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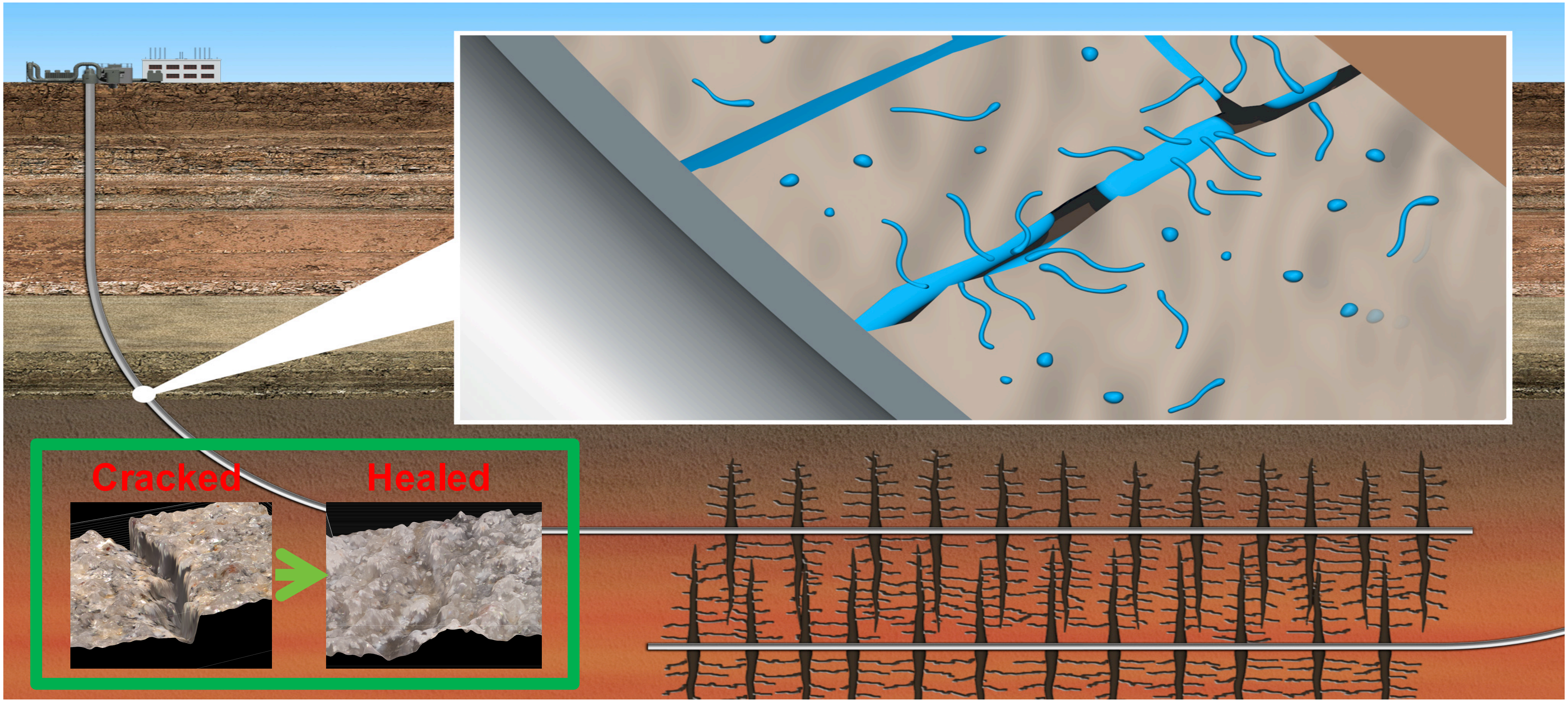


Self-Healing & Re-Adhering Cements with Improved Toughness at Casing and Formation Interfaces for Geothermal Wells

Project Officer: Eric Hass
Total Project Funding: $3,000,000
November 14th, 2017

Carlos A. Fernandez (PI)
Pacific Northwest National Lab
with Brookhaven National Lab and National Energy Technology Lab

Track Name

Relevance to Industry Needs and GTO Objectives

Challenges/Barriers

- Damage of underground cement and other structures is challenging not only to repair but often to even locate
- Major factors causing failure are:
  1. Cement-well incompatibility, i.e., lack of chemical bonding to metal casing and clays/rocks
  2. Undesirable phase transitions in cement at the interfaces
  3. Mechanical, thermal, and chemical stress
- Thermally/chemically stable cements with self-healing properties and improved adhesion at casing and formation interfaces are yet to be developed

Project Objectives

- To develop advanced cement composites with the following features:

1. Self-repairing capability of cracked cement matrix

2. Re-adhering ability to casing and formation

3. Resilience to high T environment *(including thermal shock)*

4. Improved chemical stability

- All resulting in lifetime cost reduction leading to a reduction of the LCOE on geothermal power generation via:
  - A. Enhancing wellbore integrity and operational safety
  - B. Reducing frequency of wellbore intervention, associated repair costs, and temporarily production shutdown

Project Supports the following GTO Goal(s)

1. Improving processes of identifying, accessing, and developing geothermal resources
2. Identifying and accelerating near term conventional and/or blind hydrothermal resource growth
3. Accelerating a commercial pathway to and securing the future of Enhanced Geothermal Systems
4. Overcoming deployment barriers
5. Collaborating on solutions to subsurface energy challenges

Methods/Approach

Summary of 3y-project plan (so far, no deviation from original plan):

FY16: a. Screening novel polymer-cement and inorganic-cement composites that outperform conventional wellbore cement by retaining +90% mechanical strength when subjected to different EGS-representative thermal and chemical environments.

b. Demonstrate self-repairing capability.

FY17: a. Down-select polymer-cement and inorganic-cement composites based on re-adhering capability to casing after mechanical (shear) separation

b. Demonstrate multiple re-adhesion to casing after materials weathering under different thermal and chemical EGS-representative conditions.

FY18: **Synthesis of a hybrid inorganic-polymer cement composite(s) that synergistically combine the properties of the best-performing (organic and inorganic) composites** towards amplifying the range of EGS fields at which these advanced materials can be deployed at followed by:

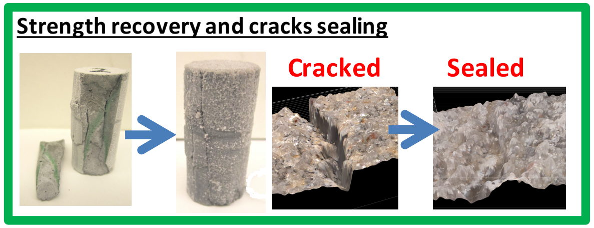
a. Long-term (one month) high temperature (up to 300C) performance evaluation including self-healing capability
b. Evaluation of cement-rock interface bond strength and re-adherence after exposure to different EGS's thermal & chemical conditions
c. Evaluation of slurry pumpability following API standards

Tasks performed at EGS-representative conditions

1. **Additives-cement slurry compatibility (FY16)**
   a. Slurry homogeneity b. Slurry density c. Slurry viscosity and consistency at 85C

2. **Bulk mechanical properties (FY16)**
   a. Compressive strength b. Fracture toughness c. Young Modulus
   d. Before and after 1-month exposure of material to:
      i. 6 cycles of 25C-300C
      ii. H2SO4 pH 1-2 brine at 90C
      iii. 15,000 ppm CO2 in brine at 90C for 1 month

3. **Self-repairing capability (FY16)**
   a. After shear fracture
   b. Compressive strength before and after heal event
   c. Permeability before and after heal event



X-ray Microtomography of a fracture before and after healing in an inorganic-cement composite


HP/HT reactors for cement weathering at different EGS-representative conditions

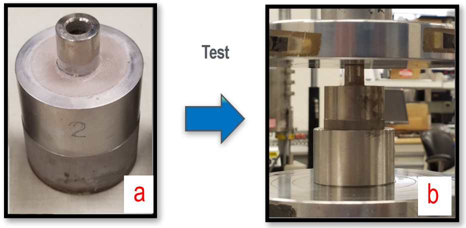
Methods/Approach

Tasks performed at EGS-representative conditions (cont.)

4. **Cement-casing interface mechanical properties (FY17)**
   a. Shear bond strength at cement-steel interface before material's weathering (lap-shear and/or pipe-shear)
   b. Shear bond strength at cement-steel interface after material's exposure (1 week) to:
      i. 6 cycles of 25C-300C
      ii. H_2SO_4 pH 1-2 in 1wt% NaCl brine at 90C
      iii. 15,000 ppm CO_2 in 1wt% NaCl brine at 90C
   c. Re-adhesion (healing) capability at cement-steel interface after shear separation before material's weathering
   d. Re-adhesion (healing) capability at cement-steel interface after shear separation after material's exposure (1 week) to:
      i. Identical conditions as in b.

Lap-shear testing

5. Chemical analysis including atomistic simulations (FY16- FY17)
   a. SEM/EDX, X-ray diffraction spectroscopy (XRD), CT scan, FTIR, synchrotron high-resolution XMT,
   b. X-ray fluorescence spectroscopy (XAS), X-ray absorption near edge structure spectroscopy (XANES),
   c. Surface area analysis and pore size distribution analysis



New pipe-shear testing

5. Will the advanced cements last? Long-term thermal stability and healing ability (FY18)
   a. One month curing followed by compressive strength, permeability, and adhesion to casing analysis
   b. Shear fractures followed by permeability analysis and healing materials at 200-300C temperatures
   c. Perform post-healing tests (cement matrix and cement-casing interface) including:
      I. Compressive strength (recovery)
      II. Permeability reduction
      III. Re-adhesion (adhesive strength recovery)

6. **Cement-formation interface mechanical properties (FY18):** Identical approach to item 4 replacing steel with granite

7. **Rheological and placement tests (thickening time) (FY18):**
   a. Under typical simulated pressure and Bottom Hole Circulating Temperature (BHCT) according to API standards

HP/HT multi-fluid rheometer

Technical Accomplishments and Progress: **Polymer-Cement Composites**

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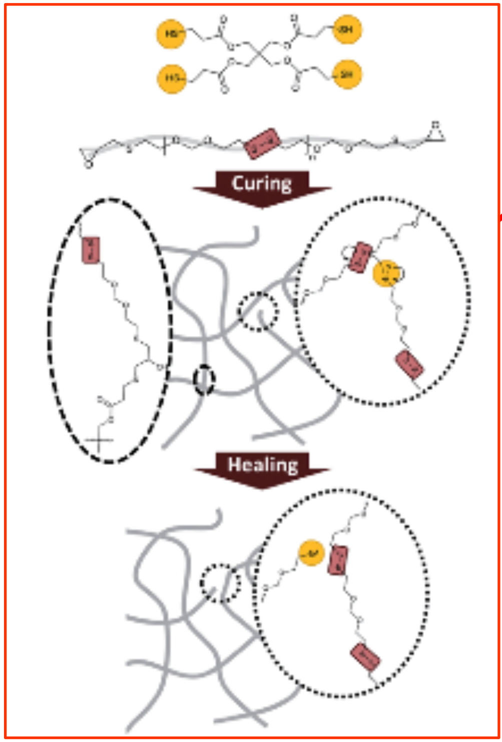
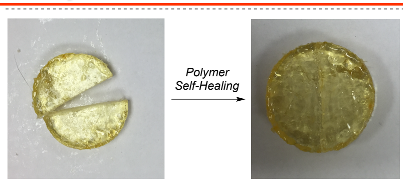
Concept Summary

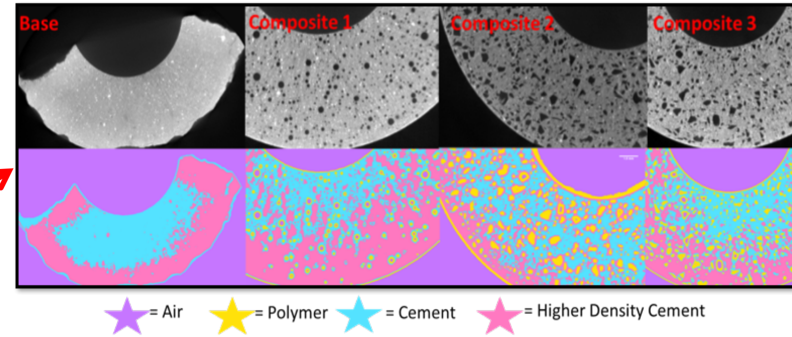
Combine a self-healing polymer w the cement to create a self-healing polymer-cement composite material



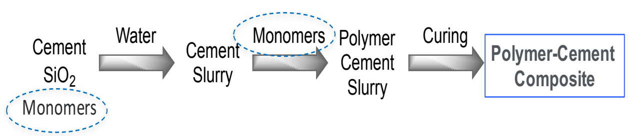


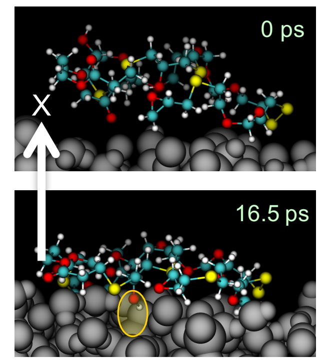
All milestones met on time and budget

“Molecular Velcro”: Reversible Interactions for multiple and fast self-healing



How the composite is made?

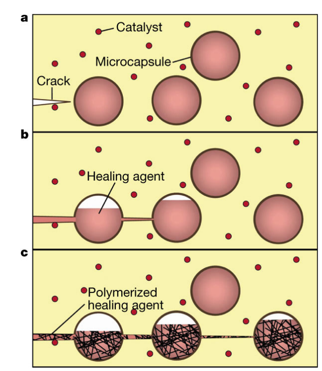




Atomistic simulations confirmed **healing due to reversible and dynamic polymer-cement and polymer-polymer debonding-bonding**

Polymer chemistries:

- Thermally-stable monomers, and crosslinkers
- Polymer molecules anchored to cement matrix and interfaces via coordination bonds, covalent bonds, H-bonding, and/or van der Waals interactions
- Introduce self-healing properties in bulk cement and self-re-adhesion at cement-formation and cement-casing interfaces



Current state of the art: Microcapsules

Technical Accomplishments and Progress: **Polymer-Cement Composites**

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Tests statistics

+35 polymers
Cement H
Silica flour

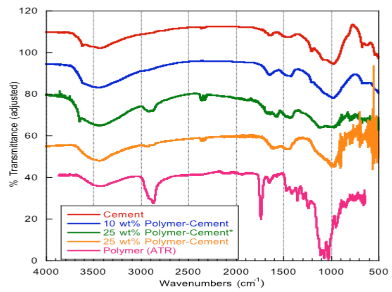
+590 samples tested

3 environments

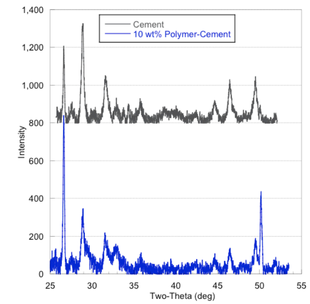
Rheological, thermal, chemical and spectroscopic analysis

FY16 M1 met: identify at least 2 organic-based and 2 inorganic-based cement composites for initial screening
FY16 M2 met: Identify at least 1 organic and 1 inorganic slurry with flowability (3 hours at 85° C) similar to OPC slurries.

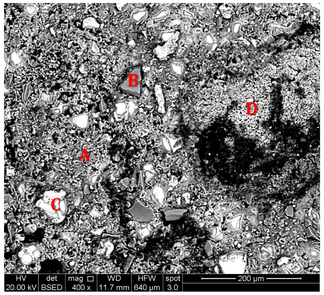
Polymer presence confirmed by FTIR



Two main phases, xonolite and quartz when curing at 85C

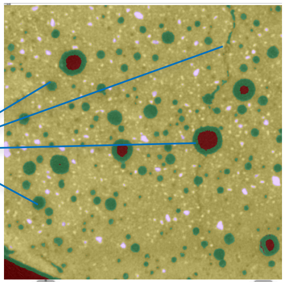


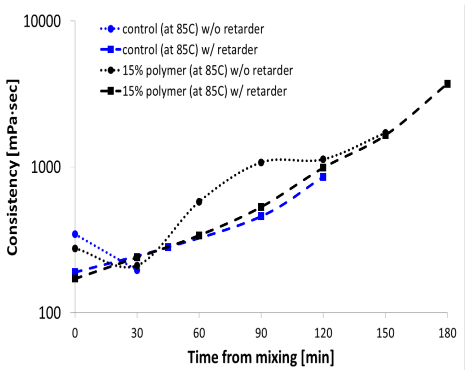
SEM/EDX: Areas rich in C & S due to polymer presence



Polymer homogeneously distributed in cement matrix (XMT)

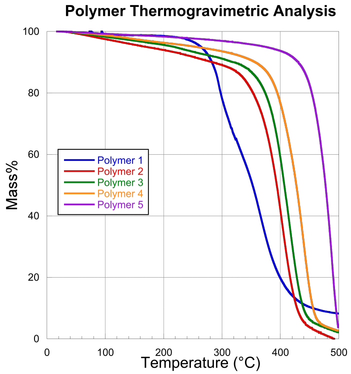
Polymer



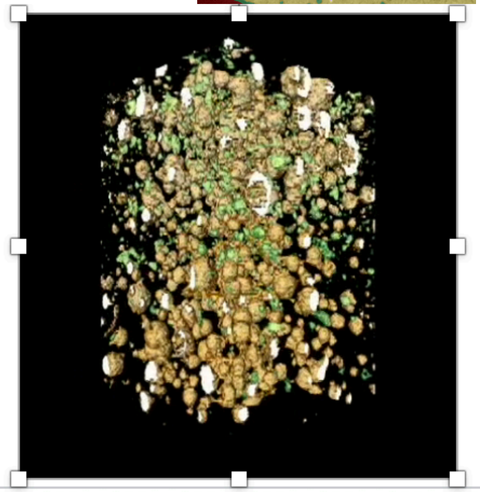


Slurry consistency

1. Polymer cement slurries show similar rheological properties to traditional well cements
2. Use of a retarder might not be required



TG suggests high thermal stability (250-430 C !)



Technical Accomplishments and Progress: **Polymer-Cement Composites**

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Cement composites resistance to EGS environments

FY16 M3 met: At least one cement composite with structural fracture toughness >0.006 $MN/m^{3/2}$

FY16 M4 met: Cement composite(s) with structural toughness ≥90% with respect to unexposed cement after weathering

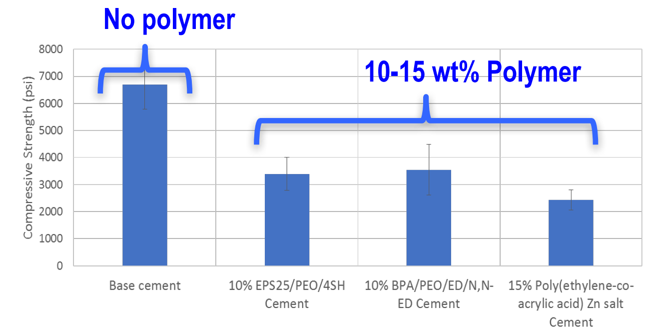
Note: PNNL/NETL was limited to 250C for curing or thermal weathering (instead of originally proposed 300C

Geothermal well criteria:

Compressive strength >1000psi

Fracture toughness > 0.006 MN $m^{-3/2}$

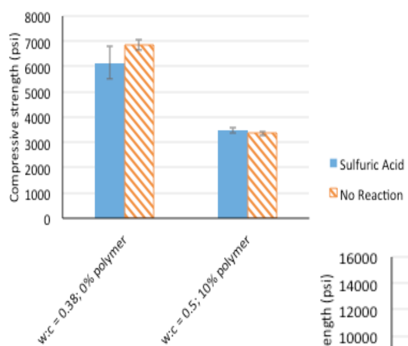
Compressive strength **BEFORE** weathering

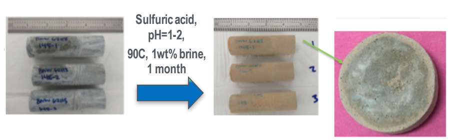


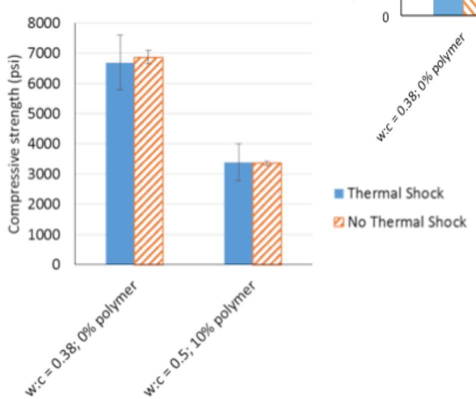
Fracture toughness before weathering:
Polymer-cement = 0.007 MN $m^{-3/2}$
Base cement = 0.011 MN $m^{-3/2}$

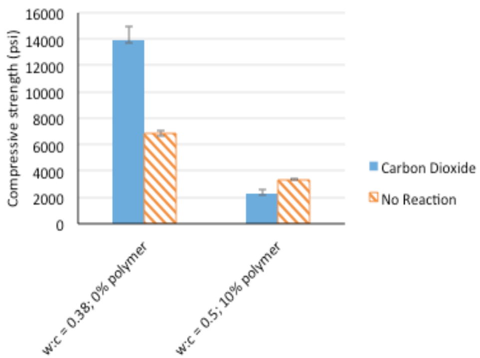
Young Modulus before weathering:
Polymer-cement = 7.0 GPa
Base cement = 11.3 GPa

Compressive strength **AFTER** exposure to thermal shock, mineral acid/brine, CO_2/brine









Compressive strength after weathering

Polymer-cement

- Remained unchanged when exposed to:
  - ✓ Six thermal shock cycles
  - ✓ High temperature mineral acid
- Decreased by 30% when exposed to:
  - ✓ High HP/HT CO_2 / brine

Conventional cement

- Only 7% decrease after thermal shock and 13% decrease after mineral acid exposure.
- Doubled by carbonation

Technical Accomplishments and Progress: **Polymer-Cement Composites**

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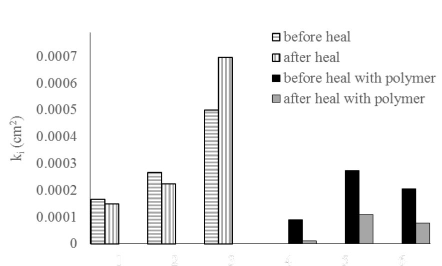
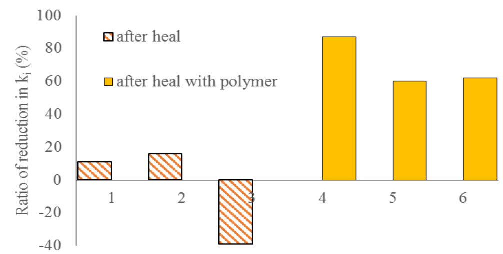
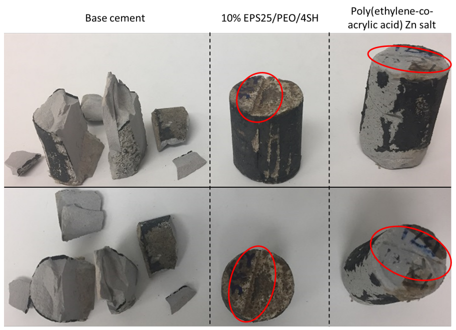
Polymer-cements **reduced permeability by 62-87%** on shear-generated fractures (apertures up to 0.5mm !)

Cement composites self-repairing ability





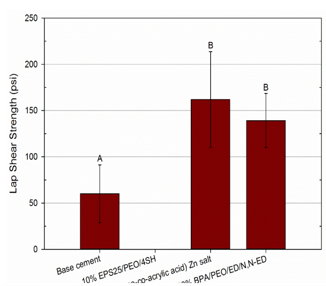


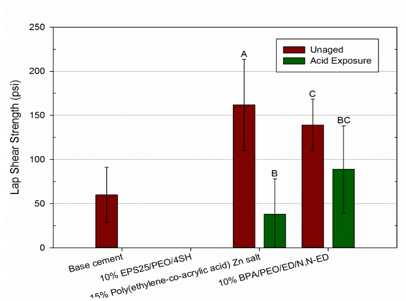
FY17 M1 met: Cement composites with shear bond strength @ carbon steel (CS) /cement joint +30%> OPC

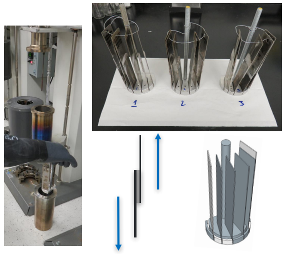
FY17 M2 and Go/No-go met: At least one cement formulation with ≥30% higher resistance to shear debonding at steel interfaces with respect to OPC after weathering

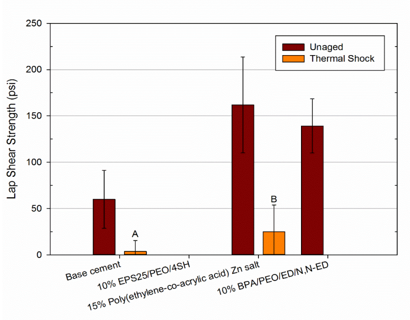
Note: Large variance in shear tests values using lap-shear method made these tests very challenging

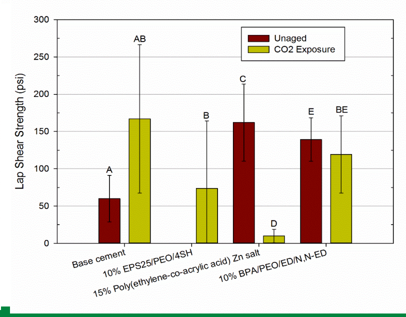
Cement composites adhesion to steel casing











Before Weathering:

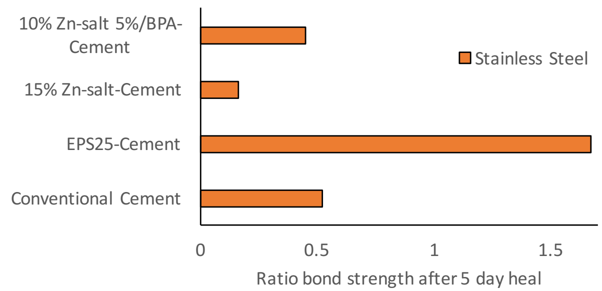
- Polymer-cements **outperform (by nearly 3X)** conventional cement's adhesive strength to SS casing

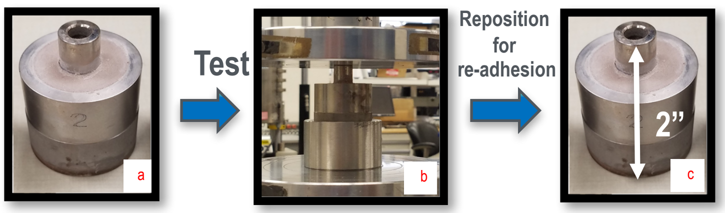
After weathering:

- ***Thermally-shocked samples:*** **polymer-cements outperform by 6X** base cement
- ***Sulfuric acid attack:*** polymer-cements **outperform by 40X** base cement
- ***CO_2 brines:*** **Polymer-cements** have statistically **similar adhesion** to base cement.

Technical Accomplishments and Progress: Polymer-Cement Composites

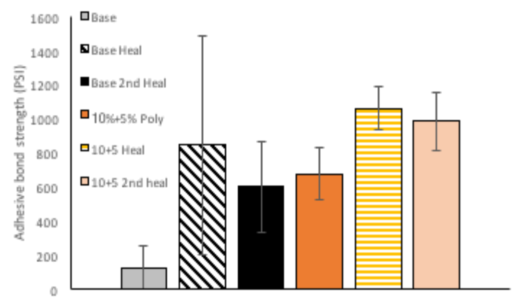
Cement composites multiple re-adhesion (healing) to steel casing



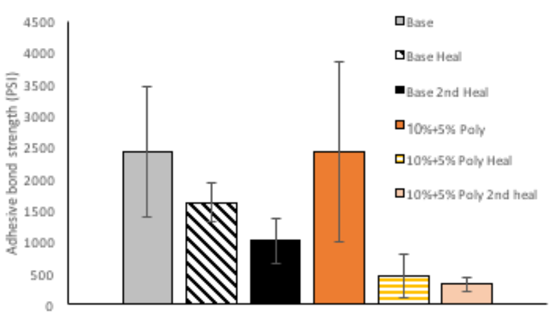


FY17 M3 met:

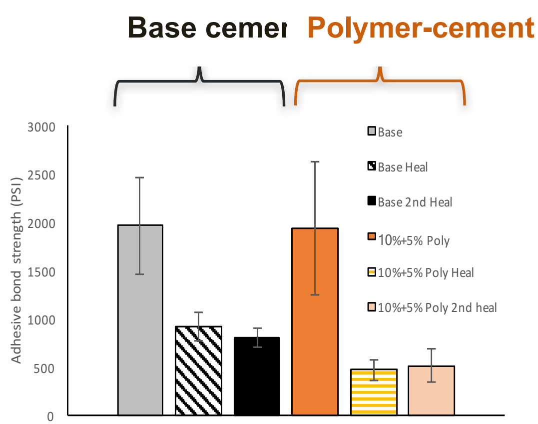
- shear bond strength recovery rate >80% for debonded cement/carbon steel (CS) joint samples, compared with that before re-adhering,
- identify at least one cement technology that self-adhere to the CS casing and base cement when cured at 300C after mechanical/chemical and/or thermal stresses
- **Note:** base cement showed surprisingly high shear bond strength with this pipe shear method



Thermal shock



CO_2 exposure



H_2SO_4 exposure

Re-adhesion BEFORE weathering (top plot):

- One polymer-cement show 167% casing adhesive strength recovery

AFTER weathering (left plots):

- ***Thermally-shocked samples:*** polymer-cements **outperform by 20-40%** conventional cement with **recovery rates of up to 150%**
- ***Sulfuric acid attack:*** polymer-cements **show significantly lower adhesive strength recovery in the 1st healing event** and **higher adhesive strength recovery in the 2nd healing event** compared to conventional cement
- ***CO2 brines:*** similar to sulfuric acid attack

Technical Accomplishments and Progress: **Polymer-Cement Composites - Summary**

- **Mechanical properties:** Three composites **met the wellbore requirements.** The composites seem to be more ductile than conventional cement (**40% lower Young Modulus**). **FY16 Milestones Q1 and Q3 met**
- **Rheological properties:** Could be deployed in the same way conventional cement is. **FY16 Milestone Q2 met**
- **Thermal stability:** Could, in principle, be applied in T ranges between **60C-300C**
- **Self-repairing:** Demonstrated bulk cement **reduction in fracture permeability between 62% and 87% (apertures as large as 0.5mm).** Mechanism: dynamic & reversible bonding at cement-polymer and polymer-polymer.
- **Bulk cement resistance to EGS environments:** Resistance to all extremely harsh geothermal environments (thermal and chemical stresses). **FY16 Milestone Q4 met**
- **Adhesion strength to (stainless) steel casing: Outperform (by up to 300%)** conventional cement. **FY17 Milestone Q1 met**
- **Casing adhesion resistance to EGS environments:** Either match **(CO_2/brine)** or **outperform by 6X (thermal shock)** and **by 40X (mineral acid)** conventional cement. **FY17 Milestone Q2 and Go/No-go met**
- **Cement-casing re-adhesion (healing): FY17 Milestone Q3 met**
  - **Before weathering:** Two cement composites **recovered 71% and 167% of original adhesive strength**
  - **After thermal shock: Outperforms** conventional cement in multiple healing events after thermal shock (**150% recovery rate).**
  - **After chemical stress: Shows significantly lower % of adhesive strength recovery after the 1st self-repairing event** but **higher % recovery after the 2nd repairing event** respect to conventional cement
- **Cost:** estimated in $0.40/lb, **8X of base cement** (Cement H/SiO_2). Working to reduce it to the proposed 3X of base cement.
- **One publication, three pending / One patent application / Six Presentations / One press release / Data uploaded to GDR**

Inorganic-Cement Composites

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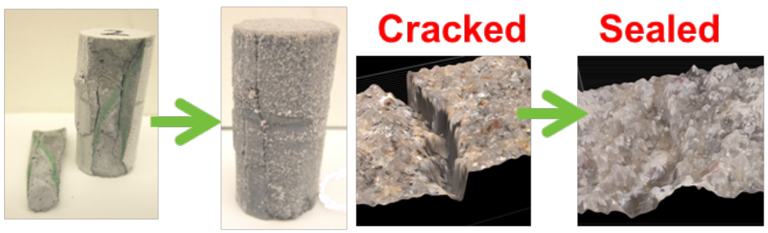
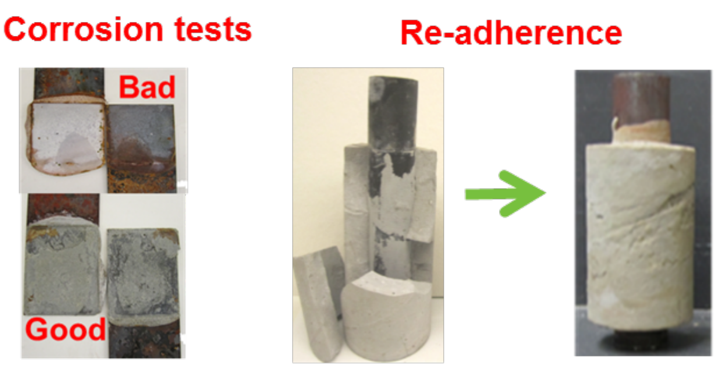
Methods/Approach

Three environments, 300°C (water, carbonate, geo-brine)

Strength recovery and cracks sealing



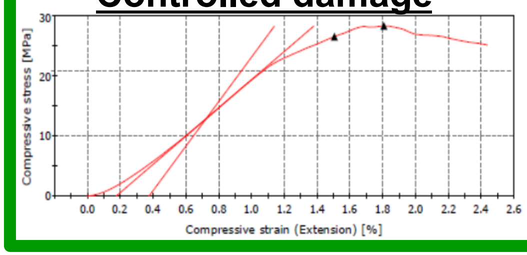
Bond recovery, corrosion protection

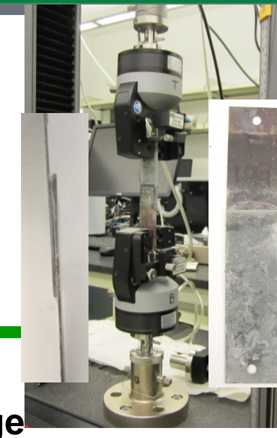


Bond durability

- Thermal Shock: 350C dry heat → 25C water
- $scCO_2$ brine, 30days, 90C
- Acid resistance, pH 0.6, 30 days, 90C

Controlled damage





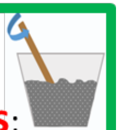
Compressive and bond strengths before and after the repeated damage

Establishing Mechanism of healing

- XRD
- FTIR/TGA
- SEM+μEDX and μEDX mapping
- Raman
- CT scan
- 3D Optical Microscope

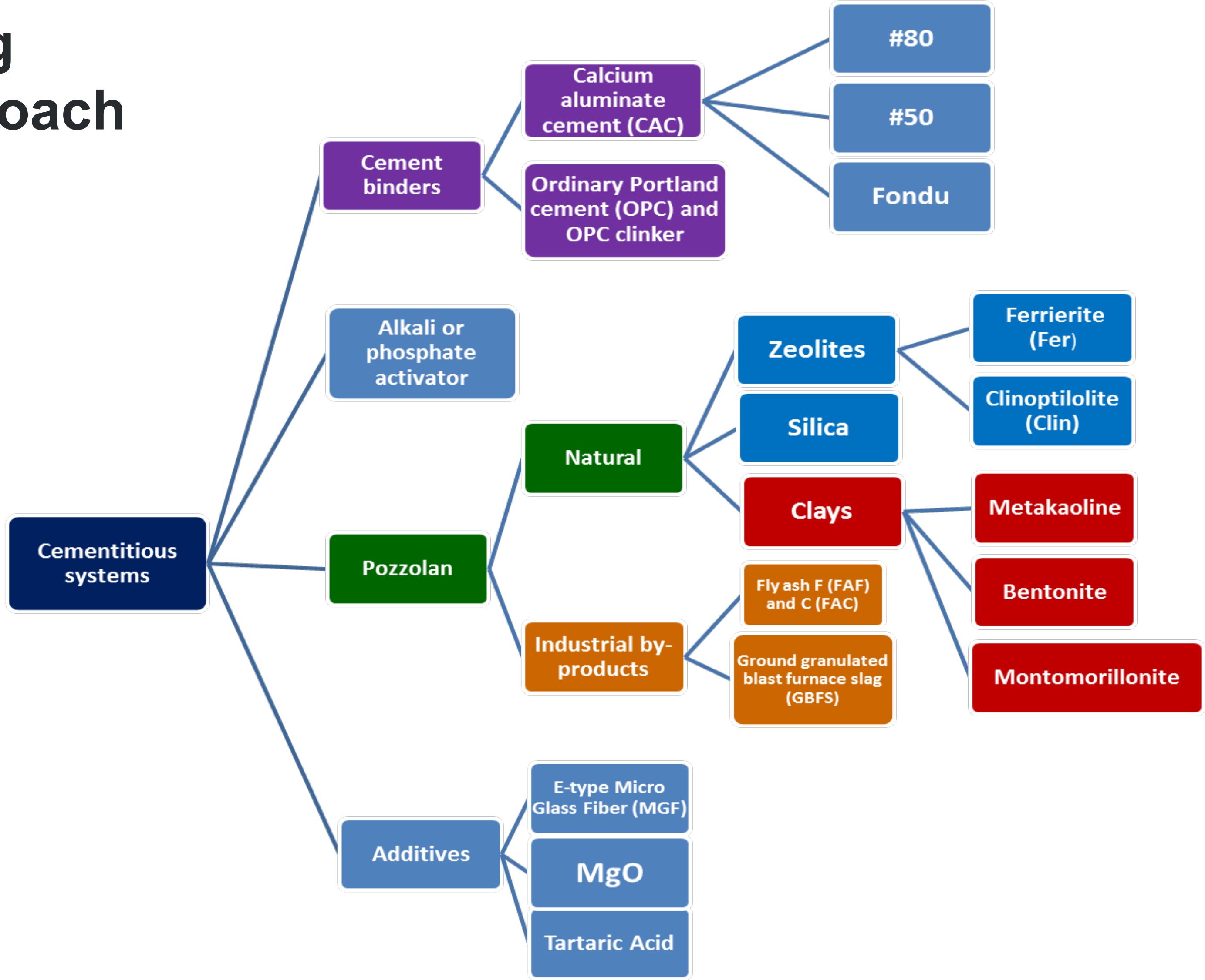
Self-healing cements – approach 300°C

Tests statistics



48 formulations;
4 cement binders;
8 pozzolans;
3 healing aid additives
635 samples tested

3 environments



Technical Accomplishments and Progress: **Inorganic-Cement Composites**

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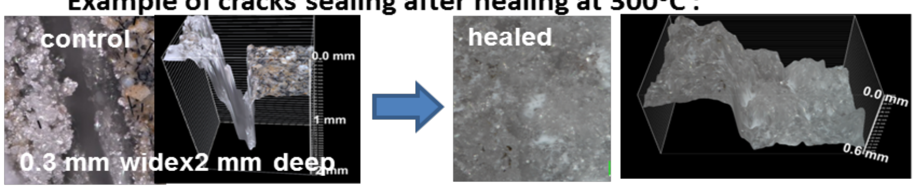
Examples of Matrix strength recovery: A+>100%; A 80-99%; B 60-79%; C<60%

Cement system	Curing Environment (270°C and 350°C)			
	Water	Alkali Carbonate	Geothermal brine	Thermal shock
Class G/SiO_2	C	B	B	A
CAC (#80)/FAF (TSRC)	**A**	**A**	**A**	**A+**
CAC(#80)/Zeolite 1	A	A	A+	A+
Class G/SiO_2/Zeolite 1	C	A	C	N/A
OPC/Zeolite 2/SiO_2(FlexCem)	A+	A	C	A+
CAP/FAF	C	C	A	A+
GBFS/FAC	B	B	B	A
GBFS/FAC/Zeolite 1	A	A	A	A
FAC/FAF	C	B	C	A

Formulations with Micro Glass Fibers (MGF)			
	Water	Alkali Carbonate	Geothermal brine
Class G/SiO_2/MGF	A	A	A
CAC (#80)/FAF/MGF	**A+**	**A+**	**A+**
CAC(Fondu)/FAF/MGF	A+	A+	A+
CaP/FAF	C	B	A
FAC/FAF/MGF	C	C	B
GBFS/SiO_2/MGF	A	A+	B

Example TSRC/MGF healing in water at 300°C :

Example of cracks sealing after healing at 300°C :



Technical Accomplishments and Progress: **Inorganic-Cement Composites**

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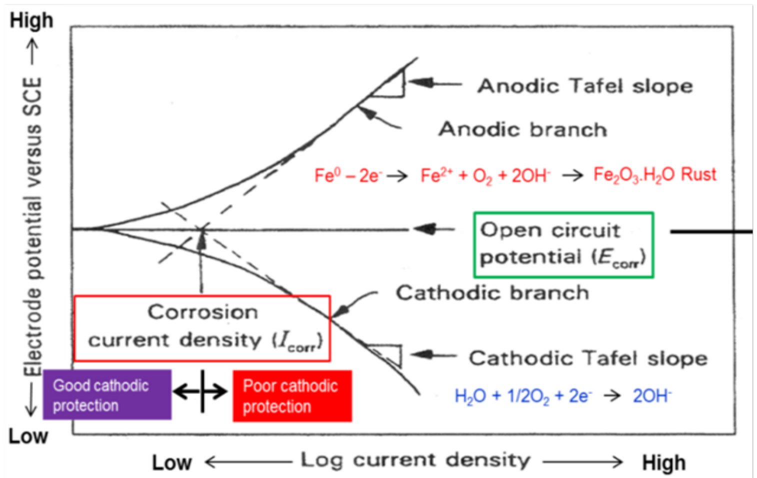
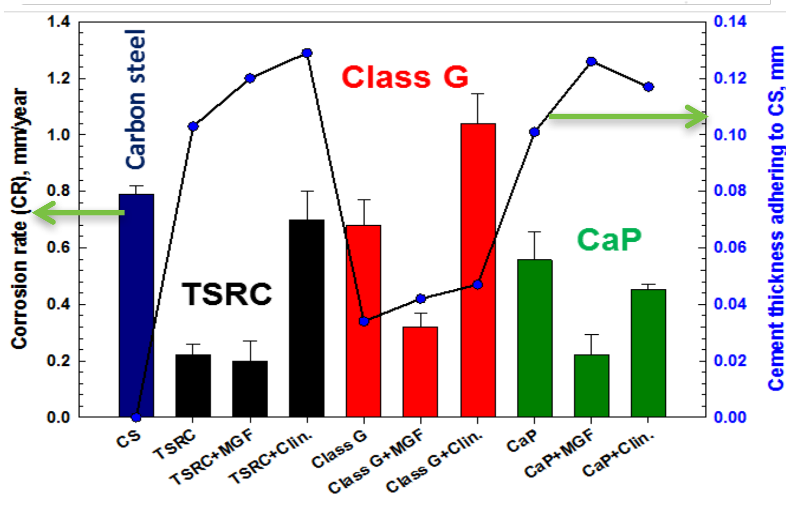
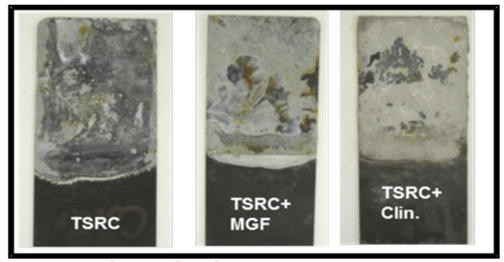
Examples of Interface strength recovery, corrosion protection of Carbon Steel (CS)

Corrosion rate (mmpy) of CS

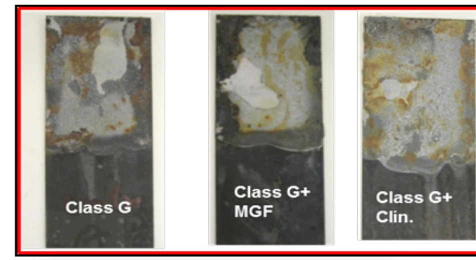




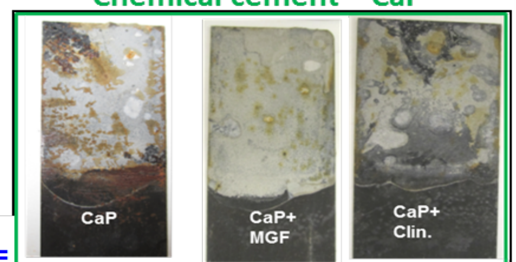
Alkali-activated cement - TSRC



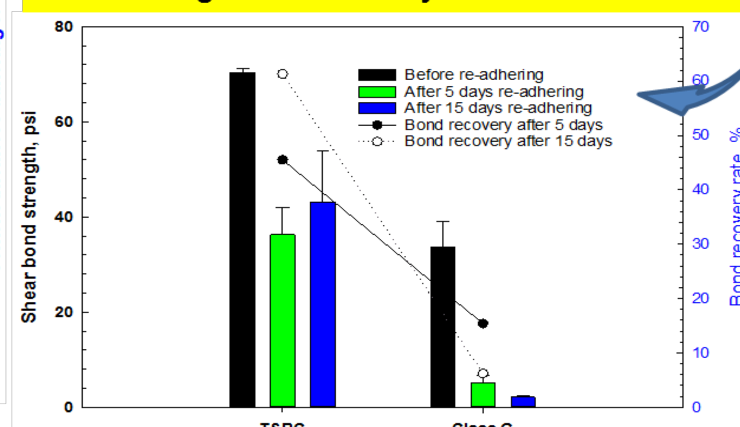
OPC-based cement – OPC/SiO_2



Chemical cement - CaP

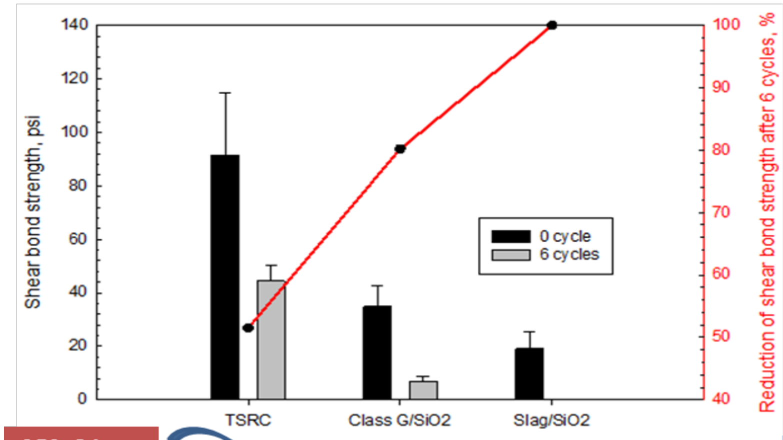


Bond strength and recovery: non confined tests



Bond-healing improves at longer time (15 days) for TSRC but not for class G/SiO_2 blend

Bond durability



350°C heat

~25°C water

TSRC

Hair crack Development after 6 cycles

Class G/SiO_2

Wide crack Development after 6 cycles

Slag/SiO_2

Catastrophic failure after 6 cycles

Shrinkage crack after 300°C autoclave

Acid samples

Slag

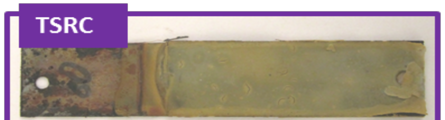
Broken after 20 days

Class G

Broken after 18 days

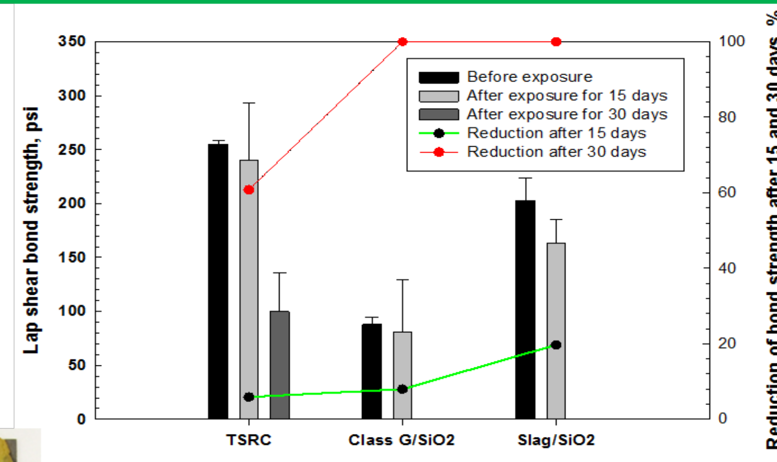
Interfacial bond erosion failure

TSRC

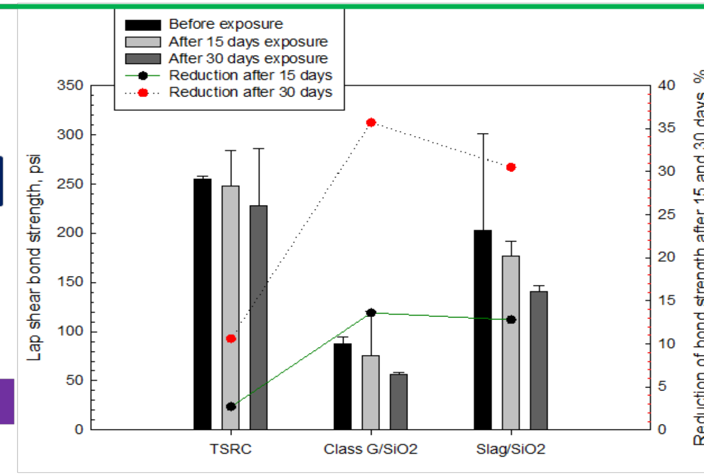


TSRC remained intact after 30 days

30 days pH 0.6 H_2SO_4/brine exposure test results at 90°C



30 days pH 5.5 $scCO_2$/brine exposure test results, 90°C



Technical Accomplishments and Progress: Inorganic-Cement Composites - Summary

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Results

1) Various cement chemistries, including 4 cement binders , 8 pozzolanic materials and 3 healing aid additives are tested (635 cement matrix and cement-metal interface samples prepared and evaluated);
2) Matrix strength recoveries of more than 100% and cracks sealing achieved for several cements in water, carbonate and geo-brine after repeated damage tests and healing at 300^{o}C;
3) Bond recoveries of more than 60%, more than 5 times lower corrosion rate than for common well cement, more than 2-times lower corrosion rate after 5-day healing compared to that before healing (decreased permeability).

Major Healing Factors

1) Moderate Young's modulus (YM), ranging from 1×10^5 to 3×10^5 psi, to avoid brittle fractures
2) Crack-plugging by new crystalline and amorphous reaction products in matrix and at interfaces formed by the cement surfaces and reactants from different thermochemical environments,
3) Utilization of alkali metals-incorporated CaO-Al_2O_3-SiO_2 type of pozzolanic additives as healing aides to accelerate healing in water, CO_2, and brine environments,
4) Attractive-physical and chemical bonds at interfaces between cement-derived hydration products and CS.
5) Void-free (low permeability) coverage of CS surfaces by specific amorphous and crystalline phases, and extension of this coverage by prolonged cement's hydration time
6) Great re-adhering properties of broken cement to cement remaining on CS (as for matrix recovery).

Cost

Current cost of the best performing formulation is ~7.2x(common well cement) (OPC/SiO_2); more economical options are under evaluation (if successful the cost of the advanced cement would be ~3x(common well cement))

Data Sharing and Collaboration

Published 4 peer-reviewed papers and 6 talks (4 invited talks); GRC-2016 best presentation award

Research Collaboration and Technology Transfer

- PNNL signed an NAA with Halliburton where the later performed rheological studies on polymer-cement composite slurries. Halliburton showed special interest in the polymer-cement technology.
- Lafarge Holcim has also shown interest on our polymer-cement composites and we will begin conversations during FY18 towards potential opportunities for licensing and commercialization
- BNL collaborated with Trabits group on evaluation of new cement-zeolite composites developed with support of EERE office of DOE.

Future Directions

- Synthesis of a **hybrid inorganic-polymer cement composite that synergistically combine the properties of the best-performing (organic- and inorganic-) cement composites** to amplify the range of EGS fields at which these advanced materials can be deployed at*
- Evaluate long-term stability at EGS temperatures (one month) and slurry pumpability following API standards.
- A comprehensive technical report will be generated with all material's info including material's cost together with identifying potential stakeholders for technology licensing and field deployment.

Milestone or Go/No-Go	Status /Expected Completion Date
FY17-M4: At least one cement composite with +90% reduction in permeability and/or +90% recovery of compressive strength after self-repairing from mechanically induced radial cracks (tensile failure)	Predicted by October 30th
FY18-M1: At least one cement composite thermally-stable at 200C for 5days for further evaluation. At least one cement composite thermally-stable at 250C for 5days for further evaluation. At least one cement composite thermally-stable at 300C for 5days for further evaluation.	
FY18-M2: Fit-for-purpose cement composites: A. cement composite with self-healing capability and re-adhering (to casing) capability with thermal stability in the 200-250C range for up to one month; B. cement composite with self-healing capability and re-adhering (to casing) capability with thermal stability in the 250-300C range for up to one month	
FY18-M3: At least 2 cement composites that meet field requirements based on API procedures w/ controlled thickening times of at least 90min @ 85^{o}C. - (Minimum) one cement composite with shear strength at formation (granite or other representative lithology) interfaces equal to or no lower than 70% with respect to the same material before re-adhering. - (Minimum) one cement composite that self-re-adhere to the formation with a +70% recovery after exposed to thermal and/or chemical stresses.	
FY18-M4: A technical report on (minimum) two fit-for-purpose formulation(s). Identification of at least one stake holder for technology transfer. Two per-reviewed publications. Determine if additional lab-scale tests specific to a geothermal site are required with the identified stakeholder.	

Summary Slide

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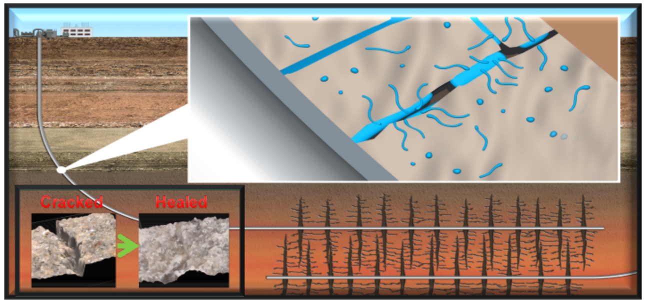
- This project **demonstrated** the synthesis of **advanced inorganic-cement and (patent-pending) organic (polymer)-cement composites** with **enhanced tolerance to extreme thermal and chemical environments found in EGS** (maintaining near-original mechanical properties)

- Both, inorganic-cement and organic-cement composites posses **self-repairing capability w/ strength recoveries after damage of more than 90%** and/or **permeability reduction of up to 87%** (fractures as large as 500μm).

- Both, inorganic-cement and organic-cement composites posses **strong adhesion to steel casing (up to 300% higher** than conventional cement) and re-adhering capability w/ **strength recoveries after damage of 70-167%**

- Re-adhesion capability is, for most cases, maintained after exposure to EGS thermal and chemical environments

- Work is ongoing to determine:
  a. Long-term stability at EGS temperatures
  b. Adhesion and re-adhesion capability to formation
  c. Slurry pumpability



- **Goal is to:**
  1. Generate **fit-for-purpose cement composites** that can be deployed in a **wide (and complementary) range of EGS fields**, ***outperforming conventional wellbore cement in terms of durability and reliability***.
  2. Approach potential stake holders for **technology licensing and field deployment**. Once identified, additional work specific to a geothermal field might be required

- Milestones/deliverables met on time and budget (no deviation from plan). Cost as of FY17-Q3: $ 1,557,222