**Predicting Compressive Stress Relaxation of TFE/P Polymers in Simulated Production Fluid (SPF)**
**A study of comparative changes in compressive stress relaxation after aging in SPF**

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ABSTRACT

TFE/P polymers have a long, successful history of solving difficult sealing problems in the oilfield where sour hydrocarbons are encountered. The supplier's challenge has been to achieve low compression set and low compressive stress relaxation using commonly accepted cure systems. A new TFE/P polymer has been introduced to address this issue. This paper examines different grades of TFE/P polymers, including the newest grade, to examine differences in compression set, compressive stress relaxation, and Arrhenius predictions of the compressive stress of these materials when subject to long term compression.

# INTRODUCTION

## Background

The need to seal against increasingly corrosive oilfield environments, particularly "sour gas" and "sour crude", fortunately coincided with the development of the FEPM class of polymers in the 1970s. The first FEPM polymer, known today as Aflas®, is a copolymer of tetrafluoroethylene and propylene.  FEPM rubbers are remarkable on account of their strong resistance to both alkaline and acidic sealing conditions as compared to FKM'S, which age rapidly in a high pH environment.

One of the primary shortcomings of Aflas is its susceptibility to high compression set absent highly engineered formulation and processing. Consequently, AGC introduced a new grade of FEPM known as Aflas 600 X™, to help mitigate the compression set problem for processors and application engineers using molded Aflas products in the field.

The primary objective of this paper was to test the claims about Aflas 600X by comparing its ability to retain sealing capability in an oilfield environment compared to that of its predecessor known as Aflas 100H. While compression set remains an important attribute of any compounded elastomer, interest has shifted to the stress response of a material subject to prolonged to deflection. Subsequently, developments in the polymer industry have led to widespread acceptance of compression stress relaxation (CSR) as an effective measure of a polymer's sealing lifetime. The trouble lies in efficiently estimating how CSR changes over the lifetime of a seal, which can be as long as several years. A common method to test a polymer's resistance to aging-induced degradation of physical properties is the Arrhenius analysis.

## Objective

The objective of the study was to compare the ability of Aflas 100H and Aflas 600X to retain sealing force in simulated production fluid (SPF: see ISO 23936-2:2011). Percent retained compressive strength was chosen as the primary metric by which to monitor degradation in sealing capability. Of additional interest was the potential for the Instron Universal Testing Machine to accurately and reproducibly measure compression stress relaxation of elastomers at low strain.

## Scope

### *Elastomers:*

The two subject polymers studied were different grades of FEPM. The FEPM class of elastomers is defined by ASTM D1418-01a:

> FEPM – "A fluoro rubber of the polymethylene type only containing one or more of the monomeric alkyl, perfluoroalkyl, and/or perfluoroalkoxy groups, with or without a cure site monomer (having a reactive pendant group)"

FEPMs, being a relatively new class of polymers, are not subdivided into different "types" as the FKM's are within ASTM D1418. The defining characteristic of this class of fluoro-elastomers is the distinct absence vinylidene fluoride in their molecular constitution. FEPM polymers, at this point in time, are differentiated from one another by manufacturer and the manufacturer's grade. For purposes of this study, Alfas 100H and Aflas 600X were analyzed.

*Environment:*

A simulated production fluid ("SPF"), as described in ISO 23936-2:2011(E), was used to closely replicate the type of environment observed in downhole drilling. Specifically, a non-aromatic, sweet multi-phase fluid per A.1.i capped with nitrogen.

Aging was conducted at 170°C, 200°C, and 230°C for four different time periods: 48, 168, 336, and 672 hours.

*Evaluation:*

Evaluation of an elastomer's sealing capability depends in large part upon the desired application. Traditionally, tensile stress-strain curves have been used as a proxy to estimate an elastomer's mechanical properties. Most rubber sealing applications take place under compressive strain, however, meaning that tensile data is not always useful in inferring an elastomer's suitability in sealing applications. This inertia in the market is slowly changing, as engineers are beginning to realize that compressive stress-strain data are a more fundamental quantity to understand a seal's performance. Importantly, the advent of cost-effective means to accurately measure the low strains necessary for compressive stress-strain testing has allowed the industry to change its standards to reflect this new knowledge.

The viscoelastic phenomenon of compressive stress relaxation, is a temperature-dependent process which arises from two separate etiologies. The first, physical stress relaxation, occurs at lower temperatures and on shorter time scales when realignment of polymer chains and entanglements dominates the kinetics of the strained rubber matrix. The second, chemical stress relaxation, is caused by long service times at high temperatures and is associated with degradation of the polymer backbone and/or the crosslink network. Typically, the latter etiology is more critical in determining the useful service lifetime of a rubber seal. The long time scales required to measure chemical stress relaxation, however, make it an expensive and difficult process. This paper therefore explores the use of Arrhenius analysis using physical stress relaxation measurements to probe seal lifetime.

## EXPERIMENTAL

The primary goal of this paper was to assess the efficacy of a novel FEPM product, Aflas 600X, as compared to Aflas 100H. Thus, two rubber compounds were studied using identical formulations except for their base polymers, which were selected as Aflas 600X and Aflas 100H respectively. The formulations are displayed in *Figure 1*.

| **AFLAS 100H Formulation** | |
|---|---|
| Constituent | PHR |
| Aflas 100H | 100 |
| MT 990 Carbon Black | 30 |
| TAIC | 3 |
| Peroxide | 1 |
| Calcium Stearate | 1 |

| **AFLAS 600X Formulation** | |
|---|---|
| Constituent | PHR |
| Aflas 600X | 100 |
| MT 990 Carbon Black | 30 |
| TAIC | 3 |
| Peroxide | 1 |
| Calcium Stearate | 1 |

- Both compounds press-cured for 10 minutes at 170°C (338°F)
- Both compounds post-cured for 4 hours at 200°C (392°F)

*Figure 1 – (Left) Depicts the formulation for the Aflas 100H compound, denoted 100H in this paper. (Right) Depicts the formulation for the Aflas 600X compound, denoted 600X in this paper.*

As mentioned previously, compressive stress relaxation (CSR) was selected as a key indicator of sealing lifetime. Numerous methods exist for examining fixed-strain CSR, though most use one of the test specimen geometries detailed in ASTM D6147 Section

7.1.1. For the purposes of this study, the cylindrical disc of diameter 13.0 mm and height 6.3 mm (hereinafter “CSR buttons”) was selected due to its simple geometry and ease of molding. Stress response under compressive strain was measured using an Instron Universal Testing System equipped with a compression attachment.

Aging of test specimens followed the recommendations of ISO 23936-2-2011 and occurred in simulated production fluid (SPF) in stainless steel aging vessels purged with ultra-high purity nitrogen gas. Samples were aged for 48, 168, 336, and 672 hours at 170°C, 200°C, and 230°C (see *Table 1* below).

| | |
|---|---|
| Aging period | • 48 hours (2 days)<br>• 168 hours (1 week)<br>• 336 hours (2 weeks)<br>• 672 hours (4 weeks) |
| Test Specimen | • ASTM D6147 CSR Button |
| Test Fluid | • Non-aromatic: 70 % heptane, 30 % cyclohexane |
| Multi-phase | • 30% Nitrogen, 10% water, 60% test-fluid |
| Test Temperatures | • 170°C<br>• 200°C<br>• 230°C |

*Table 1: Experimental test matrix.*

## Methodology

The present study is a comparative one and therefore focuses on highlighting the differences between the resistance of Aflas 100H and Aflas 600X to a defined mixture of common oilfield fluids at high temperature. In pursuit of this goal, the authors have utilized an Arrhenius analysis to determine the temperature-dependence of compressive stress degradation in rubber.

## *Arrhenius Analysis – Methodology:*

The Arrhenius analysis is a simple method which models a presumed exponential relationship between service temperature and degradation time. This principle is known as time-temperature superposition and holds generally for most rubber compounds. The precise form of the Arrhenius equation can be found in Equation 1[1].

Eq. 1 - $$k = Ae^{\frac{-E_a}{RT}}$$

An alternate form of the equation, obtained by taking its natural logarithm, provides Equation 2 for a straight line. This equation is used to model the aging data obtained during elastomer lifetime prediction studies.

Eq. 2 - $$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

Equation 2 can be used to extrapolate the test data to temperatures outside the tested ranges, allowing prediction of elastomer lifetimes for temperatures where testing would be prohibitively long.

## *Aging of Elastomers – Methodology:*

Elastomer aging was conducted to match the recommendations of ISO 23936-2:2011 as closely as possible. The experimental compounds were aged for four different test durations at three different temperatures, with six samples tested and averaged per data point (48, 168, 336, and 672 hours at 170°C, 200°C, and 230°C). The times and temperatures were selected based on prior knowledge of Aflas service performance.

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[1] Where k=degradation reaction rate constant, A=pre-exponential factor, $E_a$=degradation reaction activation energy, R=universal gas constant, T=reaction temperature.

While 230°C is an acceptable service temperature for Aflas (albeit on the upper edge), the highly volatile SPF fluids contraindicated a higher test temperature. This limited the acceleration of aging, resulting in measured properties that were more similar than intended across the three test temperatures.

### *Compression Testing – Methodology:*

CSR and compressive strength data for each compound were measured at a fixed deflection of 25%, a common strain encountered in a typical sealing application. An Instron Universal Testing Machine equipped with compression platens was used to replicate the general outline of ASTM D575. Briefly, the standard recommends conditioning the test specimens with two cycles of compression and release, followed by fixing the specimens at the desired deflection for an unspecified amount of time. The standard recommends 168 hours; as the present study is meant to probe physical relaxation, a twenty (20) minute relaxation period was chosen instead. The stress-strain protocol described above results in test data which look similar to *Figure 1* below, albeit with different property magnitudes. *Figure 2* shows a schematic representation of how max compressive strength and CSR are calculated from the raw data.

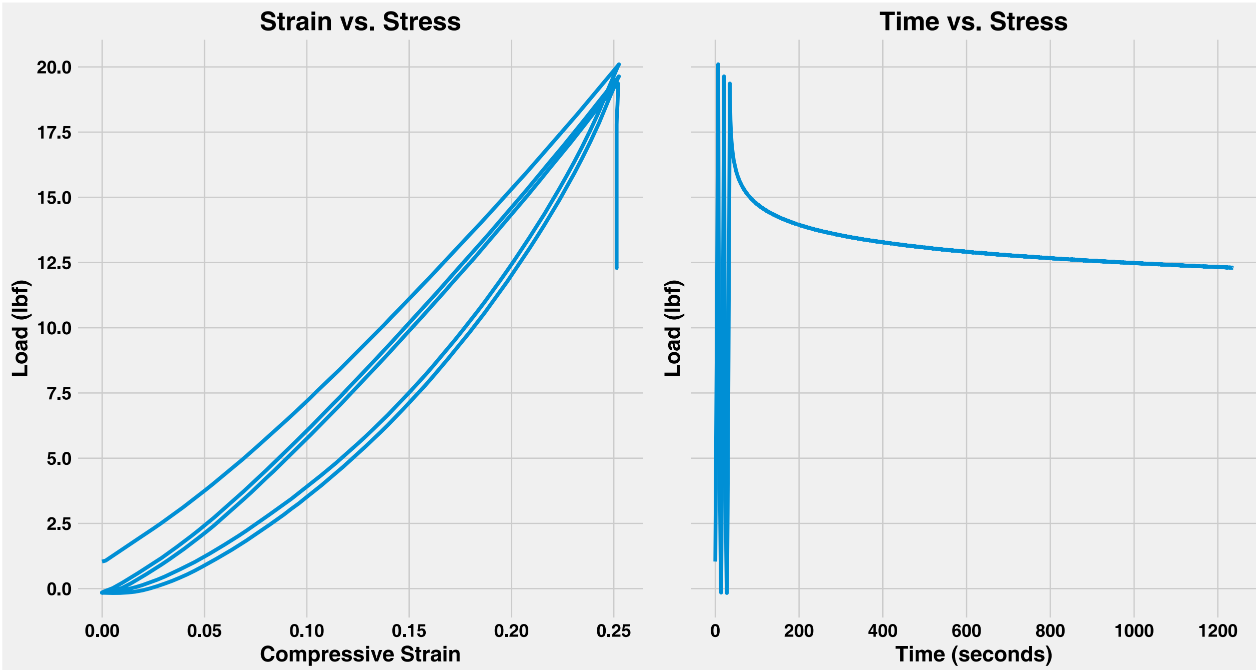


*Figure 1 – Compression stress-strain behavior of an arbitrary test specimens. Sample shown is a CSR button comprised of 100H test compound, aged for 168 hours at 200°C*

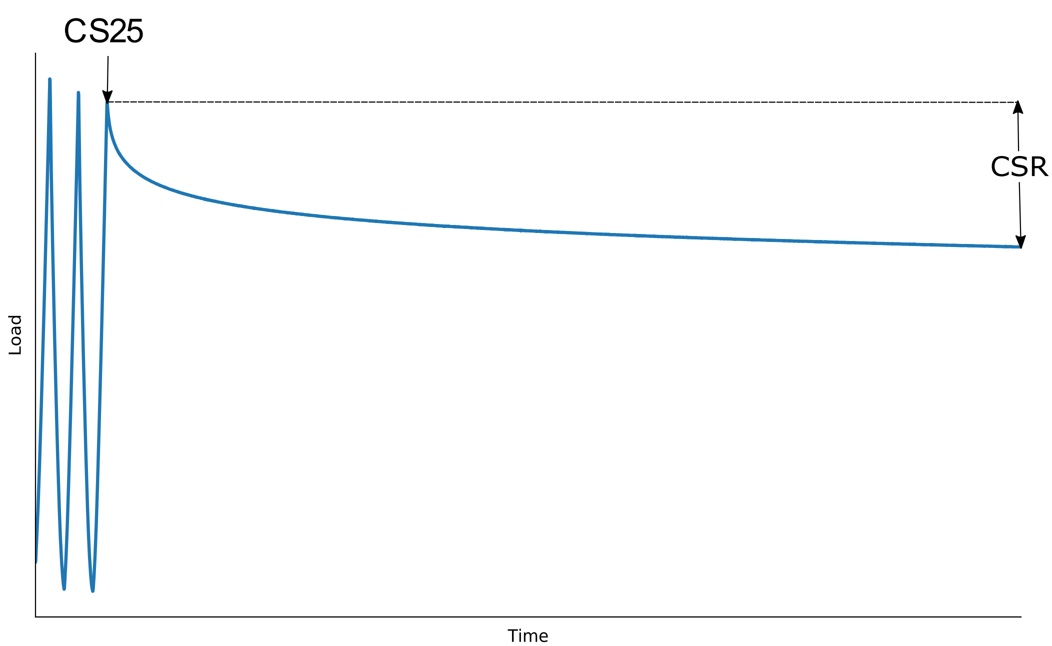


*Figure 2 – Compression stress-strain behavior of an arbitrary test specimens. In this case, the sample shown is a CSR button comprised of 100H test compound, aged for 168 hours at 200°C*

## RESULTS AND DISCUSSION

### *1. Compression Properties of Aflas Compounds Aged in SPF*

Compression properties were considered in the present study due to their relevance as a metric of a rubber compound's sealing performance. The key properties measured using the Instron were total compressive stress relaxation (CSR) and maximum compressive stress. Since maximum compressive strength occurs at maximum deflection (25%), this measurement can be thought of as M25 in compression (hereinafter referred to as "CS25"). These properties were grouped by compound and temperature and plotted against aging time, to provide a sense of how each compound performs in sealing applications. The plots are shown in *Figure 3* (Total CSR) and *Figure 4* (CS25).

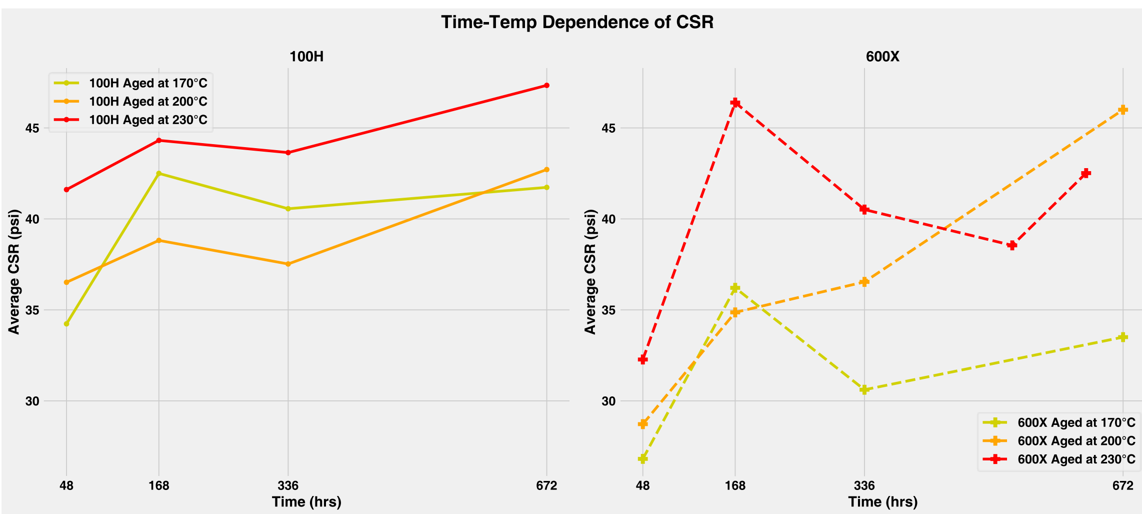


*Figure 3 – Effect of aging time and aging temperature on the observed CSR in 100H (left) and 600X (right).*

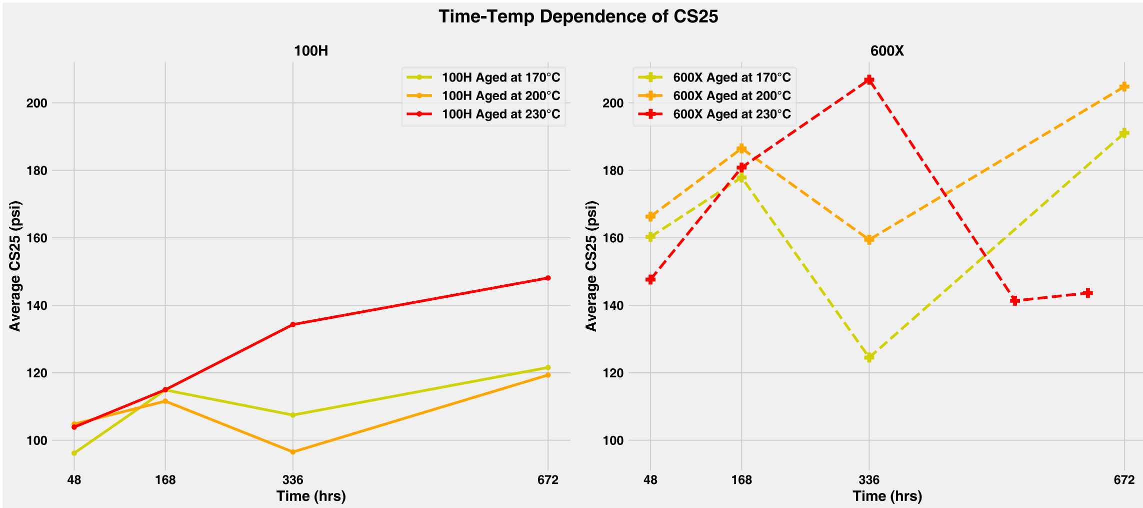


*Figure 4 – Effect of aging time and aging temperature on the observed CS25 in 100H (left) and 600X (right).*

A few interesting trends are immediately apparent. Of note, the Aflas 600X compound displays significantly greater compressive strength as compared to Aflas 100H (Figure 4, right). Further, it is evident that the compound modulus *increases* as it ages, in contrast to the effect of aging on most tensile modulus properties. This effect is mild, except upon aging at 230°C.

Shifting focus to stress relaxation, both 100H and 600X display similar CSR values across the set of data (see *Figure 3*). This was unexpected, as intuition might suggest that 600X would have elevated CSR commensurate with its higher compressive strength. Regardless, the observation implies that 600X is able to *retain* its sealing force more effectively than 100H in the SPF.

To better account for stress relaxation from a baseline measurement, the authors examined the percent loss of CS25 with respect to the maximum compressive strength to allow for a more direct comparison between how aging affects the relative compressive stress relaxation of each compound. The CSR and compressive strength data were recombined into a single measure (see Eq. 3) and identified as "Percent Loss of CS25".

Eq. 3 - $$\% \, Loss \; of \; CS25 = \frac{CSR}{CS25}$$

These data are plotted in *Figure 5* below. Percent Loss of CS25 values proved to be more chaotic and unfit for lifetime prediction. They do, however, confirm the suspicion that 600X retains its compressive strength better than 100H under short term strain.

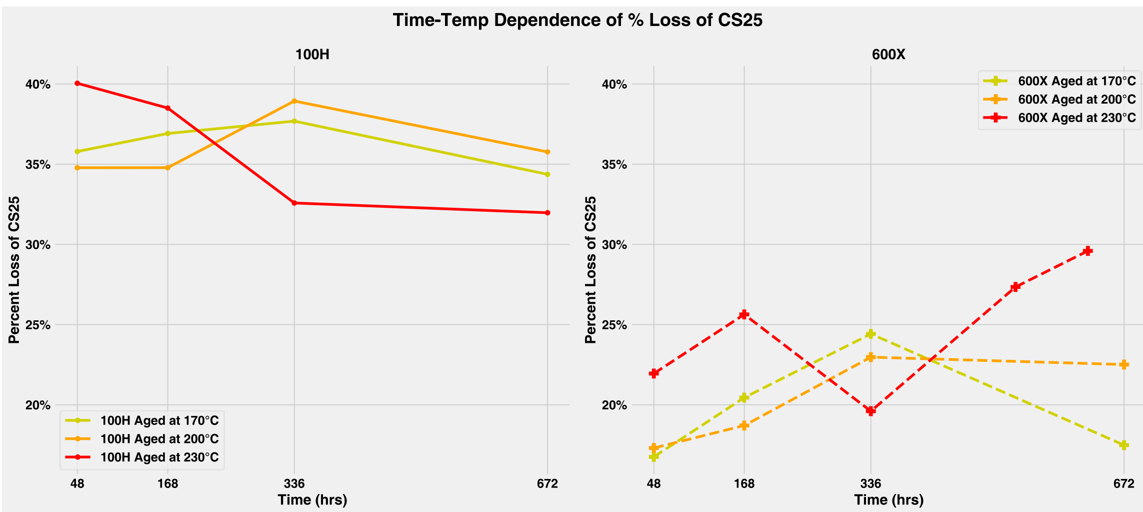


*Figure 5 – Effect of aging time and aging temperature on the Percent Loss of CS25 relative to max compressive strength.*

A final measure, the percent retention of a property, was borrowed from ISO 23936-2:2011 to make the data amenable to Arrhenius analysis. "Percent Retained CSR" (see Eq. 4) and "Percent Retained CS25" (see Eq. 5) values were compared to a baseline (in this case, 48-hour aging data for each temperature), to get a direct sense of how aging impacted physical properties.

Eq. 4 - $$\% \, Ret. CSR = 100 * \left(\frac{CSR}{CSR_i}\right)$$

Eq. 5 - $$\% \, Ret. CS25 = 100 * \left(\frac{CS25}{CS25_i}\right)$$

These data are summarized in *Figure 6* and *Figure 7*.

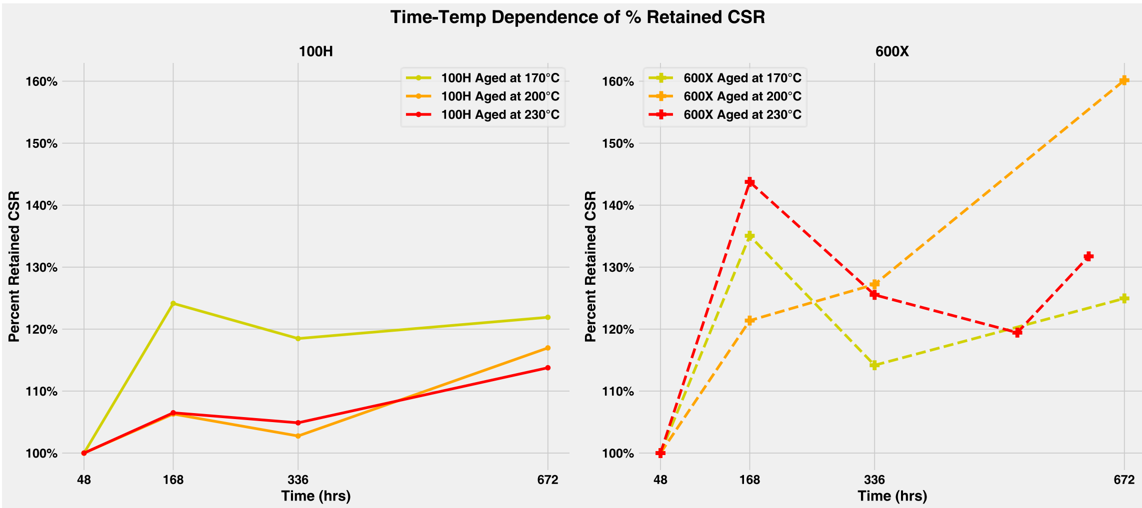


*Figure 6 – Effect of aging time and aging temperature on the percent retained CSR.*

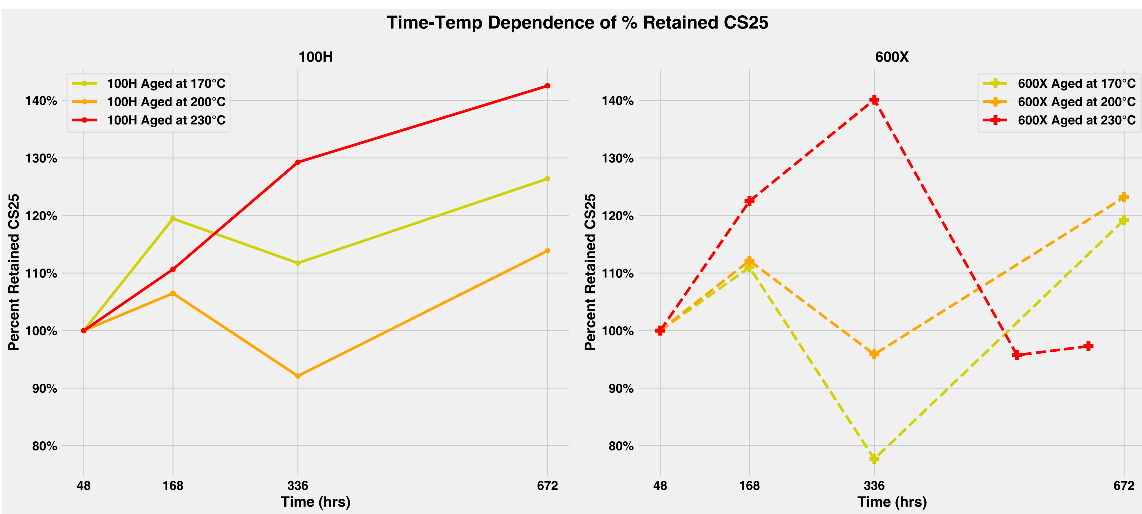


*Figure 7 – Effect of aging time and aging temperature on the percent retained CS25.*

The figures indicate that both compounds mostly retained their properties except upon aging at 230°C. It appears that aging at 230°C impacts both compounds' physical properties roughly equivalently. The retention of compressive strength in Aflas 100H offers validation of this material's merit in difficult sealing conditions. That 600X performs comparably to 100H suggests it could find use in the demanding industry of oilfield completions.

*2. Lifetime Prediction using Arrhenius Method*

A primary objective of this paper is to determine whether Instron compression testing can be used for accurate lifetime predictions. While the Arrhenius method can successfully model most thermal aging data, it is often difficult to assess the accuracy of the obtained results without accompanying in-application lifetime data. Interesting results arise nonetheless from the analysis in this case.

Percent retained CSR data were fitted for each compound and test temperature using linear regression (see e.g. *Figure 8*). Extrapolated lifetime estimates were calculated using the lines of best fit, assuming failure occurs when a property reaches ±50% of its baseline value. The natural logarithm of the reciprocal of these lifetime estimates were plotted against their reciprocal temperatures (*Figure 9* and *Figure 10*).

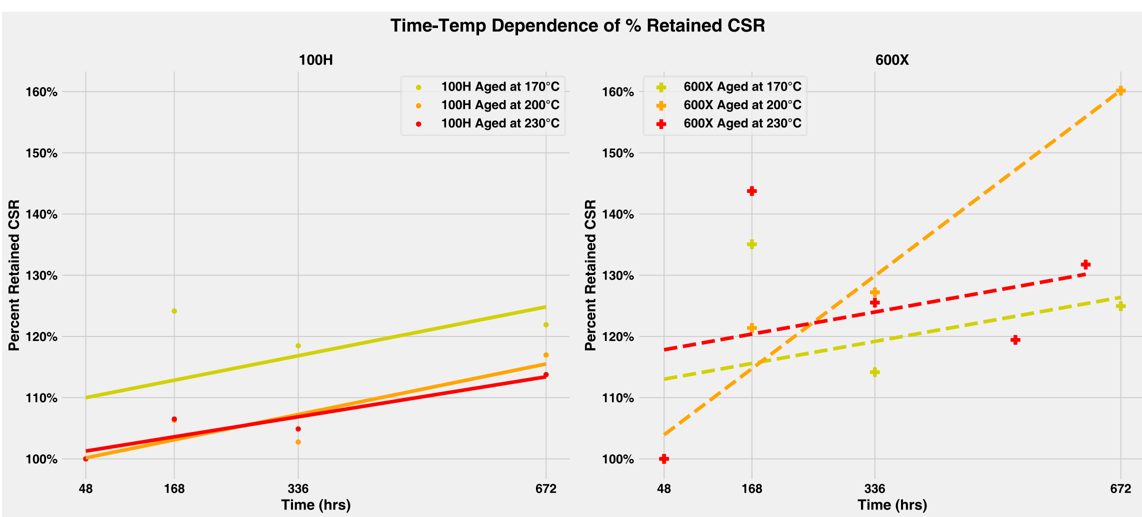


*Figure 8 – Effect of aging time and aging temperature on the percent retained compressive strength.*

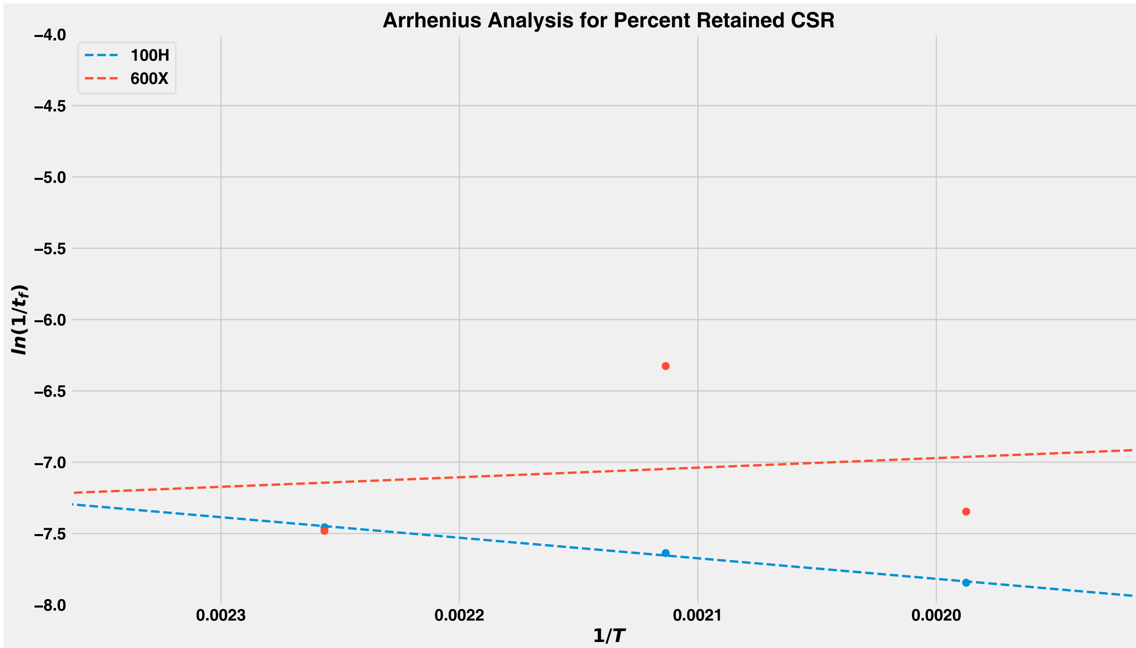


*Figure 9 – Fitting of Arrhenius model to percent retained CSR data for the two experimental compounds.*

The 100H data in the left half of *Figure 8* provides a good illustration of the difficulty in using physical relaxation data for lifetime prediction. The small relaxation magnitudes prevented sufficient separation across aging temperatures to adequately fit the Arrhenius model. This manifests as lines of best fit with nearly identical slopes. In fact, the slopes become smaller as aging temperature increases, a fact which is reflected in the negative slope of the Arrhenius model (see *Figure 9*). A negative Arrhenius slope is not inherently undesirable, though the observation that CSR increases with degradation (*Figure 3*) means it is in this case. Similar results were obtained for the 600X, with no clear relationship between temperature and property degradation. Thus, explicit lifetime predictions were excluded from the analysis to avoid misrepresenting the materials.

*3. Discussion of Experimental Error*

Elastomer lifetime studies traditionally track tensile property degradation across time and temperature. The data presented above were erratic when compared to these more traditional means of assessing elastomer lifetime. A large contributor to the observed lack of temperature dependence was the high degree of experimental error in measuring compression properties. *Figure 10* and *Figure 11* reproduce the CSR (*Figure 3*) and CS25 (*Figure 4*) data presented in the results section above. Included in the figure are errorbars, which are shown as plus or minus the standard deviation of the sample.

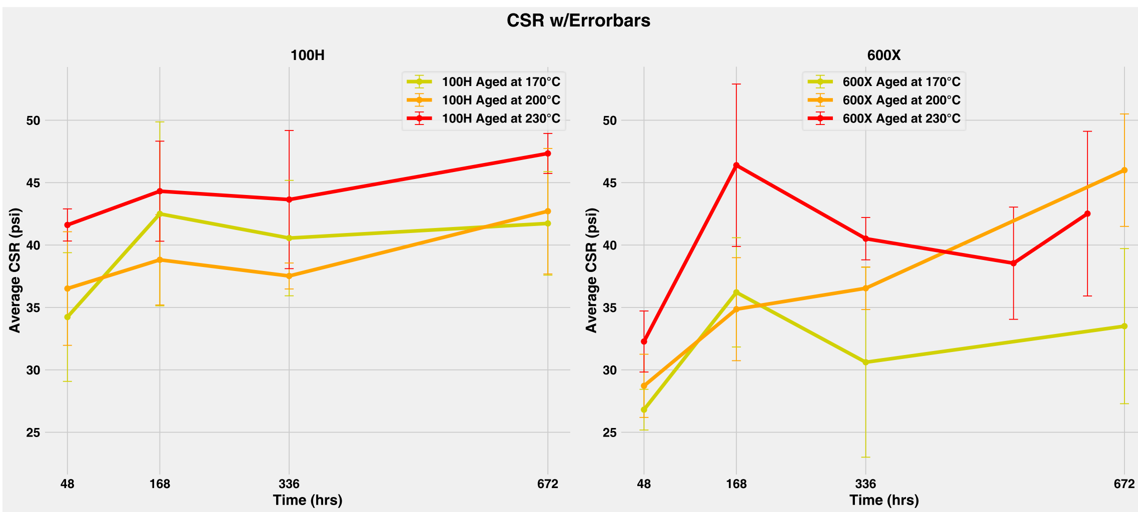


*Figure 10 - Effect of aging time and aging temperature on the observed CSR in 100H (left) and 600X (right). Errorbars showing deviation within sample groups are included.*

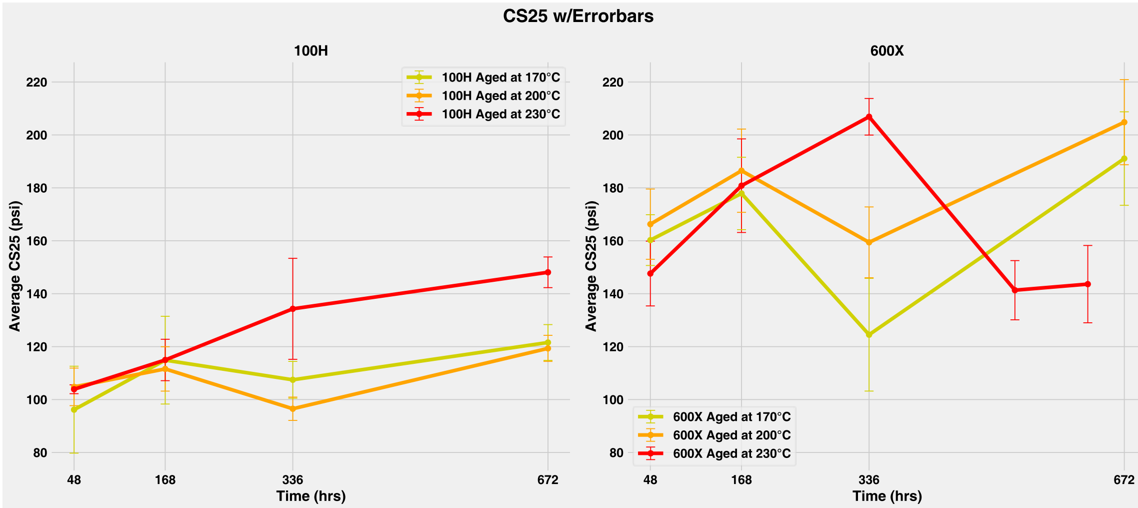


*Figure 11 - Effect of aging time and aging temperature on the observed CS25 in 100H (left) and 600X (right). Errorbars showing deviation within sample groups are included.*

The large overlap between sample groups in the above figures explains the inability to apply an Arrhenius model. The causes of the overlap are unknown but could arise from two possible sources: (1) an inherent lack of an Arrhenius relationship between compression properties and aging time/temperature or (2) deficiencies in the experimental design or measuring equipment. The first option is unlikely, as several authors have found considerable success in estimating elastomer lifetime using more elaborate schemes of testing compression properties.

It is far more likely that the current state of the Instron compression setup prevents sufficiently accurate measurements of stress relaxation for the purposes of Arrhenius analysis. Consider that the ASTM D6147 buttons used in this study have a height of 6.3 mm (0.248 in). To achieve 25% deflection, the Instron would need to apply a strain of 1.575 mm (0.062 in), a difficult level of precision to obtain with a standard Instron. More precise means of achieving low strains on small rubber specimens would likely decrease experimental error. Using a larger specimen geometry would have a similar impact, leading to higher load values and requiring less precision.

## SUMMARY

Increasingly harsh sealing environments in the oil and gas industry have necessitated the development of novel elastomers and new ways to test their efficacy in applications. The present paper focused on creating a protocol to test degradation of elastomer compression properties in a simulated production fluid (see ISO 23936-2:2011). The protocol was designed to provide comparative data to differentiate between the applicability of two FEPM polymers, Aflas 100H and Aflas 600X, to oilfield sealing environments. While small design flaws prevented prediction of elastomer lifetime using the Arrhenius method, the original goal of differentiating the two polymers was successfully achieved. Aflas 100H, a polymer with a long history in oil and gas, displayed greater thermal stability with regards to both its compressive strength and compressive stress relaxation. This speaks to the potential of Aflas 100H to retain its sealing force, especially with proper compounding. Aflas 600X, a newcomer to the FEPM market, shows considerable promise due to its heightened compressive strength relative to Aflas 100H. While it appears to have a lower thermal threshold for degradation, it still provides a similar sealing force as that of Aflas 100H after degradation. The results presented herein warrant further testing of Aflas 600X in order to assess its utility in the oilfield.