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 (Al₂O₃ / AlPO₄) Cements (APCs)
- Calcium Phosphate (Ca₅(PO₄)₃(OH)) Cements (CPCs)
- Wollastonite / Aluminum Phosphate (CaSiO₃ / AlPO₄) Cements (WAPCs)
- Fly Ash / Aluminum Phosphate Cements
- Other Commercially Available Cements (as Applicable)
Aluminum Phosphate Cements (APCs)

$\text{Al}_2\text{O}_3^* + 2\text{H}_3\text{PO}_4 \rightarrow 2\text{AlPO}_4 + 3\text{H}_2\text{O}$

- Based on Wagh et al., 2003 using Inexpensive Starting Materials (Al$_2$O$_3$ and H$_3$PO$_4$).

- 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 °C at both Ambient (0.1 megapascal MPa) and Elevated Pressure (up to 1 (MPa)).

* Al$_2$O$_3$ is present in excess with respect to H$_3$PO$_4$ 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 (H₃BO₃) and gadolinium oxide (Gd₂O₃) as neutron absorbers.

Effects of Additives II:
Catapal B (AlOOH), gibbsite (Al(OH)₃), and metakaolin as aluminum sources.
Ammonium dihydrogen phosphate (NH₄H₂PO₄), sodium pentahydrogen phosphate, (NaH₅(PO₄)₂) and ammonium pentahydrogen phosphate NH₄H₅(PO₄)₂ as phosphate sources.
APCs at Elevated Pressures (~1 MPa)

- Reaction between $\text{Al}_2\text{O}_3$ and aqueous $\text{H}_3\text{PO}_4$ at 150 – 200 °C at ~1 MPa for 0.5 to 2 days yields well consolidated monoliths.

- Reactants ‘set’ to produce one or more binder phases: berlineite ($\alpha$-$\text{AlPO}_4$), $\text{AlPO}_4 \cdot \text{H}_2\text{O}$ and $\text{AlPO}_4$ – cristobalite.

- Subsequent curing at 250 °C for 8 hours yields berlineite ($\alpha$-$\text{AlPO}_4$), and/or $\text{AlPO}_4$ – cristobalite.

- It is unclear which $\text{AlPO}_4$ phase is more effective as a binder.

- Adequate unconfined compressive strength measured at 5.5 MPa.
APCs at Ambient Pressure (0.1 MPa)

- The reaction \( \text{Al}_2\text{O}_3 + 2\text{H}_3\text{PO}_4 \rightarrow 2\text{AlPO}_4 + 3\text{H}_2\text{O} \) takes place at \( \geq 130 \) °C. Product water as steam causes large voids as APCs set at ambient pressure.

- Additional aluminum sources such as gibbsite (\( \text{Al(OH)}_3 \)) 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 °C.

- \( \text{NH}_4\text{H}_2\text{PO}_4, \ \text{NaH}_5(\text{PO}_4)_2, \) and \( \text{NH}_4\text{H}_5(\text{PO}_4)_2 \) were also tested as alternative phosphate sources.

- APC with metakaolin and \( \text{NaH}_5(\text{PO}_4)_2 \) 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.

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Wollastonite Aluminum Phosphate Cements (WAPCs)

- In the presence of a wollastonite (CaSiO₃) filler, Al(OH)₃ reacts with aqueous NaH₅(PO₄)₂ to make well consolidated monoliths.

- Mixtures are set by slowly ramping temperature to 130 °C, then are cured at 250 °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.
Calcium Phosphate Cements (CPCs)

\[ \text{Ca}_4(\text{PO}_4)_2 \text{O} + \text{CaHPO}_4 \rightarrow \text{Ca}_5(\text{PO}_4)_3(\text{OH}) \]

- Tetracalcium Phosphate (TTCP) and Dibasic Calcium Phosphate (DCPA) react aqueously at room temperature to form CPC (hydroxyapatite).

- Set time is rapid \( \leq 25 \) 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 \( \text{K}_3\text{PO}_4 \) solution (in \( \text{H}_2\text{O} \)) for complete dissolution.

- Produces CPC monoliths composed of hydroxyapatite with some residual starting product (TTCP) that negatively affects strength and integrity.
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 °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.
Selected References


Selected References


Questions?