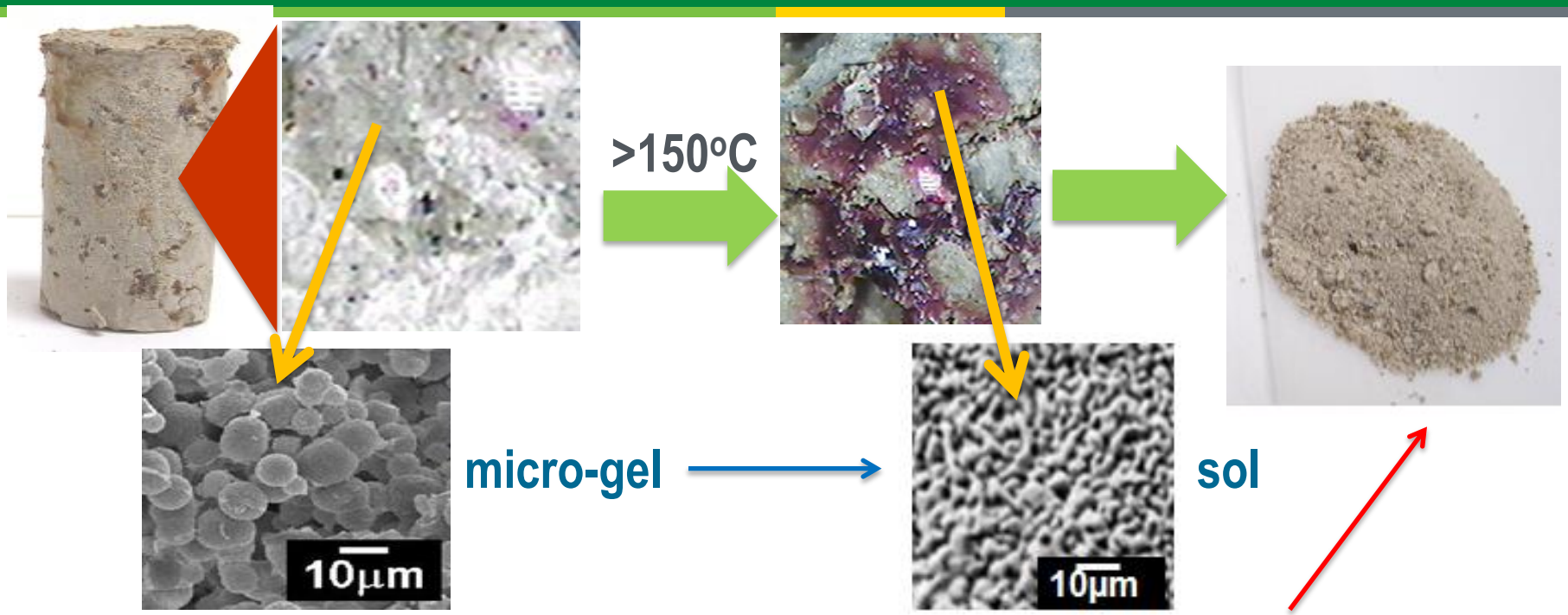

PVA gel-incorporated cement at 85°C

Pulverized cement by gel →sol conversion

Self-degradation technology by *in-situ* gel → sol phase transition

Temporary Sealer Materials

Project Officer: Joshua Mengers
Total Project Funding: $120,000
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: Using BNL-developed cementitious sealing material, the objectives of this project are 1) to develop an advanced self-degradation enhancing additive, which aids in converting bulk cement into fine powder at ≥150^{o}C, 2) to design set-controllable formula at 85^{o}C, 3) to determine mechanical behaviors of sealer before self-degradation, 3) to evaluate solubility of degraded cement in less-or non-corrosive acids at 90^{o}C, and 4) to develop plugging technology using self-decomposable PVA fiber for 0.5 to 2.0 in. wide slots.

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

Eight material criteria for self-degradable sealers:

- One dry component product
- Plastic viscosity, 20 to 70 cp at 300 r.p.m
- Maintenance of pumpability for at least 3 hours at 85°C
- Compressive strength >2000 psi at 85°C
- Be self-degradable at ≥150°C
- Expandable and swelling properties; >0.5% of total volume of sealer
- Excellent plugging performance through fractures of up to 2.0 in. wide spacing at ~ 85°C
- Solubility ≥70wt% of degraded cement in acid at 90°C.

Accomplishments, Results and Progress

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Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Task 1. Develop advanced self-degradation enhancing additive	Completed -T. Sugama and T. Pyatina "Utilization of PVA flakes in promoting self-degradation of temporary cementitious fracture sealing material," GRC Transaction 38 (2014) 331-338. 2014 GRC Best Presentation Award -T. Sugama and T. Pyatina "Effect of sodium carboxymethyl celluloses on water-catalyzed self-degradation of 200°C-heated alkali-activated cement," Cement & Concrete Composites 55 (2015) 281-289.	April 2014
Task 2. Test plugging performance of self-decomposable PVA fiber for 0.5 X 0.5 in. slot	Completed	July 2014
Task 3. Assess effect of PVA fiber on improving toughness of sealer	Completed	October 2014
Task 4. Formulate set-controllable cementitious sealer	Completed	January 2015
Task 5. Evaluate less- or non-corrosive acid to dissolve a crumbled sealer	As of March 2015, 60% completed	
Task 6. Develop plugging technology for 1.5-2.0 in. slots		

Cement System

Alkali-activated pozzolana cements as matrix

-Class C fly ash as major cement-forming material

-Granulated blast-furnace slag as minor cement-forming material

Additives

-Sodium metasilicate (SMS) as alkali activator

-PVA (Mw 195,000) flake as self-degradation promoter

-PVA fiber (6 and 19 mm long x ~15μm diam.) as self-decomposable bridging material

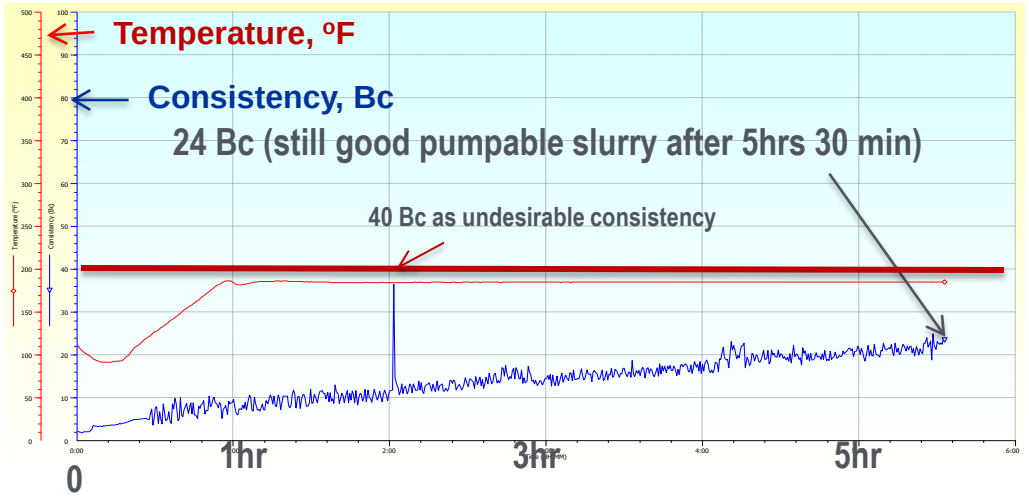
-MgO as volume-expanding additive

-Sodium gluconate (SG) as fiber wetting and set-control additive

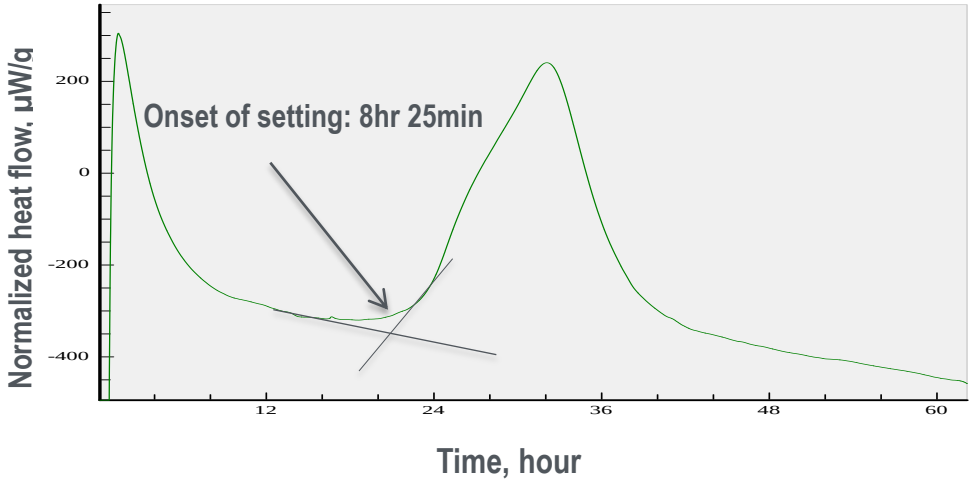
Major hydration product at 85^{o}C

Calcium silicate hydrate (C-S-H phase I)

Thickening time measurements of sealer slurry at 85°C by HPHT consistometer under dynamic condition at 5500 psi, followed by micro-calorimeter at 85°C under static condition



Chandler HPHT Consistomer



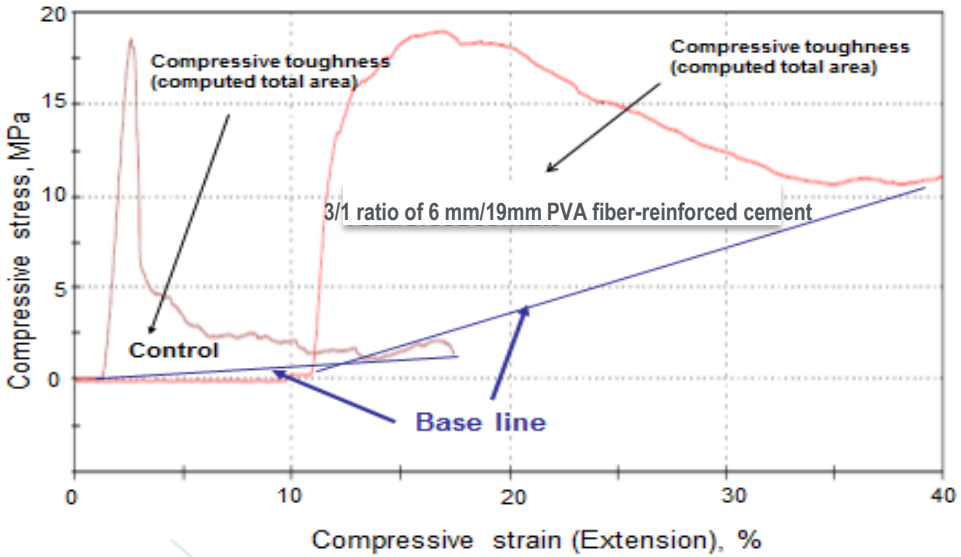
Isothermal Micro-calorimetry

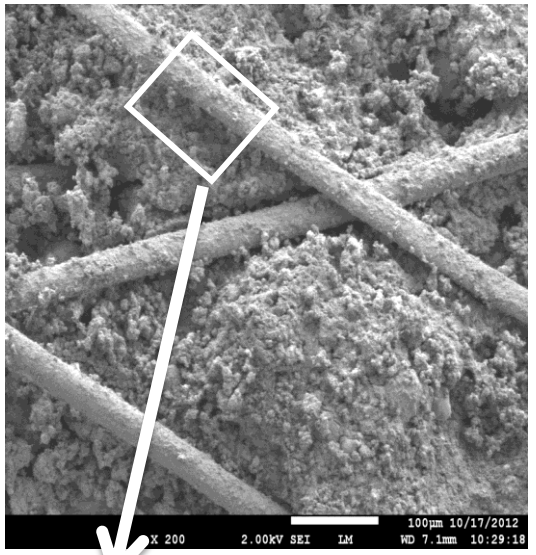
Comparison of plugging performances of sealers made by the combination of 19 mm- and 6 mm-long PVA fibers for 0.5-in. wide x 6-in. long x 0.5 in. high slot nozzle

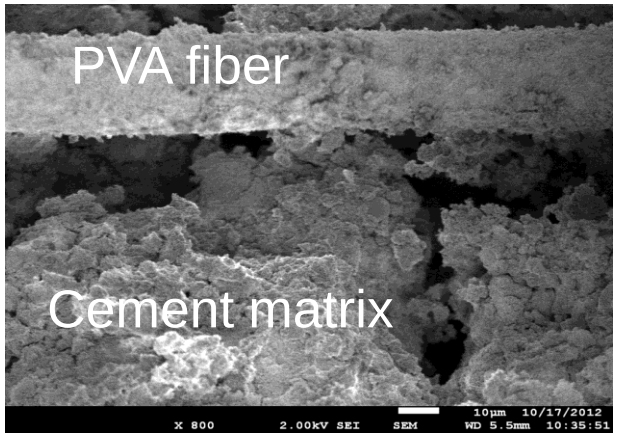
Fiber	Content, wt%	Filtration loss of sealer, wt%					
		20 psi pressure	50 psi pressure	100 psi pressure	200 psi pressure	500 psi pressure	1000 psi pressure
PVA (6mm)	5	100	100	100	100	100	100
PVA (19 mm)	4	32.7	100	100	100	100	100
PVA (19mm) PVA (6mm)	2.0 1.0	2.8	10.9	100	100	100	100
PVA (19mm) PVA (6mm)	2.0 2.0	5.8	0	0	0	0	0
PVA (19mm) PVA (6mm)	1.0 3.0	4.1	8.9	0	0	0	0

High-pressure slot plugging apparatus

Compressive-strength and-toughness for non-reinforced and PVA fiber-reinforced cements after autoclaving at 85ºC

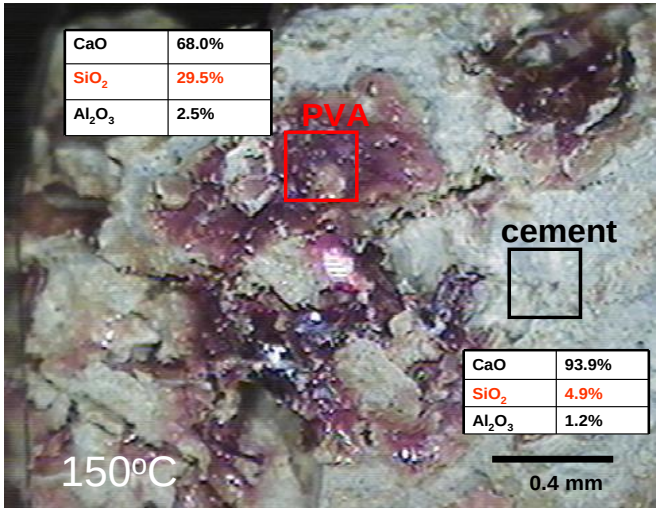


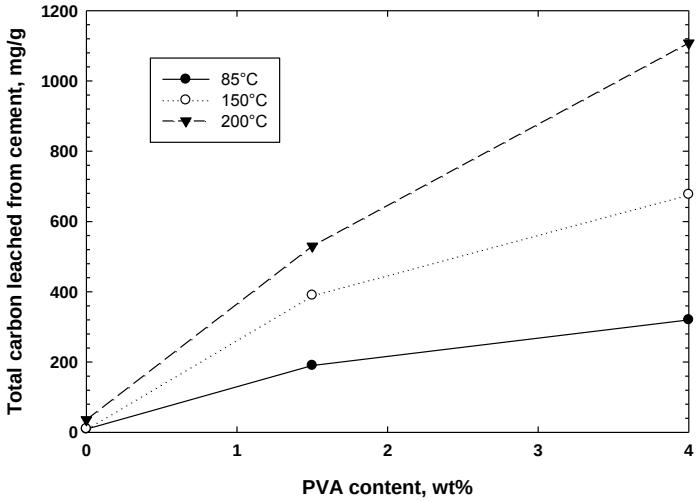


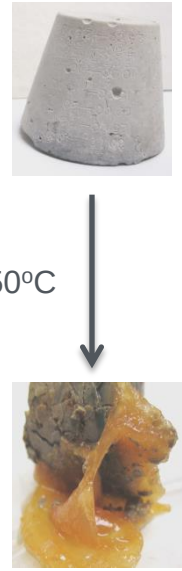


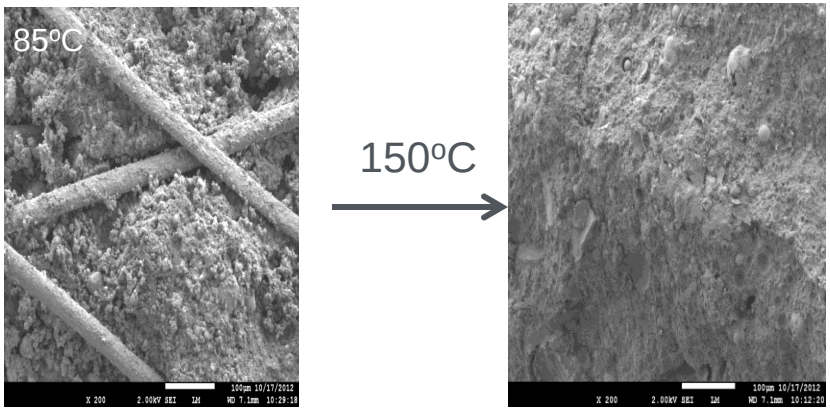
	Compressive strength, psi	Compressive toughness, N-mm/mm^3
Control (no PVA fiber)	2390	0.41
PVA fiber-reinforced cement	2479	3.94

Leaching of PVA from cement at 85,150, and 200°C

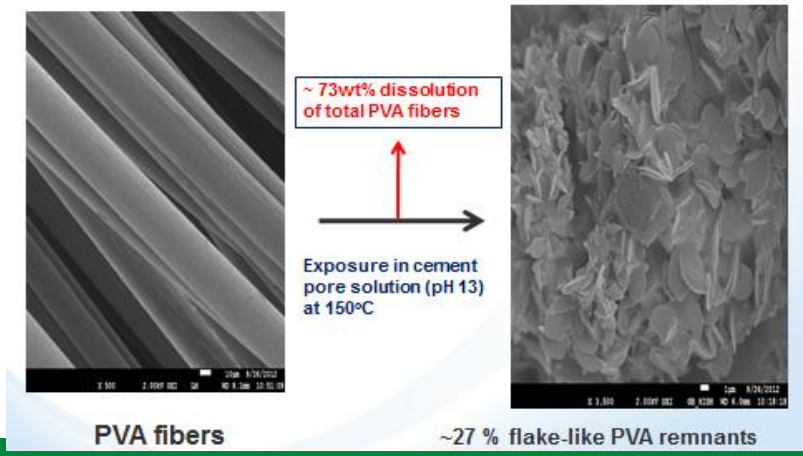








Self-decomposed PVA fiber (right) in cement at 150°C

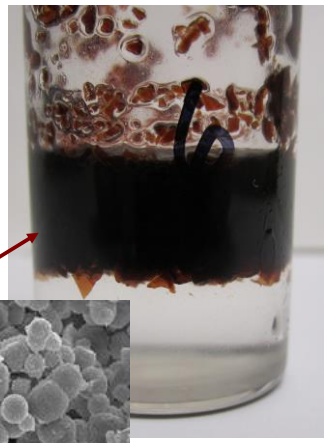


PVA micro-gels formed in PVA/SMS mixed solution at 85°C and gels⟶sol transition at ~150°C

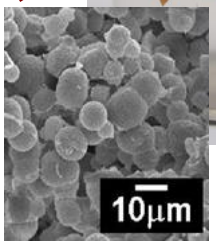
PVA solution

85°C

+ SMS



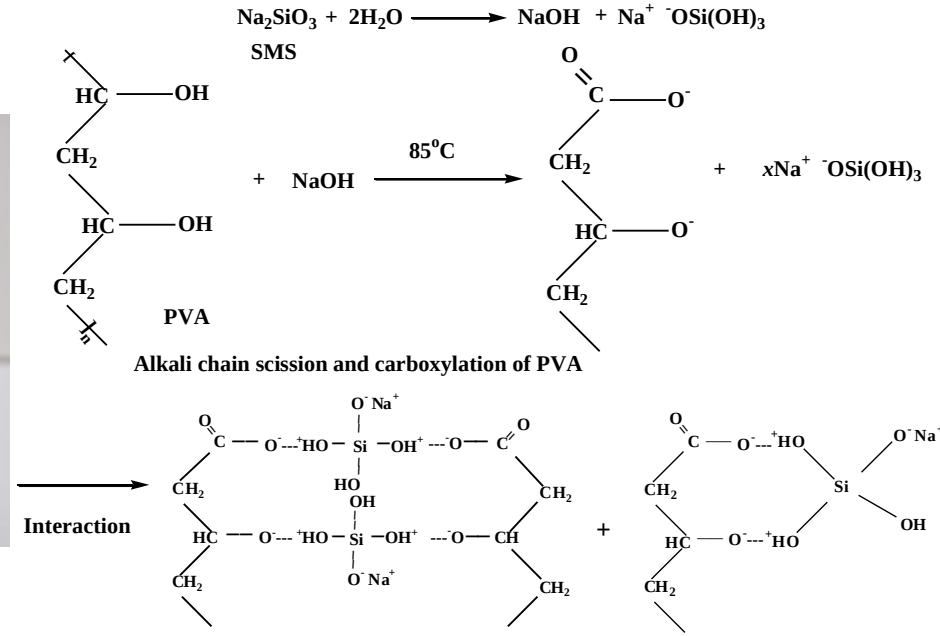
PVA gels

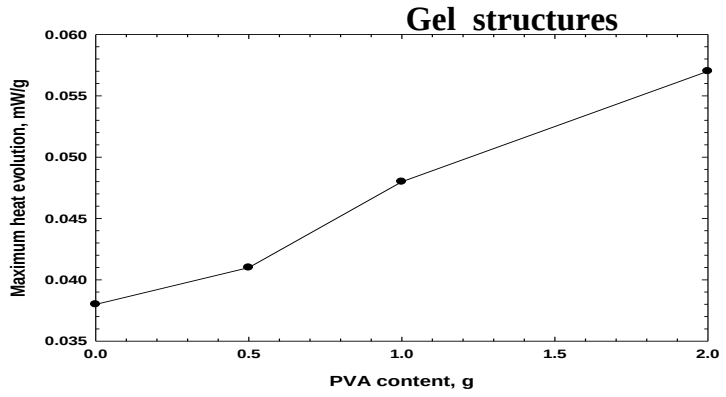


150°C

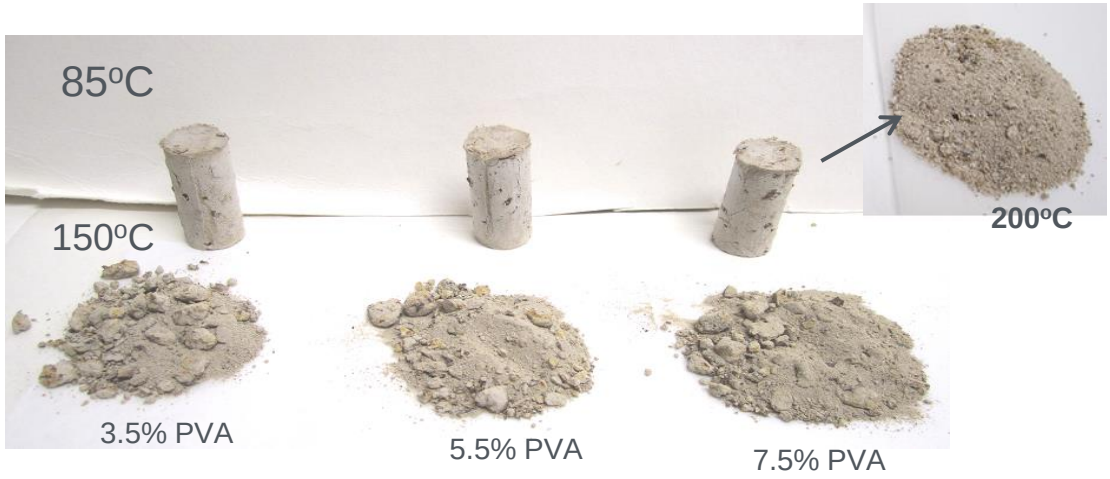
PVA sol

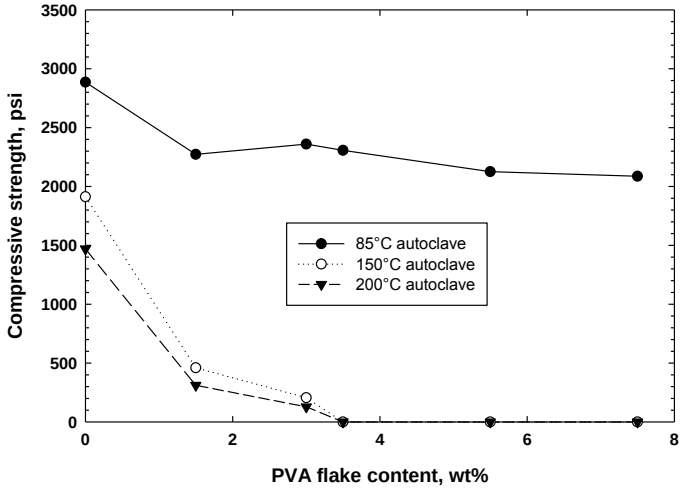
Reaction route to form PVA gel and gel's chemical structure

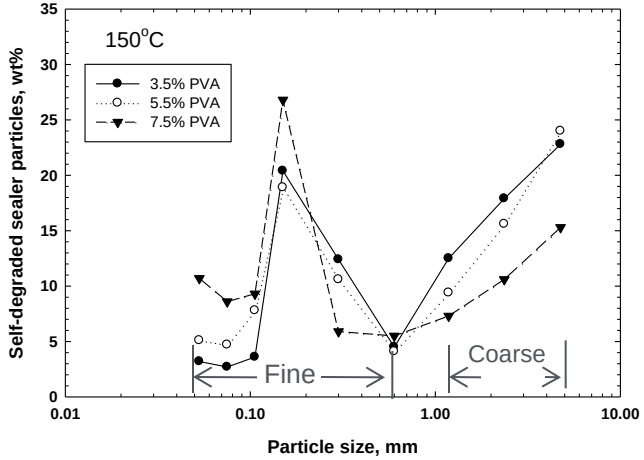


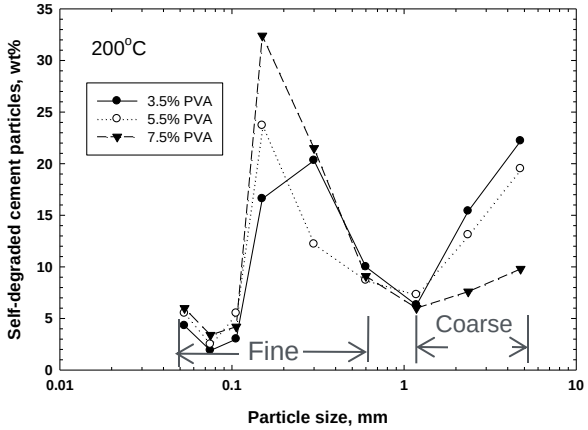


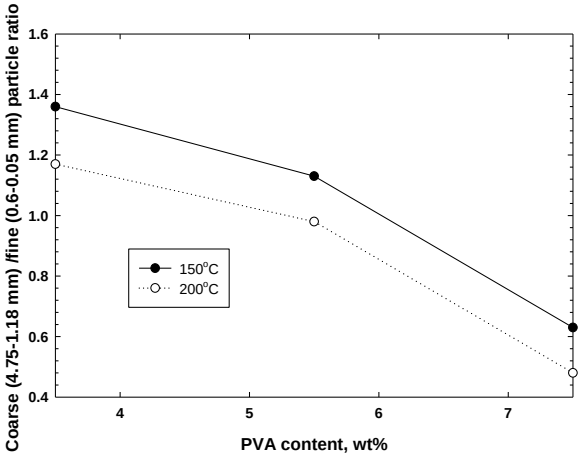
Self-degradation and compressive strength at 150 and 200°C for 85°C-cured PVA fiber-bridged cements



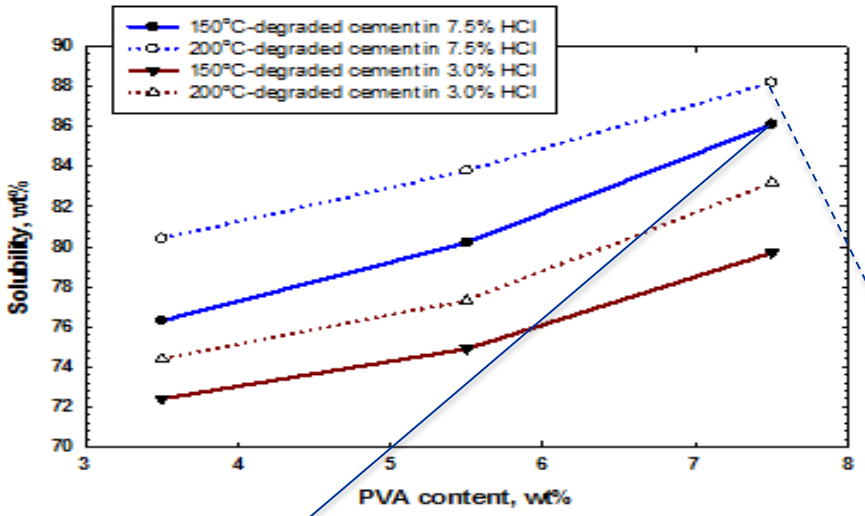


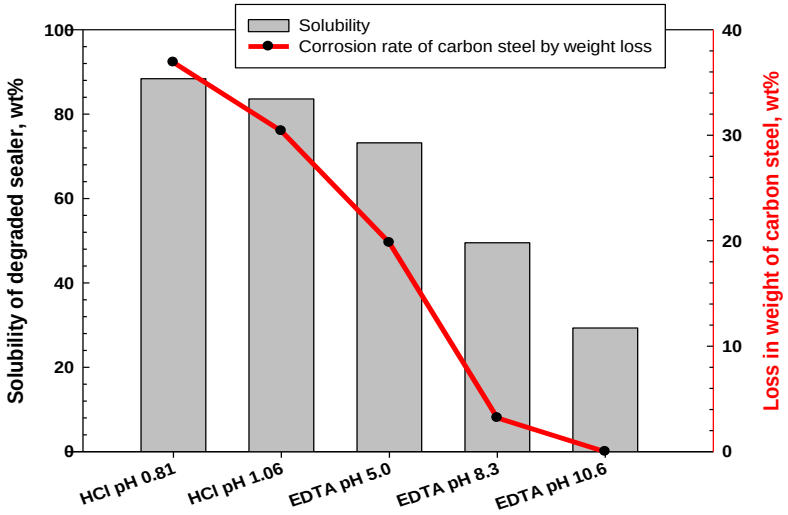


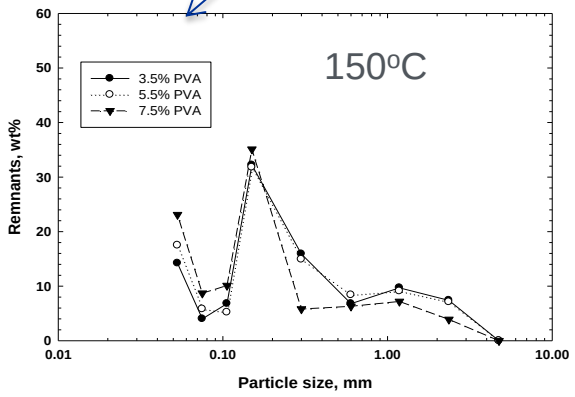


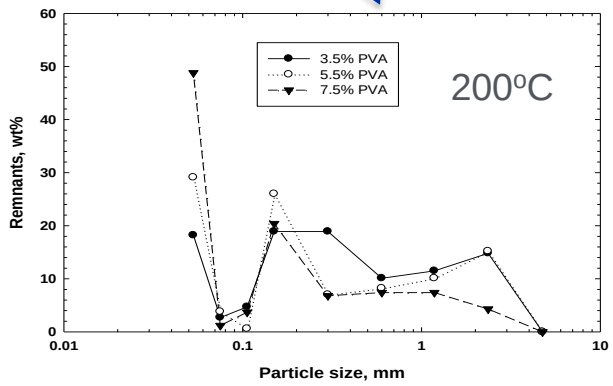


Solubility of self-degraded cement in mineral (HCl) and organic (EDTA) acids at 90ºC and particle size distribution of remnants

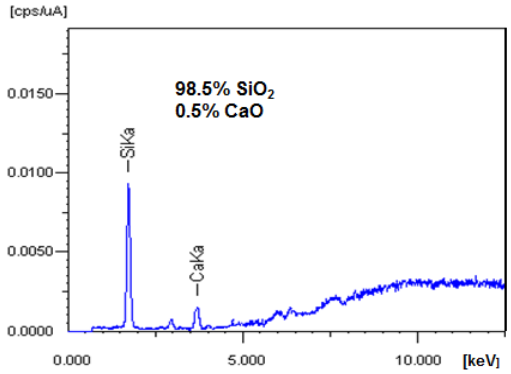








Chemical composition of remnants



Future Directions

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Milestone or Go/No-Go	Status & Expected Completion Date
Task 1. Upgrade current high-pressure API slot apparatus to be capable of being raised to hydrothermal temperature of 250°C.	May 2016
Task 2. Conduct in-house scale-up demonstration of temporary sealer performance from plugging and degradation to dissolution.	Aug. 2016
Task 3. Deliver report covering all information obtained in FY 2015 to DOE and prepare peer-reviewed journal article.	Oct.2016
Task.4 Complete technology transfer to geothermal industry	Dec.2016
Go/no-Go Decision	

Summary

	FY2014 (Nov. 2013-Oct. 2014)	FY2015 (Nov. 2014-Mar. 2015)
Target/Milestone	•Develop advanced self-degradation promoter •Test plugging performance of self-decomposable PVA fiber •Assess mechanical behavior of PVA fiber-reinforced sealer	•Develop set-controlling additive suitable for sealer formula at 85^{o}C •Evaluate performance of less- or non-corrosive acids in dissolving crumbled sealer
Results	•The combination of PVA-flake and -fiber not only adequately plugged 0.5 x 0.5 in. square slot under pressure of 1000 psi, but also served in converting bulk cement into fine powder with average particle size of 0.3 mm at hydrothermal temperatures 150-200^{o}C. •PVA fiber offered improved toughness of the sealer.	•For former target, sodium gluconate as set controlling additive maintained pumpability >8 hours of cement slurry. •For the latter, organic EDTA mild acid (pH 5) dissolved 75 wt% of crumbled sealer at 90^{o}C and contributed to a minimal corrosion of steel casing compared with that of HCl (pH 0.8).