APPENDIX E
FCT DOCUMENT COVER SHEET [1]

Name/Title of
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Recommendations for Filler Material Composition and Delivery
Method for Bench- Scale Testing
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QA program which meets the requirements of

   ☒ DOE Order 414.1   ☐ NQA-1-2000   ☐ Other

This Deliverable was subjected to:

☒ Technical Review   ☐ Peer Review

Technical Review (TR)	**Peer Review (PR)**
Review Documentation Provided	**Review Documentation Provided**
☐ Signed TR Report or,	☐ Signed PR Report or,
☐ Signed TR Concurrence Sheet or,	☐ Signed PR Concurrence Sheet or,
☐ Signature of TR Reviewer(s) below	☐ Signature of PR Reviewer(s) below

Name and Signature of Reviewers

Charles Bryan/SNL

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Recommendations for Filler Material Composition and Delivery Method for Bench-Scale Testing

Fuel Cycle Research & Development

Revision History

Version	Description
Recommendations for Filler Material Composition and Delivery Method for Bench-Scale Testing (SFWD-SFWST-2018-000490 Rev. 0) Milestone: M4SF-18SN010305024 Work Package: SF-18SN01030502 WBS: 1.08.01.03.05 Sandia Review and Approval: SAND2018-****	Submitted to the U.S. Department of Energy, Office of Spent Fuel and Waste Science and Technology.

Sandia National Laboratories

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Acknowledgments

**Recommendations for Filler Material Composition and Delivery Method for
Bench-Scale Testing**

**Sandia National Laboratories
March, 2018**

1. Introduction

This report supplements *Joint Workplan on Filler Investigations for DPCs* (SNL 2017) providing new and some corrected information for use in planning Phase 1 laboratory testing of slurry cements as possible DPC fillers. The scope description is to "Describe a complete laboratory testing program for filler composition, delivery, emplacement in surrogate canisters, and post-test examination. To the extent possible specify filler material and equipment sources."

This report includes results from an independent expert review (Dr. Arun Wagh, retired from Argonne National Laboratory and contracted by Sandia) that helped to narrow the range of cement types for consideration, and to provide further guidance on mix variations to optimize injectability, durability, and other aspects of filler performance.

2. Cementitious Filler Compositions for Testing

The planned range of cement types for laboratory screening (SNL 2017) was discussed with Dr. Wagh, resulting in changes that are reflected in Table 1. The overall effect was to narrow the range of cement types, while increasing the number of variants (e.g., plasticizers and retarders). The discussions also helped to identify a new filler concept: whereas the $AlPO_4$ (berlinite) cement type had been previously identified, its setting behavior was recognized as favorable to filling DPCs (see discussion below).

First, two cement types considered previously (SNL 2017) were rejected. Calcium-aluminate cement (CAC) produces sets fast and is strongly alkaline. Testing of CAC as DPC filler, given that it could be aggressive to spent fuel cladding (pH > 10), is deferred until a need arises. Addition of sulfate to CAC chemistry promotes growth of Ca-Al-S-H_2O compounds, particularly ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$). Ca-sulfoaluminate cement (CASC) can be less alkaline than CAC (Langton et al. 2011), however, ettringite breaks down with dehydration to an amorphous form at ~50°C, and further disassociates to bassanite ($CaSO_4 \cdot 0.5H_2O$) and monosulfate ($Ca_4Al_2O_6(SO_4)$ $\cdot 12H_2O$) at ~110°C (Fridrichova et al. 2016). Accordingly, CASC is thermally unstable and likely unsuited for DPC fillers. Another possible objection is growth of ubiquitous metal-oxidizing, sulfate-reducing bacteria that could accelerate corrosion.

Corrosion of DPC internals by fillers could be important for: 1) spent fuel Zircaloy cladding, and 2) aluminum used in neutron absorber plates, thermal shunts, and Metamic® basket components. Zircaloy cladding is highly resistant to acids and bases, and maintaining its integrity would mean avoiding compositions that are specifically aggressive to Zircaloy (e.g., fluoride and concentrated strong acids), and maintaining filler pH around neutral (e.g., between 4 and 10, although Zircaloy is resistant to more extreme pH). For aluminum corrosion the main concern is corrosion leading to H_2 gas generation after filling and sealing of the canister, but before waste package breach in the repository. This can be limited somewhat if the filler pH is circum-neutral, but dewatering each DPC after the filler has solidified is probably needed to limit the rate and extent of aluminum metal corrosion.

2.1 Aluminum-Phosphate Cement

Aluminum complexes with phosphate have been investigated for decades (Wilson and Nicholson 1993, Chapter 6). According to these authors: "…the species present in 50% phosphoric acid solution containing aluminum appear to be H_3PO_4, $H_6P_2O_8$, $H_2PO_4^-$, $H_5P_2O_8^-$, $AlH_3PO_4^{3+}$, $AlH_2PO_4^{2+}$, $Al(H_2PO_4)_2^+$, and $Al(H_3PO_4)_n$ where n ≥ 2, of unknown protonation." The aluminous complexes generally do not form precipitates at near-neutral or mildly acidic pH and near-ambient temperature. However, aluminum phosphate complexes are apparently polymeric which could affect the flow properties of a cement mix. Note that these statements assume acidic to mildly acidic conditions; as pH becomes alkaline, Al-hydroxide complexes form leading to precipitates such as gibbsite ($Al(OH)_3$).

As Al dissolves, viscosity is reported to increase markedly (Wagh 2018, personal communication). Aluminum oxide (typically α-Al_2O_3, the corundum polymorph) is very slow to dissolve near ambient temperature, so the viscosifying effect would be delayed in a DPC filler slurry subject to gradual heating. One of the effects of heating in thermal-setting aluminum phosphate cement (APC) would be to dissolve Al_2O_3. However, in the design of phosphate cements for use in geothermal boreholes, a recognized problem is that when solubilities of various oxides (SiO_2, Al_2O_3, $CaSiO_3$) increase, flash-setting may result (Wagh 2016, Chapter 16). Alumina solubility reaches a maximum at 118°C in phosphate solution, but for the system Al-PO_4-H_2O, precipitates are not reported in the sparse literature on APC until temperature of 150°C. In a high-temperature water (steam) environment the precipitates are hydrates variscite or metavariscite (polymorphs of $AlPO_4 \cdot 2H_2O$), or wavellite ($Al_3(PO_4)_2(OH)_3 \cdot 5H_2O$). If the set material is then allowed to dry at 150°C, these apparently convert to anhydrous berlinite ($AlPO_4$). The mineral grain density increases with berlinite formation, and the effect on the set cement is not known although shrinkage or cracking have not been reported. By analogy to Mg-K-PO_4 cement discussed below, decrepitation should not occur as the hydrates convert to the anhydrous form. Another option is to heat the Al-PO_4 slurry directly to 150°C in air (i.e., without a pressure vessel), but again, the composition and texture of the final precipitate are not known. These options for heating and dewatering APC should be investigated early in the test series.

Setting via gel behavior has been reported ("aluminum-phosphate gel" described by Wilson and Nicholson 1993, Section 6.5.4). However, this was in a chemically mixed system containing glass, silica, fluoride, etc. Wagh (2016, Chapter 16) suggested that amorphous aluminum hydrophosphate (referred to by the author as $Al(H_3PO_4)_n$) forms in borehole cement at ~100°C, but the result is apparently in a suspension or fine slurry, and readily pumpable. Observation of complexation and polymerization behavior will be an important objective for testing.

Orthophosphoric acid (50%, pH 1.5 at ambient temperature) is recommended as the initial liquid in the mix for borehole cement (Wagh 2016, Table 16.2). If too acidic for DPC application (e.g., for Zircaloy cladding) neutralization may be possible without forming precipitates, for example by adding a small amount of finely particulate, microcrystalline or amorphous $Al(OH)_3$. As suggested by Wagh (2016) the $Al(OH)_3$ releases Al ions into solution quicker than the alumina, while not changing the desired cement bonding or temperature behavior discussed above. The amount of $Al(OH)_3$ specified (2.2% w/w or 28 mmol, per 100 g dry powder), is approximately 10% of the molality of H_3PO_4 (48.4 g of 50% solution or 250 mmol, per 100 g dry binder powder including Al_2O_3, $Al(OH)_3$, and boric acid retarder; Wagh 2016, Table 16.2). If much of the $Al(OH)_3$ dissolves at acidic conditions, this may be enough for neutralization. This should be determined from slurry pH measured after mixing. Increased $Al(OH)_3$ may also significantly

decrease setting time (Wagh et al. 2006) although this may not be important for DPC application if setting can be controlled by temperature.

The Al:P ratio in the APC binder is approximately 4:1 (Wagh 2016, Section 16). Class F fly ash can be added as a mildly reactive aggregate or conditioner, to control slurry consistency and to impart more strength to the final product. Class F is favored because it contains less Ca (which could react rapidly with phosphate in the mix) than Class C, and contains only moderate amounts of carbon (inert, graphitic, dark in color). APC setting behavior should be tested without fly ash addition, and interaction of 50% H_3PO_4 and fly ash, without alumina, should also be tested to understand the potential effects on pH, setting behavior, and slurry thickening at T < 150°C.

A goal of APC mix design should be to limit the amount of water, which forms porosity when anhydrous $AlPO_4$ eventually forms (either during direct heating of slurry under air or by dewatering of previously formed hydrous cement phases). In addition, as the mix is heated to 100°C and higher, pressure curing may be needed to prevent boiling (actually 95°C at the elevation of Albuquerque). The vapor produced by boiling could cause large, irregular macropores to form, and premature dewatering of the mix could degrade the setting behavior. The vapor pressure of water at 150°C is approximately 5 atm (absolute), which is within the internal pressure rating of many DPCs – on the order of 7 bars (gage) (SNL 2017, Table 3). This means that pressure curing in situ is possible for many DPCs.

Plasticizers (typically organic surfactants) may be effective for reducing the amount of water in APC mixes but no results have been reported. Plasticizers such as colloidal clay materials (e.g., inorganic attapulgite – Attagel®) could help to decrease water content in the mix while maintaining fluidity. The possibility of reducing the amount of water using plasticizers should be investigated, although the amount of added organic material should be minimized to inhibit radiolytic gas formation and possible microbial growth. Retarders may not be needed given the temperature-dependent setting behavior of APC.

Literature data on the physical properties of cured APC were not found for this review, but by analogy to MKP cements discussed below, porosity will be up to 35%, and connected micropores can be expected in the paste phase of the final set product if boiling is controlled. Permeability is likely to be significant, possibly enough to allow moisture removal as suggested by SNL (2017, Section 7.2.3).

Ingredients for testing APC (Al_2O_3, $Al(OH)_3$, 50% H_3PO_4, Class F fly ash) are widely available. The purest alumina (~99%) is calcined (> 1,050°C) to drive off chemical water; this is a common industrial commodity (Aluchem, Inc. 513/733-8519, www.aluchem.com). Typical industrial product has particle size ranging from 44 to 75 μm, and may be ground (more surface area) or unground. Alumina powder at the finest grade available ("reactive" alumina, mean particle size <10 μm) forms a very smooth and readily pumped slurry (Wagh 2018, personal communication). Reactive grade is recommended for testing, unless it produces undesirable properties or composition in the final cured product, in which case a blend of finer and coarser grades could be used. Fly ash (Class C, Class F, etc.) is available from various sources but previous experience suggests Boral Material Technologies (800/292-5354). A plasticizer that could work with APC (Wagh 2018, personal communication) is Norlig A, a Ca-lignosulfonate (LignoTech USA, 715/359-6544).

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2.2 Magnesium-Potassium-Phosphate Cement (Ceramicrete®)

The starting mix should be 0.9:2:3.1:5 parts (w/w) MgO, H_2O, KH_2PO_4, and Class F fly ash. These ratios yield equimolar portions of MgO and KH_2PO_4 which is stoichiometric, but the ratios are typically simplified to 1:2:3:5 for $MgKPO_4$ (MKP) cement, producing a slight molar excess of MgO. Note that Mg is a minor constituent of fly ash (~1% MgO by weight in oxide analysis).

Boric acid has been extensively tested as a retarder (Wagh 2016). NaCl was also suggested (Sugama 2016) but could facilitate corrosion in a DPC. Fluidity may be increased by increasing water (and setting time might be extended). Plasticizer admixtures (a few percent) when they are effective, are known to increase cement fluidity, and inhibit settling of fine aggregates, without additional water.

Increasing the fly ash filler, or possibly adding another filler such as quartz sand which is inert, will be necessary to slow setting time. This occurs for two reasons: 1) the heat capacitance of additional filler slows the temperature rise and the resulting thermal acceleration of the binder reaction, and 2) introducing more relatively inert surface area may tend to decrease the availability of the acid solution for reaction with MgO. Reported setting times of 30 to 60 minutes for MKP cement include the effect of fly ash at the proportion given in Table 1. Significantly longer setting time will be needed for DCP filler application.

Alumina may also be effective for retarding set, replacing all or part of the fly ash. Powdered alumina is relatively unreactive, so fine particle size can be used without causing setting reactions (except elevated temperature approaching 150°C). Use of "reactive" grade Al_2O_3 could greatly increase its surface area compared to MgO, so that even weak affinity with PO_4 species in solution would tend to compete with formation of MKP.

Thermal activation is especially important because MKP cement binder will have completely set when its temperature reaches approximately 50°C, and the binder reaction is exothermic (Wagh 2018, personal communication). It may be impractical to maintain T < 50°C everywhere inside a loaded DPC for the ~2 hours that it could take to fill the canister with cement. Note that KH_2PO_4 dissolution in water is mildly endothermic, and when the mix temperature returns to ambient, mixing can be taken as complete.

The crystalline species actually produced during set is $MgKPO_4 \cdot 6H_2O$, which dehydrates to $MgKPO_4$ when the temperature is raised to approximately 100°C or greater. Disintegration of the solidified grout does not occur on dehydration (Wagh 2018, personal communication). Thus, an intact low-water grout filler could be obtained in a DPC by dewatering the cured cement, during heating >100°C. Final porosity will be strongly affected by the amount of water in the initial mix, and could be on the order of 25%. The pore structure created by dewatering the MKP hydrate is reported to be fine with micron-scale pores that tend to be connected (Wagh 2018, personal communication). The cured cement may therefore have limited permeability due to connected, but fine pores (e.g., < 1 md). Measurement is discussed with other follow-on testing (Section 4.3).

Sources for MgO which has been calcined to appropriate consistency (i.e., for reaction slowing; Wagh 2018, personal communication) include Martin-Marietta Magnesia Specialties (MagChem P98 pulverized magnesia, 410/780-5500, www.magnesiaspecialties.com). The production method for KH_2PO_4 is also important; grinding produce angular particles that decrease fluidity. A spray-dried powder form of KH_2PO_4 is recommended (producer ICL Performance Products, distributed by Brenntag North America, Inc., 773/586-2002, www.brenntag.com). Fly ash can be obtained

from the supplier identified above, and the plasticizer identified above could work with MKP cements also (Wagh 2018, personal communication). Boric acid is a common laboratory reagent and needed only in small amounts for Phase 1 testing.

2.3 Ca-Phosphate Cement (hydroxyapatite)

To produce stoichiometric hydroxyapatite ($Ca_5(PO_4)_3(OH)_2$, HAP) at near-neutral pH the Ca:P ratio should be 1.67. Most $Ca-PO_4$ salts have lower ratios, with tetracalcium phosphate ($Ca_4(PO_4)_2O$, TTCP) the only higher ratio at 2. TTCP is alkaline and more soluble than dicalcium phosphate anhydrous ($CaHPO_4$, DCPA) which is near-neutral. Using other inorganic, basic Ca-compounds such as CaO as supplemental sources for reaction with acidic phosphate solutions, would be unworkable for DPC fillers because of rapid reaction. Low-solubility compounds of Ca and phosphate in solid form, are used in Ca-phosphate cement (CPC) to prevent flash-setting.

Studies on CPC typically describe combining TTCP with DCPA as dry powders, each ground to fineness (e.g., mean grain size ~15 µm) in equimolar amounts, for biomedical applications. A relatively small amount of $CaCO_3$ (1 µm mean grain size) may be added as a source of free Ca, along with fillers such as silica or fly ash. Setting begins in minutes, and full cure can be complete in 4 hours (Wagh 2016, Chapter 13). Setting is strongly exothermic (on the order of 70 kJ/mol or 10^6 kJ per DPC, using data from Wagh 2016, Appendix A), and the setting reaction is thermally accelerated. Retarders and aggregate fillers would therefore be required to extend setting time significantly, for DPC applications. Increasing the grain size of TTCP and DCPA could also be helpful to slow down setting, and simplify preparation of the powders.

Testing should investigate citric acid as a retarder following Sugama's (2006) work on Ca-aluminate-phosphate cements (discussed below). Citric acid forms a barrier layer on the surfaces of Ca-bearing grains, which can be broken down to a greater or lesser degree as setting progresses. The same effect could occur in a Ca-phosphate mix with Ca contributed by low-solubility solid phases. Sugama's basic ingredient was Ca-aluminate cement (CAC), and a solution of Na-pyrophosphate as the acid ingredient. Thus, a difference with CPC is that the ingredients TTCP and DCPA both contain Ca and phosphate, and citric acid could act on both phases. Citric acid would likely break down slowly at temperature, but the products are other organic molecules for which the effects on corrosion and gas generation in DPCs are not known.

Class F fly ash is recommended, varying the concentration from 30 to 90% of the total weight of all dry ingredients, to slow setting and increase fluidity. The initial water content should be 10% of total weight, or that needed to produce a workable slurry (which may be >10%). The effect of additional water should be evaluated by increasing in steps of 3%. Citric acid should be investigated as a retarder, at concentrations of 2, 4, and 6% of the total powder weight, following Sugama (2006). Ultimately, for DPC filler application setting time will be the major challenge, so testing should focus on retarding and then move on to fluidity and other objectives.

TTCP is commercially available only in small quantities, and is used mainly for bone cements. Kilogram-level quantities might be obtained at some expense from reputable suppliers with effective quality control programs, or it could be synthesized as discussed below. DCPA and citric acid are readily available as laboratory reagents. The relative scarcity of TTCP means that experimental protocols should be designed to minimize batch size (Section 4).

2.4 Ca-Aluminate-Phosphate Cement (ThermaLock®)

Ca-aluminate-phosphate cement (CAPC) evolved through collaboration of Brookhaven National Laboratory (BNL) with industry, supported by the U.S. Department of Energy, to develop a high-temperature cement for use in geothermal boreholes. The result was successful in that the service life of CAPC is an order of magnitude greater than for previous Portland cement based formulations. The reasons for this stability are the formation of crystalline phases (instead of gel) including HAP, boehmite (γ-AlOOH), hydrogarnet ($3CaO \cdot Al_2O_3 \cdot 6H_2O$), and analcime ($NaAlSi_2O_6 \cdot H_2O$) (Sugama 2006).

Halliburton made the CAPC formulation available in 1999 as ThermaLock®, a one-part dry powder product for mixing with water. Developments from the collaboration that *may* be included in ThermaLock® include the following (Sugama 2006): use of citric acid retarder, mixing with Class C and Class F fly ash in 70/30 proportion, styrene acrylic emulsion added as corrosion inhibitor, and micro-fiber reinforcement. Major ingredients for a similar formulation (Wagh 2016, Table 16.2) are: monocalcium aluminate ($CaAl_2O_4$) 24% w/w of dry ingredients, Na-polyphospate ($(NaPO_3)_n$) 40%, and fly ash 36%.

Whereas ThermaLock® has been demonstrated repeatedly in geothermal wells as deep as 18,000 feet, it has known pumpability and retarded set (~4 hours). The purpose of testing should be to compare with other mixes and evaluate suitability for the DPC filler application. Modifications to as-procured ThermaLock® cement are not anticipated without consultation with Halliburton (i.e., without additional information on its composition).

2.5 Ordinary Portland Cement

Many pre-mixed 1-part formulations are available for self-leveling cement applications, such as flooring underlayment, embossing, etc. Most of these contain sand and Portland cement, modified with a polymer plasticizer. They have setting time on the order of 30 minutes or less. These cements can be pumped, but this is not typically an objective. Importantly, the slurry pH and cured cement pH are too alkaline for DPC filler application (pH > 11).

Low-pH OPC grout is a niche application where metal corrosion, or other chemical interactions such as radionuclide sequestration, are objectives. Low-pH formulations have been developed for nuclear waste repository applications to enhance stability and durability, reduce corrosion of engineered barriers, and limit complexation of dissolved radionuclides at high pH. A review by Holt (2008) reports that low-pH injection grout for fractured rock, can be formulated with any class of cement, and silica fume content >20% of the dry powder weight. The slurry pH can be decreased to pH 11, and possibly lower through mix design. Water:binder ratios between 0.4 and 2.0 (binder includes cement and silica, not aggregates or fillers such as fly ash) have been found effective. Silica fume in large proportions apparently delays setting time, although possibly not initial setting that would be important for DPC filler applications. Increased mixing water is widely known to increase porosity and decrease strength, while improving flow properties. Addition of silica fume may recover some of that strength. The author notes that high-silica OPC-based grout has exhibited adverse shrinkage in response to drying.

A recent experimental study investigated cements for grouting deep boreholes for disposal of nuclear waste (Collier et al. 2015). They used Class G oil well cement (median particle size 16.5 μm) partially replaced by silica fume (median 17 μm). Polycarboxylate poly-ether plasticizer Sika Viscocrete 3110® functioned at temperatures well above 100°C, while a sulfonate-based

organic plasticizer degraded at 90°C (Collier et al. 2015). The Viscocrete admixture functioned as both a plasticizer and set retarder. It produced an initial increase of consistency for a few minutes, followed by approximately 2 hours of consistency *decrease* to 0 Bc (corresponding to a very low viscosity). This condition was maintained, for example, for more than 3 hours at 120°C with plasticizer addition of 2% (weight of binder, i.e., silica and cement dry powders). Setting time (determined by a needle penetration method such as ASTM C403) was at least 4 hr for plasticizer loading of 1% or greater. Superplasticizer loading and temperature of setting did not appear to affect final strength.

Following these studies, and recognizing that a generic OPC design cannot nearly represent the range of variation of available Portland-based cement formulations, a simple formulation is recommended here combining Class G oil well cement (for elevated temperature conditions), silica fume, polycarboxylate plasticizer (e.g., Viscocrete 3110®), and Class F fly ash filler. The initial binder:filler and water:binder weight ratios should both be 1:1, and the ratios should be independently varied up and down in increments of 30%. The initial plasticizer concentration should be 2%, which can be decreased to 1% when a promising recipe is found.

Sources for Class G cement include GCC Rio Grande (Tijeras, NM, 505/281-3311). Silica fume that conforms to ASTM C1240 (*Standard Specification for Silica Fume Used in Cementitious Mixtures*) is available from Sika Corp. as Sikacrete-950DP® (201/933-8800, usa.sika.com). Plasticizer Sika Viscocrete 3110® is available as an aqueous liquid, from the same source. Larger particle sizes can be obtained as precipitated amorphous silica from PPG Silica Products (www.ppgsilica.com), or ground silica that is typically quartz with increased inhalation hazard (not recommended). Sourcing for Class F fly ash is discussed above.

Table 1. Refined cement slurry recipes for laboratory screening and exploratory variations.

Material	Starting Recipe for Screening	Notes on Variants
Al-Phosphate Cement (APC)	Based on Wagh (2016) deep/geothermal cement: Calcined alumina (Al_2O_3, e.g., 10-50 μm)　49% Aluminum hydroxide ($Al(OH)_3$) nucleant　1% Class F fly ash　50% 50% H_3PO_4 solution　~45 mL/100 g dry alumina Water　Sufficient for slurry; not more than ~50 mL per 100 g fly ash	• Vary fly ash from 0 to 75% of powders, in steps of 25%. • Vary $Al(OH)_3$ content: 0 and 3% to test for effect. • Increase water in steps of 15% of initial amount, only as needed to achieve fluidity and setting behavior. • Add plasticizer at 1% and 3% as needed to achieve fluidity and setting behavior, while decreasing water. • Samples must be heated to 150°C for hours to cure. This can be attempted at ambient pressure in an oven, but boiling may prevent proper cure. • Curing may need to be done in a pressure vessel placed in the oven, exposing samples to a steam environment at 150°C (5 atm pressure). • Check curing time by extending cure to 7 days for representative samples. • Calorimetry will not be effective by the method described (insulated cup). • Aluminum hydrophosphate will form as a possible precipitate during cure as T→ 100°C. This should be investigated by direct observation. • If a retarder is needed, which is unlikely, 1 to 3% boric acid has been recommended (see text).
Mg-K-Phosphate (MKP) Cement	Typical Ceramicrete® recipe (Wagh 2018, personal communication): MgO, calcined (w/w of dry powders)　10% KH_2PO_4 powder　34% Class F fly ash (reactive)　55% Water　22% of total dry powders Boric acid retarder　≥ 0.5%	• This Ceramicrete® recipe is self-consolidating (flows into complex forms) and may also be self-leveling. • Recipe is stoichiometric for $MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O \rightarrow MgKPO_4 + 6H_2O$. • Much of the MgO is unreacted, but the fly ash forms PO_4 compounds. • MgO is calcined to reduce reactive surface area, to limit the setting rate. (Increasing MgO surface area cannot be used to neutralize slurry pH.) • Increase boric acid in 1% increments if needed, but there may be little additional retarder effect at >3%. • Increase water in small increments (e.g., 3% of dry powders) as needed for fluidity. • Add plasticizer (see text) at 1% and 3% if needed, decreasing water, to prevent bleed and control final porosity.
Calcium-Phosphate Cement (CPC)	Typical bone cement binder recipe (Wagh, 2018 personal communication) with aggregates: Binder TTCP 73%, DCPA 27%　40% Class F fly ash　60% Water　(sufficient to produce slurry) Citric acid retarder　4%	• Binder proportions should be stoichiometric for hydroxyapatite (Ca/P = 1.67). • Vary citric acid retarder from 0 to 6% in steps of 2% following Sugama (2006) work with CAPC. • Note that citric acid may not be effective and a different retarder may be needed. • Vary fly ash from 30 to 90% to retard set. • Water requirement will be at least 10% of total weight; increase in steps of 3% to increase fluidity and retard set.
Ca-Aluminate-Phosphate Cement (CAPC)	Haliburton ThermaLock®　(according to instructions)	• Pre-mixed dry cement product; mix according to instructions. • Refer to Sugama (2006) for composition and potential variations, if pre-mixed composition does not suffice.
Ca-Aluminate Cement (CAC)	Deferred because of potential setting time, heat generation, and alkaline corrosivity issues.	
Ca-Sulfo-aluminate Cement (CSAC)	Deferred because of potential setting time, heat generation, alkaline corrosivity, and microbial activity issues.	
Generic OPC Grout	Cement recipe reported by Collier et al. (2015): Class G oil well cement　38% Silica fume (submicron)　10% Class F fly ash　50% Viscocrete 3011® liquid (mix first with water)　2% Water　100% of binder (cement, fume, plasticizer)	• Viscosity may increase in the first few minutes, then decrease steadily for ~2 hours, due to the plasticizer. • Vary fly ash up/down from reference by 30% of initial amount. • Vary water up and down by 30% of initial amount. • Vary silica fume up and down by 50% of initial amount (goal is slurry pH ≤ 10), • Decrease plasticizer to 1% after a promising mix is found. • Curing at elevated temperature may change results.

3. Delivery Systems and Canister Filling Concepts

Grout mixing options for cement testing include: small planetary mixer (kitchen type, bowl capacity up to ~5 liters) or a larger vertical-shaft floor mixer (commercial kitchen or cement lab, bowl capacity up to ~130 liters, www.hobartcorp.com/products/food-prep/mixers). As mixer size increases, handling batches becomes more difficult as they could weigh on the order of 100 kg. Mixed cement would be conveyed to bench-scale tests by pouring, which for large batches would require a portable crane, and possibly transferring mixed product into a bottom-pour ladle for use.

If greater delivery is needed, a small grout plant can be configured to include one or more batch mixers and a progressive cavity pump with its own feed hopper (www.chemgrout.com/products). Mixed grout is transferred to the hopper and pumped, while another batch is mixed. System delivery capacity ranges from 7.5 to 50 lpm for these relatively light, skid-mounted, electrically powered units. At the lower end of this range dry ingredients could be handled manually in sacks, but as the capacity increases handling of bulk quantities (or many sacks) would require additional equipment. The upper end of this range could have sufficient

Oil well cement is nearly always mixed in batch mixers, with multiple mixers set up for the stages of a cement job. Mixer batch capacities in the range 20 to 100 bbl (3 to 15 m^3) are common. These are coupled with diesel-powered pumper units to deliver slurries and liquids to the well at required rates. Setting times for oil well cements are similar to DPC cement slurry fillers, so the pace of operations and types of equipment would be similar, although the scale of oil well cementing equipment is probably several times larger than needed for DPCs.

Continuous static mixers are used for spray applications, where two or more separate liquid or slurry feeds are combined under pressure at the point of delivery. The concept could be adapted to DPC applications, noting that two or more mixers and pumps would still be needed to feed the components.

For Phase 1 testing a small batch mixer of the simple planetary design will be used. For tests requiring greater volume (such as those described by SNL 2017), a larger vertical-shaft mixer will be used, or an integrated mixer and pump such as that sold by ChemGrout. For full-scale DPC filler operations a cementing system would resemble oil well cementing, since the volume would be similar to one cement stage (each canister would hold about 6 m^3 or about 40 bbl). However, the DPC filler system would be considerably smaller because the pumping rate is several times less.

For all forseeable cement slurry fillers testing, batch mixing will be used. Small planetary or larger vertical-shaft floor mixers will be used for bench-scale laboratory work. Mixer bowls will be small enough for lifting and pouring by one or two technicians (batch size up to ~25 liters). For a future demonstration test requiring larger quantities, an integrated batch mixer/pump system may be used, at the lower end of the size range discussed above.

4. Testing Methods

Phase 1 testing will be supported by pre-test thermochemical calculations, within the limitations of the databases. In particular, Pitzer constants for the Al-PO_4-H_2O system are scarce. Modeling will be helpful for interpreting exothermic setting, and understanding endothermic dissolution behavior (e.g., KH_2PO_4).

4.1 Mixing and Thermal Treatment of Cement Samples

Mixing will be done in a variable-speed planetary mixer with mixing forks (nominal 1.5-liter batch size in a 5-liter bowl). The total mixing duration will be on the order of 3 to 5 minutes for each batch, whereupon the slurry will be transferred to another container and tested repeatedly using a flow cone device (Ford cup, see below). During the transfer, samples for temperature monitoring, bleed measurement, and archival will be poured. All containers used for APC must withstand 150°C. The archival sample molds for other cement types must also withstand 150°C.

TTCP will be purchased in dry powder form at an appropriate level of purity (e.g., >90%). However, if a supplier is not available then it will be prepared from a mixture of DCPA and $CaCO_3$ powders fired at 1,500°C for 6 hours in a muffling furnace, quenched, re-ground, and sieved while minimizing exposure to humidity. The crucible will be covered for transfers (at ambient temperature) from and to the particle control workstation.

Temperature in loaded dual-purpose canisters will rise to approximately 150°C within approximately one day after slurry injection (SNL 2017). Peak temperature can be controlled by choosing waste that meets age and burnup requirements, and by maintaining the outer canister temperature. Cement samples will therefore be cured at elevated temperature to observe the final curing characteristics at in situ conditions. The environment inside a canister during curing will be steam, with a pressure up to the vapor pressure of water at 150°C (about 5 bars).

For Phase 1 testing thermal curing will begin 2 hours after mixing, in an oven at ambient pressure, controlled at 150°C. A ramp-up temperature function may be used, and curing time will be varied to determine how long is needed (a simple compressive strength test on cooled samples may be used at this point). APC likely cures differently at temperature depending on whether pressure is also controlled (water may boil off before hydrous precipitates such as variscite can form). Samples will be heat treated at 150°C both under air, and sealed in a certified pressure vessel in a steam environment. The same steam cure at 150°C may also be used for other promising mixes.

Based on present understanding there is no reason why ambient-stored samples could not be later cured at 150°C if needed for testing purposes (except for $AlPO_4$ cement which will not cure at ambient temperature). After curing, samples will be stored at ambient laboratory conditions (e.g., 25°C and RH ~ 30%) until needed for other testing.

4.2 Testing for Screening of Candidate Fillers

Ford Cup

Low viscosity self-leveling grouts are needed that can penetrate DPC interstices. Viscosity screening will rely on application of ASTM Method D1200–10 *Standard Test Method for Viscosity by Ford Viscosity Cup*. The flow cone method ASTM C-939 would require significantly larger sample batches, on the order of 3 liters. The Ford cup resembles a flow cone, but smaller. Ford cup measurements will be done after 30, 60, 90 and 120 minutes of setting (measurements cease when the cement sets). Significant deviation between duplicates, particularly for Ford cup results with the possibility of ≥120 minute setting time, will be tested a third time. Note that $AlPO_4$ cement must be cured in an oven, so Ford cup measurements will be made during heating at appropriate time/temperature intervals, if curing is done at ambient pressure. If pressure-curing is used then Ford cup measurements will be possible only during the 2 hours after mixing before samples are loaded into the pressure vessel. The Ford cup has a long handle and can readily do this safely at

>100°C without removing the container from the oven, if the technician is careful and protected from spatter.

Phase 1 screening testing is expected to require several months. More detailed viscometry or consistometry (for curing at temperature and pressure), for a down-selected group of cement mixes, will be considered for a future phase of testing.

Thermal Evolution

Thermal evolution of promising mixes will be evaluated by pouring freshly mixed cement into insulated, disposable containers with embedded temperature sensors (e.g., medical probe with disposable plastic sleeve). Temperature will be monitored until cure is reasonably complete (hours to days). This method will serve as an index test for comparing the heats of reaction for various mixes, and identifying mixes that set rapidly and may be thermally activated.

Water Bleed, Slurry pH, and Archival Samples

Slurry separation will be evaluated by observing a sample placed in a graduated cylinder immediately after mixing, for at least 3 hours (based on ASTM C940 but with smaller sample volume). The filled cylinder will be placed upright where there is no vibration. Separation of liquid and solid fractions should be visually undetectable until the cement sets. Plastic graduates will be used where possible to prevent breakage (glass graduates for thermal curing), and sacrificed at the conclusion of each test.

The slurry pH will be measured using pH paper, wiping off the solids to obtain an immediate reading. This is a low precision measurement but will suffice to classify each mix as acidic (pH < 4), circum-neutral (pH 5 to 9), or alkaline (pH > 10). The pH of cured cement (by grinding and slurrying) will be considered for a future phase of testing.

Samples will be poured into 2-inch diameter cylindrical molds for later measurement of physical, mechanical, and flow properties, grain structure, etc. Two such samples will be poured for each batch. Samples may be aged at representative waste-canister temperature (e.g., 150°C) prior to testing, hence all such samples will be cast in heat-resistant molds (e.g., resistant plastic, or aluminum).

4.3 Follow-On Testing

Cement mixes can be rejected from further consideration because of setting time or loss of fluidity before 2 hours, bleed (which implies phase separation), or poor texture (friability) after set. A small number (e.g., 10 to 20) of mixes will be recommended for further study after Phase 1. Follow-on testing can fine-tune the mixes, and produce additional types of data pertinent to the DPC filler application (SNL 2017):

Slurry Properties

- Viscosity measurements on slurries made by rheometer (wherein the mixture is mechanically sheared between moving plates or cylinders) or consistometer (a paddle mixer in an environmental vessel simulating evolution of high T,P conditions).

- Contact angle measurement with an optical goniometer, between cement slurries (e.g., liquid fraction) and stainless steel, aluminum, and zirconium alloy oxide surfaces.

- Calorimetry by instrumental analysis. Measured cement setting enthalpies will be used to predict and optimize setting times, and model chemical thermodynamics, for representative temperature trajectories.

Properties of Cured Cements

- Thin section optical analysis and x-ray diffraction studies for phase identification in cured cement. Supplement segregation study (see below) to characterize dispersion of B_4C particles.

- Moisture content and phase identification from thermal-gravimetric analysis (TGA) of cured cement.

- Physical properties (porosity, grain density, compressive strength) on cured samples, including samples taken by sub-coring and sectioning. Evaluate chemical bonding effects and compositional uniformity.

- Gas permeability of just-cured samples (Wagh 2016, Section 16.2.5) using an approach such as ASTM Method C204 *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 of filled DPCs.

- Thermal properties of uncured and cured material, along with calorimetry to measure heat of formation during cure. Thermal analysis will use uncured and cured heat dissipation properties and evolution of setting enthalpy to model the actual thermal regime during filling.

- Measurement of setting expansivity along representative in situ temperature/curing trajectories, and during dewatering. Measurement of the coefficient of linear thermal expansion on cured samples. Used to predict mechanical loading of canister during operations and after disposal.

Dispersion of Neutron Absorbing Phase

- Segregation testing using an approach such as ASTM Method C1610 *Standard Test Method for Static Segregation of Self-Consolidating Concrete Using Column Technique*. Mixes will substitute B_4C particles (e.g., 10% of dry powders) for a portion of fly ash. Cured samples are sectioned to characterize variability in the distribution of entrained particles.

Long-Term Durability

- Durability testing performed by leaching at representative and over-driven temperature (autoclave) conditions. Similar to "product consistency tests" performed on cements, with possible changes such as extended duration.

- Intentional dissolution of cured cement (e.g., acid leaching) to evaluate retrievability of spent fuel from grouted canisters.

- Radiolytic damage and gas production on exposure to gamma radiation (10^8 Gy), a test which takes approximately 1 month in Sandia's radiation testing facility. Irradiation can then be followed by durability testing (e.g., leaching) to detect damage that could be significant to long-term durability after waste package breach.

A next phase of follow-on testing incorporating these testing methods is anticipated to require an additional 12 months. Based on results from follow-on testing, a more advanced testing program can be developed for pre- and post-test examination in unit-cell, separate effects, and demonstration tests (see SNL 2017). The follow-on tests described above constitute a reasonable basis for planning future work.

Summary

The cement types recommended for Phase 1 testing have been narrowed, and a key prospect has been identified that is thermal-setting and may be ideally suited as a DPC filler (APC, Wagh et al. 2006). Technically challenging CPC, which produces environmentally stable hydroxyapatite but sets quite rapidly, is retained for investigation. MKP cement and CPAC are retained because they represent decades of research at ANL and BNL, respectively, and produce resistant phosphate-compounds. CPAC has also been commercialized by Halliburton as a successful product for cementing geothermal wells. A generic Portland cement based formulation for borehole application has also been identified (from among many alternatives) for comparison to phosphate cements on pH and other factors. Thus, the number of cement types has been minimized to include three independent phosphate chemistries plus an additional combination, and a Portland cement benchmark.

Each cement type has been described in terms of a reference mix recipe with key quantities specified, and recommended variations to optimize injectability, setting properties, cohesion of the cured product, circum-neutral pH, and long-term stability to radiation and groundwater. Key specifications for ingredients have been identified, especially particle sizes for dry powders. Vendor sources for all ingredients have been identified except for TTCP, which is expensive and used in small quantities for bone cement. TTCP may need to be synthesized in the laboratory for Phase 1 testing.

To reduce the use (and disposal) of cement ingredients, and to decrease testing costs, batch size has been decreased to 1.5 liters (by a factor of one half) by selecting an alternative method for measuring working time (Ford cup). Other aspects of Phase 1 testing have been defined and simplified so that investigators can focus effort and design and testing of alternative mixes that produce desired behaviors.

Follow-on testing of a few selected cement mixes is described, that will evaluate: chemical and physical properties of slurries and cured cements; reaction with cladding, aluminum, and other mateirals present in DPCs; dispersion of neutron absorbing material; and long-term durability. As testing advances beyond Phase 1 larger cement batches may be needed, for which commercially available mixing and pumping equipment has been identified.

Standards Identified

ASTM Method C939 – *Standard Test Method for Flow of Grout for Preplaced-Aggregate Concrete (Flow Cone Method)*

ASTM Method C940 – *Standard Test Method for Expansion and Bleeding of Freshly Mixed Grouts for Preplaced-Aggregate Concrete in the Laboratory*

ASTM Method D1200 –*10 Standard Test Method for Viscosity by Ford Viscosity Cup*

ASTM Method C403 – *Time of Setting of Concrete Mixtures by Penetration Resistance*

ASTM Method C204 – *Standard Test Methods for Fineness of Hydraulic Cement by Air-Permeability Apparatus*

ASTM Method C1610 – *Standard Test Method for Static Segregation of Self-Consolidating Concrete Using Column Technique*

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