

Phosphate Cement Development for Dual Purpose Canister Fillers

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INTRODUCTION

Commercial generation of energy by nuclear power plants in the United States (U.S.) has produced thousands of metric tons of spent nuclear fuel (SNF), the disposal of which is the responsibility of the U.S. Department of Energy (DOE) [1]. Utilities typically utilize the practice of storing this SNF in dual-purpose canisters (DPCs). As of March 2022, there are over 3,000 DPCs in storage in the United States that contain SNF. While DPCs were designed, licensed, and loaded to meet NRC requirements and preclude the possibility of a criticality event during SNF storage and transport, they were not designed or loaded to preclude the possibility of a criticality event during the regulated postclosure period following disposal.

Criticality in an as-disposed DPC is not possible unless a moderator, most likely water is present [2]. This requires that both the DPC disposal overpack and the DPC itself must be breached so that water can enter to potentially facilitate criticality. Once water has entered the DPC, the reactivity of the SNF in a DPC is controlled by multiple factors. These include fissile mass in the fuel rods, the presence of neutron absorbers in the fuel, in the water, or integral to the basket, the presence of moderator, moderator volume and temperature, basket geometry, and fuel temperature.

There are several options for the disposal of SNF stored in DPCs in a geologic repository. One is to repack the SNF into canisters that are designed to remain subcritical during the regulated postclosure period following disposal. A second option is the direct disposal of DPCs. While DPCs were not designed for ‘as is’ disposal, analyses are currently underway to assess this possibility. These assessments are focused on the post-disposal behavior of SNF in a DPC, particularly the probability and consequences of criticality during a 1 Ma-year postclosure period in several geologic disposal media [2]. A third option, and the focus of the current paper, is to fill the void space of a DPC with a material before its disposal that significantly limits the probability of criticality over the post-closure regulatory period.

The effectiveness of a filler material to mitigate criticality will ultimately depend on its ability to reduce moderation effectiveness in a DPC. To do so will require that the filler exhibit several attributes including: (1) neutron moderator displacement by filling a substantial amount of the DPC free volume; (2) minimal intrinsic ability to moderate neutrons; (3) a smooth pourable and low viscosity slurry that

takes several hours (~8) to begin setting and (4) a minimal compaction or volume reduction (10%) after infiltration and solidification [3,4]. Because the cement is required to serve as a structural material, a modest compressive strength of 500 pounds per square inch (psi) or 3.45 megapascal (MPa) is targeted. Materials that exhibit these attributes and are currently under consideration as DPC fillers include low-melting point metals and chemically bonded phosphate cements.

Sandia National Laboratories (SNL) is focused on the development of chemically bonded phosphate cements. Numerous compositions have been explored including aluminum phosphate cements (APCs), calcium phosphate cements (CPCs), magnesium potassium phosphate cements (MKPs), Fly ash phosphate cements (FAPCs), Wollastonite aluminum phosphate cements (WAPCs) and calcium aluminate phosphate cements (CAPCs).

This paper updates research currently being conducted for the DOE that is focused on a promising subset of phosphate-based cements. Currently, the APCs and CAPCs show the most promise and have been selected for further development and advanced testing. However, the WAPCs form well consolidated cements but short set times (2 hours or less) make them less appealing for the use case. Nevertheless, recent formulation changes (including the addition of grossite and BPO_4) have increased set times to 8 hours making them a viable third option.

RESULTS

Aluminum Phosphate Cements (APCs)

Aluminum phosphate cements (APCs); more specifically aluminum oxide / aluminum phosphate ($Al_2O_3 / AlPO_4$) cements, are those in which Al_2O_3 serves as the filler material bound by an $AlPO_4$ binder formed by the reaction of Al_2O_3 with various phosphate sources. These cements as originally developed are described in some detail in [5]. The basic formula utilizes an excess of Al_2O_3 reacted with dilute phosphoric acid (H_3PO_4 in water) to form a smooth pourable slurry that is stable for months at room temperature. If the slurry is heated (130 to 170 °C) at ambient pressure, the product is a very hard $Al_2O_3/AlPO_4$ cement with large voids (Figure 1) likely caused by steam expansion from the reaction between Al_2O_3 and H_3PO_4 to form the $AlPO_4$ binder phase.

Numerous attempts to eliminate large void formation involved the use of aluminum-based additives (modifiers) including gibbsite $\text{Al}(\text{OH})_3$ boehmite (AlOOH), metakaolin (nominally $\text{Al}_2\text{Si}_2\text{O}_7$) and grossite (CaAl_4O_7). In addition, a variety of phosphate sources including sodium pentahydrogen diphosphate ($\text{Na}_4\text{H}_5(\text{PO}_4)_2$), ammonium pentahydrogen diphosphate ($\text{NH}_4\text{H}_5(\text{PO}_4)_2$), sodium hexametaphosphate ($(\text{NaPO}_3)_6$) and others including recent experiments with BPO_4 . The use of these alumina-based modifiers and alternative phosphate sources are described in detail in several reports produced by SNL [6, 7, 8].



Figure 1. Standard APC cement sample with large voids.

With respect to the APC cements, grossite (Figure 2) appears to be a more effective modifier than metakaolin or gibbsite based on the strength achieved in a number of cements developed to date.



Figure 2. APC cement sample with grossite modifier.

Considering the DPC environment post-filling, the radiation dose to filler materials within a DPC could approach 50 MGy. An initial evaluation of irradiation effects was performed at the SNL Gamma Irradiation Facility (GIF) at a dose of 25 MGy using a ^{60}Co gamma radiation source. A comparison of irradiated and unirradiated APC-Grossite samples shows no significant degradation in macro-

properties (unconfined compressive strength, UCS) after exposure to gamma radiation (Table I).

Table 1. UCS of APC-grossite samples.

Sample	UCS psi / MPa
APC-grossite (unirradiated)	990 / 6.8
APC-grossite (irradiated)	920 / 6.3

In comparison with pure APCs, the APC / grossite cements offer considerably smaller pores, expansion ratios close to unity, modest but acceptable compressive strengths, and reasonable working times before setting is initiated (~8 hours). However, the hydrolytic stability of this APC-grossite is very poor. After being heated in a pressure vessel under autogenous pressure at 250 °C for seven days the sample disintegrated (Figure 3).



Figure 3. APC-grossite post hydrothermal testing.

Modest strengths and the very poor performance during hydrothermal testing make these cements less desirable for the use case.

Calcium Aluminum Phosphate Cements (CAPCs)

CAPCs specifically grossite (CaAl_4O_7) and hibonite ($\text{CaAl}_{11}\text{O}_{18}$) are fillers bound by an aluminum phosphate that serves as the binder. Both grossite and hibonite were found to be effective cementitious materials when combined with sources of phosphate. Aqueous mixtures of grossite with $(\text{NaPO}_3)_6$, and mixtures of hibonite with phosphoric acid (H_3PO_4) and sodium dihydrogen phosphate (NaH_2PO_4), produce cements long set times (> 8 hr), and low shrinkage upon cure (< 5%). The grossite CAPCs (Figure 4) are also notable for hydrolytic stability after being heated in a pressure vessel under autogenous pressure at 250 °C for seven days (Figure 5).

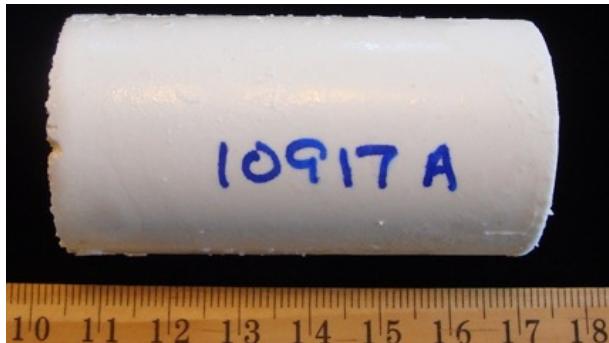


Figure 4. Grossite CAPC cement sample.

Measured compressive strengths (Table 2) are remarkable as compared to the other cement compositions under study but equally remarkable is the reduction in mechanical strength (~50%) after exposure to 25 MGy of gamma radiation.

TABLE 2. UCS of grossite CAPC samples.

Sample	UCS psi / MPa
CAPC-grossite (unirradiated)	6,380 / 43.0
CAPC-grossite (irradiated)	3,320 / 22.9



Figure 5. Grossite CAPC cement sample post-hydrothermal treatment.

X-ray diffraction studies [8] revealed an observable elevation in peak background between 15-40° 2θ which may be due in part to the degradation of CAPC-grossite crystalline phases and/or the creation of a new amorphous phase by irradiation of the cement. Changes in structure as a result of irradiation could be affecting mechanical properties. Additional studies to assess this possibility are underway.

Substantial working times (≥ 8 hr.) and hydrolytic stability at elevated temperature make the grossite-based

CAPCs intriguing candidates for the DPC use case. However, the apparent loss of mechanical strength after irradiation requires further investigation and possible mitigation although it should be noted that the post-irradiation strength exceeds the requirement of 500 psi/3.45 MPa by a considerable margin and is stronger than nearly all cements tested over the course of this three-year investigation.

With respect to hibonite-based CAPCs (Figure 6), we again observe long slurry working times (>8 hr.) and retain a substantial mechanical strength post-irradiation (Table 3). However, unlike the grossite-based CAPCs they lack hydrolytic stability at very high temperature (250 °C) and are observed to partially disaggregate after the 7-day hydrothermal test described above (Figure 7).

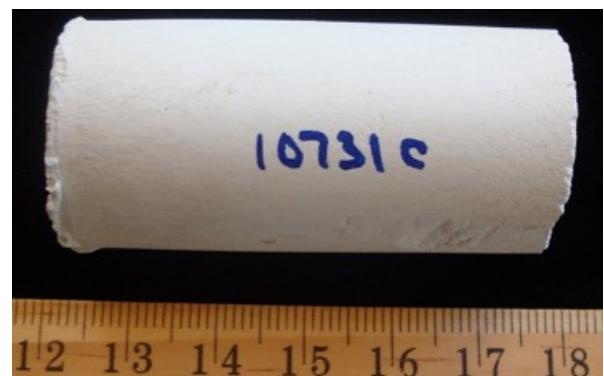


Figure 6. Hibonite CAPC cement sample.

Table 3. UCS of hibonite CAPC samples.

Sample	UCS psi / MPa
CAPC-hibonite (unirradiated)	Sample irregular and displays numerous cracks; not tested.
CAPC-hibonite (irradiated)	2,020 / 13.9

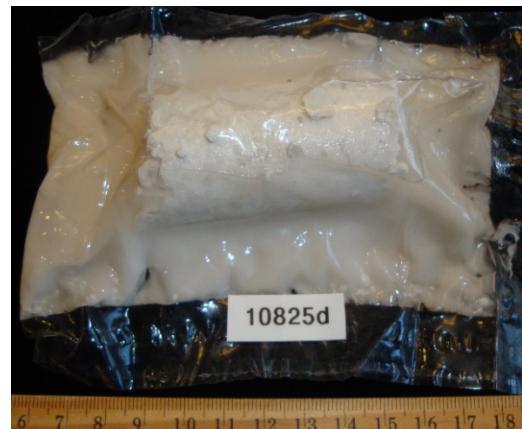


Figure 7. Hibonite CAPC cement post-hydrothermal testing.

Wollastonite Aluminum Phosphate Cements (WAPCs)

Wollastonite (CaSiO_3) forms a cementitious material when combined with a phosphate source. Wollastonite phosphate cements (WAPCs) are cements in which CaSiO_3 serves as the filler material bound by a calcium phosphate that serves as the binder. When wollastonite is combined with a low pH source of phosphate such as H_3PO_4 , the working time before setting initiates is very short (< 1 hr). Combining wollastonite with a higher pH phosphate source such as NaH_2PO_4 produces a cement with a slightly increased set time but low compressive strength (Figure 8). Alumina-based modifiers including gibbsite, boehmite, metakaolin and grossite (CaAl_4O_7) can be used to improve compressive strength.

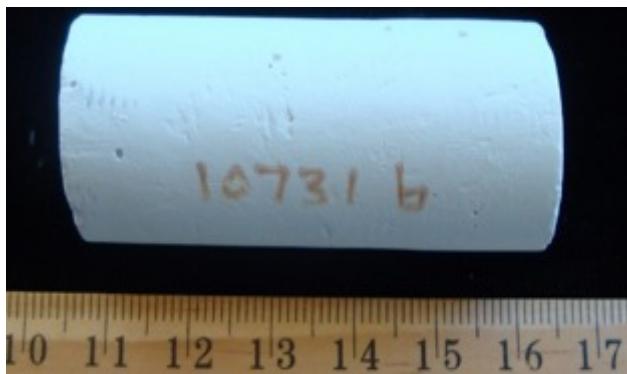


Figure 8. WAPC-grossite cement sample.

That said, wollastonite-based slurries offer the advantage of zero shrinkage upon setting and are hydrolytically stable at high temperatures (250 °C) (Figure 9), so we investigated whether the combination of alumina modifiers and higher pH phosphate sources can overcome the limitations of set time and low compressive strength (Table 4).

Table 4. UCS of WAPC-grossite samples.

Sample	UCS psi / MPa
WAPC-grossite (unirradiated)	Sample has a number of penetrating cracks; not tested.
WAPC-grossite (irradiated)	320 / 2.2

We have recently found that compressive strength can be improved by adding small amounts (as low as 5 mole percent) grossite to wollastonite. Working time was increased to greater than 8 hr by using a coarser grade (lower surface area) of wollastonite together with the use $\text{Na}(\text{PO}_3)_6$ and/or BPO_4 as the phosphate source.



Figure 9. WAPC-grossite cement sample post-hydrothermal testing.

SUMMARY AND CONCLUSIONS

The performance of APCs with relatively low compressive strength and poor stability under hydrothermal conditions make them less than desirable for the DPC use case. Meanwhile, grossite as a primary filler material or as a modifier has resulted in marked improvements in the properties of several DPC cement filler candidates. Grossite CAPCs have substantial mechanical strength even after irradiation. However, the significant decrease in strength observed post-irradiation requires further investigation before it is advanced as a material for the use case. As a modifier, grossite improves strength and set times of the APC and WAPC cements. Hibonite CAPCs also show considerable promise although their degradation under hydrothermal conditions is a potentially significant liability. With recent improvements in working time and compressive strength, the WAPCs remain in contention as viable candidates for the DPC use case.

ENDNOTES

This is a technical paper that does not take into account contractual limitations or obligations under the Standard Contract for Disposal of Spent Nuclear Fuel and/or High-Level Radioactive Waste (Standard Contract) (10 CFR Part 961). For example, under the provisions of the Standard Contract, spent nuclear fuel in multi-assembly canisters is not an acceptable waste form, absent a mutually agreed to contract amendment. To the extent discussions or recommendations in this paper conflict with the provisions of the Standard Contract, the Standard Contract governs the obligations of the parties, and this abstract in no manner supersedes, overrides, or amends the Standard Contract.

This paper reflects technical work which could support future decision making by DOE. No inferences should be drawn from this paper regarding future actions by DOE,

which are limited both by the terms of the Standard Contract and Congressional appropriations for the Department to fulfill its obligations under the Nuclear Waste Policy Act including licensing and construction of a spent nuclear fuel repository.

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