section 6.2) will be used to support selection of filler materials for testing in subsequent phases.

Dry Particulate Filler Self-Leveling Flow Test

This phase will also include selection and testing of dry particulate fillers, to determine if useful self-leveling flow behavior needed for DPC filling can be produced.

7.3.3 Phase 3 Physical Model Studies

Cement Filler Separate Effects Tests

Testing will be similar to the Phase 2 unit-cell testing, but will include other processes and may be performed in different configurations and at larger scale. A heated cell will be filled to represent waste heating, and cement curing will follow a realistic time-temperature trajectory based on pre-test simulations. Cement filler materials will include loading with particulate neutron absorbing material. Separate effects tests will be instrumented for temperature, pressure, and other internal conditions, for model validation. Configuration may be varied, e.g., alternative drain/vent port arrangements. Results from this phase will be used to support selection of filler materials and test conditions, and simulation methods, for mock-up testing in Phase 4.

Molten Metal/Metal Alloy Filler Separate Effects Tests

Further testing will simulate canister filling, including use of different fillers (e.g., higher melting points), different canister configurations, and at larger scale. The test cell may be modified for realism or to facilitate more tests. Filling will be performed through a drain port, i.e., bottom-up. A heating system will be used to maintain the temperature of the canister and the filler material above the melting point. Internal components of the test cell may be heated to simulate decay heat. Once the induction heater is off, the filler material will solidify. A conceptual diagram of the

experimental configuration is shown in Figure 8. The mock-up will be instrumented to measure important parameters such as temperature, flow rates, and heating parameters. Filling progress will be observed and recorded through a high temperature window in the cell, with a dual camera (visual and thermal). Following solidification, non-destructive and destructive tests will be performed to evaluate void filling and uniformity of composition and material properties. Results from this phase will be used to support selection of filler materials and test conditions, and pre-test simulation methods, for follow-on testing.

This phase may also include selection and testing of a glass filler, using a similar test cell and an appropriate heating system (i.e., oven). The need for glass testing will be based in part on the degree of success obtained with metal/metal-alloy fillers having attributes (e.g., toxicity, material cost, filling temperature) considered promising for implementation in DPCs containing nuclear fuel.

7.3.4 Phase 4 Scaled Demonstration

A DPC mock-up will be fabricated with sufficient realism and size to convincingly demonstrate canister filling with integrated thermal, rheological, and chemical effects. The means of handling, mixing, and pumping significant quantities of cement fillers will be part of the demonstration. The mock-up will be instrumented for model validation. Following solidification, non-destructive and destructive tests will be performed to evaluate injectability and void-filling performance, and examine for damage to simulated fuel. Full-process testing will be used to validate the predictive multi-physics computational model. This testing and final documentation will complete the cement filler data, and the dry particulate filler data, intended for future use.

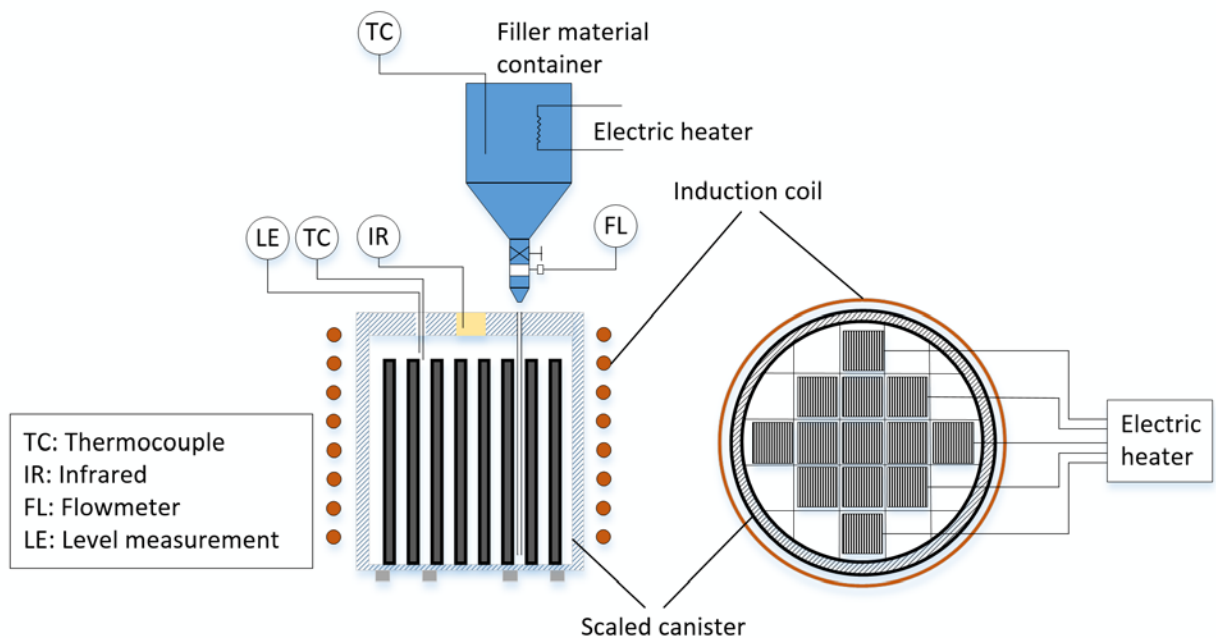


Figure 8. Conceptual diagram of a scaled mockup demonstration test with induction heating, for metal/metal alloy fillers. A similar configuration with a different heating scheme is proposed for testing cement fillers.

8. Summary and Approach to Implementation of DPC Fillers

The overall proposed fillers R&D program is described in Sections 6 and 7, and summarized in Table 9. This workplan covers a reasonably complete set of technical questions with regard to DPC filler implementation and effectiveness. Both cement slurry and molten metal fillers are covered, with additional investigation of dry particulate fillers and molten glass. A wide range of tests on filler materials, unit-cell tests, and scaled mockup demonstration tests is included, with the expectation that testing needs will narrow as more is learned. Detailed test planning will be done for each test or test series performed, that includes technical procedures, hazard analyses, safety controls, and environmental controls, consistent with the requirements of the institution (e.g., ORNL or SNL).

Phasing will provide opportunities for replanning to address technical developments, resource availability, or other priorities. The technical maturity of DPC fillers is low (pre-conceptual) and the phase timing proposed here will allow maturation in an effective manner typical of major development projects.

The proposed program carries two types of fillers (low-temperature cements, including chemically bonded cements, and molten metal/metal alloy fillers) through all phases to final documentation. No selection between these two types is currently planned, although that may be possible in the future during the phases, based on the information to be collected.

This program will produce a demonstration of filler emplacement in a mockup canister at an appropriate scale, with extensive supporting information and data. If further work on fillers is conducted after that, it would proceed to conceptual design, prototyping, integration with a repository concept of operations, engineering design, licensing, etc., with an appropriate nuclear quality assurance program established at that time.

Table 9. Summary of lab testing, technical analysis, numerical simulation, bench-scale testing, and demonstration across multiple phases.

Phase 1 ^A	Phase 2	Phase 3	Phase 4
6.1 Testing for Cement Materials	6.2 Testing and Analysis for Molten Metal/Metal Alloy and Glass Materials		
<ul style="list-style-type: none"> • Injectability • Durability (leaching) 	<ul style="list-style-type: none"> • Injectability (continued) • Durability (leaching irradiated samples) • Retrievability/Recoverability 	<ul style="list-style-type: none"> • Gas Generation • Postclosure Performance 	
	6.3 Testing and Analysis for Dry Particulate Filler Materials		
7.1.1 Supporting Analysis for Cement Fillers <ul style="list-style-type: none"> • Thermochemical Analysis of Cement Composition and Cure • Postclosure Leaching Analysis • Natural Analogues • DPC Shell Pressure Rating • Fate of Hydrogen Gas in Sealed Canisters 		7.1.2 Supporting Analysis for Metal/Metal Alloy and Glass Fillers <ul style="list-style-type: none"> • Literature Review and Technology Survey 	
7.2.1 Phase 1 Numerical Simulation <ul style="list-style-type: none"> • Criticality • Thermal • Flow • Filler Dose Analysis 	7.2.2 Phase 2 Numerical Simulation <ul style="list-style-type: none"> • Coupled Thermal-Flow • Radiolysis • Pre-Test Predictions 	7.2.3 Phase 3 Numerical Simulation <ul style="list-style-type: none"> • Coupled Thermal-Flow • Coupled Thermal-Flow-Mechanical • Pre-Test Predictions • Postclosure PA 	7.2.4 Phase 4 Numerical Simulation <ul style="list-style-type: none"> • Pre-Test Predictions • Final Project Documentation
7.3.1 Phase 1 Physical Model Studies <ul style="list-style-type: none"> • Molten Metal/Metal Alloy Filler Phase 1 Activities 	7.3.2 Phase 2 Physical Model Studies <ul style="list-style-type: none"> • Cement Filler Unit-Cell Testing • Molten Metal/Metal Alloy Filler Unit-Cell Testing • Dry Particulate Filler Self-Leveling Flow Test 	7.3.3 Phase 3 Physical Model Studies <ul style="list-style-type: none"> • Cement Filler Separate Effects Tests • Molten Metal/Metal Alloy Filler Separate Effects Tests 	7.3.4 Phase 4 Scaled Demonstration <ul style="list-style-type: none"> • Final Project Documentation
Notes: ^A Many Phase 1 activities can be supported in FY18 with currently available resources.			

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