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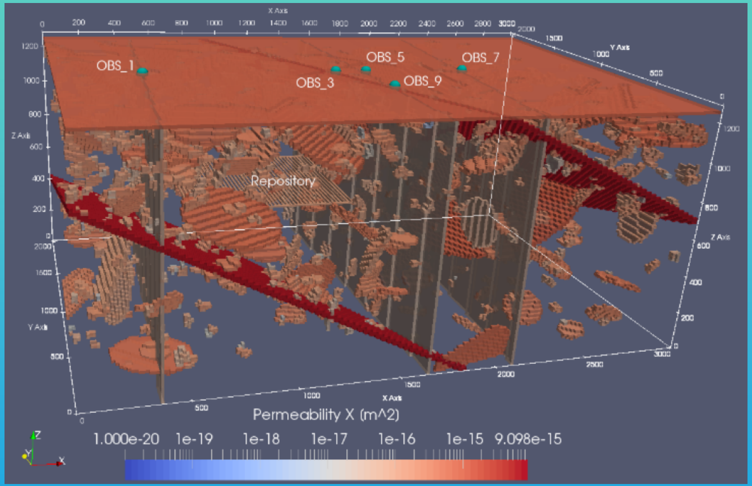

Progress on DPC Cement Filler Development

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Options for Dual Purpose Canister (DPC) Disposal*

*Spent Nuclear Fuel (SNF) currently stored in DPCs at numerous sites across the US.

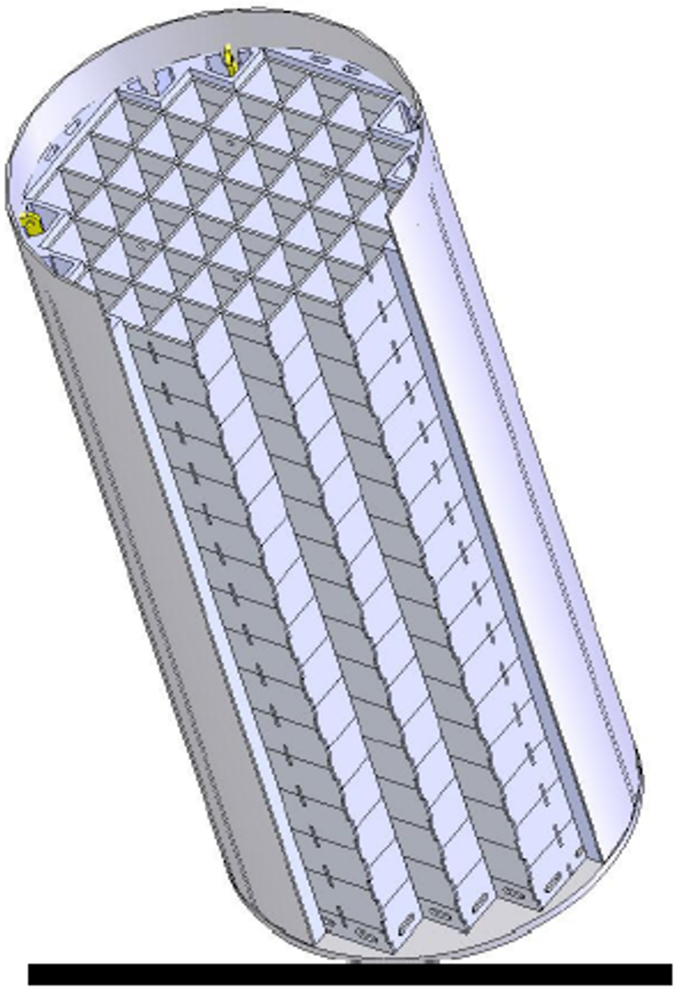
Repackage the SNF into canisters that are designed to remain subcritical during the regulated post-closure period following disposal.

Alternatives Under Evaluation:

Direct Disposal of DPCs.

Fill and dispose DPCs with a material that significantly limits criticality over the post-closure regulatory period.

*As of June 2022 there are more than 3,700 DPCs in storage across the U.S.



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Attributes for DPC Fillers

- Moderator Displacement
- Material Compatibility
- Ease of Injectability
- 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 / non-corrosive
- Set at elevated temperature
  - Long room temp working times availabl
- Very low solubilities
- Self-bonding
- Radiation stable
- Radionuclide sequestration

$CaSiO_3$ / $Al(OH)_3$ with sodium phosphate

Phosphate Cements Under Evaluation

Phosphate cements: aqueous phosphate with materials containing CaO and/or Al_2O_3.

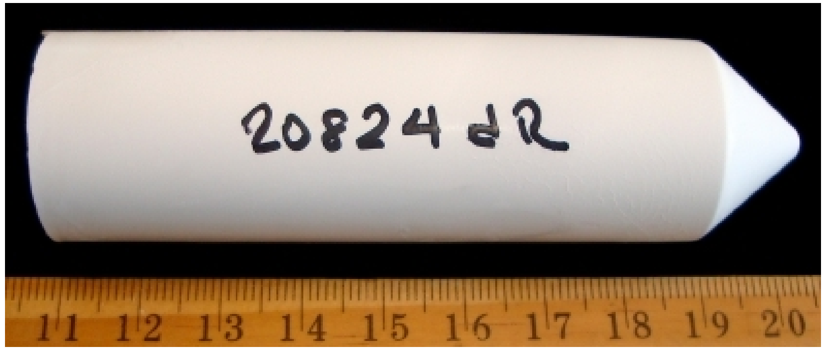
Examples of reactants:

Aluminum Oxide (corundum), $Al(OH)_3$

- $CaSiO_3$ (wollastonite)
- Calcium aluminate ($Ca_3Al_2O_6$, $CaAl_2O_4$,
- $CaAl_4O_7$, $CaAl_{12}O_{19}$)
- Blends of the above oxides

Phosphate sources:

- Orthophosphate (H_3PO_4, $NH_4H_2PO_4$, NaH_2PO_4)
- Polyphosphate ($Na_5P_3O_{10}$, $(NaPO_3)_3$,
- $(NH_4PO_3)_X$, $(NaPO_3)_6$)
- Boron phosphate (BPO_4)



1:1 $CaSiO_3$ / $CaAl_4O_7$ with $(NaPO_3)_6$

$CaAl_4O_7$ with $(NaPO_3)_6$

Advanced Testing of PO_4 Cements

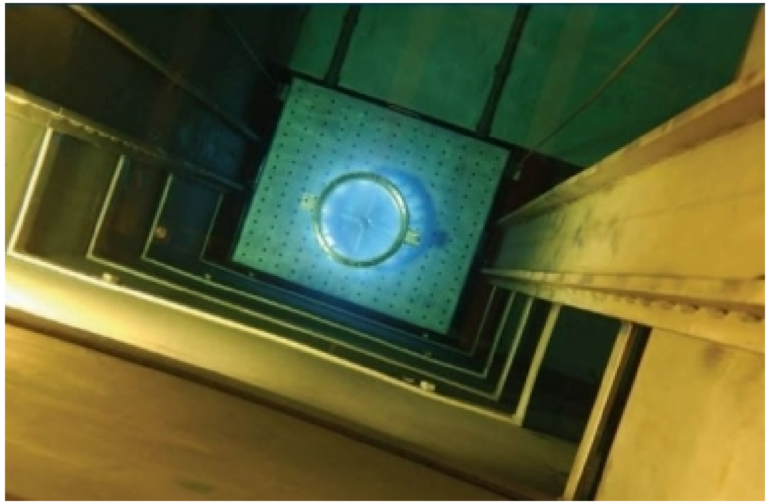
^{60}Co gamma radiation testing:

24 2”x1” samples of 6 compositions were made.

2 samples of each composition were exposed to ~25 MGy ^{60}Co gamma over 2 weeks.

The compositions:

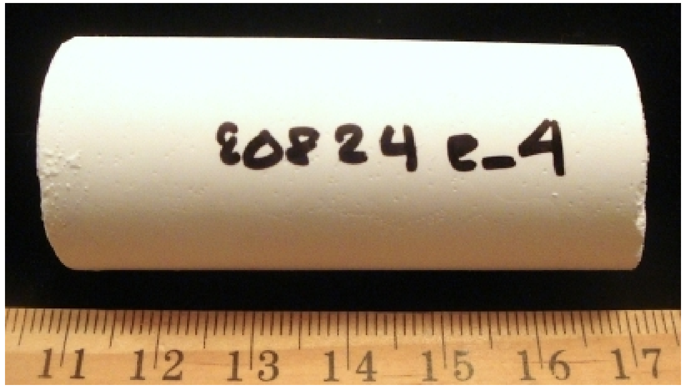
- $CaAl_4O_7$ / $CaSiO_3$ with polyphosphate (2)
- $CaSiO_3$ / $Al(OH)_3$ with BPO_4
- $CaAl_4O_7$ / $GdAlO_3$ with polyphosphate
- $CaAl_4O_7$ with polyphosphate
- $CaAl_4O_7$ / $CaAl_2O_4$ with polyphosphate



Hydrothermal testing:

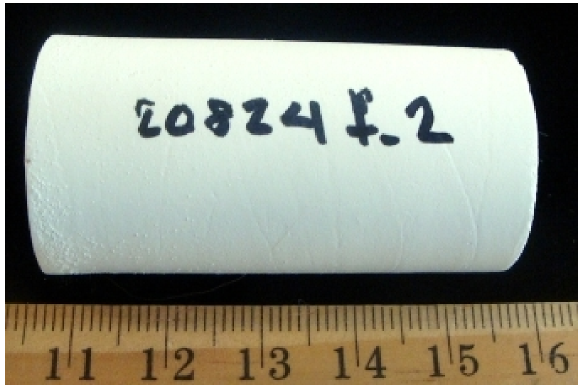
One sample of each irradiated cement was immersed in water at 250 C / 39.8 MPa for 7 days.

Gamma Radiation / Hydrothermal Test Results



Contains AlOOH and ($Ca_5(PO_4)_3OH$) by XRD. $CaSiO_3$ was not detected.

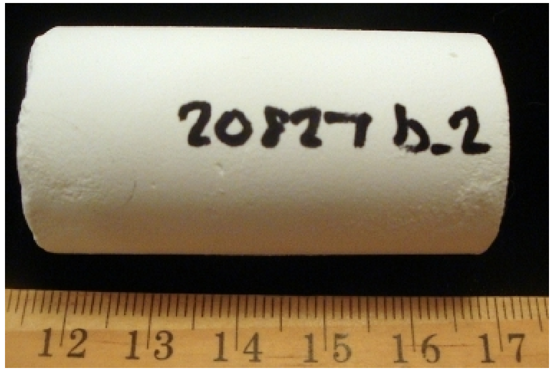
1:9 $CaSiO_3$ / $CaAl_4O_7$ with $(NaPO_3)_6$	UCC Strength (MPa)	Young's Modulus (GPa)	Poisson's Ratio
pre- ^{60}Co	n/a	n/a	n/a
post- ^{60}Co	54.7	10.0	0.14
^{60}Co + H_2O / 250 °C	67.2	25.1	0.23



Contains $CaSiO_3$, $Ca_5(PO_4)_3OH$, and $AlPO_4$.

1:24 $CaSiO_3$ / $CaAl_4O_7$ with $(NaPO_3)_6$	UCC Strength (MPa)	Young's Modulus (GPa)	Poisson's Ratio
pre- ^{60}Co	4.7	2.3	0.16
post- ^{60}Co	5.5	3.2	0.15
^{60}Co + H_2O / 250 °C	5.1	2.4	0.08

Gamma Radiation / Hydrothermal Test Results



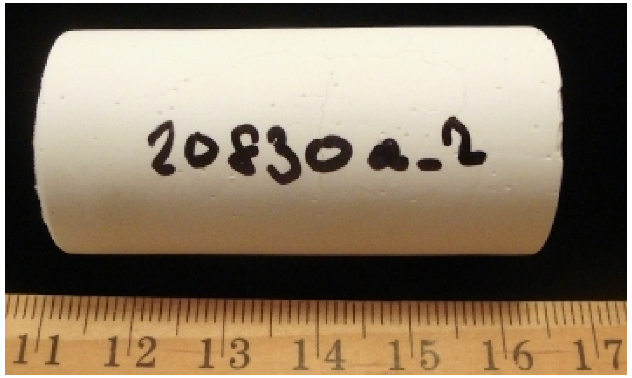
Contains $CaSiO_3$ and $Ca_9Al(PO_4)_7$.

Consists of an undetermined phase.

10:1 $CaSiO_3$ / $Al(OH)_3$ with BPO_4	UCC Strength (MPa)	Young's Modulus (GPa)	Poisson's Ratio
pre- ^{60}Co	8.3	43	n/a
post- ^{60}Co	6.1	1.67	0.13
^{60}Co + H_2O / 250 °C	0.8	25.1	n/a

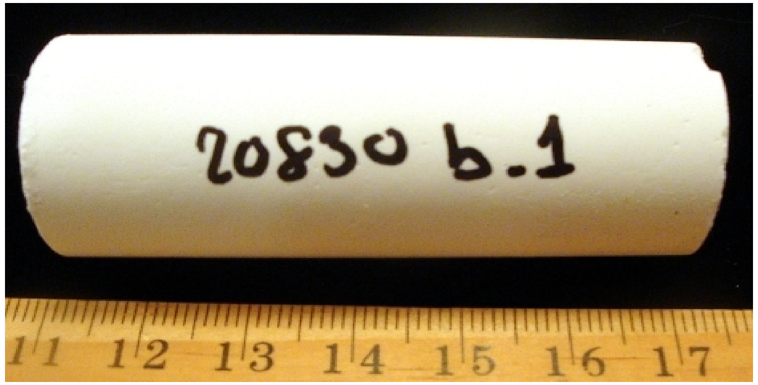
1:17 $GdAlO_3$ / $CaAl_4O_7$ with $(NaPO_3)_6$	UCC Strength (MPa)	Young's Modulus (GPa)	Poisson's Ratio
pre- ^{60}Co	65.0	24.5	0.21
post- ^{60}Co	n/a	n/a	n/a
^{60}Co + H_2O / 250 °C	33.9	5.5	0.23

Gamma Radiation / Hydrothermal Test Results



Contains AlOOH and $Ca_5(PO_4)_3OH$.

$CaAl_4O_7$ with $(NaPO_3)_3$ and $(NaPO_3)_6$	UCC Strength (MPa)	Young's Modulus (GPa)	Poisson's Ratio
pre- ^{60}Co	69.7	12.8	0.21
post- ^{60}Co	53.6	22.7	0.18
^{60}Co + H_2O / 250 °C	53.6	20.8	0.24



Contains AlOOH and $Ca_5(PO_4)_3OH$.

1:4 $CaAl_2O_4$ / $CaAl_4O_7$ with $(NaPO_3)_6$	UCC Strength (MPa)	Young's Modulus (GPa)	Poisson's Ratio
pre- ^{60}Co	67.6	24.5	0.2
post- ^{60}Co	36.1	8.05	0.13
^{60}Co + H_2O / 250 °C	36.7	9.0	0.17

Observations

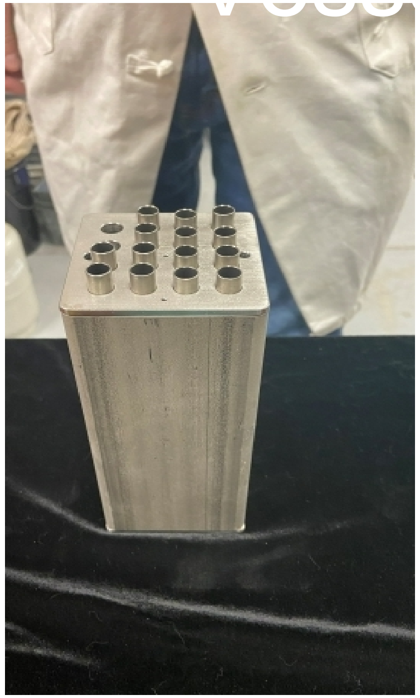
- Radiation by itself had little effect on external appearance or crystal structure.

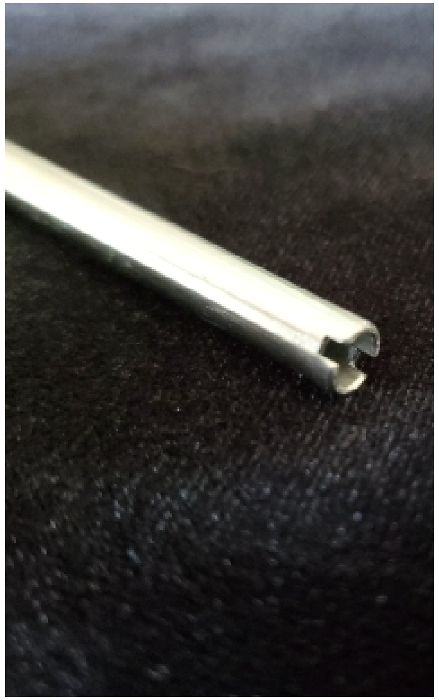
- UCC measurements indicate samples were, on average, weakened by ^{60}Co γ irradiation.

- Hydrothermal exposure altered crystal structures of cement monoliths without changing gross morphology. In one case UCS increased.

- In-situ generation of $Ca_5(PO_4)_3OH$ has the potential to sequester both actinides (e.g., U and Pu) and fission products (Sr).

Subscale DPC Filler Test Vessel





70 mm x 70 mm x 168 mm tall 304 stainless steel vessel.

16 cartridge heaters sheathed in zircaloy fuel rods, input voltage to heaters controlled by variable transformer.

Cement inlet tube designed to represent “drain pipe” with restricted flow.

Weight monitored during filling to observe weight gain / loss over time.

Temperature monitored by two thermocouples during the experiment.

Subscale DPC Filler Test: Pure $CaAl_4O_7$ / $(NaPO_3)_6$

Set power to achieve internal temperature of ~260 °C while the test fixture was closed.

Inlet tube is registered at the top of the vessel.

With the vessel on a scale, filling is initiated at a rate of 7 g / minute and completed after 2.6 hours when the vessel reached capacity.

Temperature at end of fill was 98.3 °C (boiling point of water). Heating was continued for another 43 hr until weight stabilized (presumed set), temperature 215.9 °C.

A 20 ton press was used to remove the cured material; cement may have been damaged upon extraction.

Conclusions and Recommendations

- $CaAl_4O_7$ / $CaSiO_3$ blends with polyphosphate show considerable promise with respect to durability based on preliminary irradiation and hydrothermal testing.

- Cement alteration to hydroxylapatite, an actinide and Sr getter, may be valuable.

- Increased strength upon hydrothermal exposure may be from self healing and/or self sealing. We will investigate.

- Future work will focus on using $CaAl_4O_7$ / $CaSiO_3$ phosphate cements in DPC mock-ups of increasing scale and complexity.