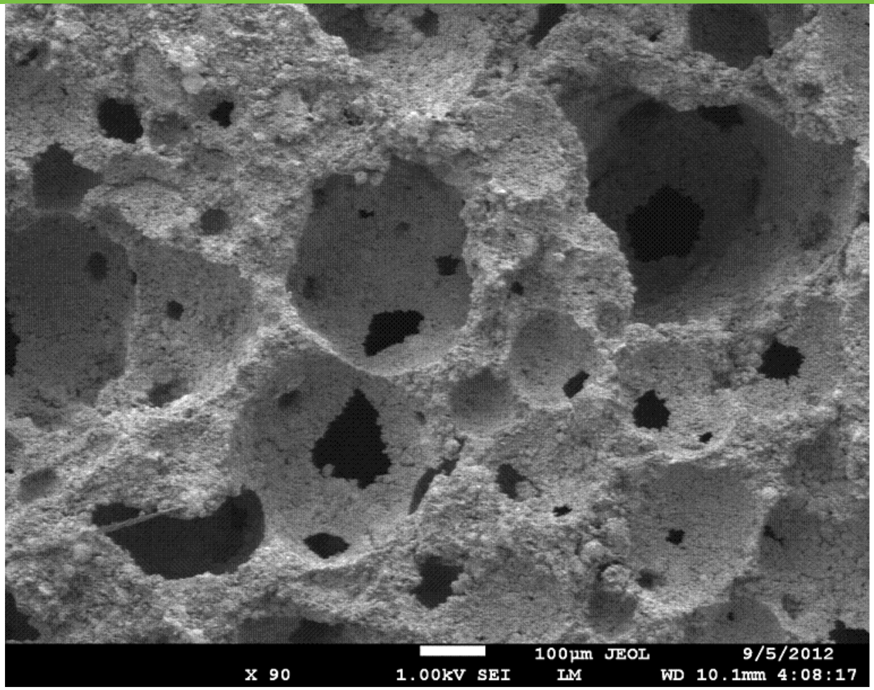

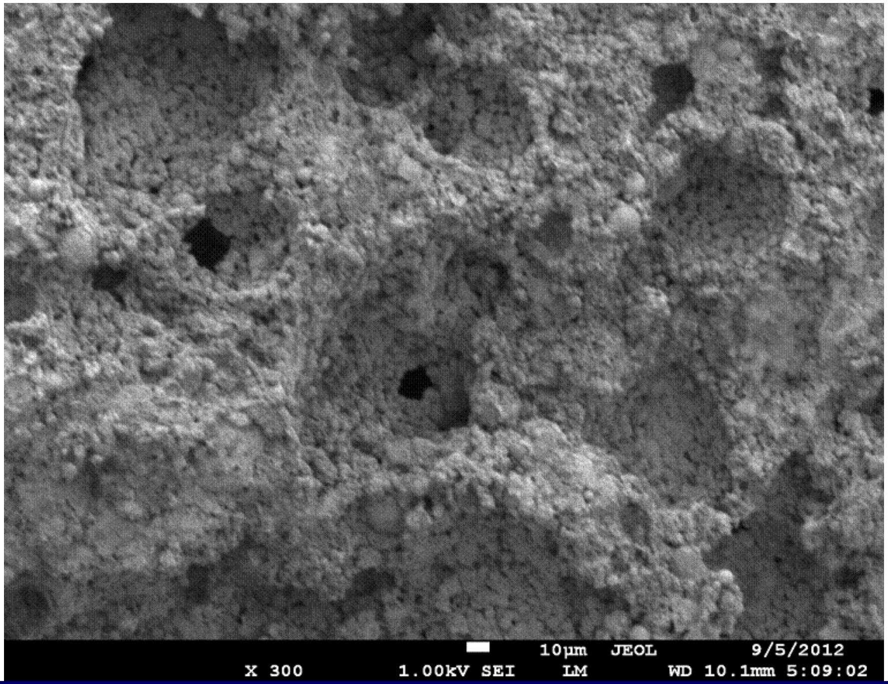

Microstructure developed in conventional foamed (left) and corrosion-resistant foamed cements (right)

Multifunctional Corrosion-resistant Foamed Well Cement Composites

Project Officer: Dan King/Greg Stillman
Total budget: $300 K
April 24 , 2013

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

Presenter Name: Dr. Toshifumi Sugama

Relevance/Impact of Research

Objectives: The thrust of this project is to develop cost-effective multifunctional corrosion-resistant foamed cement composites for carbon steel-based casings in EGS wells, to characterize their properties, and to transfer developed technology to cost-sharing industrial partners.

Impact: When a field-applicable corrosion-resistant foamed well cement possessing all required properties is formulated, it will provide the following five bottom-line benefits for EGS wellbore integrities:

1. Extension of the carbon steel-based casing's lifecycle;
2. Reduction of capital investment instead of using very expensive corrosion-resistant titanium and zirconium alloys, stainless steel or clad materials;
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 some capital investment.

Scientific/Technical Approach

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

1) Slurry density of foamed cement, < 1.3 g/cm^3;

2) Maintenance of pumpability for at least 3 hours;

3) Thermal and hydrothermal stability >300°C

4) Corrosion rate of carbon steel casing < 70 milli-inch/year;

5) Compressive strength, > 1000 psi after five superheating-cooling cycles (one cycle: 500°C heat for 24 hrs and 25°C water-quenching for 4 hrs) as thermal shock resistance test;

6) Water permeability, < 1 x 10 $^{-4}$ Darcy;

7) Bond strength to steel casing and granite rock, > 30 psi;

8) Resistance to CO_2-induced mild acid (pH ~ 5.0) at 300°C, < 5 wt% loss after 30 days exposure;

9) Fracture toughness, > 0.006 MN/m$^{3/2}$ at 300°C, 24 hour-curing time;

10) No shrinkage;

12) Thermal conductivity < 0.5 W/m.K;

13) Total raw material cost < $0.20/lb.

Accomplishments, Results and Progress

Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Task 1. Develop thermal shock-resistant cements	Completed. S. Gill, T. Pyatina, and T. Sugama "Thermal shock-resistant cement," GRC Transactions, 36 (2012) 445-451. 2012 GRC Best Presentation Award	March 2012
Task 2. Develop formulation of air-foamed light weight cements	Completed.	Jun 2012
Task 3. Develop corrosion inhibitors for foamed cement	Completed. T. Sugama, S. Gill, T. Pyatina, R. Keese, A. Khan, and D. Bour "Corrosion-resistant foamed cements for carbon steel," BNL informal report, January (2013).	December 2012
Task 4. Deliver interim report to DOE	Completed. Two reports	December 2012
Task 5. Complete technology transfer to cost-sharing industrial partners	Completed. Schlumberger, Baker Hughes, and Geodynamics	December 2012

Accomplishments, Results and Progress

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Synthesis of Thermal Shock-resistant Cement (TSRC)

Hydrothermal synthesis of new cement consists of three cementitious phases, *hydro-garnet*, *hydro-ceramic*, and *hydro-Al oxide*, from starting materials including *refractory calcium aluminate cement (RC)*, *Class F fly ash*, and *sodium silicate*

$CaO.Al_2O_3$
$CaO.2Al_2O_3$
RC

$+ \; H_2O \xrightarrow{\text{hydrothermal reaction at 200℃}}$

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

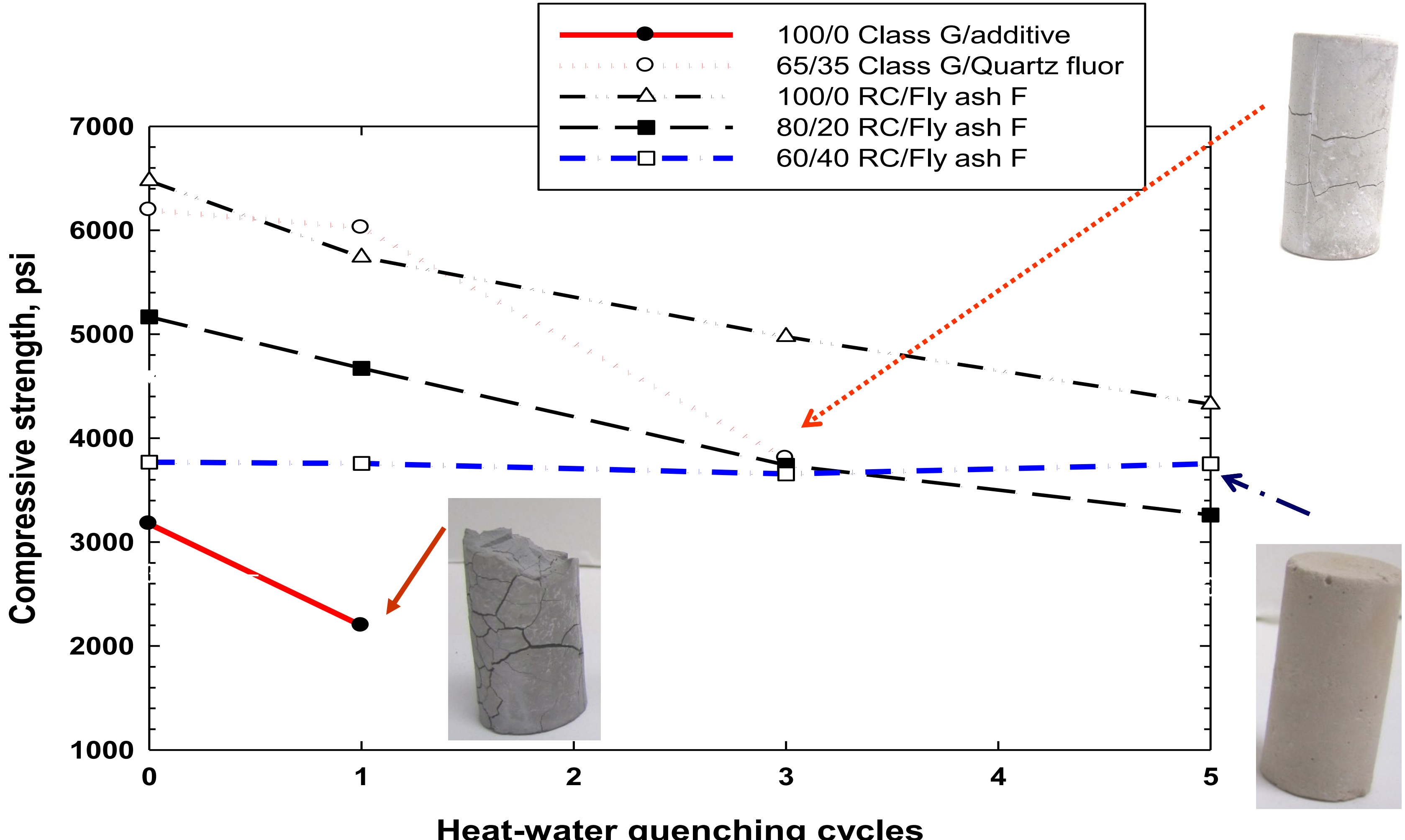
$3Al_2O_3.2SiO_2$
SiO_2
Class F fly ash

$+ \; Na_2O.SiO_2$ (1/1 NaO_2/SiO_2 ratio) $+ \; H_2O \xrightarrow{\text{hydrothermal reaction at 200℃}} Na_4Al_3Si_3O_{12}(OH)$

Hydroxysodalite

Hydro-ceramic

Thermal shock-resistance test (one cycle: 500°C annealing for 24 hrs + 25°C water-quenching for 5 hr)



Phase compositions formed in TSRC after 5 cycle testing

$Ca_3Al_2Si_2O_8(OH)_4$ + $Ca_5Al_2(OH)_{12}$ + $Na_4Al_3Si_3O_{12}(OH)$ + gamma-AlOOH

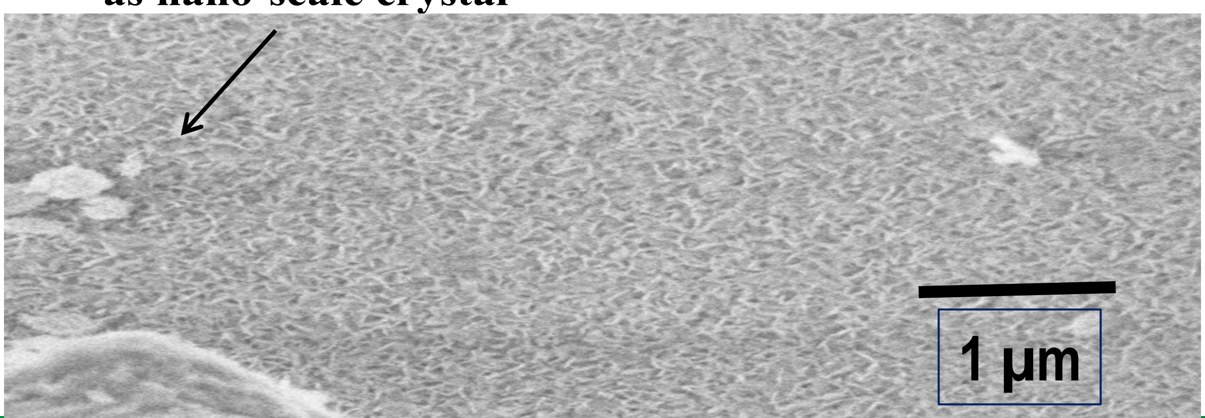
Hydrogrossular | Katoite | Hydroxysodalite | Boehmite

Hydro-garnet | Hydro-garnet | Hydro-ceramic | Hydro-Al oxide

500°C, CO_2

$Na_8Al_6Si_6O_{24}CO_3$+ >> + $CaCO_3$ + gamma-Al_2O_3

Carbonated sodalite
as nano-scale crystal

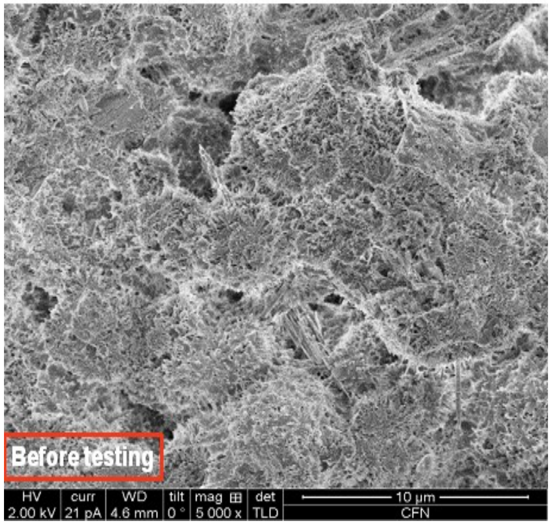


Phase compositions formed in Class G/quartz flour system after 1 cycle testing

$$\underset{\text{1.1 nm tobermorite}}{Ca_5(OH)_2Si_6O_{16}.4H_2O} + CaO.SiO_2.H_2O + \underset{\text{Portlandite}}{Ca(OH)_2}$$

$$\Big\downarrow \; 500°C,\ CO_2$$

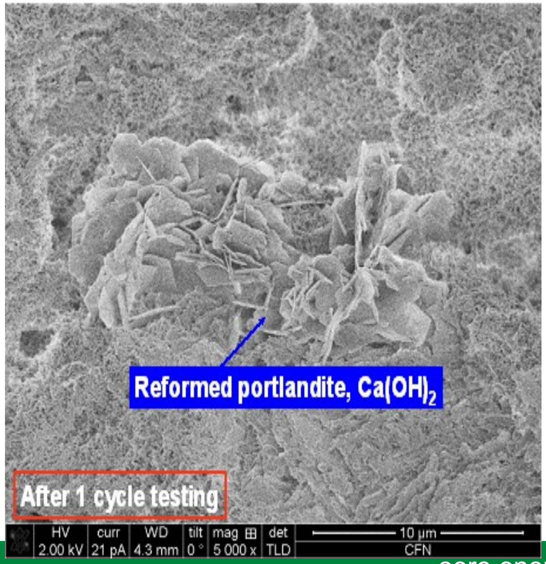
$$\underset{\text{Lime}}{CaO} + \underset{\text{Calcite}}{CaCO_3} + \underset{\text{Portlandite}}{Ca(OH)_2} + \gg + \underset{\text{1.1 nm tobermorite}}{Ca_5(OH)_2Si_6O_{16}.4H_2O} + CaO.SiO_2.H_2O$$



Phase transformation of portlandite in hydrated Class G cement under dry and wet conditions

$$Ca(OH)_2 \xrightarrow{500°C,\ CO_2} \begin{matrix} CaCO_3 \\ + \\ CaO \end{matrix} \xrightarrow{\text{water}} Ca(OH)_2$$

in-situ **volumetric expansion of cement by reformation of portlandite**



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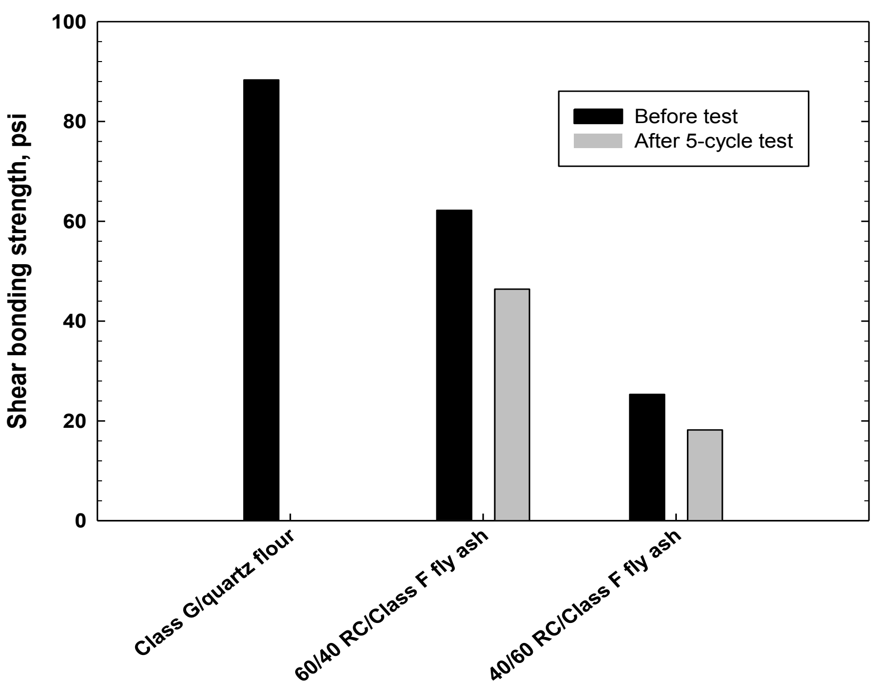
Cool water-thermal stress cycle test for cement sheaths (One cycle: 350°C heated-25°C cool water passing in tube)

~25°C water

Class G/quartz flour cement sheath after 1 cycle

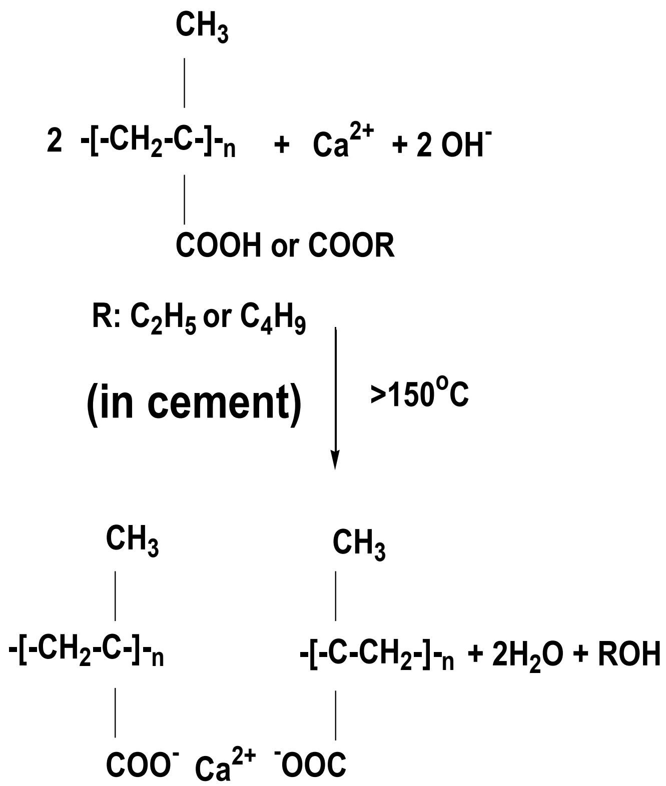
New cement sheath after 5 cycles

Shear bonding strength at interfaces between cement and casing before and after 5 cycle testing

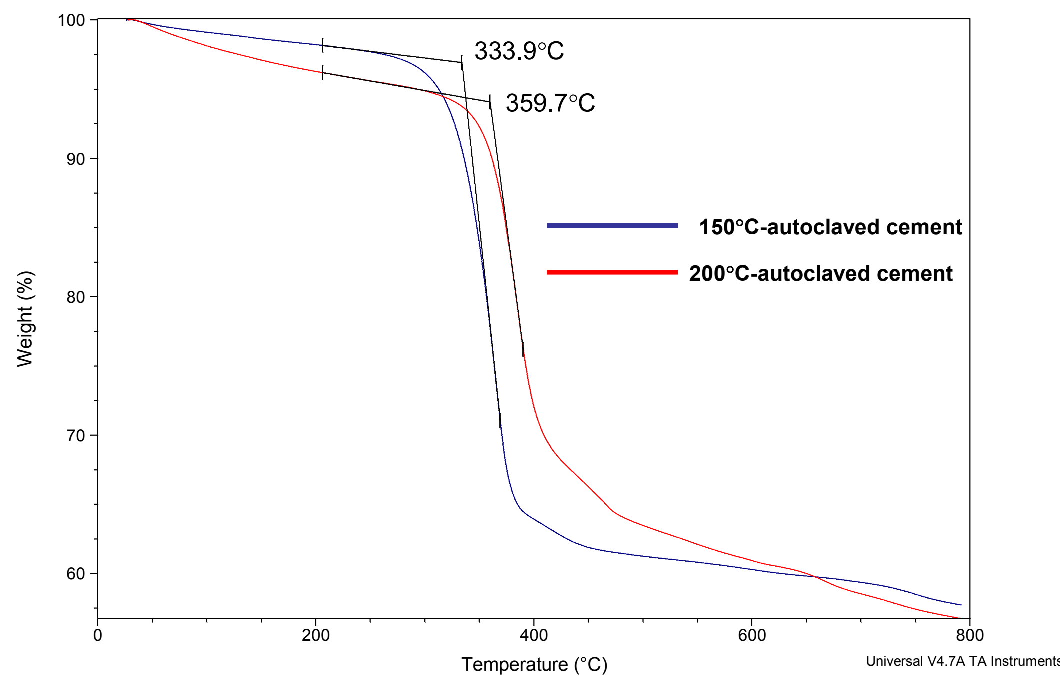


Corrosion-resistant foamed TSRC for carbon steel

High-temperature Corrosion Inhibitor: Acrylic polymer (AP)

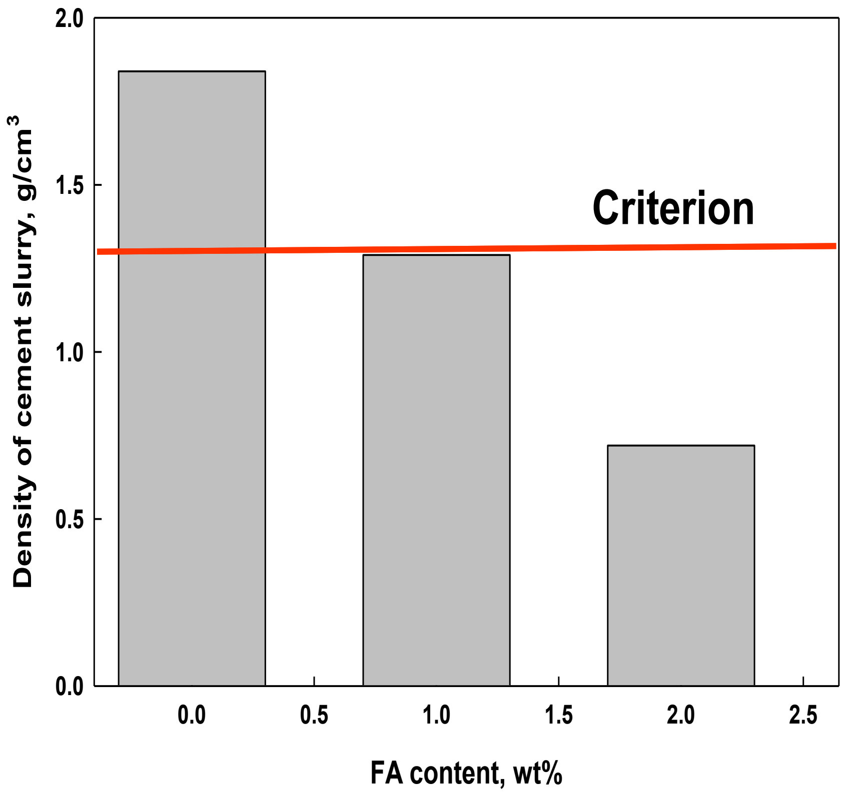


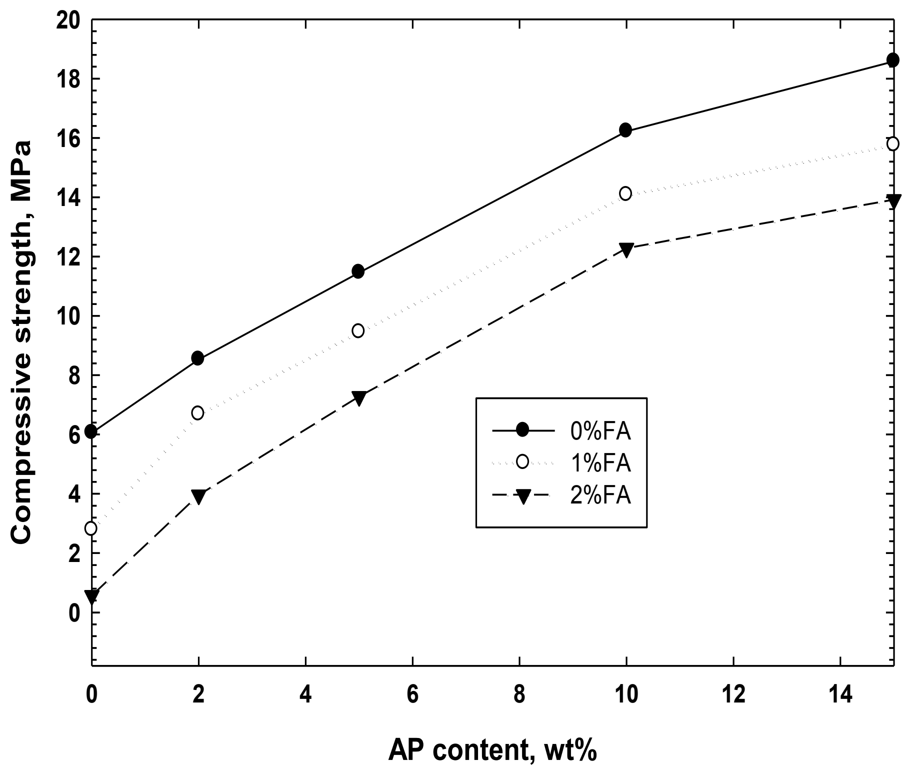
Thermal stability of Ca-complex AP formed in cement



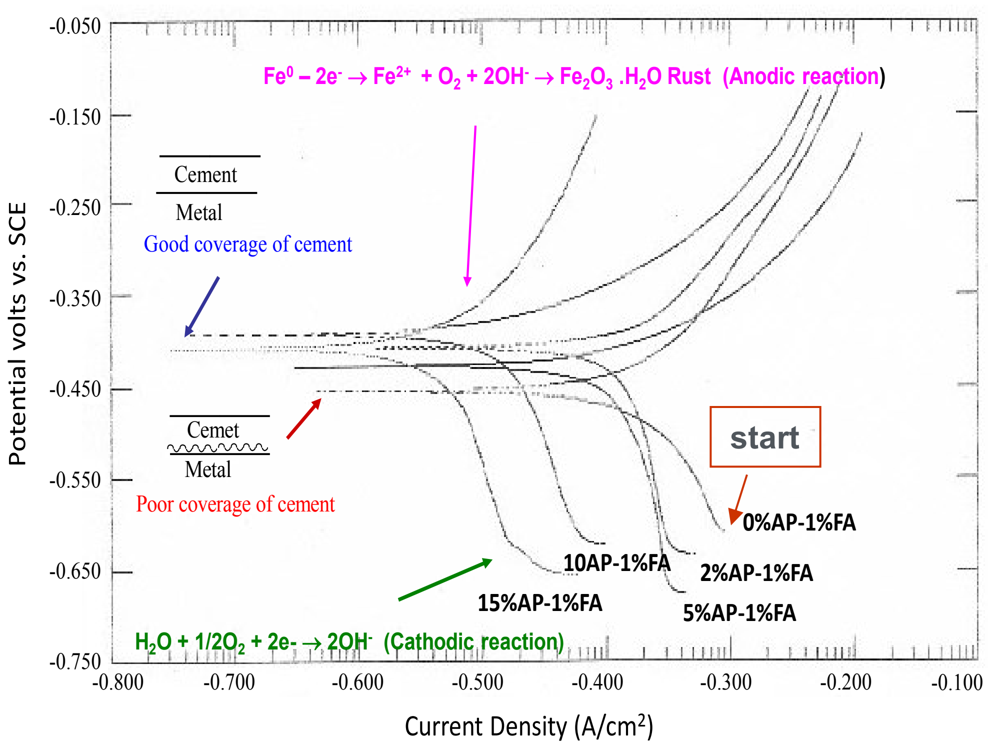
Slurry density of foamed cements and compressive strength of AP-modified and non-modified foamed cements after autoclaving at 200°C

Foaming Agent (FA): Cocamidopropyl dimethylamine oxide

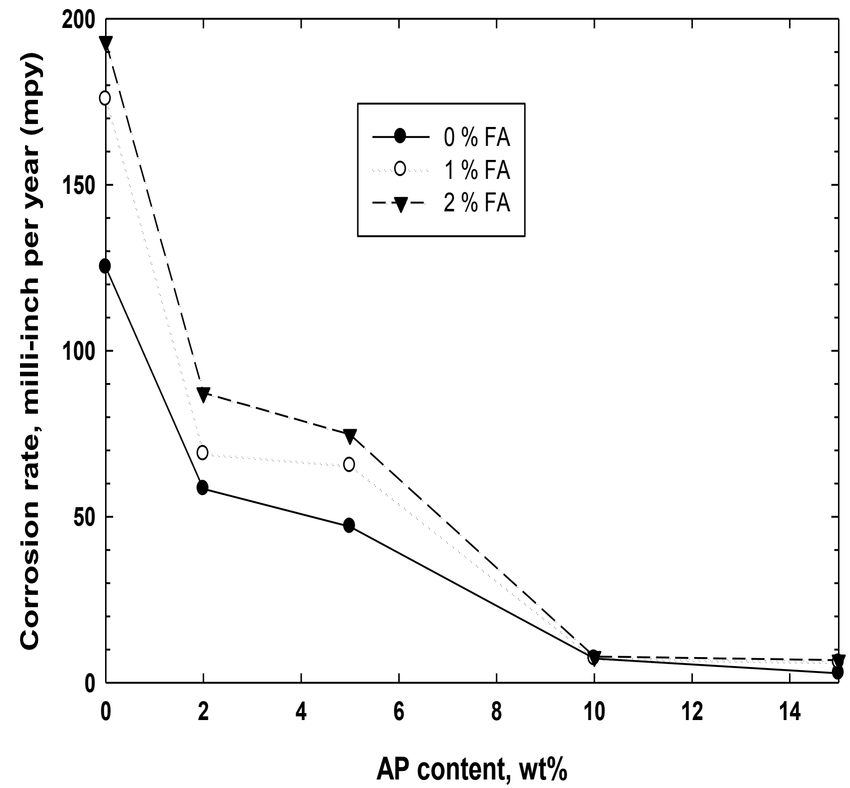




DC polarization diagrams for carbon steel panels coated with unmodified and AP-modified foamed cements after autoclaving at 200°C



Corrosion mitigation of carbon steel by AP-modified foamed cements



Future Directions

Milestone or Go/No-Go	Status & Expected Completion Date
Task 1. Complete thermal stress resistant test for 300°C-cured foamed TSRC	Apri.2013
Task 2. Develop high temperature-stable corrosion inhibitors ≥300°C	Jun. 2013
Task 3. Develop toughness enhancing additives	Aug.2013
Task 4. Develop setting control additives	Nov.2013
Go/no-go decision	
Task 5. Deliver interim report covering all information obtained in FY2013 to DOE and prepare peer-reviewed journal article	Dec.2013
Task.6 Complete technology transfer to geothermal industry	Dec.2013

Mandatory Summary Slide

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Thermal shock-resistant cement (TSRC) and 200°C-withstanding corrosion inhibitor suitable for foamed TSRC were developed in FY 2012.

	FY2012 (Dec. 2011- May 2012)	FY2012 (Jun. 2012- Jan. 2013)
Target/Milestone	**Complete annealing-water quenching test.**	**•Complete density and electrochemical corrosion tests. •Meeting with industrial partners to evaluate its technical feasibility and to address future R&D direction.**
Results	**Formulated thermal shock-resistant cement.**	**•Developed two specific additives, foaming agent and corrosion inhibitor suitable for TSRC. •Report covering all data was prepared and set to DOE and industrial partners for review.**

Project Management

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Timeline:

Planned Start Date	Planned End Date	Actual Start Date	Current End Date
December 2011	December 2012	December 2011	December 2012*

Budget:

Federal Share	Cost Share	Planned Expenses to Date	Actual Expenses to Date	Value of Work Completed to Date	Funding needed to Complete Work
$300 K	0	$300 K	$250 K	$300 K	0

*** Some work ongoing with carry forward funds**