PROCEEDINGS, 48th Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 6-8, 2023
SGP-TR-224

Self-healing Cements for Low- and High-temperature Applications

Zihao Li,[1] Chao Zeng,[1] Lirong Zhong,[1] Susan Petty,[2] Geoffrey Garrison,[2] Hamid Najafi,[3] Marc Brennen,[3] and Carlos A. Fernandez[1]*

[1]Pacific Northwest National Laboratory, [2]AltaRock Energy Inc., [3]Resource Cementing

Carlos.Fernandez@pnnl.gov

Keywords: Geothermal, self-healing, wellbore, cement, polymer

ABSTRACT

Wellbore cement in geothermal environments is subjected to a number of mechanical, thermal (up to 400°C), and chemical (CO_2, H_2S, mineral acids, concentrated brines) stress regimes over its lifetime. As a result, wellbore failure at the cement lining due to thermal, mechanical, and or chemical stresses is one of the most common drivers of reservoir intervention during geothermal energy production. Wellbore intervention is expensive and time-intensive since involves production shutdowns and repairs with an average cost of $1.5 million per wellbore without taking into consideration the economic losses because of production stoppage. Similarly, long-term storage of CO_2 considers very low or no leakage from the formation. Cement is not stable in a CO_2 environment and becomes vulnerable when a wellbore is exposed to CO_2 injected into the surrounding formation for permanent storage. To address these problems, Pacific Northwest National Laboratory has developed scalable self-healing cement formulations for geothermal and carbon storage applications with capability for full recovery of structural integrity. The cement technology is distinctly different from other competing cements because it is the only technology that: (1) offers fast (less than 24h) and complete recovery of structural integrity and mechanical strength and over multiple damage and healing events, (2) does not require time-intensive manipulations or staff training for cement preparation and placement, (3) adheres to steel casing and wellbore rock, and (4) is resilient to high-temperature and chemically corrosive environments. This work will report on experimental as well as modeling results obtained this far on this 2020 R&D100 award winner technology.

1. INTRODUCTION

It is essential to ensure the cement sheath in a geothermal wellbore environment can maintain its mechanical integrity over the long term if zonal isolation is to be preserved for the duration of the well's useful life. Alterations in the wellbore's multiple conditions, such as temperature, pressures, including casing pressure and formation pressure, or even nearby tectonic stresses can all contribute to wellbore stresses to a magnitude significant enough to generate cracks on the cement sheath (Nelson and Guillot, 2006). The capacity of a cement sheath to maintain its structural integrity when subjected to varying stresses in the subsurface environment is greatly dependent on the mechanical properties of the cement including its bonding to the casing and the rock that surrounds it. These properties include ductility and tensile strength as well as interfacial adhesive strength and resistance to shear stress (Shortall et al., 2015).

Thermal shock is a significant threat to geothermal wellbore infrastructure. In addition, geothermal reservoirs and wellbores are subjected to harsh chemical environments, such as excessive mineral acidity, high brine concentration, and carbonated conditions. To reduce the risk of wellbore failure, considerable work is taking place to provide wellbore cements with the desired mechanical properties and chemical and thermal stability, including the development of cement compositions containing both inorganic and organic additives. For example, Rockett et al., (1979) and Sugama (2006) developed phosphate-bonded cements, and their mechanical properties were successfully evaluated after exposure to geothermal environments. Zeldin et al., (1980) also developed organic as well as inorganic cement materials. Bour and Hernandez (2003) created a foamed calcium aluminate cement with enhanced mechanical durability which was successfully implemented in a geothermal well. Nevertheless, although tremendous progress has been made in the development of cementitious materials to exploit in high-temperature subsurface settings, there are still substantial material's limitations for them to be the used over the lifetime (30+ years) of the wellbore (Wu et al., 2012; Van and De Belie, 2013). For example, self-healing cements with the required adhesion at the casing and formation interfaces in geothermal environments have not yet been developed (Sugama, 2006).

Similarly, the goal of Carbon Capture and Storage (CCS) is the safe and permanent storage of CO_2 in the target CO_2-storage reservoir. If CO_2 leaks out from reservoir and escapes back into the atmosphere, the motivation to apply CCS worldwide and, as a result, to mitigate atmospheric CO_2, is significantly diminished. CO_2 leakage can have severe adverse effects since it (a) may contaminate subsurface resources, such as hydrocarbon reserves and freshwater aquifers; (b) it can affect ecosystems at the land surface or in the vadose zone; and (c) it may collect in low-lying areas leading to harmful effects, such as suffocation of plants and animals, including humans.

Regardless of the subsurface application, cements with self-healing capability are the way to go if we wish to provide with long-term insulation between casing and formation rock and maintain wellbore integrity and operability in carbon storage or geothermal reservoirs without the need for costly interventions.

By adding chemical and/or thermally stable polymers to wellbore cement, the Pacific Northwest National Laboratory (PNNL) has recently produced two unique self-healing cement composites for their application in carbon storage and geothermal environments. These novel cement slurries have the rheological characteristics equivalent to conventional well cement formulations without the need of retarders.

Although the average compressive strength of novel self-healing cement is not as high as that of conventional wellbore cement, it is nevertheless eligible for wellbore applications with values significantly above 1000 psi while simultaneously bringing about higher ductility and self-healing ability to the cementitious material (Childers et al., 2017). In this study, we report the rheological and mechanical properties, including consistency, density, setting time, self-healing capability, of two polymer-cement formulations developed for low and high-temperature applications.

2. MATERIALS AND METHODS

2.1 Self-healing Polymer and Polymer-Cement Synthesis

This study involves the incorporation of two different polymers to cement in the form of monomers and crosslinkers. Monomer thioplast EPS25 (640 g/l equivalent epoxide) was supplied by Akzo Nobel, while monomers N, N-methylene-bis-acrylamide (99%) (MBA), 1,4-butanediamine (99%) (BDA), poly(ethylene glycol) diglycidyl ether (PEO) (250 g/l equivalent epoxide), and crosslinker pentaerythritol tetrakis (3-mercaptopropionate) (4SH) were purchased from Sigma-Aldrich. Deionized water was used for all experiments. In addition, Ordinary Portland cement (Type-I/II) was supplied by Sakrete and Class H cement was supplied by LaFarge from the Joppa Plant, and Silica flour (200 mesh) was obtained courtesy of U.S. Silica.

The synthesis of MBA-BDA copolymer and the crosslinking reaction of EPS25/PEO/4SH are shown in **Figure 1**. In the case of MBA-BDA, the polymeric system was synthesized first, followed by drying it and grinding it to incorporate it as a final polymeric product in the cement slurry. The synthesis was performed following a previous approach (Wang et al., 2020), where the Aza-Michael addition of MBA-BDA copolymer is carried out at 35 °C for 24 hours in the presence of $MeOH/H_2O$. Acetone is then added to precipitate the finished copolymer. After the solvent is removed, the MBA-BDA polymer was five times washed with acetone before being dried for 48 hours at 50°C under vacuum. The polymeric product is a glassy polymer that is milled at a high speed to create a powder. This powder, in a concentration of 10wt% based on dry solid mix, is added to a mix of cement:silica flour 70:30 followed by adding water to a water-to-cement (w/c) ratio of 0.54.

In the case of EPS25-based polymer, the precursors (EPS25, PEO, and 4SH) are separately mixed in an aluminum pan and immediately added in a 10wt% concentration (based on dry mix) to the cement/silica flour/water slurry made with a cement:silica flour mass ratio of 70:30 and a w/c ratio of 0.71. Unlike the MBA/BDA polymer, the polymerization and crosslinking reaction of EPS25/PEO/4SH (shown on Figure 1, right) occurs at the same time of the hydration process of cement/silica flour.

Control cement samples, which are cement and silica flour without polymer added, were prepared by mixing cement powder and silica flour in a 70:30 mass ratio. The powder mixture was then mixed with deionized water uniformly for 15 minutes forming a cement slurry with w/c ratio of 0.54. Cement samples composition are depicted in **Table 1**. The slurry is transferred to plastic molds (diameter: 1 inch; length: 4 inch) to obtain the solidified cement samples. Molds will be placed in a small container and this container inside a larger container containing water and covered fully. In the case of EPS25-modified cement samples, this container is placed for curing inside an oven at 85C for 24h followed by removing the molds and placing the cylindrical samples in a Parr reactor to cure for 5d at 200C in 100% relative humidity. The MBA/BDA-cements were cured at ambient temperature and 100% relative humidity for further investigations.

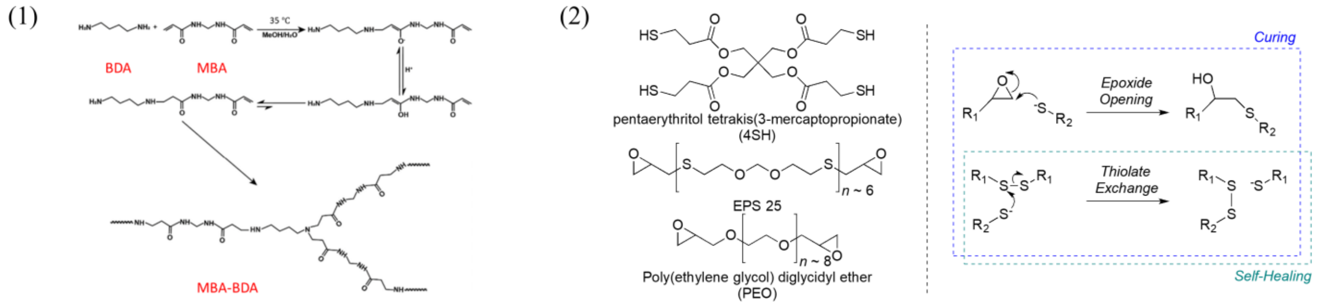


Figure 1: (1) MBA and BDA copolymer and synthesis of MBA-BDA polymer (Jian et al., 2023); (2) Molecule structures of EPS25, 4SH, and PEO and the illustration of curing and self-healing process of polymer EPS25/PEO/4SH (Childers et al., 2017).

Table 1: Control cement and self-healing cement (MBA/BDA, EPS25/PEO/4SH) in this study.

	Control Cement	MBA/BDA-cement	EPS25/PEO/4SH-cement
Cement (g)	210	210	210
Silica flour (g)	90	90	90
Water (g)	113.4	113.4	150
MBA/BDA (g)	0	30	0

EPS25 (g)	0	0	11.2
PEO (g)	0	0	11.2
4SH (g)	0	0	7.6

2.2 Rheological Properties

A rheometer (Anton Paar MCR 301) was used to evaluate the workability of cement slurries. Shear stress/shear rate plots as a function of time were obtained at 25, 70, and 120°C to determine the plastic viscosity via the Bingham model, which are suggestive of the following chemical reactions: cement hydration and polymerization/crosslinking. All sample mixes were subjected to shear stress measurements for up to 180 minutes in the shear rate range of 0–800 sec^{-1} under the torque operation limit of 200 mN·m. During each run, the shear rate was increased from 0 to 800 sec^{-1} and subsequently decreased at the same rate from 800 to 0. Since cement slurry often exhibits non-Newtonian behavior, the upward (i.e., increasing shear rates) and downward (i.e., lowering shear rates) shear rate runs were used to get undisturbed and dynamic yield stresses, respectively. The slope of the plots represents the plastic viscosity of the slurry. In addition to rheological properties, Vicat needle tests were performed for determining the initial and final setting time of the cementitious materials. Both, plastic viscosity and setting times are critical parameters to determine the workability/pumpability of cement and the amount of water required in the slurry. The later affects the curing time of cement, where too much water would decrease the strength of cement materials, while insufficient water would impact the completion of hydration reactions, also resulting in a reduction in strength. Unmodified (control) cement and polymer-cement composites were tested using a manual Vicat needle apparatus.

2.3 Mechanical Properties

Cylindrical samples prepared for compressive strength tests were made of 1" in diameter and 3.75" in height. Replicate (minimum triplicate) compressive strength tests were performed on cement samples with the same (w/c) ratio in the case of control and MBA/BDA-cements, a cement samples with a w/c ratio of 0.71 for EPS25-based cements. C_{s0} denotes the compressive strength of control cement samples. The compressive strength of these samples was measured in two stages. In the first stage, a vertical loading displacement of 0.001"/sec was applied until 300 lbf load was reached. After this targeted load was reached, the rate of loading displacement was decreased to 0.0001"/sec for the remaining of the test and until a 10% drop in load was seen. After each test the samples were healed for 5d at room temperature (22°C, control cement I/II and MBA/BDA-cement) or high temperature (200 °C, control cement H and EPS25-based cement) and 100% relative humidity before a new compressive strength test was performed. This cycle of healing and compressive strength testing was performed in these samples, where C_{si} denotes the compressive strength C_s at a certain round i of measurement, and the ratio $C_{si}/C_{s(i-1)}$ represents the restored compressive strength ratio. Visual observation showed that only small (below 500 microns aperture) microfractures were developed in the samples during each test, particularly in polymer-modified cements. The compressive strength was computed using the maximum compressive load reported. When the first cycle of compressive strength test finished, the tested samples will be aged for at least 5 days at room temperature (22°C) or high temperature environment (200 °C) and 100% relative humidity. This cycle of healing and compressive strength testing was repeated weekly for a few weeks.

3. RESULTS AND DISCUSSIONS

3.1 Vicat Needle Test and Density Measurement

Figure 2 illustrates the Vicat needle test results of control cement and self-healing cement including MBA-BDA-cement I/II and EPS25/PEO/4SH-cement H. **Table 2** shows the density of each cement used in this study. Except for the control cement with a comercial superplasticizer (lignosulfonate), all other cements will lose plasticity and attain the lowest needle depth in the first 25 hours. Unmodified (control) cement had the shortest hardening time among the groups. The setting time for MBA-BDA cement is slightly longer than the control sample. Based on the results of tests conducted on three EPS25-cement groups, we can conclude that cement H has longer setting times as compared to cement type I/II as expected. Surprisingly, EPS25-cement with the higher w/c ratio resulted in a shorter hardening time. The addition of lignosulfonate will dramatically lengthen the cement's setting period.

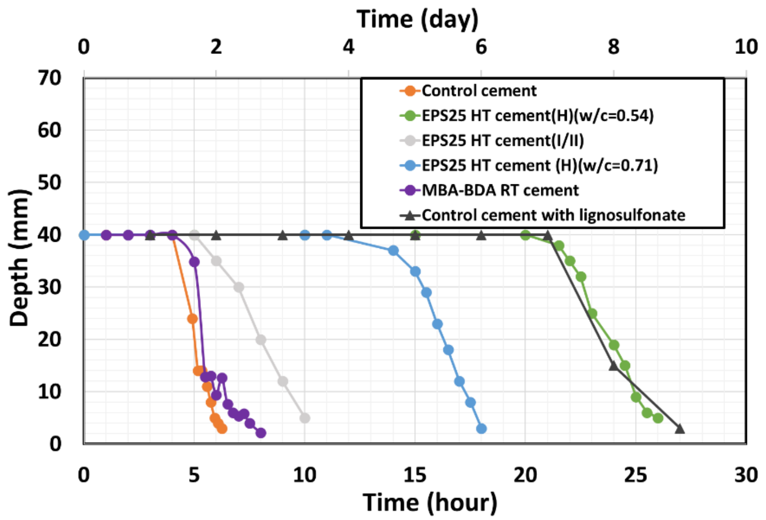


Figure 2: Vicat needle test results of control cement and self-healing cement. Top abscissa axis refers to control cement with lignosulfonate.

Table 2: Density measurement of cements in this study.

Mud balance test	Density (g/cm^3)
Control cement (I/II)	1.945
EPS25/PEO/4SH-cement H	1.775 (within 10% of control cement H)
Control cement H	1.950
MBA/BDA-cement I/II	1.970 (within 10% of control cement I/II)

3.2 Plastic viscosity

The viscosity of cement slurries is critical for the cement to be workable throughout the pumping process. To be injected in the well bore, the cement slurry must not only flow through the center of the wellbore and through the annulus at ambient (carbon storage) and high-temperature conditions (geothermal), but also being to harden right after and set within the first 24h. The rheological properties of a standard control cement were determined on a slurry with 70 wt% cement, 30 wt% silica flour, and a w/c ratio of 0.54. From the stress vs. shear rate plots at different temperatures, the undisturbed yield stress (the minimum stress required to initiate flow from a stationary state), the dynamic yield stress (minimum stress required to maintain a steady flow), and the plastic viscosity (slope of the upward stress/shear rate plot) can be regarded as a function of time.

Figure 3 shows the rheological properties of control cement I/II, control cement I/II with superplasticizer, and self-healing MBA-BDA cement including undisturbed yield stress, dynamic yield stress, and consistency at ambient temperature (25°C). As shown in **Figure 3 Error! Reference source not found.**, control cement with and without superplasticizer have similar viscosity values at each time which is unexpected since superplasticizer should increase cement workability. Nevertheless the values of undistubrbed shiel stress and dynamic yeild stress are lower than unmodified control cement in the first 75 min showing the thinning effect of the superplasticizer. MBA-BDA self-healing cement has a unique variation of plastic viscosity upon hydration. The viscosity slightly decreases with mixing time while control cement with and without superplasticizer increases, both reaching a plateau at around 120 minutes. The value of undisturbed yield stress and dynamic yield stress of MBA-BDA are higher than the control cement I/II with and without superplasticizer as well. We hypothesized that the MBA-BDA polymer dissolution in the aqueous slurry is kinetically controlled in this process. As time evolves MBA-BDA polymer slowly dissolves in the cement slurry with the resulting adsorption of polymer moieties on the surface of cement particles via hydrogen bonding (Deng et al., 2015; Reid et al., 2017) between -NH functionalities in the polymer and oxygen atoms in the unhydrated cement grains as well as between =O functionalities in the polymers and -OH at the Calcium Silicate Hydrate (C-S-H) hydration products (Rawal et al., 2010). In this fashion, the cement grains are functionalized with long chain and crosslinked MBA-BDA polymer moities, which makes the slurry thicker as compared to control cement and cement with superplasticizer.

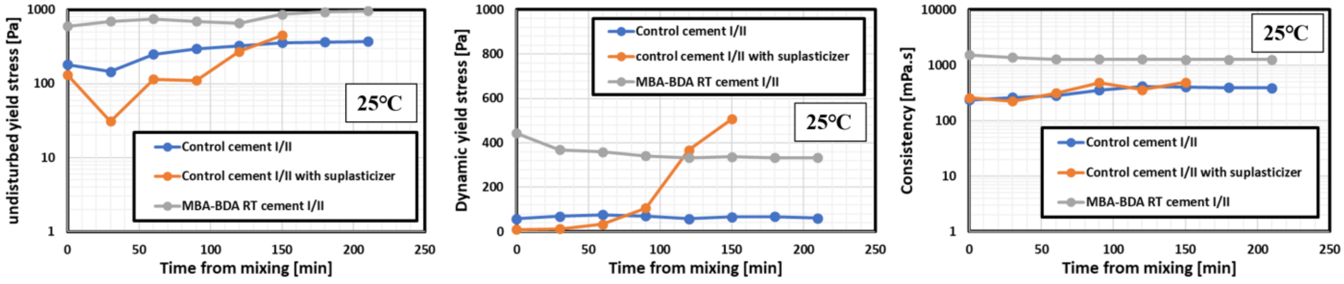
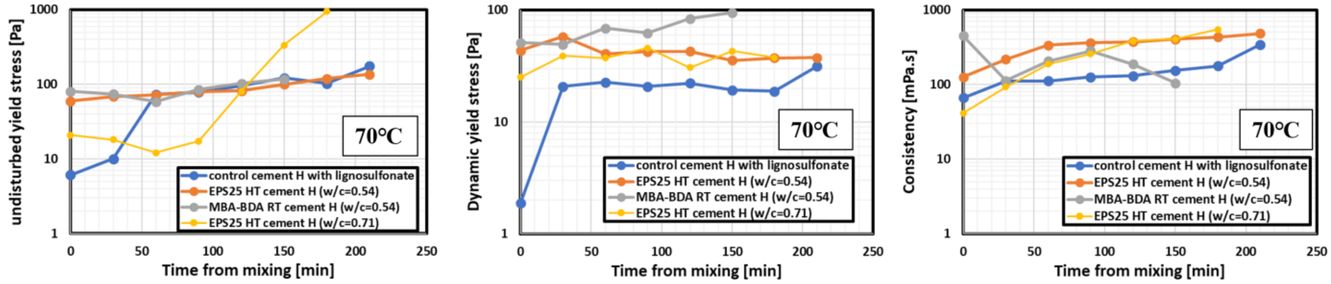


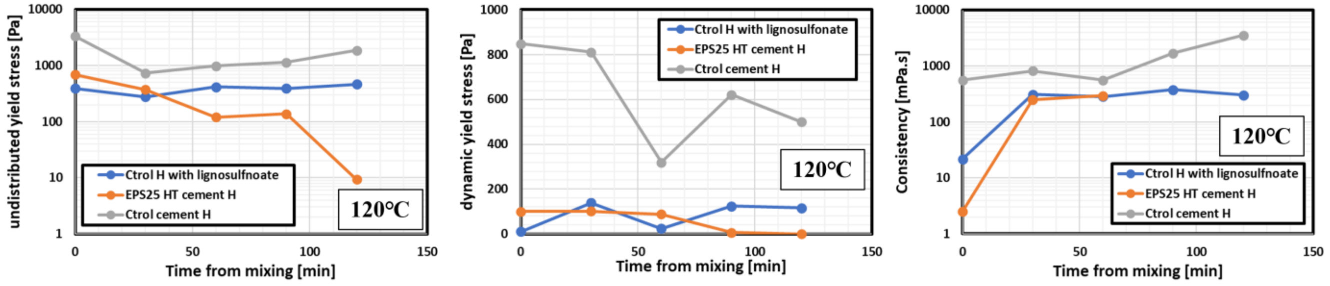
Figure 3: Undisturbed yield stress, dynamic yield stress, and consistency of control and MBA-BDA cements at 25°C.

Figure 4 illustrates the static and dynamic yield stress as well as plastic viscosity as a function of time for MBA/BDA-cement and EPS25 polymer-cement slurries at 70°C, and EPS25 polymer-cement at 120°C. At 70°C, a higher w/c ratio results in lower undisturbed yield stress and plastic viscosity for the first 120 min and this difference disappears in later times. The dynamic yield stress, however, remains independent of w/c ratio at 70C. Control cement with superplasticizer shows very similar values of undisturbed yield stress and plastic viscosity and relatively lower values of dynamic yield stress respect to EPS25-cement which implies that the EPS25-based polymer acts as a superplasticizer and retarder in the slurry by aiding to the flowability of cement H as well as reducing hydration rates of cement by coating the unhydrated cement grains during mixing. MBA-BDA-cement slurry also shows similar values of undisturbed yield stress and plastic viscosity and slightly larger values of dynamic yield stress at 70C making it suitable for deployment at this temperature, similarly to EPS25-cement.

At the highest temperature evaluated, 120°C, MBA/BDA-cement type H is not suitable showing a fast hydration process (data not shown) which could be due to low thermal stability of the polymer, making this formulation only suitable for low temperature and even at 70C in carbon storage settings. In the case of EPS25 polymer-cement slurry tested at 120°C the undisturbed yield stress and dynamic yield stress of EPS25 slurry slightly decreases with time until about 100 min while the plastic viscosity increases. A similar behavior is observed for control cement H with superplasticizer while unmodified control cement showed the highest values of undisturbed, dynamic yield stress as well as viscosity as anticipated. Unlike cement H, EPS25-based cement H can, in principle, be pumped for at least 120 min without the addition of superplasticizer. This is, once again, potentially due to the EPS25 polymer aiding to the workability of cement H though it also acts as a retarder delaying hydration as shown in Figure 2.



Rheological properties of MBA-BDA and EPS25 cements with control cements at **70°C**.



Rheological properties of EPS25 cements with control cements at **120°C**.

Figure 4. Rheological properties of slurries of control cement and self-healing cement at 70°C and 120°C.

3.3 Compressive Strength and compressive strength Recovery

Figure 5 illustrates the average compressive strength of control cements and MBA/BDA-cement. As shown in Figure 5(1), the control cement's compressive strength, especially after 4th round of testing, decreases continuously with a significant level of data uncertainty or variability. This would be particularly apparent in the recovery ratio data in Figure 5(3), where the recovery's uncertainty is higher than the average for nearly every test. Consequently, the recovery ratios for all rounds of testing on unmodified materials are misleading, ranging from 49% to 101%. MBA/BDA self-healing cement samples (Figure 5(2) and 5(4)) demonstrate more uniform compressive strength across all rounds of testing, and the resulting recovery ratios illustrate the capability of cement for self-healing, which can be found in Test #1 to #3 and Test #4 to #6. We don't have a plausible explanation for the compressive strength and recovery ratio drops from Cycle 3 to Cycle 4, but it could be associated to a significant increase in damage after the 3rd round of testing, where larger fractures were generated instead of the controlled formation of microfractures. However, the rise in mechanical strength recovery (4th test and after) suggests a combination of self-healing and extended hydration periods (Huang et al., 2013; Yuan et al., 2019). When a recovery ratio greater than 100% was achieved, it shows that the mechanical strength recovery is the result of both the ongoing hydration of the cement sample (autogenous healing), and the self-healing process (autonomous healing). Due to the absence of self-healing capability, this phenomenon is not observed in control cements.

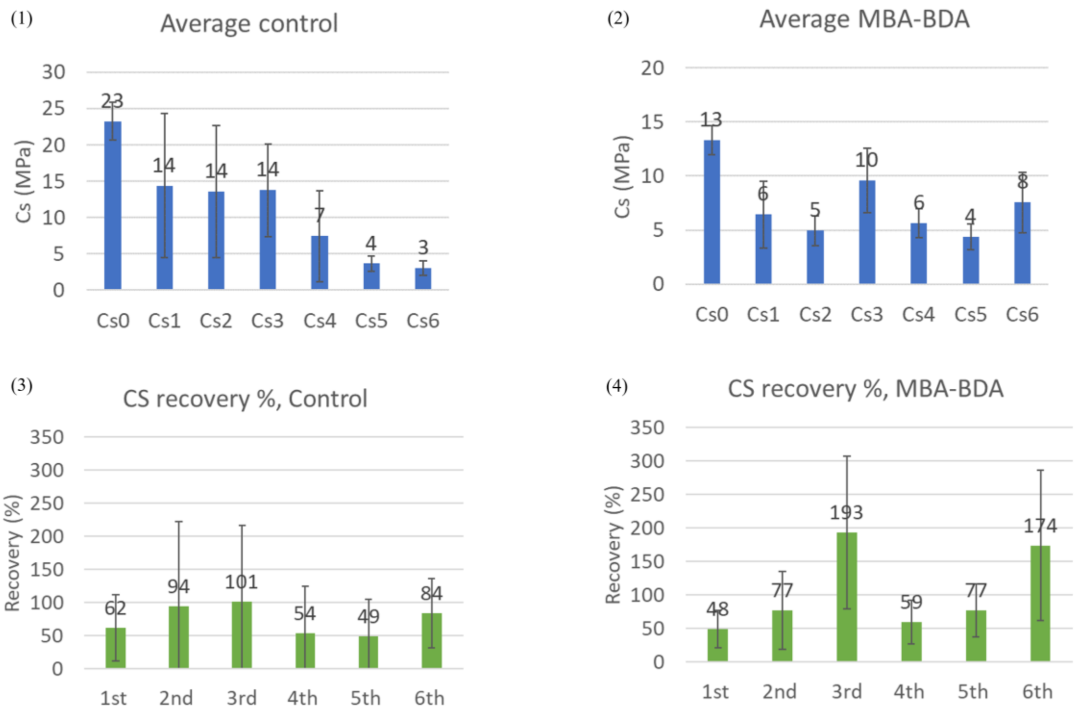


Figure 5: Average compressive strength of (1) control cement and (2) MBA-BDA self-healing cement; compressive strength recovery of (3) control cement and (4) MBA-BDA self-healing cement. Every test was run on (at least) six samples of each formulation, and there was a 7-day aging period in between each test.

The compressive strength and compressive strength recovery analysis of EPS25-based cement samples on 1” diameter by 3.75” length cylindrical samples are work in progress. The first values averaged 2,900 psi on as prepared samples after 1 day curing at 85C followed by 5 days of curing at 200C. These values are comparable to the compressive strengths measured in previous investigations after 28 days of curing (Mangadlao et al., 2015; Vipulanandan and Mohammed, 2015). We then prepared additional samples to perform multiple damage (compressive strength) / healing tests. Preliminary results showed a lower compressive strength than previous samples but still above (7.3 MPa) wellbore requirements. More importantly, impressive recovery rates of 113% and 107% on samples healed at 200C after first and second damage (compressive strength) tests were attained (**Figure 6**).

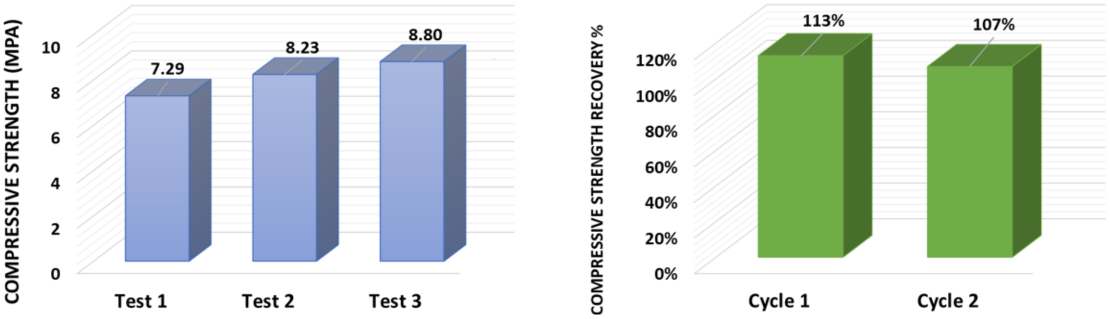


Figure 6. Compressive strength and compressive strength recovery rate for EPS25-based cement.

4. SUMMARY

In conclusion, we have introduced two unique self-healing polymer-cement composites, MBA-BDA-cement I/II for ambient temperature applications such as in carbon storage, and EPS25/PEO/4SH-cement H, which is suggested for use as geothermal wellbore cement. This study examined the rheological properties and compressive strength of these two polymer-cement composites. We demonstrated that the setting times of polymer-modified cements were longer than control cement with no additives. The plastic viscosity (a measure of workability) at 25C and 70C was higher for polymer-modified cements than control cement with superplasticizer but still within the pumpable values (in the range or below 1,000 cP). At 120C polymer-modified cement show similar plastic viscosity (and below 1,000 cP) to control cement with superplasticizer. Even though compressive strength of polymer-modified cements is lower than conventional cement, the values are significantly above the wellbore requirements. The ability of these polymer-cements to self-heal was established by repeated compressive strength / healing tests showing recovery values significantly higher and more consistent than control cement as demonstrated for MBA/BDA-cement after seven damage/healing events. EPS25-cement also show promise as a self-healing wellbore cement with the first and second recovery values being 113% and 107% respect the original compressive strength, potentially due to a combination of self-healing and continuous hydration (autogenous healing) as it was observed in MBA/BDA-cements at ambient temperature. Future research will evaluate the ability of these composite cements to withstand common geothermal settings, such as highly concentrated brines, mineral acid, and thermal stress (geothermal applications), as well as supercritical carbon dioxide (carbon storage applications).

Acknowledgements

The authors would like to thank the Department of Energy’s Geothermal Technology Office and Fossil Energy Office for the funding support. We would also like to thank Chevron for the damage/healing tests on EPS25-cements. PNNL is operated by Battelle for the U.S. DOE under Contract DE-AC06-76RLO 1830.

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