

## Distribution of Stresses to Improve Mechanical Properties of the Oil Well Cement

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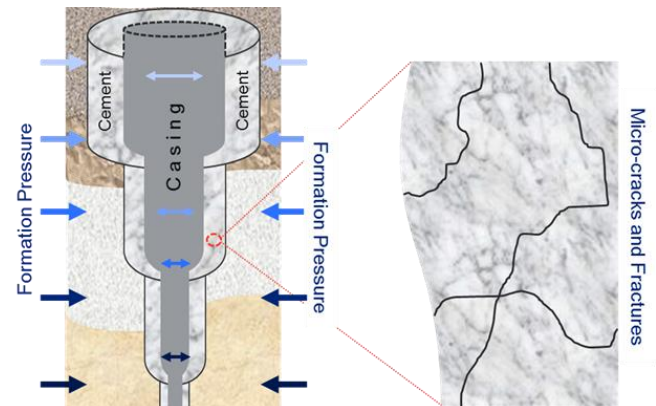
### Abstract

Breakdown in the cement sheath in the oil well may result in an unexpected shutdown of oil and gas production. This novel additive provides excellent distribution of stresses within an oil well's cement sheath, which transpires from the formation under downhole conditions. The frequent repairing of the cement sheath will result in expensive restoration costs and a reduction in the overall production. Therefore, it is highly desirable that the cement placed at the time of oil well construction should have anticipated mechanical properties. We have developed a next-generation additive that can effectively distribute stresses throughout the cement matrix, thereby reducing the formation of micro-cracks and fractures. A polymeric additive having mechanical linkages, unlike traditional polymers, is developed using innovative materials chemistry. The polymer chains can slide through pulley-type crosslinks inherent to the polymer networks. This mechanism allows the effective distribution of stresses over repeated cycles. The synthesized additive was blended with cement at various ratios and the cement slurries were cured at 300 °F and 3000 psi for 4 days. The mechanical properties, e.g., compressive strength and Young's modulus, were measured under a confined pressure of 3000 psi at temperature of 300 °F. We have observed a unique mechanism where the cement's compressive strength remained unaltered, although the elastic properties of the cement have improved under extreme downhole conditions. The additive developed in this research will minimize the remedial costs and improve the lifespan of the oil well by efficiently absorbing stresses during the production of crude oil.

### Introduction

Primary cementing is one of the most important operations executed on the well in the course of oil well construction. The cement is placed in the annulus between the rock formations of the wellbore and casing, to provide zonal isolation (Hadin 1965; Lu et al. 2019; Zheng et al., 2017). Zonal isolation prevents the communication of fluids between zones in the well. Complete and durable zonal isolation is the foremost goal of cementing. The quality of the cement job has a direct impact on the economic longevity the well throughout the life of producing

oil and gas well. The efficacy of the primary cementing operation is governed by the well production and performance over the life of the well. It is estimated that about 15% of primary cementing job fails, costing the petroleum industry USD 450 million annually in the repairing the cement sheath. Several precautions have been implemented to avoid failure in the cement, e.g. variations in the procedure for placing the cement, incorporation of additives to improve the curing behavior, changes composition in the Portland cement, blending elastic materials, and many more (Khalifeh et al 2016; Vipulanadam and Mohammed 2015). However, these precautions are not able to overcome the failure in the oil well cement sheath.



**Figure 1. The origin of zonal isolation loss in the oil well cement sheath — the differential pressure during production creates uneven distribution of stresses within cement matrix, resulting in formation of micro-cracks and fractures.**

The failure in the cement is typically observed at two operational stages, (1) at the time of the placement of the cement — improper balancing of the pressures that allows gas and fluid influx into the cement-filled annulus and movement of pipes, and (2) during production, uneven distribution of forces on the cement sheath, generated from the pressure difference (Boul and Ajayan 2019; Alsaba et al. 2020; Ridha et al. 2013). The present deliver technology focuses on the addressing the uniform distribution of forces exerted in the

course of production on the set-cement matrix. For any oil well construction process to be successful, it is highly desirable that cement should have excellent long-term resilience (Maagi et al 2019; Vipulanandan et al. 2015). It is important that the cement should show very good mechanical properties to offer a pressure tight seal between casing and formation (Figure 1). During production of oil or gas, there may be thermally induced dynamic pressure differentials between casing and formation, and it is this differential pressure that can create stresses on to the cement sheath. These concentrated stresses generate cracks or fractures in the cement and result into serious consequences, e.g., safety, reduced production and eventually decreases total life of the oil well.

In the current study, we have employed novel additive based on the polyrotaxanes chemistry (PR). This additive is composed of mechanically linked cross-links in addition to covalent linkages that allow stress distribution through sliding motion at sub-nanometer scale. The cement formulation with and without PR additive were formulated and the cement slurries were evaluated to understand the rheology, consistency, and fluid loss properties. The mechanical properties such as compressive strength and elastic modulus were also measured under confined pressure and high temperature to demonstrate effect of PR in the oil well cement.

## Experimental

### Materials

The cement used for the cement slurry design is Class G cement and its chemical composition is SiO<sub>2</sub> (21.6 wt%), Al<sub>2</sub>O<sub>3</sub> (3.6 wt%), Fe<sub>2</sub>O<sub>3</sub> (4.9 wt%), CaO (64.22 wt%), MgO (1.6 wt%), SO<sub>3</sub> (2.5 wt%), Na<sub>2</sub>O (0.48 wt%), loss on ignition (0.6 wt%), and insoluble residue (0.5 wt%). Dispersion, fluid loss additive and retarder were obtained from the commercial sources. Silica flour was obtained from Sigma-Aldrich. All the chemicals were used as received without any purification.

### Cement slurry formulation

We have conducted several experiments to optimize the cement slurry formulation. However, the current study emphasizes on the optimized cement designs and their properties.

**Table 1. Cement Slurry Formulations – Control and PR-Cement.**

Composition	Control	PR-Cement
Class G, g	298.4	297.4
Silica Flour, g	104.5	104.1
PR, g	-	5.9
Retarder, g	0.7	0.7
Dispersant, g	1.2	1.2
Fluid loss additive, g	2.1	2.1
Water, g	162.7	161.4

The blending of cement slurries was carried out according to API standard mixing procedure and the composition of Control and Cement with Polyrotaxane (PR-Cement) is presented in Table 1. The defoamer 7500L (1 mL) was also added in each cement slurries. The density of the control and PR-Cement found to be  $1.9 \pm 0.04$  g/cc ( $15.87 \pm 0.33$  lb/gal), measured on set-cement samples at ambient conditions.

### Characterization

The mixing of additives, cement and water were carried out on a constant speed mixer (Model 686CS, Fann Instrument). The mixer is designed to mix cements to comply with API standard for well cementing. The fluid loss properties of control and PR-Cement slurries was performed on a Fann fluid loss analyzer. The high pressure high temperature consistometer (Model 8340, Chandler Engineering) was employed to measure the thickening time at 3000 psi. The consistency of cement slurries was evaluated in Bearden units of consistency (Bc). The M3600 Viscometer (Grace Instrument) was used to study the rheological properties of cement slurries. Ultrasonic Cement Analyzer (UCA, Model 4265HT, Chandler Engineering) was used to measure compressive strength. The mechanical properties under the confined environment were measured through a triaxial measurement system (AutoLab 3000, New England Research, Inc.). AutoLab 3000 is a customizable servo-hydraulic operated system for triaxial measurements with software-controlled arbitrary stress paths on specimens at in situ stress conditions, pore pressure, and temperature. It consists of a pressure vessel with an internal piston for differential stress and servo-hydraulic intensifiers for differential stress, confining, and pore pressure. The cylindrical, 2 (length) × 1 (diameter) in., cured cement samples were loaded in the loading cell and the compressive strength and Young's modulus were measured under variable pressure and temperature conditions.

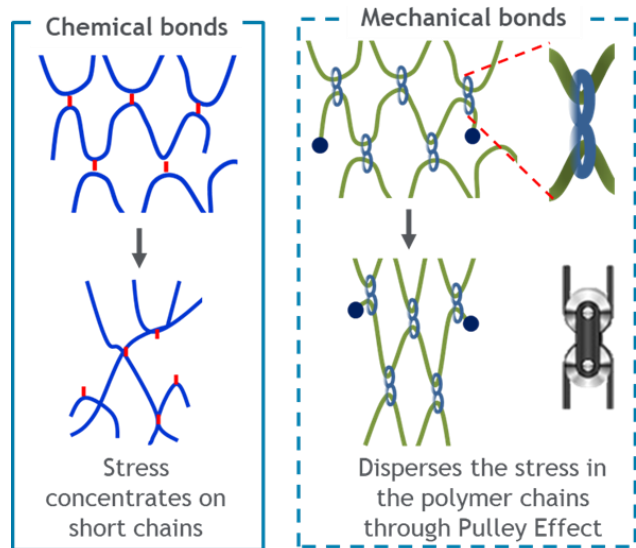
## Results and discussion

### Chemistry of polyrotaxanes

The polymeric additive developed in the present study is distinctly different from the traditional polymer/elastomer additive. The traditional additives have strong covalent bonding while the novel additive — Polyrotaxanes — have both mechanical bonds and chemical bonds (Harada et al. 2009; Wenz et al. 2006). In traditional polymers, chemical bonds/crosslinks break down upon repeated cycle of stresses because of uneven distribution of stresses (Figure 2). Since the stresses are concentrated on the shorter chains, they lose the effectiveness over a period of time. We envision, a cement additive endowed with pulley-like cross-links in its polymeric network. The force requires to lift an object directly/without pulley is higher than the force require to lift the same object with a system of pulleys (Choi et al. 2017; Imran et al. 2014).

Inspired by this principle, we have installed cyclic molecules such as cyclodextrin (Patel et al. 2017) at the crosslinks of the polymer network in the PR additive. When we apply forces on to this type of mechanically linked polymer network, the stress is not concentrated on short linkages,

however, it uniformly distributed throughout the matrix (Patel et al. 2021). Thus, these sliding motions at the molecular level act as molecular machines in the cement matrix and enable unprecedented elastic behavior. The PR additive is comprised of three materials: the linear polymer, the cyclic molecule, and the stopper molecule, forming necklace-like structure. The cyclic ring can rotate as well as slides upon external forces, providing structural rearrangements



**Figure 2.** Installing pulleys in the traditional polymeric network, as movable cross-links, for uniform distribution of stresses. Cyclic molecules threaded on to the linear polymer chain to form necklace-like materials — Polyrotaxanes. Cyclic ring can rotate and slides, generates molecular motions.

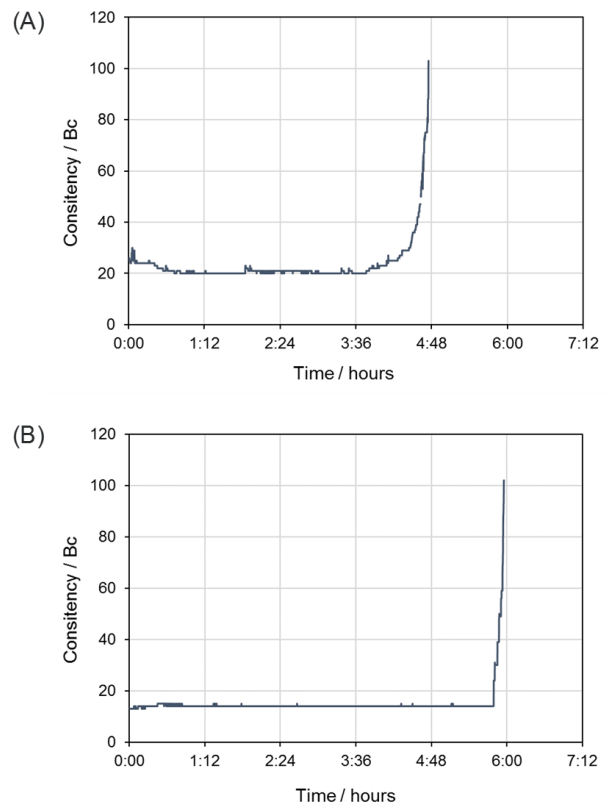
### Rheology, thickening time, and fluid loss

The rheology of the cement slurries plays significant role in the final mechanical properties of the set-cement. The rheology of the cement slurries can also provide the information on suspendibility, pumpability and equivalent circulating density.

**Table 2.** Rheological properties for Control and PR-Cement at 77 °F and 180 °F

RPM	77 °F		180 °F	
	Control	PR-Cement	Control	PR-Cement
3	6	6	6	6
6	8	10	7	10
100	93	102	86	98
200	152	171	147	167
300	198	215	178	205
600	273	297	265	292
PV, cP	75	82	87	87
YP, lbf/100ft <sup>2</sup>	123	133	91	118

The entrapment of gas bubbles can also be eliminated by controlling the rheological behavior of cement slurries. The flow properties of the cement slurries — Control and PR-Cement — were measured by Fann 35 Couette coaxial cylinder rotational viscometer at ambient and 180 °F (Table 2). Dial readings for both slurries showed no significant changes in the viscosity when the slurries were conditioned at 180 °F. Although we have observed shear thinning of the cement slurries at higher temperature, the low rpm values are persistent with the low temperature dial readings. The rheology of cement slurries can further be modified based on the well conditions by varying the quantity of additives.



**Figure 3.** Thickening time for (A) Control and (B) PR-Cement at 180 °F and 3000 psi. Control: 70 Bc, 100 Bc at 4.4 and 4.45 hours respectively. PS-Cement: 70 Bc, 100 Bc at 5.56 and 5.57 hours respectively.

The thickening time is related to the pumpability of the cement slurries and controlling the gas migration during the cement curing transition. For drilling operation, the thickening time of the cement slurries should be high to prevent unwanted hardening of the cement before completing displacement process. There is a critical time between these two phases that last several hours. In this period, the cement slurry no longer behaves as a liquid with hydrostatic pressure nor as an impermeable solid. During this transition time, gas migration leading to pressure buildup and loss of zonal isolation. The right-angle set of cement slurries has been considered as one of the solutions to overcome these consequences. Thickening times for Control and PR-Cement slurries at 180 °F and 3000

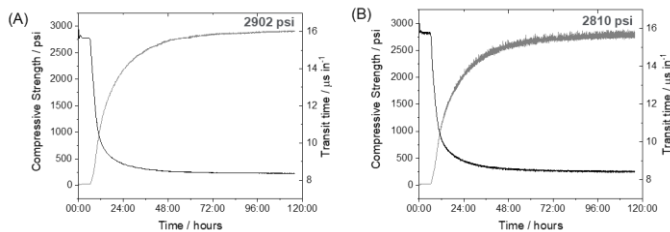
psi were evaluated using a Chandler HPHT consistometer (Figure 3).

We have optimized the cement slurries design to make sure that they demonstrate right-angle transition to minimize gas migration and provide minimum time for completing displacement process. The thickening time of Control is 4.4 and 4.45 hours for 70 Bc and 100 Bc, respectively. Similarly, the thickening time of Control is 5.56 and 5.57 hours for 70 Bc and 100 Bc, respectively. The thickening time can be adjustable by varying the quantity of retarders according to the requirement of the well operation.

The fluid loss of the cement slurries is optimized within the range of API standard. The cement slurries were conditioned at 180 °F for 1 hour before measuring the fluid loss. The fluid loss obtained for Control and PR-Cement is 24.5 (API 49 mL) and 24 (API 48 mL) mL respectively at 180 °F.

### Mechanical properties

The compressive strength development under 3000 psi and 180 °F of cement slurries (Figure 4), Control and PR-Cement, were determined through a high temperature Ultrasonic Cement Analyzer (UCA). We have not observed strength retrogression over 5 days at these conditions for both samples. Furthermore, the compressive strength for PR-Cement is 2810 psi compare to 2902 psi for the Control, clearly demonstrate the effect of PR and introduction of elastic behavior in the set-cement.

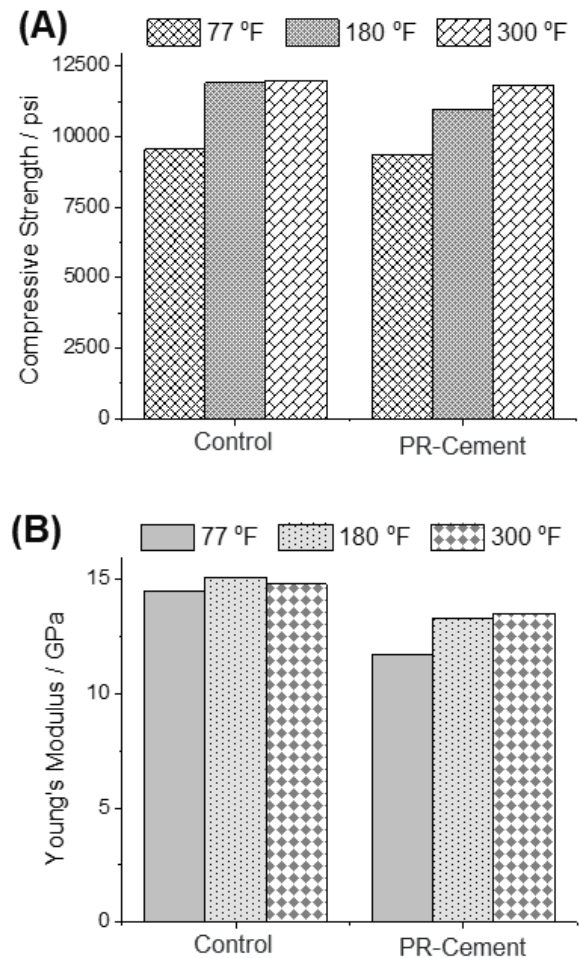


**Figure 4. Compressive measurement for (A) Control and (B) PR-Cement on high temperature Ultrasonic Cement Analyzer (UCA) at 180 °F and 3000 psi.**

The compressive strength and Young's modulus were measure using NER Autolab 3000. This instrument has allowed us to obtain the mechanical properties under high pressure and high temperature. Autolab 3000 is equipped with axial loading system, a confining pressure supply system, temperature jacket, and data acquisition software. Cylindrical samples (1" diameter/2" length) were employed for these measurements. The cement samples are jacketed and placed between steel end-caps. Static mechanical properties were measured using Linear Variable Differential Transformer sensor (LVDTs), which were mounted on the sample to measure axial deformation and radial deformation.

After the sample was placed in a triaxial cell, a confining pressure of 3000 psi was applied. The cyclic axial load was applied in the form of triangular waveforms. Each sample was deformed over three cyclic loading series. In each cyclic loading series, a differential stress of 3000 psi was applied during the cyclic loading; and various peak axial stresses were

applied during the cyclic loading. Because uniaxial stress was applied on the sample, this module was used to calculate Young's modulus using LVDTs to measure sample strain.



**Figure 5. Mechanical properties under confined pressure of 3000 psi at 77 °F, 180 °F and 300 °F. (A) Compressive strength and (B) Young's modulus for Control and PR-Cement.**

The compressive strengths for Control and PR-Cement were measured at ambient, 180 °F, and 300 °F under confined pressure of 3000 psi (Figure 5A). The compressive strength for Control was 9550, 11900, and 12000 psi at 77, 180, 300 °F, respectively. The higher compressive strength at high temperature is arising from the further curing of the cement matrix. PR-Cement has demonstrated compressive strength of 9330, 10950, and 11800 psi at 77, 180, 300 °F, respectively. Generally, it is established that the incorporation of polymeric or rubbery additives into the cement substantially reduces the compressive strength. However, PR has minimal effect on the compressive strength in PR-Cement. We have seen an unprecedented integrity of the cement sample, PR-Cement, even after 27-29 % displacement or reduction in size. Control sample undergo deformation and the cement sample was crushed into pieces after analysis. Interestingly, the amount of PR in PR-Cement is 1 % bowc and it demonstrated excellent

stress distribution characteristics that hold together cement particles under extreme conditions.

The Young's modulus for Control and PR-Cement was also calculated from the cyclic stress-strain tests (Figure 5B). The cements samples were subjected to cyclic stress of 3000 psi under confined pressure of 3000 psi. The cyclic tests were running over 5 cycles and the identical tests were carried out for minimum three samples of each formulation design. Young's modulus for Control was found to be 14.5, 15.1, and 14.8 GPa at 77, 180, and 300 °F. PR-Cement has demonstrated the Young's modulus of 11.7, 13.3, and 13.5 GPa at 77, 180, and 300 °F, respectively. The lower Young's modulus with comparable compressive strengths to the control correspond to an improved strain tolerance in the materials. PR-Cement showed low Young's modulus compare to Control at all temperature ranges and under confined pressure. Pointing toward the fact that PR, indeed, facilitate the introduction of elastic properties into cement matrix.

## Conclusions

We have introduced a novel additive for oil well cement to provide enhanced mechanical properties under downhole condition. Polyrotaxanes additive is composed of pulley-type cross-links, which facilitate the uniform distribution in the cement matrix, provide shock absorption properties, and minimize the formation of micro-cracks and fractures. It is expected that this additive can substantially reduce the huge resources spend on remedial jobs on well cement and increase total life span of the oil well by blending only 1 %bwoc PR in cement. Facile synthetic approach of producing PR allow the large-scale manufacturing. PR has transformed brittle cement into tough without compromising compressive strength. The thickening time, fluid loss, rheological properties can be altered through selecting various retarder, dispersant and fluid loss additive, and the addition of PR has shown minimum effect on these properties.

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