U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

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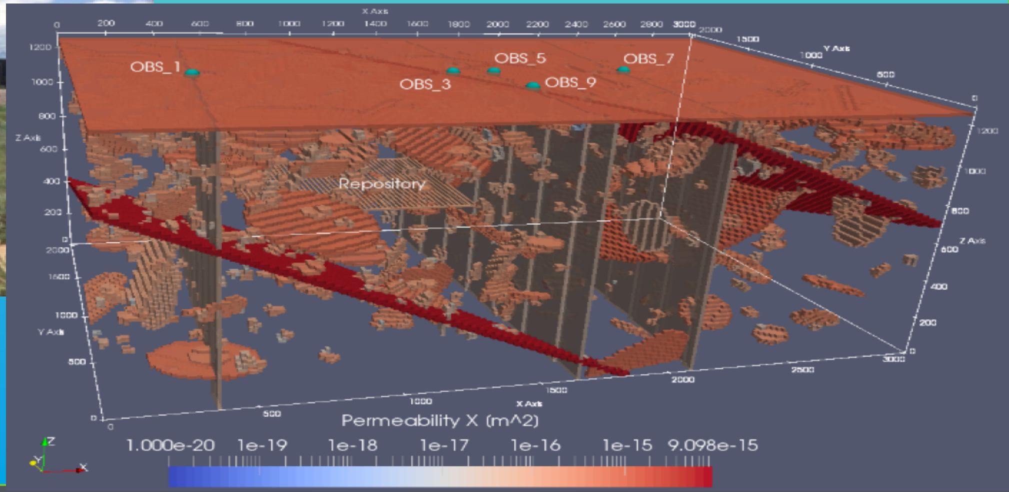

Ongoing Research and Development: Cement Filler Testing and Analysis

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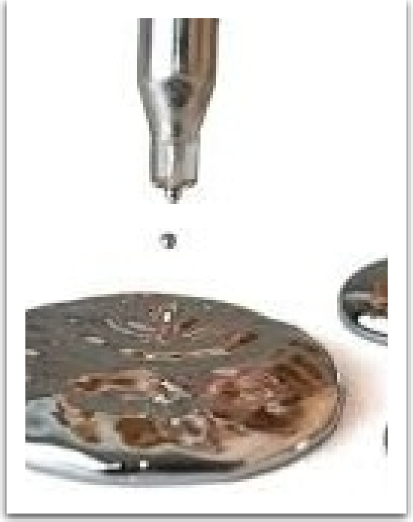
Key Attributes for DPC Fillers

- 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

Features of Phosphate Cements:

- Intrinsic neutron moderation is limited.
- Addition of neutron poisons possible (B_4C, Gd-oxides)
- Slurry properties vary but can be modified.
- Strengths, porosities, etc. vary but can be modified.
- Near Neutral pH
- Very low solubilities (at near neutral pH)
- Self-Bonding
- Radionuclide Sequestration

Phosphate Cements Under Evaluation

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

DPC Filler Target Property Requirements

- Slurry Properties
  - Low viscosity < 1,000 cPi.
  - Non-Newtonian fluid flow (shear thinning) is likely beneficial.
  - Slow set or thermal set – slurry working time of 8 hours.
  - Aggregate grain size < 100 µm.
  - Minimal (or beneficial) reactions between slurry and DPC components.
  - Thermal stability over a wide range of temperatures 50 – 250 ^{o}C.

DPC Filler Target Property Requirements

- Cement Properties
  - Set times of hours to days.
  - Porosity well connected and ≤ 35% with permeability ≈ 10 mD
  - Expansion Ratio (solid volume / fluid volume) ≈ 1.0
  - Strength ≥ 5 MPa unconfined compressive strength (UCS).
  - Near neutral pH.
  - Chemically stable or alterable to stable phases over significant periods of time under repository conditions.

Aluminum Phosphate Cements (APCs)

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

* Al_2O_3 to H_3PO_4 ~5:1

- Simple Acid-Base Reaction with 2 Compounds (4 elements) in Water. (Wagh et al., 2003). Patented!
- Inexpensive Starting Materials (Al_2O_3 and H_3PO_4).
- Reactants form Smooth Pourable Slurries in Water that are Stable for Days at RT.
- Near Neutral pH Post Set.
- Thermal Set Cement, Reaction Initiates at ~130 ^{o}C at Room Pressure.
- Chemical water is generated as $AlPO_4$ binder forms.

Aluminum Phosphate Cements (APCs)

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

- Simple ambient pressure and hydrothermal experiments produce poor products.
  - Cements with significant macro-porosity observed in ambient pressure experiments at various temperatures and times.
  - Hydrothermal experiments in Parr Vessels produce poorly consolidated cements.

Early Attempts…

0.1 MPa Pressure 150 °C

~0.2 MPa Pressure 150 °C

Modified APC Formulations

- The reaction $Al_2O_3 + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2O$ takes place at ≥ 130 °C. 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.
- Al sources react with phosphates at room temperature, causing APCs to begin setting below 100 °C.
- $NH_4H_2PO_4$, $NaH_5(PO_4)_2$, and $NH_4H_5(PO_4)_2$ were also tested as alternative phosphate sources.


Standard APC at Ambient Pressure


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

APCs: Challenges and Opportunities

- Porosity tends to be high (> 40%) and permeability low (0.1-1 mD) in the APC variants.
  - Varying the Al_2O_3 starting material (reactive vs calcined Al_2O_3) and the use of $NH_4H_2PO_4$ as a phosphate source (pH = 4) shows promise for porosity/permeability and expansion control.
  - Aluminum modifiers, particularly metakaolin, also show promise for porosity/permeability control.
  - The addition of neutron poisons can mitigate porosity concerns but permeability must improve so that water can escape during cement setting. The addition of B-based materials and Gd-oxides tend to reduce strength, more research is necessary.

APCs: Challenges and Opportunities

A large number of aluminum phosphate phases are observed as products (α-$AlPO_4$, β-$AlPO_4$, y-$AlPO_4$, $AlPO_4 \bullet H_2O$, $AlPO_4$ zeolite, amorphous aluminum phosphate phases)…

- $AlPO_4$ polymorphs and even the amorphous aluminum phosphate phases can be effective binders.

And…

- Preliminary geochemical modeling indicates $AlPO_4$ polymorphs and $AlPO_4 \bullet H_2O$ likely to alter to variscite $AlPO_4 \cdot 2(H_2O)$ while Al_2O_3 will likely alter to boehmite (AlOOH) with a significant increase in cement solid volume.

Calcium Aluminate Phosphate Cements (CAPCs)

- Calcium aluminates are synthesized by heating CaO and Al_2O_3 blends at high temperatures.
- Krotite $CaAl_2O_4$ aka 'CA' reacts with phosphate to form a cement (developed and patented by Sugama, BNL).
- CA also reacts with water to form CAH bonded cements but Grossite ($CaAl_4O_7$) aka 'CA2' is only weakly hydraulic.
- Grossite ($CaAl_4O_7$) aka 'CA2' & Hibonite ($CaAl_{12}O_{19}$) aka 'CA6' were synthesized and reacted with phosphoric acid.

Grossite Phosphate Cement

Calcium Aluminate Phosphate Cements (CAPCs)

Grossite ($CaAl_4O_7$) reactions with H_3PO_4

- Binder phase is currently unknown and likely amorphous.
- Shrinkage can be minimal (ER=0.98).
- Recent experiments with grossite and alternative phosphate sources (sodium hexametaphosphate) are increasing working times to days.
- Starting pH's range between ~3-6.
- Binder phase is likely hydrous and an assessment of water and/or H_2 gas generation upon irradiation will be initiated soon.

Summary and Next Steps

- Currently APCs and CAPCs show the greatest promise for continued development.
- Continue process and formulation optimization of both cements.
- 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?