AADE-24-FTCE-032

Synthetic Insoluble Organic Matter in Cement and Elastic Stiffness Estimation

Thomas Heinold, Abdullah M. Salman, Saudi Aramco; Elizabeth Q. Contreras and Stacey M. Althaus, Aramco Americas: Aramco Research Center—Houston

---

Abstract

The mechanical behavior of synthetic and insoluble polymers in cement is measured using a triaxial loading cell. The new synthetic organic matter is insoluble to solvents and chemically inert. Polymers are synthesized for mechanochemical properties such as flexibility or rigidity are controlled using different monomers. Specifically, polymers are synthesized using monomers that mimic the flexibility of nylons using long carbon-chain monomers and the rigidity and strength of polyamides using aromatic monomers to produce a family of polymers known as aramids. Kevlar and Nomex are common examples of aramids within aerospace and military applications.

Cement samples are prepared using polyamide admixtures. Once set, cement samples undergo confined cyclic stress tests to demonstrate the molecular basis of various elastic profiles of new composite materials. The methodology towards elastic stiffness shows reliable means of predicating cyclic stress-strain responses under confinement relevant to oil and gas industry applications.

Mechanical response shows material elasticity increases and fracture strain decreases with strain rate. This is best illustrated using cyclic strain-stress curves to show reversible loading and unloading based on carefully engineered polymer cement additives. Results show a compressible hyper elastic sample is designed in comparison to neat cement at confined cyclic loading and unloading parameters. A molecular level understanding is achieved in polymer structures with hexagonal moieties and their effects on overall cement mechanical properties.

Introduction

The single most critical element of the well construction process is to maintain zonal isolation in a cement annulus. Common established best cementing practices promoting the placement of a competent hydraulic annular seal are well documented. After the cement installation in the wellbore, maintaining annular isolation does depend on mechanical response and post cementing stresses (Mueller et al. 2004).

During the construction of oil and gas wells, an annular cement sheath experiences a variety of repetitive triaxial stresses. Changes in downhole conditions such as temperature and pressure (resulting from stimulation treatments, obligatory casing pressure testing, change of wellbore fluid, reservoir depletion/injection, etc.) can induce significant radial, tangential and compressive stress, potentially becoming so severe that they compromise well integrity

Such cyclic stress-strain events in oil and gas wells can lead to cracks or micro annuli development in the annular cement sheath. Cement mechanical failures are detrimental to wellbore integrity as they can result in fluid migration from subterranean formations to surface, leading to loss of zonal isolation and unwanted annular pressure buildup.

The ability to accurately predict cement failure over the lifetime of a well is a significant challenge for the oil and gas industry where frequent and continuous stress cycling can occur in wells. Obtaining such information is precisely the most value for measuring the effects from cumulative cement sheath damage and may be of the most critical impact.

While unconfined uniaxial studies are reliable and easily performed, they are limited in capturing more subtle and detrimental impact, particularly cumulative fatigue damage. In the past the perception for judging cement mechanical properties was to look at unconfined uniaxial compressive strength (UCS) and Young's modulus (YM). However lessons learned from failed cements show the limitation of this traditional approach. A more informative analysis from triaxial load cells at confined pressures up to 40 MPa (5,800 psi) yield hysteresis loops that best illustrate how cements respond to cyclic stress-strain and fatigue behavior (Contreras et al. 2021).

Cement integrity can be quantitatively measured by cumulative damage models commonly used in applied metallurgy and composite materials. In this study, non-metallic aramid materials are added to reinforce High Sulfate Resistant (HSR) oil well cement and undergo multiple mechanical tests to screen polyaramid structure response using cyclic triaxial measurements (Zhang et al. 2019, Kaiser et al. 2005) for competent cement systems with higher resistance to fatigue and failure.

Wellbore Construction Challenges

When constructing an oil or gas well, cement plays a critical role in providing well integrity including hydraulic isolation and structural support. As the well is drilled through many different formations, it passes through different rock layers that can include aquifers and hydrocarbon bearing zones.

A special portland cement is commonly utilized to isolate these zones. Since oil well cements have to perform over a wide range of pressures and temperatures and are exposed to subterranean conditions they differ from ordinary Portland cements used in the construction industry. They require greater consistency from batch to batch and are produced under more rigorous conditions than ordinary construction cements.

The American Petroleum Institute (API) designates eight classes of well cements A through H. In general, the classification are arranged in line with the depths, temperature and pressure to which a cement may be placed under. In this work a high sulfate resistant (HSR) API class G cement was utilized for all experimental work. (Nelson et al. 2006)

Once the well reaches the production zone, cement integrity for the entire lifetime of the well is required, for safety purposes, environmental reasons, and for long-term production. During the life of the well, the cement sheath encounters many challenges. Specifically, thermo-mechanical cyclic stress from significant variations in temperature and pressure. Cement is strong, but it may not be as flexible to withstand these stress cycles (Riley et al. 1974). When cement breaks, loss of zonal isolation occurs.

It has been well documented that a significant number of oil and gas wells worldwide experience annulus integrity issues in one or more casing strings during their lifetime. While every effort should be made to ensure well integrity is met and maintained during all stages of the well life cycle, gaps in zonal isolation practices, sometimes lead to well barrier defects that manifest themselves through the presence of sustained casing pressure (SCP) (**Figure**).

This is commonly the result of a well component leak that permits flow of a fluid across a wellbore barrier element. In the outer shallower casing strings, it is often caused by incomplete or poor cement bonding due to poor cement placement practices or because formation fluids channel through unset cement. Furthermore, pressure and temperature changes from well production events can contribute to the development of micro annuli or cracks in the cement. These defects once created are very difficult and costly to remediate with an extremely low success rate. Therefore, ensuring a proper primary cementing strategy including appropriate material selection is of a prime importance (Heinold et al. 2020).

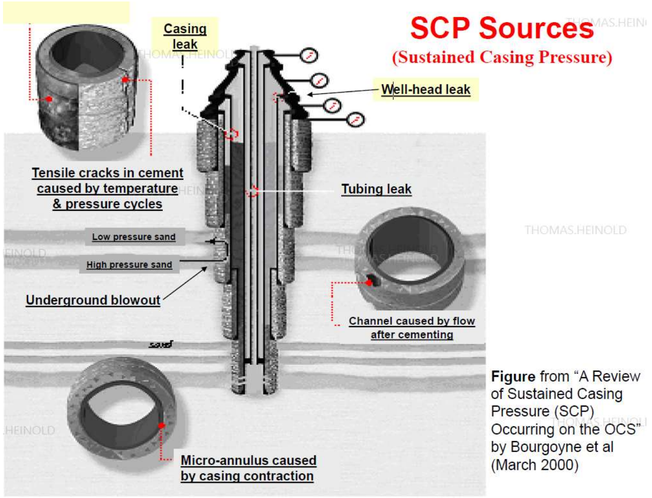

Figure from “A Review of Sustained Casing Pressure (SCP) Occurring on the OCS” by Bourgoyne et al (March 2000)

Figure 1- Sustained Casing Pressure Sources

Materials

A library of polyaramids from a family of polymers, such as Kevlar, Nomex and Nylon, with a large range of elasticity and structural effects on stress-strain rates are prepared and used as non-metallic reinforcement (NMR) in oil well cement (**Figure**). Polyaramid admixtures are prepared as a dry polymer and added to the dry blend of cement and cured under pressure and temperature. The cured cement samples are tested using a triaxial loading cell at 40 Mpa (5,800 psi).

Polyaramid Admixtures Synthesis

The polymers developed here are highly aromatic polymers produced by mixing a carboxylated crosslinker with diamine monomer groups to form amide polymers (Essawy et al. 2010, Kohnle et al. 2009, Matsusaka et al. 2012). In designing different polymer moieties, two types of monomers provide a range of structural outcomes, from more rigid to more flexible admixtures (Contreras and Althaus 2021).

Where two of the three diamine monomers are highly aromatic and electron dense and the remaining monomer, aliphatic and more flexible (**Figure**). A crosslinker that is tri-functionalized is used to make high molecular weight polymers that are highly insoluble, high performing, and high temperature resistant. For these reasons, aramids are chemically inert and insoluble, including in several organic solvents, such as a dimethylformamide, strong acids, and alkaline cement environments at temperatures up to 350 °F.

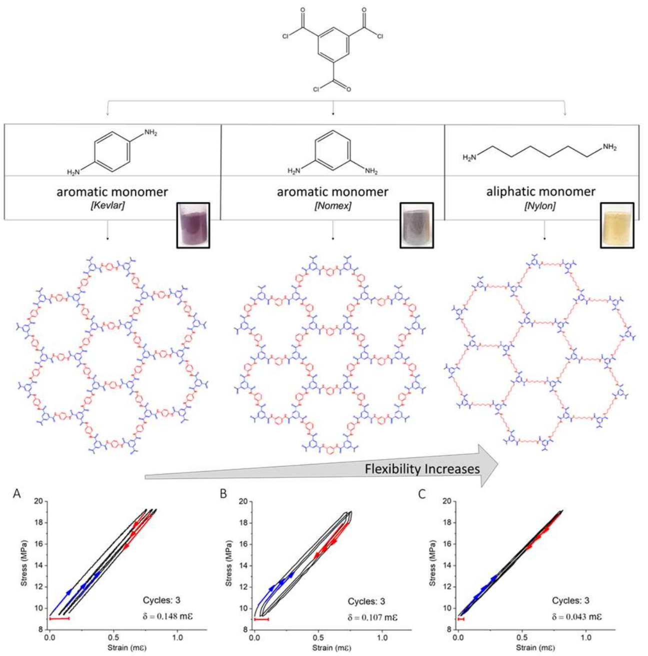

Figure 2- Various monomers in the synthesis of aramids; molecular level understanding on overall cement mechanical properties; and graphs showing reversible strain of hardened cement and more elastic and favorable cement systems. Stress-strain cyclic tests (up to 40 MPa overbearing load) of aramid-reinforced cements demonstrate how A) the more rigid aramid provides enhanced mechanical properties in comparison to neat cement; B) the less rigid aramid polymer allows for less cumulative damage along the x-axis; and, C) the most flexible polymer makes cement more elastic, mitigating cement breakage.

Table 1. Cement samples in Figure (A-C) in comparison to neat cement. Sample characterization and properties, such as density (ppg), permanent deformation (δ), Young's modulus (YM), Poison's ration (PR), and compressive strength (CS) illustrate cement performance.

Properties		Neat	1A	1B	1C
density	ppg	16.4	16.1	16.2	16.1
δ	a.u.	0.30	0.15	0.11	0.04
YM	psi	2.2E+06	1.9E+06	1.9E+06	1.7E+06
PR	a.u.	0.19	0.21	0.25	0.28
CS	psi	12,691	11,792	11,197	10,863

Portland Cement Samples and Confined Cyclic Test

The cement specimen were prepared in accordance with API Recommended Practice for Testing of Well Cements 10B-2. The cement slurries comprised of API Class G (HSR) Portland cement and 3% (w/w) polymer were mixed, placed in 2 inches diameter by 4 inches long brass molds and then cured in pressurized curing chambers at 180°F and 20 MPa (2,900 psi) for three days.

All cylindrical cement samples are jacketed and placed between steel endcaps. Linear Variable Differential Transformer sensors (LVDTs) are mounted to measure axial and radial deformation at ambient temperature. The three primary types of measurements obtained from this study using a triaxial loading cell are Young's modulus (YM), Poison's ratio (PR), and compressive strength (CS) as seen in (**Table 1**).

Static confined triaxial loading measurements at high pressures up to 75 MPa (10,900 psi) are possible with a triaxial press. The testing equipment consists of an axial loading system, a confining pressure supply system, and data acquisition software (**Figure**).

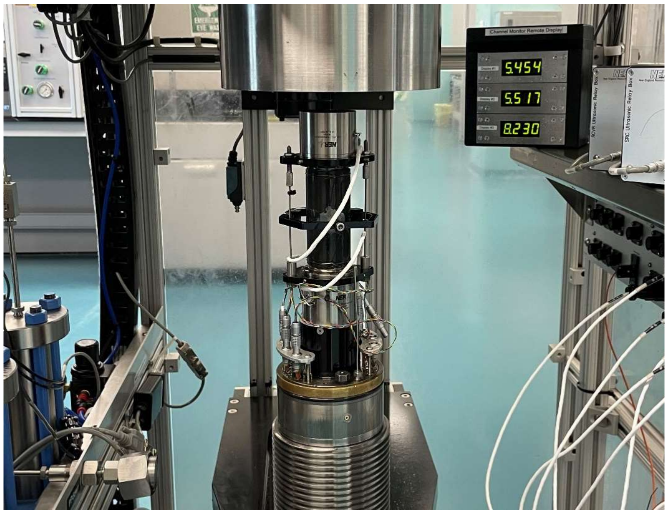

Figure 3 - Example of equipment which can achieve triaxial testing results

The triaxial press was programed to measure the stress-strain response at room temperature. (**Figure** 4).

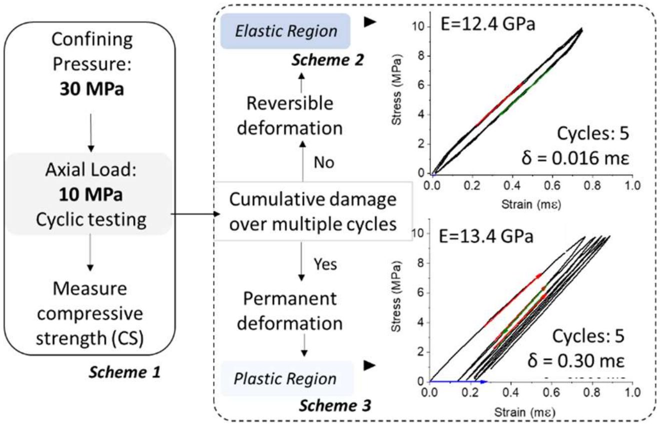

Figure 4: Sample-independent Protocol at 40 mPa maximum confining pressure to screen for high integrity samples. Cyclic testing illustrates sample elasticity (Scheme 2) or plasticity (Scheme 3).

Experiments of triaxial cyclic testing on NMR cements were placed under 30 MPa (4,350 psi) confining pressure (load rate 0.2 MPa/s) and cyclic testing at 0 to 10 MPa (1,450 psi) uniaxially (load rate 0.2 MPa/s) for up to 5 cycles to best illustrate cement performance. In addition, confined peak compressive strength is measured by applying increasing axial loads at a rate of (0.694 MPa/s) until the sample failed. (Contreras et al, 2023)

Results and Discussion

The mechanical parameter characterization of a cement sheath impacts the output of a wellbore stress models as it relates to the prediction of the ability of the cement sheath to withstand the expected changes in temperature, pressure and reservoir conditions.

Of vital importance is the accuracy of the input values of Young's Modulus of a material, which can be derived by a number of possible methods. Dynamically or acoustically determined Young's Modulus (usually by resonance techniques or by ultrasonic means) will generate the highest Young's Modulus values (Mueller et al. 2004).

The Young's modulus and the Poisson's ratio determination uses a stress-strain uniaxial compressive loads to the cylindrical sample versus time and displacement. Statically determined Young's Modulus (by means of compressional testing) will produce lower values than the same material evaluated dynamically.

In the past the perception for judging the mechanical properties of cement was to look at compressive strength. However ongoing lessons learned from wells experiencing sustained annular pressure showed the limitation of this traditional approach. Changes in downhole conditions in terms of temperature and pressure can induce sufficient stresses to destroy the integrity of the cement sheath, cause long-term gas migration, and sustained annular pressure.

Triaxial testing applies a second stress to the axial pressure normally using an apparatus which can apply a radial pressure to the cylindrical sample. The application of the radial pressure is first and the axial pressure is second.

In this study, the mechanical behavior of cement systems subject to cyclic loading was investigated (Gorninski et al. 2004, Kim et al. 1996). A series of triaxial compressive stresses are performed to examine the fatigue behavior of different cement systems when subjected to cyclic loading. Cement reliability can be quantitatively measured by cumulative damage models, such as Miner's rule, which is commonly used in applied metallurgy and materials (Fatemi et al. 1998, Kindrachuk et al. 2015). Miner's Rule generally describes reaching failure when damage fraction reaches 1:

$$\sum_{i=1}^{k}\left(\frac{n}{N_i}\right) = 1 \qquad \text{(eq. 1)}$$

Where:

n	total number of cycles at a given amplitude that a specimen is subjected to during its lifetime
N	total number of cycles at a given amplitude that the specimen can survive as determined by laboratory tests
k	number of the different amplitude levels of the cucles

where the damage fraction is a function of stress and n cycles. When the damage fraction reaches 1, failure occurs as a result of cumulative fatigue damage from cement fractures and micro annuli formation; and the lifetime of the cement will be exhausted from irreversible plastic deformation with loading and unloading stresses.

Insoluble organic polymers called polyaramids are synthetically prepared with a range of elasticity and stiffness for overall effects on cement-organic matter composites and materials strength. That is, addition of aramids into cement enhances cement mechanical properties. Aramids are from a family of polymers known to be high strength and high performing. These polymers are added up to 3% bwoc as free-flowing powders to the dry cement blends of various slurry designs.

Using a triaxial loading cell for confined mechanical testing (30 MPa, or 4350 psi), axial strain (10 MPa or 1,450 psi) is asserted on a cement cylinder. The radial strain is monitored for 5 cycles of loading and unloading. With aramid-reinforced cement, young modulus (YM) decreases and improves with increased polymer moiety flexibility. Under cyclic testing, creeping events vary between samples as permanent deformation is mitigated and fracturing events decrease as reinforced cements return increasingly to its original state after loading and unloading of the axial strain (**Table 1**).

Collectively, the data on elasticity and high compressive strength shows the value of new polymer additives for long term zonal isolation cement sheath integrity of oil and gas wells.

Conclusions

In this study polymers synthesized for mechanochemical properties, such as flexibility or rigidity are controlled using different monomers. Specifically, polymers are synthesized using monomers that mimic the flexibility of nylons using long carbon-chain monomers and the rigidity and strength of polyamides using aromatic monomers to produce a family of polymers known as aramids.

Kevlar and Nomex are common examples of aramids with aerospace and military applications as fibers and composites. Next, cement samples are prepared using polyamide admixtures embedded into cement within freshly prepared slurries. Once set, the hardened samples undergo confined cyclic stress tests to demonstrate the molecular basis of various elastic profiles of new composite materials in bulk.

Methodology towards elastic stiffness shows reliable means of predicating cyclic stress-strain responses under confinement relevant to the oil and gas industry in many applications.

Acknowledgments

The authors would like to thank Timothy P. O'Connell, Diana Rasner, Kenneth Johnson and Roland Martinez for assistance in the synthesis and characterization of the polymers, for the expertise in operating triaxial loading cells, for cement sample preparation, and for different aspects of this research.

Nomenclature

API	American Petroleum Institute
a.u.	arbitrary unit
bwoc	by weight of cement
°F	Degree Fahrenheit
Mpa	Megapascal
ppg	pounds per gallon
psi	pounds per square inch
w/w	weight by weight
%	percent

References

1. Bourgoyne, A.T Jr., Scott, S. L. and Manowski, W. 2000. A Review of Sustained Casing Pressure Occurring on the OCS, final report submitted to US Department of Interior Minerals Management Service, Washington, D.C.
2. Contreras, Elizabeth Q., and Stacey M. Althaus. 2021. "Design of aromatic polyamides to modify cement performance under triaxial cyclic tests." MRS Communications 11 (6):777-782.
3. Contreras, Elizabeth Q., Heinold, Thomas, Martinez F. Roland, Johnson, D. Kenneth, "Effect of Stress Triaxiality on Creep Deformation of Polyaramid-Reinforced Elastic Cements" IMECE International Mechanical Engineering Congress and Exposition. https://doi.org/10.1115/IMECE2023-113350.
4. Essawy, Hisham, and Klaus Tauer. 2010. "Polyamide capsules via soft templating with oil drops—1. Morphological studies of the capsule wall." Colloid and Polymer Science 288 (3):317-331.
5. Fatemi, A., and L. Yang. 1998. "Cumulative fatigue damage and life prediction theories: a survey of the state of the art for homogeneous materials." International Journal of Fatigue 20 (1):9-34.
6. Gorninski, Jane Proszek, Denise C. Dal Molin, and Claudio S. Kazmierczak. 2004. "Study of the modulus of elasticity of polymer concrete compounds and comparative assessment of polymer concrete and portland cement concrete." Cement and Concrete Research 34 (11):2091-2095.
7. Heinold, Thomas, D. Steve Porter, Urooj Qasmi, and Salim Taoutaou. 2020. "A Step Change in Cementing Mitigating Sustained Casing Pressure." SPE Annual Technical Conference and Exhibition, October 26–29, 2020.SPE-201469-MS https://doi.org/10.2118/201469-MS
8. Kaiser, Trent M. V., Victor Ying Ben Yung, and Russ M. Bacon. 2005. "Cyclic Mechanical and Fatigue Properties for OCTG Materials." SPE International Thermal Operations and Heavy Oil Symposium, November 1–3, 2005.SPE-97775-MS https://doi.org/10.2118/97775-MS
9. Kim, Jin-Keun, and Yun-Yong Kim. 1996. "Experimental study of the fatigue behavior of high strength concrete." Cement and Concrete Research 26 (10):1513-1523.
10. Kindrachuk, Vitaliy M, Marc Thiele, and Jörg F Unger. 2015. "Constitutive modeling of creep-fatigue interaction for normal strength concrete under compression." International Journal of Fatigue 78:81-94.
11. Kohnle, Maria-Verena, Ulrich Ziener, and Katharina Landfester. 2009. "Synthesis of styrene–butadiene rubber latex via miniemulsion copolymerization." Colloid and Polymer Science 287 (3):259-268.
12. Matsusaka, Nami, Toyoko Suzuki, and Masayoshi Okubo. 2012. "Effects of stirring prior to starting emulsion polymerization of styrene with nonionic emulsifier on particle formation and its incorporation." Colloid and Polymer Science 290 (6):561-567.
13. Mueller, Dan T, Virgilio GoBoncan, Robert Lee Dillenbeck, and Thomas Heinold. 2004. "Characterizing casing-cement-formation interactions under stress conditions: impact on long-term zonal isolation." SPE Annual Technical Conference and Exhibition held in Houston, Texas, U.S.A., 26–29 September 2004. SPE-90450-MS https://doi.org/10.2118/90450-MS.
14. Riley, V. R., and I. Razl. 1974. "Polymer additives for cement composites: a review." Composites 5 (1):27-33.
15. Nelson, Erik, "Well Cementing", 2nd Edition, 2006
16. Zhang, Zhen, Zhengfei Hu, and Siegfried Schmauder. 2019. "Fatigue Behavior of 9–12% Cr Ferritic-Martensitic Steel." In Handbook of Mechanics of Materials, edited by Siegfried Schmauder, Chuin-Shan Chen, Krishan K. Chawla, Nikhilesh Chawla, Weiqiu Chen and Yutaka Kagawa, 1629-1674. Singapore: Springer Singapore.