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Progress Toward the Development of Cement Fillers for Dual Purpose Canisters

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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 store this SNF in dual-purpose canisters (DPCs). And, 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, on the order of 10,000 to 1,000,000 years [2]. As of March 2019, there are over 2,700 DPCs in storage in the United States that contain SNF [3].

Criticality in a disposed of DPC is not possible unless a moderator, in this case, water is present. This requires that both the DPC disposal overpack and the DPC itself must be breached so that water can enter [2]. Once water has entered the DPC, the reactivity of the SNF is controlled by multiple factors including enrichment and burnup of the fuel; 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 [4].

There are several options for the disposal of SNF stored in DPCs in a geologic repository [5]. One is to repackage the SNF into canisters that are designed to remain subcritical during the regulated postclosure period following disposal. For example, this option was considered for the Yucca Mountain performance assessment (PA) where the SNF would be packaged into transportation, aging, and disposal (TAD) canisters specified for performance with site-specific conditions. Analyses determined that that the probability of a TAD in-package postclosure criticality event was low enough to exclude it from further consideration in the PA [6, Section 2.1.2.2]. However, repackaging presents challenges that include increased disposal cost, estimated at approximately $20B [7]. Further, repackaging SNF presents increased risk to workers both in terms of dose exposure and a variety of other operational safety and health concerns.

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 the postclosure regulatory 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 criticality over the post-closure regulatory period. A rough estimate for the cost of filling a DPC is \$200K [7] resulting in a total cost of \$0.54B to fill all the DPCs currently in storage, or about \$2B to fill all the DPCs currently projected to be loaded in the U.S. This cost could much higher and still represent a substantial cost savings over repackaging [7].

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 more than 60% of the DPC free volume; (2) a minimal intrinsic ability to moderate neutrons and (3) a minimal compaction or volume reduction (10%) after infiltration and solidification. Additional desirable physical, chemical and operational attributes of filler materials are summarized elsewhere [5].

Materials that exhibit these attributes [5] and that are currently under consideration as DPC fillers include low-melting point metals and cements that are primarily phosphate-based. Oak Ridge National Laboratory (ORNL) is currently researching metals and glasses while Sandia National Laboratories (SNL) is researching cement materials because the encapsulation of radioactive waste in the U.S. and other countries is already an important application of chemically bonded phosphate cements [8].

Recently, phosphate-based cement materials have been assessed and recommended for study as potential DPC filler materials [9,10]. While commonly considered cements, they are more accurately described as chemically bonded ceramics as they exhibit ionic or covalent bonds instead of the hydrogen bonds and van der Waals bonds that are active in ordinary Portland cements (OPCs) [8]. However, they also exhibit some of the properties of cements because most, with one important exception described below, are mixed and set at low temperature.

Beyond the desired properties for fillers referenced above, phosphate ceramics have several properties that make them attractive as potential DPC fillers. They are inorganic, nontoxic, have neutral pH, and are insoluble (at near-neutral pH). They are made from low-cost and often naturally occurring materials, they have reasonably long set (working) times of an hour or longer, and they are self-bonding, meaning that a second layer will bond to a previously set layer [9].

This paper describes research currently being conducted for the DOE that is focused on a subset of the phosphate-based materials that have been recommended for study that include: (1) alumina/aluminum phosphate or APC, is a composite material composed of $Al_2O_3/AlPO_4$; (2) calcium phosphate cement or CPC, comprising hydroxyapatite, which has the chemical formula $Ca_5(PO4)_3(OH)$; (3) magnesium potassium phosphate or MKP which has the chemical formula $MgKPO_4$; and (4) a novel fly ash phosphate cement.

RESULTS

Aluminum Phosphate Cement (APC)

APC materials have been described in some detail [11]. The basic formula utilizes an excess of Al_2O_3 reacted with as dilute phosphoric acid (H_3PO_4 in water) to form a smooth pourable slurry. In addition, other phosphate sources including ammonium hydrogen phosphates such as ammonium pentahydrogen diphosphate ($NH_4H_5(PO_4)_2$) are also under investigation. The alumina and the phosphate source react to yield an aluminum phosphate binder phase, which can be $AlPO_4$, and/or a hydrous aluminum phosphate phase such as $AlPO_4 \cdot H_2O$, or possibly an amorphous phase. Because the components react very slowly at room temperature, with a noticeable change in viscosity of the Al_2O_3 /H_3PO_4 / H_2O slurry occurring only after several days, the production of densified cementitious bodies requires heating of the slurry in excess of 130 °C in either a 'wet' pressurized steam atmosphere or 'dry' ambient pressure atmosphere. The 'wet' process is accomplished by reacting the slurry in a sealed container with an excess of water present. In the steam atmosphere at 150 to 200 °C the alumina and phosphate react to yield both $AlPO_4$ and $AlPO_4 \cdot H_2O$. Conversion of the hydrous phase and full densification of the sample may be accomplished by additional heating at ambient pressure. The final $Al_2O_3/AlPO_4$ product is a dense, hard composite material with small isolated pores. If the slurry is heated at ambient pressure, the product is a very hard $Al_2O_3/AlPO_4$ material but this 'dry' process frequently results in densified bodies with large voids likely caused by steam expansion from the reaction between Al_2O_3 and H_3PO_4.

Our best results to date have been obtained by mixing Al_2O_3 and $NH_4H_5(PO_4)_2$ with the addition of a small amount of metakaolin in a 50% aqueous solution. The ratio of Al_2O_3 to metakaolin is in the range of 5 to 10 wt percent, and the mole ratio of Al to total P is approximately 10. A water reducer such as a lignosulfonate or a polyacrylate may be added to reduce viscosity. Boric acid (H_3BO_3) may optionally be included at between 3 and 10 wt. percent with respect to alumina. The resulting slurry is heated slowly (on the order of several °C per hour) to a temperature between 130-200 °C *at ambient pressure*. This produces a strong monolith that contains minimal observable macroporosity and is resistant to attack by water at 200 °C. The Al_2O_3 / metakaolin / phosphate cements also offer low porosity and possibly moderate thermal conductivity.

Calcium Phosphate Cement (CPC)

CPC or hydroxyapatite has been developed for medical/dental repair of bones and teeth [12,13]. It has the added benefit in that it is a very effective sorbent for a variety of radionuclides including the actinides, uranium, strontium and radium [14]. There are well-established routes to prepare CPC primarily based on its use for clinical applications. However, these synthesis routes typically have the disadvantage of fast set times and because the starting materials are produced in small quantities for clinical use there is the added disadvantage of relatively high cost.

Experimental work has begun by using a well-established method of producing CPC with tetracalcium phosphate (TTCP) and dibasic calcium phosphate (DCPA) mixed water with a 73:27 weight ratio to form a smooth flowable slurry [9]. To increase set time, several potential calcium chelating agents including citric acid, formic acid, malonic acid and others have been added to the baseline TTCP/DCPA/water mixture in various amounts. The predominant effect of these additives was longer working time, but after setting the final CPC products were typically poorly consolidated and easily disaggregated. More recently, we have begun to explore the use of longer chain carboxylic and dicarboxylic acid chelators. The use of 1,12 dodecanedicarboxylic acid (DDDA) has begun to show promising results. Because the DDDA is insoluble in neutral water, it requires the addition of a potassium phosphate solution to achieve solubility. This excess phosphate content appears to shift equilibrium towards the formation of a solid precipitate. Meanwhile the DDDA appears to serve a two-fold purpose in CPC synthesis. First, dicarboxylic acid chelation slows the formation of hydroxyapatite, resulting in a longer viable working window. Second, the twelve-carbon chain appears to have acted as a surfactant to improve slurry flow.

Because common dental cements have limited commodity-scale production and high cost, the application of DDDA to CPC formation using more commonly available, less expensive reagents, for example, calcium hydroxide and potassium phosphate solution, is under investigation.

Magnesium Potassium Phosphate (MKP) Cement

Magnesium potassium phosphate cements are high strength materials that are used in a number of construction applications including road repair. They are resistant to temperature swings, road salt, and maintain bond strength better than other construction materials [8]. They tend to cure more slowly than other chemically bonded cement types and can therefore be used more readily in large monolithic pours. Preliminary research on this cement material was initiated using a commercially available MKP cement. The baseline product and the baseline product with a boron carbide (B_4C) additive (~9 wt% B_4C) have been evaluated to date. Initial testing of the baseline product resulted in the formation of a dense, hard monolith. However, very fast set times were observed after adding water to the dry cement product, on the order of 5 to 10 minutes. Similar experiments with the boron carbide modified product resulted in much longer working times ~ 30 minutes. The resulting monoliths are dense, with modestly high strengths, but they disaggregated over a period of ~24 hours when immersed in distilled water. We continue to work with the vendor to develop a modified MKP product with high strength and an increased working time.

Fly Ash Phosphate Cement

A serendipitous discovery during experiments to examine the use of various ratios of fly ash as a filler for APC cements led to the production of a surprisingly dense fly ash phosphate cement. These cements are the product of reaction between coal fly ash and a source of phosphate. A typical cement mixture starts with Class F fly ash, H_3PO_4, and H_2O in a 5:1:1 weight ratio (fly ash: H_3PO_4: H_2O). A water reducer such as lignosulfonate or polyacrylate may also be added. Reactive alumina may be incorporated as well although higher ratios of alumina to fly ash produce friable monoliths that are easily disaggregated. The mixture forms a thin paste or slurry, which thickens to a soft paste over several hours. Upon heating the cement to 130 - 200 °Cat ambient pressure, it loses most of the water and forms a hard, porous concrete monolith. Cohesion improves upon addition of 5-10 wt. % H_3BO_3 to the starting material. The binder phase is not well characterized since it appears amorphous and may be a glass phase. Efforts to characterize this amorphous binder phase are underway.

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