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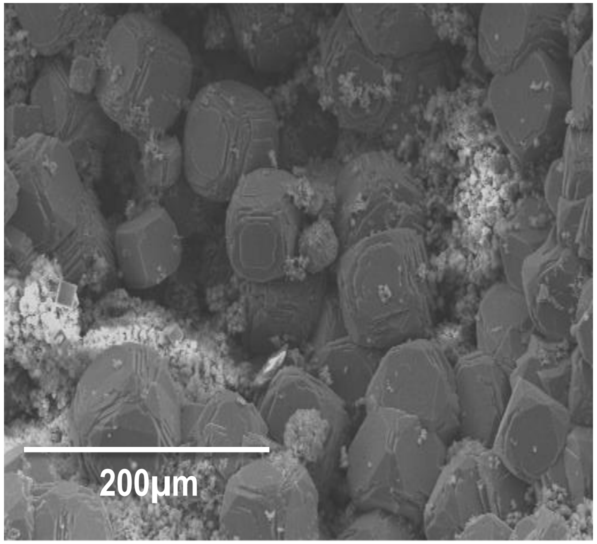
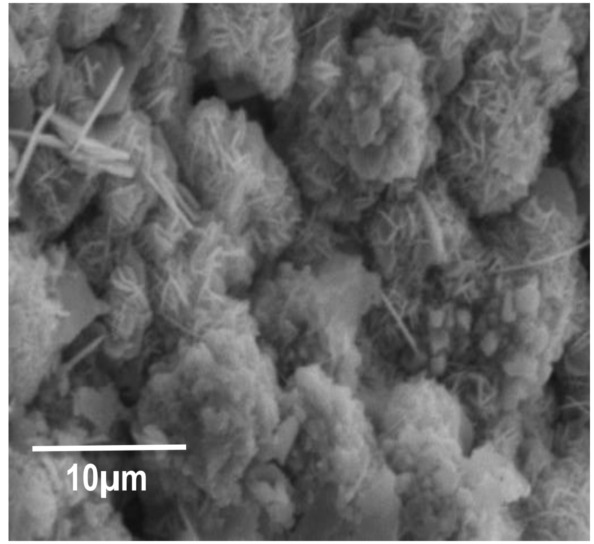
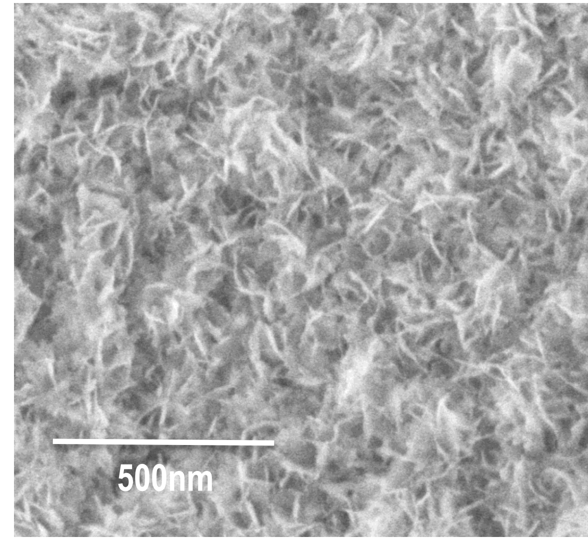


Analcime ($NaAlSi_{12}O_6.H_2O$)



Thomsonite ($NaCa_2Al_5Si_5O_{20}.6H_2O$)



Hydroxysodalite [$Na_4Al_3Si_3O_{12}(OH)$]

Three major hydro-ceramic crystals formed in BNL-formulated thermal shock-resistant cement (TSRC)

Multifunctional Corrosion-resistant Foamed Well Cement Composites

Project Officer: Joshua Mengers

Total Project Funding: $420,000

May 11-14, 2015

Principal Investigator: Dr. Toshifumi Sugama
Co-PI: Dr. Tatiana Pyatina

Presenter Name: Dr. Toshifumi Sugama
Brookhaven National Laboratory

Relevance/Impact of Research

Objectives: **The thrust of this project is to develop cost-effective multifunctional corrosion-resistant foamed cement composites for carbon steel (CS)-based casings in both hydrothermal and EGS wells, to characterize their properties, and to transfer developed technology to cost-sharing industrial partner under CRADA.**

Impact: **When a field-applicable corrosion-resistant foamed well cement possessing all required properties is formulated, it will provide the following five benefits for hydrothermal and EGS wellbores:**

1. **Lifecycle extension of the carbon steel-based casings;**
2. **Reduction of capital investment by using stainless steel or clad materials instead of very expensive corrosion-resistant titanium and zirconium alloys;**
3. **Decrease in well operation and maintenance (O&M) costs;**
4. **Reduction of substantial expenditures for abandoning, re-drilling, re-cementing, reconstructing or repairing wells brought about by the failure of well cement;**
5. **Cost-effective cements will reduce capital investment.**

Scientific/Technical Approach

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The field applicable multifunctional cements will be formulated to meet the following eleven material criteria:

1) Slurry density of foamed cement < 1.3 g/cc (10.8 ppg);
2) Maintenance of pumpability for at least 3 hours;
3) Thermal and hydrothermal stability >300°C
4) Compressive strength > 1000 psi after five superheating-cooling cycles (one cycle: 600°C heat with CO_2 for 24 hrs and 25°C water-quenching for 4 hrs) as thermal shock resistance test;
5) Corrosion rate of carbon steel (CS) casing < 50 milli-inch/year;
6) Impedance to corrosive ion conductivity >10K ohms;
7) Bond strength to CS casing and granite rock > 70 psi;
8) Resistance to CO_2-induced mild acid (pH ~ 5.0) at 300°C < 5 wt% loss after 30 days exposure;
9) Compressive toughness > 0.2 N-mm/mm^3 after 300°C- 24 hour-autoclaving;
10) No shrinkage;
11) Thermal conductivity < 0.5 W/m.K.

Accomplishments, Results and Progress

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Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Task 1. Develop alternative thermal shock-resistant cement (TSRC)	Completed.	March 2014
Task 2. Develop set-control additive suitable for TSRC	Completed. T. Pyatina and T. Sugama "Set-controlling additive for thermal shock resistant cement," GRC Transaction 38 (2014) 251-257.	May 2014
Task 3. Develop toughness enhancing additive	Completed. T. Sugama and T. Pyatina "Toughness improvement of geothermal well cement at up to 300°C," J. Composite Materials 4 (2014) 177-190.	August 2014
Task 4. Assessment of interfacial bond durability between TSRC and carbon steel casing	Completed.	February 2015
Task 5. Develop advanced high-temperature inorganic anodic corrosion inhibitors	As of March 2015, 70 % completed	
Task 6. Evaluate resistance of TSRC to acid		
Task 7. Long-term corrosion- and thermal shock-resistance testing under CRADA with Schlumberger		

Synthesis of Thermal Shock-Resistant Cement (TSRC)

Hydrothermal synthesis and products for new hybrid cements consisting of initial-binding phase (IBP) and alkali-activated Class F fly ash (CFFA) as secondary-binding phase. Alkali activator is sodium metasilicate (SMS).

Benefits for use of *pozzolana-latent CFFA* as industrial by-product

1. Reducing the total raw material cost of cement, based upon its low cost of $ ~ 0.02/lb, compared with $~0.06/lb of Ordinary Portland Cement (OPC).
2. Abating CO_2 footprint incurred from OPC manufactures.

IBP

$CaO.Al_2O_3$ / $CaO.2Al_2O_3$ (Refractory calcium aluminate (RCA)) $+ SiO_2 + H_2O \xrightarrow{200-300^oC}$

- $Ca_3Al_2Si_2O_8(OH)_4$ Katoite silician — Hydro-garnet
- $Ca_5Al_2(OH)_{12}$ Katoite — Hydro-garnet
- gamma-AlOOH boehmite — Hydro-Al oxide

$CaO.SiO_2$ (calcium silicate (OPC)) $+ SiO_2 + H_2O \xrightarrow{200-300^oC}$ Tobermorite $Ca_5Si_6O_{15}(OH)_2.4H_2O$ — Calcium silicate hydrate

Class F fly ash (CFFA)

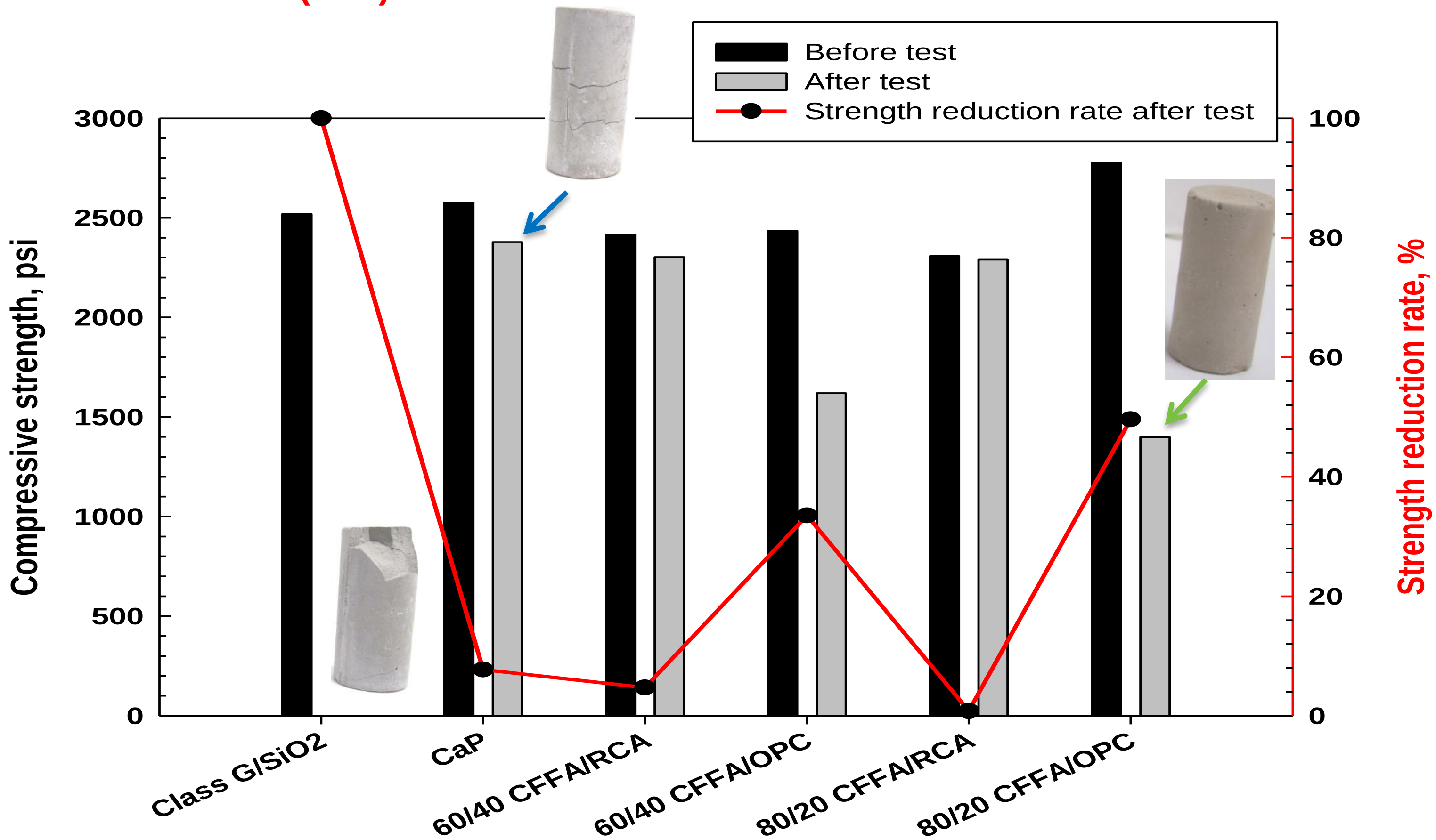
$3Al_2O_3.2SiO_2$ / SiO_2 $+ Na_2O.nSiO_2 + CaO + H_2O \xrightarrow{200-300^oC}$

- $Na_4Al_3Si_3O_{12}(OH)$ Hydroxysodalite
- $NaCa_2Al_5Si_4O_{20}\cdot 6H_2O$ Thomsonite
- $NaAlSi_2O_6.H_2O$ Analcime

Hydro-ceramic

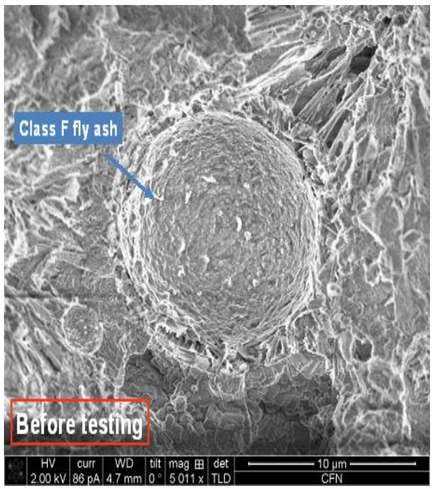
5-cycle thermal shock-resistance test (one cycle: 600°C annealing for 24 hrs + 25°C water-quenching for 5 hr)

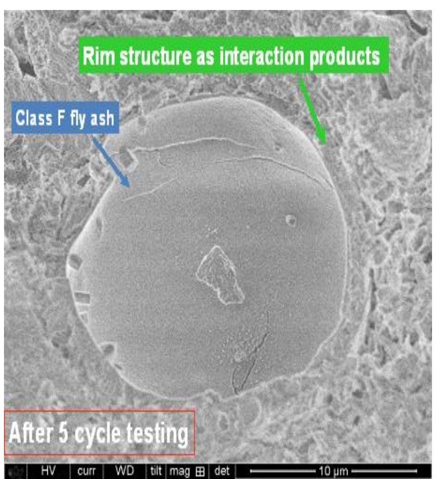
Reference cements: 70% Class G + 30% Quartz (Class G/SiO_2) and Calcium aluminum phosphate cement (CaP)



Phase transformations in CFFA-rich TSRC after 5 cycle testing

+





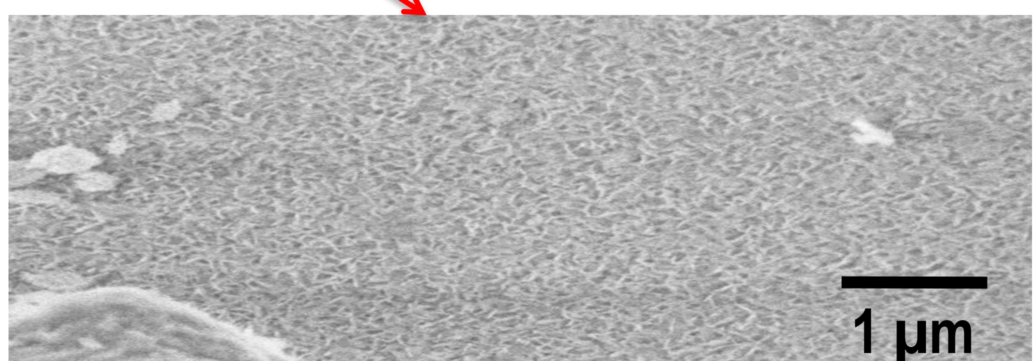
$Na_4Al_3Si_3O_{12}(OH)$ Hydroxysodalite (Hydro-ceramic) + $Ca_5Al_2(OH)_{12}$ Katoite (Hydro-garnet) + gamma-AlOOH Boehmite (Hydro-Al oxide) + $Ca_5Si_6O_{15}(OH)_2.4H_2O$ Tobermorite (Calcium silicate hydrate)

600°C, CO_2

$Na_8Al_6Si_6O_{24}CO_3$ + >> + $CaCO_3$ + gamma-Al_2O_3 + $Ca_5Si_6O_{15}(OH)_2.4H_2O$

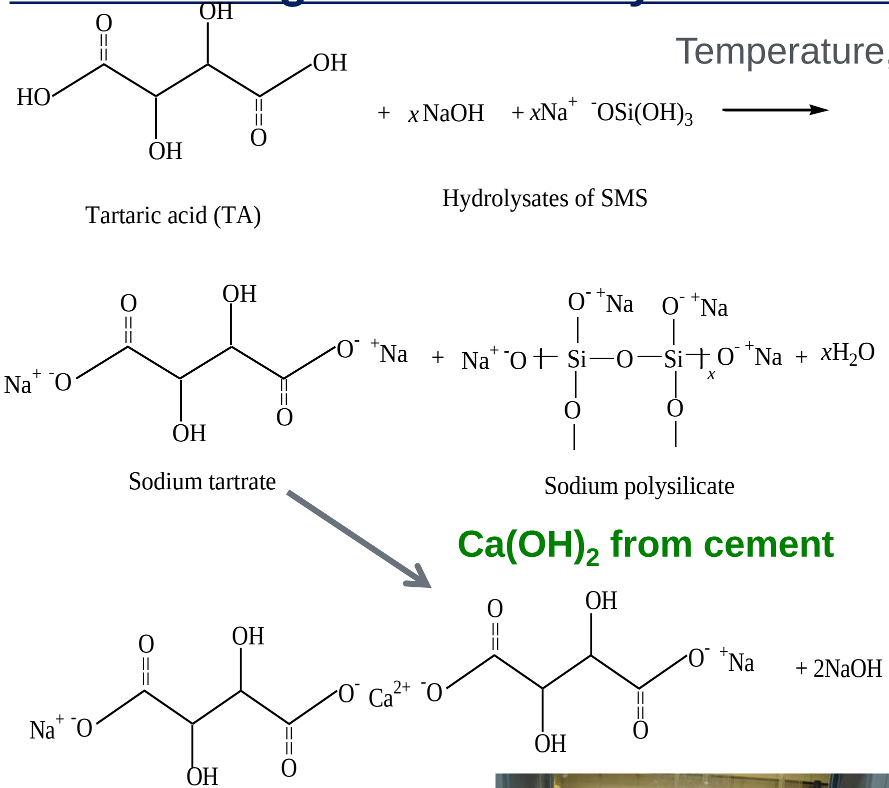
Carbonated sodalite as nano-scale crystal

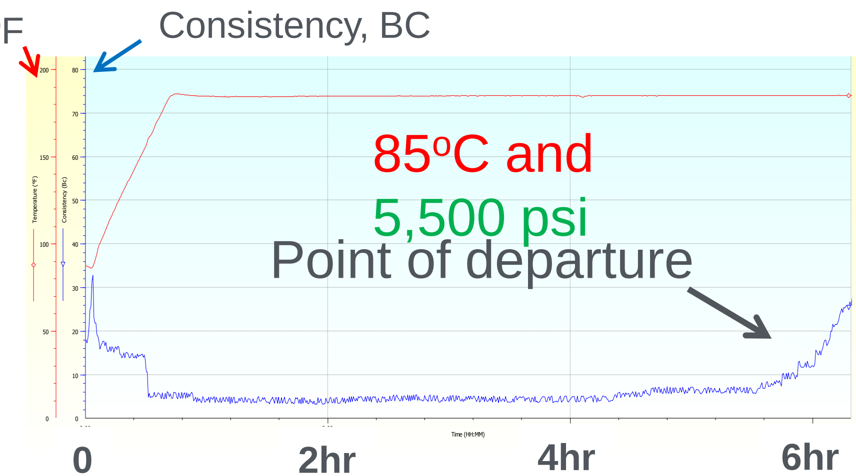
SEM image

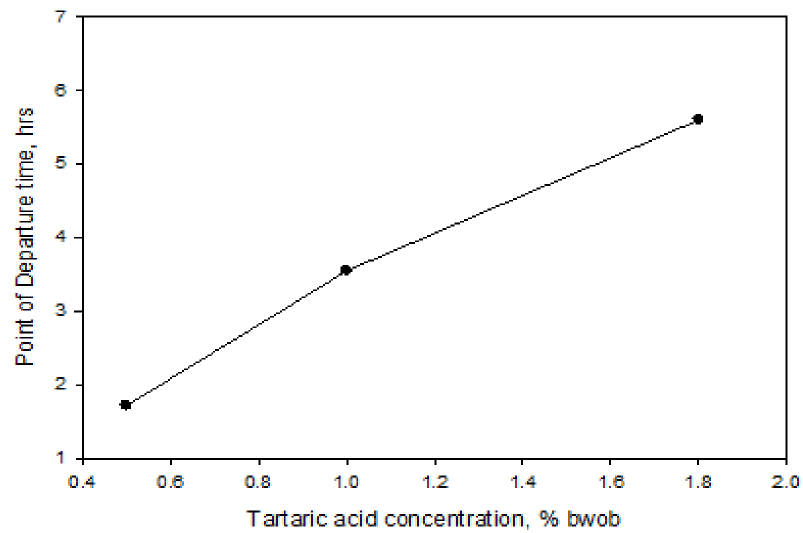


Set-controlling additives at 85ºC

Set-retarding mechanism by TA and HTHP consistomer test results

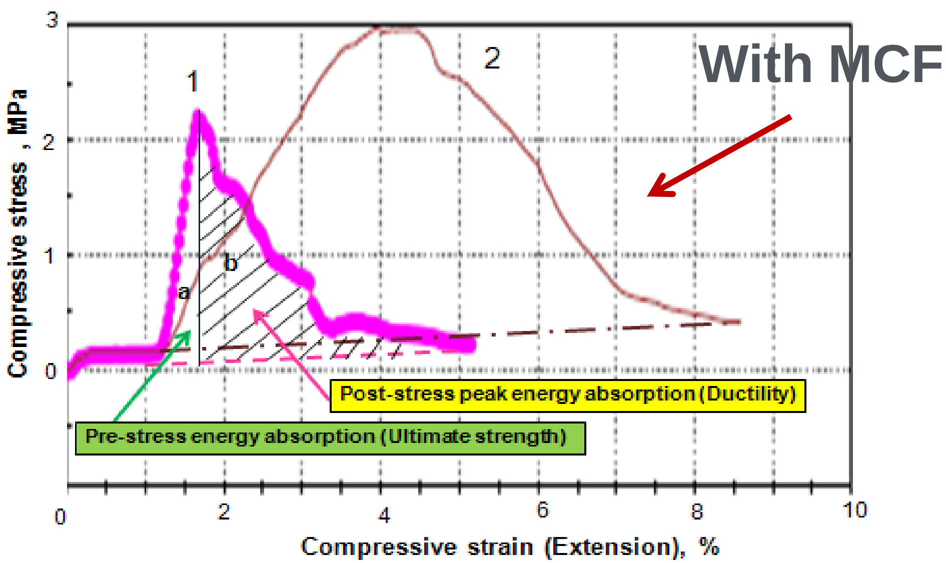


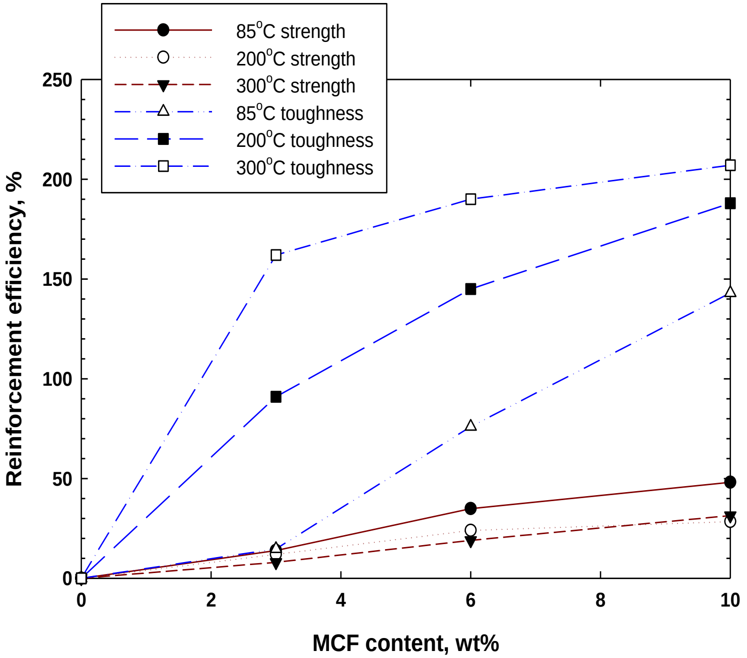


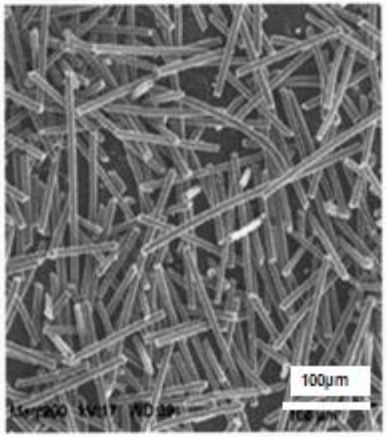


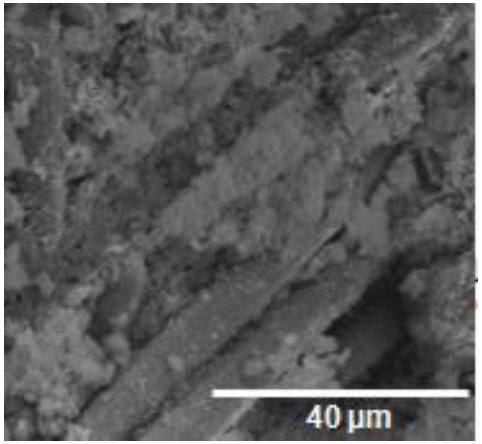
Chandler HTHP Consistometer

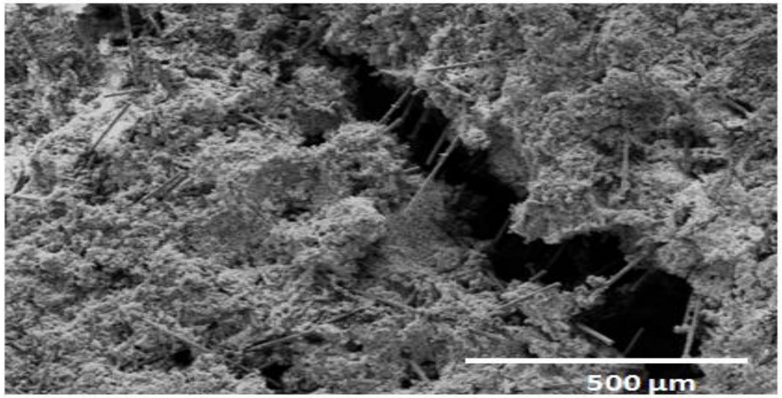
Toughness improvement by micro-carbon fiber (MCF)











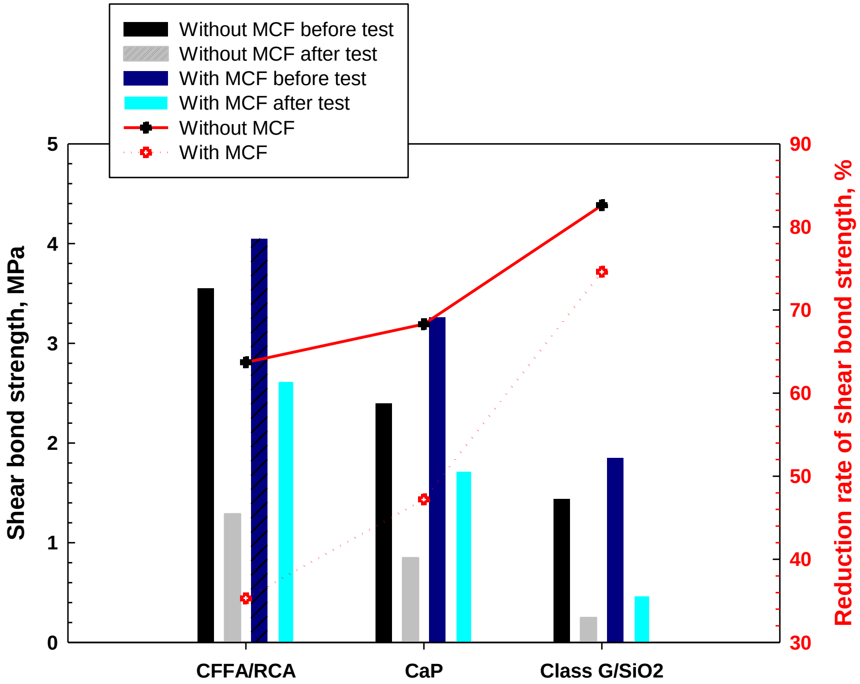
Adherence durability of MCF-reinforced and unreinforced cement sheath to steel casing

7-cycle thermal-water cooling tensional stress test for cement sheaths (One cycle: 350°C heated-25°C cool water passing in tube)

~25°C water

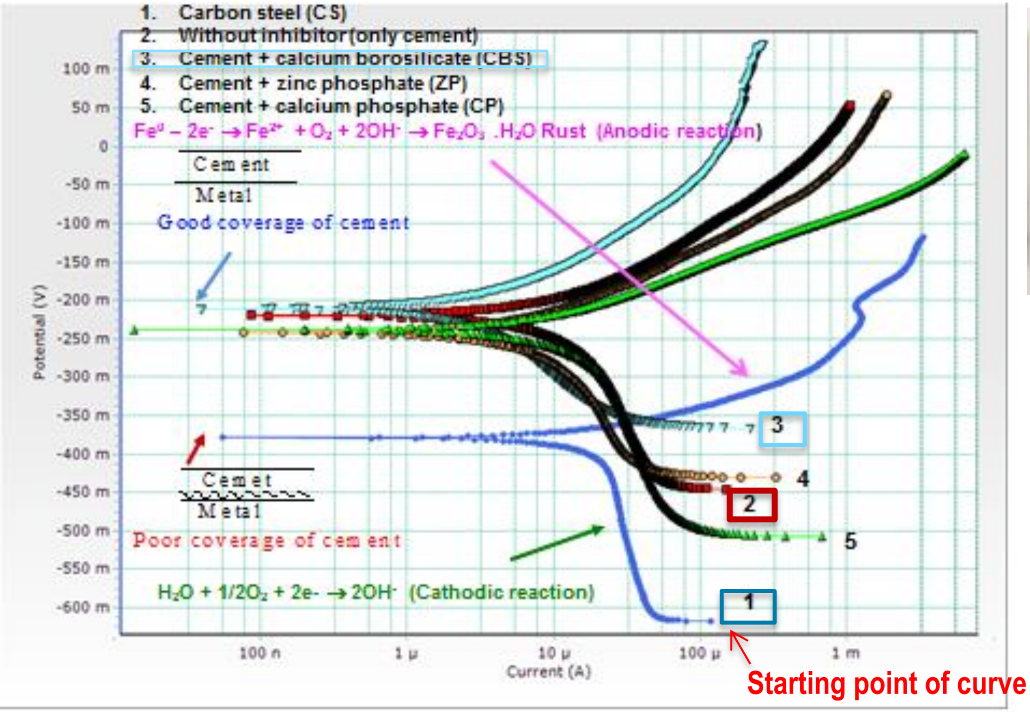
Class G/SiO_2 sheath after 1 cycle

MCF-reinforced Class G/SiO_2sheath after 7 cycle



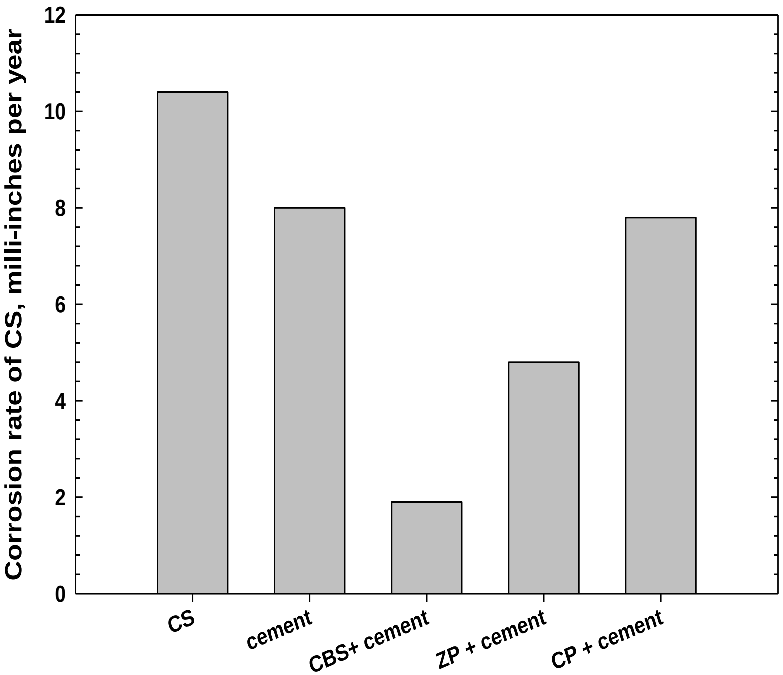
Shear bonding test

High-temperature Inorganic Anodic Carbon Steel (CS) Corrosion Inhibitors Suitable for TSRC in brine

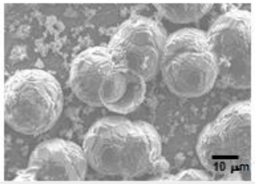


Cement-coated CS coupon sample (coating thickness, 1-1.5 mm) after autoclaving 300°C for 24 hrs

Corrosion rate of CS coated and uncoated with cement

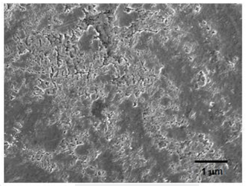


Cement-derived passive layer over CS surfaces at 300°C



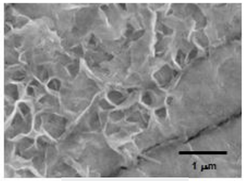
Without inhibitor

Analcime, $NaAlSi_2O_6.H_2O$



ZP

Amorphous $NaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$



CBS

Future Directions

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Milestone or Go/No-Go	Status & Expected Completion Date
Task 1. Optimize inexpensive CFFA/OPC formula	Mar.2016
Task 2. investigate bond durability at cement/rock and /clay mineral interfaces	Jun. 2016
Task 3. Assess thermal insulating properties	Sep. 2016
Task 4. CRADA with Schlumberger	Sep .2016
Task 5. Deliver annual report covering all information obtained in FY2016 to DOE and prepare peer-reviewed journal article	Dec.2016
Go/No-go Decision	

Summary

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Alternative thermal shock-resistant cement (TSRC) possessing toughness and controlled set, and 300°C-withstanding corrosion inhibitor suitable for foamed TSRC were developed through FY 2014 to March in FY 2015.

	FY2014 (Oct. 2013-Sep. 2014)	FY2015 (Oct. 2014- Mar. 2015)
Target/Milestone	-Complete annealing-water quenching test. -Complete HTHP consistomer test. -Complete toughness measurement.	•Complete interfacial bond durability test at TSRC/steel casing joint. •Complete electrochemical corrosion test.
Results	-Formulated alternative TSRCs. -Developed set-controlling additive suitable for TSRC. -Developed tough, crack-arresting TSRC.	•Identified a potential of micro-carbon fiber for improving adherent durability of TSRC to casing surfaces. •Developed 300^{o}C-withstanding inorganic anodic corrosion inhibitor suitable for TSRC.