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

Analcime \((\text{NaAlSi}_{12}\text{O}_{6}\cdot\text{H}_{2}\text{O})\)

Thomsonite \((\text{NaCa}_{2}\text{Al}_{5}\text{Si}_{5}\text{O}_{20}\cdot6\text{H}_{2}\text{O})\)

Hydroxysodalite \([\text{Na}_{4}\text{Al}_{3}\text{Si}_{3}\text{O}_{12}\cdot\text{OH}])\)

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

Presenter Name: Dr. Toshifumi Sugama
Brookhaven National Laboratory

This presentation does not contain any proprietary confidential, or otherwise restricted information.
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.
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 CO₂ 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 CO₂-induced mild acid (pH ~ 5.0) at 300°C < 5 wt% loss after 30 days exposure;
9) Compressive toughness > 0.2 N-mm/mm³ after 300°C-24 hour-autoclaving;
10) No shrinkage;
11) Thermal conductivity < 0.5 W/m.K.
<table>
<thead>
<tr>
<th>Original Planned Milestone/ Technical Accomplishment</th>
<th>Actual Milestone/Technical Accomplishment</th>
<th>Date Completed</th>
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<tbody>
<tr>
<td>Task 5. Develop advanced high-temperature inorganic anodic corrosion inhibitors</td>
<td>As of March 2015, 70 % completed</td>
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<td>Task 6. Evaluate resistance of TSRC to acid</td>
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<td>Task 7. Long-term corrosion- and thermal shock-resistance testing under CRADA with Schlumberger</td>
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Accomplishments, Results and Progress

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 pozolana-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 CO₂ footprint incurred from OPC manufactures.

![Reaction Diagram]

**IBP**

$\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow 200 \text{ - } 300^\circ \text{C}$

**Refractory calcium aluminate (RCA)**

$\text{CaO} \cdot \text{SiO}_2 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow 200 \text{ - } 300^\circ \text{C}$

**calcium silicate (OPC)**

**Class F fly ash (CFFA)**

$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{Na}_2\text{O} \cdot n\text{SiO}_2 + \text{CaO} + \text{H}_2\text{O} \rightarrow 200 \text{ - } 300^\circ \text{C}$

$\rightarrow \text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{(OH)}$

$\rightarrow \text{Hydroxysodalite}$

$\rightarrow \text{NaCa}_2\text{Al}_5\text{Si}_4\text{O}_{20 \cdot 6}\text{H}_2\text{O}$

$\rightarrow \text{Thomsonite}$

$\rightarrow \text{NaAlSi}_2\text{O}_6\cdot\text{H}_2\text{O}$

$\rightarrow \text{Analcime}$

$\rightarrow \text{Hydro-ceramic}$

$\rightarrow \text{Tobermorite}$

$\rightarrow \text{Calcium silicate hydrate}$
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/SiO₂) and Calcium aluminum phosphate cement (CaP)
Phase transformations in CFFA-rich TSRC after 5 cycle testing

\[
\begin{align*}
\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH}) & \quad \text{Ca}_5\text{Al}_2(\text{OH})_{12} & \quad \text{gamma-AlOOH} & \quad \text{Ca}_5\text{Si}_6\text{O}_{15}(\text{OH})_{2.4}\text{H}_2\text{O} \\
\text{Hydroxysodalite} & \quad \text{Katoite} & \quad \text{Boehmite} & \quad \text{Tobermorite} \\
\text{Hydro-ceramic} & \quad \text{Hydro-garnet} & \quad \text{Hydro-Al oxide} & \quad \text{Calcium silicate hydrate}
\end{align*}
\]

\[
600^\circ\text{C}, \text{CO}_2
\]

\[
\begin{align*}
\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3 & \quad >> \quad \text{CaCO}_3 & \quad \text{gamma-Al}_2\text{O}_3 & \quad \text{Ca}_5\text{Si}_6\text{O}_{15}(\text{OH})_{2.4}\text{H}_2\text{O} \\
\text{Carbonated sodalite as nano-scale crystal} & \quad & & \\
\end{align*}
\]

SEM image

1 µm
**Set-controlling additives at 85°C**

*Set-retarding mechanism by TA and HTHP consistomer test results*

\[
\text{Tartaric acid (TA)} \quad \xrightarrow{\text{Hydrolysates of SMS}} \quad \text{Sodium tartrate} \quad \xrightarrow{\text{Sodium polysilicate}} \quad \text{Ca(OH)\(_2\) from cement}
\]

**Temperature, °F**

**Consistency, BC**

85°C and 5,500 psi

Point of departure

**Set-controlling additives at 85°C**

**Set-retarding mechanism by TA and HTHP consistomer test results**

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\text{Hydrolysates of SMS}
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\]
Toughness improvement by micro-carbon fiber (MCF)

Accomplishments, Results and Progress

With MCF

Post-stress peak energy absorption (Ductility)

Pre-stress energy absorption (Ultimate strength)

Reinforcement efficiency, %

MCF content, wt%

85°C strength

200°C strength

300°C strength

85°C toughness

200°C toughness

300°C toughness

Compressive stress - MPa

Compressive strain (Extension), %

MCF content, wt%

0 2 4 6 8 10

Reinforcement efficiency, %

0

50

100

150

200

250

85°C strength

200°C strength

300°C strength

85°C toughness

200°C toughness

300°C toughness

100μm

40μm

500μm
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$_2$ sheath after 7 cycle
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_{2}O_{6}.H_{2}O

ZP
Amorphous NaO-Al_{2}O_{3}-SiO_{2}.H_{2}O

CBS

# Future Directions

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<thead>
<tr>
<th>Milestone or Go/No-Go</th>
<th>Status &amp; Expected Completion Date</th>
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<tbody>
<tr>
<td>Task 5. Deliver annual report covering all information obtained in FY2016 to DOE and prepare peer-reviewed journal article</td>
<td>Dec. 2016</td>
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<tr>
<td>Go/No-go Decision</td>
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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.

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<tr>
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<td>Complete annealing-water quenching test.</td>
<td>Complete interfacial bond durability test at TSRC/steel casing joint.</td>
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<td>Complete HTHP consistomer test.</td>
<td>• Complete electrochemical corrosion test.</td>
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<td>Complete toughness measurement.</td>
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<tr>
<td>Results</td>
<td>Formulated alternative TSRCs.</td>
<td>Identified a potential of micro-carbon fiber for improving adherent durability of TSRC to casing surfaces.</td>
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<td></td>
<td>Developed set-controlling additive suitable for TSRC.</td>
<td>• Developed 300°C-withstanding inorganic anodic corrosion inhibitor suitable for TSRC.</td>
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<td>Developed tough, crack-arresting TSRC.</td>
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