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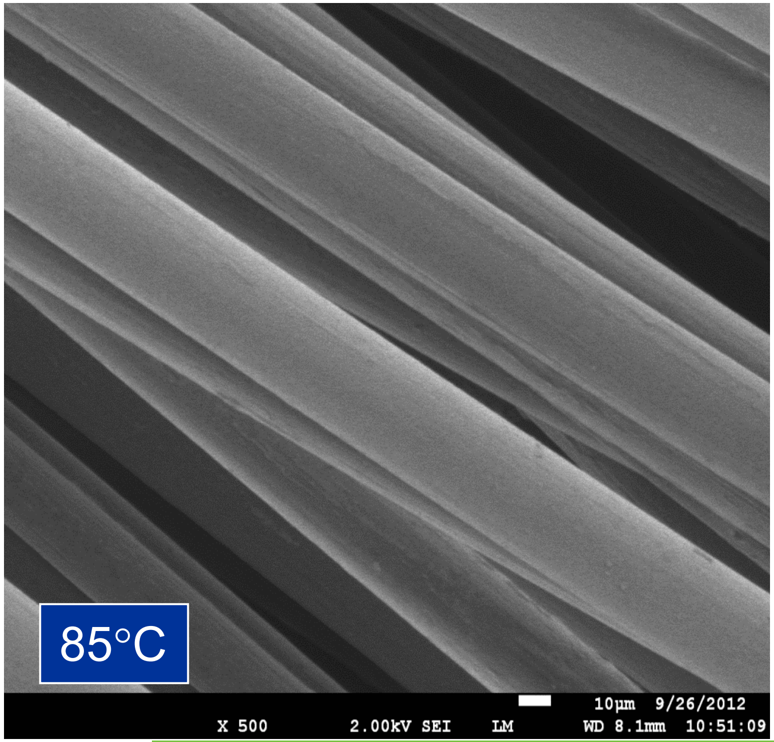

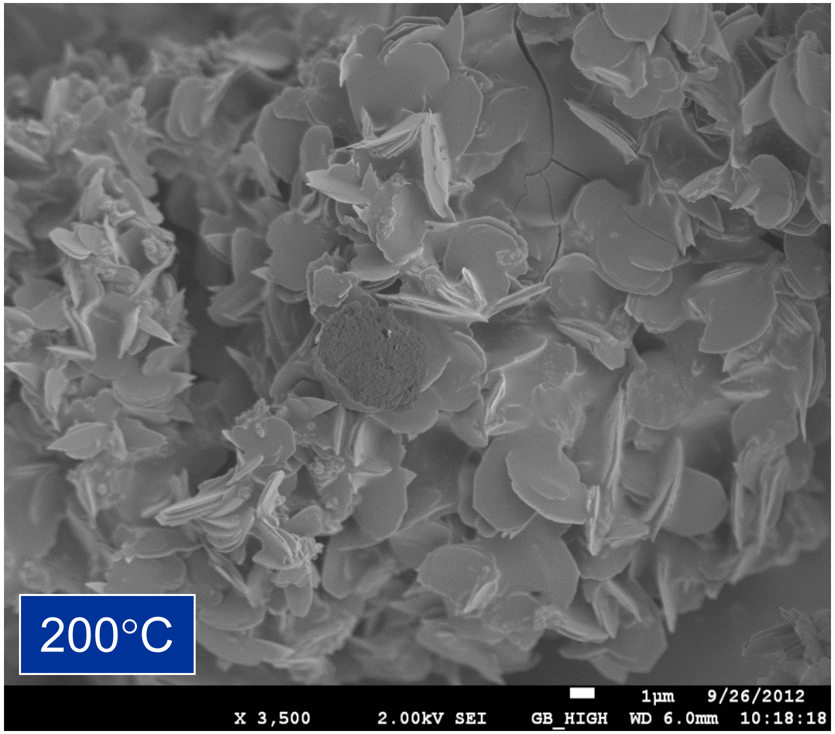

Self-decomposable fibrous bridging additive for sealers

Self-degradable Temporary Cementitious Sealers

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

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Objectives: Using BNL-developed temporary fracture sealing materials, objectives of this project are 1) to develop an advanced self-degradation enhancing additive, 2) to find specific bridging additive, which aids the sealer in plugging adequately the fractures at 85°C and to degrade itself at ≥200°C, 3) to evaluate the compatibility of sealers with drilling fluid, and 4) to transfer developed technology to cost-sharing industrial partners.

Impact:

- Reduction of total costs of sealing and multi-fracture drilling operations including the elimination of three major issues,1)lost-circulation problem, 2)additional isolation liners, and 3)managed pressure drilling, and also the use of inexpensive raw material.
- New science and technology regarding self-degradable cementitious materials.

Scientific/Technical Approach

BNL-developed self-degradable sealers met the following nine material criteria:

- One dry component product
- Plastic viscosity, 20 to 70 cp at 300 r.p.m
- Maintenance of pumpability for at least 1 hour at 85°C
- Compressive strength >2000 psi
- Be self-degradable after contact with water at ≥200°C under a certain pressure
- Expandable and swelling properties; >0.5% of total volume of sealer
- Excellent plugging performance through fractures of ~0.04 to 0.25 in. wide spacing at ~ 85°C
- Anti-filtration properties
- Material cost which was equal or less to that of conventional Ordinary Portland Cement (OPC)-based sealers.

Accomplishments, Results and Progress

Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Task 1. Develop advanced self-degradation promoter	Completed. -T. Sugama, T. Pyatina, and T. Butcher "Self-degradable cementitious sealing materials in enhanced geothermal system," in Materials Challenges in Alternative and Renewable Energy, Ceramic Transactions, 239 (2012) 137-153. -T. Sugama and T. Pyatina "Sodium carboxymethyl celluloses (CMCs): Self-degrading promoters of temporary cementitious sealing materials," BNL Informal report, September (2012).	May 2012
Task 2. Develop self-decomposable bridging additives under API slot testing evaluation	Completed. -T. Sugama, T. Pyatina, S. Gill, B. Iverson, and D. Bour "Self-decomposable fibrous bridging additives for temporary cementitious fracture sealers in EGS wells," BNL informal report, December (2012).	September 2012
Task 3. Assess compatibility of sealer with drilling fluid	Completed.	October 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, Halliburton and Geodynamics	December 2012

Alkali-activated pozzolana cements for temporary sealer

Based upon all experimental works in FYs 10 and 11, the granulated blast-furnace slag (S)/Class C fly ash (C) blending system was selected as cement-forming material, and the following additives were use to design self-degradable fracture sealers.

Additives

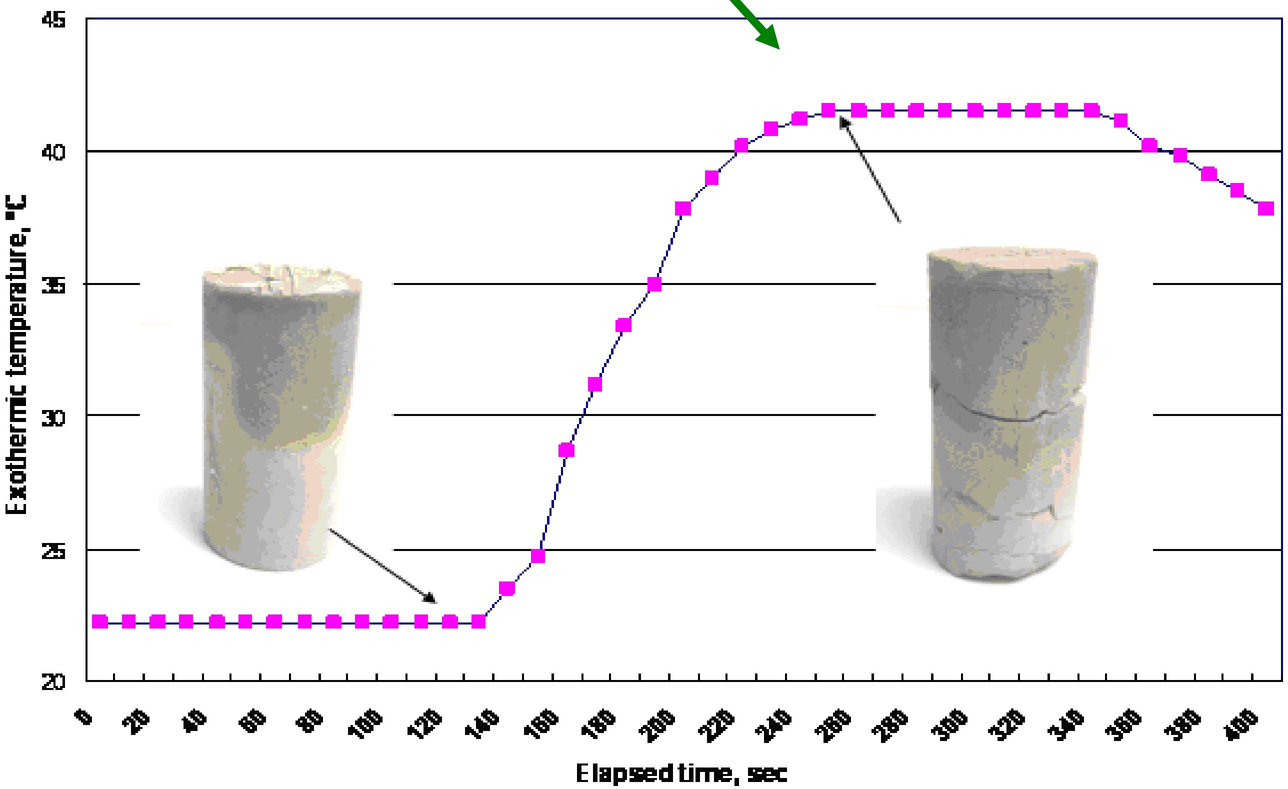
-Sodium silicate as alkali activator.

-Sodium carboxymethyl cellulose (CMC) as self degradation promoter.

-Magnesium oxide (MgO) as expansive agent.

-Polyvinyl alcohol (PVA) fiber as self-decomposable bridging material.

1. Direct immersion of ≥200°C-heated sealers in water.
2. After autoclaving for 24 hours at 200°C.
3. Water impregnation after heated sealers were cooled down to room temperature.



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Hydrothermal reactions between sodium silicate and slag or Class C fly ash

$$Na_2O.SiO_2 \xrightarrow{\text{Hydrolysis}} Na^{+} + {}_{y}(H_3SiO_4)^{-} + {}_{z}OH^{-}$$

sodium silicate

1/1 NaO_2/SiO_2 ratio

$$CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO + {}_{z}\,OH^{-} + {}_{y}\,(H_3SiO_4)^{-} \xrightarrow{\text{200°C-autoclave}} CaO.SiO_2.H_2O + {}_{n}\,Al(OH)_4^{-} + {}_{m}\,Mg^{2+} + NaOH$$

slag

C-S-H (I) phase

$$\rightarrow Ca_5(OH)_2Si_6O_{16}.5H_2O$$

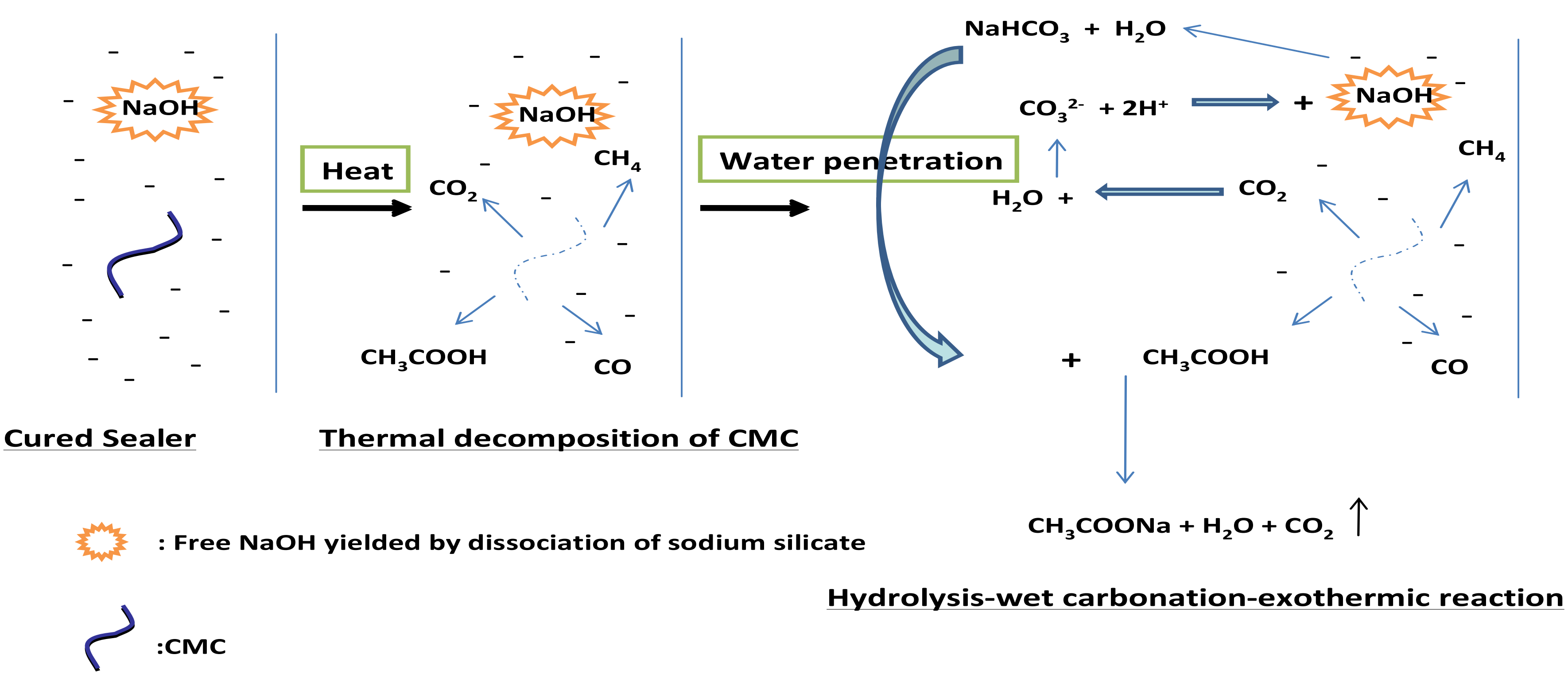
Tobermorite

$$3CaO.Al_2O_3,\ CaSO_4,\ CaO,\ SiO_2 + {}_{z}\,OH^{-} + {}_{y}\,(H_3SiO_4)^{-} \longrightarrow Ca_5(OH)_2Si_6O_{16}.5H_2O + {}_{n}\,Al(OH)_4^{-} + {}_{m}\,SO_4^{2-} + NaOH$$

Class C fly ash

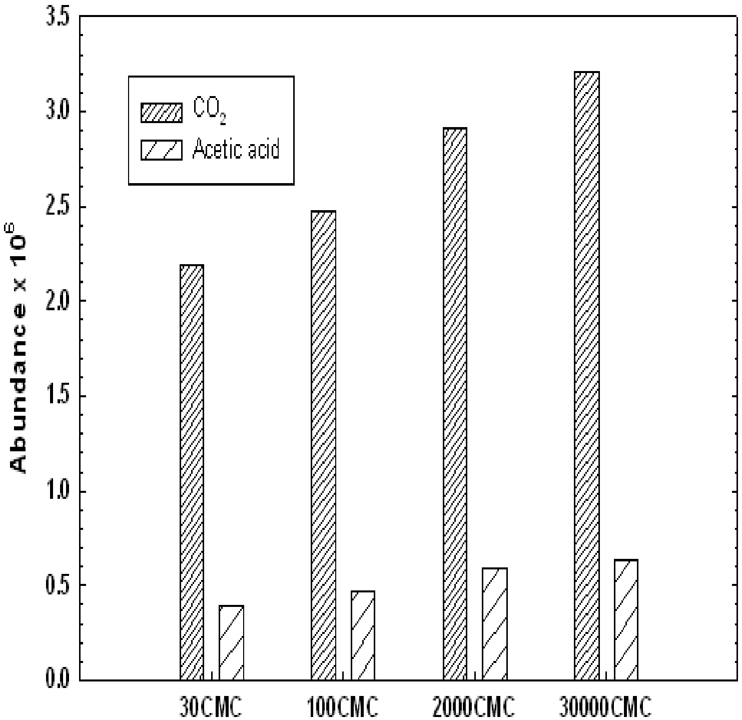
Tobermorite

Self-degradation Mechanism

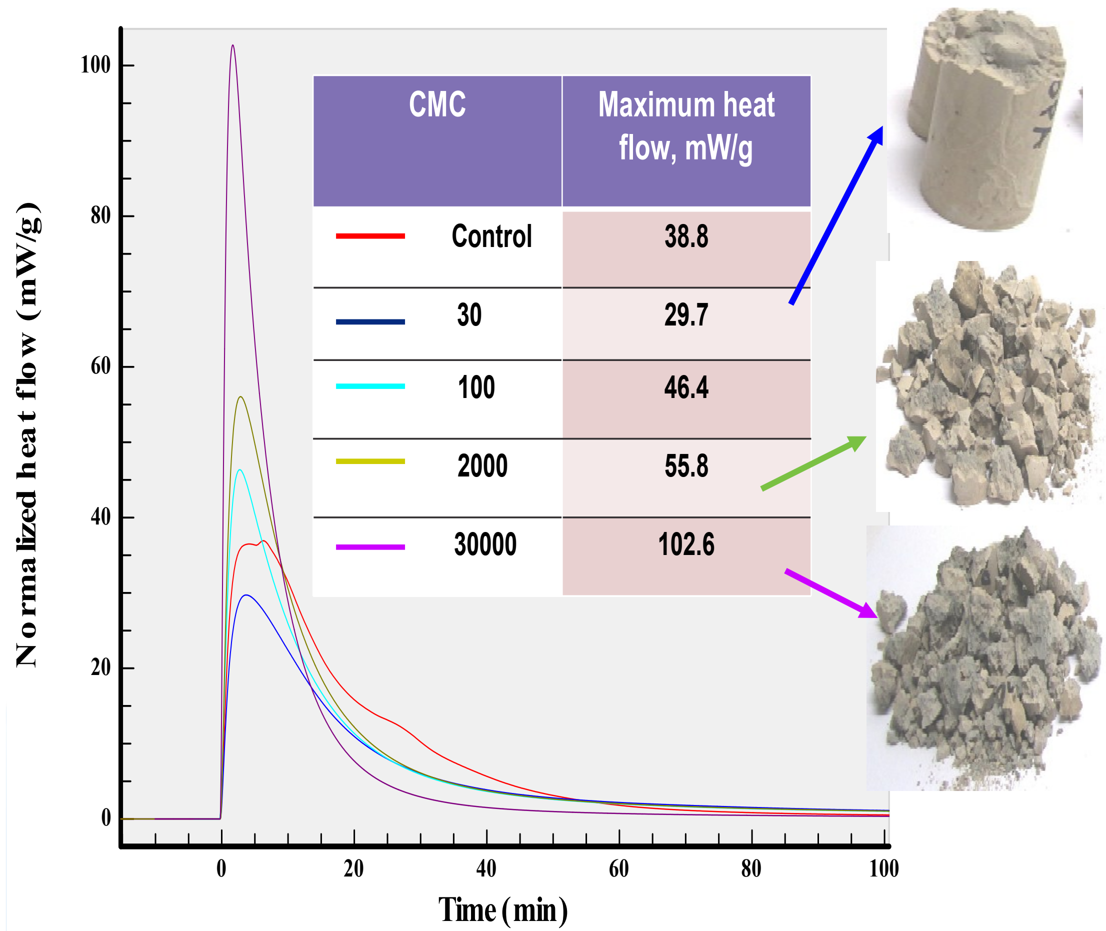


Py-GC/MS abundance of CO_2 and acetic acid emanated from 200°C-heated CMC self-degradation promoters with various molecular weight (MW)

30CMC: 80,500MW
100CMC: 133,400 MW
2000CMC: 224,000 MW
30000CMC: >224,000 MW



Exothermic heat energy generated in 200°C-heated sealer containing CMCs with various MW after contact with water



CMC	Maximum heat flow, mW/g
Control	38.8
30	29.7
100	46.4
2000	55.8
30000	102.6

Accomplishments, Results and Progress

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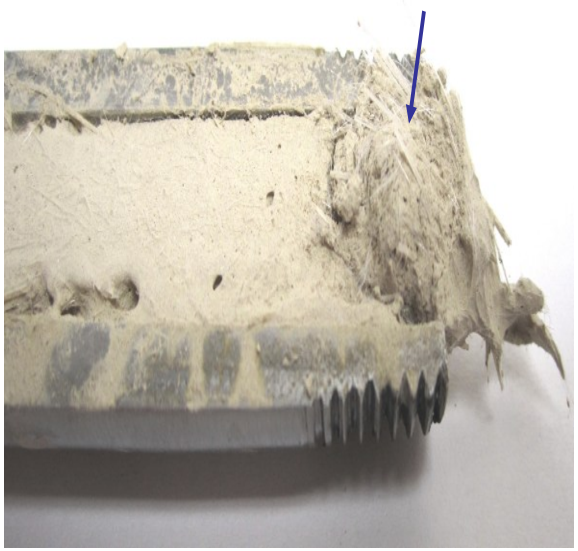
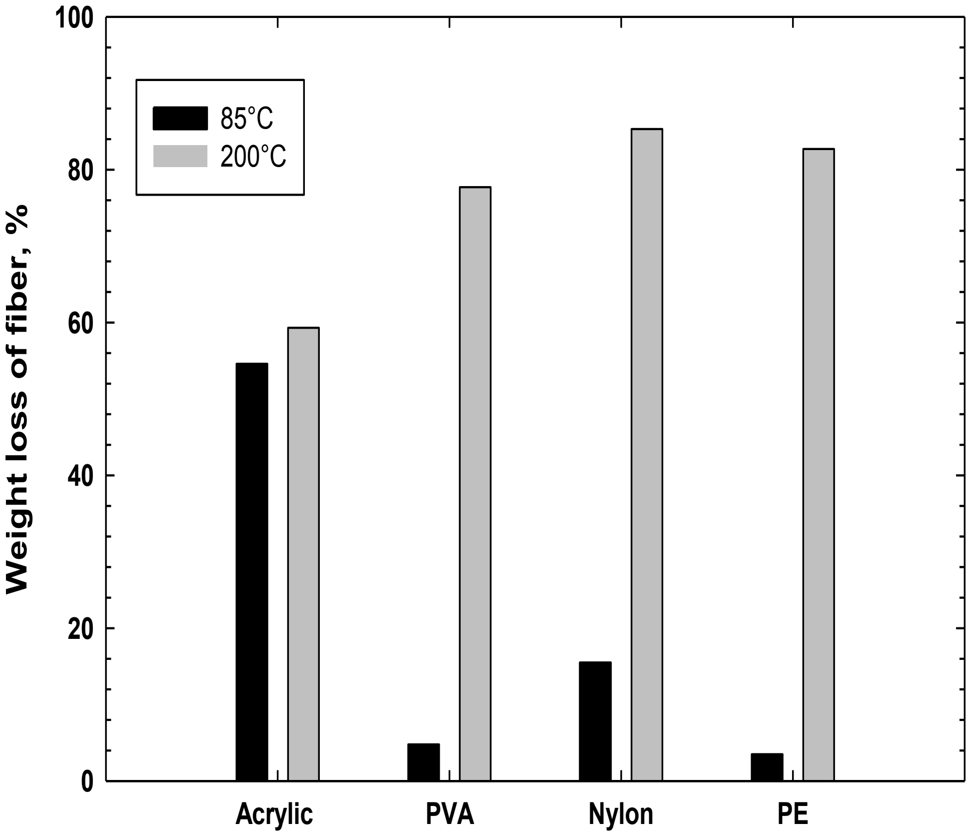
Comparison of plugging performances of sealers made by the combination of 19 mm-long PVA and 6 mm-long PVA, nylon, or PE fibers for 1-in. wide x 6-in. long x 0.24 in. high slot nozzle

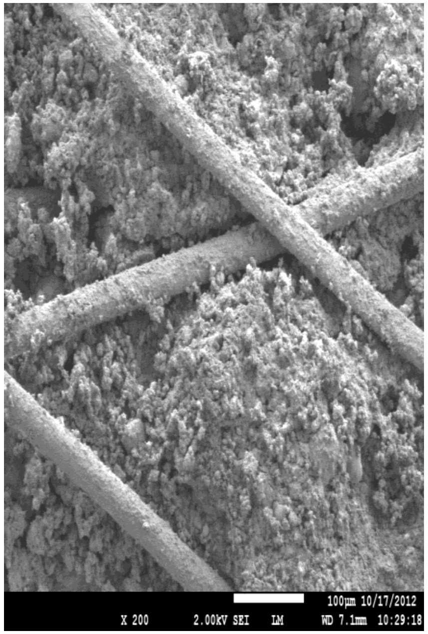
Fiber	Content, wt%	Filtration loss of sealer, wt%					
		20 psi pressure	50 psi pressure	100 psi pressure	200 psi pressure	500 psi pressure	700 psi pressure
PVA (6mm)	4	100	100	100	100	100	100
PVA (19 mm)	2	17.4	25.8	100	100	100	100
PVA (19mm) PVA (6mm)	1.0 0.5	1.6	0	0	100	100	100
PVA (19mm) PVA (6mm)	0.5 1.0	10.6	0	0	0	0	0
PVA (19mm) Nylon (6mm)	0.5 1.0	6.4	2.9	1.4	0	0	0
PVA (19 mm) PE (6mm)	0.5 1.0	7.1	14.9	27.5	100	100	100



Weight loss of acrylic, PVA, nylon, and PE fibers treated with pH 13.7 cement pore solution at 85°C and 200°C

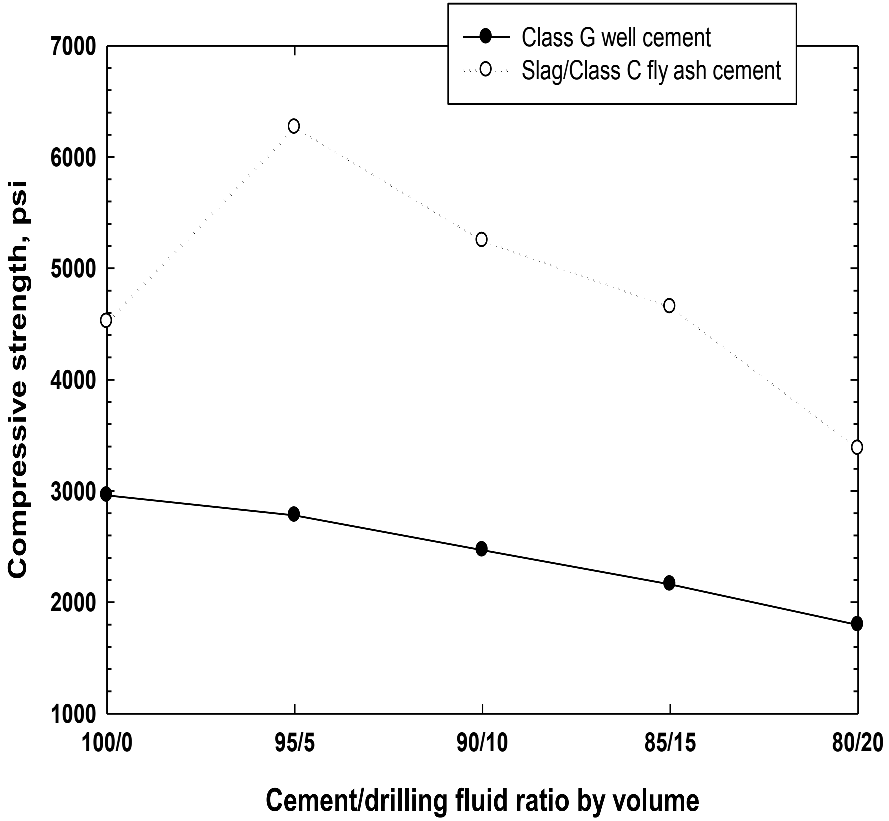


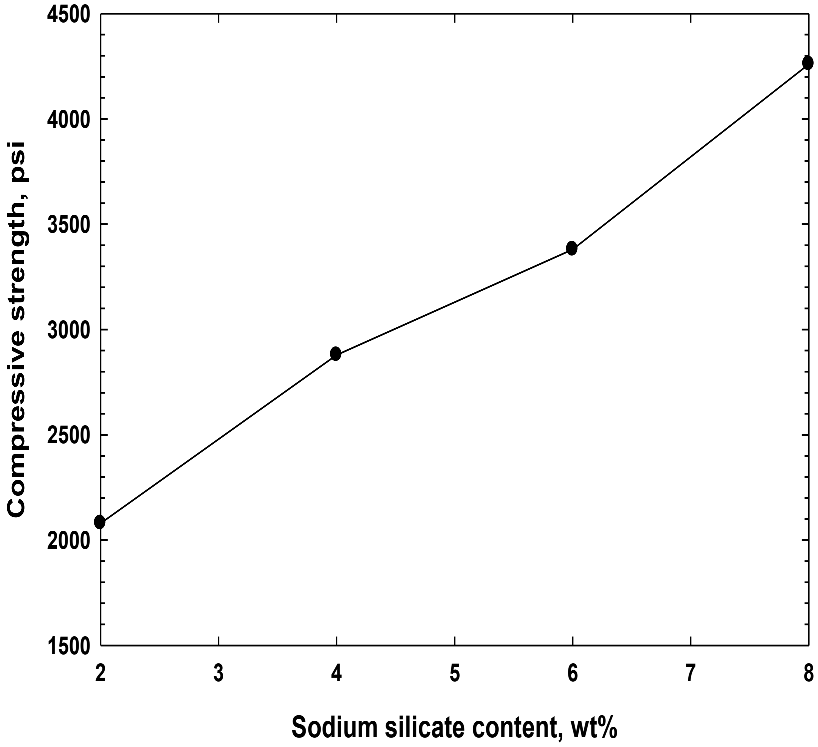
PVA fibers in 85°C-autoclaved sealer (left) and self-degraded sealer at 200°C (right)



Compatibility test of sealer with drilling fluid

Formula of water-based drilling fluid: 0.27% caustic soda, 0.53% Lignosulfonic acid, 0.27% polyanionic cellulose, 0.27 % xanthan gum, 1.5% barite, 5.3% bentonite gel, and 91.9% water.





Future Directions

Milestone or Go/No-Go	Status & Expected Completion Date
Task 1. Develop self-pulverizing technology of degraded sealers	Apr. 2013
Task 2. Optimizing a field-applicable formula of sealer slurry	Aug. 2013
Task 3. Develop the plugging technology of sealers in a large slot size, ranging from 1 to 3 in. wide spacing	Sep.2013
Task 4. Determining mechanical behaviors of optimized formula	Oct.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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Two specific additions, CMC with >224,000 MW as self-degradation promoter and PVA-based bridging fibrous material, offered advanced properties of BNL-developed temporary sealer. Additionally, the sealer had a good compatibility with water-based drilling fluid.

	FY2012 (Jan. 2012-Aug. 2012)	FY2012 (Sep. 2012-Jan. 2013)
Target/Milestone	•Improve self-degradation performance of sealer. •Develop self-decomposable bridging additive.	•Assess compatibility of sealer slurry with drilling fluid. •Meeting with industrial partners to evaluate its technical feasibility and to address future R&D direction.
Results	•For former target, the magnitude of sealer's self-degradation depended on MW of CMC additive. •For latter, PVA fiber not only adequately plugged slot with 0.25 in. wide at 85°C, but also effectively decomposed at 200°C.	Report covering all data was prepared and set to DOE and industrial partners for review.

Project Management

Timeline:

Planned Start Date	Planned End Date	Actual Start Date	Current End Date
January 2012	January 2013	January 2012	January 2013*

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**