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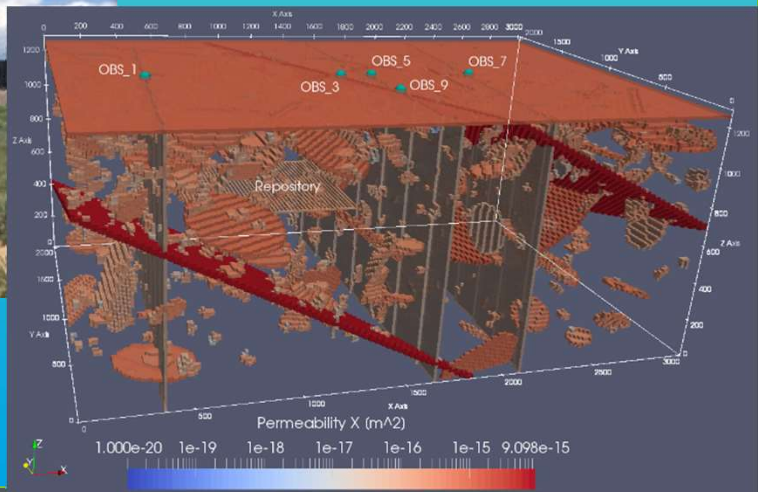
Spent Fuel and Waste Science and Technology (SFWST)



Ongoing Research and Development: Cement Filler Testing and Analysis

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U.S. Nuclear Waste Technical Review Board Virtual Meeting

July 27 28, 2020

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SAND2020 7279 PE

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Key Attributes for DPC Fillers

- Material Compatibility
- Ease of Injectability
- Moderator Displacement
- Minimal Intrinsic Neutron Moderation
- Minimal Gas Generation
- Long-Term Chemical Stability
- Radionuclide Sequestration

Phosphate-Based Cements

Low Melting Point Metals

Phosphate Cements as DPC Fillers

Advantages of Phosphate Cements:

- Inorganic
- Nontoxic
- Near Neutral pH
- Very Low Solubility (at near neutral pH)
- Self-Bonding
- Radionuclide Sequestration

Phosphate Cements Under Evaluation

- Aluminum Oxide / Aluminum Phosphate (Al_2O_3 / $AlPO_4$) Cements (APCs)
- Calcium Phosphate ($Ca_5(PO_4)_3(OH)$) Cements (CPCs)
- Wollastonite / Aluminum Phosphate ($CaSiO_3$ / $AlPO_4$) Cements (WAPCs)
- Fly Ash / Aluminum Phosphate Cements
- Other Commercially Available Cements (as Applicable)

Aluminum Phosphate Cements (APCs)

$Al_2O_3^* + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2O$

- Based on Wagh et al., 2003 using Inexpensive Starting Materials (Al_2O_3 and H_3PO_4).
- Reactants form Smooth Pourable Slurries in Water that are Stable for Days.
- Acid-Base Reaction Results in Near Neutral pH Post Set.
- Set Temperatures Typically at 150-200 ^oC at both Ambient (0.1 megapascal MPa) and Elevated Pressure (up to 1 (MPa)).

* Al_2O_3 is present in excess with respect to H_3PO_4 at ~5:1

Early Attempts…

0.1 MPa Pressure 150 °C

~0.2 MPa Pressure 150 °C

APC Experimental Approach

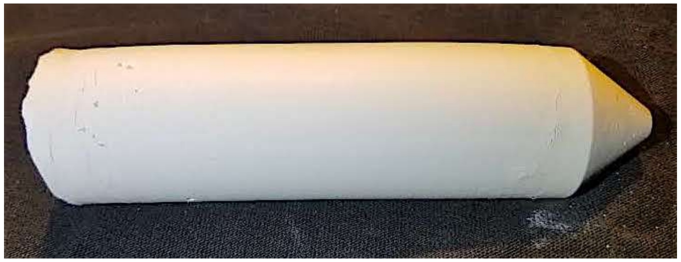
Vary Pressure, Temperature and Time

Effects of Additives I:

Boric acid (H_3BO_3) and gadolinium oxide (Gd_2O_3) as neutron absorbers.

Effects of Additives II:

Catapal B (AlOOH), gibbsite ($Al(OH)_3$), and metakaolin as aluminum sources.
Ammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium pentahydrogen phosphate, ($NaH_5(PO_4)_2$) and ammonium pentahydrogen phosphate $NH_4H_5(PO_4)_2$ as phosphate sources.



APCs at Elevated Pressures (~1 MPa)

- Reaction between Al_2O_3 and aqueous H_3PO_4 at 150 – 200 ^oC at ~1 MPa for 0.5 to 2 days yields well consolidated monoliths.
- Reactants 'set' to produce one or more binder phases: berlinite (α-$AlPO_4$), $AlPO_4 \bullet H_2O$ and $AlPO_4$ – cristobalite.
- Subsequent curing at 250 ^oC for 8 hours yields berlinite (α-$AlPO_4$), and/or $AlPO_4$ – cristobalite.
- It is unclear which $AlPO_4$ phase is more effective as a binder.
- Adequate unconfined compressive strength measured at 5.5 MPa.

APC sample in Pyrex tube (1.25 in x 5 in) after setting and curing.

APCs at Ambient Pressure (0.1 MPa)

- The reaction $Al_2O_3 + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2O$ takes place at ≥ 130 ^oC. Product water as steam causes large voids as APCs set at ambient pressure.
- Additional aluminum sources such as gibbsite ($Al(OH)_3$) and metakaolin reduce or eliminate expansion and large void formation during setting of the cement.
- These sources react with acid phosphates at room temperature, causing APCs to begin setting below 100 ^oC.
- $NH_4H_2PO_4$, $NaH_5(PO_4)_2$, and $NH4H_5(PO_4)_2$ were also tested as alternative phosphate sources.
- APC with metakaolin and $NaH_5(PO4)_2$ additives yielded a unconfined compressive strength of 9.5 MPa.
- Binder phase(s) for the ambient pressure APCs is unidentified in almost all cases and likely amorphous.

Standard APC at Ambient Pressure

APC with metakaolin and $NaH_5(PO_4)_2$ at Ambient Pressure

Wollastonite Aluminum Phosphate Cements (WAPCs)

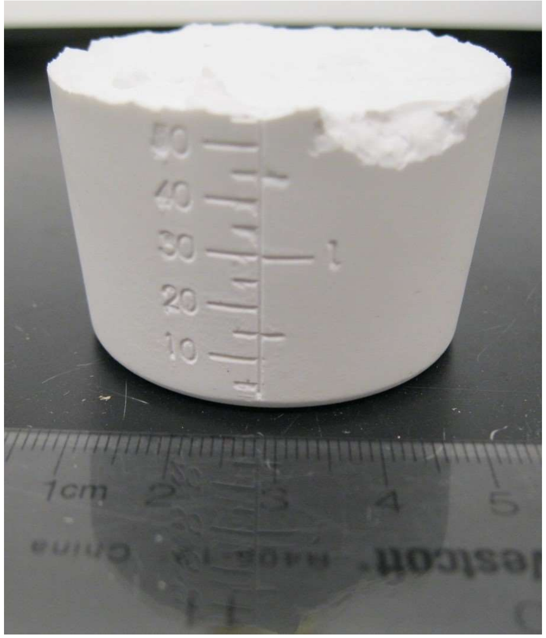
- In the presence of a wollastonite ($CaSiO_3$) filler, $Al(OH)_3$ reacts with aqueous $NaH_5(PO_4)_2$ to make well consolidated monoliths.
- Mixtures are set by slowly ramping temperature to 130 ^{o}C, then are cured at 250 ^{o}C.
- Unconfined compressive strength for WAPC material pictured (11.5 MPa) was greater than all APCs tested.
- Binder phase(s) cannot be identified by XRD and could be amorphous and/or possibly a glass.

WAPC Monolith

Calcium Phosphate Cements (CPCs)

$Ca_4(PO_4)_2O + CaHPO_4 \rightarrow Ca_5(PO_4)_3(OH)$

- Tetracalcium Phosphate (TTCP) and Dibasic Calcium Phosphate (DCPA) react aqueously at room temperature to form CPC (hydroxyapatite).
- Set time is rapid ≤ 25 minutes. Calcium chelators (carboxylic acid-based) were explored to increase set times to 2-3 hours.
- Dodecanedioic Acid (DDDA) a Dicarboxylic Acid was determined to be most effective but required the use of 1 M K_3PO_4 solution (in H_2O) for complete dissolution.
- Produces CPC monoliths composed of hydroxyapatite with some residual starting product (TTCP) that negatively affects strength and integrity.



CPC Monolith

Summary and Next Steps

- Currently APCs and WAPCs show the greatest promise for continued development.
- Continue process and formulation optimization of both cements.
- Development of CPCs that set at elevated temperatures (100-200 ^{o}C) is underway.
- Measurements of filler porosity as well as their permeability to water and gas are also underway.
- Future work includes:
  - Radiation stability and long term solubility testing on optimized products.
  - Develop in-package chemistry models with fillers.
  - Small scale testing of fillers in DPC mock ups.

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Questions?