CSI TECHNOLOGIES

Final Report

Title: Resin Compared to Cement as a Sealant for OCS Wells

Contract No: E17PC00004
Date: October 12th, 2018
Version: 1.4

QUALITY SYSTEM CERTIFICATION
DNV·GL
ISO 9001

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ACRONYMS AND ABBREVIATIONS

API:	American Petroleum Institute
ATR:	Attenuated Total Reflectance
bbl:	Barrel
Bc:	Bearden Unit of measurement for Thickening Time
BHCT:	Bottom hole circulating temperature
BHST:	Bottomhole static temperature (°F)
BPF:	Bisphenol F
BSEE:	Bureau of Safety and Environmental Enforcement
bwoc:	By weight of cement
°C:	degrees Celsius Temperature
Ca(OH)Br:	Calcium Hydroxide Bromide
Ca(OH)Cl:	Calcium Hydroxide Chloride
CFR:	Code of Federal Regulations
cm^{-1}:	wavenumber
DSC:	Differential Scanning Calorimetry
°F:	degrees Fahrenheit Temperature
FEA:	Finite element analysis
ft:	foot
FTIR:	Fourier Transform Infrared Spectroscopy
g:	grams
gps:	Gallons per sack
HSE:	Health, Safety, and Environment
in:	inch
in^3:	cubic inches
in/in:	inch per inch
$In\text{-}lb_f$:	Inch-pounds
J/g:	Joule per gram
lb/gal:	pound per gallon
Lb_f/in^2:	pounds per square inch
LVDT:	Linear Variable Differential Transformer

Me:	Methyl
min:	minutes
ml:	milliliter
mm:	millimeter
MPSV:	Multipurpose Service Vessel
NA:	Not Applicable
NORSOK:	Norsk Sokkels Konkuranseposisjon
OCS:	Outer Continental Shelf
OH:	Hydroxide
PACE:	Plugging and Abandonment Collaborative Environment
pH:	potential of hydrogen
psi:	pounds per square inch
RP:	Recommended Practice
SME:	Subject Matter Expert
T_g:	Glass transition temperature
TGA:	Thermal Gravimetric Analysis
UCA:	Ultrasonic Cement Analyzer
UK:	United Kingdom
XRD:	X-Ray Diffraction
XRF:	X-Ray Fluorescence
YP:	Yield Point (lb/100ft^2)

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1.0 EXECUTIVE SUMMARY

The purpose of this project was to evaluate performance of epoxy, phenolic, polyester, and furan resin-based compounds as sealants for petroleum wells in the OCS. The main goal of the research was to evaluate the resin formulations to determine viable options for application in the OCS. Additionally, this research assessed the resin options against the current well sealant of choice – Portland cement. This assessment includes sealant performance, operational guidelines, availability, cost, regulatory and HSE considerations.

Conclusions and recommendations are provided below:

- As part of the Scope, an Industry Advisory Group was formed and participated actively throughout the project providing useful insight and guidance concerning utility of resin sealants for OCS wells. Specific insight and experience with resin for remedial application related to resin price, seal performance, and difficulty of application. This practical, authentic knowledge supplied a realistic foundation for assessing resin's sealant utility.

- The Industry Advisory Group concluded that remedial and abandonment seals were the highest anticipated use of resin sealant in the OCS. Experiences of successful resin sealant applications following multiple sealing attempts using Portland cement coupled with potential of superior resin barrier durability bolstered confidence in the class of materials.

- Four distinct resin chemistry classes that were utilized in the testing as potential well sealants were epoxy, phenolic, polyester, and furan. These resins chemistry were studied and found that broad chemical compositions would be applicable in well applications since the Industry primarily only uses epoxy

- Papers referenced in the Literature Review including SPE papers and patents describing fundamental long-term sealant performance studies emphasized the lack of complete understanding of seal failure mechanisms and properties required to ensure seal durability.

- Resin sealants in general cost roughly 15 to 50 times more than Portland cement on a per-cubic-foot basis. Higher cost of resin sealant can be justified if the indicated potential of superior barrier function is confirmed through field experience to reduce risk of leaks or catastrophe.

- Resin sealants can provide cost savings when considering the operational costs in the life of the well. In primary remediation of a Deepwater well the resin can provide well cost savings. In primary remediation of a Shelf well the cement is more cost saving than resin. In plug and abandonment of a Deepwater well in both upper and lower zones the resin can provide well cost savings. In plug and abandonment of a Shelf well in both upper and lower zones the resin can provide well cost savings.

- No petroleum regulatory entity has developed regulations for resin well sealants although several industry organizations are developing performance specifications and guidelines. Most providers of commercial resin well sealant declined to provide materials for comparative testing. So resin manufacturers provided component chemicals for each identified resin type, and viable formulations of each resin class were formulated for testing at conditions representing a range of application conditions for OCS wells. Simulated application conditions were developed to cover those existing in Shelf and Deepwater wells from conductor pipe to production and included temperatures and pressures applicable to both primary and remedial/abandonment operations. Specific application conditions are detailed in Section 6.0 of this report. Several commercially-available resins were included in the testing as they were offered. Laboratory and large-scale evaluations of these resin formulations (both designed from chemical supplier materials and as submitted by commercial resin formulation suppliers) were conducted and compared to results of appropriate Portland cement designs. Resin and Portland cement designs are detailed in Table 8 on page 58 of this report.

- Physical and chemical properties as well as seal performance characteristics of each of these resin formulations confirmed that these resins from each of these chemical types can function as well sealants. In general, resin seal performance and durability test results were superior to those of Portland cement. Long-term exposure of resins and Portland cements to well fluids and temperatures revealed that chemical resistance and mechanical durability of resins were superior to those of Portland cement in these environments. In fact, certain Portland cement designs deteriorated drastically over six months when exposed to completion brines.

- It is important to note that several resin formulations demonstrated unsatisfactory mechanical properties, stability, or seal durability. A portion of these resins were formulated from supplier materials and others were commercially available. In several cases formula adjustments produced acceptable results when retested. This exercise emphasized that resin chemistry is not a sealant cure-all. Proper design of mechanical properties and reaction kinetics at temperature, well geometry and seal volume are required to achieve viable resin seals. This finding emphasizes that designers, appliers, and regulators of resin well sealants must ensure that materials are properly formulated to produce durable seals under application conditions. Additionally, temperature increases driven by resin's exothermic curing reaction can drive rapid hardening, thermal expansion and subsequent shrinkage that can detrimentally affect seal performance if not controlled during design formulation. Cohesiveness of these non-aqueous sealants coupled with improved bonding performance indicates possible lowered volume requirements of resin to produce durable well seals.

- Operationally, resins can be designed for placement in all well conditions that currently employ Portland cement. Resin viscosity is generally higher than that of Portland cement but resin fluids realistically can be mixed and placed with traditional mixing and pumping equipment. Manufacturers indicate resin supply chain for well service is achievable. Handling resins on offshore platforms requires considering handling and containment of the organic resin components, additional cleaning fluids, and consequences of exothermic reaction occurring at surface.

- Mechanical Performance Property tests performed on the epoxy, polyester, furan, and phenolics Resin investigated their tensile strength and bond capabilities with respect to producing a durable well barrier formation: the higher the tensile and bond strength, the better the barrier. Results concluded the resins exhibited higher bond and tensile strength than the sample Portland Cements tested.

- Degradation and durability exposure tests were also performed on the epoxy, polyester, furan, and phenolics Resins to investigate their tensile strength after long term exposure to well fluids. Results proved that when exposed to brines or hydrocarbons representative of fluids existing in a well, the mechanical properties of resins remained generally stable with time. When testing commonly used Portland cement in the same fluids, approximately half of the cements tested showed significant degradation during the same time period. The resin tests showed to have a higher tensile strength for superior performance of resin sealants when exposed to well fluids over cement.

- In the Small and Large Scale Annulus Seal Stress test, the model utilized was indicative of casing run into a wellbore hole. When testing commonly used Portland cement in both models, the seals failed with lower cumulative stress than resin. However; several resin compositions did fail this physical testing. The determining factor for an annulus seal application usage would be the composition of the resin, which would need to be customized based on the environment exposure it would be presented in. This test reinforces the cautionary observation that there are no standards for resin applications and not all resins are universally applicable for utilization as well sealants.

- Overall results of this investigation indicate that properly-designed and applied, all four types of resins, generally performed superior to Portland cement due largely to the positive performance aspects as outlined below:
    - Increased bond strength
    - Increased tensile strength
    - Degradation durability
    - Durability under stress
    - Impact Resistance
    - Lowered Young’s Modulus and higher Poisson’s Ratio

This recommendation addresses the contradictory circumstances that BSEE resin regulation development requires a performance database to establish acceptable controls and limits while operators resist using resin sealants because they do not produce barriers “recognized” in BSEE regulations.

The recommended approach is based on BSEE initiating cooperative program with OCS operators to quickly amass a performance database for resin sealants form which regulation constraints (volumes, mechanical properties, confirmation testing, etc.) will progress. This recommended pathway, discussed in detail in Section 13.4 of this report, consists of 6 steps:

- BSEE elicits cooperative assessment of resin sealant performance on OCS:
- Assess past resin success on OCS.
- Establish resin qualification protocol.
- Communicate incentive for resin performance assessment to the industry operating on OCS.
- Establish resin design, placement, and performance regulations.

Include resin sealant regulations into 30 CFR 250.1715, 30 CFR 250.1721, 30 CFR 250 415, etc. as warranted

- BSEE’s Current position in regulation development for resin for OCS wells is in its initial development phase because no historical resin performance as a sealant for use in oilwell exists.

When current BSEE regulations were initially developed for Portland cement, the material had already been in use as the OCS well industry's only sealant.

- Development of regulations depends in part on creating an acceptance context similar to that formed for cement prior to original regulation development. A step-by-step process to develop regulations is included in Figure 143.

- Industry standards and guidelines for resins used as well barriers are issued from the UK and NORSOK. An API task group (SC10/WG05: Well Abandonments) is currently developing a recommended best practice document that covers alternative well sealants to Portland cement. The recommended practice in development could be used to develop guidelines for establishing resin sealant performance regulation. When API writes this for sealant, BSEE could incorporate this into their regulations.

2.0 INTRODUCTION

2.1 Objective

The objectives of this project are to evaluate performance of various resin-based compounds as sealants for petroleum wells in the OCS and to compare them against the current well sealant of choice – Portland cement. Specific objectives are to:

- Close the gap in understanding regarding the fundamental chemical and physical interactions of resin materials relevant to their use as well sealants.
- Evaluate all commercially available and proprietary resin materials for suitability as a wellbore sealant.
- Quantify the long term stability and long and short term performance under OCS well conditions of the currently available, viable resin products.
- Using numerical and physical models, evaluate the seal integrity of all viable resin products.
- Compare the material performance and seal integrity of the resin products versus Portland cement under the same conditions.
- Develop operational guidelines necessary for implementing resin in the OCS including sourcing, supply chain, handling and placement.
- Evaluate HSE considerations for all stages of resin design and implementation, as well as the improvements that may be seen with improved wellbore sealants.
- Evaluate well sealant cost versus benefit for both resin and Portland cement over the range of applications and conditions.
- Evaluate the current regulatory and industry standards with regards to resin as a wellbore sealant, and propose example regulation guidelines for best implementing resin as a wellbore sealant.
- Safe and effective well operation depends on a stable, well sealant that isolates hydrocarbon flow to the surface, prevents inter-zonal flow of formation fluids, and contains well operations from drilling through final abandonment. In the OCS, this sealant must withstand a surprisingly harsh environment and various stresses imposed by well construction, completion, production, and intervention. When quantified over a well's operational lifetime, the magnitude of energy applied to the well tubulars, sealants, and borehole as an integrated system is significant. Maintaining a sealed annular space throughout the life of the well is a key to significantly reduced cost and HSE risk.

2.2 Conclusions and Recommendations

The conclusions listed here are brief statements of significant information collected and interpreted from outcomes of the investigation. Each of these statements are explained and supported in detail later in this report. Refer to Sections 4 through 13 for details of data analysis, interpretation of results, and development of information.

Results of this study produced fifteen general conclusions regarding resins as well sealants for OCS wells:

1. Four distinct resin chemistry classes have application potential as well sealants: epoxy, phenolic, polyester, and furan. The chemistry defining each of these four resins is described in Section 7.0 of this report. These resins are commercially available, can be mixed and placed, and can be

formulated to produce durable well seals with superior mechanical properties, barrier performance and chemical stability to those of Portland cement.

2. Laboratory performance results indicate that resins from each chemical class can be formulated to produce long-term seal durability and stability. Epoxy and polyester resin formulations along with several blended compositions were successfully formulated at each of the design conditions. Furan resin was formulated for design temperatures of 150°F and 240°F while phenolic resin design could only be achieved at 240°F. The crosslinking chemistry of these two resin chemical types required heat to drive the reaction.

3. A major cautionary conclusion followed from the realization that resin chemistry cannot be applied universally as a well sealant. Resin sealants are not a “one-size-fits-all” remedy. Formulation of applicable designs for any of the resin chemical classes requires attention to design conditions, performance requirements, and formulation chemistry not unlike Portland cement. In reality, exothermic reaction and associated stresses that can develop in resin sealant as it cures impose additional maximum temperature increase and set time design constraints on resin sealants. Failure to tailor a resin formulation to meet well placement requirements and *in situ* seal criteria will usually produce inadequate barriers.

4. Furan and phenolic resin designs tested herein were formulated by the investigators from commercially-available components. These formulations met minimum design criteria for the higher-temperature designs described in Section 6.0, but were not optimized with respect to seal performance because these investigators lacked sufficient design experience with these resins to optimize designs within the scope of this project. Commercial sealants formulated from these resin components can be expected to perform better due to design optimization not attempted during this investigation.

5. Crosslink chemical reaction that results in hardening of all resin classes produces significant exothermicity during the time resin is setting, bonding, and developing solid properties. This exothermicity can produce a significant temperature increase especially in larger-volume applications such as setting plugs in large-diameter pipe. Effects of the exothermicity (particularly methods to mitigate temperature increases) should be factored into the resin design. Failure to account for internal stress generation that can result in bond failure.

6. All resins samples tested displayed excellent stability up to 150˚C (302°F) with only minor weight loss over duration of curing conducted in this investigation.

7. The general sealing performance of resins was substantially better than that of Portland cement.

8. Several Portland cement formulations deteriorated markedly after exposure to brine. Mechanism for this degradation was determined to be acid/base reaction with hydrated calcium ions being the source of acidity. This degree of deterioration was not exhibited by the resins. Generally, resins were less affected by exposure to well fluids than Portland cement.

9. Overall performance (mechanical properties, bond strength, and chemical resistance) of resin lends itself to using less resin sealant volume to produce a barrier that performs comparably to a barrier established with currently prescribed volumes of Portland cement.

10. Laboratory data indicate resins can be mixed and placed in situations and with equipment and conduits routinely employed for Portland cement in OCS. Lower resin volume, higher resin viscosity, and solids addition necessitate thorough, precise mixing of resin components compared to mixing Portland cement. Batch mixers are therefore better suited to mix resin rather than on-the-fly mixers routinely used for cement. Reaction control to prevent reaction in the mixer for low-temperature resin applications, clean up of resin from mixing equipment, and handling of returns/excess at the surface are more complicated with resins compared to Portland cement. Mixing small resin volumes in smaller batch mixing equipment of capacity similar to designed job volume and equipped with effective agitators and recirculation loop alleviates these potential handling difficulties.

11. Resin sealants in general cost roughly 15 to 50 times more than Portland cement on a per cubic foot basis. Significantly less resin volume can produce durable seals. It is estimated that sealant volumes can be reduced by 25% making resin still a more costly option.

12. Higher cost of resin sealant can be justified if potential of superior barrier function is confirmed through field experience to reduce risk of leaks or catastrophe.

13. No petroleum regulatory entity has developed regulations for resin well sealants. Several industry organizations are developing performance specifications and industry best practices guidelines for resin sealants.

14. A process is proposed to establish meaningful regulations for resin well sealant application on the OCS. This pathway is based on the assumption that current regulations governing Portland cement sealant applications are adequate. Thus, regulations governing barrier establishment using resin sealants can be of similar structure with sealant volumes and heights adjusted to account for improved performance. Resin sealant performance metrics on which to base volumes and heights do not exist as they did for Portland cement when initial cement regulation development began in the 1950's. So no historical performance basis exists for minimum barrier volume and height. The proposed pathway maps steps working with operators and resin service companies to identify well candidates for resin application, establish provisional regulations, apply resin, monitor performance, and optimize based on success.

15. The exothermic resin curing reaction can degrade bond durability. This potentially damaging phenomenon, which is not a factor with Portland cement, should be regulated with limits of maximum temperature increase and maximum increase rate.

Specific conclusions ensuing from each individual task are listed below. All the conclusions stated herein are documented and supported within the Discussion of Results for each task in Sections 3 through 11.

2.2.1 Task 1.0 Conclusions - Formation of Industry Advisory Group

1. Industry Advisory Group was formed and participated actively throughout the project providing useful insight and guidance concerning utility of resin sealants for OCS wells. Specific insight and experience with resin for remedial application related to resin price, seal performance, and

difficulty of application. This practical, authentic knowledge supplied a realistic foundation for assessing resin's sealant utility.

2. The Industry Advisory Group concluded that remedial and abandonment seals were the highest anticipated use of resin sealant in the OCS. Experiences of successful resin sealant applications following multiple sealing attempts using Portland cement coupled with potential of superior resin barrier durability bolstered confidence in the class of materials. Resin's higher cost coupled with the general industry opinion that Portland cement functions well as a primary well construction sealant lead to the group's opinion that wide adoption of resin sealants for primary cementing is unlikely in the OCS.

2.2.2 Task 2.0 Conclusions - Review of Previous Work

Two previously-written reports, discussed in Section 5.0 and presented in their entirety in the Appendix, contain detailed descriptions of work reported in the literature and specific conclusions drawn from the review. Broad, basic conclusions based on the review that defined boundaries of this investigation are stated here.

1. Four service companies currently offer resin well sealants commercially. Literature indicates these materials are chemically classified as either epoxy or polyester. Range of application conditions and operational scenarios are broad. A significant number of resin applications described are remedial treatments. Reports describing successful application of these commercial products provide anecdotal support of resin seal potential.

2. Major categories of resin well sealant materials discussed in previously reported literature include epoxy, polyester, furan, and phenolics. This previously-reported work supports fundamental evaluation of resin chemistry that could be used as well sealant.

3. Papers describing fundamental long-term sealant performance studies emphasized the lack of complete understanding of seal failure mechanisms and properties required to ensure seal durability. Lab evaluations of resins emphasized functional knowledge gaps created by the major differences between resins and Portland cement. Mechanical property comparisons illustrated resin's superiority, but other mechanical, thermal, and chemical issues arise that are outside the industry's normal focus. These identified gaps correlate to those gaps identified in this investigation and support the need to address effects of exothermicity timing and magnitude, volume changes, and adhesion over time as a function of sealant volume or geometry.

2.2.3 Task 3.0 Conclusions - Gathering Area Conditions in the OCS for Resin Application

Guided by input from the Industry Advisory Group and past BSEE investigations, a total of 6 OCS well configurations (3 Shelf and 3 Deepwater) were identified. A range of sealant application conditions was chosen (temperature, pressure, volume, application type) at various representative points along each example configuration to establish test conditions and primary and remedial/abandonment sealant property requirements encountered in these wells. Sealant performance and design criteria identified from each of these conditions were condensed into three test temperatures (80°F, 150°F, and 240°F) at which to evaluate resin performance. Conditions all along the well path were represented by these three temperatures. A range of Portland cement formulations commonly used in primary or remedial/abandonment OCS well applications covering these typical locales along the well were designed and tested for comparison to resins.

2.2.4 Task 4.0 Conclusions - Fundamental Chemical Evaluation of Resins

1. When considering thermal stability in air and in brines, the epoxy resins appear to be the best candidates for sealing of OCS oil wells. Furthermore, laboratory results demonstrate that resin chemistry can be manipulated to create compositions with thermal stability sufficient to produce highly durable well seals.
2. Resins in general possess better mechanical properties and chemical resistance than those of Portland cement. Fundamentally, resin sealants can produce more durable well barriers than Portland cement.

2.2.5 Task 5.0 Conclusions - Laboratory Evaluation of Resin Performance Properties

1. Useful well sealants were formulated from resin in each of the four chemical categories. This successful laboratory demonstration implies that viable well sealant could be formulated from each of these resin chemical classes. Thus, each of the identified resin chemical categories can be considered as potential alternatives to Portland cement for well application.

2. As indicated from laboratory results from this investigation, resin mechanical properties were generally superior to those of Portland cement. Higher tensile strength, shear bond, and hydraulic bond indicate potential for superior performance of resin sealants.

3. Mechanical properties of resins remained generally stable with time when exposed to brines or hydrocarbons representative of fluids existing in a well. Portland cement mechanical properties degraded, significantly in some formulations.

2.2.6 Task 6.0 Conclusions - Seal Integrity and Numerical Evaluation of Resin Performance

1. Results of small-scale seal integrity testing, discussed in detail in Section 8.1.5 of this report, reveal that resins in general produce more durable seals than Portland cement. Large-scale physical modeling of seal integrity, discussed in Section 8.1.6 of this report, mirrored the results of small scale. These results further support the generally increased durability potential of well seals formed form resins compared to those of Portland cement. Several resin formulations did fail this physical testing which reinforces cautionary alert that resins are not universally applicable as well sealants. Design and performance testing are required to ensure function of resin sealant at application conditions.

2. These small-scale laboratory results are confirmed by FEA using numerical models developed for previous Portland cement projects as discussed in detail in Section 9.0. The lab testing and FEA modelling demonstrate that the FEA analysis can predict cement and resin failure with good accuracy. Although some of the resin samples experienced immediate failure, this was likely as a result of the exothermic reaction induced by the curing process. It was generally observed that the samples that did not fail or had a significant number of cycles to failure in the lab also performed well in the analysis. It should be noted that sealant response is influenced by many different factors such as loading conditions, confinement,

etc. Therefore, one sealant composition that performs poorly in a certain scenario may perform sufficiently in another.

Details in Section 9.0 indicate FEA tended to over predict performance of resin seals compared to the small-scale and large-scale performance. A potential theory for this discrepancy involves curing conditions of samples for which mechanical property data were gathered for FEA testing. Mechanical property specimens were cured in small volumes under well controlled temperature while small-scale and large-scale annular seal test models involved larger volumes of resin cured in different geometries that may have produced excess heat buildup due to the exothermic curing reaction. Effects of material mass and geometry (surface area to volume ratio) on resin curing have been observed to affect resin reaction kinetics and temperature build up. Resin mechanical properties measured in the lab may have developed more rapidly than they did in the annular configuration with potentially more variable curing temperature. The potential of lower actual resin mechanical properties in the model than predicted may have caused the increase in predicted resin seal durability over measured. Conversely, potentially weakened seal durability caused by temperature increase from exothermic reaction may have reduced measured resin performance.

2.2.7 Task 7.0 Conclusions - Develop Operational Guidelines

Based on Tasks 1 – 6, the operational guidelines for resin application in OCS were developed. These operational resin application guidelines deal with mixing and placement of resin sealant. Design guidelines for resin performance were considered beyond the scope of this report, but specific consideration to mixing, managing exothermicity reaction temperature increases, and clean up/disposal were addressed. Specific guidelines for resin barrier seal length were considered to be beyond the scope of this investigation.

2.2.8 Task 8.0 Conclusions - Performance Assessment of Resin Compared to Cement

1. Results of this investigation indicate that properly-designed and applied resins will generally perform superior to Portland cement as a flow barrier due largely to the positive performance aspects of resins, discussed in detail in Section 8.0:
    a. Increased bond strength
    b. Increased tensile strength
    c. Chemical resistance
    d. Durability under stress
    e. Impact Resistance
    f. Cohesive immiscibility in water allowing for fall through placement
    g. Lowered Young's Modulus and higher Poisson's Ratio – More elastic

2. Resin attributes that are less desirable than those of Portland cement include:
    a. Cost (discussed in detail in Section 12.0)
    b. Exothermic reaction can create safety hazard at surface (discussed in detail in Appendix B)
    c. Disposal of excess (discussed in detail in Section 10.0)

2.2.9 Task 9.0 Conclusions - Cost-Benefit Analysis

1. Analysis of comparative cost of resin chemical categories versus cost of Portland cement reveals that cost of resins applicable for well sealants is about 15 to 50 times that of Portland cement on a per cubic foot basis. This analysis, detailed in Section 12.0, start with manufacturer's prices for resin and estimates appropriate markups applied along the supply chain to deliver a cubic foot of retail-priced resin sealant. These values were compared with average delivered cement cost per cubic foot as suggested from informed members of the Industry Advisory Group. Results are for material cost only. Evaluation of other cost/price comparison aspects such as transportation, blending, mixing, etc., were determined to be equivalent for resin or Portland cement.

2. Resin sealants can provide cost savings when considering the operational costs in the life of the well. In primary remediation of a Deepwater well the resin can provide well cost savings. In primary remediation of a Shelf well the resin is comparable in cost to the cement. In plug and abandonment of a Deepwater well in both upper and lower zones the resin can provide well cost savings. In plug and abandonment of a Shelf well in both upper and lower zones the resin can provide well cost savings.

3. Resin's performance success documented from sealant case history reports described in the review of previous work (Section 5.0 and Appendix B) and performance/durability results reported here indicate that resin sealants can function effectively in smaller seal volumes than traditionally employed using Portland cement. With estimated sealant volumes reduced to 25% of Portland cement, resins are still significantly more expensive.

4. It is concluded by the investigators conducting this work that extra cost of resin sealant is warranted in critical applications with high risk of harm to the environment from a failed barrier and no easy access to the well for containment, control, or repair. Such applications include seals for abandonment barriers in OCS wells. This conclusion corresponds to the consensus opinion of the Industry Advisory Group in light of improved expected seal durability and associated reduction of HSE risk.

2.2.10 Task 10.0 Conclusions - Regulatory Analysis of Resin as Well Sealant

1. Current status of BSEE resin regulation development for a new sealant for OCS wells is unique because no historical resin performance database exists to verify any stated regulation. When current BSEE regulations were initially developed for Portland cement, the material had already been in use as the OCS well industry's only sealant. Design and performance regulations were developed within an historical context. No resin historical performance database exists for new BSEE regulation basis.

2. Development of regulations depends in part on creating an acceptance context similar to that formed for cement prior to original regulation development. A step-by-step process to develop regulations is recommended below and discussed in detail in Section 13.0.

3. No regulations exist both domestically and globally for resins used as well barriers.

4. Industry standards and guidelines for resins used as well barriers are issued from the UK and NORSOK. These guidelines, described in detail in Section 13.0. An API task group (SC10/WG05: Well Abandonments) is currently developing a recommended practice document that covers alternative well sealants to Portland cement. The recommended practice in development could be used to develop guidelines for establishing resin sealant performance regulation.

2.3 Recommendation

The current state of regulations for resin well sealants on OCS appears to be hindered by contradictory conditions. Technical evidence generally supports using resin sealant to reduce risk of hazards caused by a well barrier breach. However, assurance of resin sealant performance and establishment of application protocols requires substantial demonstration of actual resin performance. Regulations stating resin sealant barrier number, locations and dimensions cannot be imposed without a basis developed from actual performance data.

One approach to interrupting this cyclic challenge involves BSEE actively encouraging OCS operators to use resin sealants in their wells and monitor sealant effectiveness over time. Active documentation and review of engineering, design application, and seal durability would accelerate demonstration database gathering and analysis. An ongoing collaboration between operators using resin sealants and BSEE to evaluate resin effectiveness would speed up application use, accelerate performance assessment, and guide BSEE toward regulation limits and controls faster than amassing performance information traditionally.

Subsequent recommendations regarding broader adoption of resin sealants for use in OCS wells and establishing regulations covering resin sealants are:

BSEE Incorporates Cooperative Assessment of Resin Sealant Performance on OCS: Collaboration with OCS operators interested in evaluating resin sealants to develop evaluation protocol that produces information rapidly without increased risk.

Assess Resin Success on the OCS: Estimates of resin sealant applications from operators and service providers in the OCS concur that resin sealants, primarily epoxy resins, have been employed on hundreds of OCS well remedial or abandonment operations over the last two decades. These applications, almost always employing resin in conjunction with Portland cement, contain significant performance information. A collaborative effort of BSEE and operators mining this resin use information will provide a basis for establishing or defining resin sealant success.

Develop Provisional Resin Qualification Protocol: With the assessment of this limited performance data as a basis, BSEE would then identify initial resin performance specifications and practices deemed sufficient to confirm resin as a viable well sealant for OCS. Distinct differences in seal formation and durability between Portland cement and resin sealants identified during this investigation point to additional regulation focus on resin adhesion (shear bond or hydraulic seal) and effects of magnitude and timing of heat generated by the resin curing reaction. T

Convey requisite information to the industry operating in OCS: Once provisional resin protocols are established, BSEE then seeks collaboration among operators, API, etc. to apply resin sealants on OCS wells. These applications of resin as the only well sealant must be chosen to allow monitoring of seal performance over time (e. g. temporary abandonment) and with viable pathway to repair any seal failure that may occur. Active collaboration encouraged by BSEE to potentially reduce risk through improved well sealant acceptance would accelerate field trial.

Establish Resin Design, Placement, and Performance Regulations: Once sufficient performance data confirm resin as a viable well sealant for OCS, the information should provide adequate justification for establishing seal heights and waiting-on-sealant-time. Performance basis for resin regulations is assumed to match that of current Portland cement regulations.

Include Resin Sealant Regulations into 30 CFR 250.1715, 30 CFR 250.1721, 30 CFR 250 415, etc. as warranted: Regulation of volumes and seal function can be structured as those currently covering Portland cement. Resin performance specifications or industry guidelines can be incorporated by reference similar to the incorporation of API RP 65 (Recommended Practice for Cementing Shallow Water Flow Zones in Deep Water Wells) into 30 CFR 250.415 (e). The gap analysis of zonal isolation regulations was perused to identify industry standards for barriers, the requirements and regulations in the OCS, domestic onshore, international onshore and international offshore areas. This analysis compared and contrasted the regulations identified with current BSEE zonal isolation requirements and provide recommendations for improvement in well safety.
A flowchart describing the steps outlined to achieve the stated recommendation is presented in Section 13.4.

3.0 BACKGROUND AND REPORT STRUCTURE

A resin is defined as a liquid substance that can be converted into a rigid polymeric solid by chemical or thermal treatment. Resin reacts with a curing agent to transform from a liquid to a highly-crosslinked three-dimensional solid network. This reaction, known as curing, is chemically irreversible and generates a rigid polymer that will not melt or depolymerize after curing; therefore, they are dimensionally stable as well as chemically and thermally resistant.

This investigation was undertaken to address utility of resins as OCS well sealants. Evolution of petroleum well sealants tracks Portland cement developing into the well sealant of choice for the oil industry. Portland cement has been used as a construction material for centuries and was first utilized as a well sealant over a century ago when shallow wells created low-stress conditions for barrier function. Portland cement was inexpensive, mixable with water to form a pumpable slurry, and set to form a solid seal. As well depths, temperatures, pressures, and architecture grew harsher; technology was developed for Portland cement to extend its applicability. Thus, modified cement chemistry and grind along with hundreds of additives including set retarders, viscosity modifiers, fluid loss additives, thermal stability additives, and mechanical property enhancers have been developed to expand Portland cement's performance limits. In reality, this brittle material is far from ideal as a durable sealant in today's highly stressed well environments. When a crushing force is applied to cement, the cement is deformed beyond its capacity, and the brittle cement will shatter.

On the other hand, resin chemistry was introduced commercially around 100 years ago. The material category's benefit as a long-lasting, durable adhesive and sealant for high-temperature, high-stress applications was recognized immediately. Significant development work had produced a solid foundation of resin chemistry by the time the drilling industry first commercialized resins as a well sealant in the 1960's (Ostroot 1970). Since that time, resin's temperature range and durability have been expanded through development within the electronics, aircraft, health, and aerospace industries. Correspondingly, increasing demands for durable well sealants have pulled researchers to consider resins as sealants for wells under extreme operating conditions

The first use of synthetic resins was that of cellulose nitrate in 1860 but it was not until 8 decades later before resins found limited application in the oilfield as referenced above. Recognition of resin's penetrating ability compared to Portland cement slurry drove development of epoxy resin as sealant for gravel pack consolidation and well plugging during the 1980's and 1990's (Dartez 1994). Recent advances in epoxy chemistry have created resurgence in their use as well sealants over the past decade (Shell Oil Company 2004) (Urdaneta 2014) (Leal 2016). Resins offer many properties that suggest that they will have superior performance compared to Portland cement for annular sealing of oil wells.

Over the past decade, resin commercial well sealant development and field trials have steadily increased as evidenced by increasing number of resin application case history papers in the literature. These products and applications have usually been one-off occurrences designed for difficult or critical remedial or abandonment seal applications. Little general fundamental or background information has been supplied although numerous published articles describe particular resin attributes or design issues and illustrate successful field applications. However, these initial results of resin sealant success in curing difficult well seal issues illustrate potential for resin to deliver more durable well barriers. The prospect of improved well integrity is generating increased interest in exploration of resin's potential as a well sealant. Several industry organizations (NORSOK, PACE, Oil & Gas UK) have endeavored to expand fundamental understanding of resin well sealant potential, to categorize the myriad design and application parameters to be addressed for resin well sealants, and to develop guidelines for resin use as a well sealant. These guidelines are fully referenced and further discussed in Section 13.0.

BSEE recognized the increasing interest in resin well sealant utility in wells on the OCSs. This investigation was commissioned by BSEE to address the objectives stated above to better prepare BSEE and the OCS petroleum industry for coordinated and informed application of resin sealants if warranted.

A multi-disciplinary, collaborative approach was designed for this project to achieve the stated objectives. The team for the effort included an Industry Advisory Group composed of subject matter experts (SMEs) in the area of OCS well construction and operations, wellbore sealants, and resin products. This group of experts has provided guidance throughout the project on actual OCS wellbore conditions, operations, and issues in the construction process. The inclusion this SME group provided focus for the project and ensured the results of this project are practical and immediately applicable to OCS wells. Engineers, scientists and field experts have rounded out the remainder of the project team providing depth of knowledge to this effort. Throughout the proposed work, careful consideration to HSE concerns have been addressed including any handling, operational, or disposal issues for personnel or the environment.

This final report of the Resin versus Cement investigation is comprehensive. All work performed under this project is reported herein. The task-based structure of the report follows that of the initial proposal, Project Management Plan, and the monthly reporting format. Objectives, methods, data, and analysis are reported for each task and subtask. Results are analyzed and discussed in detail to guide the reader through the process of analyzing results to develop the conclusions and recommendations which are presented in the previous section.

4.0 TASK 1.0 - FORMATION OF INDUSTRY ADVISORY GROUP

The industry advisory group was formed to provide broad industry perspective for the investigation. Several oil companies including Conoco and Fieldwood were represented continuously throughout the project’s duration while other oil company representatives contributed to specific portions of the work. Wild Well Control provided abandonment engineering personnel for service company perspective. The advisory group requested anonymity for all participants. Several companies participated in the group on the condition that their corporate identity was not revealed.

Each participant was knowledgeable and experienced in OCS well construction, remediation, and abandonment operations. Expertise ranging from operations to engineering and design, to management were represented. Several participants had first-hand operational experience applying resin as a sealant in an OCS well.

This group was instrumental in establishing conditions for resin: Portland cement comparison described in Section 6.0 of this report. Several group meetings and one-on-one conversations provided basis for operational guidelines appearing in Section 10.0 and cost benefit analysis covered in Section 12.0. The group expressed a strong, unified belief that the first major focus of resin application in the OCS be in remedial and abandonment operations.

5.0 TASK 2.0 - REVIEW OF PREVIOUS WORK - LITERATURE REVIEW

The objective of this task was to analyze state of the art of resin as a well sealant as documented in public domain technical literature. Two reports summarizing results of this task were prepared and are presented in Appendix A. The initial report covered all information uncovered during the time initially allotted for this task. However, as resin suppliers were recruited for supply of test materials and formulations, additional technical and commercial literature were discovered prompting preparation of a supplemental report.

The reports contained complete literature review citations with summary of the reported information. The reviewed information helped identify resin classes applicable as well sealants, identify commercial suppliers of resin well sealants past and present, characterize resin sealant application issues and attempts to identify guidelines, and provide case histories of resin applications.

6.0 TASK 3.0 - GATHERING AREA CONDITIONS IN THE OCS FOR RESIN APPLICATION

This critical task set the parameters for the entire spectrum of resin comparisons. The objective was to choose a range of test conditions representative of possible resin application and exposure in both initial well construction and in remedial or abandonment work. This selection process started with exemplars for OCS and Deepwater wells used in two previous BSEE investigations (CSI Technologies 2011) (Sonnier 2015). These well designs were reviewed and modified within the Industry Advisory Group. Two Pro Forma well schematics, one from the OCS shelf (Figure 2) and one from Deepwater (Figure 3), were developed including casing strings, depth, hole size, temperature profiles, and representative sealant design criteria. Representative locations along each well were chosen to represent the application range of sealants. The Bottom hole, sea floor, and an intermediate depth locations were selected to establish the range of application testing environments (Table 1).

Temperature, pressure and sealant design requirements were assigned for primary and abandonment operations for each chosen point of interest. Representative cement compositions were specified to provide baseline data at each test point. Then resin sealants were designed for performance comparison for each application. Review of the general application conditions lead to acceptance of three test temperatures: 75^{o}F (surface), 150^{o}F (intermediate), and 240^{o}F (bottom hole) Figure 1. These three application regions served as comparison for all resin performance.

Pro Forma well schematics, temperatures and pressures, are presented in Figure 2 and Figure 3. Figure 2 and 3 are the well schematics that were used to determine the well properties listed in Table 1.

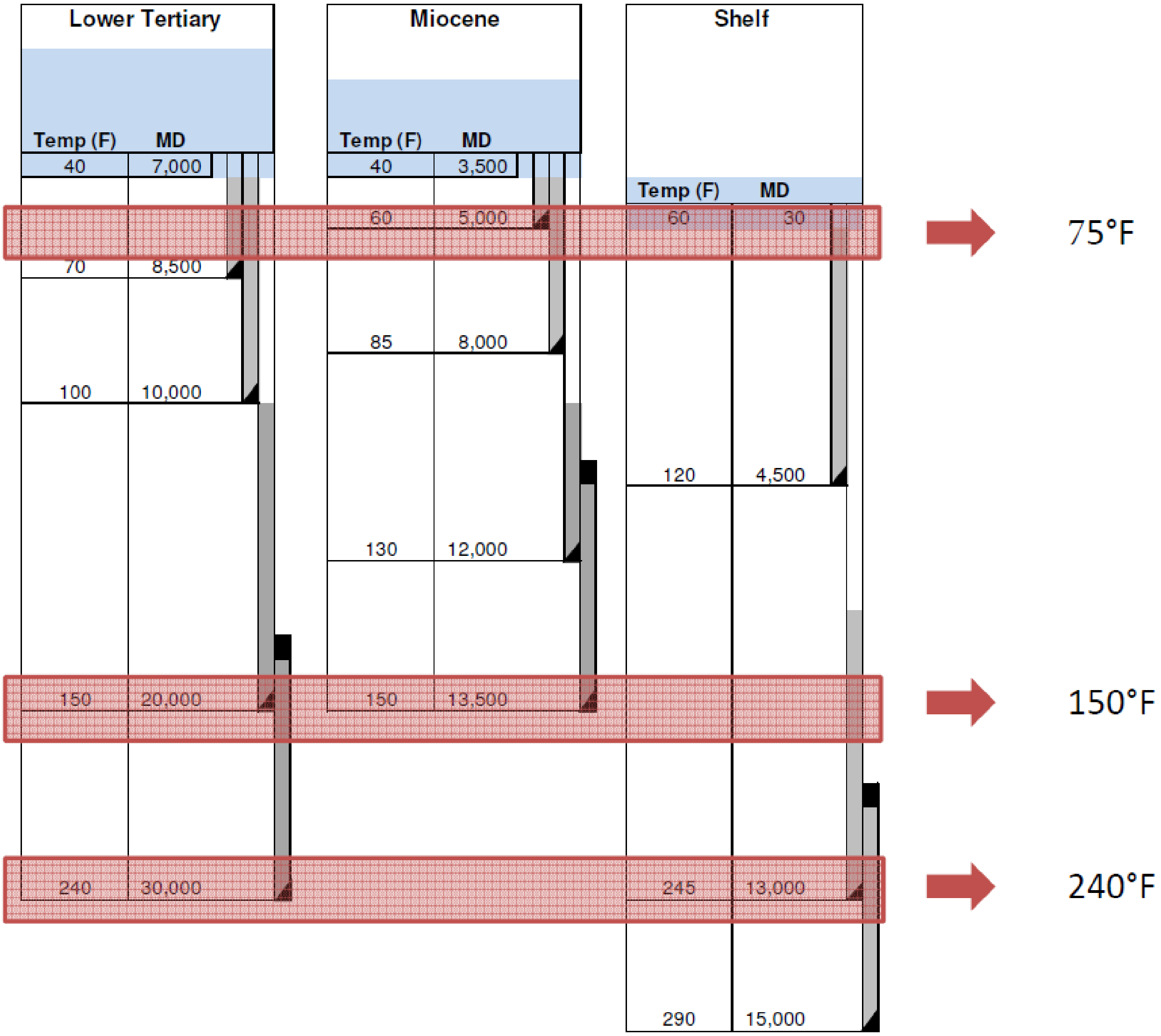
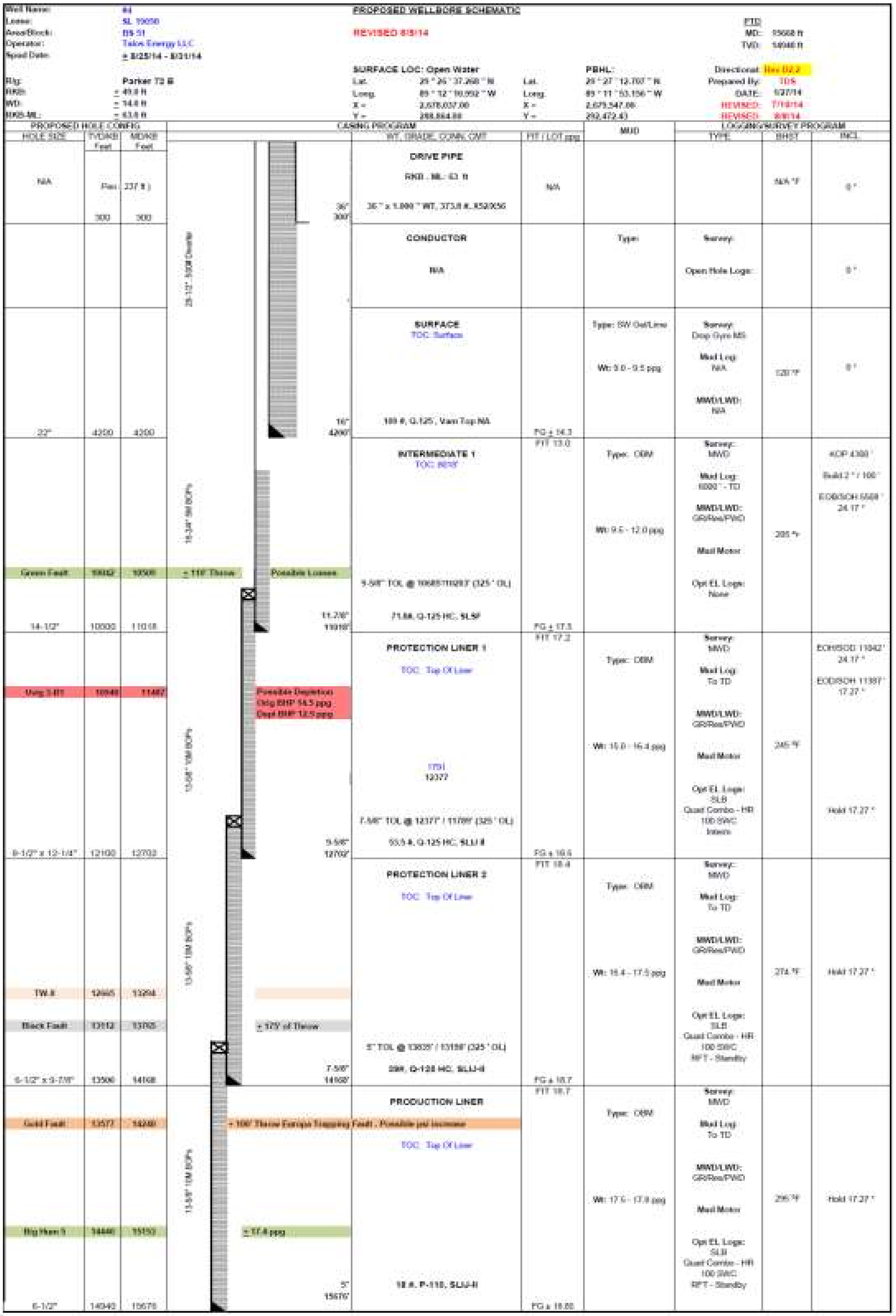


Figure 1: Well Schematic Summary



PROPOSED WELLBORE SCHEMATIC

REVISED 8/8/14

Well Name: #4
Lease: SL 19050
Area/Block: BS 51
Operator: Talos Energy LLC
Spud Date: ± 8/25/14 - 8/31/14

Rig: Parker 73 B
RKB: ± 49.0 ft
WD: ± 14.0 ft
RKB-ML: ± 63.0 ft

SURFACE LOC: Open Water
Lat. 29 ° 26 ' 37.268 " N
Long. 89 ° 12 ' 10.952 " W
X = 2,678,037.00
Y = 288,864.88

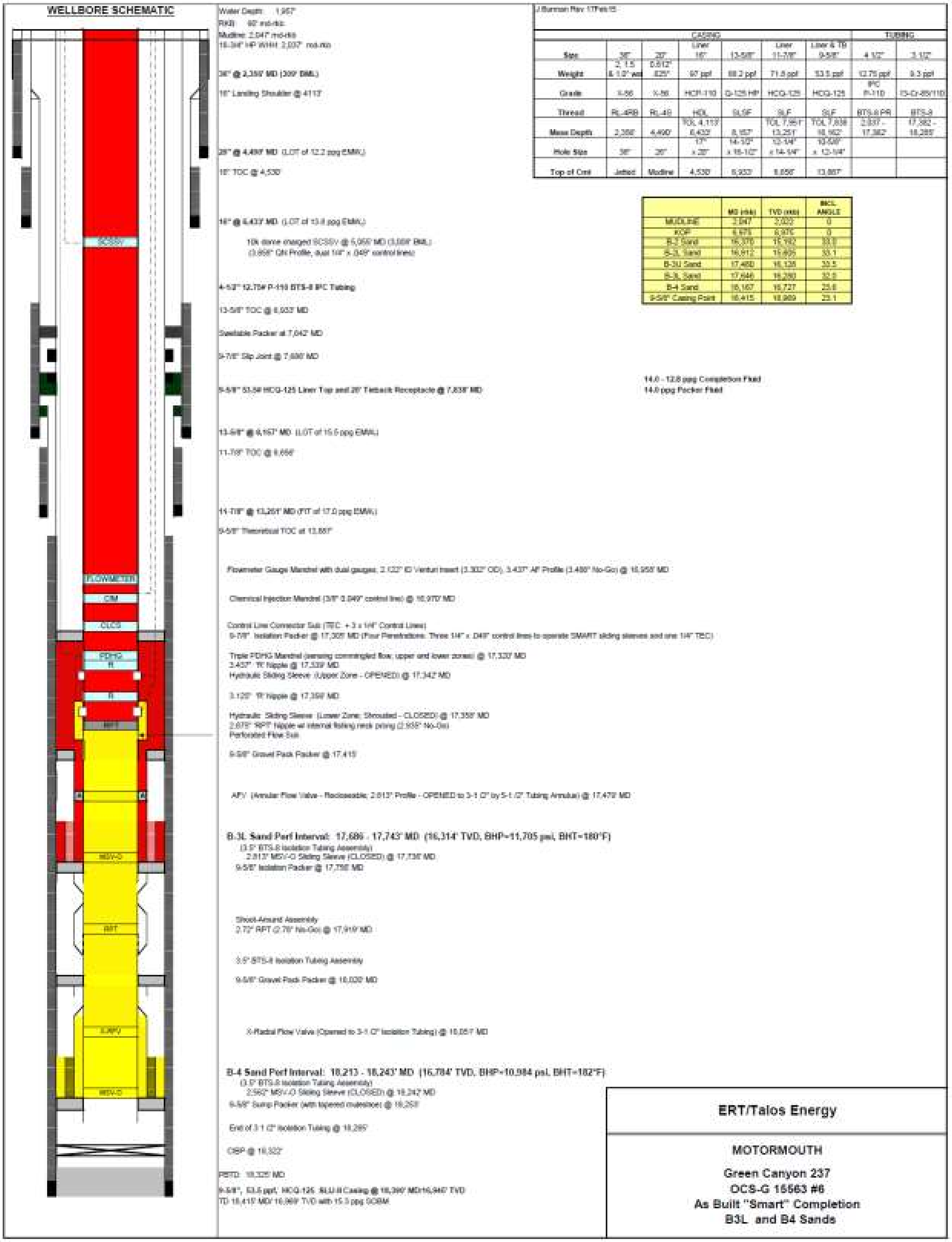
PBHL:
Lat. 29 ° 27 ' 12.707 " N
Long. 89 ° 11 ' 53.156 " W
X = 2,679,547.08
Y = 292,472.43

PTD
MD: 15668 ft
TVD: 14940 ft

Directional: Rev D2.2
Prepared By: TDS
DATE: 5/27/14
REVISED: 7/18/14
REVISED: 8/8/14

HOLE SIZE	TVDKB Feet	MDKB Feet	CASING PROGRAM	WT, GRADE, CONN, CMT	FIT / LOT ppg	MUD	TYPE	BHST	INCL
N/A	(Pen: 237 ft) 300	300	36" 300'	DRIVE PIPE RKB - ML: 63 ft 36 " x 1.000 " WT, 373.8 #, X52/X56	N/A			N/A °F	0 °
			28-1/2" 5KM Diverter	CONDUCTOR N/A		Type:	Survey: Open Hole Logs:		0 °
22"	4200	4200	16" 4200'	SURFACE TOC: Surface 109 #, Q-125, Vam Top NA	FG ± 14.3	Type: SW Gel/Lime Wt: 9.0 - 9.5 ppg	Survey: Drop Gyro MS Mud Log: N/A MWD/LWD: N/A	120 °F	0 °
			18-3/4" 5M BOPs	INTERMEDIATE 1 TOC: 8018'	FIT 13.0	Type: OBM Wt: 9.5 - 12.0 ppg	Survey: MWD Mud Log: 6000' - TD MWD/LWD: GR/Res/PWD Mud Motor Opt EL Logs: None	205 °F	KOP 4300 ' Build 2 ° / 100 ' EOB/SOH 6568 ' 24.17 °
Green Fault	10002	10509	± 110' Throw	Possible Losses					
14-1/2"	10500	11018	11-7/8" 11018'	9-5/8" TOL @ 10685'/11093' (325 ' OL) 71.8#, Q-125 HC, SLSF	FG ± 17.5				
				PROTECTION LINER 1 TOC: Top Of Liner	FIT 17.2	Type: OBM Wt: 15.0 - 16.4 ppg	Survey: MWD Mud Log: To TD MWD/LWD: GR/Res/PWD Mud Motor Opt EL Logs: SLB Quad Combo - HR 100 SWC Intern	245 °F	EOH/SOD 11042 ' 24.17 ° EOD/SOH 11387 ' 17.27 ° Hold 17.27 °
Uvig 3-B1	10940	11487	13-5/8" 10M BOPs	Possible Depletion Orig BHP 14.5 ppg Dept BHP 12.5 ppg					
				TVD 12377					
8-1/2" x 12-1/4"	12100	12702	9-5/8" 12702'	7-5/8" TOL @ 12377' / 11789' (325 ' OL) 53.5 #, Q-125 HC, SLIJ II	FG ± 16.6				
			13-5/8" 10M BOPs	PROTECTION LINER 2 TOC: Top Of Liner	FIT 18.4	Type: OBM Wt: 16.4 - 17.5 ppg	Survey: MWD Mud Log: To TD MWD/LWD: GR/Res/PWD Mud Motor Opt EL Logs: SLB Quad Combo - HR 100 SWC RFT - Standby	274 °F	Hold 17.27 °
TW-8	12665	13294							
Black Fault	13112	13765	± 175' of Throw						
6-1/2" x 9-7/8"	13506	14168	7-5/8" 14168'	5" TOL @ 13828' / 13198' (325 ' OL) 39#, Q-125 HC, SLIJ-II	FG ± 18.7				
			13-5/8" 10M BOPs	PRODUCTION LINER TOC: Top Of Liner	FIT 18.7	Type: OBM Wt: 17.5 - 17.8 ppg	Survey: MWD Mud Log: To TD MWD/LWD: GR/Res/PWD Mud Motor Opt EL Logs: SLB Quad Combo - HR 100 SWC RFT - Standby	295 °F	Hold 17.27 °
Gold Fault	13577	14240	+ 100' Throw Europa Trapping Fault , Possible psi increase						
Big Hum 5	14440	15153	± 17.4 ppg						
6-1/2"	14940	15676	5" 15676'	18 #, P-110, SLIJ-II	FG ± 18.88				

Figure 2: OCS Shelf Well Schematic



	CASING						TUBING	
Size	36"	20"	Liner 16"	13-5/8"	Liner 11-7/8"	Liner & TB 9-5/8"	4 1/2"	3 1/2"
Weight	2, 1.5 & 1.0" wall	0.812" .625"	97 ppf	88.2 ppf	71.8 ppf	53.5 ppf	12.75 ppf	9.3 ppf
Grade	X-56	X-56	HCP-110	Q-125 HP	HCQ-125	HCQ-125	IPC P-110	13-Cr-85/110
Thread	RL-4RB	RL-4S	HDL	SLSF	SLF	SLF	BTS-8 PR	BTS-8
Meas Depth	2,358'	4,490'	TOL 4,113' 6,433'	8,157'	TOL 7,951' 13,251'	TOL 7,838' 18,392'	2,037' - 17,382'	17,382' - 18,285'
Hole Size	36"	26"	17" x 20"	14-1/2" x 16-1/2"	12-1/4" x 14-1/4"	10-5/8" x 12-1/4"		
Top of Cmt	Jetted	Mudline	4,530'	6,933'	8,656'	13,887'		

	MD (rkb)	TVD (rkb)	INCL ANGLE
MUDLINE	2,047	2,022	0
KOP	6,975	6,975	0
B-2 Sand	16,376	15,192	33.0
B-3L Sand	16,912	15,605	33.1
B-3U Sand	17,460	16,128	33.5
B-3L Sand	17,646	16,280	32.0
B-4 Sand	18,167	16,727	23.6
9-5/8" Casing Point	18,415	16,969	23.1

Figure 3: OCS Deepwater Well Schematic

Table 1 summarizes the different well conditions taken from the well schematics and were used for testing the cement designs.

Table 1: Well Descriptions

Well Type	Program	Depth	Temperature BHST
OCS Shelf Well	16” Surface Lead	Seabed	70°F
	9 5/8” Liner	11,000 ft	205°F
	5” Production Liner	15,000 ft	350°F
OCS Deepwater Well	20” Surface Lead	4,490 ft	78°F
	16” Liner	6,400 ft	133°F
	9 5/8” Production Tieback	18,390 ft	201°F

7.0 TASK 4.0 - FUNDAMENTAL CHEMICAL EVALUATION OF RESINS

This task was undertaken to close the gap in understanding regarding fundamental chemical and physical behavior of resin products under well conditions. Resin chemistry was investigated to determine if resins actually exhibit attributes applicable to durable well sealant function for OCS wells. Chemistry of resins and Portland cement controlling hardening, mechanical properties, bonding, chemical resistance, and thermal stability were compared. Underlying chemical basis for resin’s heightened performance was investigated. Additionally, Portland cement performance was analyzed to assess chemical basis for any limitations in that material’s seal function.

Dr. Allen Apblett, Chemistry Professor at Oklahoma State University, pursued Task 4.0 in which the effects of temperature, well fluids, and time on various resin formulas and Portland cements were evaluated. The results are presented in two reports contained in Appendix A.

Initial thermal gravimetric data for resins analyzed in the first report supported resin utility as a well sealant. Thermally and chemically, resin sealants are more durable than Portland cement over time at temperature. Better sealing and shock resistance potential result from chemical stability and proper crosslink density. Resin chemistry can also alleviate thermal degradation. While resins were mostly abandoned in the past due to cost, potential to prevent seal failure makes consideration of resin sealant highly attractive.

Four general categories of thermosetting resin chemistry have potential application as well sealants. These chemical resin types are differentiated by the chemistry of the polymer or pre-polymer material that is crosslinked. Each of the resin chemical categories, described below, can comprise a range of variations in polymer chain length, crosslink site frequency, etc.

Epoxy Resin: Epoxy resins consist of low molecular weight pre-polymers containing multiple epoxy groups that are reacted to form a dense, highly cross-linked matrix via addition of polyfunctional molecules (hardeners and/or accelerators) such as amines or alcohols. The rate and extent of this cross-linking reaction is determined primarily by temperature, time, and the chemical nature of the epoxy resin and hardeners. The final physical properties of the cured resin are also determined by these factors. Conventional epoxy resin technologies are extremely sensitive to water, reacting exothermically and becoming deactivated by hydrolysis of the epoxide group. However, this problem has been circumvented and there are commercial epoxy resins that will actually set underwater. This has been adapted to newer oilfield epoxy resin systems that are much less sensitive to contact with water. In general, epoxy resins have the highest bonding strength of the resins used in the oilfield. The setting of epoxy resins can occur by condensation or free-radical reactions. The latter are subject to interferences during resin placement if they are exposed to radical scavengers. Epoxy resins can be stable to temperatures above 400°F and, in general, have better bonding properties and strengths than other resin systems. Epoxies can have relatively fast curing times but this can be adjusted so that restrictive placement times are not encountered.

Phenolic Resin: Phenolic resins, also known as, phenol formaldehyde resins (PF) are synthetic polymers obtained by the reaction of phenol or a substituted phenol with formaldehyde. These were the first fully synthetic commercial resins and were used for the preparation of the plastic known as Bakelite. Phenolic resins are easily set to rigid cross-linked solids through the reaction of heat and either acidic or basic catalysts. The product so-produced has excellent thermal stability. During resin placement, phenolic resins are not highly sensitive to water and will not be deactivated by limited contact with water. Indeed, the high viscosity of uncross-linked phenolic resins suppresses excessive mixing with water in the wellbore. The cross-linking and setting of phenolic resins is not highly subject to interference by chemicals present in the wellbore. Commercial base-catalyzed phenolic resins are applicable over a downhole temperature range of 90°F to 170°F and are stable to downhole temperatures up to 450°F. Phenolic resins are well known for their temperature stability and also for their comparably very high carbon yields under non-oxidative atmosphere, when compared to many other resin chemistries. Acid-catalyzed phenolic resins are considered to be most ideally applied over a downhole temperature range of 100°F to 130°F.

Furan Resin: Furan resins are oligomeric products prepared from compounds containing a furan ring that are capable, on heating or in the presence of catalysts, of converting into cross-linked polymers. The most important of these are obtained from furfuryl alcohol that is itself derived from renewable biomass materials. The resins harden slightly upon heating; the process is accelerated in the presence of acid catalysts, especially aromatic sulfonic acids or mineral acids. The hardened products have high resistance (up to 700˚F) to heat, acids, and alkalis. Furan resins are, in general, weaker resins than epoxy and phenolic resins and are applicable over a downhole temperature range (downhole temperature possibly attained by cooling) of 60°F to 350°F. Modern furan resins do not contain the monomer species but instead contain furan oligomers leading to a reduction of the reactivity of the polymerization reaction and greatly increasing the controllability of the furan resin polymerization reaction. These resins are generally set by a single-fluid process and contain an organic acid catalyst and an ester. The latter is present to react with the water formed during the condensation reaction driving the polymerization reaction further to completion and rendering a stronger hardened furan resin. Furan resins provide better control over the resin maturation time and do so over a larger temperature range compared with the epoxy resin technology. Their lower viscosity can also be beneficial to their placement in oil wells.

Polyester Resin: Polyester resins are unsaturated synthetic resins formed by the reaction of dibasic organic acids and polyhydric alcohols. The liquid resin is converted to a solid by cross-linking chains via free radical coupling of the unsaturated bonds. Cross-linking is induced by adding a compound such as a peroxide that easily decomposes into free radicals. Polyester resins are thermosetting and, as with other resins, cure exothermically so care must be taken in their formulation

Hybrid Systems: The chemistries of the resins are not always incompatible with each other so that hybrid systems with advantages over each component can be prepared. For example furan/epoxy systems are promising. Furthermore, resin systems and cements can be combined to produce so-called plastic cements that may have promise of deep well cementing.

Several gaps in the initial resin thermal gravimetric data were addressed in subsequent testing that continued until the end of the project. This fundamental testing was designed to quantify chemical and mechanical durability of resin over time and exposure to well fluids.

7.1 Thermal Gravimetric Analysis

The starting point for determining the thermal behavior of the candidate resins was to utilize a Mettler Toledo TGA/DSC 1 instrument to perform the thermal gravimetric analysis (TGA). The TGA is a procedure in which a sample is heated while measuring the sample's mass over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions including glass transition and melting temperature, adsorption and desorption of molecular compounds and chemical phenomena that include thermal decomposition and solid-gas reactions such as oxidation or reduction. The melting point for cross-linked resins coincides with the degradation point. This precludes the use of resins past their melting points. Eight candidate resin samples were analyzed using a heating rate of 5˚C/minute in an atmosphere of flowing dry air (50 ml/min) from 25˚C to 600˚C. While this instrument simultaneously provides qualitative differential scanning calorimetry (DSC) measurements along with the thermal gravimetric results, these were not used. Instead, differential scanning calorimetry measurements were performed on a much more sensitive, quantitative instrument and these will be discussed separately below. The compositions of the eight samples are provided in Table 2, of which, five of these samples were epoxy resins, one a polyester, one phenolic and one a phenolic/epoxy blend. One sample 5W consisted only of epoxy resin (a bisphenol-F (BPF)/ epichlorohydrin resin) and hardener (diethyltoluenediamine). This combination of aromatic-based resin and hardener is expected to provide superior thermal stability compared to aliphatic-based systems. Two other samples were prepared with the same resin/hardener combination and ratio but with an added weighting material plus other reagents to produce a mixture suitable for oilfield applications. One sample 15 contained 31.4% weighting material by weight while the other 16 contained 50.2 wt. %. The fourth sample, 13, was similar to 15 but used a different hardener- a mixture of a modified amidoamine and an aliphatic polyalkylene containing polyamide-polyamine with high imidazoline content derived from the reaction of tall oil with tetraethylenepentamine. These hardeners differ from epoxy resin due to their aliphatic and polymeric nature and have been reported to be superior for use in resins with a high solids content. The sixth epoxy sample 17 was based on bisphenol A with the 60/40 modified amidoamine and aliphatic polyalkylene hardener. The other three resins tested included a phenolic resin 19, a mixed phenolic/epoxy resin 18 and a polyester resin 23. These samples were selected by CSI Technologies for thermal analysis due to their mechanical performance and to also ensure that all of the target resin types were characterized.

Table 2: TGA Systems

System	Formulation
13	12 lb/gal Epoxy Resin 1 + 32.7%total weight Weighting Agent
15	12 lb/gal Epoxy Resin 3 + 31.5%total weight Weighting Agent
16	13 lb/gal Epoxy Resin 4 + 39.2%total weight Weighting Agent

17	9.3 lb/gal Epoxy Resin 5
18	14 lb/gal Phenolic 1/Epoxy Resin 5 50/50%by weight + 41.8%total weight Weighting Agent
19	14.5 lb/gal Phenolic Resin 2 + 42.8%total weight Weighting Agent
23	14 lb/gal Polyester Resin 2
5W	Epoxy Resin with no solids

The thermal gravimetric analysis traces of the eight resins are presented in Figure 4 through Figure 11.

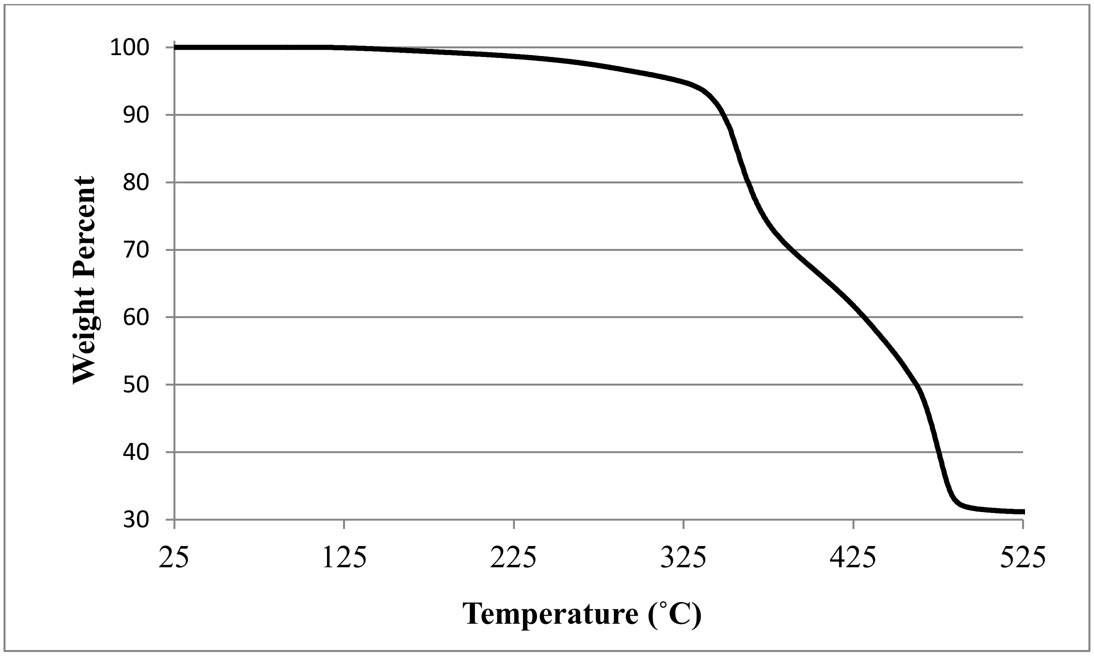


Figure 4: TGA Trace of System 13

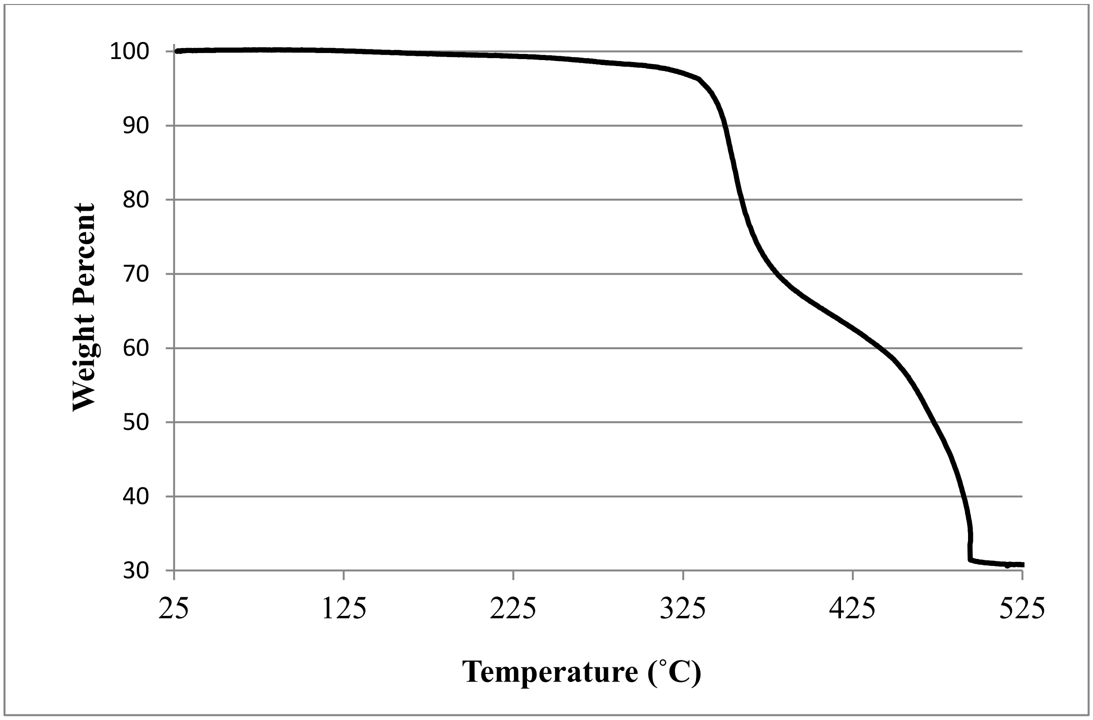


Figure 5: TGA Trace of 15

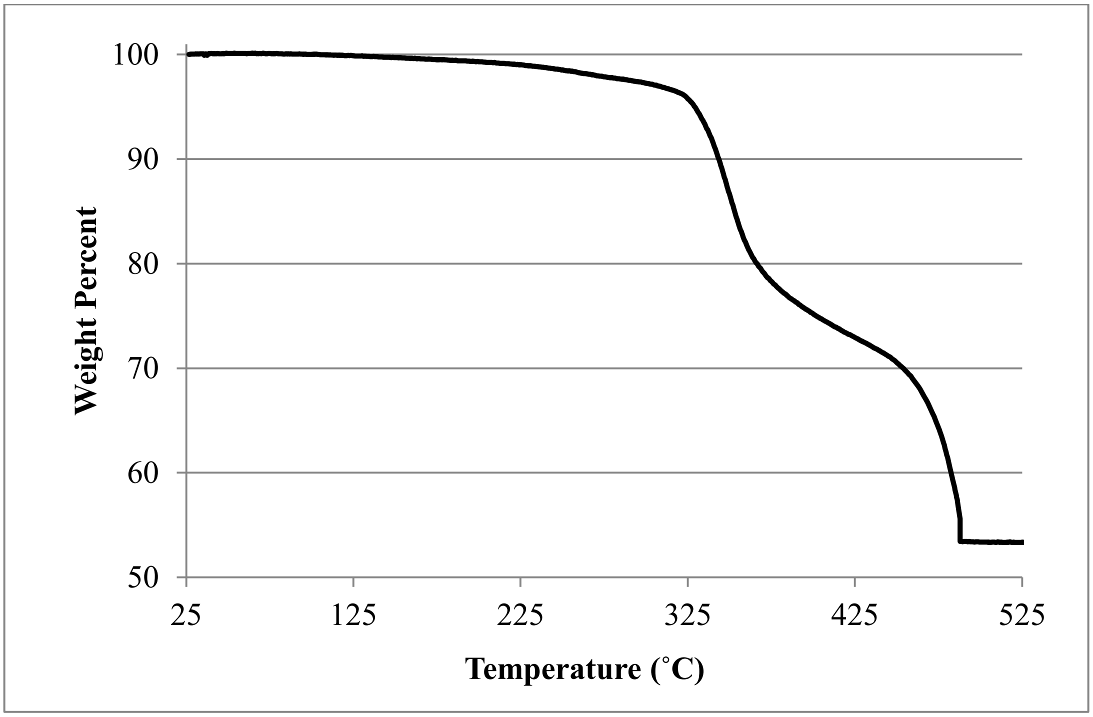


Figure 6: TGA Trace of System 16

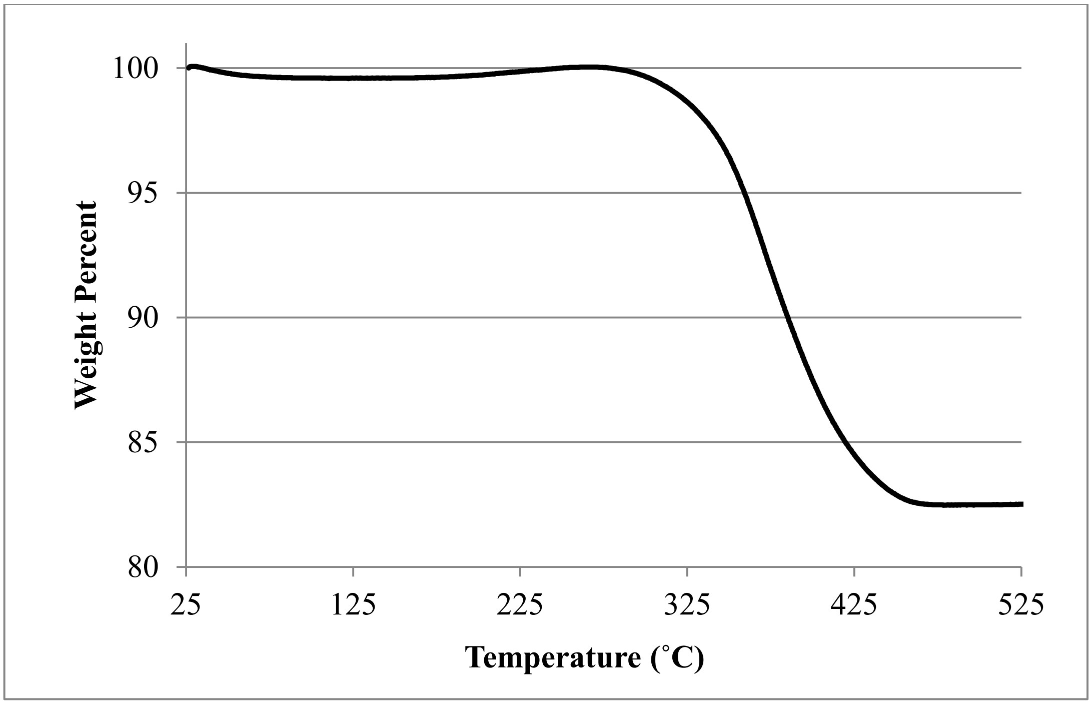


Figure 7: TGA Trace of System 19

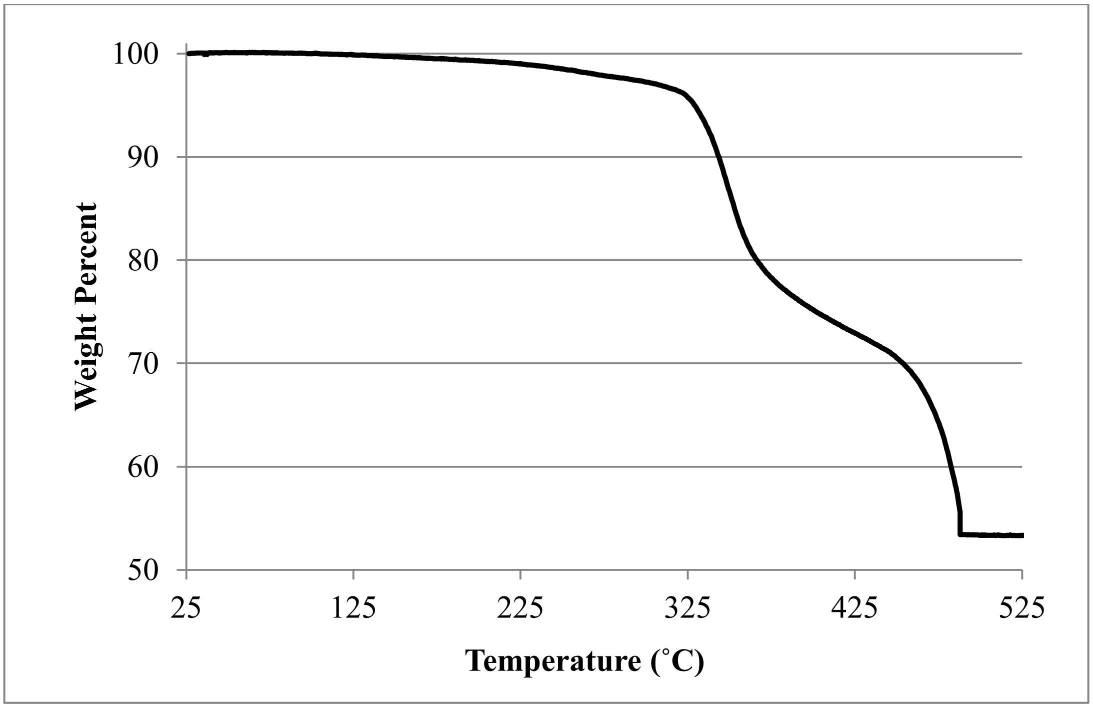


Figure 8: TGA Trace of System 17

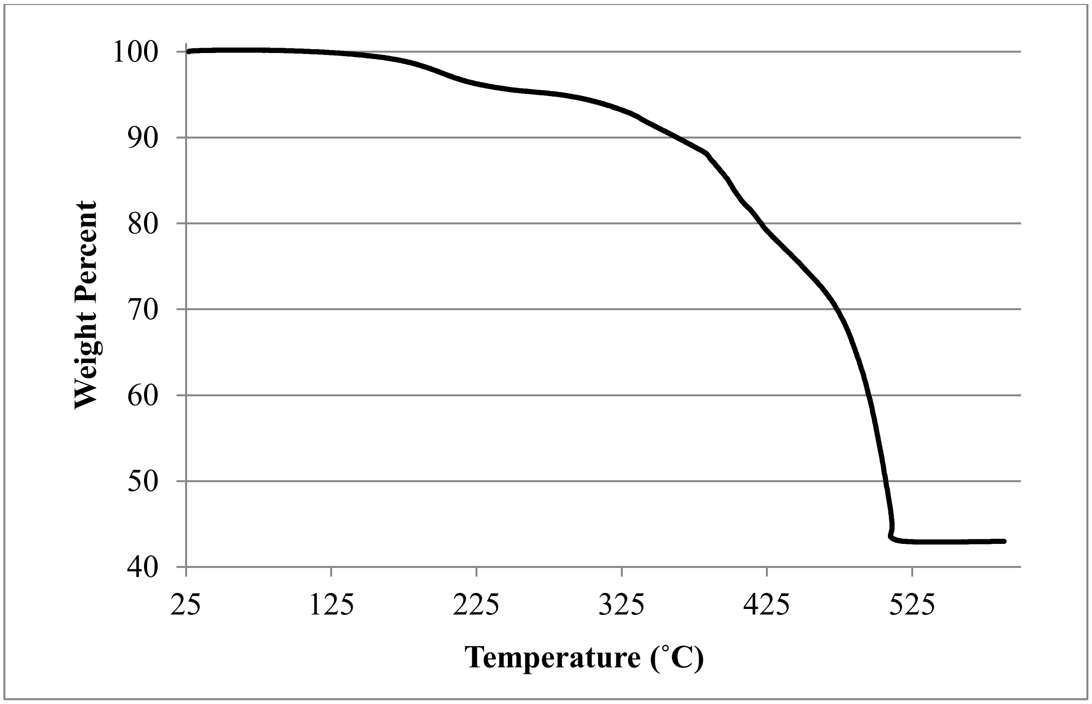


Figure 9: TGA Trace of System 18

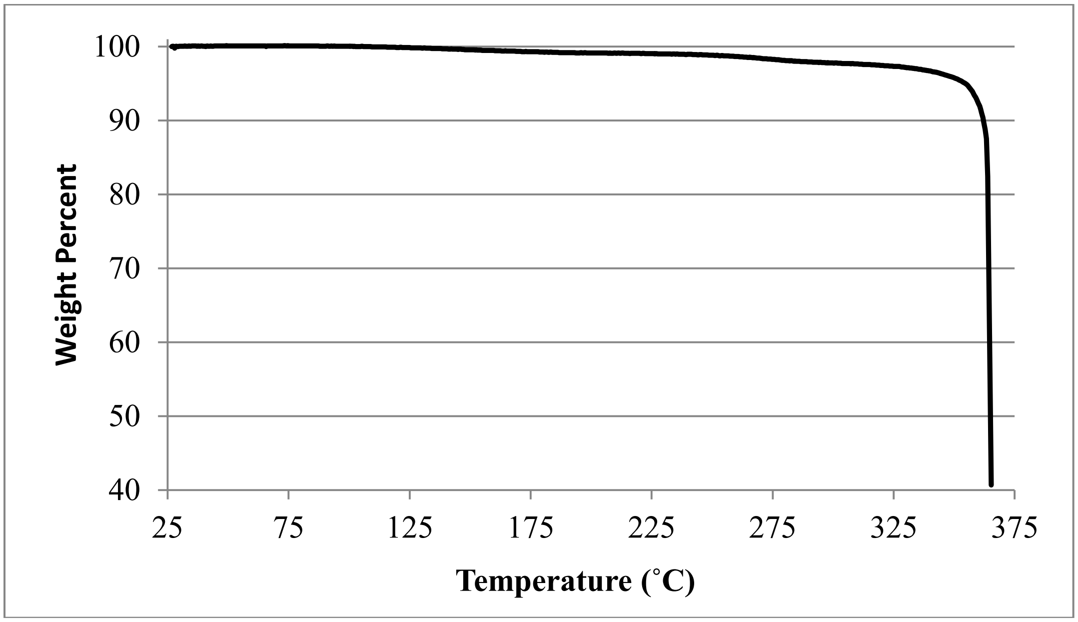


Figure 10: TGA Trace of System 5W

The pure bisphenol-f epoxy (sample 5W) hardened with diethyltoluenediamine showed high thermal stability, only beginning to decompose and combust at 348˚C. Figure 10 shows the TGA result - note that the graph is truncated due to the resin being expelled from the pan due to the violent combustion.

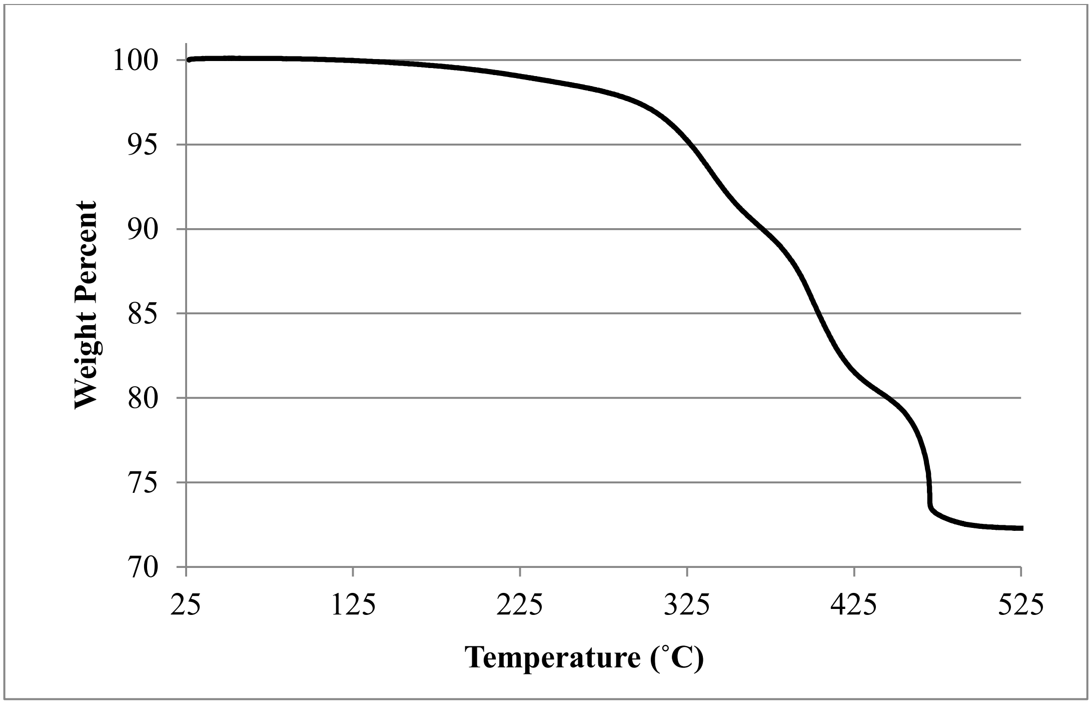


Figure 11: TGA Trace of System 23

Resin 23, a polyester based resin was also found to be quite thermally stable, decomposing above 227˚C as shown in Figure 11. There was a small mass loss above 100˚C that was likely due to release of water.

The results from the thermal gravimetric analysis experiments are summarized in
Table 3. For comparison purposes, the temperature at which a 1% loss of occurred was determined. The temperature at which the thermal degradation of the resin backbone was initiated was determined from the point where the first major mass loss occurred. Many of the samples showed weight losses (and a few showed weight gains) before the resin backbone began to degrade. These are also noted in
Table 3. Most of the losses are likely due to dehydration reactions that result from either removal of adsorbed water or condensation reactions of hydroxylated side chains. It is also possible that further thermally-activated cross-linking also occurred. The few cases where mass gains occurred can be attributed to reaction with gaseous oxygen. In order for this to lead to a weight gain, unsaturated carbons must be partially oxidized to ketones or acids or reactive methylene groups (for example, benzylic groups) are oxidized to ketone and water.

The 19 resin (Figure 7) is a phenolic resin. It had a weight loss in the TGA due to water loss up to 71˚C. It subsequently regained this mass due to an oxidation reaction upon further heating to 250˚C. At 286˚C the resin decomposed to a carbonaceous material. Note that phenolics are often used to make activated carbons.

The 18 resin, a 50/50 mixture of phenolic resin was stable to 175˚C (see TGA trace in Figure 8) but thereafter decomposed slowly to a carbonaceous solid. The initial 5.1% weight loss between 111 and 286˚C is likely due to condensation reactions of the phenolic resin that produce water as the byproduct.

For resin 5W there was a slight weight loss of 2.98% from 242 to 348˚C that is likely due to the beginning of the decomposition process as pendant groups are lost from the polymer. At low temperature, a loss of 0.68 wt. % was observed between 121 and 182˚C. This is believed to be mainly due to loss of water (see below for moisture balance results). If the temperature at which 1% weight loss is chosen arbitrarily as a comparative measure of thermal stability, it is found that the pure hardened resin is fairly stable with a temperature of 229˚C required to effect a 1% loss of weight.

Adding weighting agent prevents the violent combustion that occurs with the pristine hardened resin as was observed for resins 15 and 16 (Figure 5 and Figure 6). Instead, these resins display a two-step decomposition occurs leading to a final weight that corresponds roughly to the amount of manganese dioxide present. The presence of the various additives slightly lowers the decomposition temperatures and the temperature at which 1% of the weight loss is observed based upon the amount or resin actually present (218˚C for resin 15 and 193˚C for resin 16). Nevertheless, the resin mixtures remain very stable in the temperature regime in which they will be used. The presence of the additives also appears to slightly decrease the thermal stability of the resin backbone – the pristine resin degrades at 348˚C while the other resins are only stable to 315-324˚C. This may be attributed to the weighting agent an oxidant interacting with the polymer in a redox process.

Table 3: Results from Thermal Analysis

Sample	Temperature of 1% Weight Loss (˚C)*	Onset of Thermal Decomposition of Polymer Chain (˚C)	Other Significant Weight Losses
13	202 (177)	321˚C	0.20 %, 122-141˚C 1.00 %, 143-224˚C 3.55 %, 228-321˚C
15	254 (218)	324	0.45 %, 127-185˚C 2.26 %, 219-324˚C
16	226 (193)	315	0.43 %, 128-185˚C 2.68 %, 201-315˚C
19	318	286	0.37 % 25-71˚C Weight gain: 0.37 % 181-250
17	170	266	0.32 %, 114-154˚C 1.45%, 162-205˚C 1.30 %, 214-266˚C
18	172	286	5.10%, 111-286˚C
5W	229	348	0.68 %, 121-182˚C 2.98 %, 242-348˚C
23	227	280	2.01 %, 96-280˚C

*The number in parentheses is the temperature at which a weight loss of 1% occurs on the basis of the amount of resin present and not the full weight of the sample.

Replacement of the aromatic-based hardener with the aliphatic-based hardener led to a reduction in stability using the temperature required for a 1% weight loss as the criterion. The most comparable resins in terms of composition are 13 (aliphatic) and 15 (aromatic). The latter has a temperature for 1% weight loss (218˚C) that is 65˚C higher than that of the 13 resin (153˚C) There is also a significant weight loss in the range 140-225˚C for the epoxy resins with the aliphatic hardener (13 and 17) that was not observed for the resins with the aromatic hardener. Switching from bisphenol F to bisphenol A (resin 17) in addition to the change in hardener type produced a resin with lower stability than the 5W resin. The temperature of 1% weight loss was lowered by 59˚C and the onset of decomposition of the thermal chain was lowered by 82˚C. The difference between the two materials is the presence of two methyl groups in bisphenol A where there are 2 hydrogens in bisphenol F (Figure 12). It is possible that the methyl groups stabilize cations produced by cracking of the benzylic carbon bond and, in doing so, lower the temperature at which this thermal degradation step occurs for epoxy resins containing Bisphenol A. All of the bisphenol F epoxy resins did not begin to suffer from thermal degradation of their polymer backbones until well above 300˚C making them superior for high temperature applications.

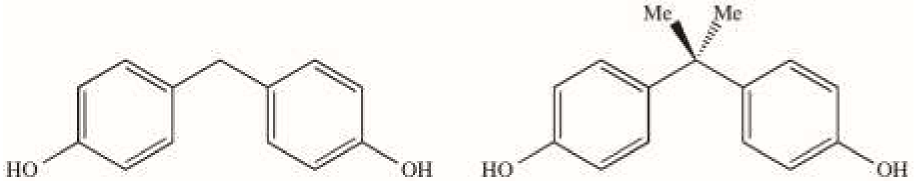


Figure 12: Bisphenol F (left) and Bisphenol A (right)

7.2 Isothermal Treatment of Resins at 150˚C in Air

In order to determine the stability of the resins in air at 150˚C, samples were tested in a moisture analysis balance. This measurement is different from thermal gravimetric analysis because the isothermal experiment allows for slow reactions and/or diffusion to reach completion. The percent weight losses for all samples and the time required to achieve these are presented in

Table 4. The results of these experiments are shown for the resins in Figure 13 through Figure 20. Notably, all loss of weight comes to completion after 20 to 300 minutes. Previously, other researchers extrapolated the initial weight-loss of epoxy resins for hundreds of years but it is evident that this weight-loss is self-limiting, not only for epoxy resins but for all resin types tested. Indeed infrared spectra shows that the weight loss of the epoxies was due to loss of water and had no effect on the resin backbone. Furthermore, the weight loss is reversible for the epoxies – after storing in 40% relative humidity, reanalysis gives a similar weight loss as measured the first time. The addition of weighting agent or the use of the polymeric hardener appears to slow the diffusion of gases out of the hardened resin. This may have important ramifications for prevention of gas seepage in oil wells. The phenolic resin 19 and the mixed phenolic/epoxy resins 18 showed higher weight losses that correlated with the phenolic content. These resins will be unacceptable if this weight loss leads to porosity or shrinkage, thus requiring more optimization of the chemical makeup of the phenolic resins. These optimizations should be achievable with the assistance of the resin manufacturers. The 23 and 15 resins were extremely stable and performed well in this experiment. The colorless resins (5W and 17) turned orange/red upon heating to 150˚C and the 23 darkened to a brown color. The other resins were too dark to discern any color changes.

Table 4: Percent Weight Loss and Time for Completion of Weight Loss for the Target Resins

Sample	Weight Loss at 150˚C	Time for Completion of Weight Loss (min)
13	2.7 %	290
15	1.0 %	90
16	1.9 %	280
19	11.0 %	200
17	3.5 %	380
18	5.4 %	330
5W	2.6 %	20
23	1.2 %	4.0

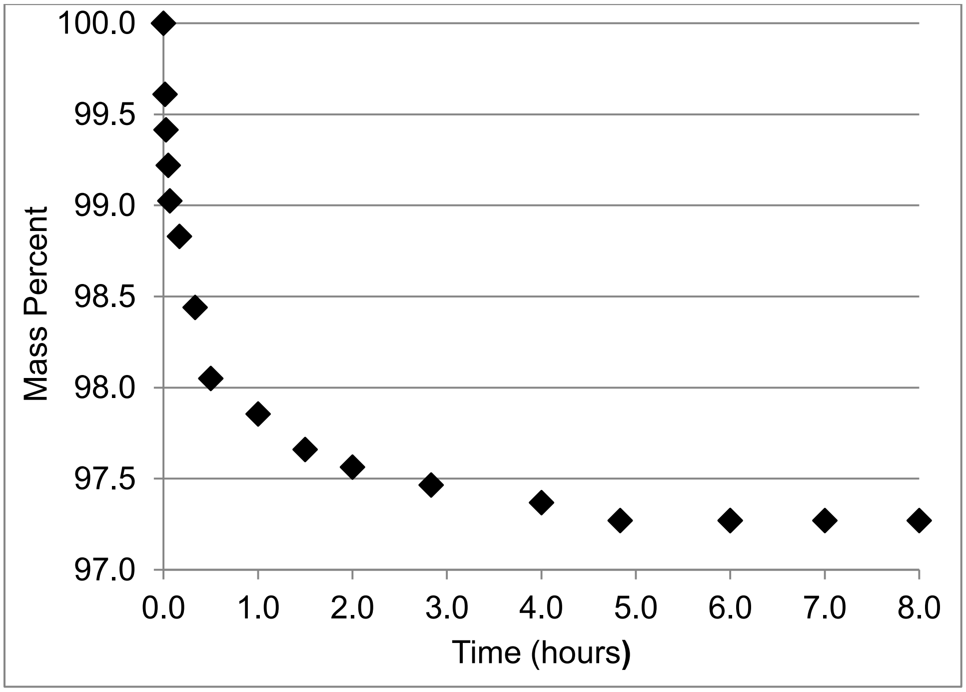


Figure 13: Moisture Balance Results for System 13

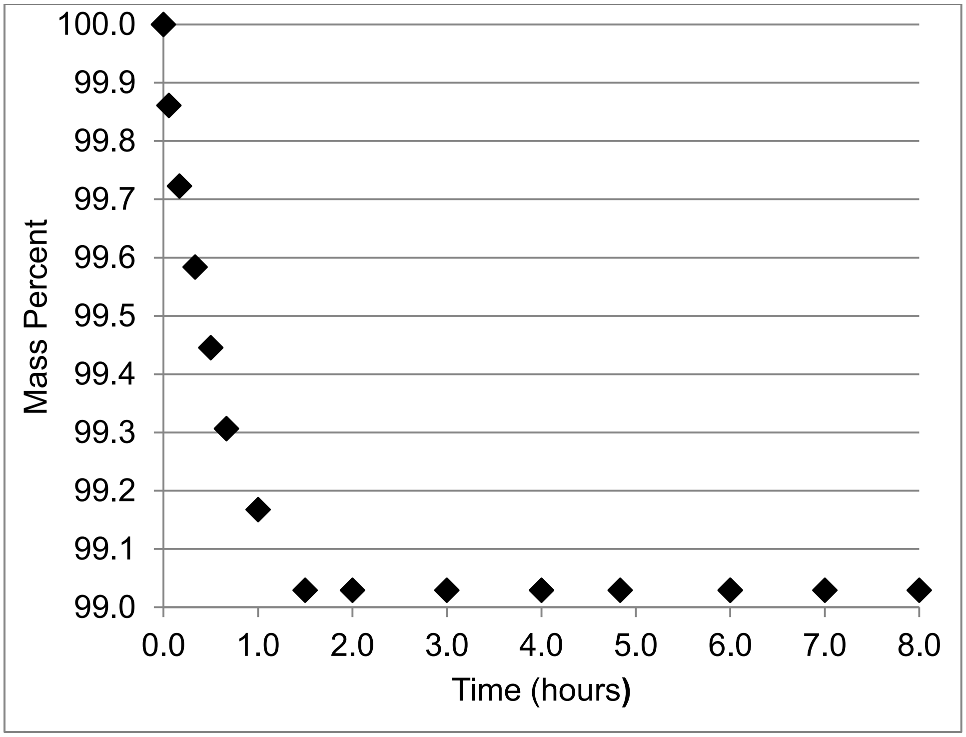


Figure 14: Moisture Balance Results for System 15

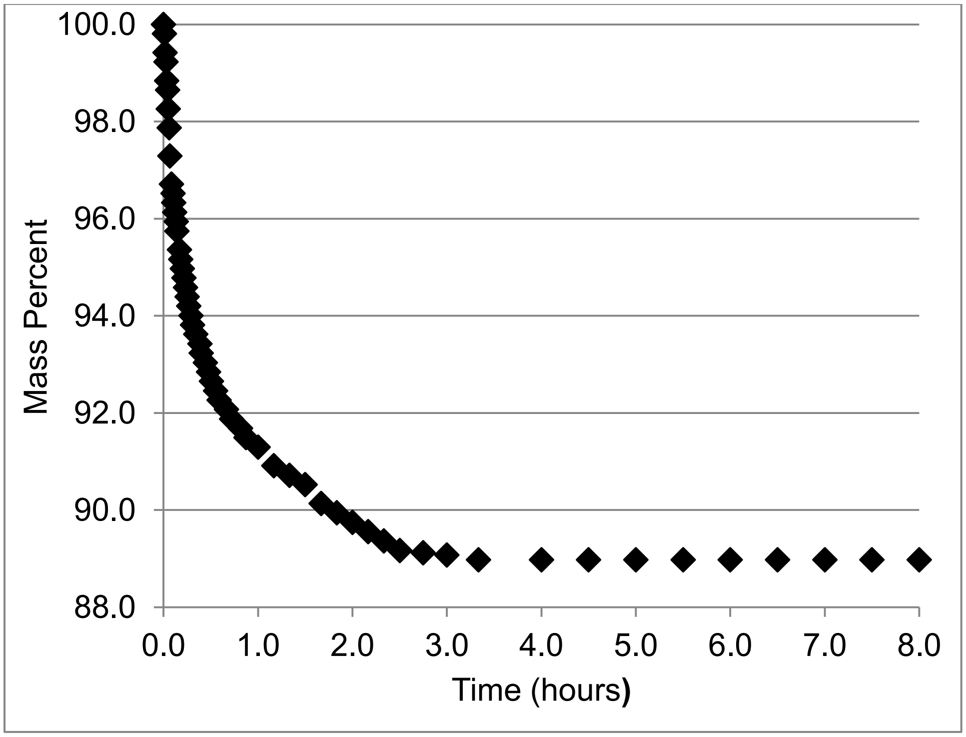


Figure 15: Moisture Balance Results for System 16

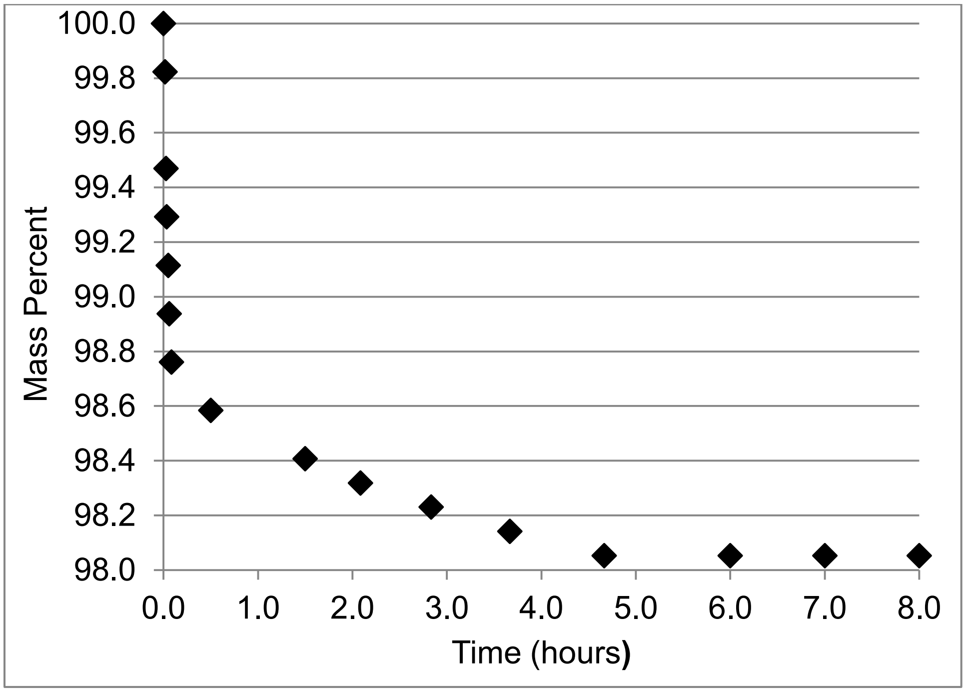


Figure 16: Moisture Balance Results for System 19

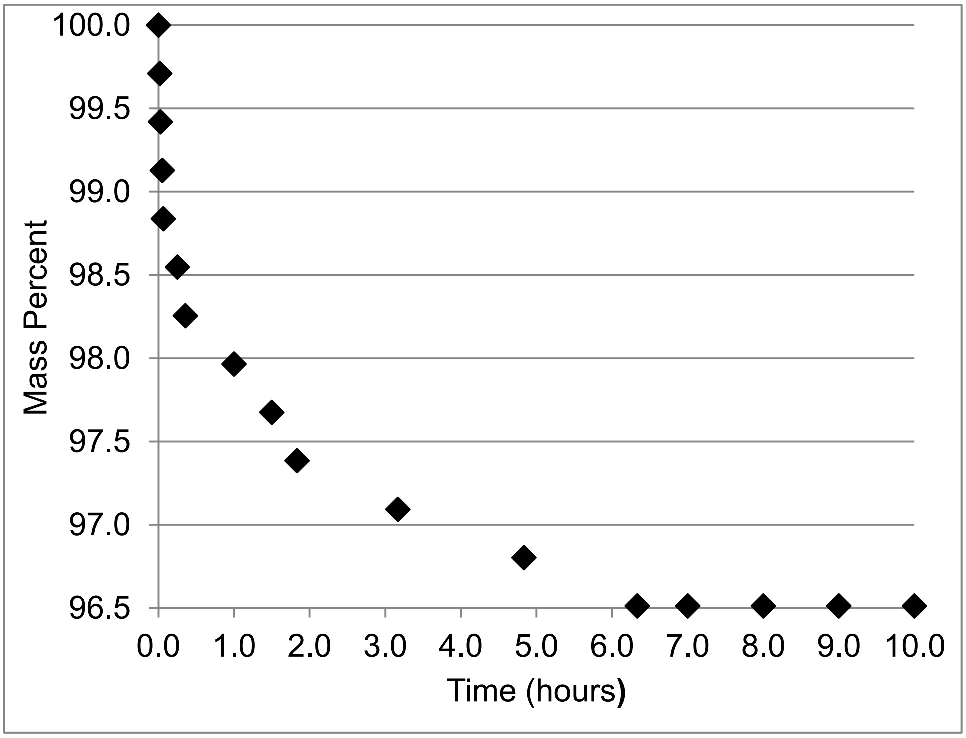


Figure 17: Moisture Balance Results for System 17

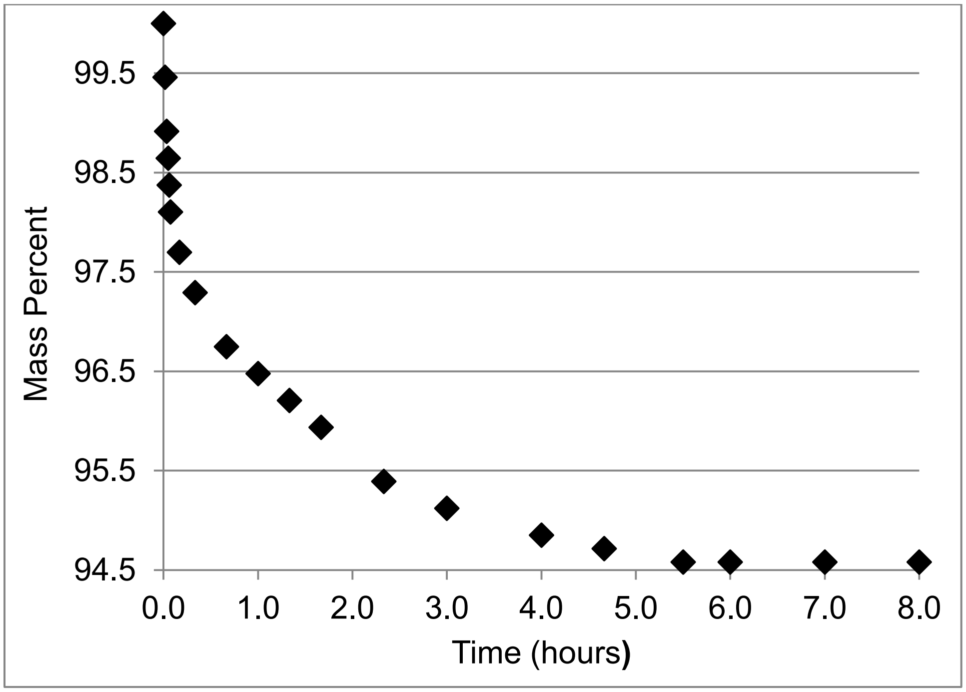


Figure 18: Moisture Balance Results for System 18

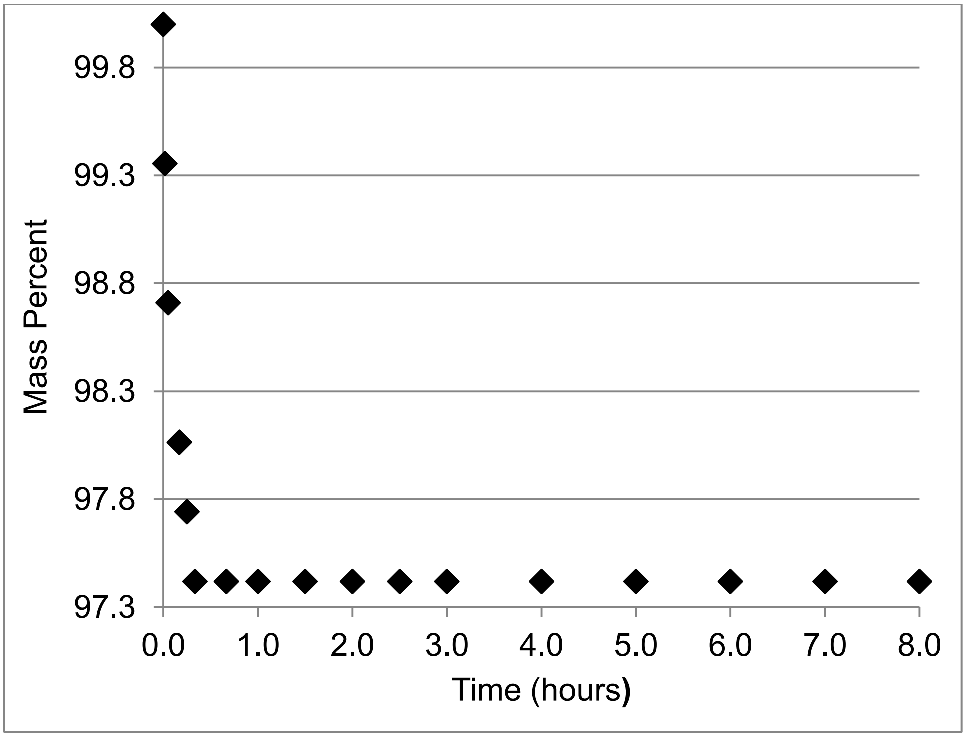


Figure 19: Moisture Balance Results for System 5W

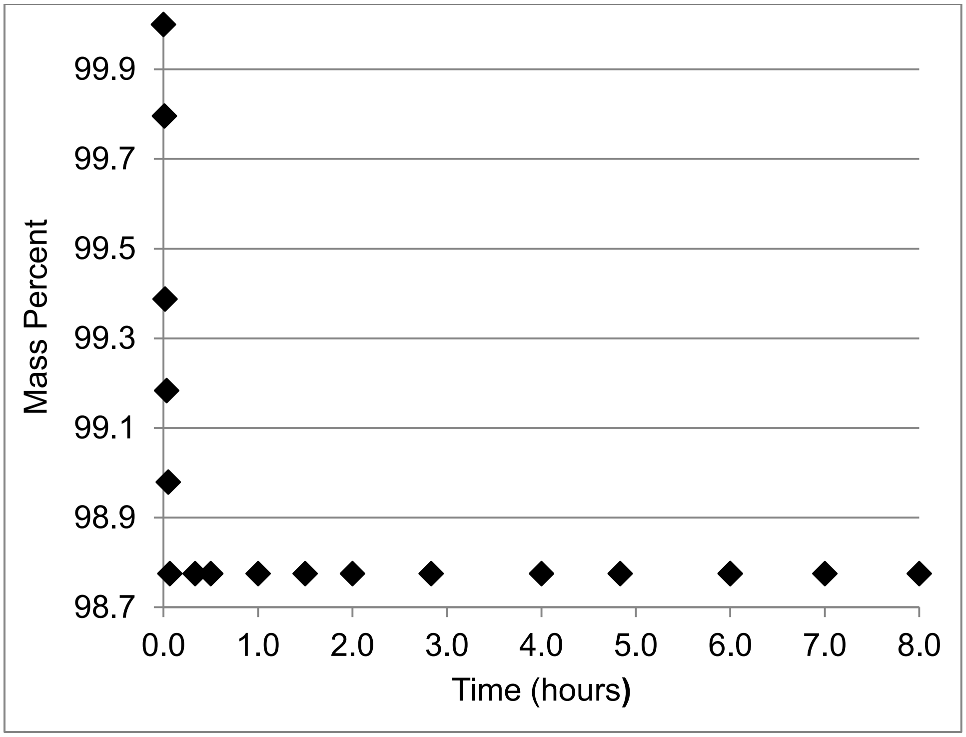


Figure 20: Moisture Balance Results for System 23

7.2 Differential Scanning Calorimetry

DSC was performed on the resins to identify any exothermicities or endothermicities associated with chemical or physical changes or any glass transitions. Experiments were performed from 40˚C to 200˚C at 2˚C per minute. The results are provided in Figure 21 to Figure 28. No glass transitions were observed but several resins showed endothermic transitions and one, resin 17, showed an exothermicity. These are enumerated in Table 5. The DSC peaks are mostly associated with loss of moisture below 100˚C.

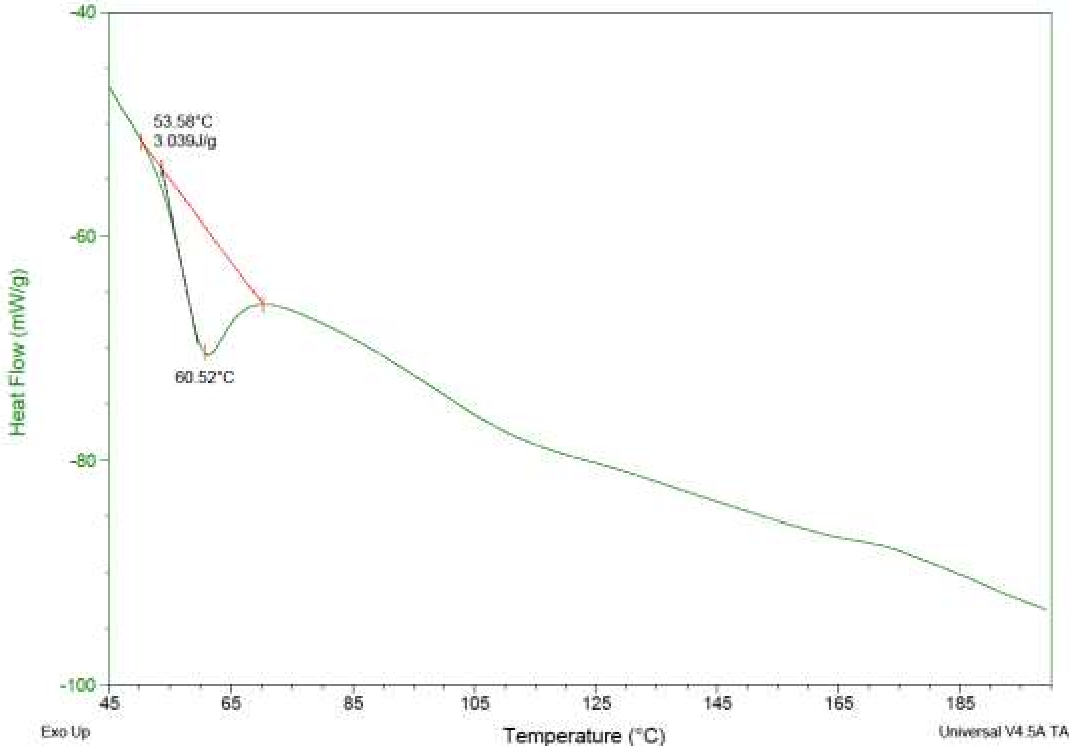


Figure 21: Differential Scanning Calorimetry Result for System 13

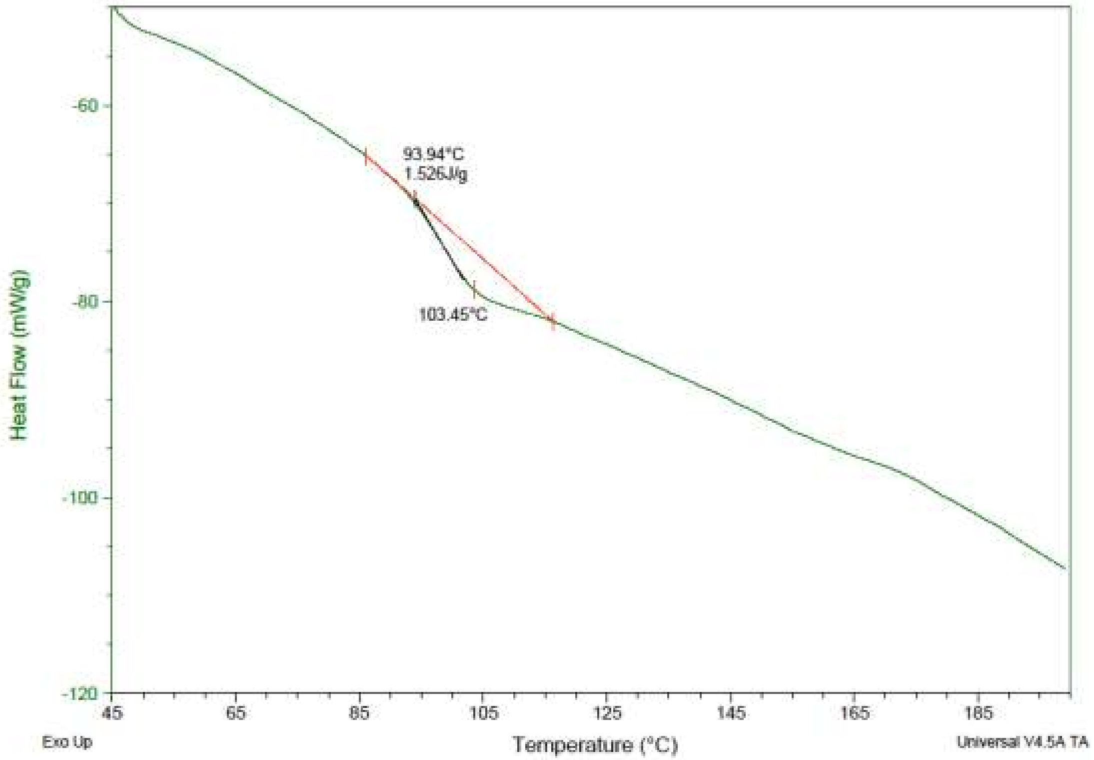


Figure 22: Differential Scanning Calorimetry for System 15

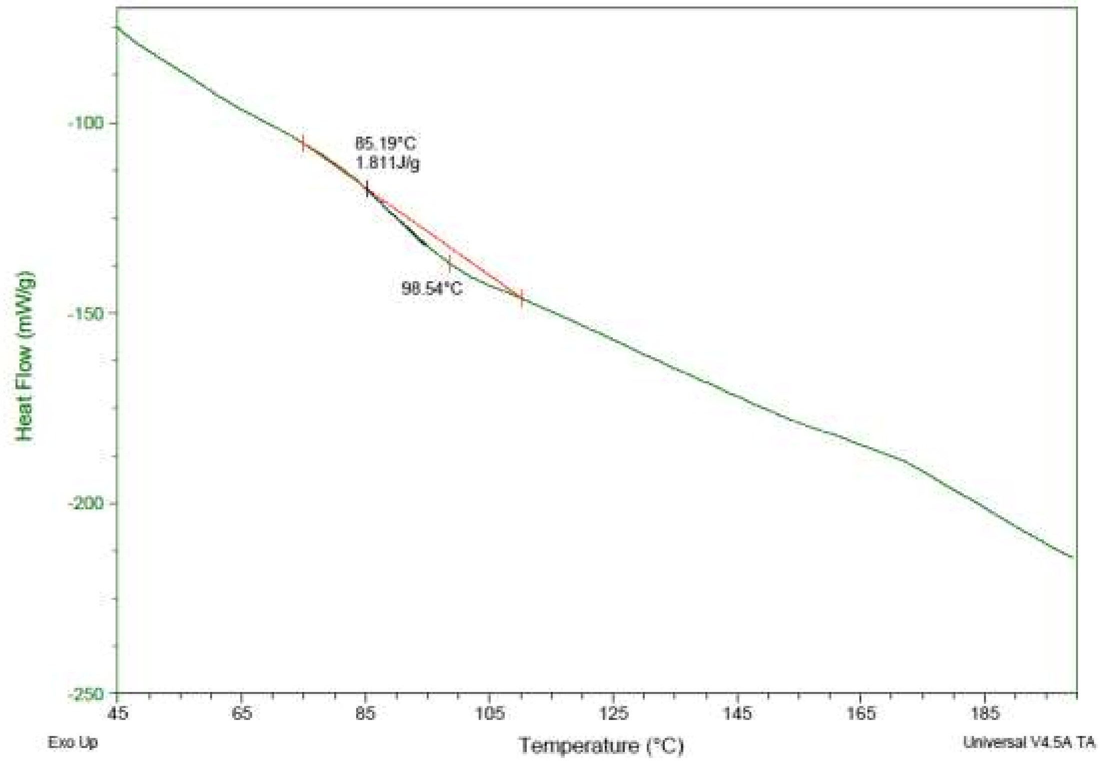


Figure 23: Differential Scanning Calorimetry Result for System 16

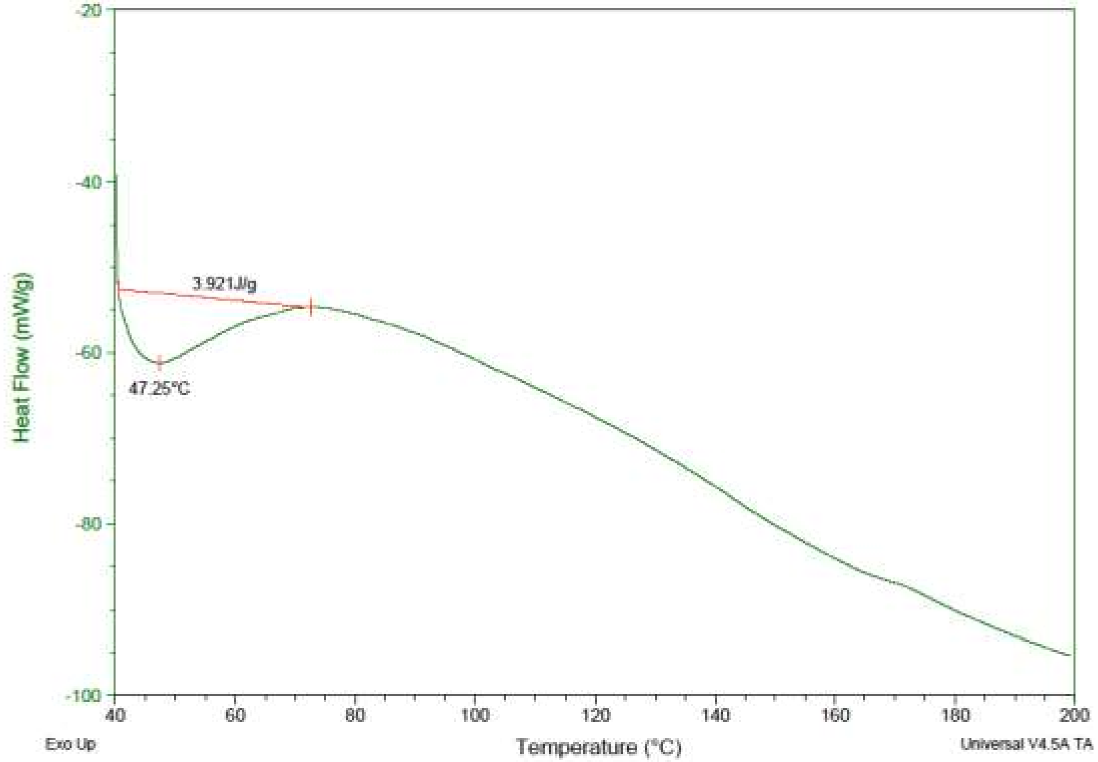


Figure 24: Differential Scanning Calorimetry Result for System 19

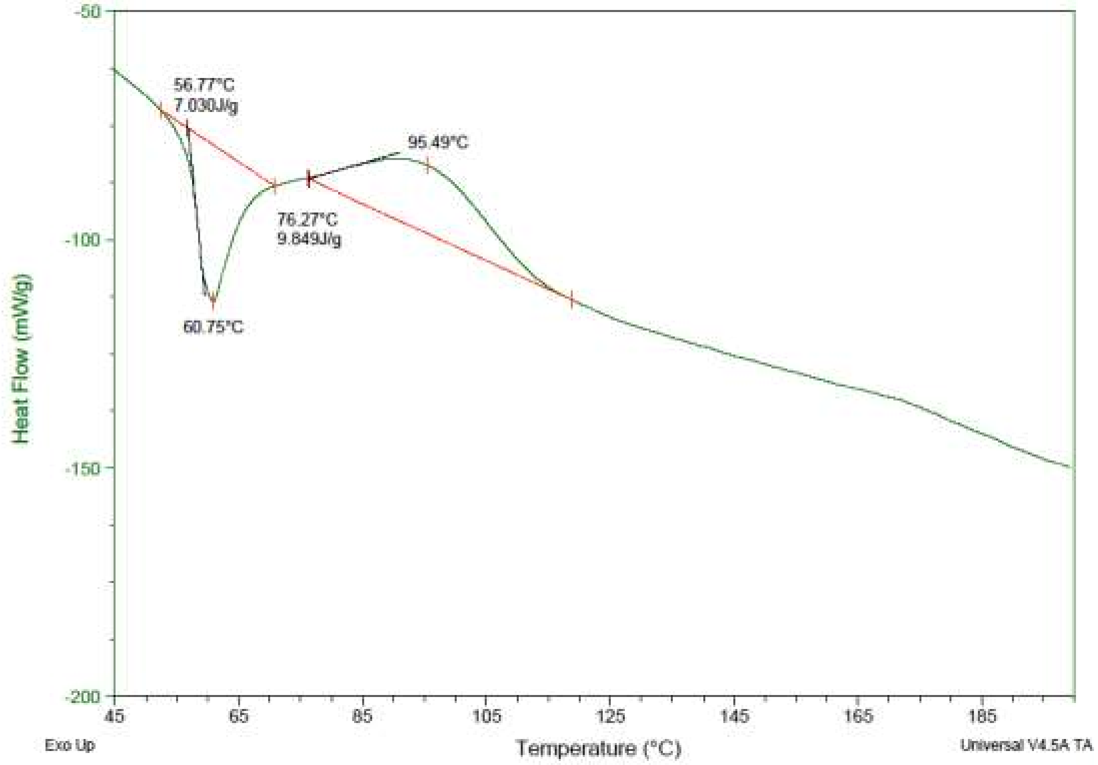


Figure 25: Differential Scanning Calorimetry Result for System 17

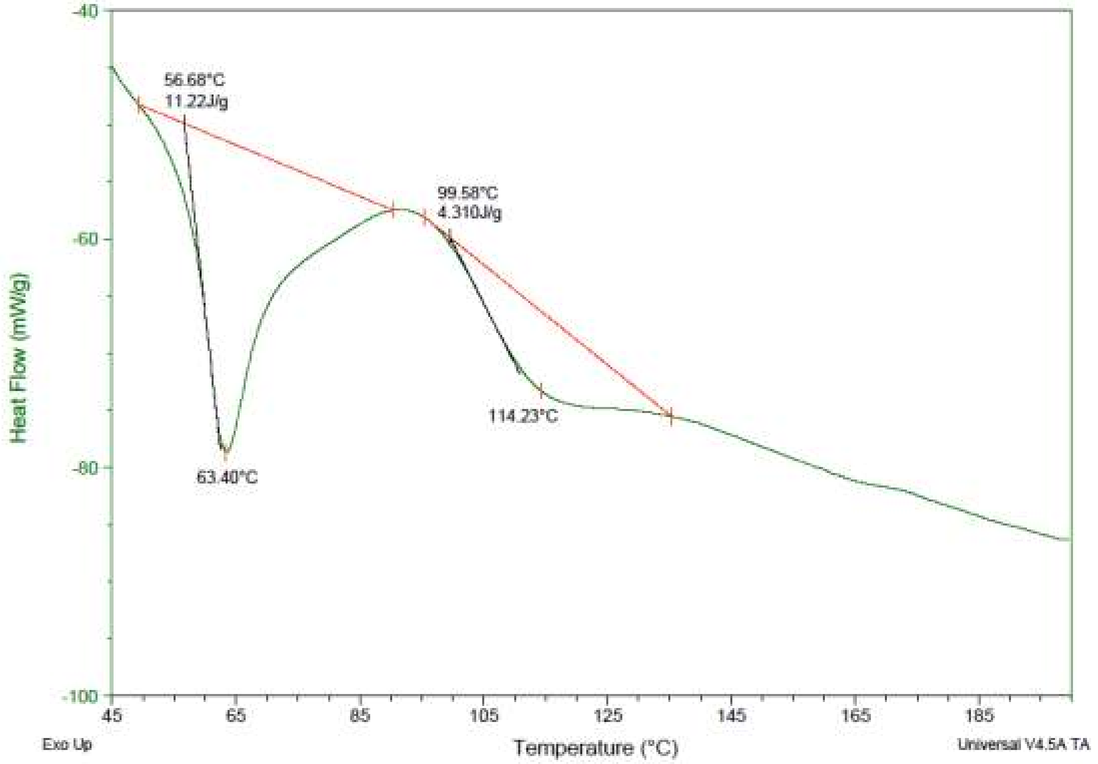


Figure 26: Differential Scanning Calorimetry Result for System 18

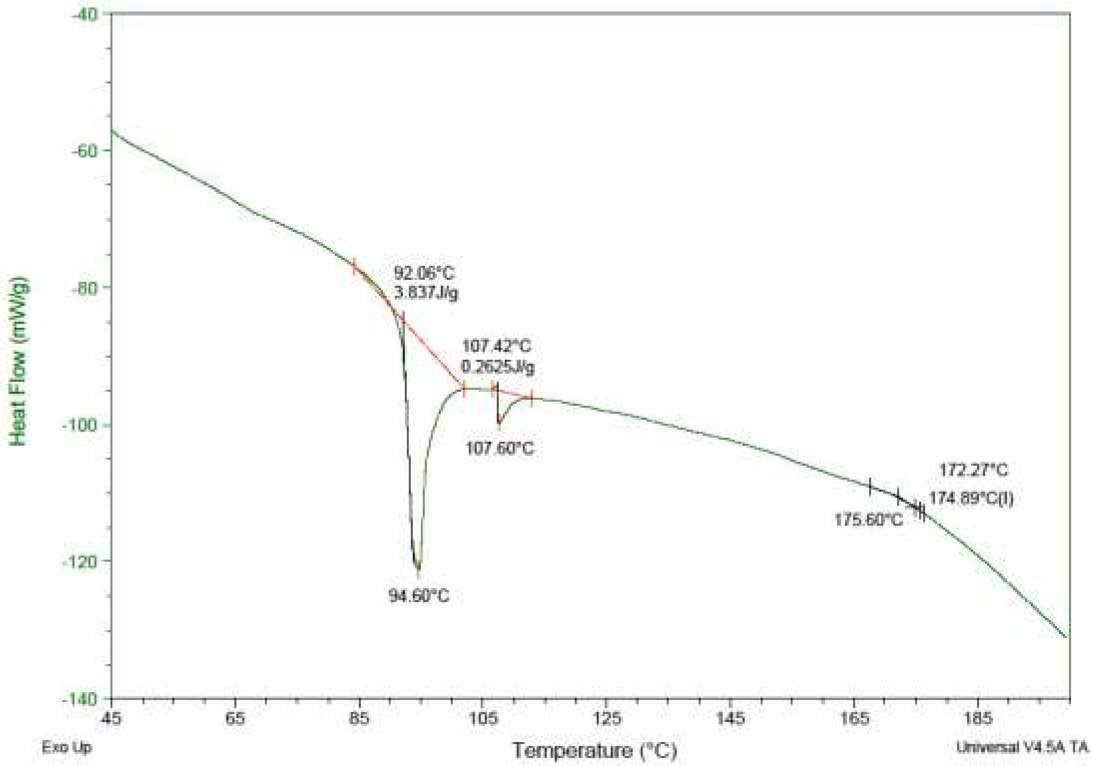


Figure 27: Differential Scanning Calorimetry Result for System 5W

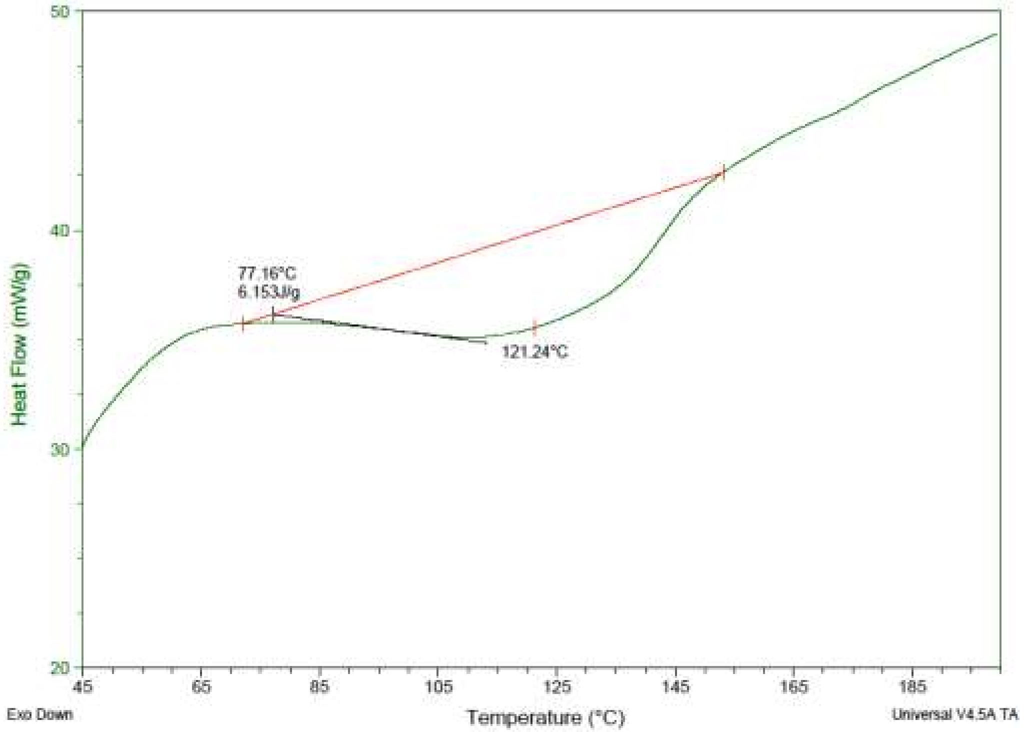


Figure 28: Differential Scanning Calorimetry Result for System 23

Table 5: DSC Results for the Resins

Sample	Onset Temperature (˚C)	Enthalpy Change (J/g)
13	53.6	3.04
15	93.9	1.53
16	85.2	1.81
19	40.0	3.92
17	56.8 76.3	7.03 -9.85
18	56.7 99.6	11.2 4.31
5W	92.1 107.4	3.84 0.27
23	77.2	6.15

7.3 Immersion of Resins in Brine and Deionized Water at 150˚C

The last set of tests was designed to test the thermal stability of the resins in aqueous systems. Two sets of experiments were performed, one with calcium bromide brine and one with deionized water. Pieces of resins were weighed and measured with a digital caliper and were then immersed individually in the test fluids (5 ml) within glass pressure tubes. The tubes were then heat to 150˚C for 24 hours. After cooling, the reins pieces were rinsed with distilled water and air-dried. The pieces were then reweighed and measures. The results are shown in Table 6 and Table 7.

Table 6: Results for Immersion of the Resins in Calcium Bromide Brine at 150°F

Sample	Mass Change (percent)	Thickness Change (percent)	Volume Change (percent)
13	-0.06	-1.7	-1.7
15	-0.44	-1.7	+5.7
16	-0.31	-4.5	-6.2
19	+6.6	+2.5	+2.3
17	-0.14	+3.9	+5.3
18	-5.2	-5.8	-9.1
5W	-0.21	+5.6	+7.2
23	-1.2	+4.2	+4.5

Table 7: Results for Immersion of the Resins in Deionized Water at 150°F

Sample	Mass Change (percent)	Thickness Change (percent)	Volume Change (percent)
13	-7.2	-7.5	-2.4
15	+0.73	0	+1.3
16	+2.1	+0.61	+1.5
19	-6.7	-2.9	-2.1
17	+0.13	-0.63	+0.38
18	+0.27	+2.7	+1.6
5W	+20.1	+36.0	+37.7
23	-7.5	-4.3	-9.3

With the exception of the resins 19 and 18, the resin samples had only small changes in mass in brine at 150˚C. Resin 19 had considerable weight gains that were accompanied by swelling of the resin. The 18 had considerable weight loss and shrunk during the experiment. Surprisingly, the resin's reactivity's were quite different and more extreme in water than in calcium bromide brine. Resin 5W had a major weight gain and correspondingly swelled remarkably. The 16 had smaller but significant weight gains with some swelling. On the other hand, resins 13, 19, and 23 had major weight losses in water at 150˚C. All of these had suspended light brown shards suspended in the water at the end of the experiments. In both immersion fluids, there were one or more epoxy resins that performed well. Considering that the emplaced resins are expected to be in contact with brines or saline waters, the calcium bromide experiments are the most appropriate for choosing resins for use in the field. Thus, the epoxy resins and the polyester resin are the most promising

7.4 Interaction of Cement with Brines

7.4.1 Acidity Changes During Immersion

In order to prevent problems posed by carbonation, 1" cement cubes were immersed in 100 ml of either calcium bromide or calcium chloride brines in gasket-sealed plastic containers. After 2 to 3 weeks the cement pieces completely crumbled. The pH of the initial calcium bromide brine was determined to be 4.5 using pH paper while that of the calcium chloride brine was found to be 4.0. After the cement pieces had fallen apart, the pH of both brine solution had risen to 6.5. Thus, an acid/base reaction is indicated as the cause of the attack of the brine on the cement. Assuming this is correct, and considering that the hydrated calcium ions are the source of acidity, it is likely that the first species formed may be slightly soluble calcium hydroxide chloride {$Ca(OH)Cl$} or calcium hydroxide bromide {$Ca(OH)Br$} species.

7.4.2 XRF Microscope Measurements

In order to monitor the progress of the reaction between the brines and the cement, a sample (System 1) provided by CSI Technologies that had clearly visible bands (Figure 29) for unreacted cement (grey), reacted cement (black), and a white efflorescence on the surface was analyzed by XRF microscopy. The relative concentrations of several key elements in each band are presented in Figure 29. In the case of most of the non-calcium metal ions, there is evidence for dissolution of metal ions leading to diminished concentrations of the black band and the presence of the elements in the effloresced white band of material. Sulfur, likely present as sulfate, also migrates in the same manner. Aluminum, on the other hand, becomes concentrated in the dark band suggesting that an aluminum-rich phase is being formed. The amount of silica in the dark band of brine-impacted cement is diminished as the aluminum-containing phase is formed.

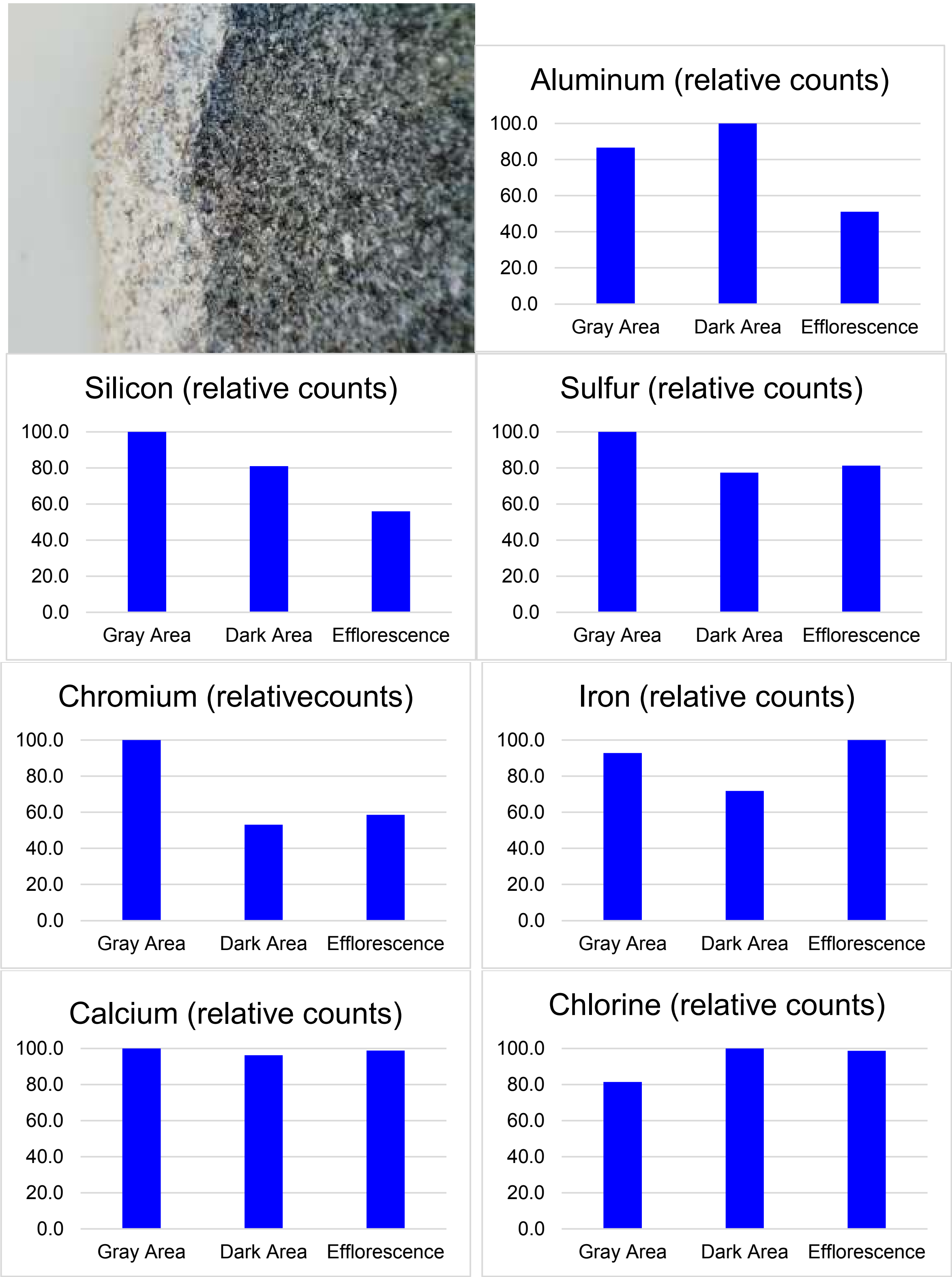


Figure 29: Picture of Cement Analysis Area and Comparison of Elemental Contents

7.4.3 XRD Diffraction of Brine-Impacted Cements

Immersion of cement pieces for six months in calcium chloride brine led to complete disappearance of diffraction peaks for all of Portland cement phases, especially Portlandite (see X-ray diffraction patterns in Figure 30 to Figure 33). A new crystalline phase was formed that was identified after much searching as a calcium aluminum chloride layered double hydroxide. These results suggest that calcium is solubilized as calcium hydroxide chloride, destroying the cementious matrix and forming the new calcium aluminum chloride layered double hydroxide along with other amorphous phases. Calcium bromide likely reacts by the same mechanism but the new crystalline product is unidentified – this may be due to the fact that calcium aluminum bromide layered double hydroxides have not been synthesized yet. This newly-discovered degradation reaction between hardened Portland cement and completion brines further underscores the drive to search for improved well sealants.

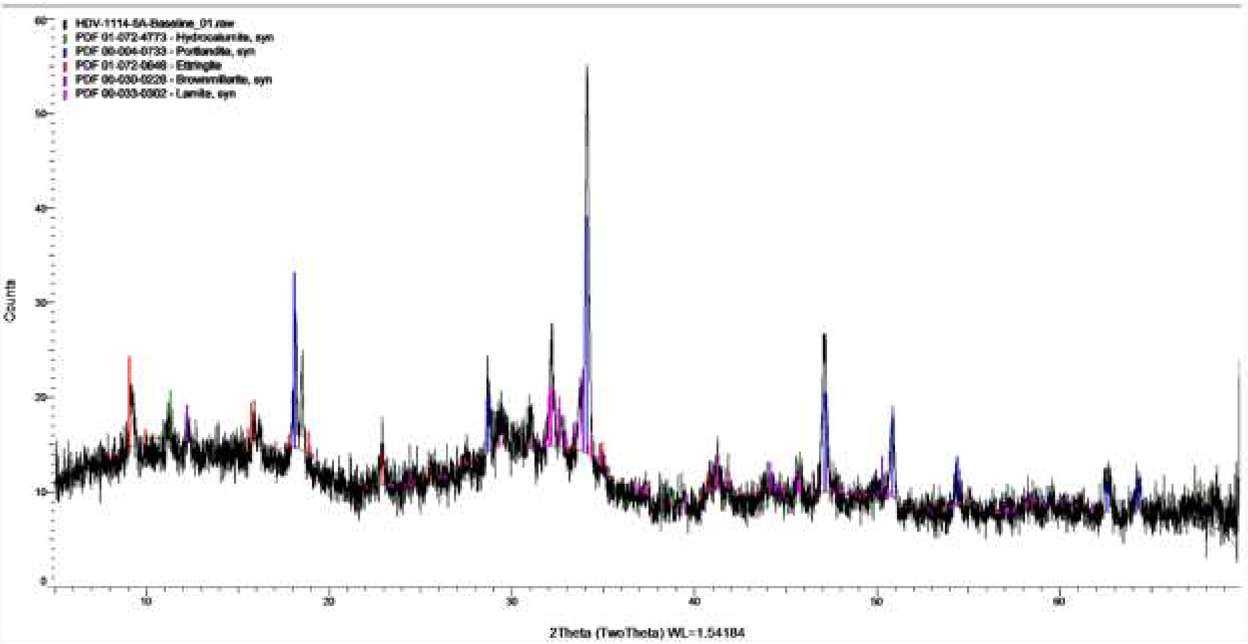


Figure 30: XRD of Baseline Cement

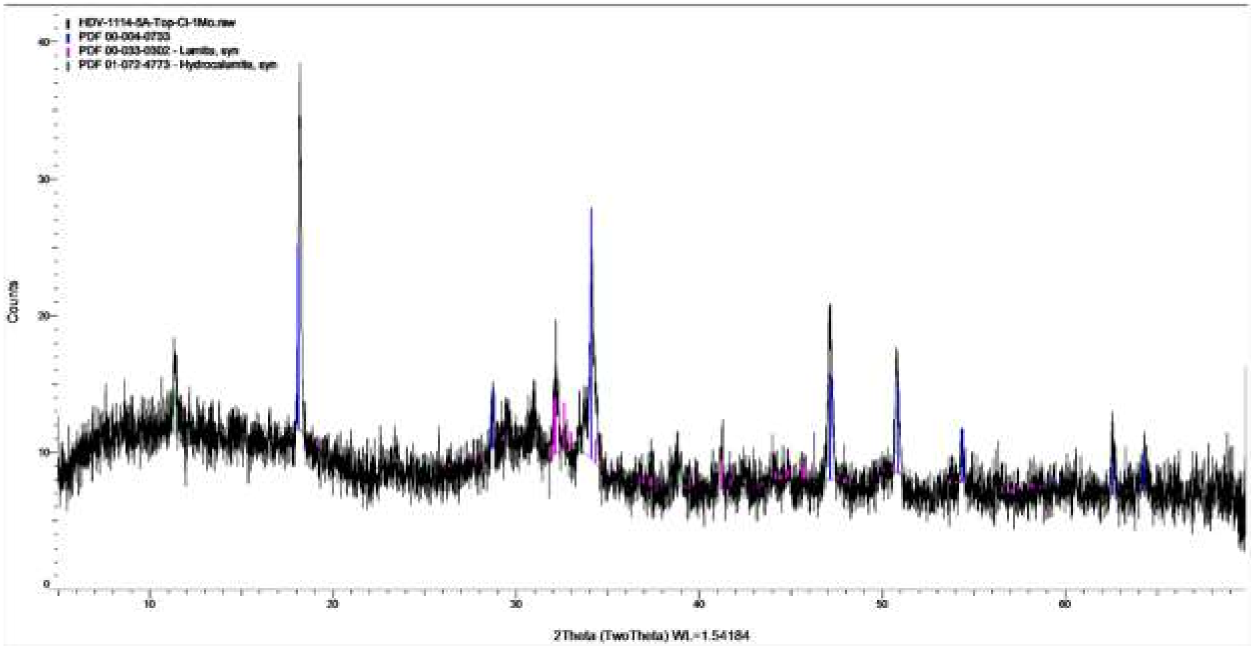


Figure 31: XRD of Cement after 1 Month Exposure to Calcium Chloride Brine

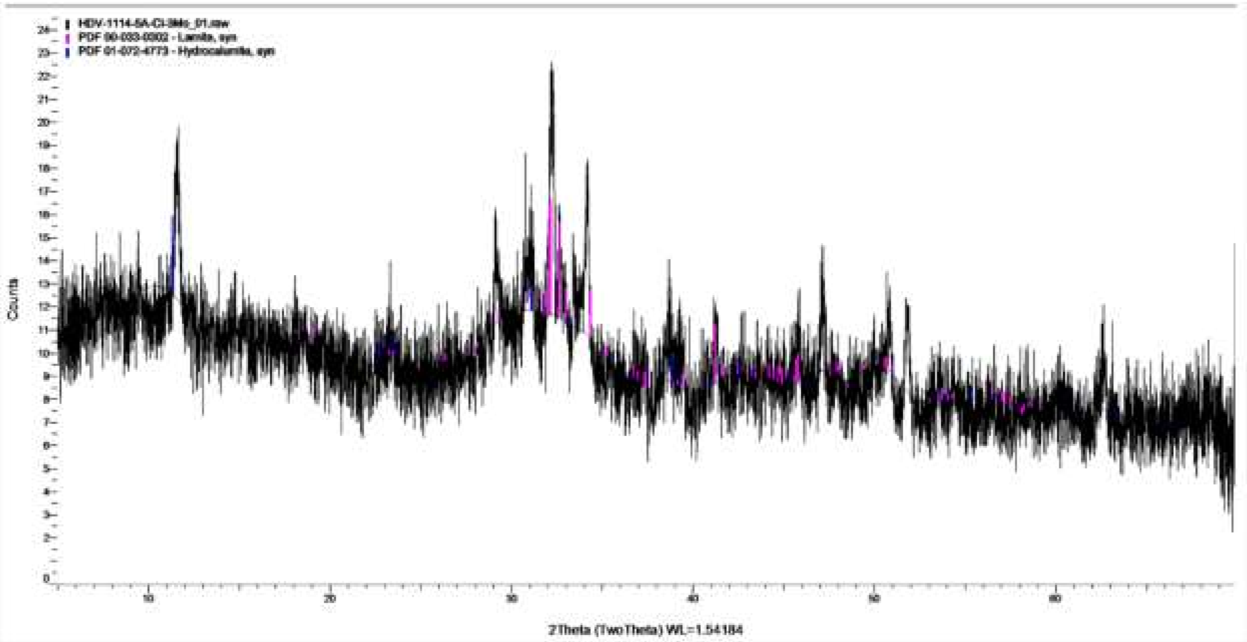


Figure 32: XRD of Cement after 3 Month Exposure to Calcium Chloride Brine

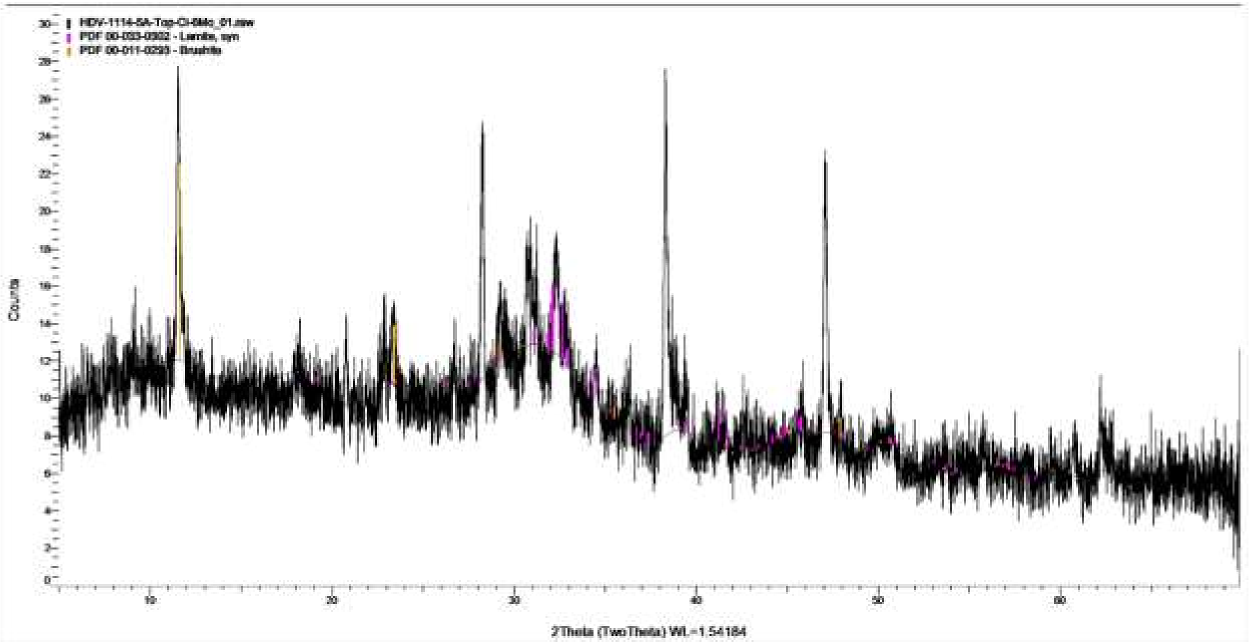


Figure 33: XRD of Cement after 6 Month Exposure to Calcium Chloride Brine

8.0 TASK 5.0 - LABORATORY EVALUATION OF RESIN PERFORMANCE PROPERTIES—SMALL SCALE

8.1 Objective

The objective of this task was to conduct small-scale laboratory testing and analysis to evaluate resin performance in a way that is comparable to data available on Portland cement.

8.1.1 Subtask 5.1-5.10 - Test Procedures

The following tests 1 – 14 are the various tests performed on either cement or resin designs. Each test is discussed in detail below.

1 Rheology: Slurry surface rheology is measured at ambient temperature with a rotational viscometer. Downhole slurry rheology is measured after conditioning in an atmospheric consistometer if the BHCT is 190°F or less. If the BHCT is greater than 190°F the slurry is conditioned under temperature and pressure in a pressurized consistometer.

2 API Thickening Time: Slurry thickening time is tested using a pressurized consistometer to simulate downhole pressure and temperature to determine how long the slurry can be pumped before setting.

3 API Static Fluid Loss: The slurry is conditioned to temperature in an atmospheric consistometer and placed in a fluid loss cell. A 1000 psi differential pressure is applied across the slurry and the amount of fluid released in 30 minutes is recorded. The fluid loss test is a representation of fluid loss from the slurry into the formation during placement.

4 API Stirred Fluid Loss: The slurry is conditioned at 190^{o}F or above in the fluid loss cell. After conditioning, the cell is rotated and a 1000 psi differential pressure is applied and the amount of fluid released in 30 minutes is recorded.

5 Free Fluid: A column of slurry is left static at downhole temperature and the volume of free fluid collected at the top of the sample is measured. This is an indication of static slurry stability.

6 UCA: Compressive strength and time to initial set is measured non-destructively with an Ultrasonic Cement Analyzer (UCA) for 24 hours or 48 hours.

7 Shear bond: This test was conducted to measure how tightly the cement is bonded to the central pipe, and was measured by mechanically forcing the inner pipe from a small-scale wellbore model. Both water wet an oil wet conditioning of the pipes before curing were tested. The simulated formation / cement sheath / central loading tube assembly was placed in a press. The cement and simulated formation was supported while axial load was placed on the central loading tube until movement was detected between the pipe and cement. The load at which this movement occurred was divided by the inner pipe area in contact with the cement to calculate the mechanical shear bond. Figure 34 shows bottom gasket, bottom plastic base, and 2x2 inch schedule 40 pipe mold. Figure 35 shows the sealant cured in the pipe along with the test jig that will be used to press the sealant until failure.

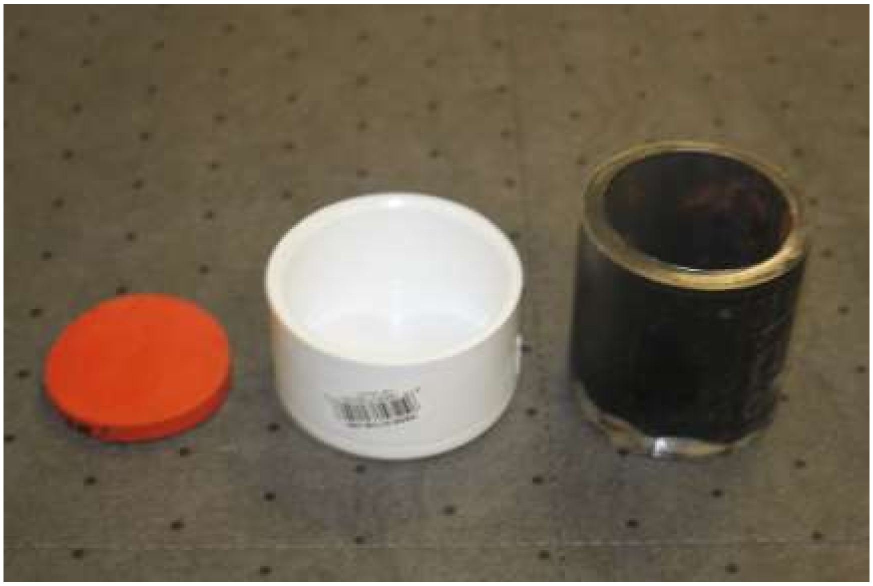


Figure 34: Shear Bond Test Mold

Figure 35: Shear Bond Test Apparatus

8 Hydraulic Bond: This test was performed on 2x6 inch schedule 40 pipe that was cured for 7 days at BHST. The pipes are configured with a bottom cap to allow for a connection to a pressure volume (PV) pump. The PV pump applies water pressure in increments of 100 psi until failure of the seal occurs or a maximum pressure reading of 1000 psi occurs.

9 Coupon Pull Test: This test was performed using a 2x2 inch schedule 40 pipe mold. The mold was fitted with rubber gaskets allowing a metal coupon to be placed in the center of the sealant as in Figure 36. Once the sealant is cured for 7 days at BHST the coupon is attached to a pulley system as seen in Figure 37 and a torque motor records the force needed to break to coupon seal.

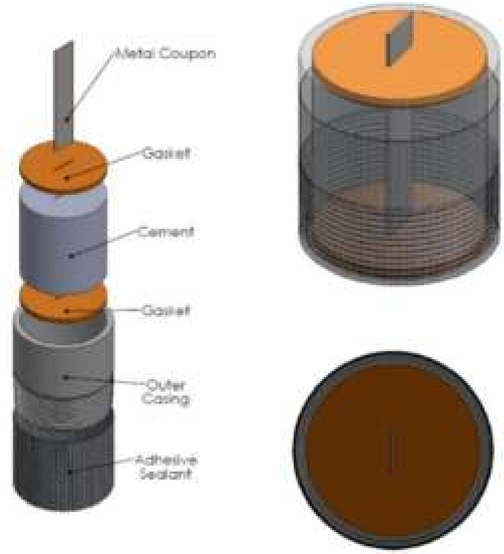


Figure 36 Coupon Pull Test Mold

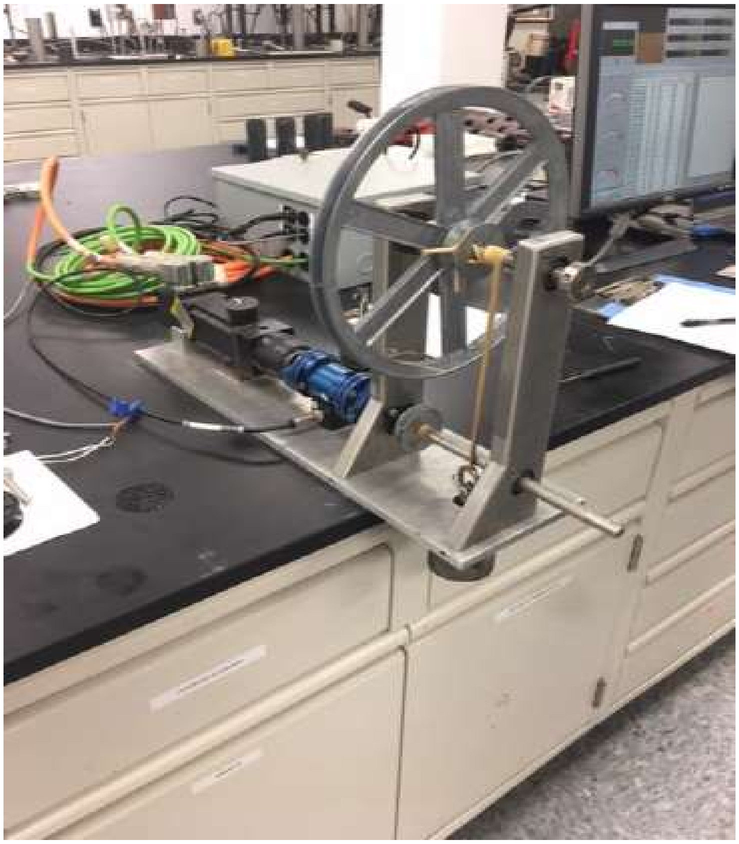


Figure 37: Coupon Pull Test Apparatus

10 Tensile Strength: This testing was performed using a splitting tensile strength method. For this test, the slurry is cured in a 2x4-in mold to make three specimens. After curing, each specimen was prepared by cutting ¼" section from each end. Those pieces were discarded, and the specimen was split into three 1 inch segments specified as top, middle or bottom. Density is then calculated for each segment using Archimedes principle. Each sample is then crushed in the testing apparatus as shown in Figure 38. The maximum reading is noted and used to calculate the tensile strength as per the equation below.

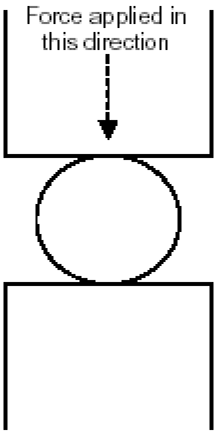


Figure 38: Diagram of Tensile Test

Tensile strength is calculated by the following equation:

Equation 1: Tensile strength equation

T (psi) = (2*F) / (Pi*L*D)

Where:
T = Tensile Strength (psi)
F = Maximum Force Recorded (lbf)
Pi = 3.14
L = Sample Length (in.)
D = Sample diameter (in.)

11 Tensile Modulus: This test was performed using the triaxial load cell with a configuration allowing a sample to be pulled apart while measuring the strain with LVDT's. Figure 39 shows the sample cured with bolts in place to allow the pulling to occur. Samples were cured for 7 days at BHST.

Figure 39: Tensile Modulus Test Specimen

12 Impact Resistance: This test consists of repeatedly dropping a steel ball on a cement bar until it breaks.

Cement slurry is poured in 5”x1”x1” bar molds and cured at BHST in a water bath for 7 days. After curing, the slurry bar is placed in the impact test apparatus shown below. A 1” ball (66.88 g) is dropped from a constant height on the cement bar. To ensure a consistent point of impact, the ball is dropped through a 1.25” PVC guide pipe placed above the slurry bar. The ball is dropped until the bar breaks, the number of impacts is recorded is defined as impact resistance of the slurry Figure 40.

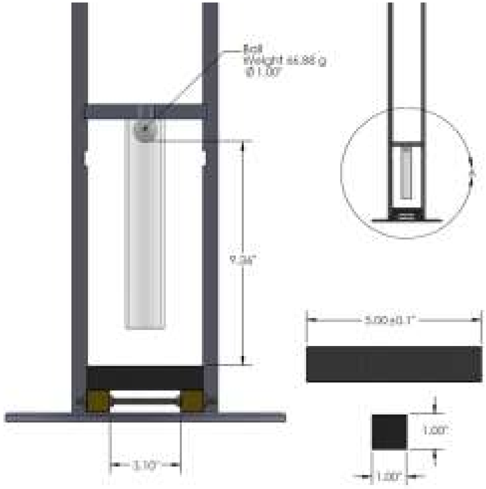


Figure 40: Impact Setup

13 Mechanical Properties: This testing consisted of unconfined compressive strength (UCS), Young's Modulus, Poisson's Ratio, and anelastic strain tests. Testing was performed using a standard load frame equipped with LVDT's. Loading for UCS was at a rate of 35psi/sec until failure. To determine Young's Modulus and Poisson's Ratio, the sample was first loaded to 5% of the UCS, then cycled from 5% to 50% of the UCS for three cycles before ending the test. The sample was fitted with LVDT's to determine radial and axial deformations during loading.

14 Anelastic strain: This test is a measure of the tendency of a sealant to permanently deform under less-than-ultimate stress loading. When combined with other mechanical properties, this behavior may explain loss of annular seal in low-intensity loading scenarios. Samples are cycled to 50% of their compressive strength up to 25 times. A plot of the strain versus time is used to calculate the anelastic strain by subtracting the strain at the last cycle for the strain at the first cycle and dividing by the number of cycles.

8.1.2 Results

There were 12 cement designs and 15 resin designs formulated for testing and are listed in Table 8.

Table 8: System Designs

System	Formulation
1	16.4 lb/gal Cement H + 0.02gps Defoamer 7011L + 2%bwoc Calcium Chloride mixed with DI water
2	16.4 lb/gal Cement H + 0.02gps Defoamer 7011L + 0.1%bwoc FR-1 mixed with DI water
3	16.4 lb/gal Cement H + 0.02gps Defoamer 7011L + 35%bwoc Silica Flour + 0.4% Kelig 32 mixed with DI water
4	16.4 lb/gal Cement H + 0.02gps Defoamer 7011L + 1%bwoc MagOxM + 0.65%bwoc NC-S-1 + 0.8%bwoc FL-17 + 1%bwoc Calcium Chloride mixed with DI water
5	16.4 lb/gal Cement H + 0.02gps Defoamer 7011L + 1%bwoc MagOxM + 0.65%bwoc NC-S-1 + 0.8%bwoc FL-17 + 0.2%bwoc FR-1 mixed with DI water
6	16.4 lb/gal Cement H + 0.02gps Defoamer 7011L + 1%bwoc MagOxM + 0.65%bwoc NC-S-1 + 0.8%bwoc FL-17 + 35%bwoc Silica Flour + 0.25% Kelig 32 mixed with DI water
7	12.0 lb/gal 65:35 Cement H:Poz + 0.3%bwoc Defoamer 7011 + 8%bwoc Bentonite mixed with DI water
8	17.0 lb/gal Cement H + 8%bwoc Hematite + 10%bwoc Silica Flour + 0.1%bwoc Defoamer + 0.9%bwoc FL-17 + 0.8%bwoc NC-S-1 + 25%bwoc 100 mesh SS + 0.1%bwoc FR-1 mixed with DI water
9	18.5 lb/gal Cement H + 40%bwoc Hematite + 10%bwoc Silica Flour + 0.1% bwoc Defoamer + 1% bwoc FL-17 + 0.5% bwoc NC-S-1 + 25% bwoc 100 mesh SS + 1% bwoc PCR-3 + 0.2% bwoc LTSA-1+ 24% bwoc micromax mixed with DI water
10	16.4 lb/gal Cement H + 0.08gps APF-27 foamed to 13.5 lb/gal Foam system mixed with DI water
11	13.5 lb/gal Cement H + 0.2% bwoc LTSA-1 + 0.15 gps sodium silicate liquid + 0.3% bwoc FL-17L mixed with Sea water
12	16.4 lb/gal Cement H + 0.01 gps defoamer + 0.3 gps FL-17L + 0.02 gps Kelig 32L mixed with DI water
13	12 lb/gal Epoxy Resin 1 + 32.7%total weight Weighting Agent
14	12 lb/gal Epoxy Resin 2 + 31.1%total weight Weighting Agent
15	12 lb/gal Epoxy Resin 3 + 31.5%total weight Weighting Agent
16	13 lb/gal Epoxy Resin 4 + 39.2%total weight Weighting Agent
17	9.3 lb/gal Epoxy Resin 5
18	14 lb/gal Phenolic 1/Epoxy Resin 5 50/50%by weight + 41.8%total weight Weighting Agent
19	14.5 lb/gal Phenolic Resin 2 + 42.8%total weight Weighting Agent
20	14.5 lb/gal Polyester Resin 1 + 50.9%total weight Weighting Agent
21	9.43 lb/gal Furan Resin 1
22	9.43 lb/gal Furan Resin 2
23	14 lb/gal Polyester Resin 2
24	14 lb/gal Polyester Resin 3
25	14 lb/gal Polyester Resin 4
26	14.5 lb/gal Epoxy Resin 6 + 50.2%total weight Weighting Agent

27	12 lb/gal Epoxy Resin 7 + 31.1%total weight Weighting Agent

Table 9 lists the settling tests which are measured with the densities of the tensile samples. Tensile strengths of the cement designs 1-12 are in typical ranges of 40 psi to 600 psi on average. Unconfined compressive strengths give typical ranges of as low as 40 psi for light weight designs to as high as 10,000 psi for higher density designs. Young's modulus was low at 3.18E+05 for the lightweight system 7 and low at 7.39E+05 for the lightweight system 11, which is to be expected. All other cement designs were in the typical range of 1.01E+06 to 3.62E+06. The Poisson's ratio were all within typical ranges of cement from 0.20 to 0.28.

Table 9: Settling, Tensile Strength, UCS, YM, and PR of Systems 1-12

	Settling lb/gal			Tensile psi			UCS	YM	PR
System	Top	Mid	Bot	Top	Mid	Bot	psi	psi	in/in
1	16.89	17.08	17.43	330	285	305	3540	1.61E+06	0.27
2	17.23	17.48	17.97	555	435	515	7630	2.78E+06	0.26
3	17.96	18.19	18.41	500	550	715	10,540	3.57E+06	0.2
4	16.98	16.95	17.08	315	300	220	4050	1.26E+06	0.23
5	16.79	16.9	17.41	545	515	510	2715	2.42E+06	0.24
6	15.27	17.51	20.01	225	680	765	6910	3.62E+06	0.24
7	12.12	12.35	12.46	35	40	50	450	3.18E+05	0.26
8	16.93	17.03	17.24	420	380	475	6310	2.20E+06	0.27
9	17.58	18.18	18.29	320	355	355	5045	1.67E+06	0.27
10	12.76	12.98	12.81	125	160	150	1310	1.01E+06	0.21
11	13.59	13.68	13.74	160	130	165	1860	7.39E+05	0.28
12	16.6	16.7	16.8	660	595	750	10,735	2.30E+06	0.22

Table 10 lists the coupon pull test results with bonds of a few designs exceeding the capacity of the instrument but most designs failed with measureable stress. No cement design passed the impact test, all failed. The tensile modulus results were similar to those obtained from Young's modulus testing in compression. Anelastic strain results showed cements to have less elasticity or ductility. Water wet shear bonds varied from as low as 93 psi to as high as 600 psi.

Table 10: Coupon Pull, Impact, Tensile Modulus, Anelastic Strain, and Water wet Shear Bond of Systems 1-12

	Coupon Pull psi		**Impact (strikes)**		**Tensile Modulus psi**	**Anelastic Strain**	**Water wet Shear Bond psi**		
System	**1**	**2**	**1**	**2**	**1**	**1**	**pipe 1**	**pipe 2**	**pipe 3**
1	+227	+236	109	5	2.59E+06	0.00120	169	282	315
2	48	+270	24	27	6.27E+06	0.00096	965	381	421
3	+281	265	57	129	3.90E+06	0.00105	254	444	185
4	229	227	21	73	3.32E+06	0.00247	413	348	624
5	202	186	57	4	3.42E+06	0.00026	651	624	542
6	245	199	43	29	3.09E+06	0.00080	696	314	288
7	52	54	1	1	too weak	0.00039	93	111	140
8	221	+271	69	39	2.96E+06	0.00081	490	324	369
9	0	80	32	42	2.34E+06	0.00050	570	334	389
10	43	220	3	4	2.61E+06	0.00018	153	147	136
11	+260	252	24	11	4.21E+06	0.00105	240	194	227
12	318	248	24	104	3.48E+06	0.00120	575	589	527

Table 11 lists the water wet hydraulic bond. Most failed before reaching 1000 psi except for System 6 which contains some expansion additive which can help in achieving higher shear bond. The oil wet shear bonds and hydraulic bonds were all lower compared to water-wet tests.

Table 11: Water Wet Hydraulic Bond, Oil we Shear Bond, and Oil wet Hydraulic Bond for Systems 1-12

	Water wet Hydraulic Bond psi			Oil wet Shear Bond psi			Oil wet Hydraulic Bond psi		
System	**pipe 1**	**pipe 2**	**pipe 3**	**pipe 1**	**pipe 2**	**pipe 3**	**pipe 1**	**pipe 2**	**pipe 3**
1	400	400	400	361	332	302	400	400	400
2	<50	<50	<50	748	294	321	<50	<50	<50
3	300	50	100	98	66	635	50	50	50
4	600	600	600	428	551	235	400	400	400
5	<50	<50	<50	352	257	224	<50	<50	<50
6	+1000	+1000	+1000	340	242	218	100	200	50
7	100	200	200	103	111	86	50	200	100
8	500	600	600	61	249	274	50	100	50
9	<50	+1000	+1000	78	133	69	50	50	50
10	<50	100	<50	56	67	75	<50	<50	<50
11	800	700	800	224	278	241	700	800	400
12	<50	<50	<50	347	256	237	<50	<50	<50

Table 12 lists standard cement testing properties of rheology at various temperatures. All values were typical for cement slurries.

Table 12: Rheologies of Systems 1-12

Systems	80°F PV/YP cp/lbf/100ft^2	75°F PV/YP cp/lbf/100ft^2	131°F PV/YP cp/lbf/100ft^2	190°F PV/YP cp/lbf/100ft^2	BHST	BHCT
1	106/31	92/29	-	-	65°F	65°F
2	55/12	-	36/17	-	150°F	131°F
3	103/11	-	-	84/15	240°F	218°F
4	206/9	277/16	-	-	65°F	65°F
5	323/14	-	260/12	-	150°F	131°F
6	335/13	-	-	206/10	240°F	218°F
7	24/35	37/38	-	-	122°F	101°F
8	282/14	-	-	145/10	245°F	190°F
9	509/54	-	-	280/24	350°F	284°F
10	60/21	521/30	-	-	80°F	65°F
11	162/20	156/20	-	-	91°F	80°F
12	463/30	-	448/42	-	201°F	162°F

Figure 42 lists the thickening times, UCA compressive strengths, free fluid, and fluid loss. All values obtained were typical for the designs. System 10 is a foamed cement and cannot be tested for UCA.

Table 13: Thickening Time, UCA, Free Fluid, and Fluid Loss for Systems 1-12

Systems	Thickening Time hrs:min			UCA				Free Fluid	Fluid Loss
	40 Bc	70 Bc	100 Bc	50 psi time	500 psi time	12 hrs psi	24 hrs psi		
1	4:18	5:33	6:40	4:37	11:54	504	1103	0.60%	-
2	2:25	2:46	2:46	2:30	3:49	1876	2706	6.40%	-
3	6:48	6:57	7:00	3:25	3:54	3382	4085	4.80%	-
4	4:21	5:17	5:42	12:37	22:07	31	602	0%	22 mls
5	5:11	5:24	5:31	6:39	7:44	1714	3221	0%	30 mls
6	4:17	4:38	4:42	4:00	4:40	2807	4157	0%	60 mls
7	4:17	-	-	10:51	N/A	54	94	1.60%	-
8	9:41	9:58	10:07	3:28	3:51	3224	3921	0.00%	52 mls
9	6:25	6:29	6:31	5:34	6:35	3044	4292	0.00%	28 mls
10	5:22	6:44	7:39	-	-	-	-	0%	-
11	9:12	11:53	14:48	9:01	34:42	109	353	0%	30 mls
12	6:22	6:29	6:32	2:04	2:49	3097	4081	0%	20 mls

Table 14 lists the rheology and hardness tests for the resin systems 13-25. Resin rheology in general is much thicker than cement, but resins have been proven field pumpable due to their Newtonian fluid properties. The hardness scale is used to assess the thickening time and set times for resin systems. Samples are cured at temperature and a puddling rod 12 inches long by 0.18 inch tip is pressed into the resin to determine the degree of hardness. The hardness scale assigns numbers to the progression of resin curing: 1 is fluid, 2 is gelled with the viscous fluid unpumpable, 3 is tacky gelled in which the resin can be easily deformed, 4 is tacky hard in which the resin can be slightly deformed and adheres to the rod, 5 is rubber hard with the resin deforming slightly, and 6 is hard denoting the resin cannot be deformed.

Table 14: Rheology, and Hardness for Systems 13-27

Systems	80°F PV/YP	75°F PV/YP	131°F PV/YP	190°F PV/YP	Hardness Scale					
					1	2	3	4	5	6
13	991/3.3	1340/1	-	-	+6hrs	24hrs		48hrs	5day	7 day
14	907/0.4	1238/2.6	-	-	+7hrs	24hrs	48hrs	5 day		6 day
15	1342/1	-	284/1	-	3hrs	4hrs			5day	7 day
16	749/5.6	-	-	112/3	+6hrs			24hrs	48hrs	6 day
17	1770/74	1021/40	-	-	3hr	4hr	7hr	10hr	24hr	2day
18	1275/5	-	326/4	-	+8hrs			24hrs		5 day
19	140/10	-	-	55/6	6hr	7hr	8hr			24hr
20	1234/28	-	588/17	-	2hrs	3hrs			4hrs	5hrs
21	5/1	-	5/1	-	+8hrs				3 day	5 day
22	5/1	-	-	5/1	1hr					2hrs
23	650/48	651/48	-	-	6hrs		7hr			24hr
24	711/86	-	700/76	-	1.5hrs			2hr	3hr	24hr
25	960/50	-	-	850/50	1hr	2hr	6hr			24hr
27	910/1	1220/3	-	-	+7hrs	24hr	48hr	5 day		6 day

Table 15 lists the settling properties as well as the tensile strength, unconfined compressive strengths, Young's modulus, and Poisson's ratio. Tensile strengths ranged from 500 psi to 4400 psi, in most cases, much higher than cements. UCS values were in the ranges of 2000 psi to 15,500 psi. Young's modulus results for the resins had a few similar to cement with the ranges of 7.35E+05 to 1.30E+06 obtained by systems 21 – 24 which were the furan and polyester systems. The other resins had lower Young's modulus in the range of 6.00E+04 to 5.30E+05. The Poisson's Ratio was much higher for resins as compared to cement.

Table 15: Settling, Tensile, UCS, YM and PR for Systems 13-27

Systems	Settling lb/gal			Tensile psi			UCS	YM	PR
	Top	Mid	Bot	Top	Mid	Bot	Psi	Psi	in/in
13	12.19	12.4	12.42	764	657	779	2865	6.00E+04	0.5
14	12.45	12.46	12.5	859	868	922	3140	6.16E+04	0.5
15	12.44	12.46	12.57	1509	1579	1623	4170	1.05E+05	0.5
16	13.15	13.38	13.69	2700	2708	3060	6455	3.00E+05	0.5
17	9.2	9.3	9.3	4329	4425	4336	13,405	4.24E+05	0.46
18	13.9	14	14.1	1002	824	1123	2360	6.90E+04	0.42
19	14.4	14.5	14.5	3020	3345	3674	11,575	5.30E+05	0.4
20	14.5	14.5	14.5	na	na	na	na	Na	na
21	9.43	9.43	9.43	2475	2450	2300	14,500	1.20E+06	0.45
22	9.43	9.43	9.43	3400	3450	3477	15,550	1.30E+06	0.45
23	14.53	14.54	14.55	1856	2112	2199	12085	1.23E+06	0.26
24	14.54	14.54	14.55	1939	1422	1500	9375	7.35E+05	0.5
25	14.53	14.54	14.55	568	654	559	2045	6.57E+04	0.5
27	12.45	12.46	12.5	750	745	760	2800	6.00E+05	0.5

Table 16 presents the coupon pull test results in which most all of the designs exhibited bonds above the maximum range of the instrument. The only system to not exhibit maximum measureable bond was system 20 which is a polyester resin that failed on average at 70 psi. All other systems either exhibited maximum bond or yielded very high strength values as compared to cement. For the impact test, all resin designs survived the maximum number of impacts. None of the systems were broken as compared to cement. Tensile modulus testing produced similar results as Young's modulus for the resins. Anelastic strain results show resins to be much more elastic and ductile than cement. Water wet shear bonds were as low as 730 psi and as high as 2500 psi. These values were generally equal to or much higher than cement bond strength results.

Table 16: Shear Bond, Impact Resistance, Tensile Modulus, Anelastic Strain, and Water wet Shear Bond for Systems 13-27

	Coupon Pull psi		Impact (strikes)		Tensile Modulus psi	Anelastic Strain	Water wet Shear Bond psi		
Systems	**1**	**2**	**1**	**2**	**1**	**1**	**pipe 1**	**pipe 2**	**pipe 3**
13	+269	+263	max	Max	8.83E+04	0.48278	1250	1325	1100
14	+263	+264	max	Max	2.68E+04	0.23650	1225	1365	1250
15	+270	+248	max	Max	1.54E+05	0.18826	1550	1830	2100
16	+238	+274	max	Max	5.80E+05	0.02825	2250	2475	2510
17	242	248	max	Max	1.44E+06	0.01419	1570	35	2330
18	241	+249	max	Max	3.02E+05	0.60703	2505	2465	2480
19	+247	+241	max	Max	1.40E+06	0.00448	2355	2215	2200
20	54	85	max	Max	na	0.35900	na	na	na
21	+245	+260	max	Max	na	0.00246	1575	1560	1580
22	+247	+253	max	Max	na	0.00286	2425	2235	2450
23	211	180	max	Max	1.50E+06	0.00345	1085	1125	1250
24	211	209	max	Max	na	0.00434	625	845	770
25	+225	+220	max	Max	1.05E+06	0.30953	785	675	725
27	+263	+264	max	Max	2.70E+04	0.25470	1300	1400	1100

Table 17 lists the water wet hydraulic bonds. All of the designs except for system 17 the bis A epoxy exceeded the test maximum of +1,000psi. System 17 achieved an average of 217 psi. Oil wet shear bonds were all high except for system 17 at 483 psi average. Oil wet hydraulic bonds for all resins exceeded 1,000 psi, except for system 17 at 383 psi average. For the resins that had high shear and hydraulic bonds, the values obtained outperformed cement.

Table 17: Water wet Hydraulic Bond, Oil wet Shear Bond, and Oil wet Hydraulic Bond for Systems 13-27

	Water wet Hydraulic Bond psi			Oil wet Shear Bond psi			Oil wet Hydraulic Bond psi		
Systems	**pipe 1**	**pipe 2**	**pipe 3**	**pipe 1**	**pipe 2**	**pipe 3**	**pipe 1**	**pipe 2**	**pipe 3**
13	+1000	+1000	+1000	1440	1525	1430	+1000	+1000	+1000
14	+1000	+1000	+1000	1475	1483	1490	+1000	+1000	+1000
15	+1000	+1000	+1000	2125	2230	2150	+1000	+1000	+1000
16	+1000	+1000	+1000	2758	2831	2956	+1000	+1000	+1000
17	200	400	50	283	1145	203	+1000	100	50
18	+1000	+1000	+1000	3091	2847	2798	+1000	+1000	+1000
19	+1000	+1000	+1000	2148	2354	2178	+1000	+1000	+1000
20	na	na	na	na	na	na	Na	na	Na
21	+1000	+1000	+1000	1537	1548	1521	+1000	+1000	+1000
22	+1000	+1000	+1000	2433	2267	2245	+1000	+1000	+1000
23	+1000	+1000	+1000	1153	1257	1375	+1000	+1000	+1000
24	+1000	+1000	+1000	746	821	742	+1000	+1000	+1000
25	+1000	+1000	+1000	842	753	851	+1000	+1000	+1000
27	+1000	+1000	+1000	1480	1520	1495	+1000	+1000	+1000

Table 18 lists the fluid loss results for some select resin designs. This property is not normally tested as resins are typically used for remedial work not requiring fluid loss control. The test is performed the same way as for cement. Filter cake formation was very thin for all resins and provided very low fluid loss values at low temperature. The fluid loss control is most attributed to the presence of solids in the resin. Fluid loss values at 190°F were in the 150-175 mls/30 min range.

Table 18: Fluid Loss Results of Resin Designs 13, 19 and 20

Systems	75°F Fluid Loss mls/30min	190°F Fluid Loss mls/30min
13	46	175
19	48	156
20	47	152

Table 19 lists the contamination tests between resin and cement. System 12 represented a cement design that was contaminated with resin systems at 10% by volume. Thickening time and compressive strengths were not affected by the additions.

Table 19: Contamination Results between Cement Design 12 and Resin Designs 13, 19, 20, and 22

System	Thickening Time at 70 Bc hrs:min	24 hr Compressive Strength psi
12	6:29	4081
10% contamination with 13	6:35	4025
10% contamination with 19	6:40	3975
10% contamination with 20	6:25	4090
10% contamination with 22	6:30	4050

Figure 41 to Figure 82 are the results of the Long Term Durability testing in various fluid exposures for baseline, 1 month, 3 month, and 6 month exposures. Testing fluids were 11.0 lb/gal calcium chloride brine, 14.0 lb/gal calcium bromide brine, nonaromatic hydrocarbon, and aromatic hydrocarbon (70% heptane, 20% cyclohexane, 10% toluene) at ambient test conditions. 11.0 lb/gal calcium chloride brine, 14.0 lb/gal calcium bromide brine, and nonaromatic hydrocarbon were the fluids at 175°F, ambient pressure test conditions. Initially a 2x4inch cylinder of sealant is cured for 7 days at either ambient or 175°F. After curing the samples are cut into 1" wafers as in being prepared for tensile strength measurements. The samples are measured for density and diameter. The baselines of the systems are tested for tensile strengths. The other columns of systems are stacked in pieces of three and labeled for traceability so that 1 month, 3 month, and 6 month can be checked for any density, diameter, or tensile change. The density and diameter changes are reported as % changes. The tensile strengths are reported as an average of three values at each timeframe and plotted on a chart.

Figure **41** lists the long term durability testing in calcium chloride brine at 175°F. Systems 3, 6, 8, and 9 showed signs of density increase over the 1 month, 3 month and 6 month cure times and are all cement designs. System 15 and 16 both epoxy resin designs showed no change.

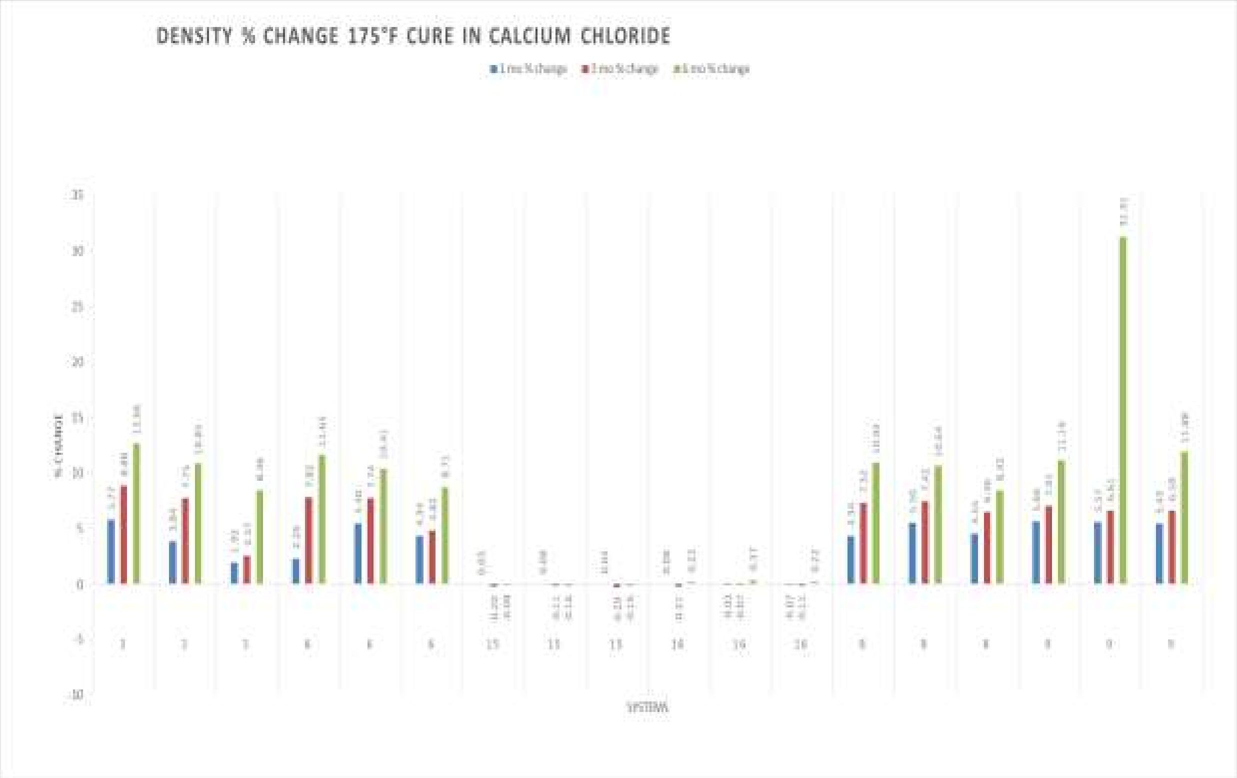


Figure 41: Density Change of Systems 3, 6, 8, 9, 15, and 16 in Calcium Chloride Brine at 175°F

Figure 42 lists the long term durability testing in calcium chloride brine at 175°F. Systems 18 (combo phenolic/epoxy), 22(furan), 25(polyester), and 26(epoxy) showed no change. System 19 a phenolic design showed some decrease in density.

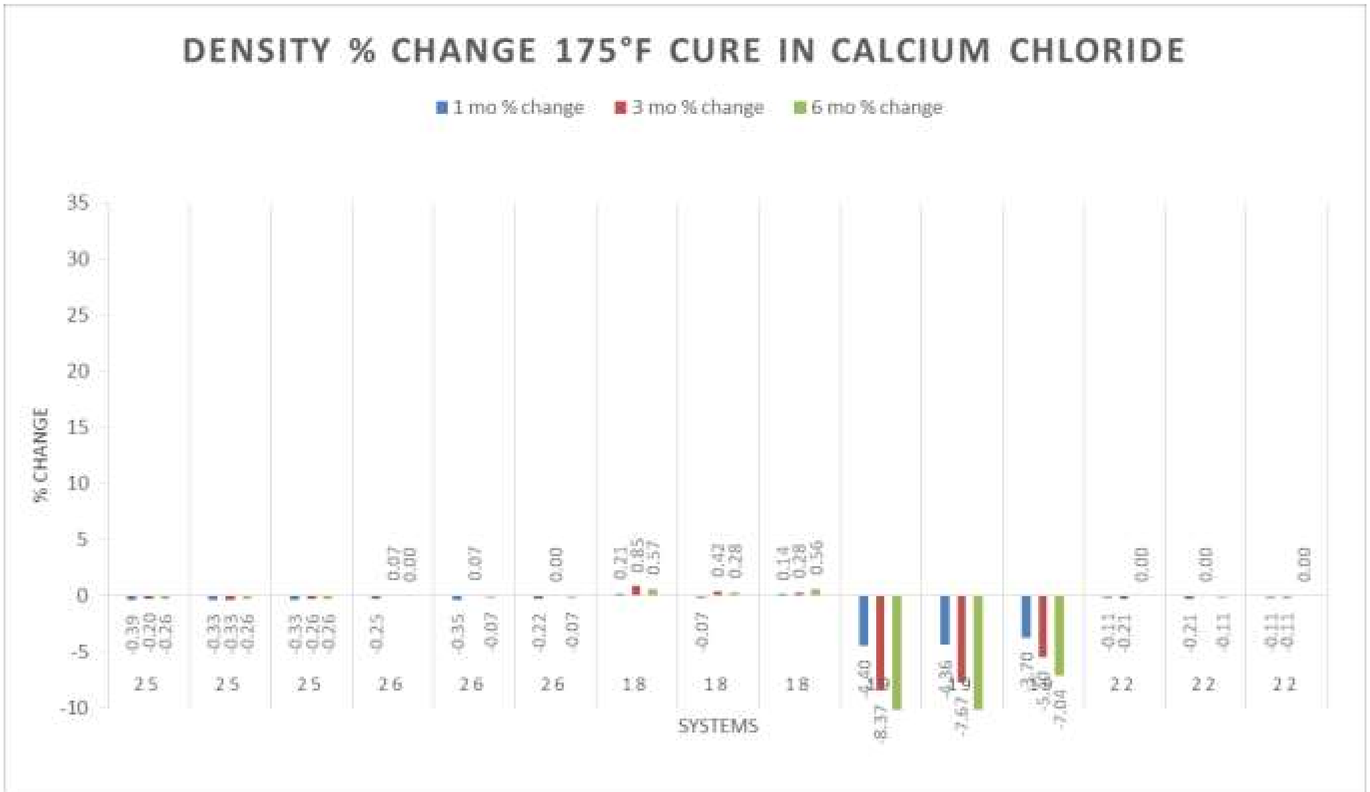


Figure 42: Density Change of Systems 18, 19, 22, 25, and 26 in Calcium Chloride Brine at 175°F

Figure 43 lists the long term durability testing in calcium chloride brine at 175°F. Systems 6 (cement), 15, and 16 (epoxy) showed no change in diameter. Systems 3 and 8 (cements) showed 3 month negative change. System 3 (cement) leveled off at 6 month. System 8 (cement) showed some increase at 6 month as well as system 9 (cement).

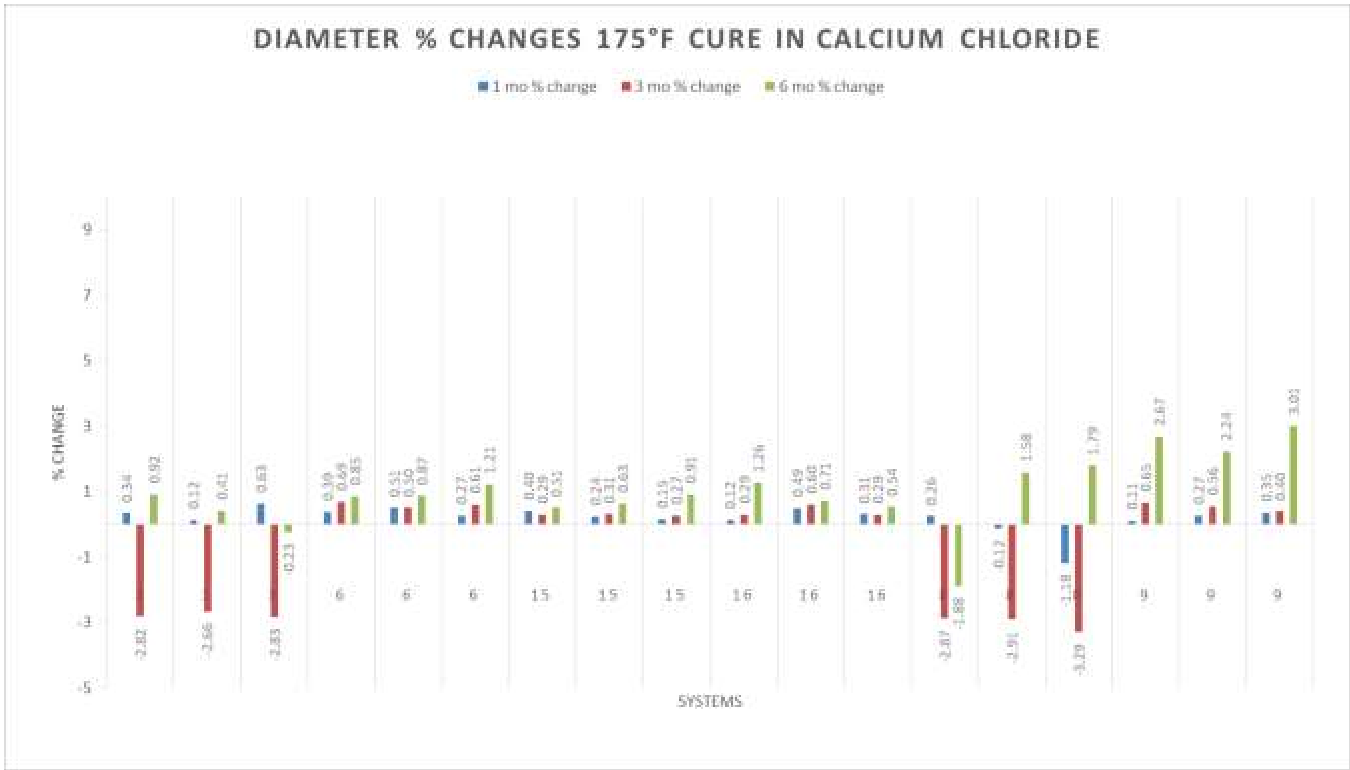


Figure 43: Diameter Change of Systems 3, 6, 8, 9, 15, and 16 in Calcium Chloride Brine at 175°F

Figure 44 lists the long term durability testing in calcium chloride brine at 175°F. Systems 18 (combo phenolic/epoxy), 19(phenolic), 22(furan), 25(polyester), and 26(epoxy) all showed no change in diameter.

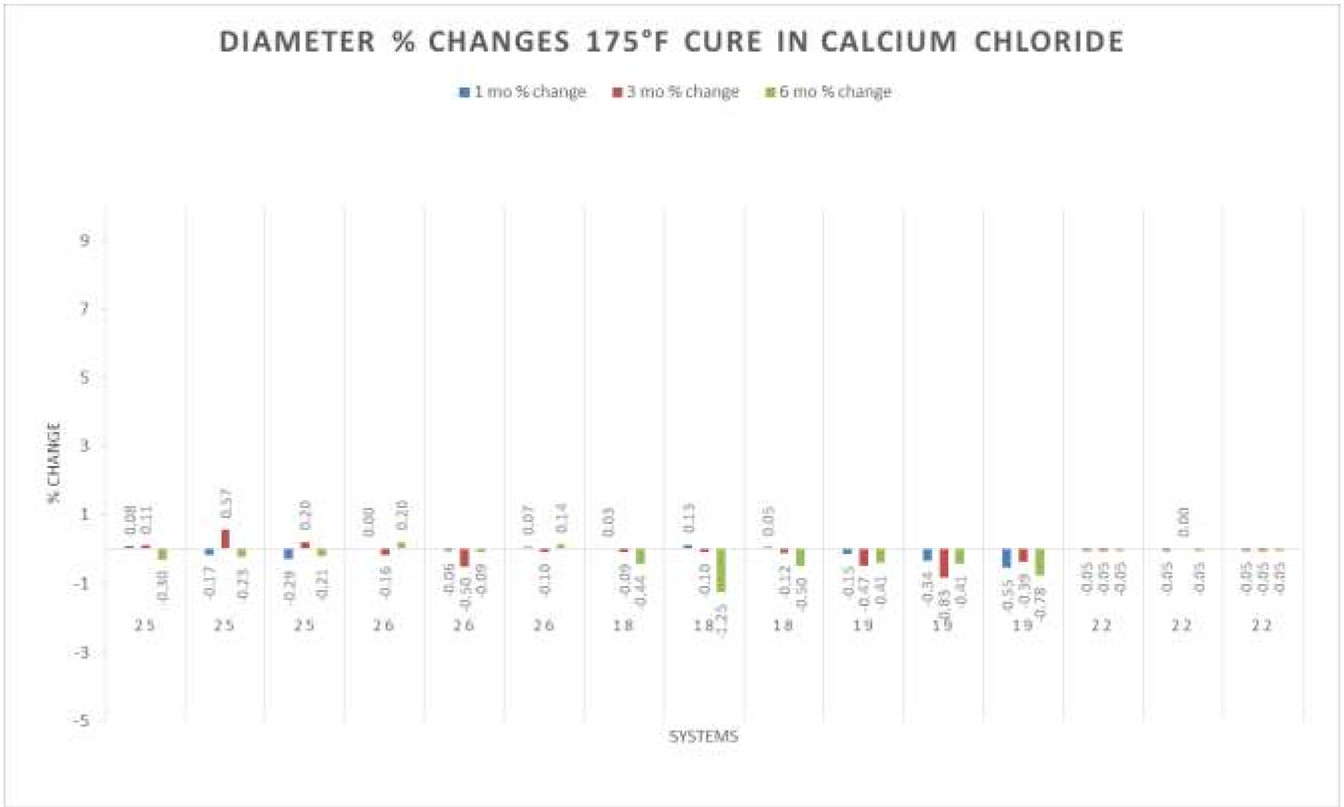


Figure 44: Diameter Change of Systems 18, 19, 22, 25, and 26 in Calcium Chloride Brine at 175°F

Figure 45 lists the long term durability testing in calcium chloride brine at 175°F. Systems 15 and 16 are epoxy resin and showed a gradual downward trend from 2700 psi to 1200 psi tensile strengths. System 26 is another epoxy resin that showed an increase from 2300 psi to 3200 psi in 3 months for tensile strengths. System 19 a phenolic resin had an initial downward trend followed by an upward trend. Systems 22 (furan), 25 and 26 (polyester) all showed either flat or slight increases over time.

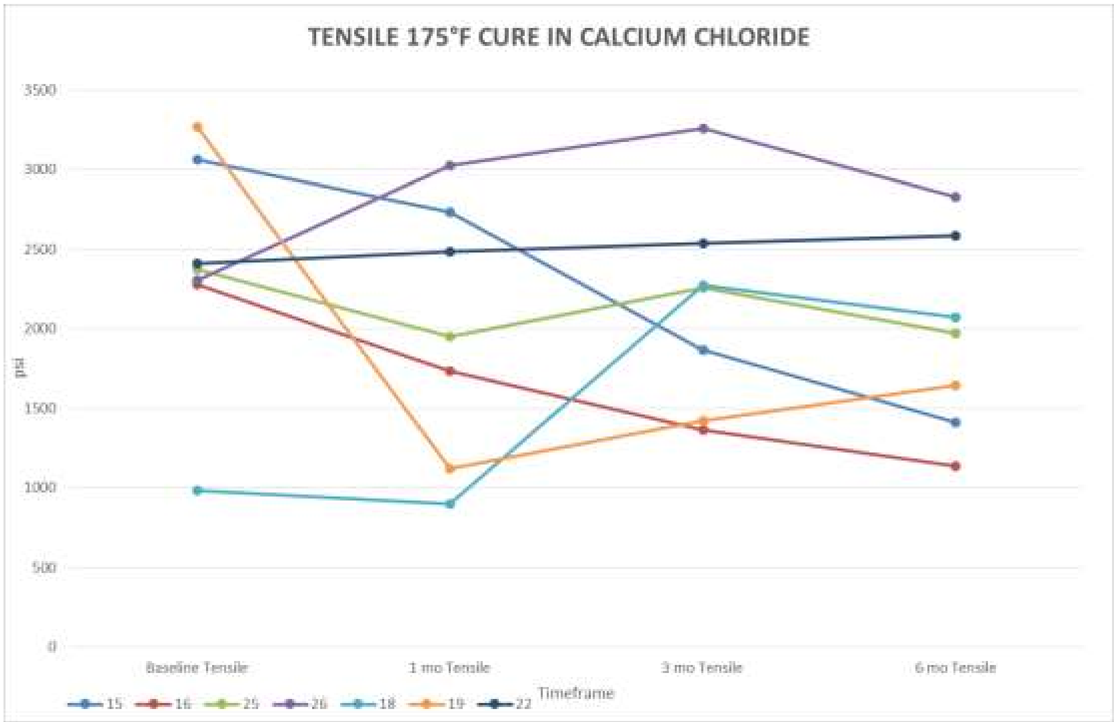


Figure 45: Tensile Strengths of Systems 15, 16, 18, 19, 22, 25, and 26 in Calcium Chloride Brine at 175°F

Figure 46 lists the long term durability testing in calcium chloride brine at 175°F. Systems 3, 6, 8 and 9 are all cement designs and all showed either a flat or upward trend for tensile strengths.

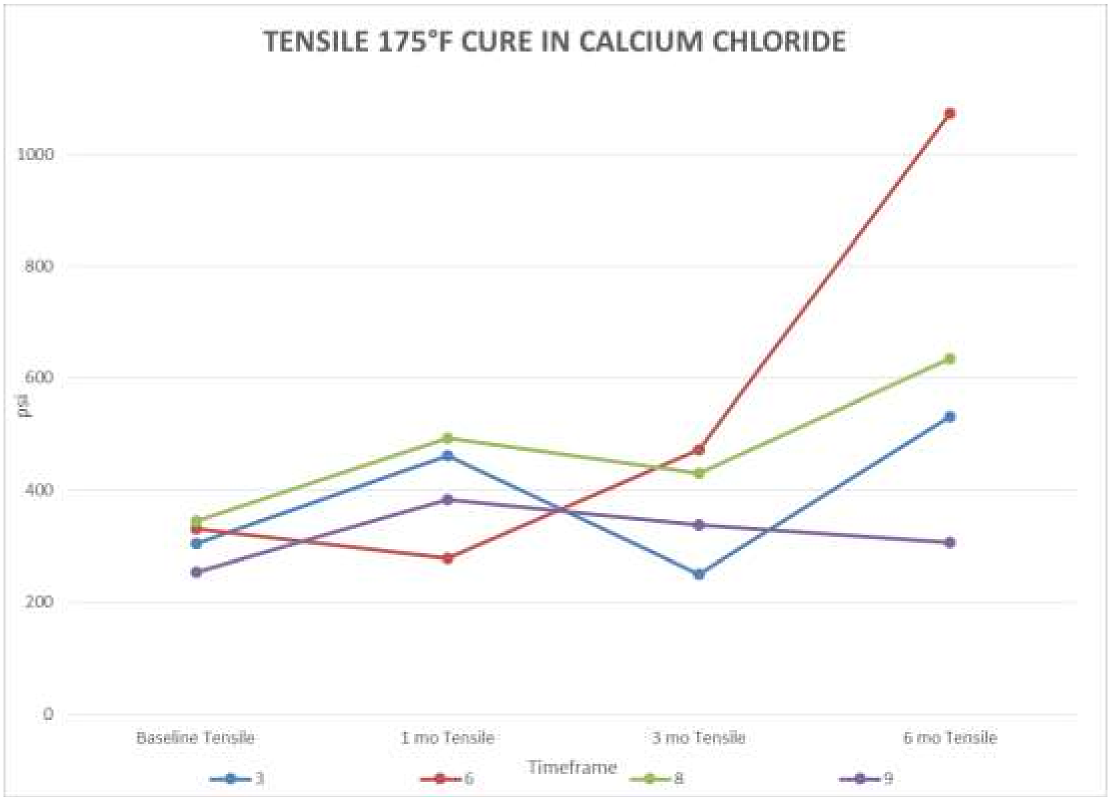


Figure 46: Tensile Strengths of Systems 3, 6, 8, and 9 in Calcium Chloride Brine at 175°F

Figure 47 lists the long term durability testing in calcium bromide brine at 175°F. Systems 3, 6, 8 and 9 (cements) all showed large increases in density over time. Systems 15 and 16 (epoxy) showed no change.

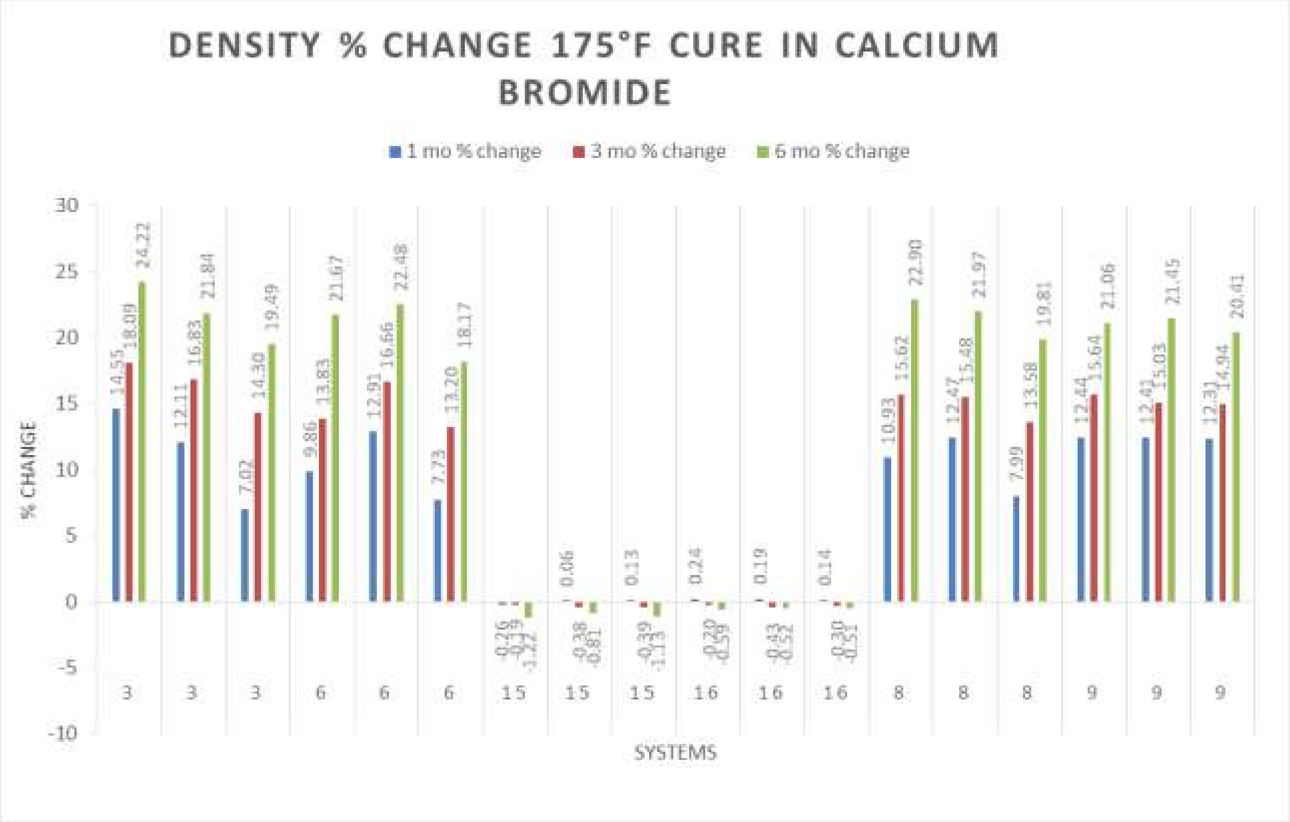


Figure 47: Density Change of Systems 3, 6, 8, 9, 15, and 16 in Calcium Bromide Brine at 175°F

Figure 48 lists the long term durability testing in calcium bromide brine at 175°F. Systems 18 (combo phenolic/epoxy), 22 (furan), 25 (polyester), and 26 (epoxy) all showed no change in density over time. Systems 19 (phenolic) showed a decrease in density over time.

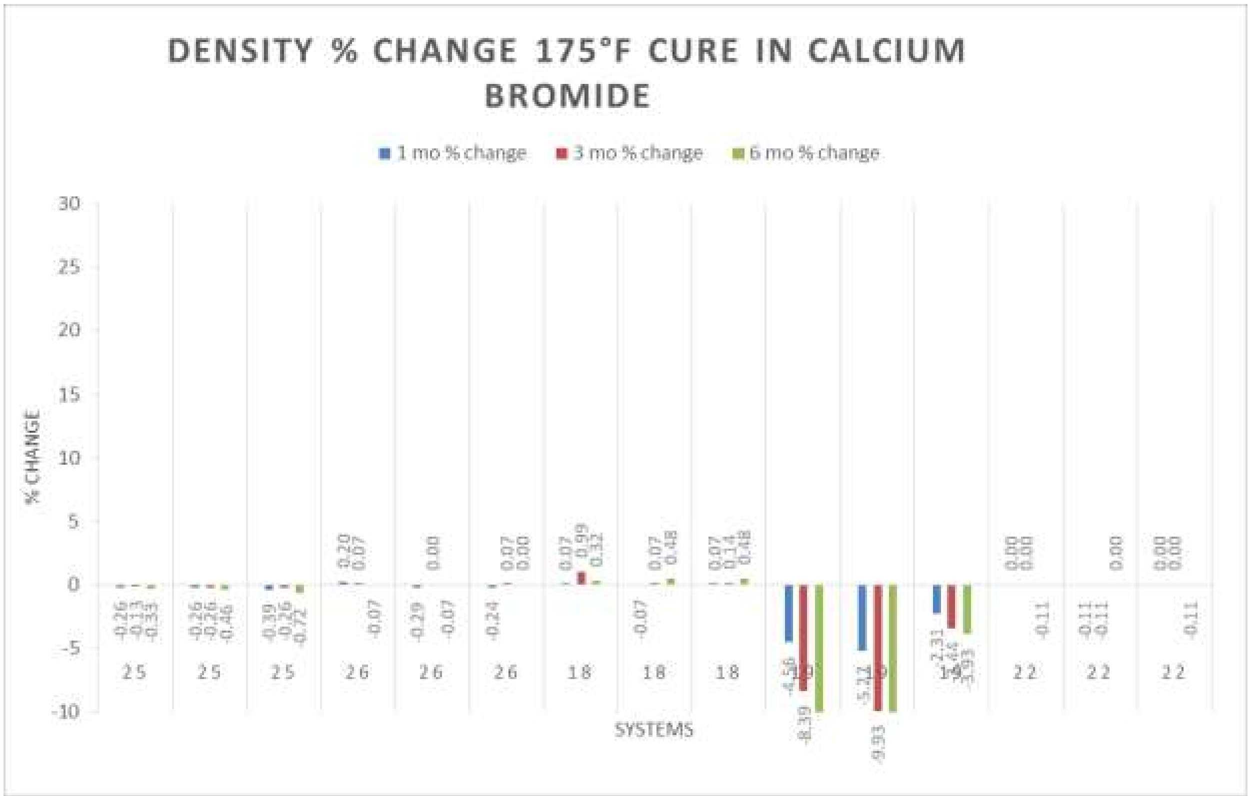


Figure 48: Density Change of Systems 18, 19, 22, 25, and 26 in Calcium Bromide Brine at 175°F

Figure 49 lists the long term durability testing in calcium bromide brine at 175°F. Systems 3, 6, 8 and 9 (cements) all show an increase in diameter at 6 month. Systems 15 and 16 (epoxy) show no change in diameter.

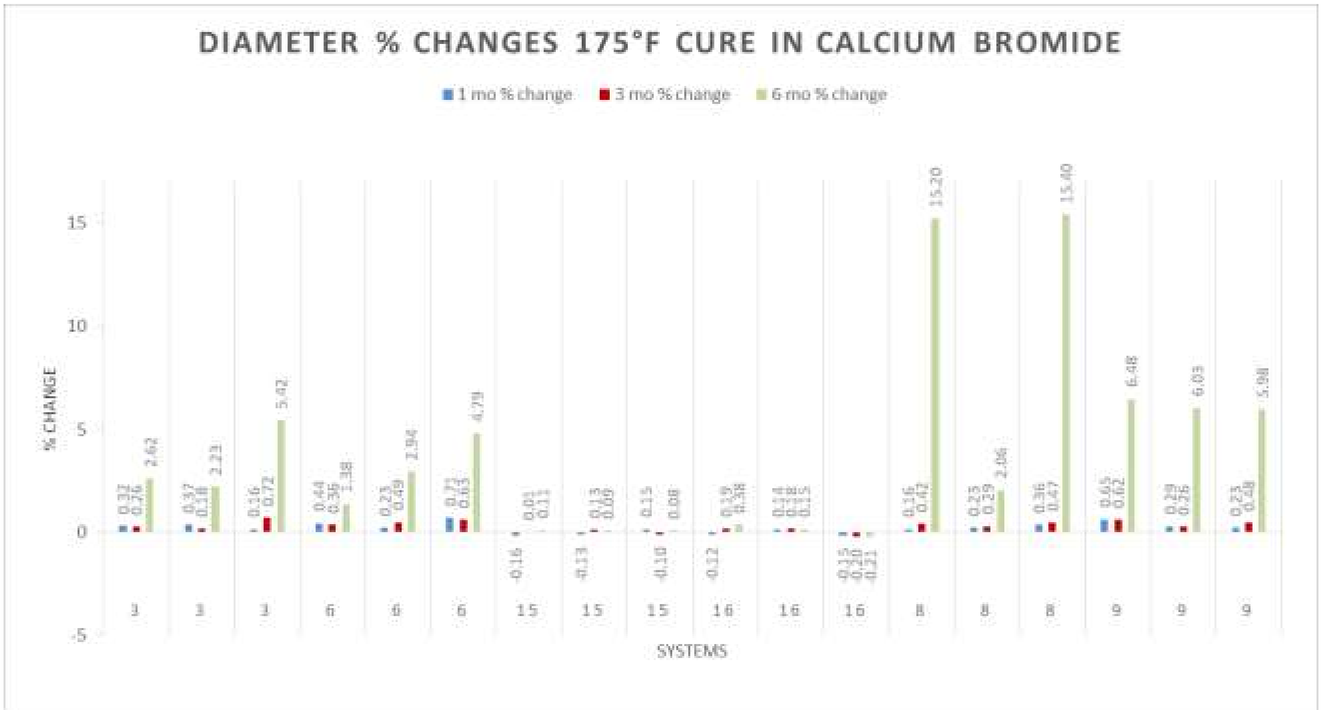


Figure 49: Diameter Change of Systems 3, 6, 8, 9, 15, and 16 in Calcium Bromide Brine at 175°F

Figure 50 lists the long term durability testing in calcium bromide brine at 175°F. Systems 18 (combo phenolic/epoxy), 19 (phenolic), 22 (furan), 25 (polyester), and 26 (epoxy) all showed little to no change in diameter.

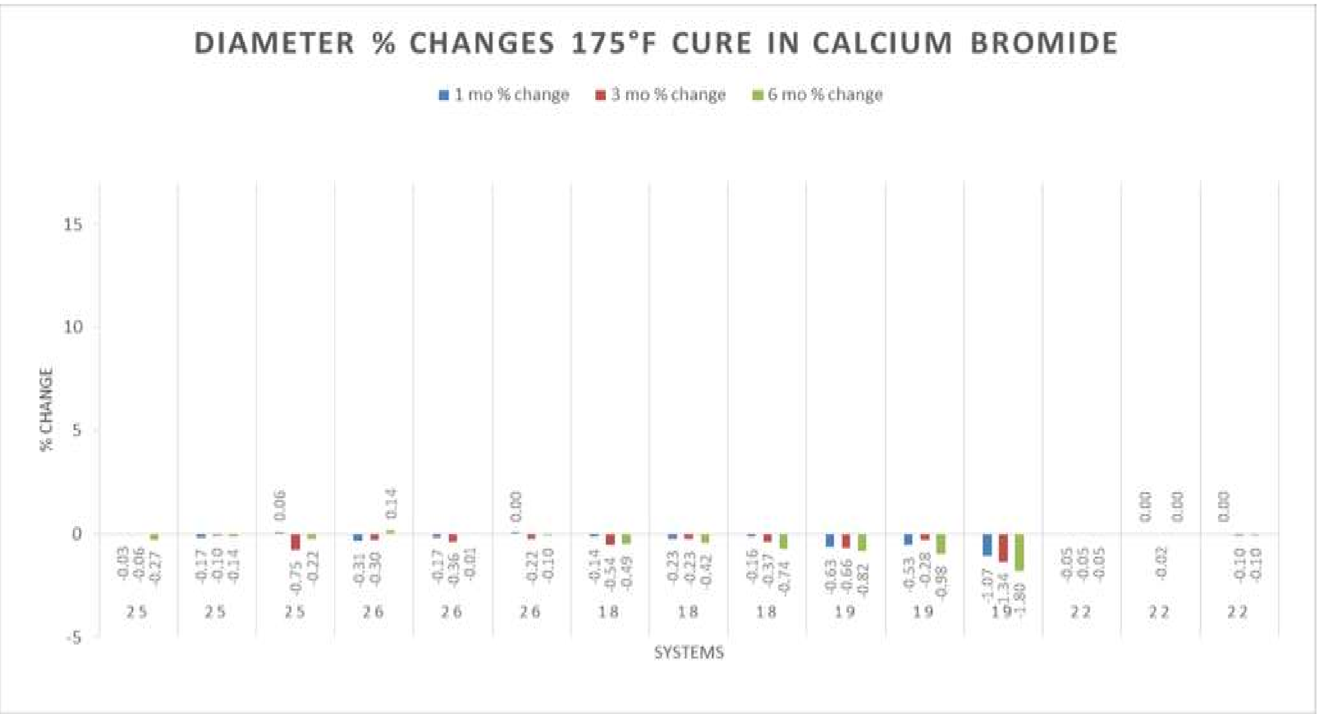


Figure 50: Diameter Change of Systems 18, 19, 22, 25, and 26 in Calcium Bromide Brine at 175°F

Figure 51 lists the long term durability testing in calcium bromide brine at 175°F. Systems 15, and 16 (epoxy) showed a downward trend initially but leveled off at 3 and 6 months at around 2000 psi tensile strength. Systems 22 (furan) and 25 (polyester) showed relatively flat trends. System 26 (epoxy) has shown an increase in tensile over time. System 19 (phenolic) had an initial drop-off but concluded with an upward trend.

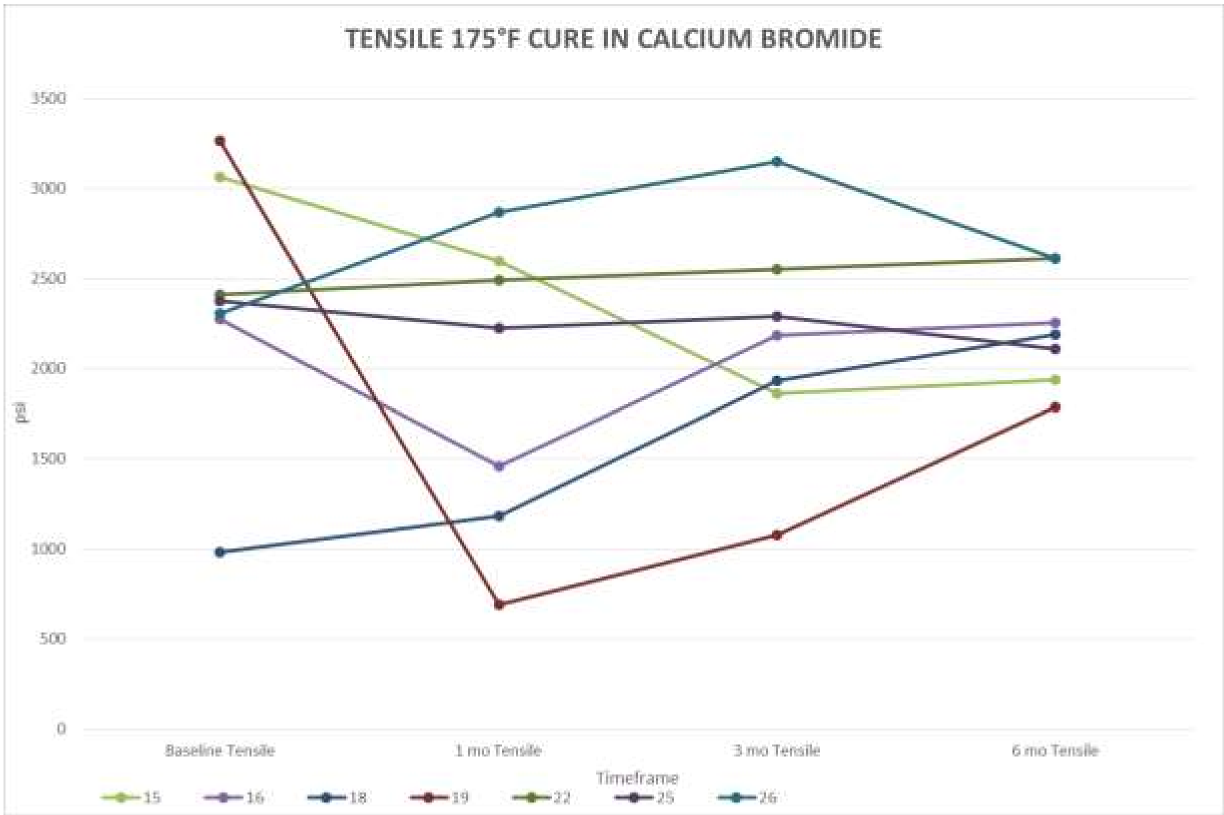


Figure 51: Tensile Strengths of Systems 15, 16, 18, 19, 22, 25, and 26 in Calcium Bromide Brine at 175°F

Figure 52 lists the long term durability testing in calcium bromide brine at 175°F. Systems 3, 6, and 8 (cements) have all shown a slight downward trend at 6 months, but are all still above initial tensile strengths. System 9 (cement) has shown an upward trend in tensile strength.

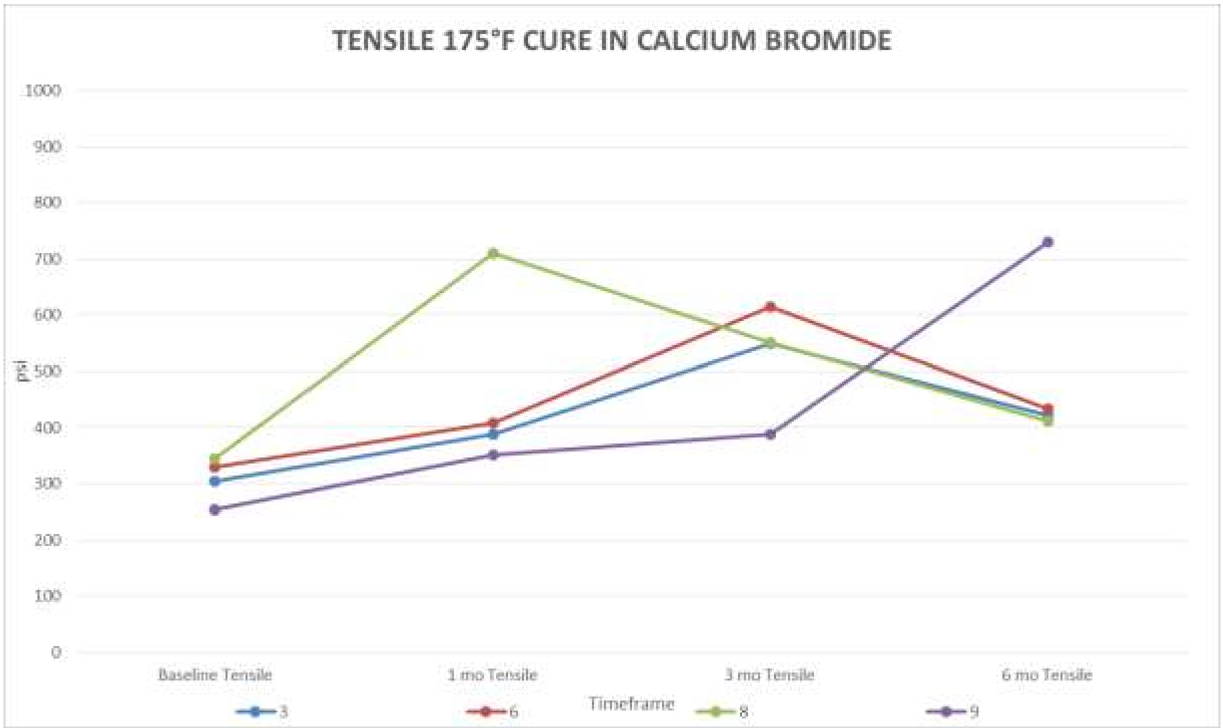


Figure 52: Tensile Strengths of Systems 3, 6, 8, and 9 in Calcium Bromide Brine at 175°F

Figure 53 lists the long term durability testing in nonaromatic hydrocarbon at 175°F. Systems 3, 6, 8, 9 (cements), 15, and 16 (epoxy) all show little to no change in density.

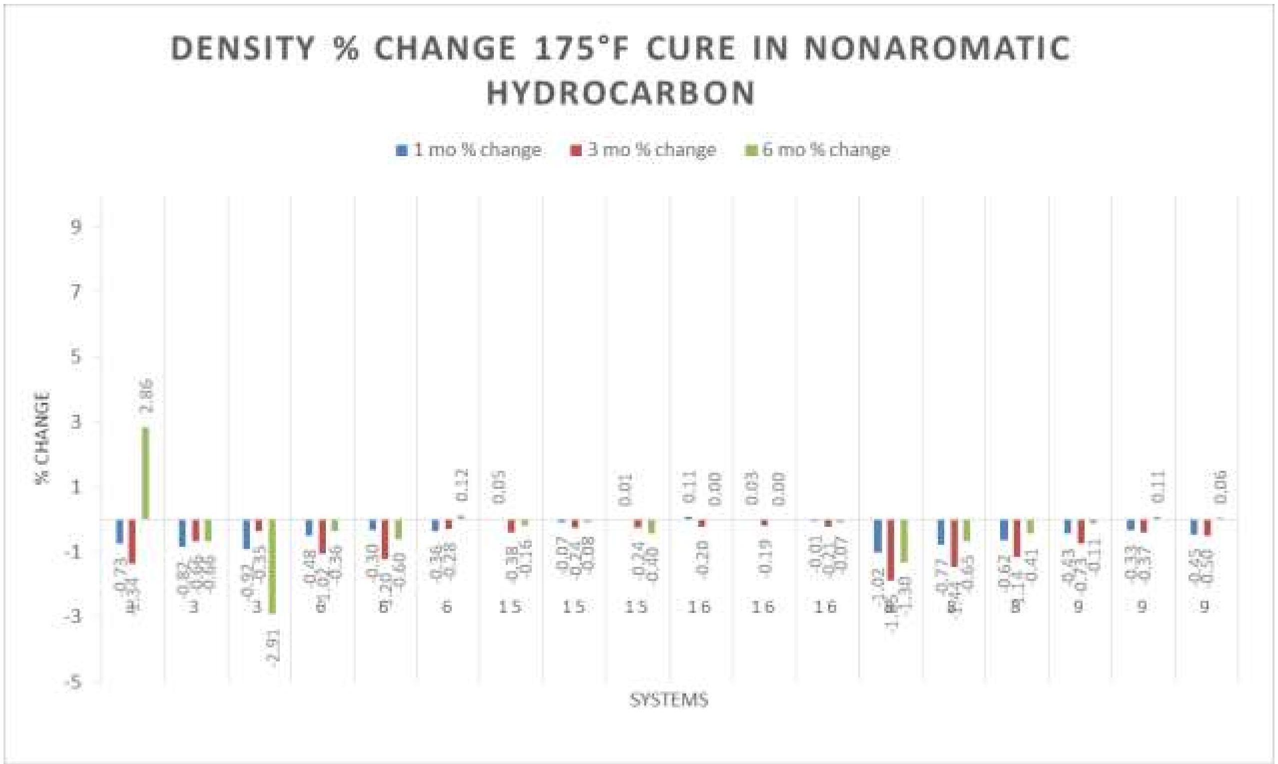


Figure 53: Density Change of Systems 3, 6, 8, 9, 15, and 16 in Nonaromatic Hydrocarbon at 175°F

Figure 54 lists the long term durability testing in nonaromatic hydrocarbon at 175°F. Systems 18 (combo phenolic/epoxy), 19 (phenolic), 22 (furan), 25 (polyester), and 26 (epoxy) all show little to no change in density.

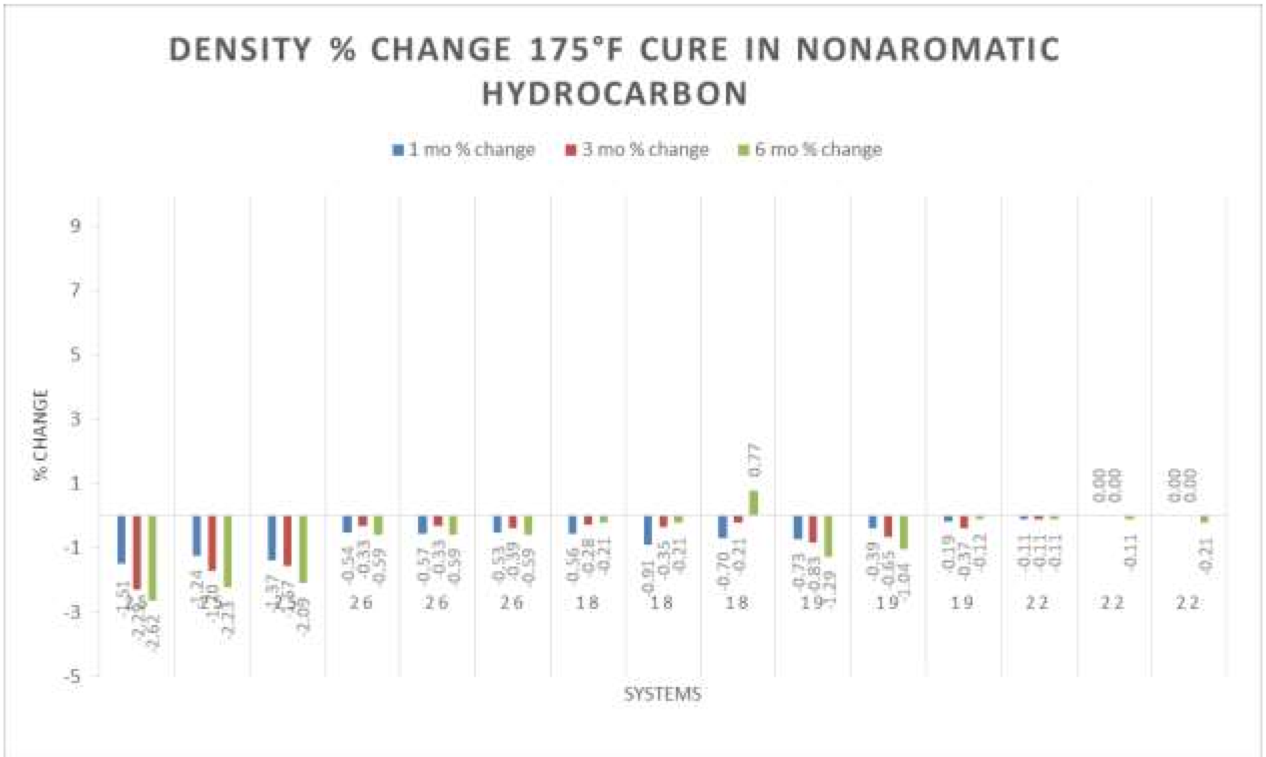


Figure 54: Density Change of Systems 18, 19, 22, 25, and 26 in Nonaromatic Hydrocarbon at 175°F

Figure 55 lists the long term durability testing in nonaromatic hydrocarbon at 175°F. Systems 3, 6, 8, 9 (cements), 15, and 16 (epoxy) all show little to no change in diameter.

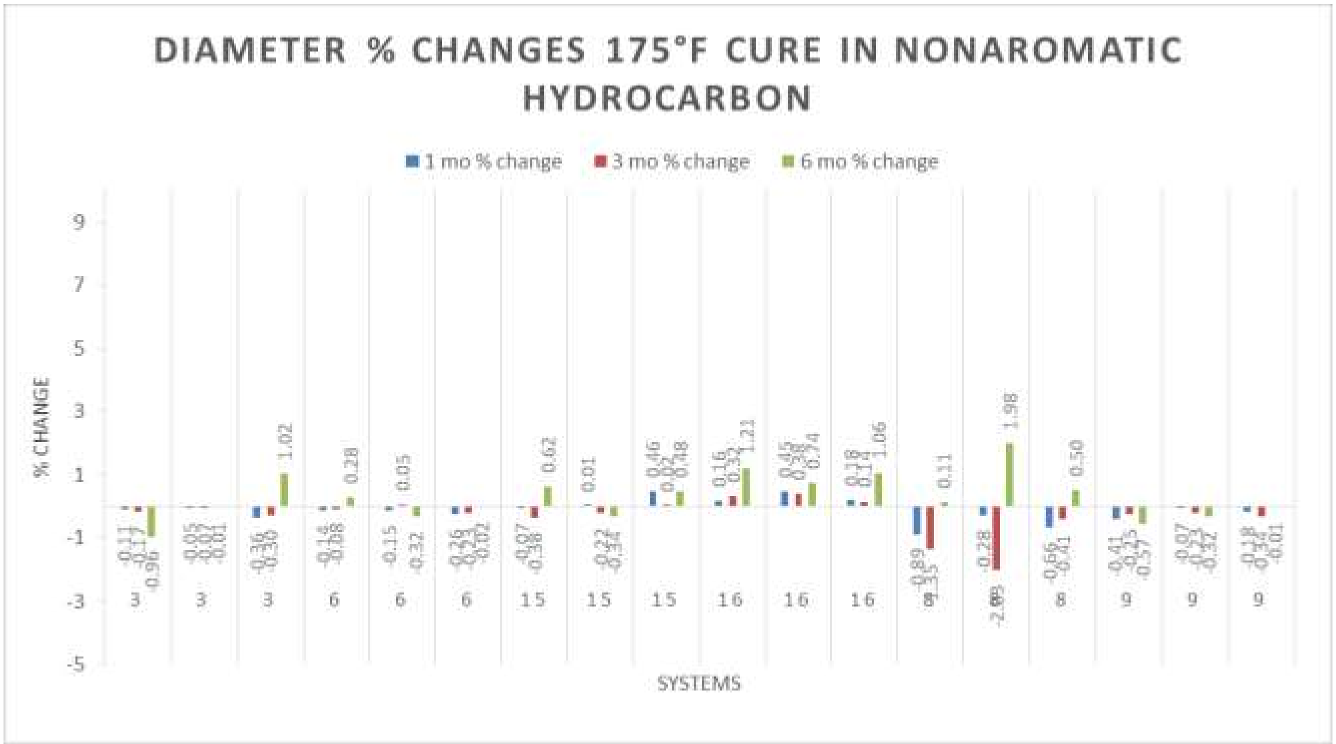


Figure 55: Diameter Change of Systems 3, 6, 8, 9, 15, and 16 in Nonaromatic Hydrocarbon at 175°F

Figure 56 lists the long term durability testing in nonaromatic hydrocarbon at 175°F. Systems 18 (combo phenolic/epoxy), 19 (phenolic), 22 (furan), 25 (polyester), and 26 (epoxy) all show little to no change in diameter.

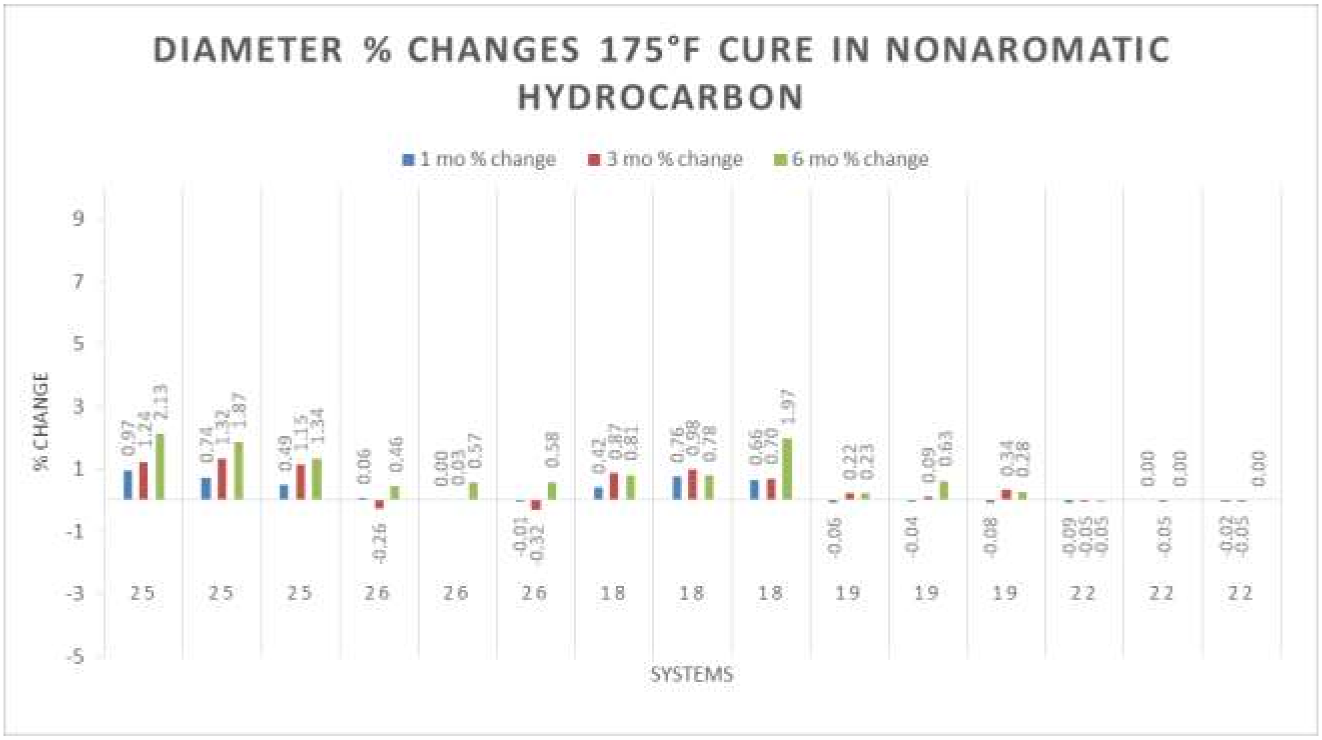


Figure 56: Diameter Change of Systems 18, 19, 22, 25, and 26 in Nonaromatic Hydrocarbon at 175°F

Figure 57 lists the long term durability testing in nonaromatic hydrocarbon at 175°F. Systems 18 (combo phenolic/epoxy) had downward and upward trends, 19 (phenolic), 15, 16 (epoxy), and 25 (polyester) all show downward trends in tensile strengths. System 22 (furan) and 26 (epoxy) show a fairly level trend in tensile strength.

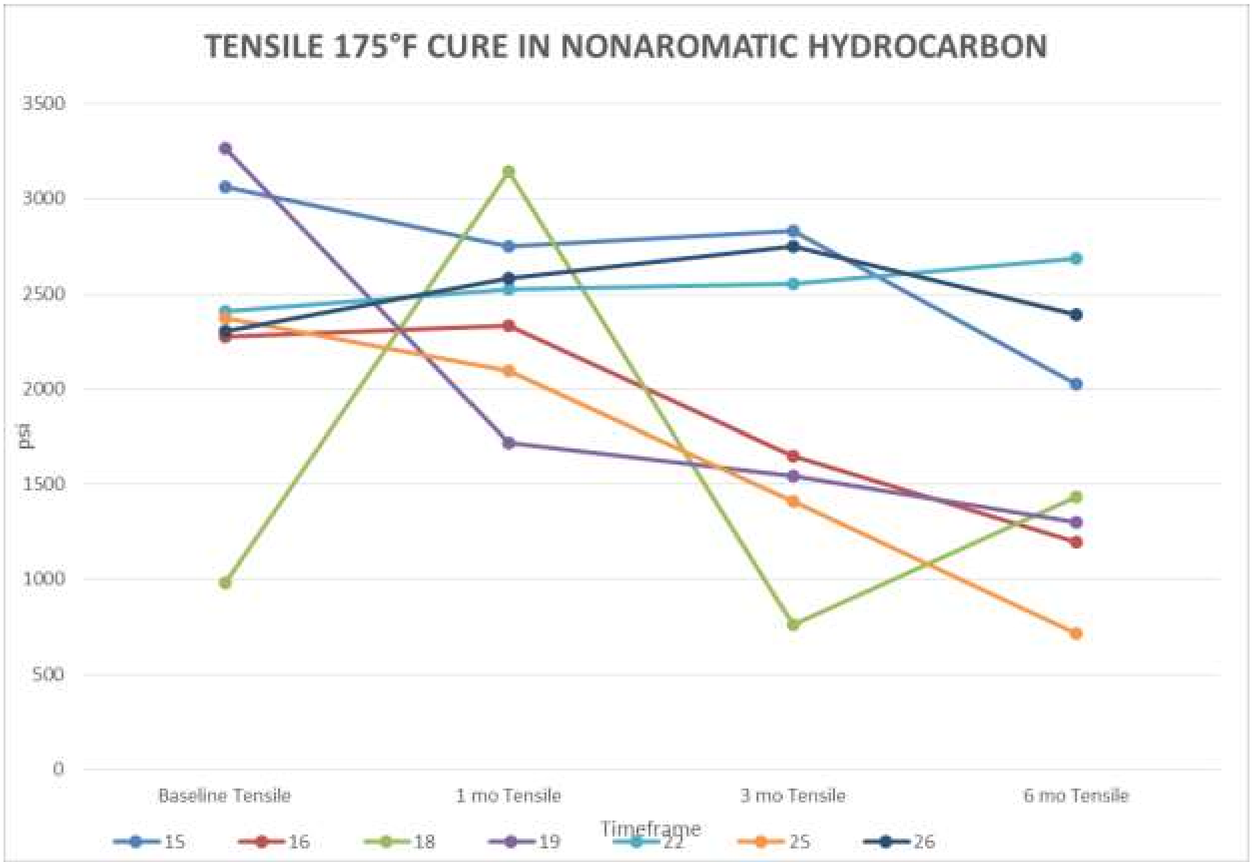


Figure 57: Tensile Strengths of Systems 15, 16, 18, 19, 22, 25, and 26 in Nonaromatic Hydrocarbon at 175°F

Figure 58 lists the long term durability testing in nonaromatic hydrocarbon at 175°F. Systems 3, 6, and 8 (cements) showed initial increases in tensile but started to show downward trends at 6 months. System 9 (cement) show an upward trend in tensile strengths.

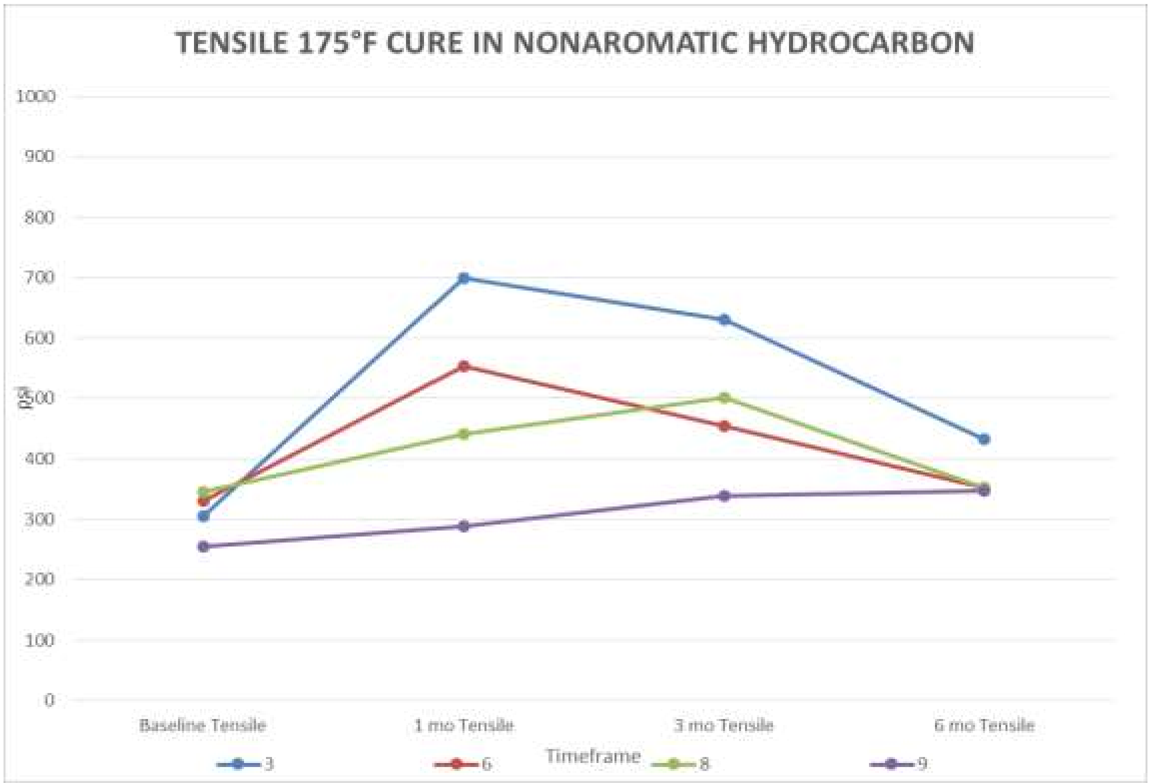


Figure 58: Tensile Strengths of Systems 3, 6, 8, and 9 in Nonaromatic Hydrocarbon at 175°F

Figure 59 lists the long term durability testing in 11.0 lb/gal calcium chloride brine at ambient conditions. System 1 and 4 (cements) showed slight increases in density at 1 and 3 month. At 6 month the samples were degraded for Systems 1 and 4 (cements) and could not be measured. Systems 13, and 14 (epoxy) showed no change. System 7 (cement) showed a large increase in density.

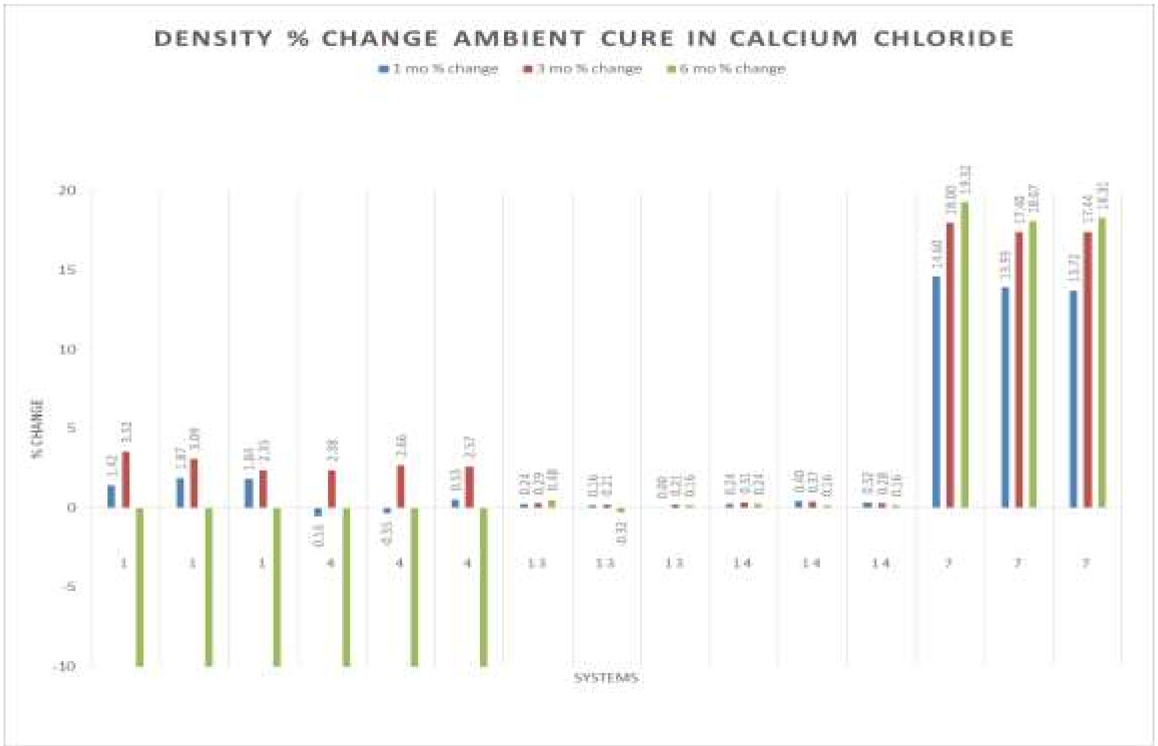


Figure 59: Density Change of Systems 1, 4, 7, 13 and 14 in Calcium Chloride Brine at Ambient

Figure 60 lists the long term durability testing in 11.0 lb/gal calcium chloride brine at ambient conditions. Systems 10 and 11 (cements) showed increases in density. Systems 17 (Bis A epoxy) and 23 (polyester) showed no change.

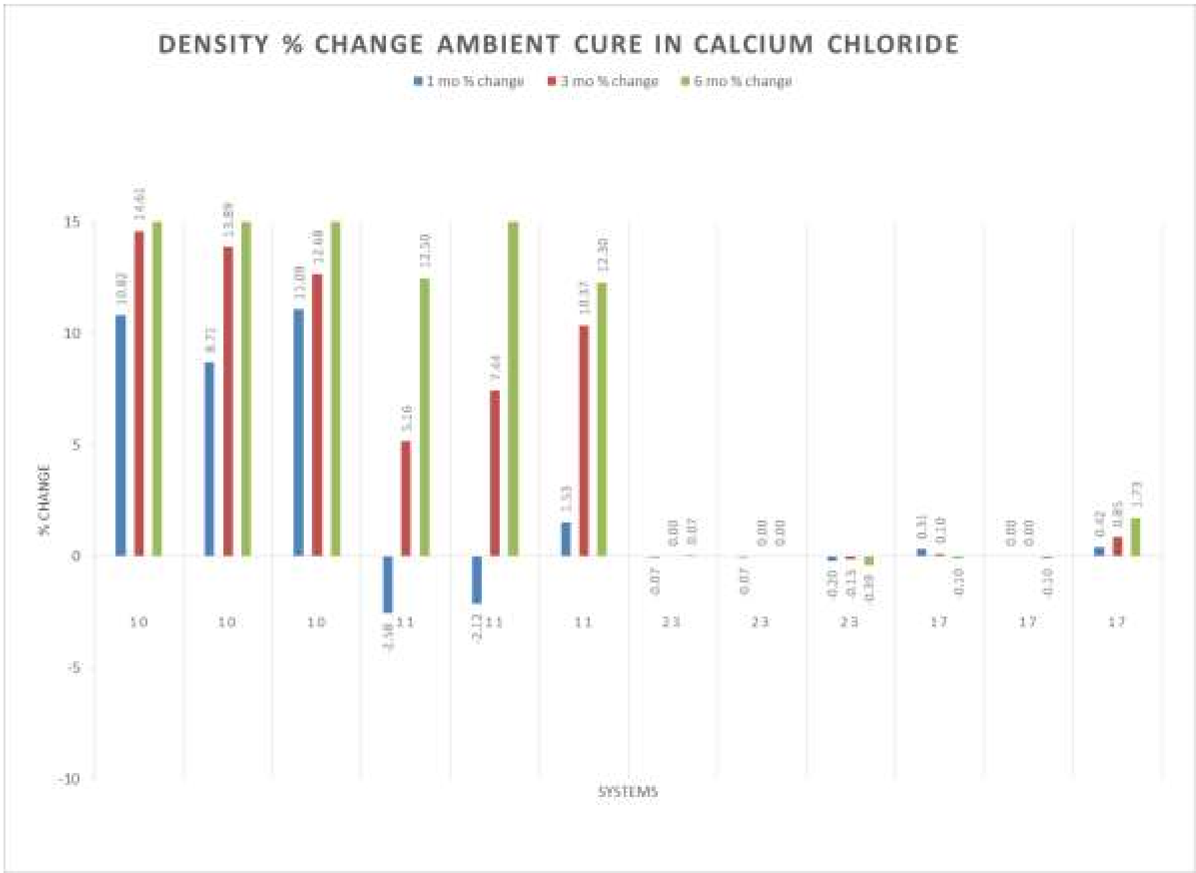


Figure 60: Density Change of Systems 10, 11, 17, and 23 in Calcium Chloride Brine at Ambient

Figure 61 lists the long term durability testing in 11.0 lb/gal calcium chloride brine at ambient conditions. System 1 and 4 (cements) showed no change in diameter at 1 and 3 month. At 6 month the samples were degraded for Systems 1 and 4 (cements) and could not be measured. Systems 7 (cement), 13, and 14 (epoxy) showed no change in diameter.

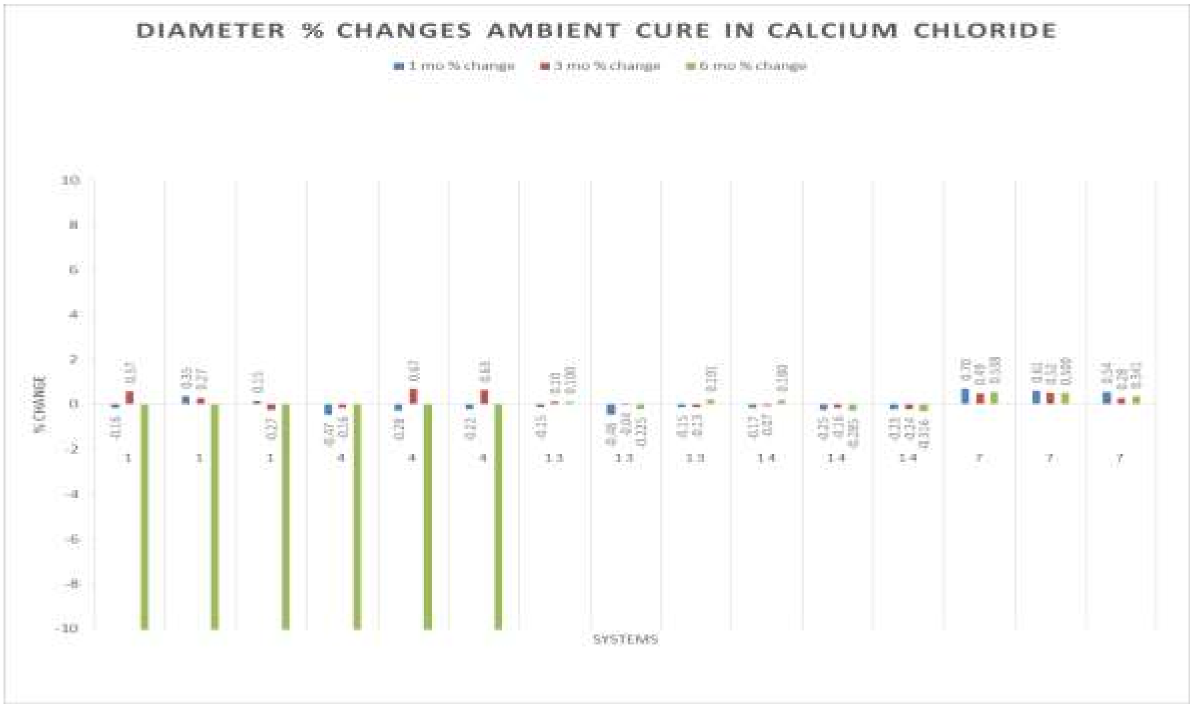


Figure 61: Diameter Change of Systems 1, 4, 7, 13 and 14 in Calcium Chloride Brine at Ambient

Figure 62 lists the long term durability testing in 11.0 lb/gal calcium chloride brine at ambient conditions. Systems 10, 11 (cements), 17 (Bis A epoxy), and 23 (polyester) showed no change in diameter.

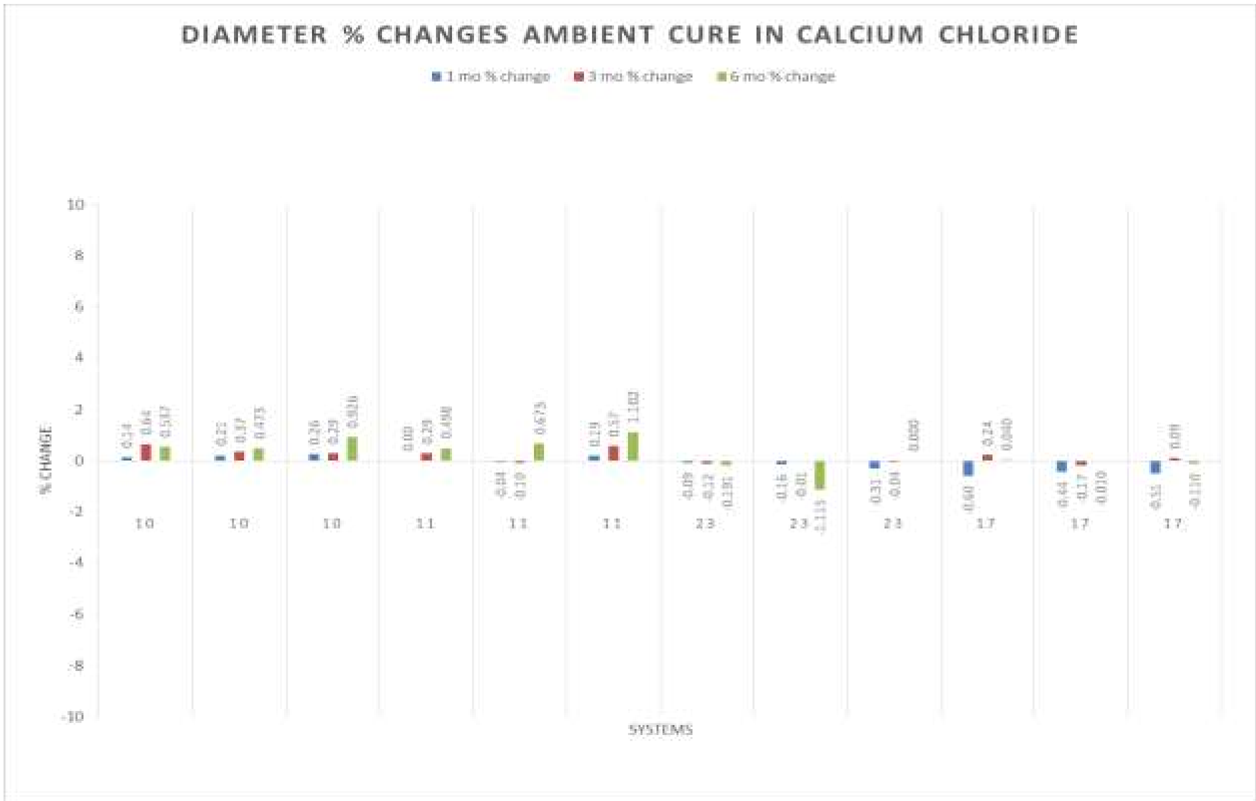


Figure 62: Diameter Change of Systems 10, 11, 17, and 23 in Calcium Chloride Brine at Ambient

Figure 63 lists the long term durability testing in 11.0 lb/gal calcium chloride brine at ambient conditions. Systems 13, 14 (epoxy), and 23 (polyester) were all relatively flat in trend for tensile strength. System 17 (Bis A epoxy) had an initial drop followed by an increase followed by a decrease.

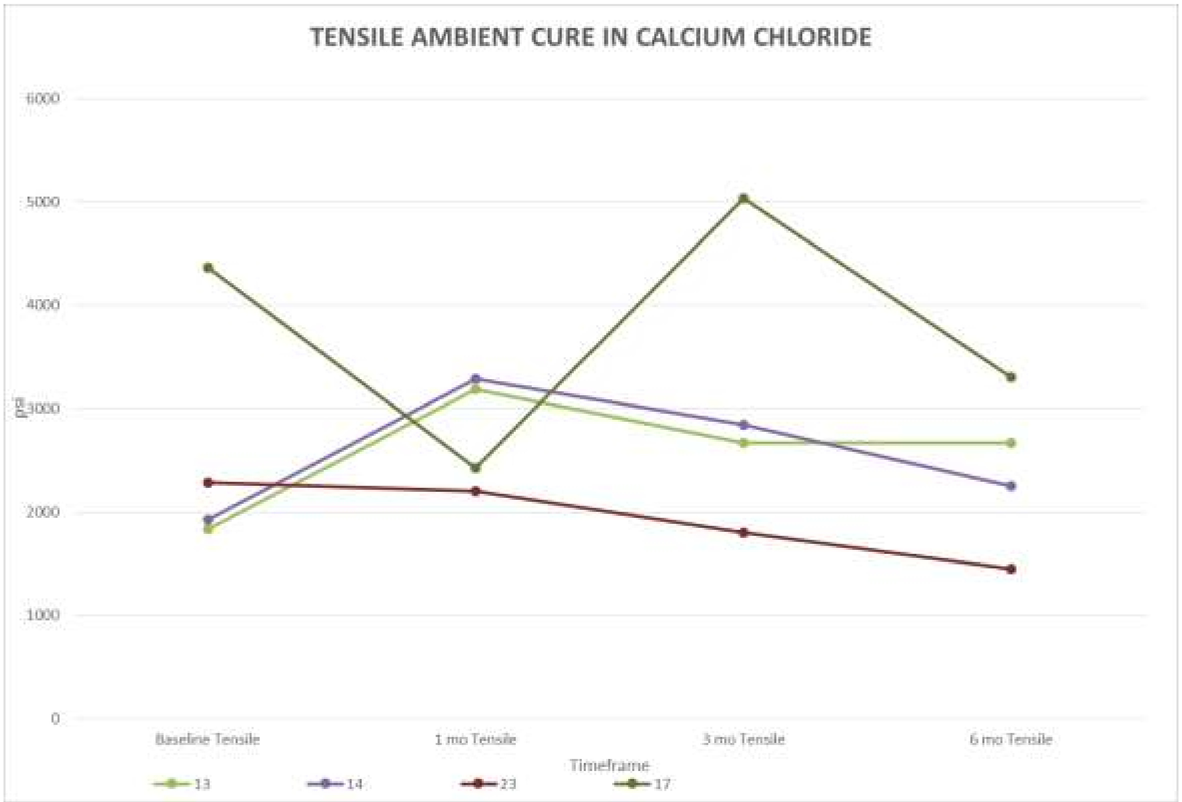


Figure 63: Tensile Strengths of Systems 13, 14, 17, and 23 in Calcium Chloride Brine at Ambient

Figure 64 lists the long term durability testing in 11.0 lb/gal calcium chloride brine at ambient conditions. Systems 7, 10 and 11 stayed fairly flat from initial to final. Systems 1 and 4 completely degraded and could not be measured for tensile strengths at 6 months.

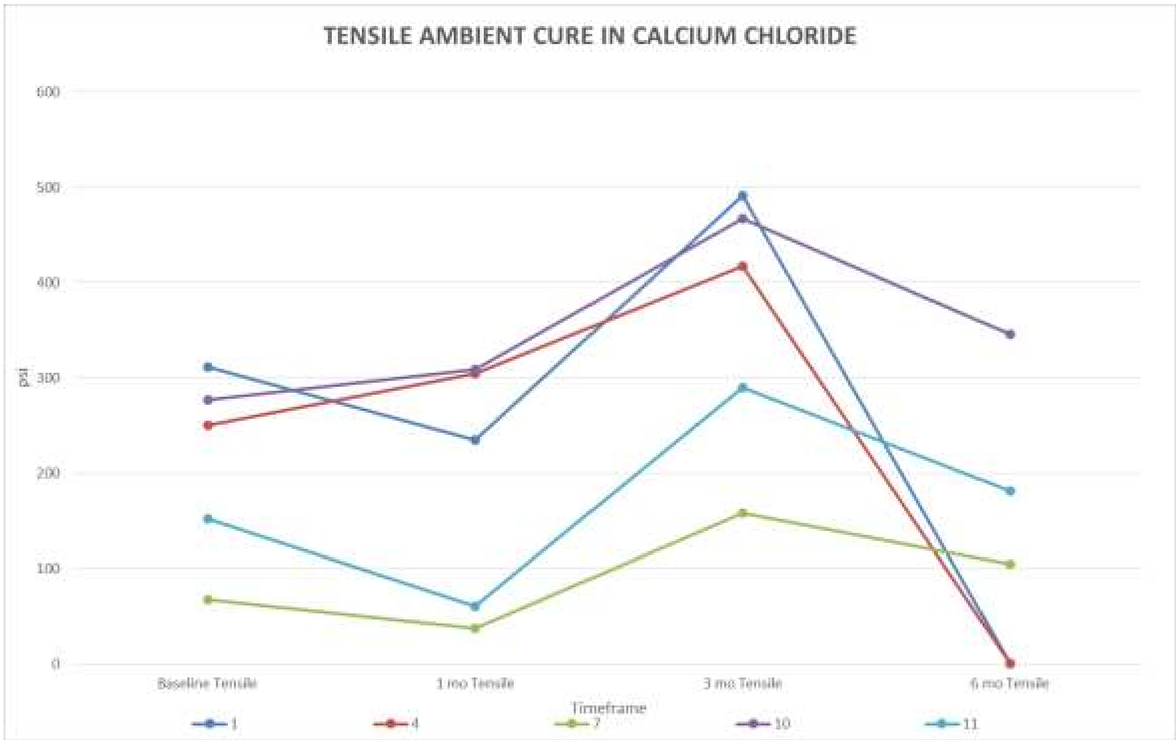


Figure 64: Tensile Strengths of Systems 1, 4, 7, 10, and 11 in Calcium Chloride Brine at Ambient

Figure 65 lists the long term durability testing in 11.0 lb/gal calcium bromide brine at ambient conditions. System 1 and 4 (cements) were degraded at 3 and 6 months and could not be measured for density. Systems 13, and 14 (epoxy) showed no change. System 7 (cement) showed a large increase in density.

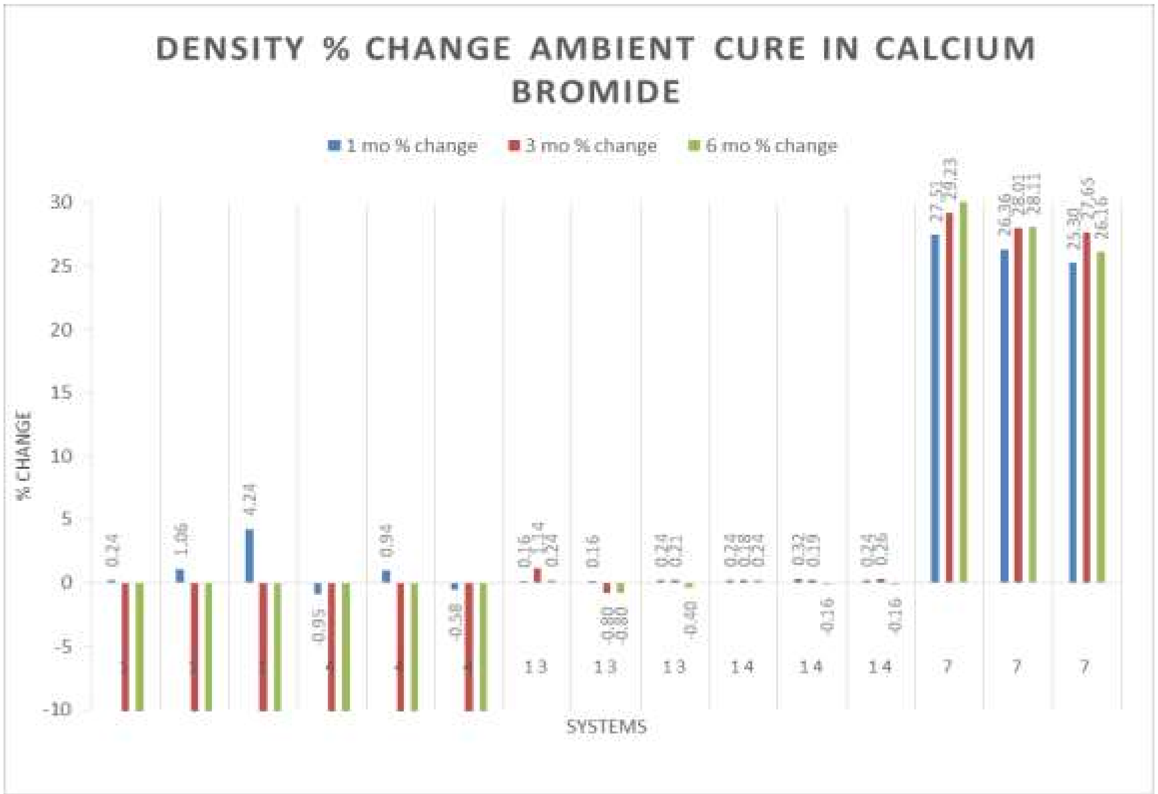


Figure 65: Density Change of Systems 1, 4, 7, 13 and 14 in Calcium Bromide Brine at Ambient

Figure 66 lists the long term durability testing in 11.0 lb/gal calcium bromide brine at ambient conditions. Systems 10 and 11 (cements) showed increases in density. Systems 17 (Bis A epoxy) and 23 (polyester) showed no change.

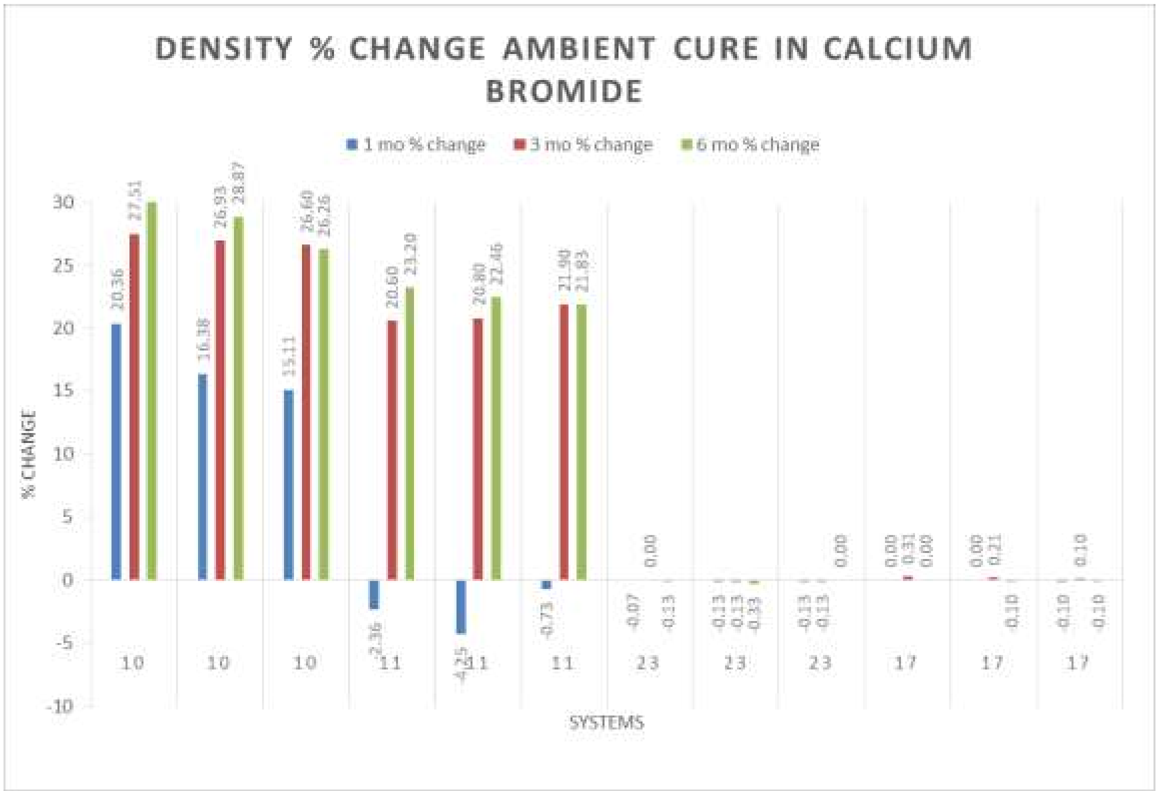


Figure 66: Density Change of Systems 10, 11, 17, and 23 in Calcium Bromide Brine at Ambient

Figure 67 lists the long term durability testing in 11.0 lb/gal calcium bromide brine at ambient conditions. System 1 (cement) could only be measured for diameter in one sample at one month. The other two samples were two degraded to measure for diameter. System 4 (cement) could not be measured for diameter at 1 month. At 3 and 6 months the samples were degraded for Systems 1 and 4 (cements) and could not be measured. Systems 7 (cement), 13, and 14 (epoxy) showed no change in diameter.

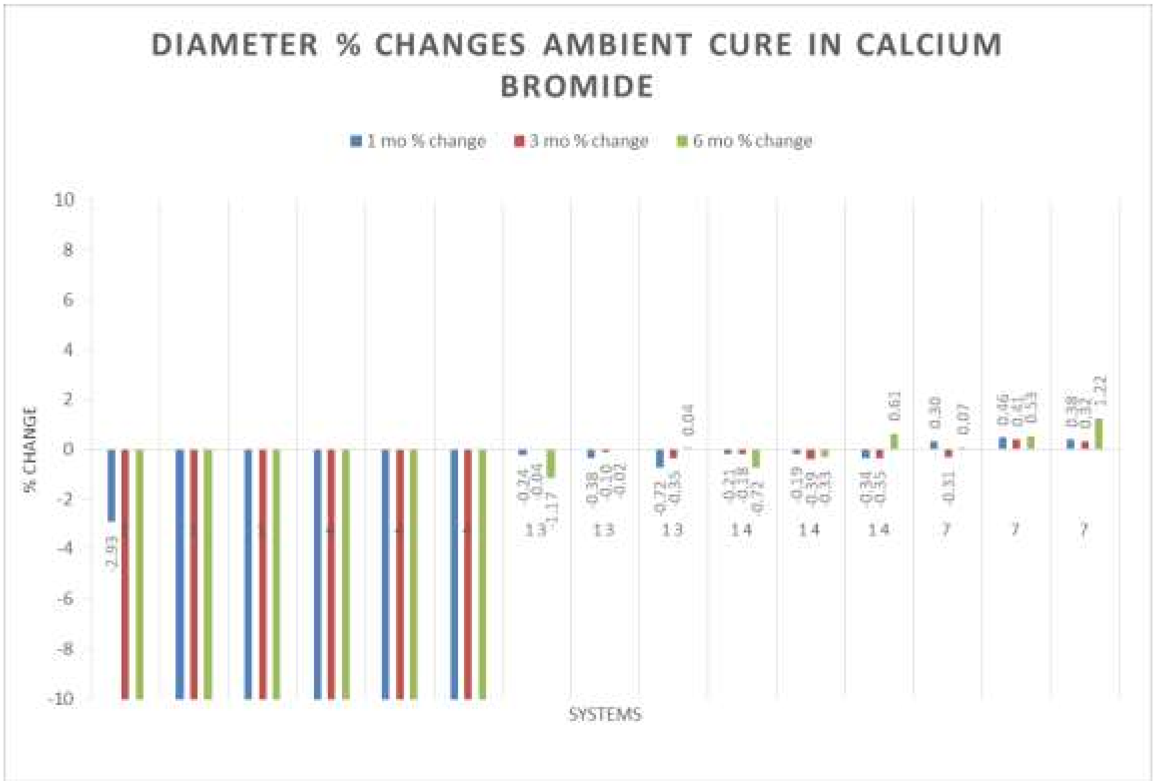


Figure 67: Diameter Change of Systems 1, 4, 7, 13 and 14 in Calcium Bromide Brine at Ambient

Figure 68 lists the long term durability testing in 11.0 lb/gal calcium bromide brine at ambient conditions. Systems 10, 11 (cements), 17 (Bis A epoxy), and 23 (polyester) showed no change in diameter.

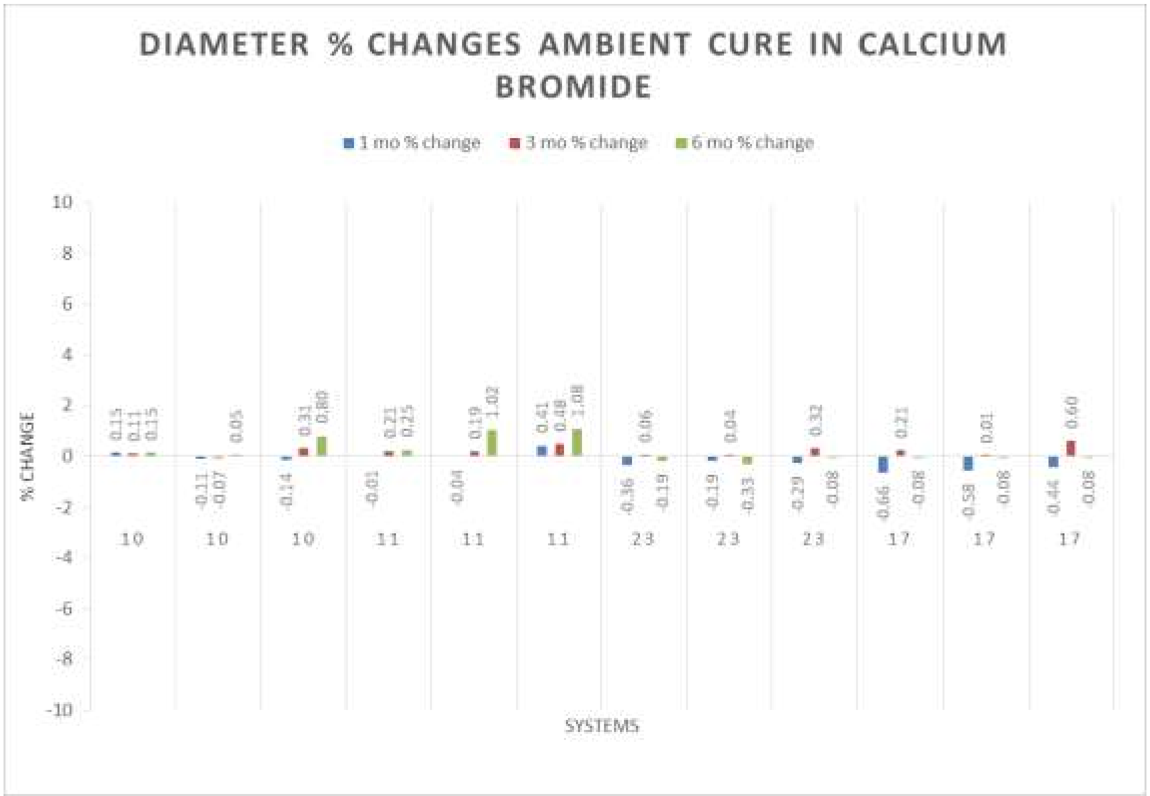


Figure 68: Diameter Change of Systems 10, 11, 17, and 23 in Calcium Bromide Brine at Ambient

Figure 69 lists the long term durability testing in 11.0 lb/gal calcium bromide brine at ambient conditions. Systems 13, 14 (epoxy), and 23 (polyester) were all relatively flat in trend for tensile strength. System 17 (Bis A epoxy) had an initial drop followed by an increase followed by a decrease.

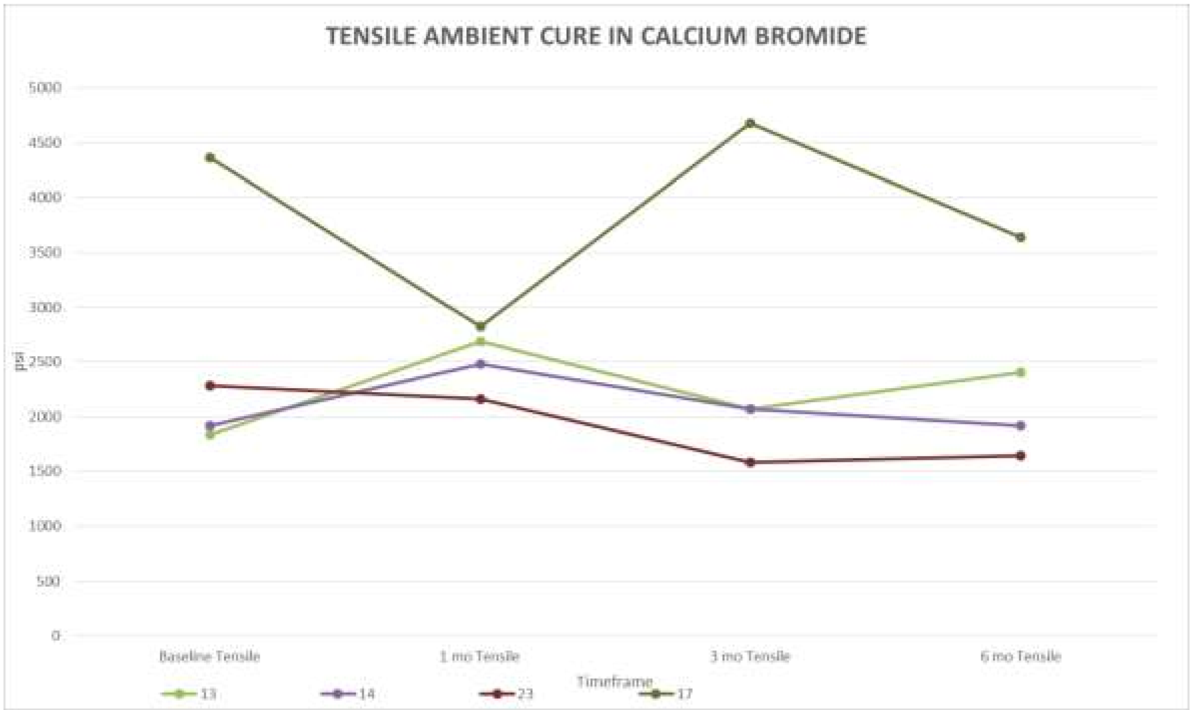


Figure 69: Tensile Strengths of Systems 13, 14, 17, and 23 in Calcium Bromide Brine at Ambient

Figure 70 lists the long term durability testing in 11.0 lb/gal calcium bromide brine at ambient conditions. Systems 7, 10 and 11 stayed fairly flat from initial to final. Systems 1 and 4 completely degraded and could not be measured for tensile strengths at 3 and 6 months.

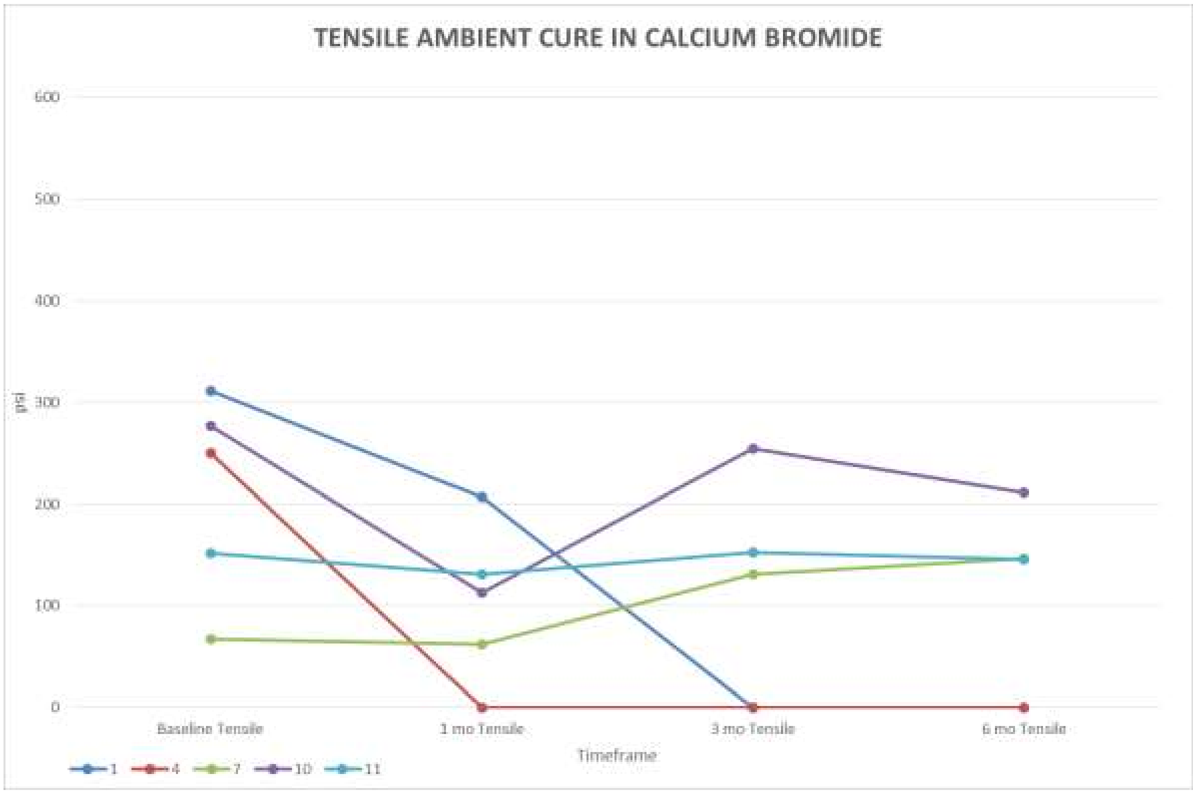


Figure 70: Tensile Strengths of Systems 1, 4, 7, 10, and 11 in Calcium Bromide Brine at Ambient

Figure 71 lists the long term durability testing in 11.0 lb/gal nonaromatic hydrocarbon at ambient conditions. System 1, 4, 7 (cements), 13, and 14 (epoxy) all showed no changes in density.

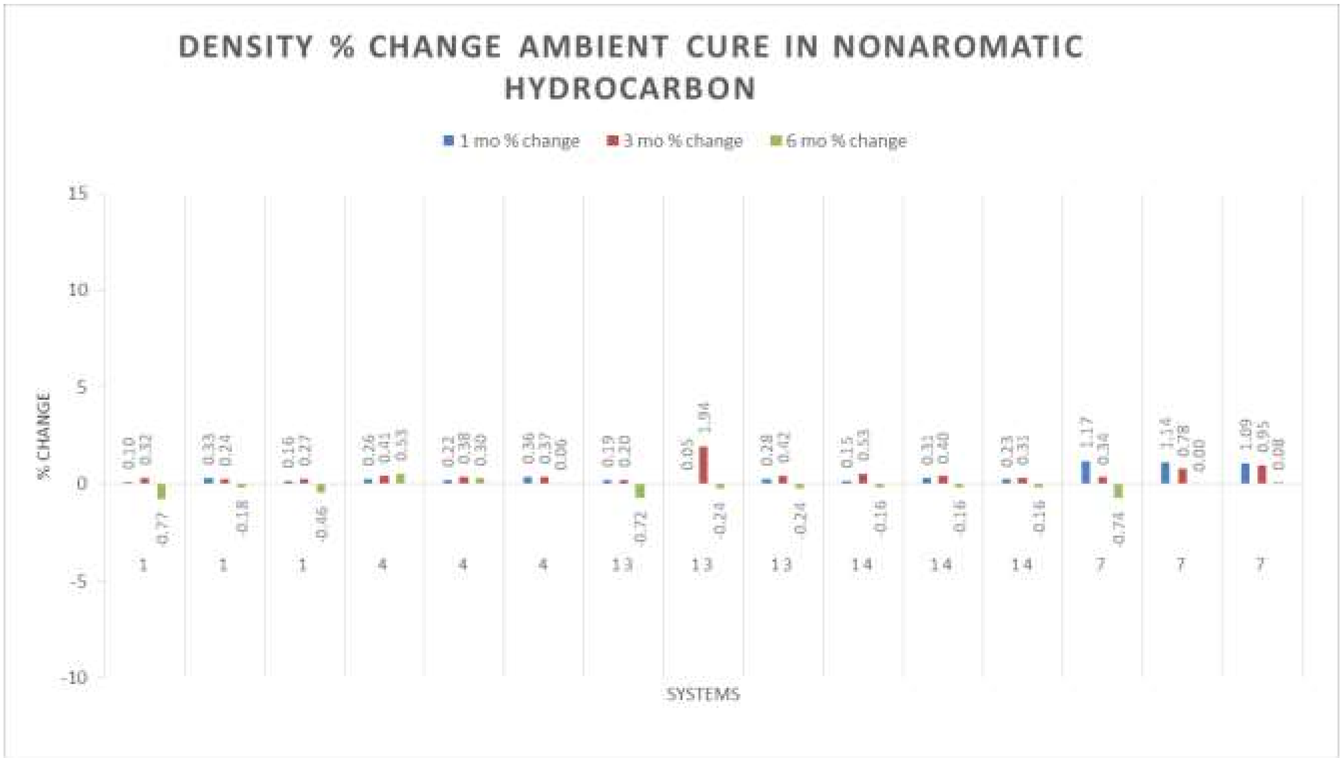


Figure 71: Density Change of Systems 1, 4, 7, 13 and 14 in Nonaromatic Hydrocarbon at Ambient

Figure 72 lists the long term durability testing in 11.0 lb/gal nonaromatic hydrocarbon brine at ambient conditions. Systems 10 and 11 (cements) showed slight changes in density. Systems 17 (Bis A epoxy) and 23 (polyester) showed little to no change.

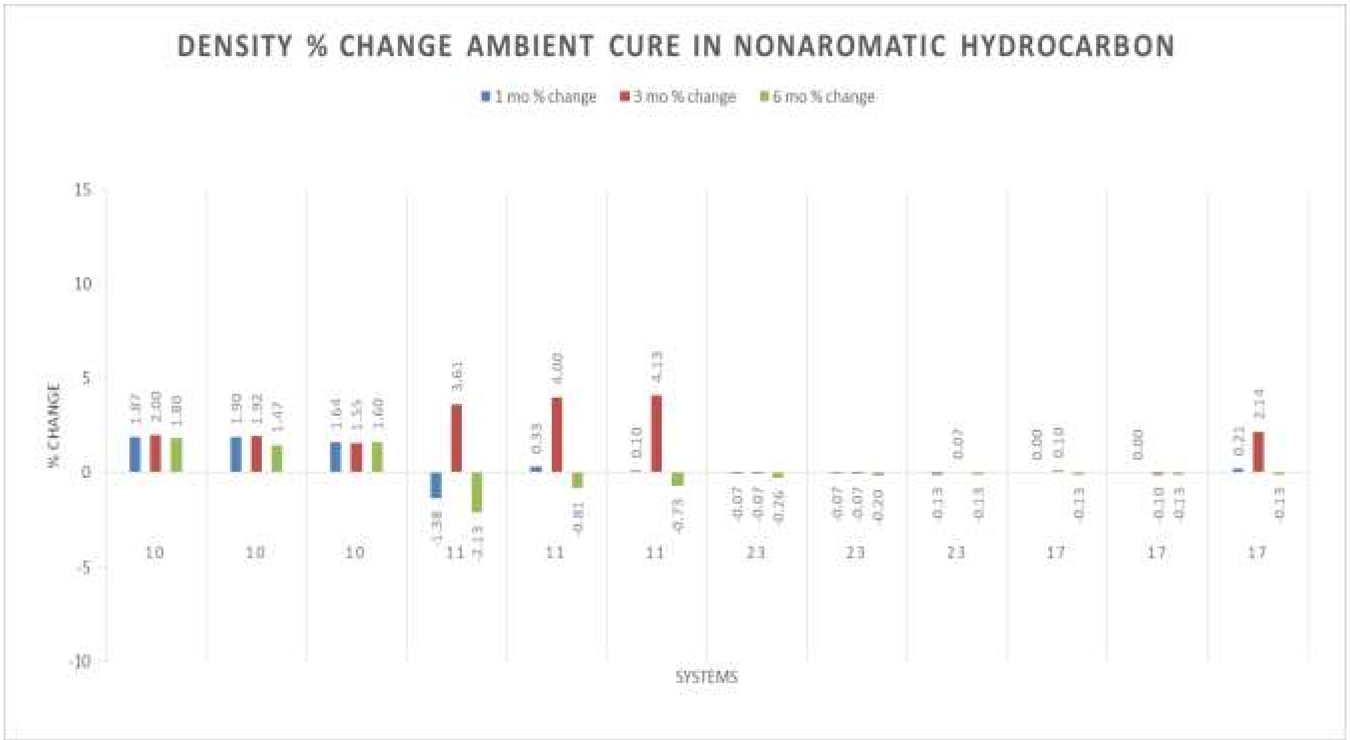


Figure 72: Density Change of Systems 10, 11, 17, and 23 in Nonaromatic Hydrocarbon at Ambient

Figure 73 lists the long term durability testing in 11.0 lb/gal nonaromatic hydrocarbon brine at ambient conditions. System 1, 4, 7 (cements), 13, and 14 (epoxy) all showed no changes in diameter.

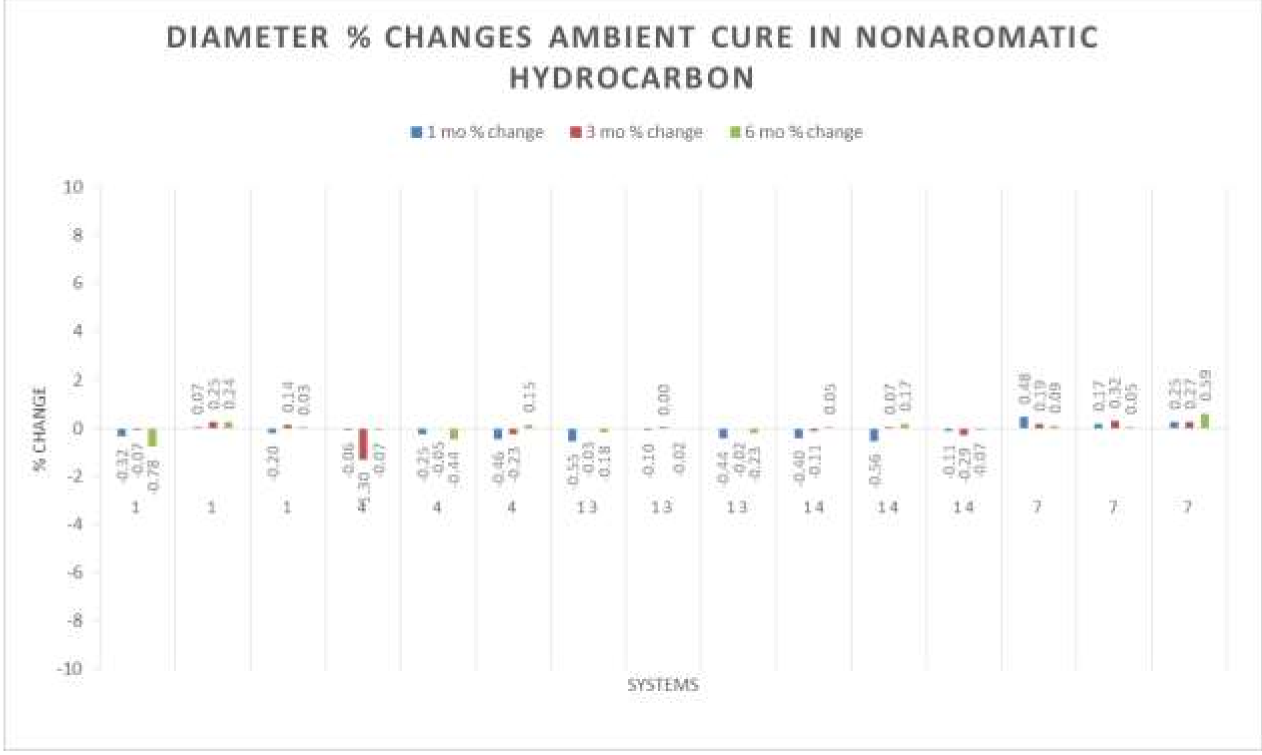


Figure 73: Diameter Change of Systems 1, 4, 7, 13 and 14 in Nonaromatic Hydrocarbon at Ambient

Figure 74 lists the long term durability testing in 11.0 lb/gal nonaromatic hydrocarbon brine at ambient conditions. Systems 10, 11 (cements), 17 (Bis A epoxy), and 23 (polyester) showed no change in diameter.

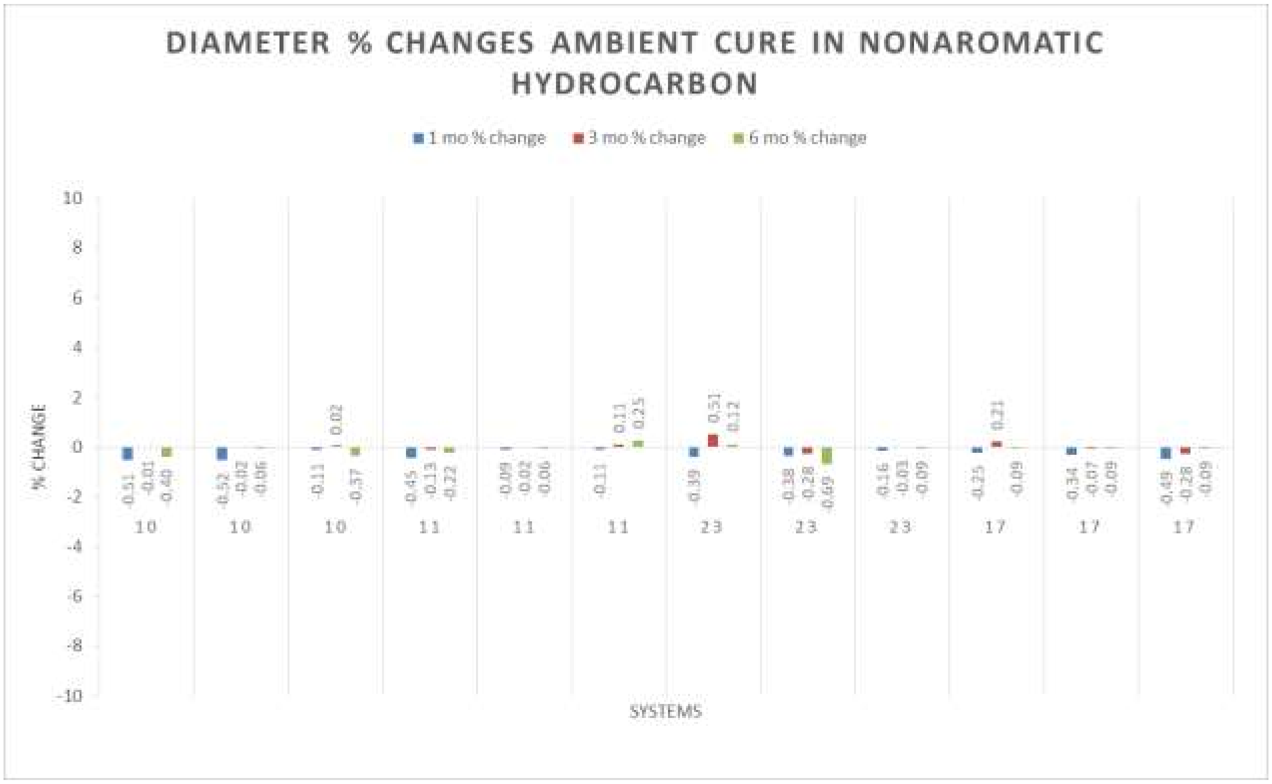


Figure 74: Diameter Change of Systems 10, 11, 17, and 23 in Nonaromatic Hydrocarbon at Ambient

Figure 75 lists the long term durability testing in 11.0 lb/gal nonaromatic hydrocarbon brine at ambient conditions. Systems 13, 14 (epoxy), and 23 (polyester) were all relatively flat in trend for tensile strength. System 17 (Bis A epoxy) had an initial drop followed by an increase followed by a decrease.

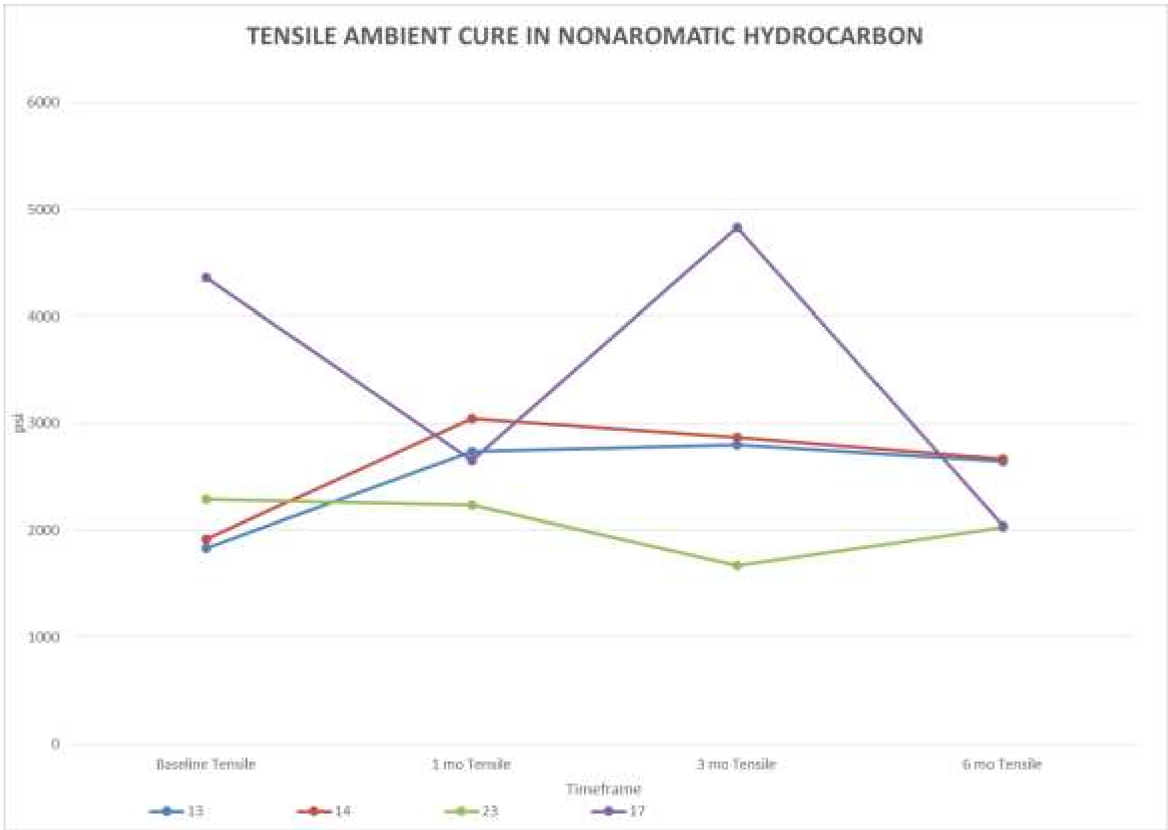


Figure 75: Tensile Strengths of Systems 13, 14, 17, and 23 in Nonaromatic Hydrocarbon at Ambient

Figure 76 lists the long term durability testing in 11.0 lb/gal nonaromatic hydrocarbon brine at ambient conditions. Systems 1, 7, 10 and 11 (cements) stayed fairly flat from initial to final. Systems 4 (cement) showed an upward trend at 6 months.

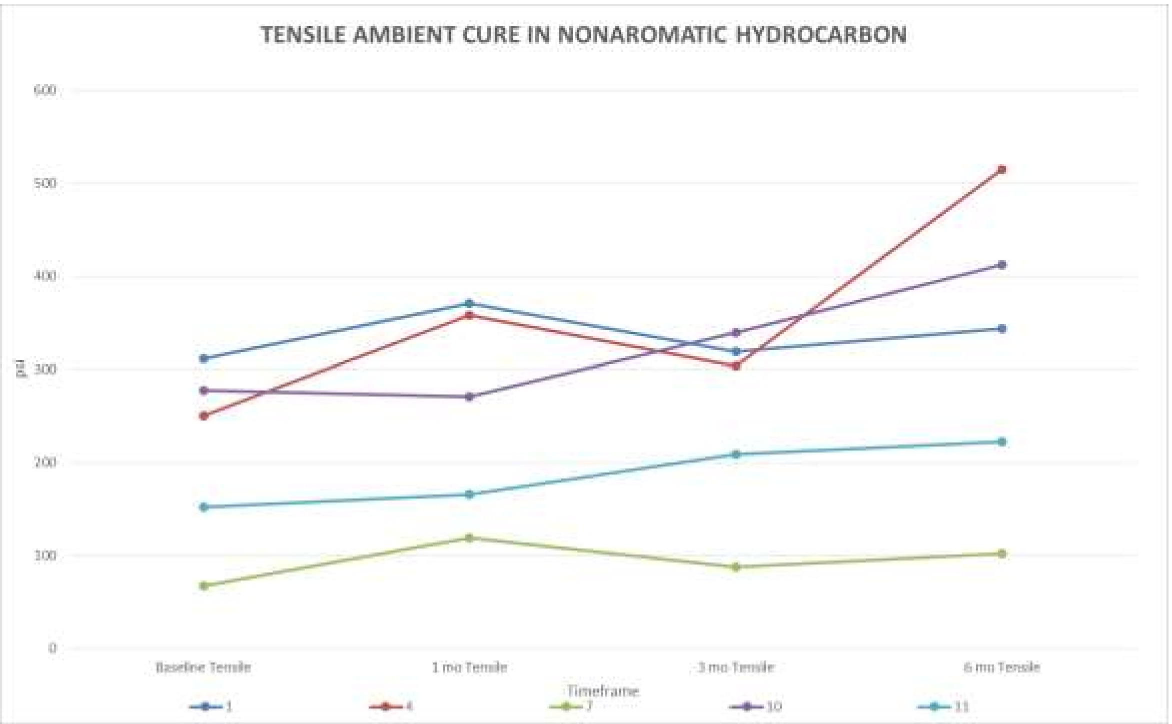


Figure 76: Tensile Strengths of Systems 1, 4, 7, 10, and 11 in Nonaromatic Hydrocarbon at Ambient

Figure 77 lists the long term durability testing in 11.0 lb/gal aromatic hydrocarbon at ambient conditions. System 1, 4, 7 (cements), 13, and 14 (epoxy) all showed no changes in density.

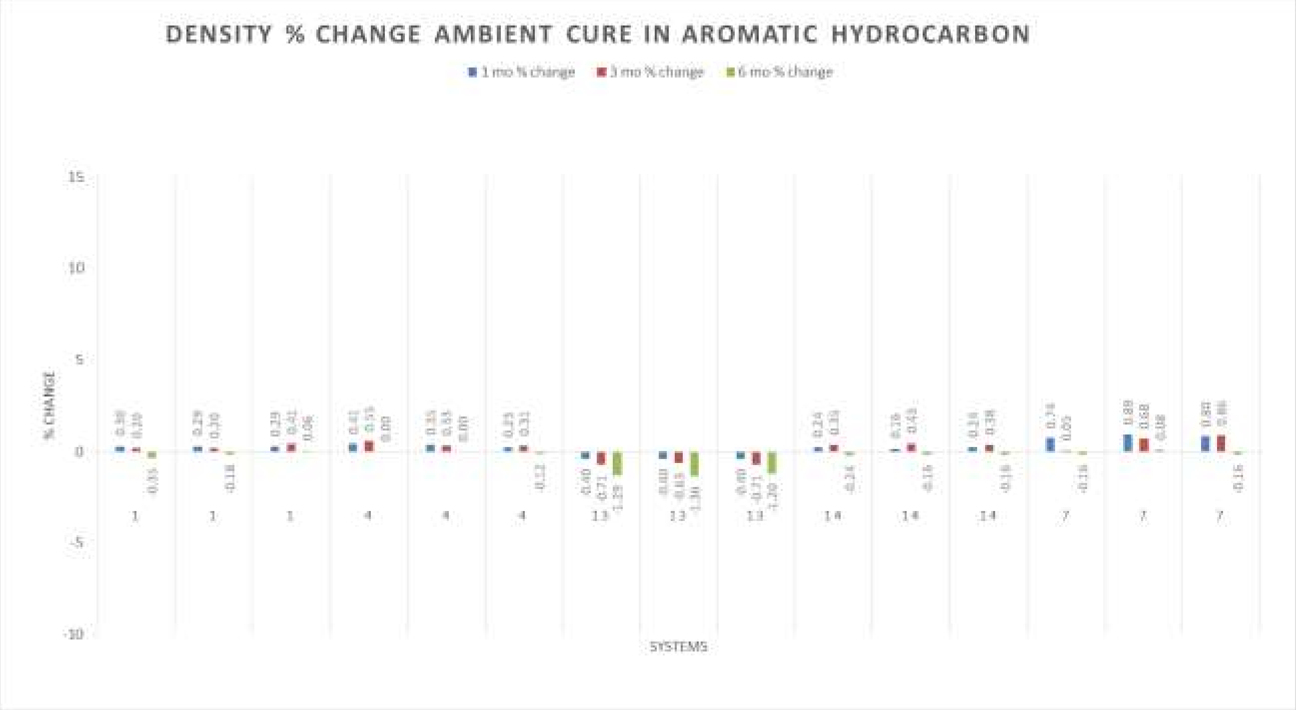


Figure 77: Density Change of Systems 1, 4, 7, 13 and 14 in Aromatic Hydrocarbon at Ambient

Figure 78 lists the long term durability testing in 11.0 lb/gal aromatic hydrocarbon brine at ambient conditions. Systems 10 (cement) showed slight changes in density. Systems 11 (cement), 17 (Bis A epoxy) and 23 (polyester) showed little to no change.

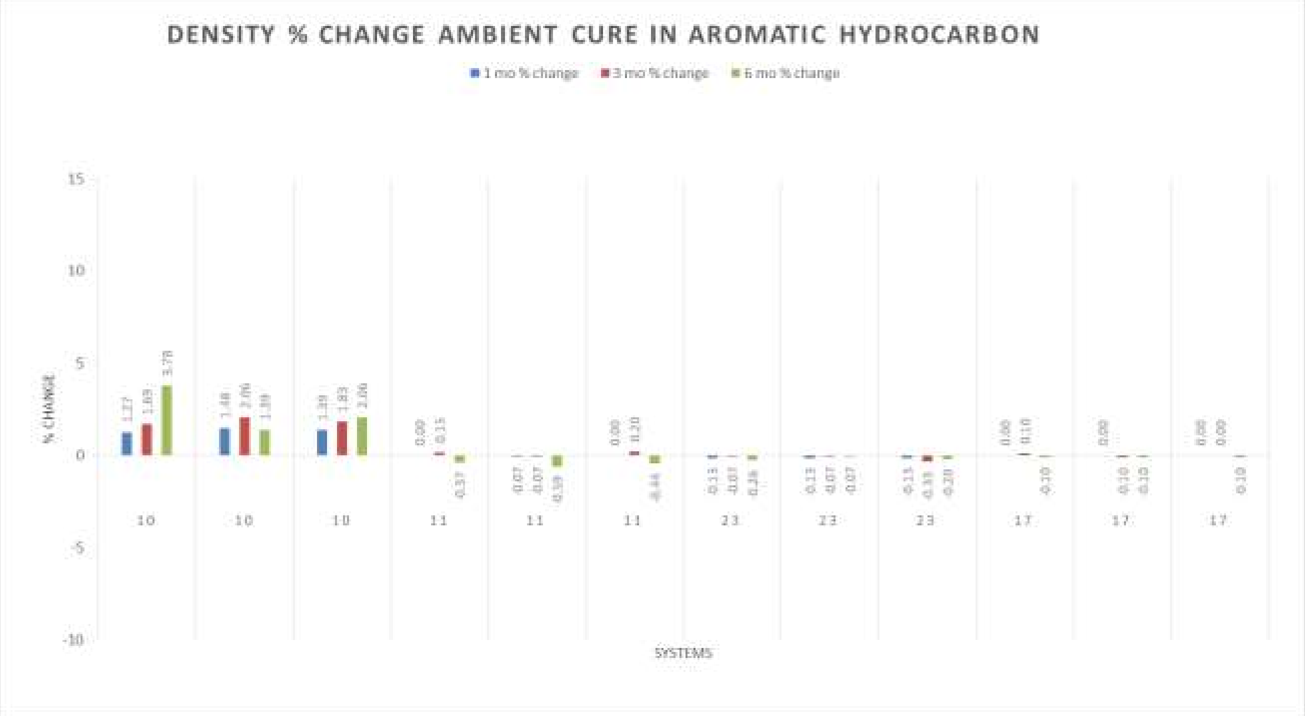


Figure 78: Density Change of Systems 10, 11, 17, and 23 in Aromatic Hydrocarbon at Ambient

Figure 79 lists the long term durability testing in 11.0 lb/gal aromatic hydrocarbon brine at ambient conditions. System 1, 4, 7 (cements), 13, and 14 (epoxy) all showed no changes in diameter.

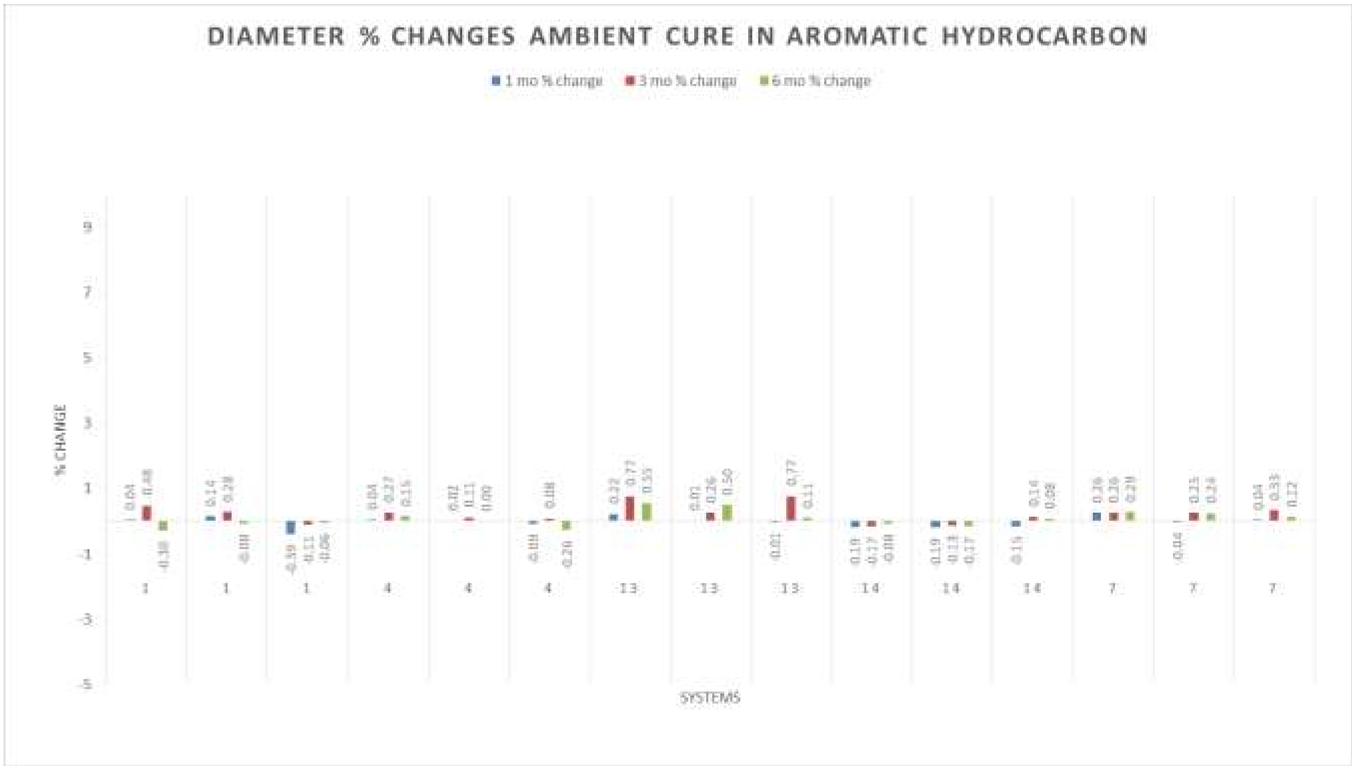


Figure 79: Diameter Change of Systems 1, 4, 7, 13 and 14 in Aromatic Hydrocarbon at Ambient

Figure 80 lists the long term durability testing in 11.0 lb/gal aromatic hydrocarbon brine at ambient conditions. Systems 10, 11 (cements), 17 (Bis A epoxy), and 23 (polyester) showed no change in diameter.

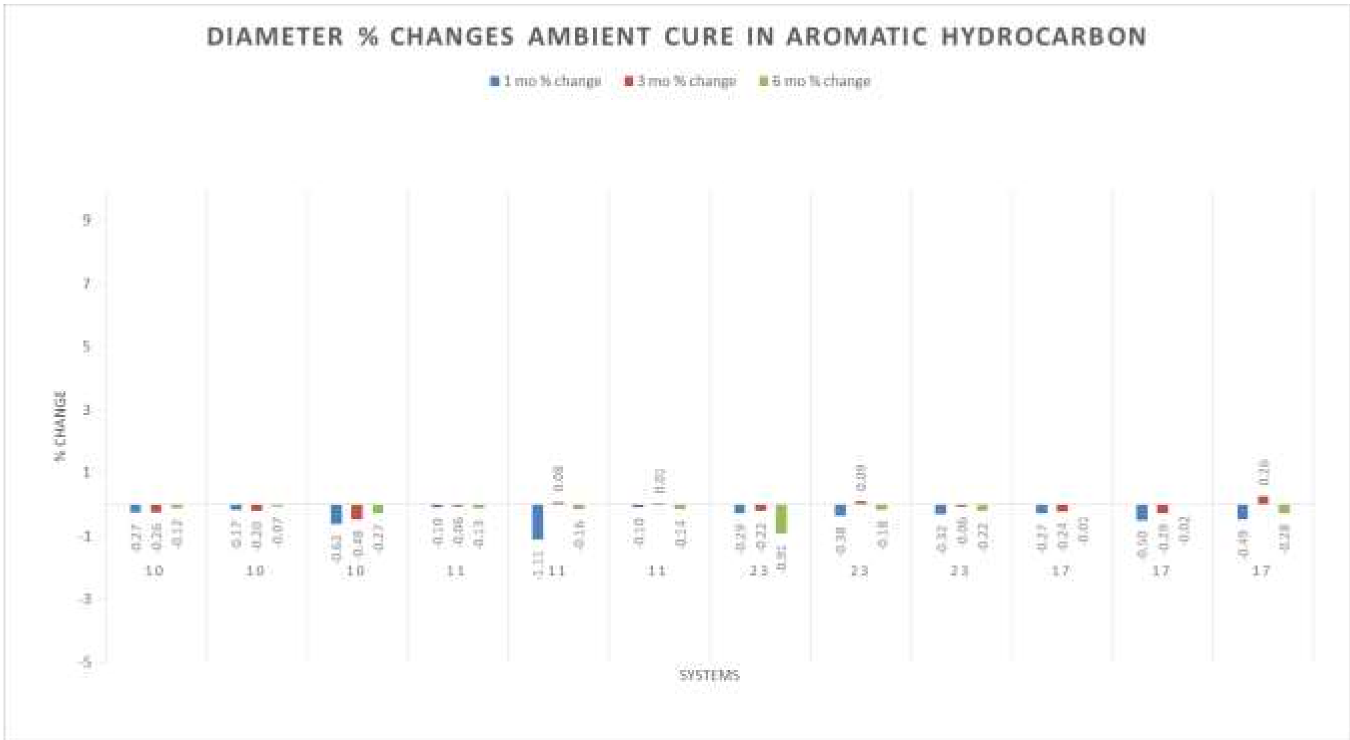


Figure 80: Diameter Change of Systems 10, 11, 17, and 23 in Aromatic Hydrocarbon at Ambient

Figure 81 lists the long term durability testing in 11.0 lb/gal aromatic hydrocarbon brine at ambient conditions. Systems 13, 14 (epoxy), and 23 (polyester) were all relatively flat in trend for tensile strength. System 17 (Bis A epoxy) had an initial drop followed by an increase.

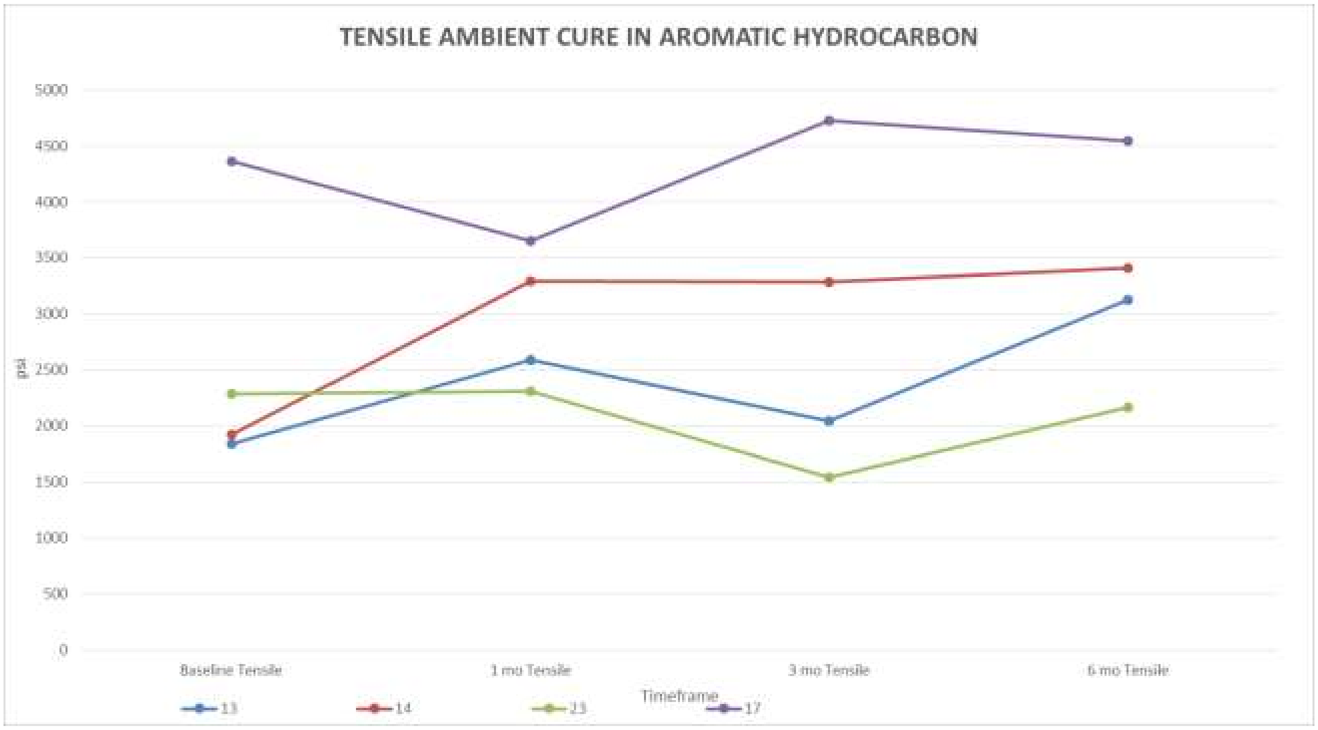


Figure 81: Tensile Strengths of Systems 13, 14, 17, and 23 in Aromatic Hydrocarbon at Ambient

Figure 82 lists the long term durability testing in 11.0 lb/gal aromatic hydrocarbon brine at ambient conditions. Systems 1, 7, and 11 (cements) stayed fairly flat from initial to final. Systems 4, and 10 (cement) showed an upward trend at 6 months.

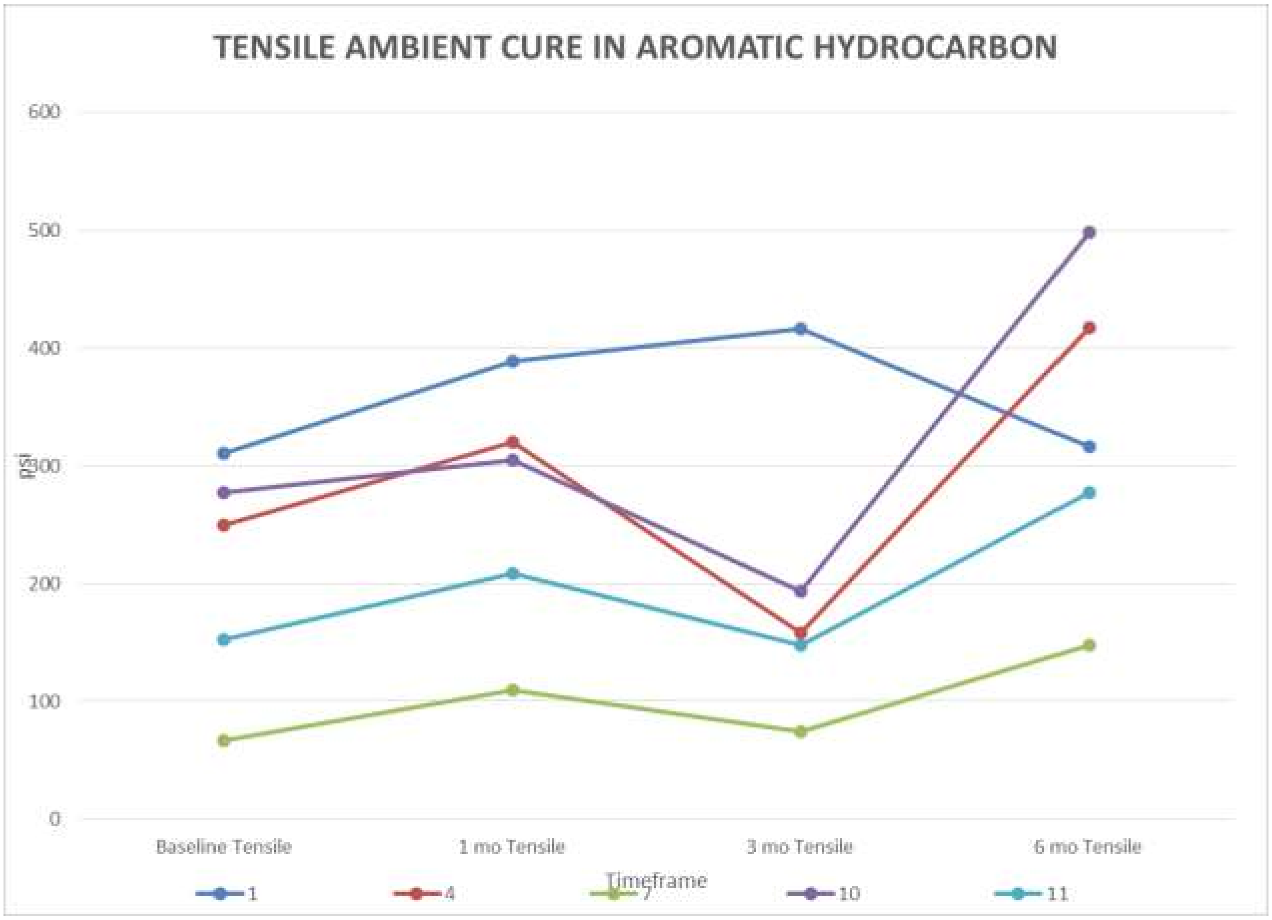


Figure 82: Tensile Strengths of Systems 1, 4, 7, 10, and 11 in Aromatic Hydrocarbon at Ambient

8.1.3 FTIR Analysis of Cements Aged in Fluids

Two inch cubes of cement were prepared using a cement with minimal additives. As a group these were designated HDV1114-5A (System 1). Three cubes were stacked as top, middle and bottom in five different solutions. One set was in water. After curing for seven days these were used for baselines. Samples 1, 2 and 3 were aged in 11 lb/gal calcium chloride ($CaCl_2$) for 1, 3, 6 months respectively. Samples 4, 5 and 6 were aged in 14 lb/gal calcium bromide ($CaBr_2$) for 1, 3, 6 months respectively. Samples 7, 8 and 9 aged in motor oil for 1, 3, 6 months respectively. Samples 10, 11 and 12 were aged in a mixed solvent (70% heptane, 20% cyclohexane, 10% toluene) for 1, 3, 6 months respectively. No visible changes were expected, but examination of the surface of each sample was planned using Fourier Transform Infrared Spectroscopy (FTIR) by Attenuated Total Reflectance (ATR). However, it was observed over time that the samples in $CaCl_2$ and $CaBr_2$ showed significant degradation. The samples in motor oil and aromatic solvent showed no degradation.

Cement aged in $CaCl_2$ and $CaBr_2$ both decomposed, but the break down was faster and more complete in the $CaBr_2$. In some cases in the $CaBr_2$ there was no cement left to sample. This is reflected in the FTIR spectra Figure 83 and Figure 84. Peaks at about 1401 cm^{-1} and 870 cm^{-1} suggest the presence of $CaCO_3$; however, the absence of a peak at about 710 cm^{-1} indicates $CaCO_3$ is not present. In the $CaCl_2$ samples these peaks are largest after three months, whereas in $CaBr_2$ they are at a maximum after one month. After six months all features in the 1550 cm^{-1} to 515 cm^{-1} have disappeared from the $CaBr_2$ samples and have greatly shrunk in the $CaCl_2$ samples. In the base line samples and the later aged samples there are peaks either side of 1000 cm^{-1} that could be due to calcium silicate. At three months in $CaCl_2$ and one month in $CaBr_2$ there large peaks about 1400 cm^{-1}, 1100 cm^{-1}, 950 cm^{-1} and 873 cm^{-1}. What these peaks are from is unclear. It would be consistent with XRF data Figure 85 to suggest these are some sort of silicates. Silicon steadily declined in the $CaCl_2$ and declined in months 1 and 3 in $CaBr_2$. There was a sample increase in month six with the $CaBr_2$ samples. It isn't clear if this is real or a sampling issue. The FTIR spectra are not indicative of just calcium silicate, but perhaps mixed silicates of calcium and aluminum, iron or some other cation.

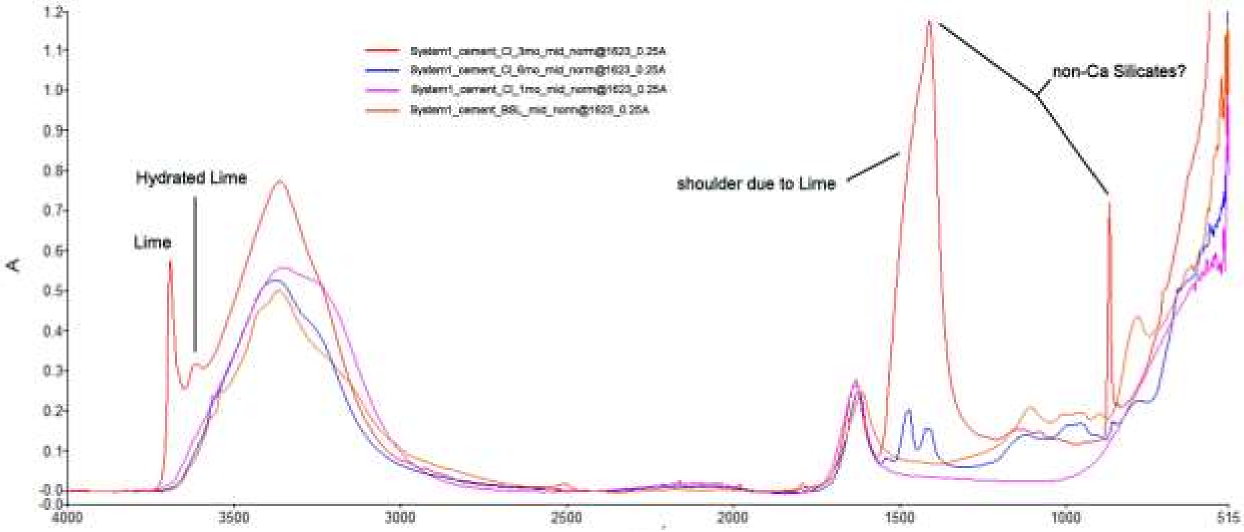


Figure 83: FTIR Cement System 1 in Calcium Chloride

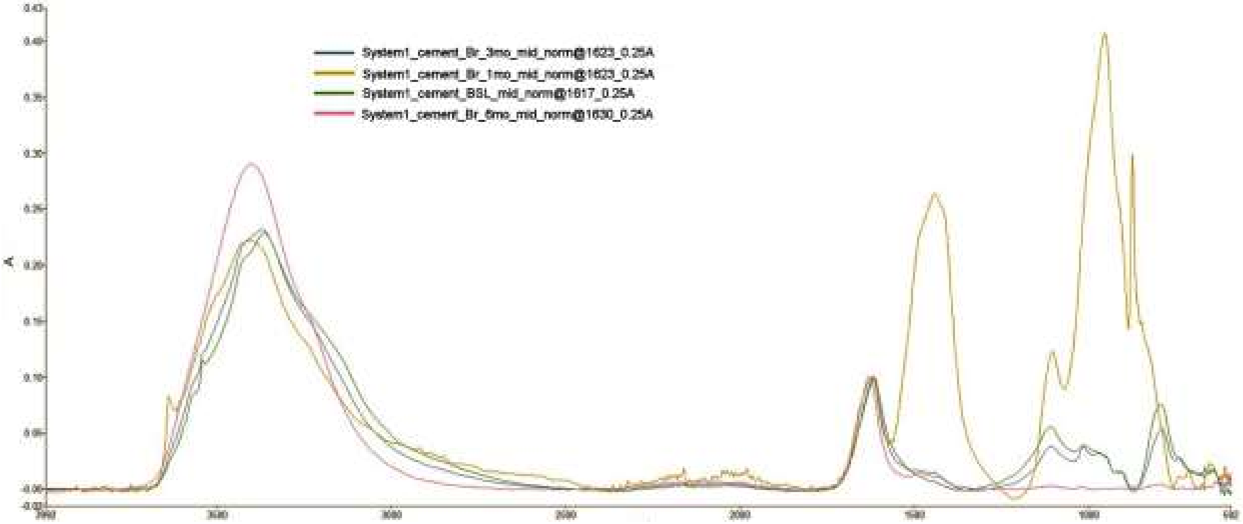


Figure 84: FTIR Cement System 1 in Calcium Bromide

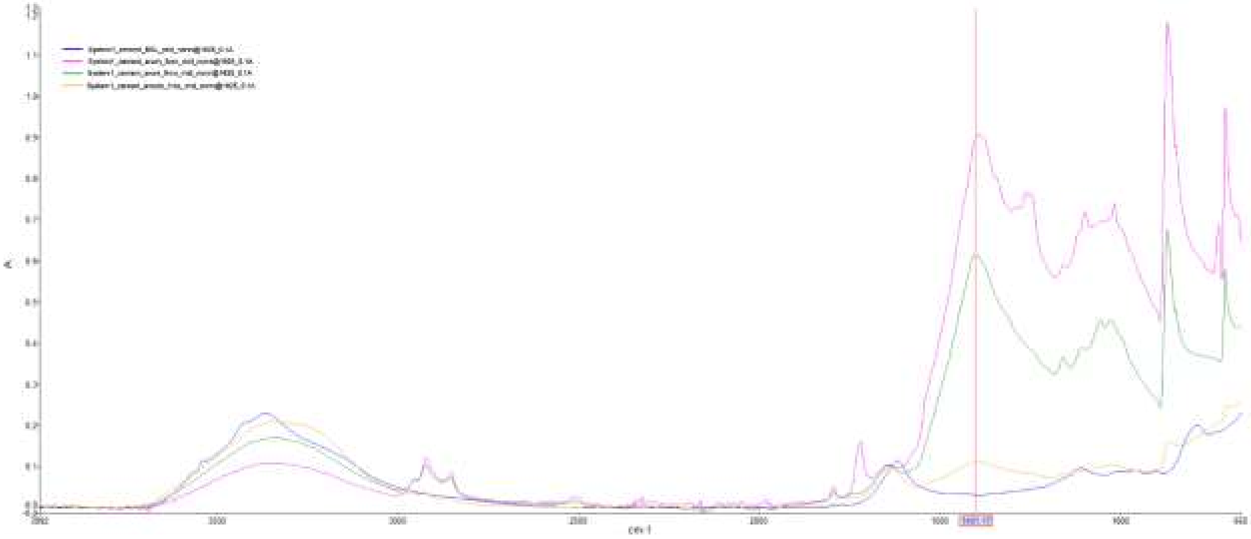


Figure 85: FTIR Cement System 1 in Aromatic Hydrocarbon

Peaks at 1401, 877 and 705 cm^{-1} clearly show the presence of $CaCO_3$. The region 1300 and 900 cm^{-1} suggests the presence of calcium silicate and possibly other silicates. These samples were aged in aromatic hydrocarbon. Samples aged in nonaromatic hydrocarbon gave similar results. No lime appears in these samples. After three and six months it can be seen that the hydrocarbons have penetrated some distance into the cement.

It would appear that in the presence of highly concentrated $CaCl_2$ or $CaBr_2$ oil field cement breaks down in a relatively short time span. The appearance of calcium carbonate, which seems to form as a normal part of cement curing, is accelerated and it is removed in the break down process. The lime also appears and disappears as a part of the break down process. Similarly the data suggests calcium silicate and possibly some other mixed silicates are generated and removed in the break down process.

8.1.4 FTIR Analysis of Resins Aged in Fluids

A range of resin samples, using different base resins, a variety of hardeners and some additives were aged for up to six months in 11 lb/gal $CaCl_2$, 14 lb/gal $CaBr_2$, additive free 30 weight motor oil or an aromatic blend of solvents. The resin samples were two inches in diameter and one inches thick. The samples were stacked in the aging solutions three high so there was a top, middle and bottom sample. Samples were pulled at one, three and six months. FTIR spectra were collected using Attenuated Total Reflectance (ATR). This allows for minimal sample preparation and views primarily the surface. Penetration is on the order of 3 – 5 mm.

In general there was little change with time or position in the stack. In the case of samples in the motor oil or aromatic solvent there were some indications that oil or solvent had penetrated into the sample somewhat. However, no great changes were observed. With the calcium chloride and calcium bromide in general no changes were observed. These trends are reflected in the spectra Figure 86 through Figure 122.

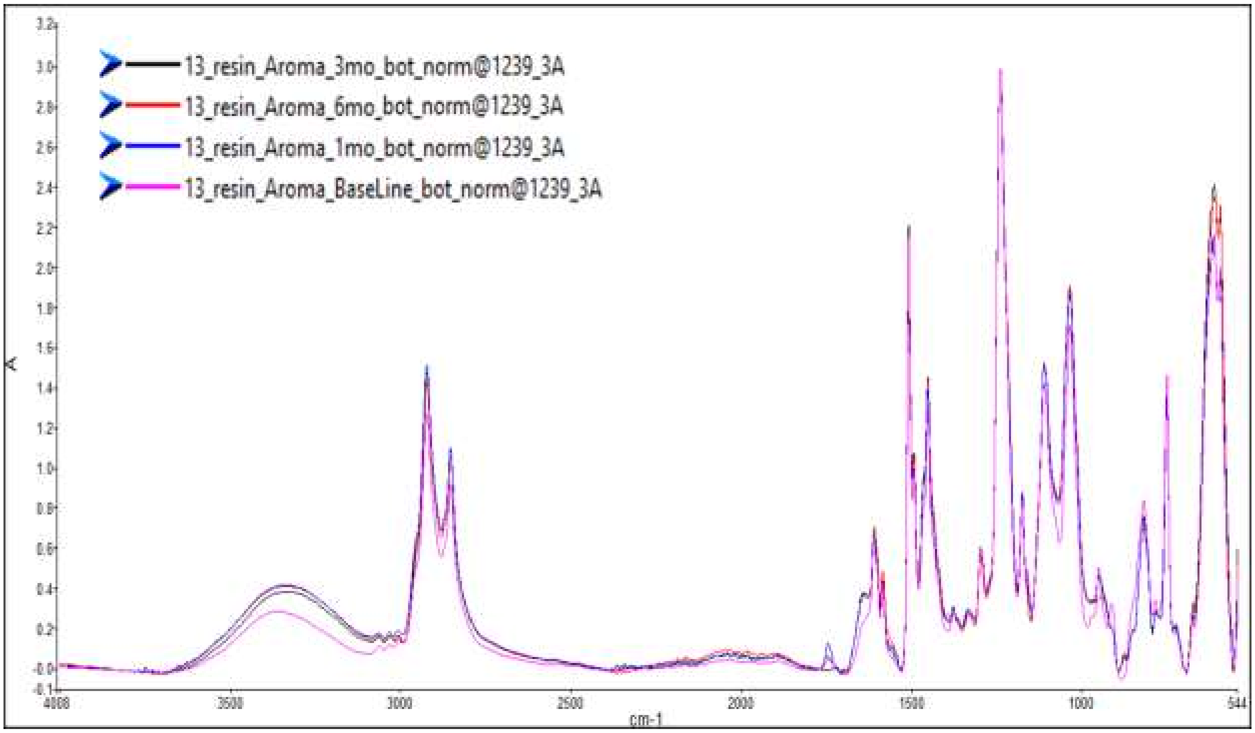


Figure 86: FTIR Resin System 13 in Aromatic Hydrocarbon

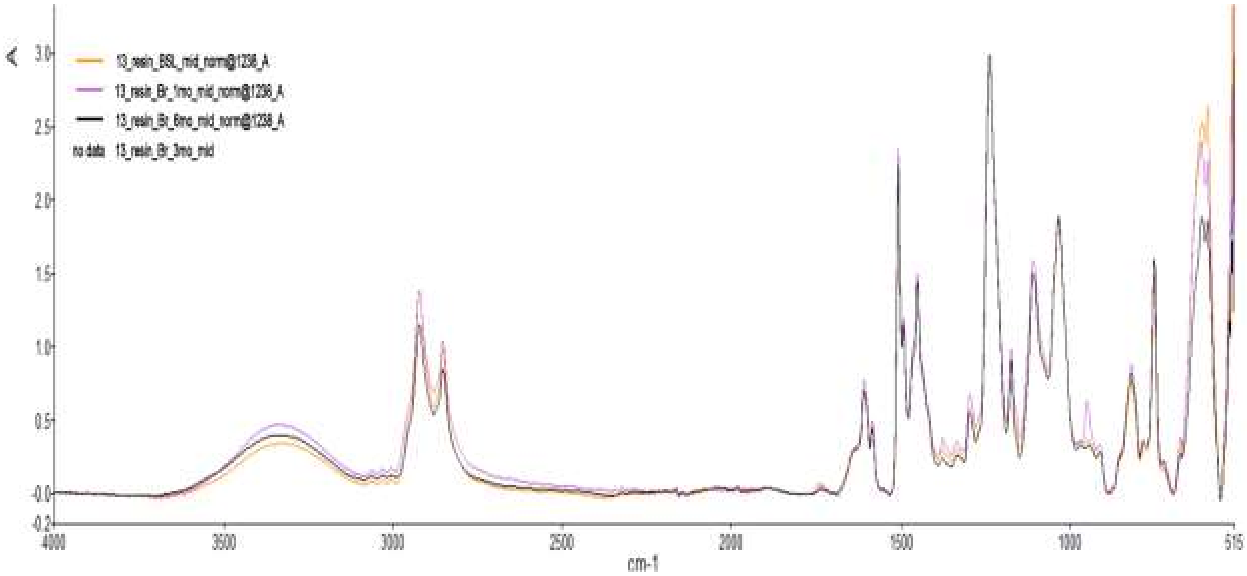


Figure 87: FTIR Resin System 13 in Calcium Bromide

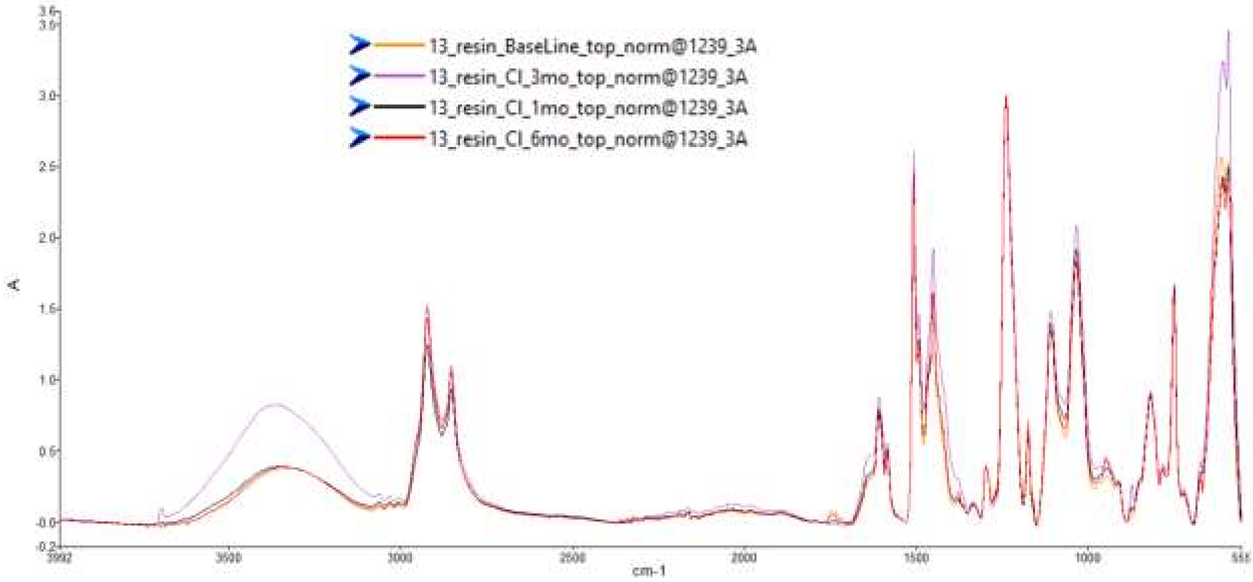


Figure 88: FTIR Resin System 13 in Calcium Chloride

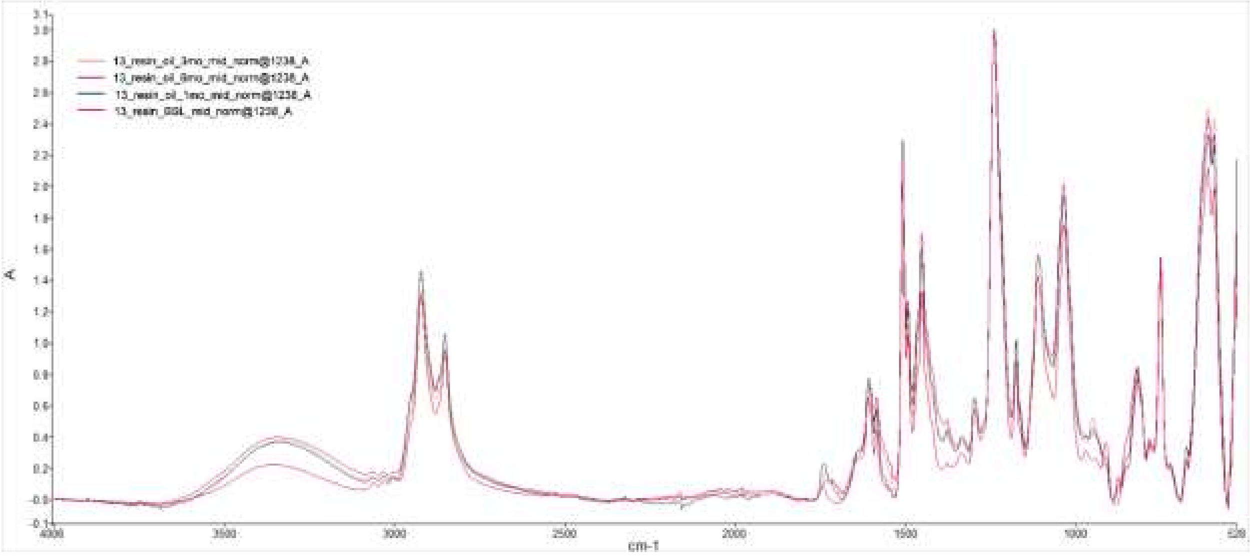


Figure 89: FTIR Resin System 13 in Nonaromatic Hydrocarbon

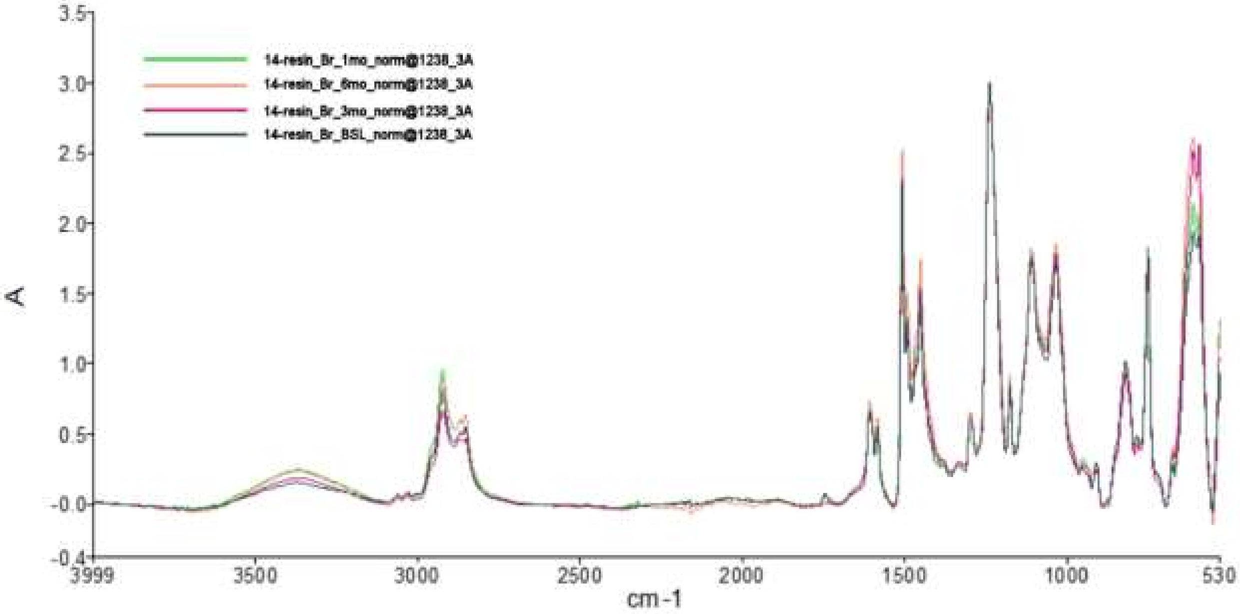


Figure 90: FTIR Resin System 14 in Calcium Bromide

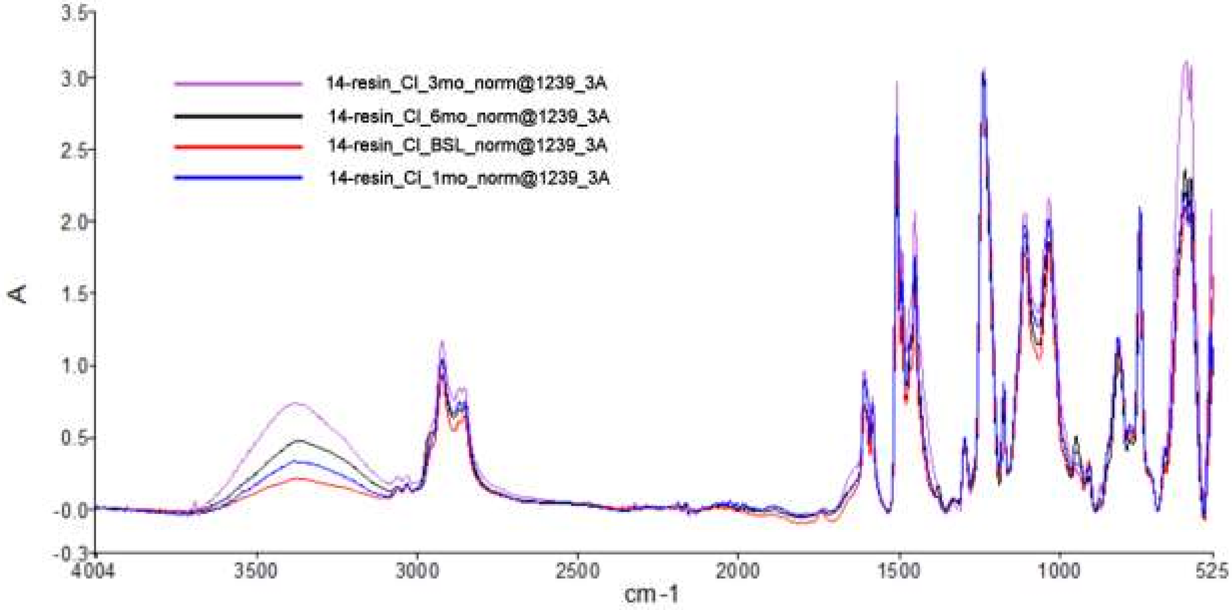


Figure 91: FTIR Resin System 14 in Calcium Chloride

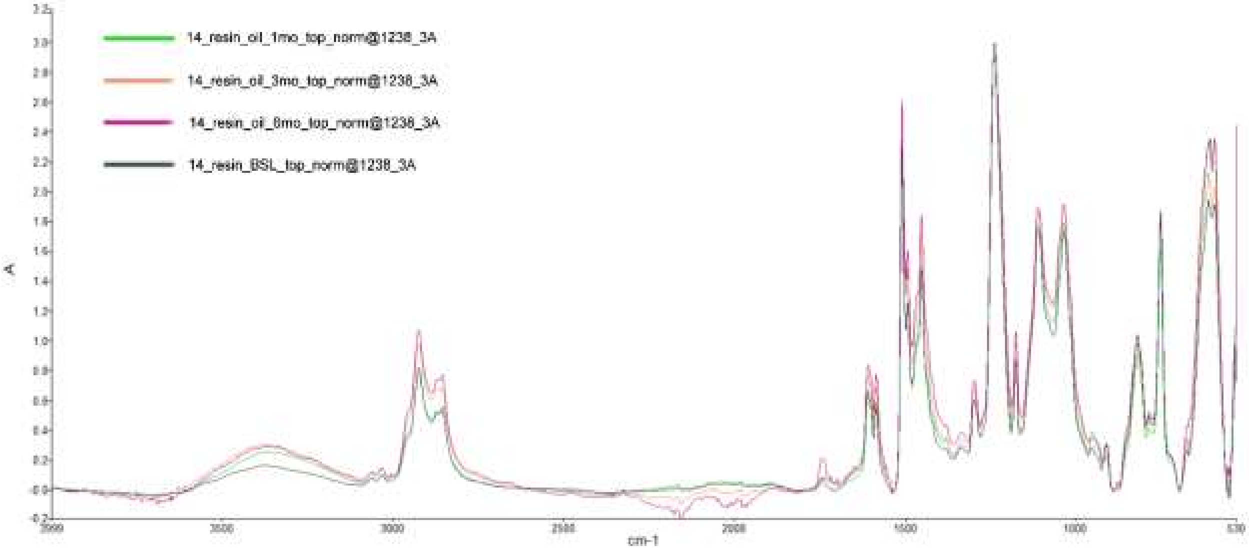


Figure 92: FTIR Resin System 14 in Nonaromatic Hydrocarbon

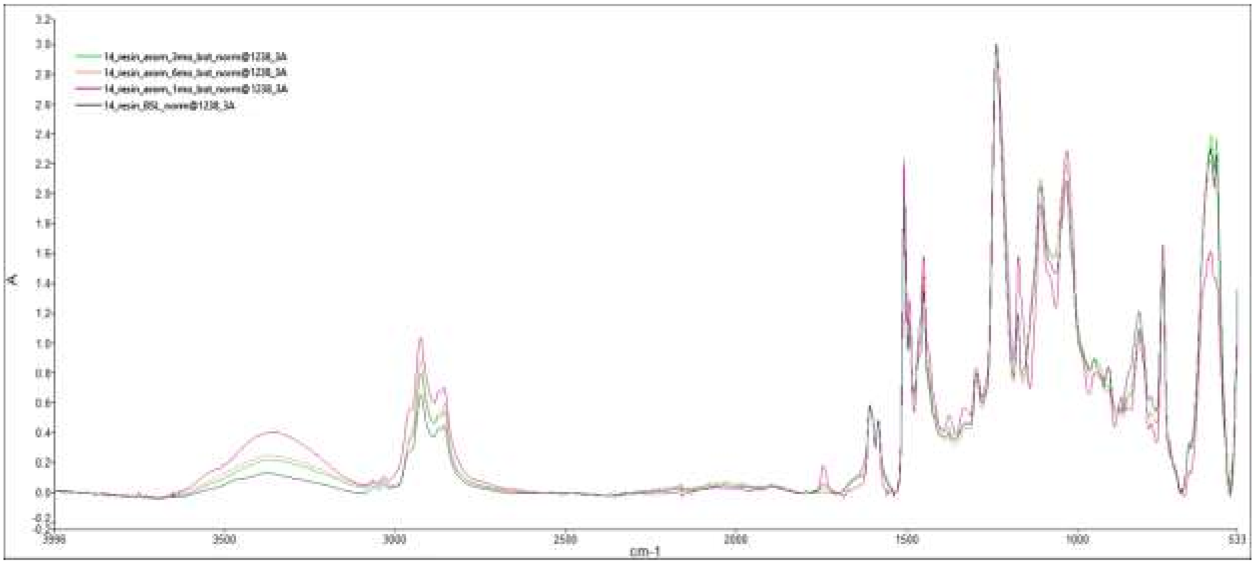


Figure 93: FTIR Resin System 14 in Aromatic Hydrocarbon

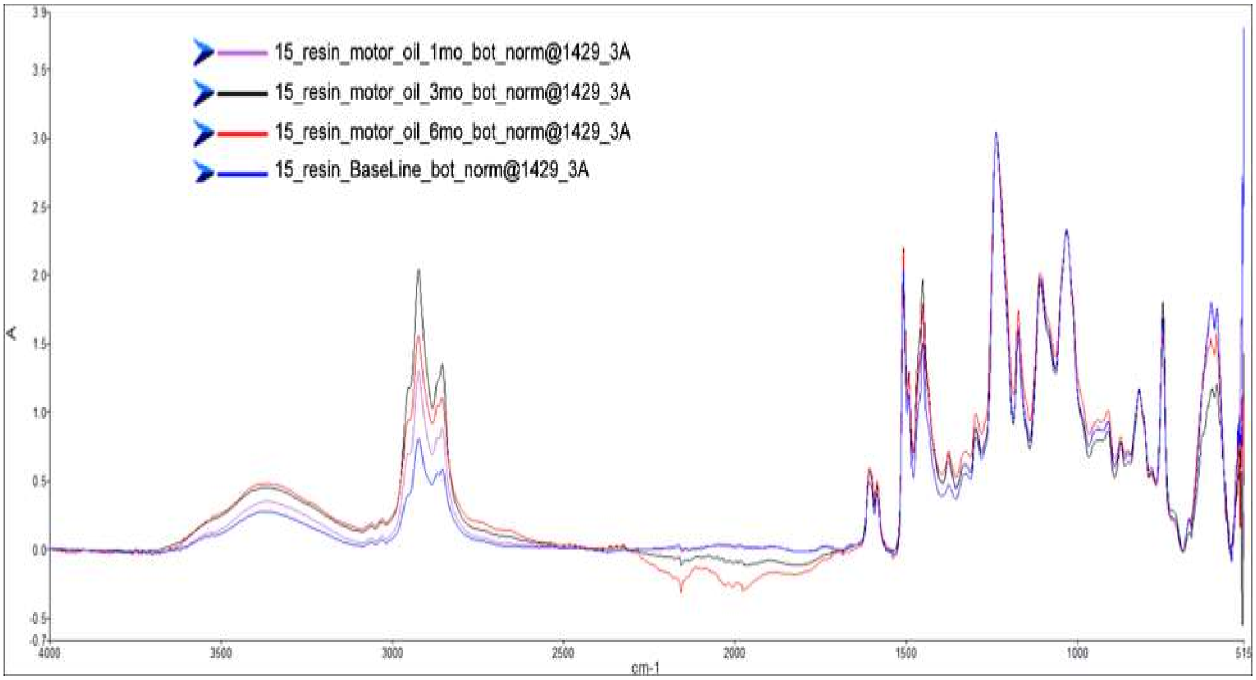


Figure 94: FTIR Resin System 15 in Nonaromatic Hydrocarbon

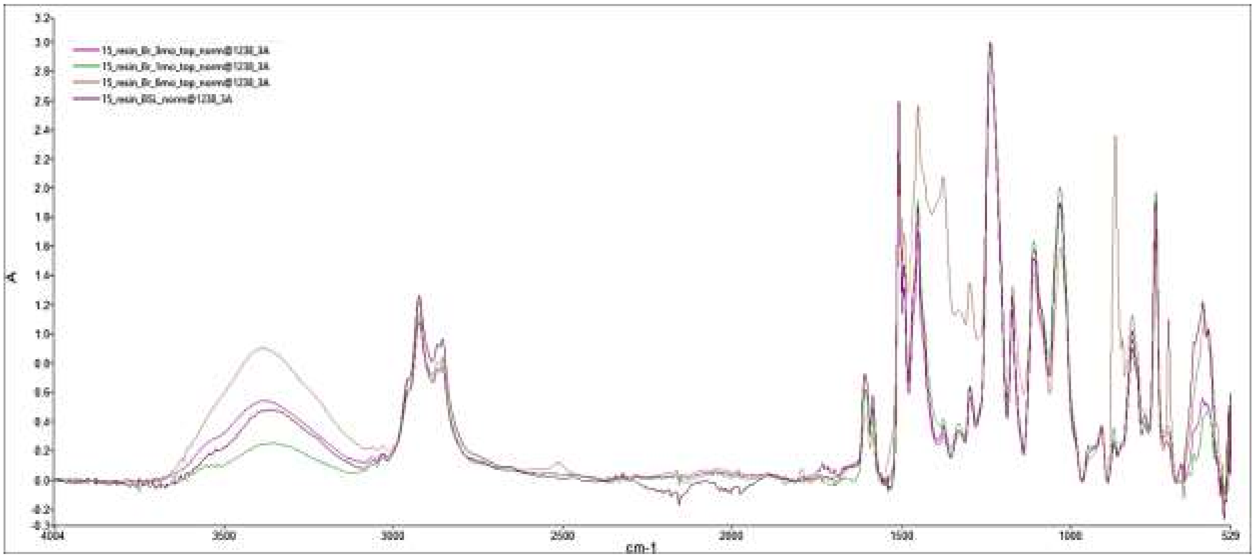


Figure 95: FTIR Resin System 15 in Calcium Bromide

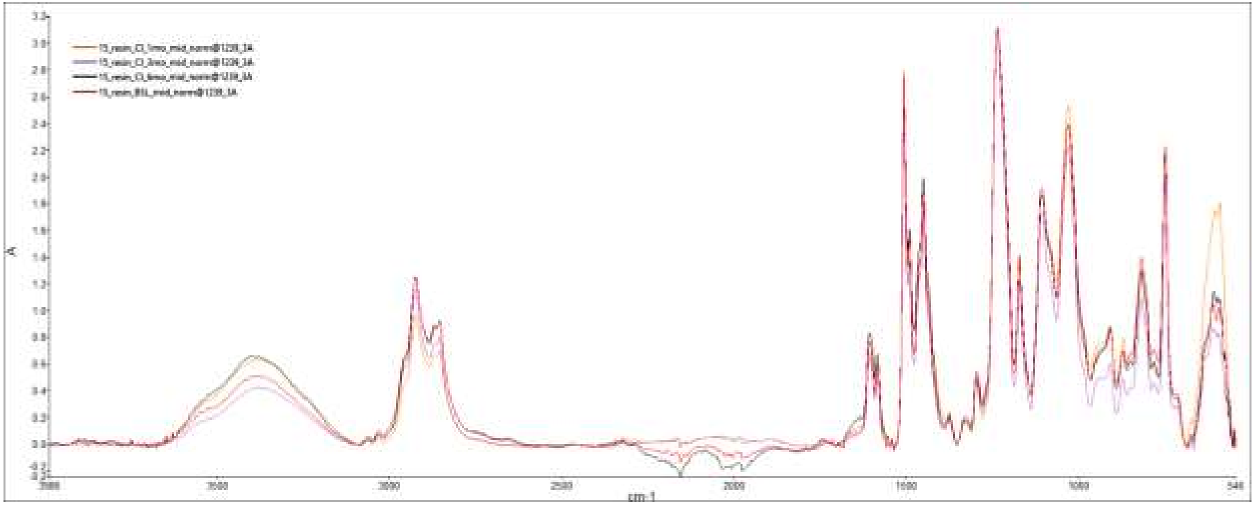


Figure 96: FTIR Resin System 15 in Calcium Chloride

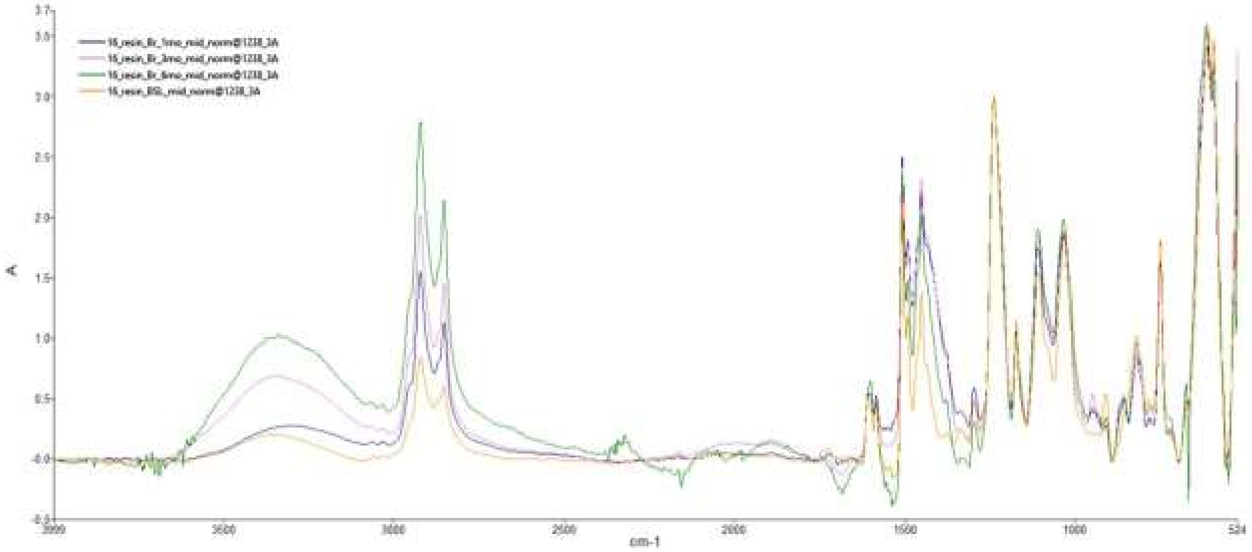


Figure 97: FTIR Resin System 16 in Calcium Bromide

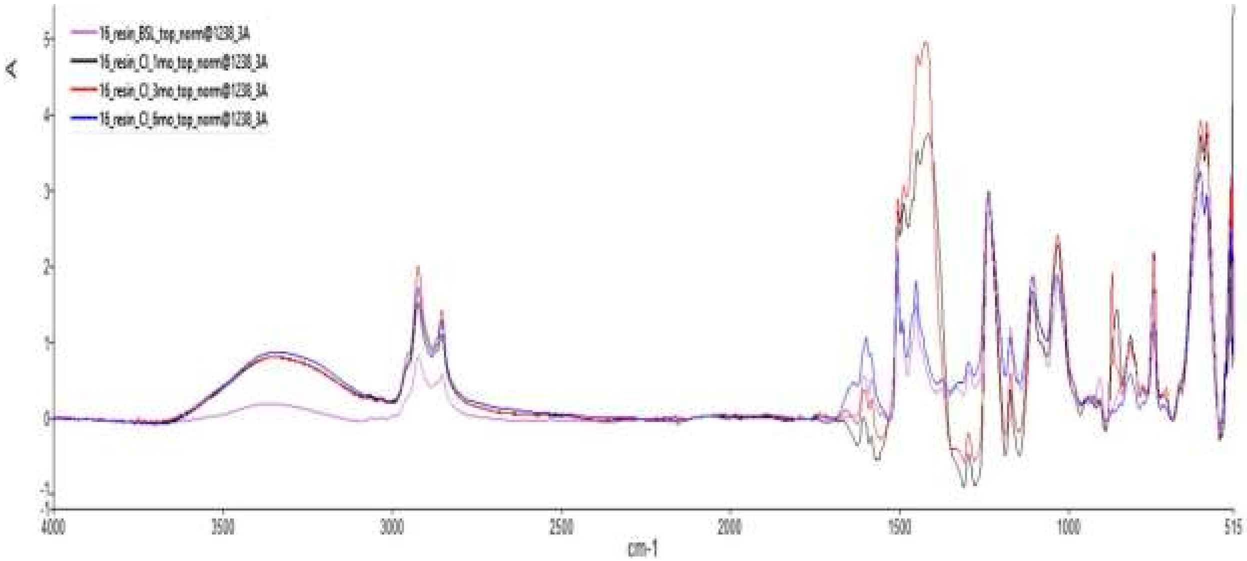


Figure 98: FTIR Resin System 16 in Calcium Chloride

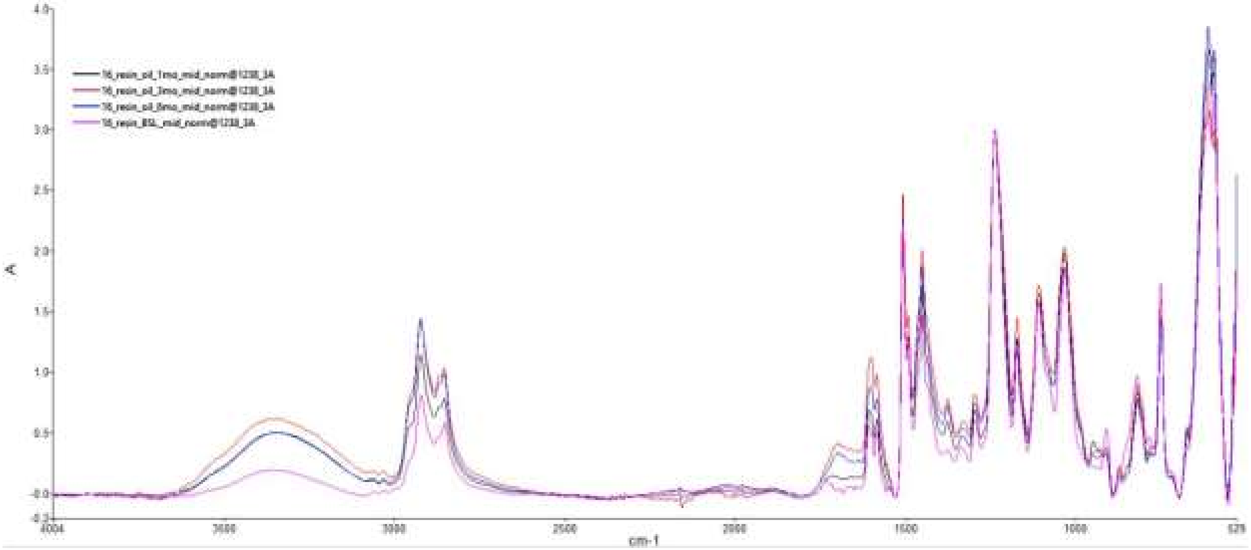


Figure 99: FTIR Resin System 16 in Nonaromatic Hydrocarbon

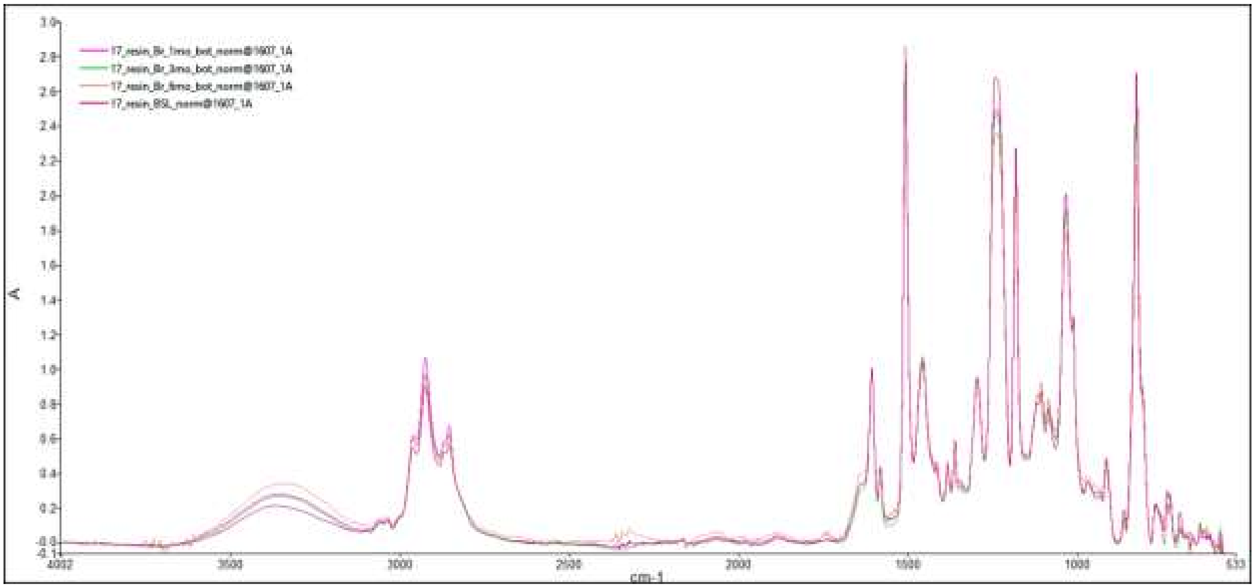


Figure 100: FTIR Resin System 17 in Calcium Bromide

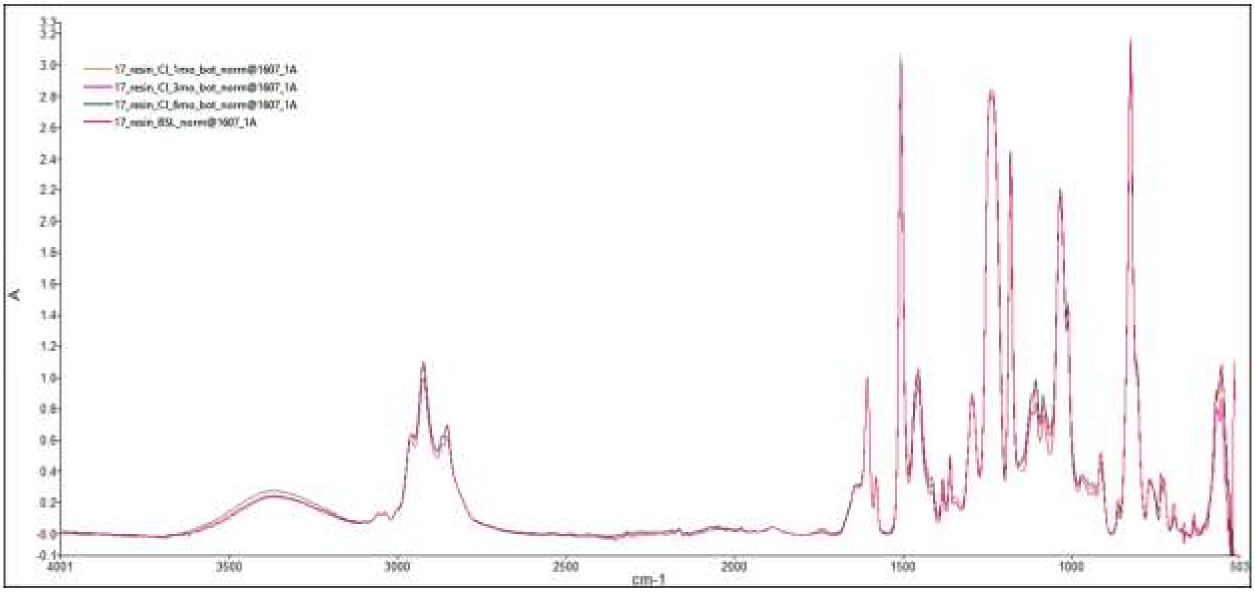


Figure 101: FTIR Resin System 17 in Calcium Chloride

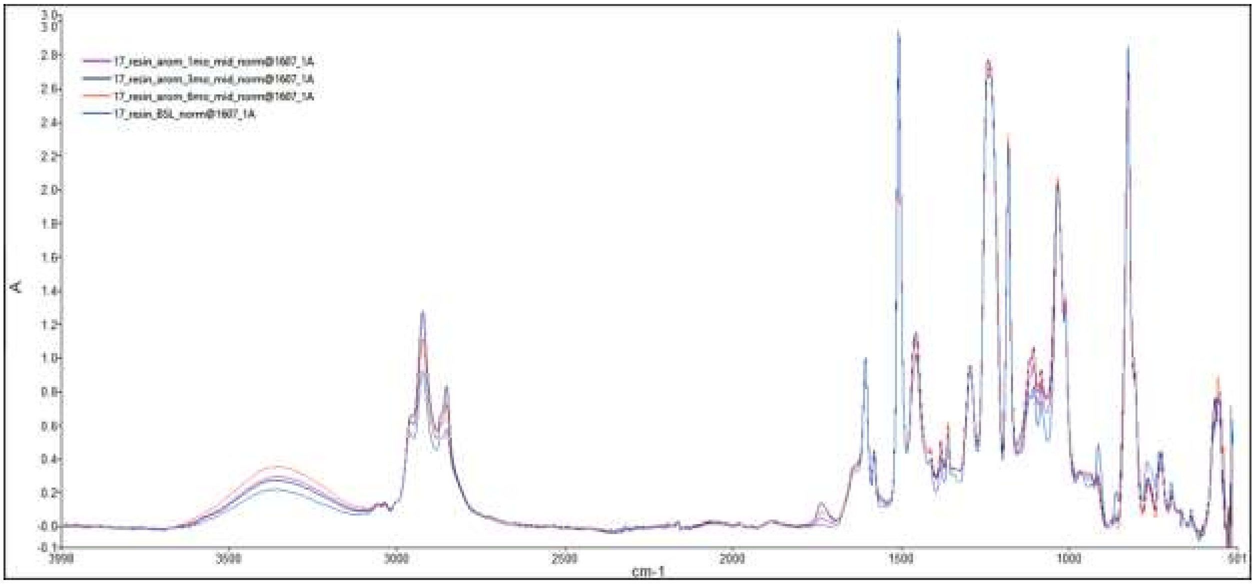


Figure 102: FTIR Resin System 17 in Aromatic Hydrocarbon

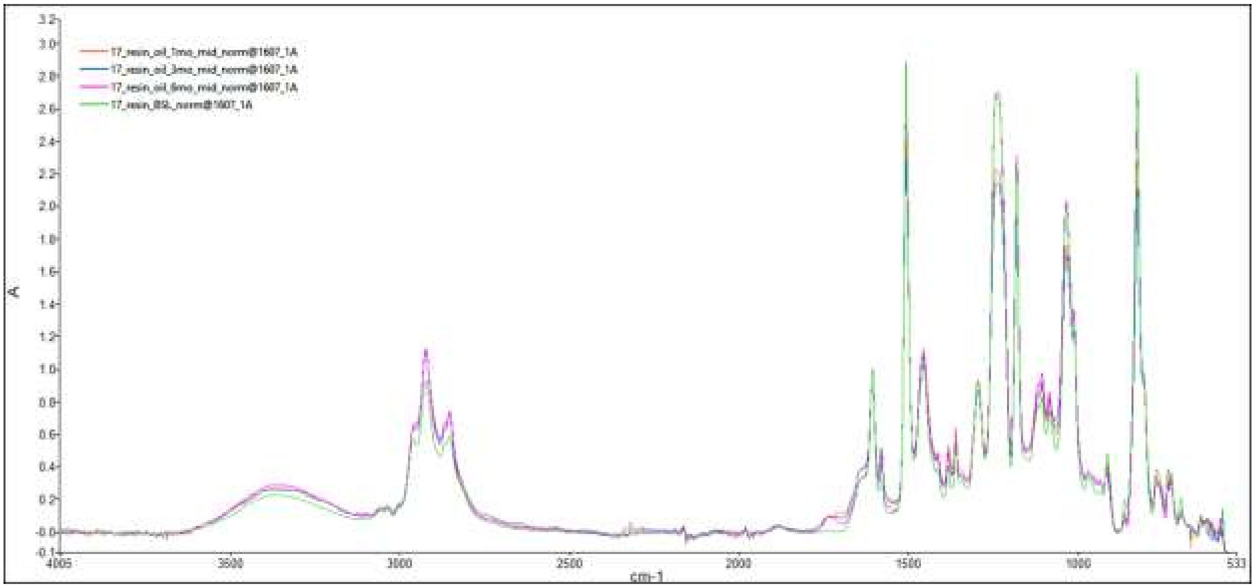


Figure 103: FTIR Resin System 17 in Nonaromatic Hydrocarbon

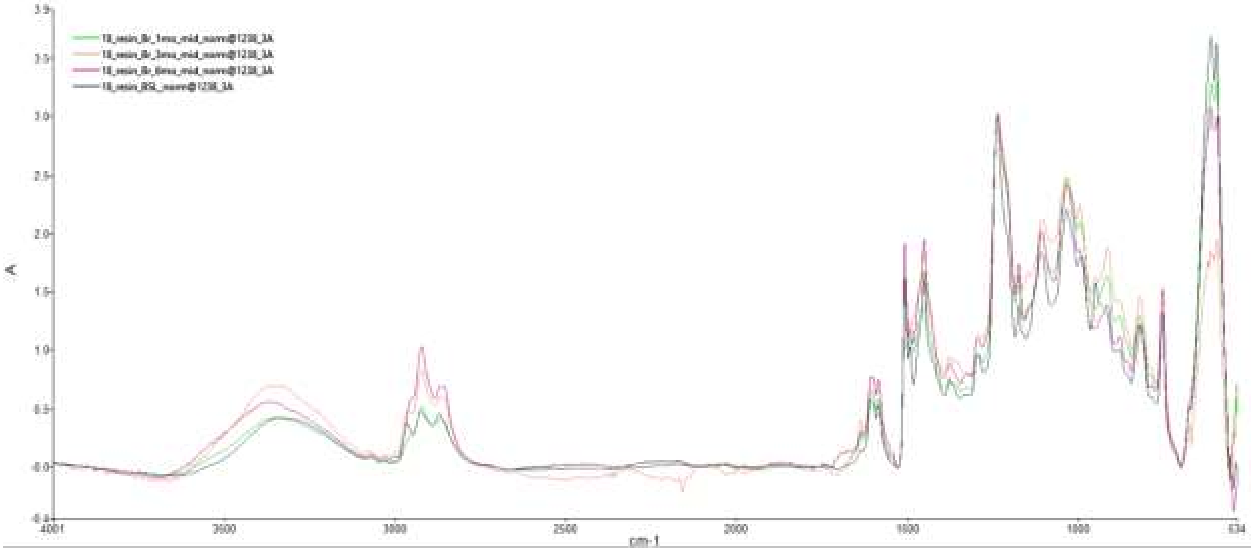


Figure 104: FTIR Resin System 18 in Calcium Bromide

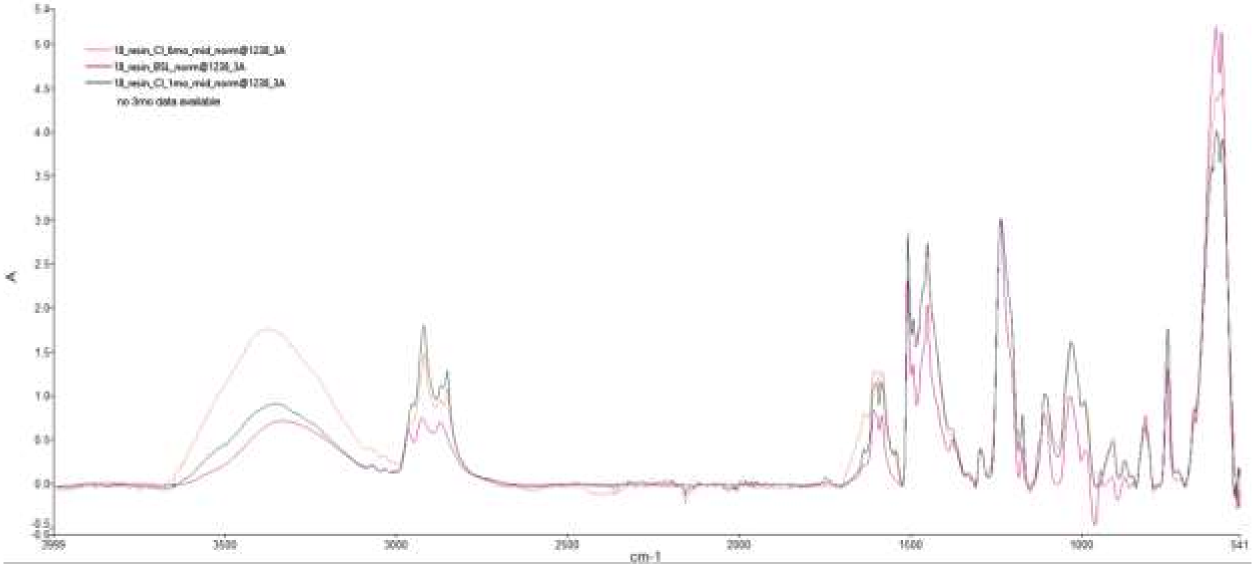


Figure 105: FTIR Resin System 18 in Calcium Chloride

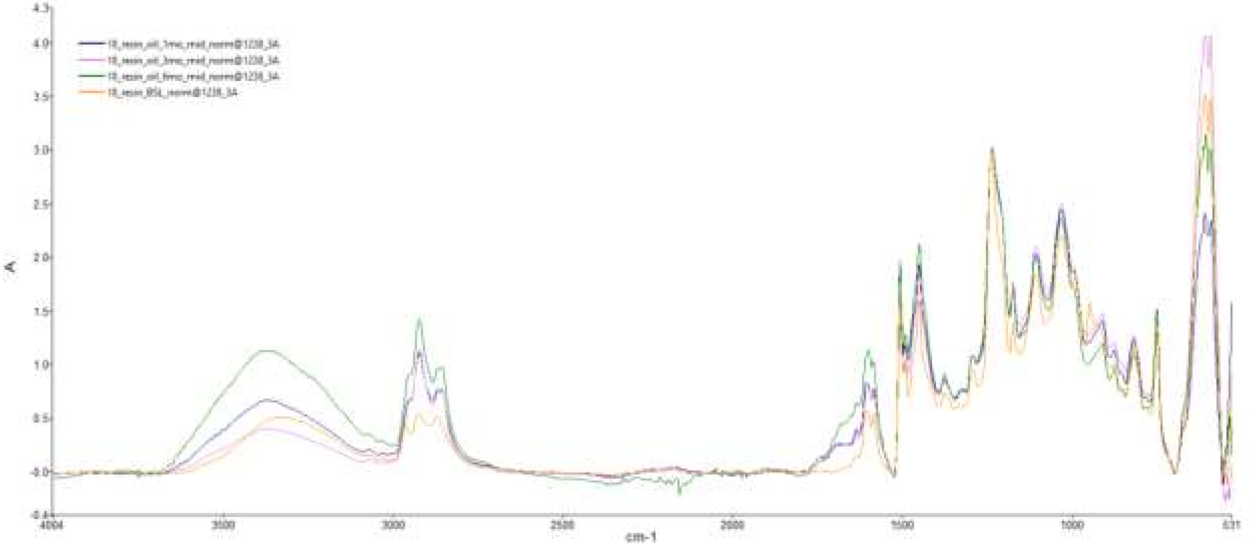


Figure 106: FTIR Resin System 18 in Nonaromatic Hydrocarbon

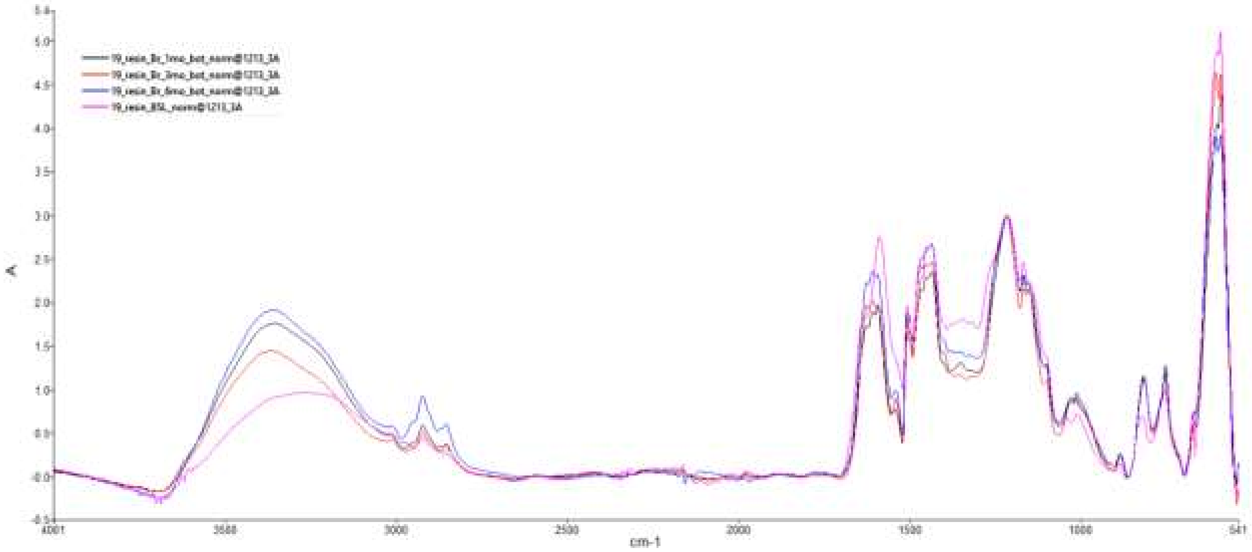


Figure 107: FTIR Resin System 19 in Calcium Bromide

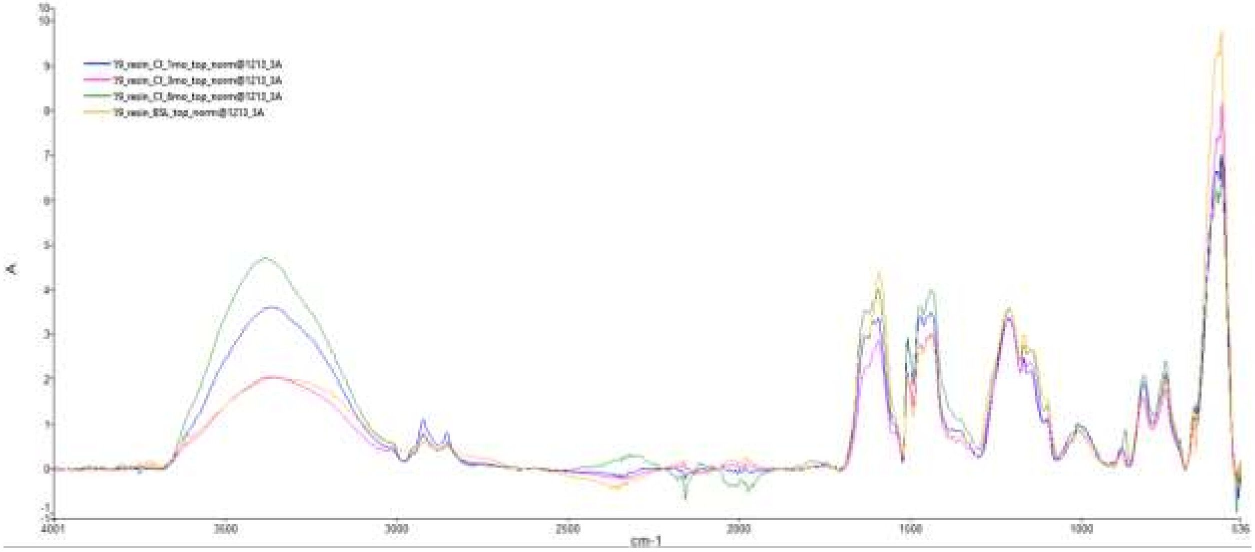


Figure 108: FTIR Resin System 19 in Calcium Chloride

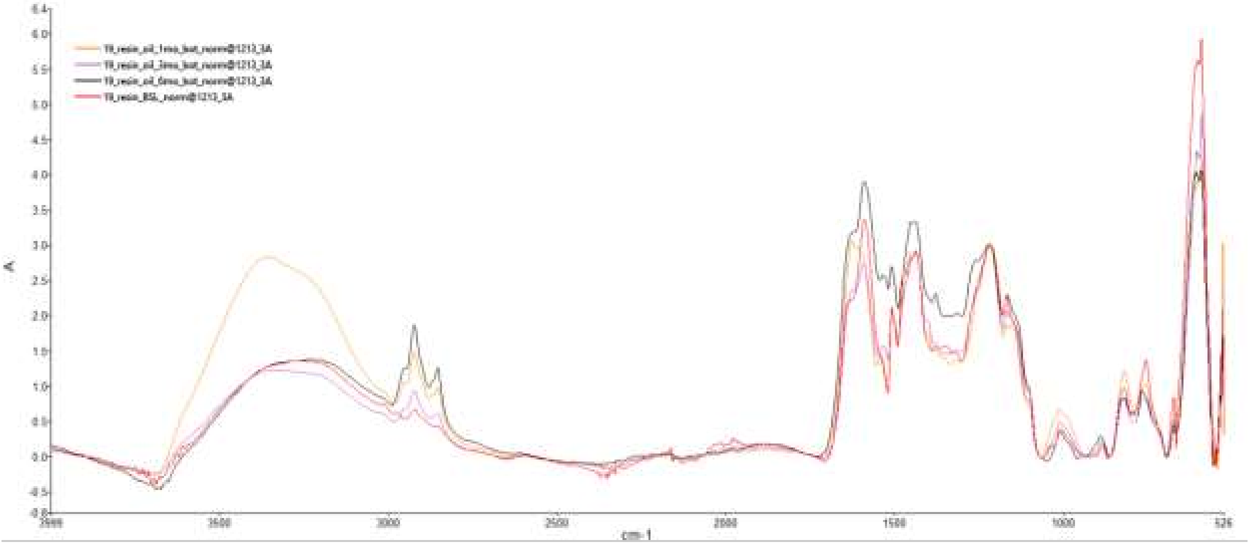


Figure 109: FTIR Resin System 19 in Nonaromatic Hydrocarbon

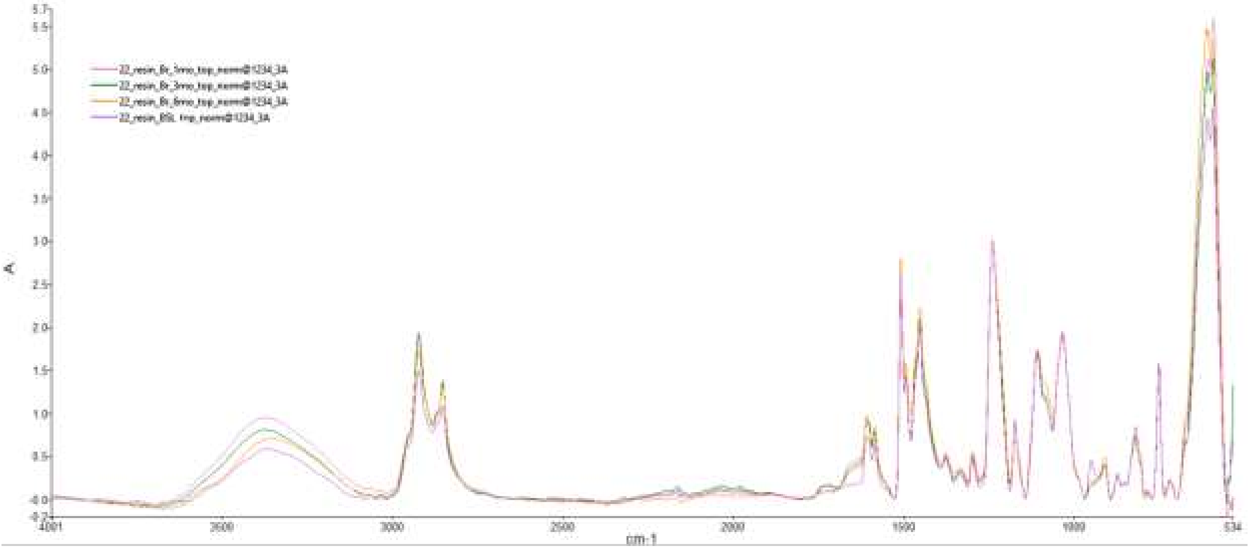


Figure 110: FTIR Resin System 22 in Sodium Bromide

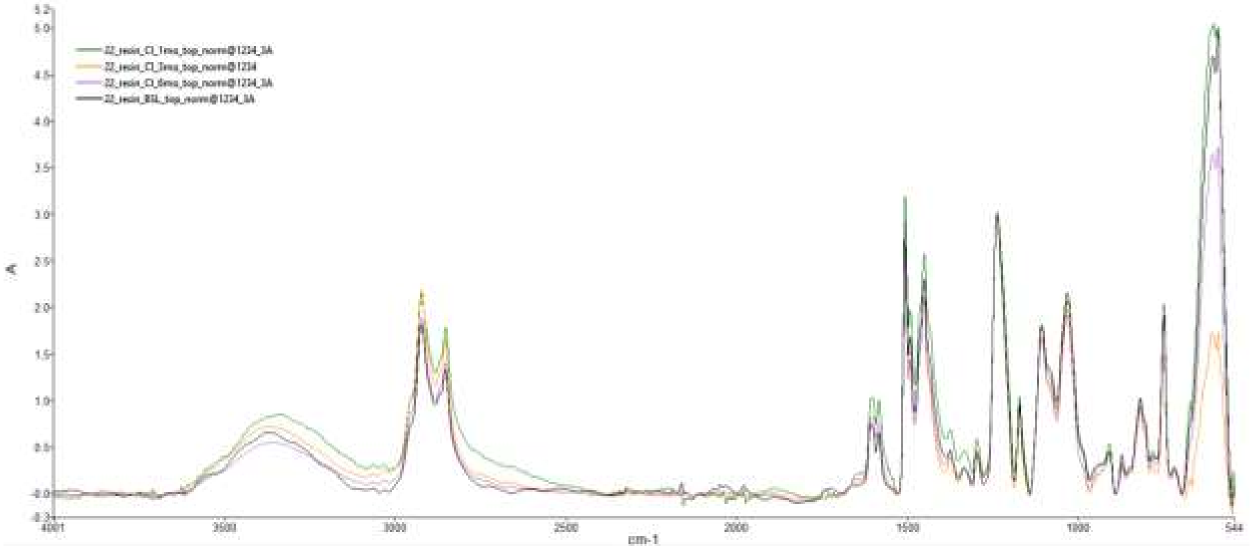


Figure 111: FTIR Resin System 22 in Calcium Chloride

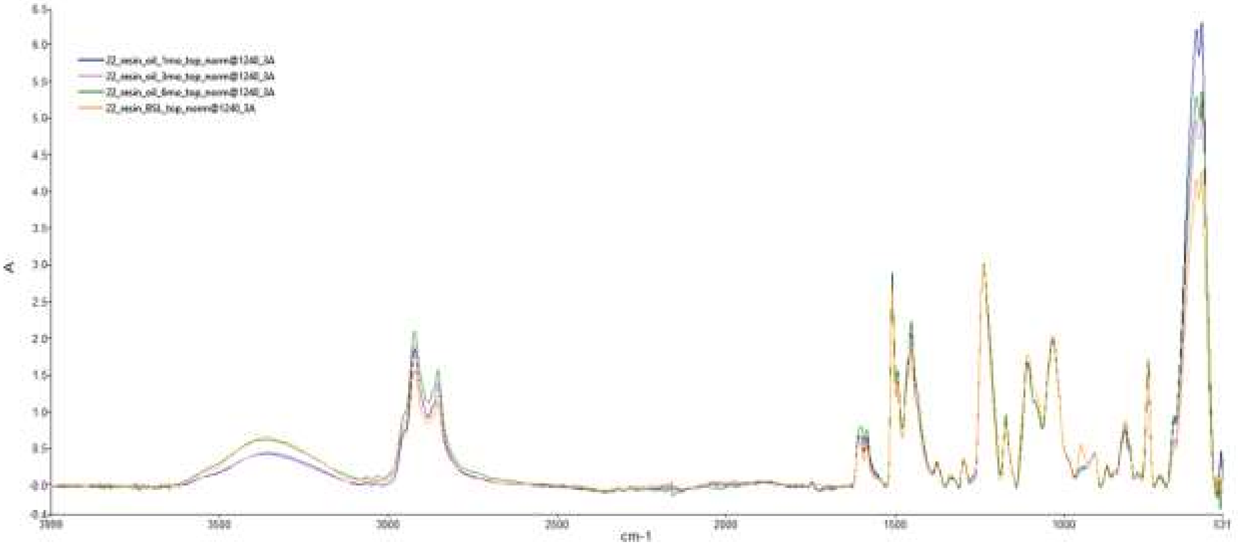


Figure 112: FTIR Resin System 22 in Nonaromatic Hydrocarbon

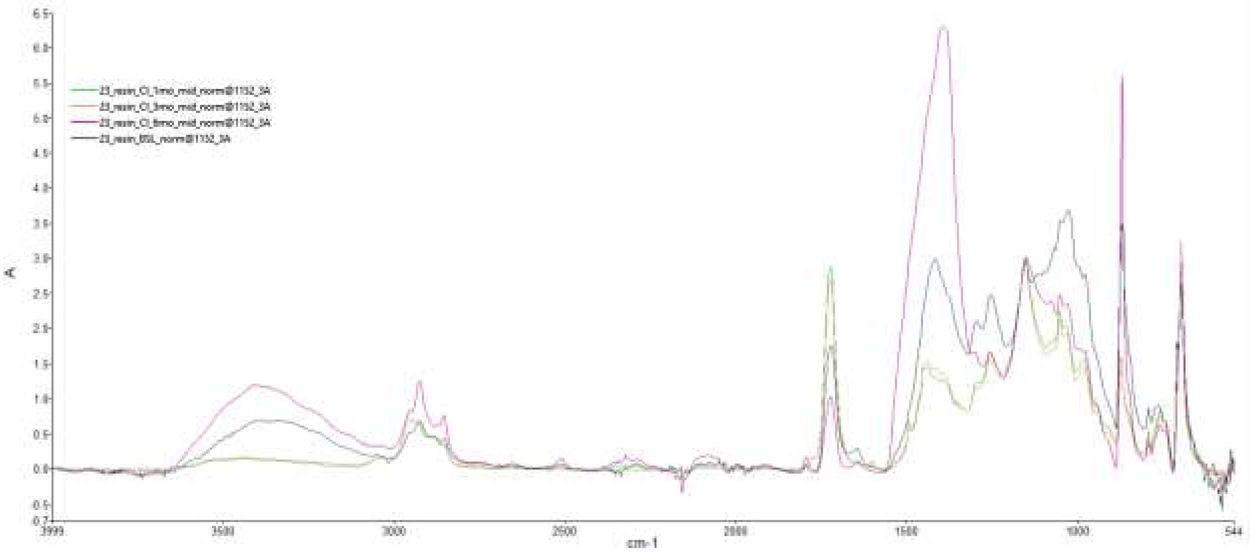


Figure 113: FTIR Resin System 23 in Calcium Chloride

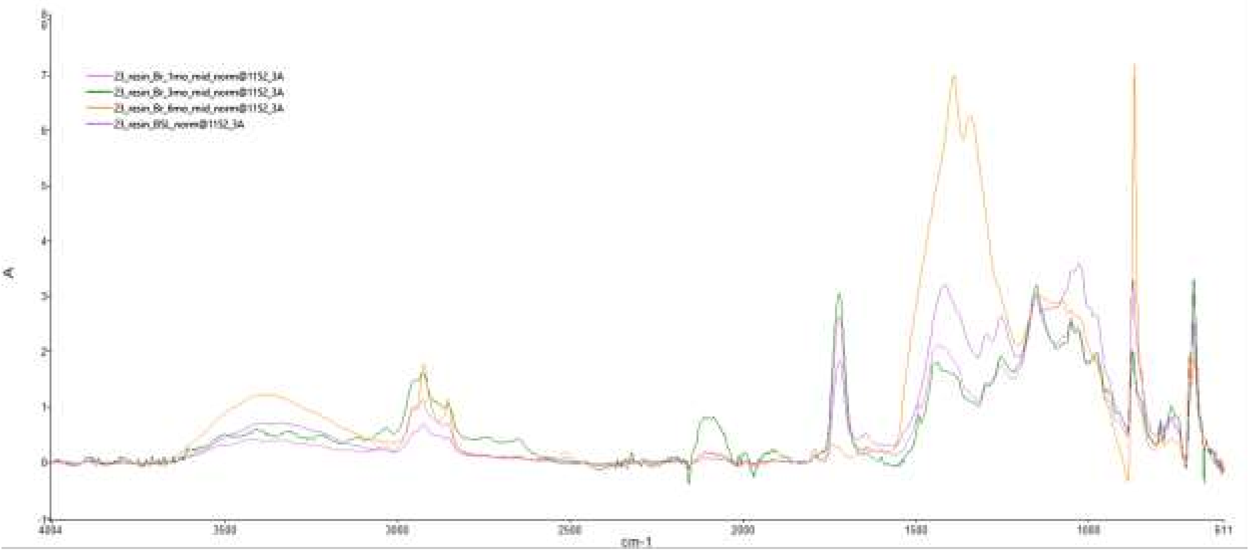


Figure 114: FTIR Resin System 23 in Calcium Bromide

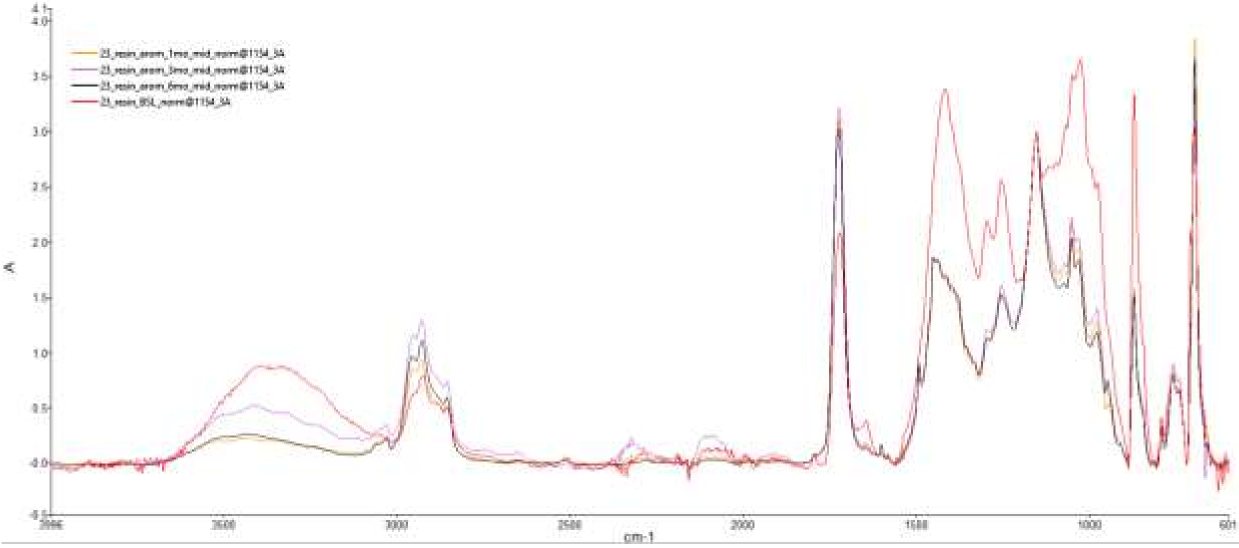


Figure 115: FTIR Resin System 23 in Aromatic Hydrocarbon

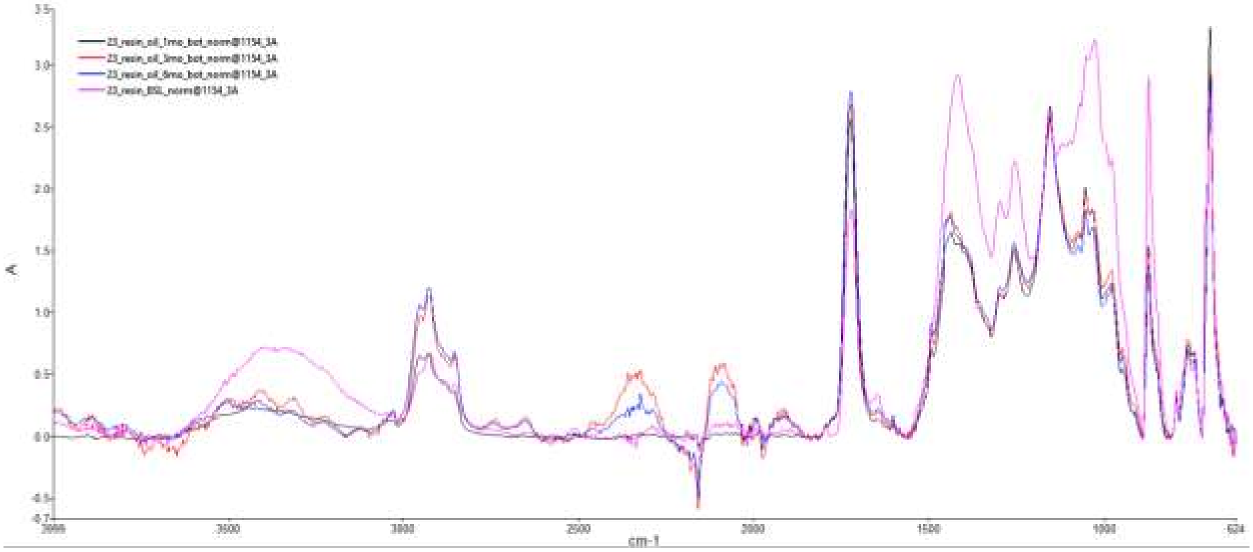


Figure 116: FTIR Resin System 23 in Nonaromatic Hydrocarbon

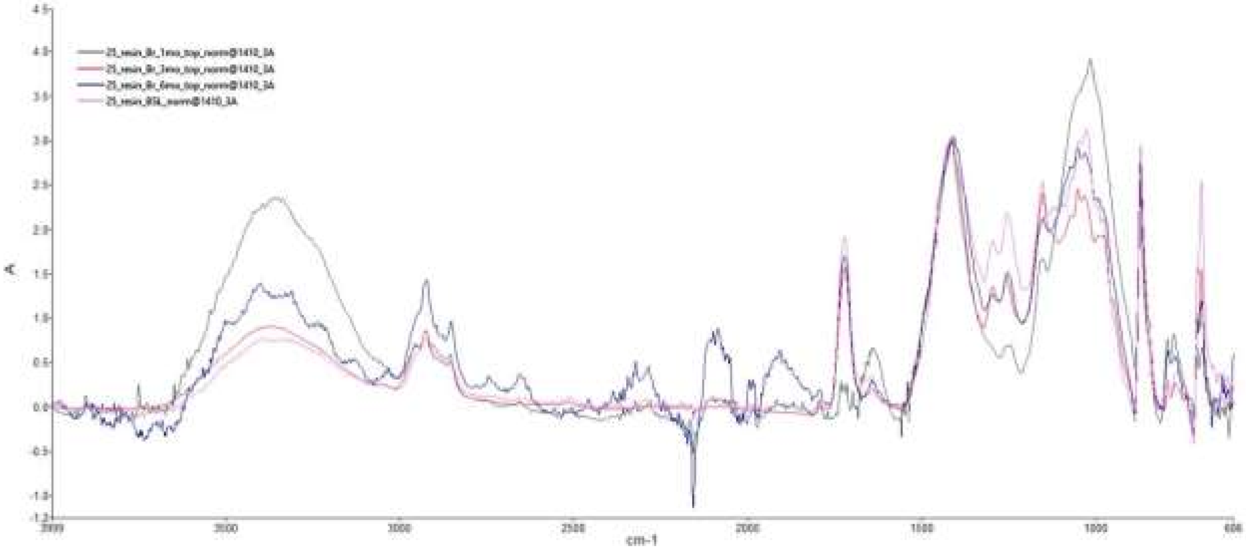


Figure 117: FTIR Resin System 25 in Calcium Bromide

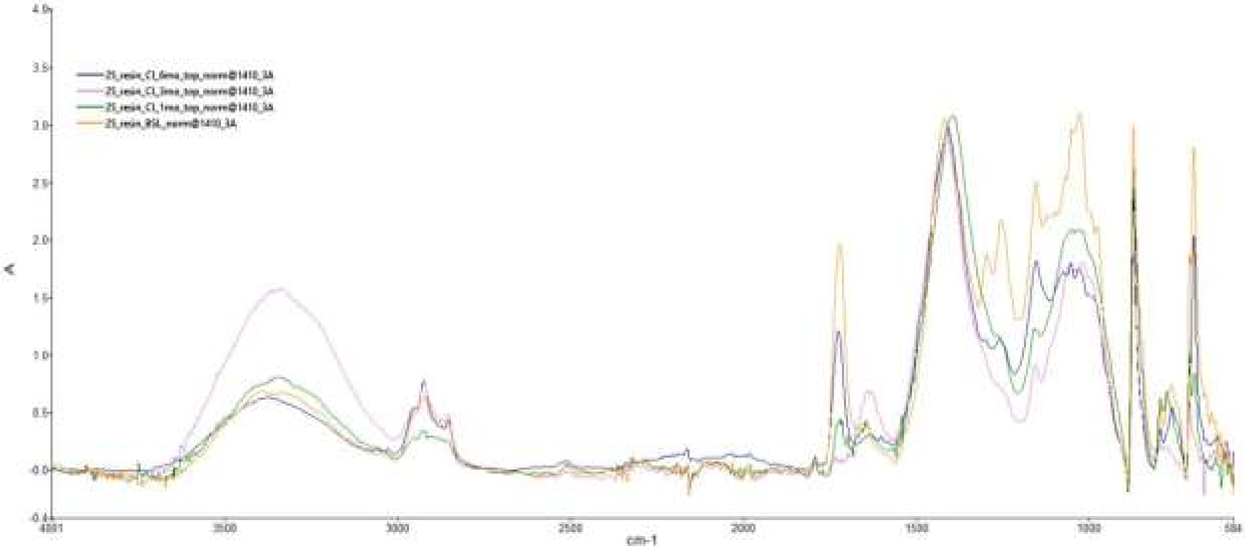


Figure 118: FTIR Resin System 25 in Calcium Chloride

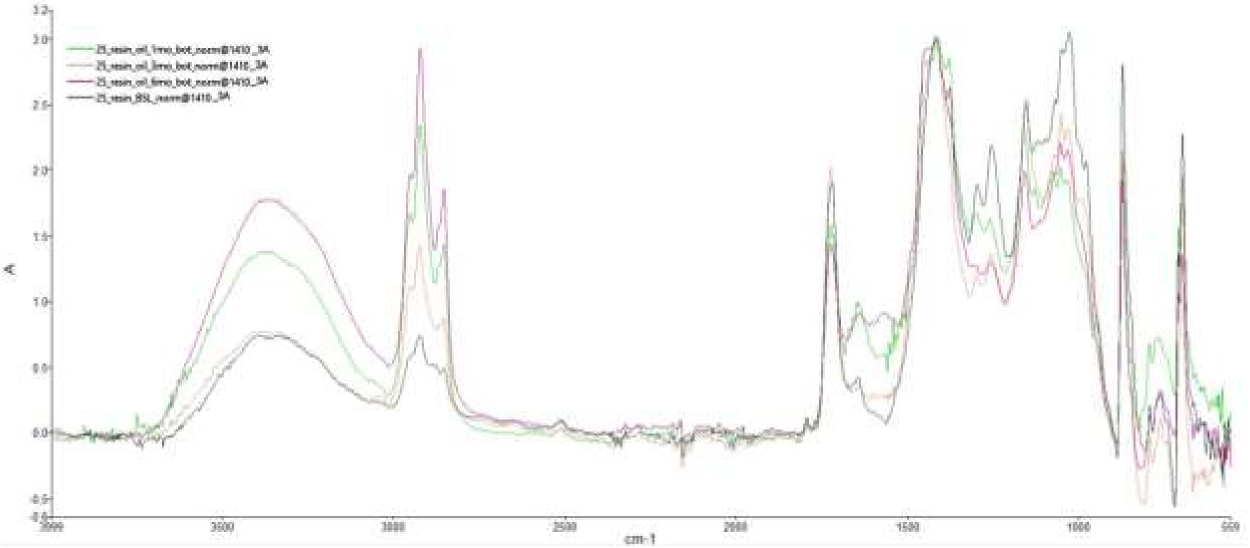


Figure 119: FTIR Resin System 25 in Nonaromatic Hydrocarbon

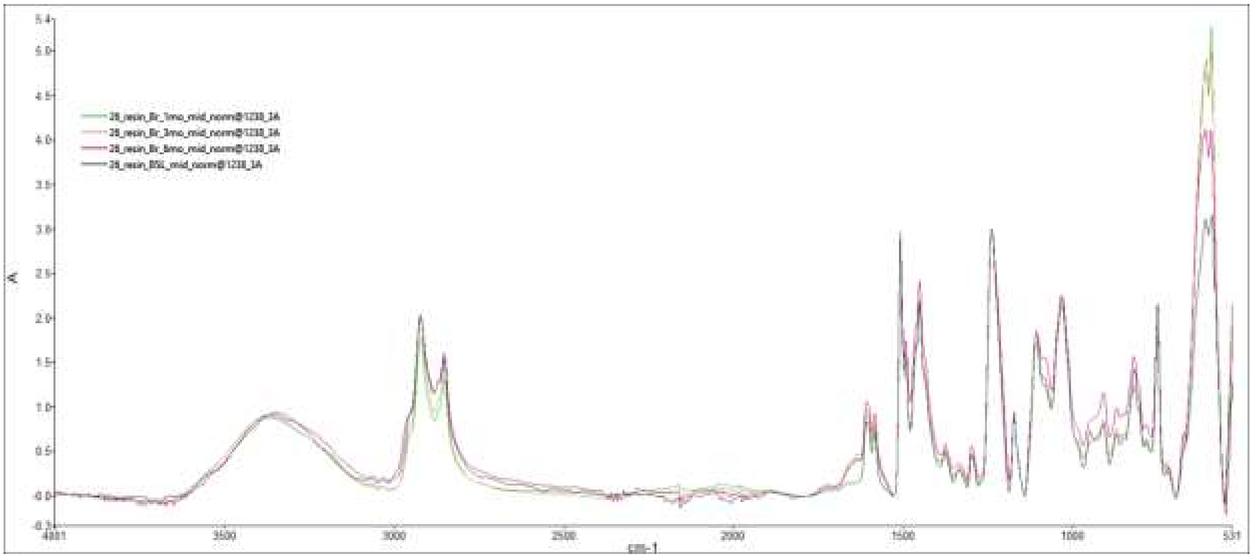


Figure 120: FTIR Resin System 26 in Calcium Bromide

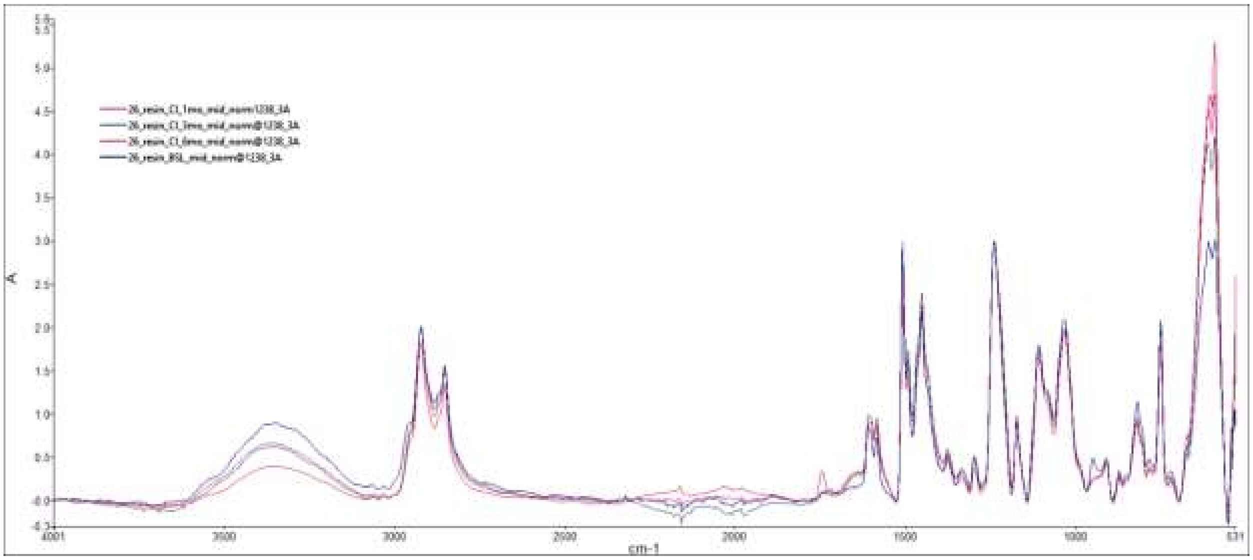


Figure 121: FTIR Resin System 26 in Calcium Chloride

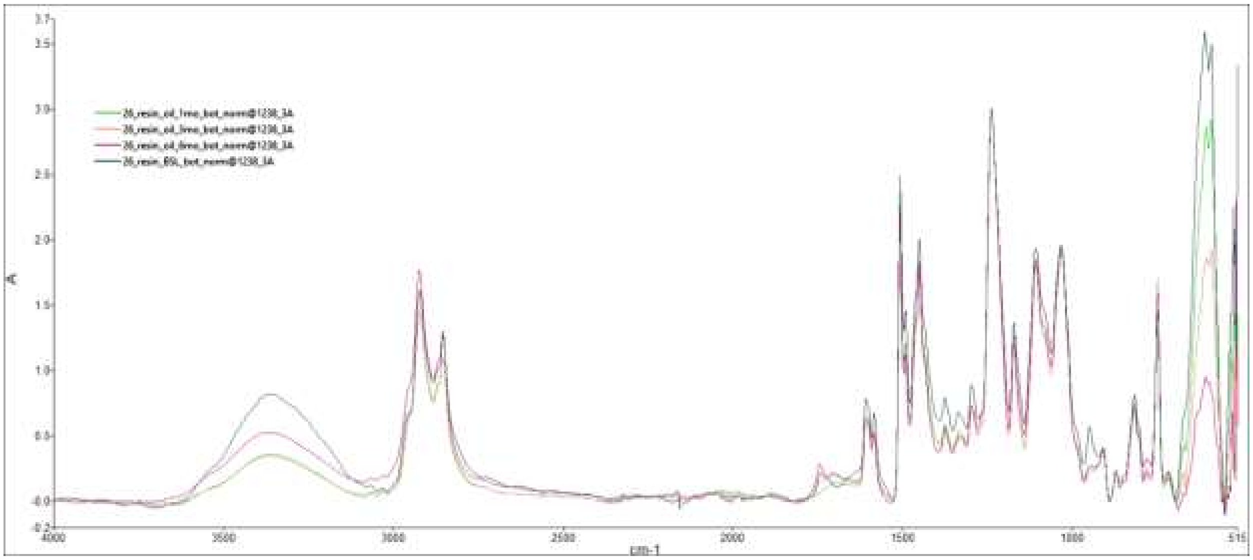


Figure 122: FTIR Resin System 26 in Nonaromatic Hydrocarbon

For most samples exposed to calcium bromide the spectra looked very similar to the spectra above done in calcium chloride. An exception to that was resin system 23. In this case there were clear changes over time and after six months changes from top to bottom as well. The changes occurred in both calcium chloride and calcium bromide. These changes can be seen in the spectra Figure 113 and Figure 114.

These changes would be consistent with acid catalyzed cross linking at an ester carbonyl group. The salt solutions are approximately pH 4 and the resin is polyester based.

8.1.5 Small Scale Pressure Annular Seal

The Annular Seal Tests were developed in order to measure the ability of cement to maintain an annular seal in a simulated small-scale wellbore. Apparatus was designed to allow the cement to be stressed by internal pipe pressure application-and-release cycles. Steel was used to simulate the formation. These represent the methodology used in the annular seal testing in this project. There are no industry standards covering this test procedure. All test fixtures were custom built for this project.

Test apparatus Figure 123 and protocols were developed for the pressure loading condition. The apparatus was designed to allow for the application of substantial energy input via hydraulic pressure cycles in the center pipe of the fixture after a sealant system was cured in the annulus of the fixture. This pressure cycling continued until seal failure was detected or the system survived 1500 cycles, the maximum practical applied energy duration. Annular pressure of 15 to 30 psi nitrogen gas was applied to detect flow when a sealant failure occurred. The hydraulic pressure cycled from 1,000 psi up to 10,000 psi with 1,000 psi increments. 25 cycles at each pressure were applied. Once reaching 10,000psi, the cycles were repeated from 0psi to 10,000 psi without any intermediate steps for up to 1500 total cycles. Calculation of total energy applied to the system from the pressure cycling yielded quantitative durability values in terms of total input energy

Assumptions for calculation energy applied to the annular seal test system from hydraulic pressure cycling in the inner pipe were:

Equation 2: Annular Seal Energy Calculation

1. Energy input into the system = pressure of the fluid x fluid volume: E (in-lb_f) = P (lb_f/in^2) x V(in^3)
2. All energy input is absorbed into the system (inner pipe-cement-outer pipe)
3. Energy input to the system is dissipated through system expansion and degradation of cement-pipe interfacial bonds

Energy values were converted from in-lb_f to joules for scaling.

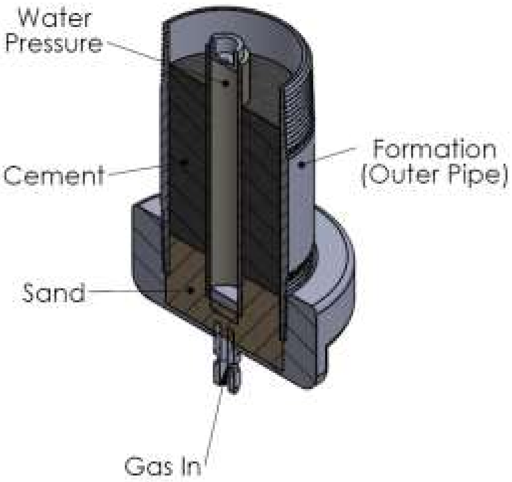


Figure 123 Pressure Annular Seal Apparatus

The small scale pressure annular seal results are listed in Table 20. Some cement designs worked well while others had immediate failures when applying pressure. This also held true for the resins, some worked well while others failed immediately. Due to the volatile nature of System 22 (furan) the test specimens required curing under pressure. The requirement to cure under pressure prevented the testing of the small scale annular seal as the test fixture was too large for the pressure curing vessel.

Table 20: Small Scale Pressure Annular Seal Results for Cements and Resins

System	Joules	System	Joules
1	+970,712	13	+979,337
2	+1,047,621	14	failed
3	failed	16	+979,337
4	+1,067,747	17	failed
5	71,159	18	+979,337
6	failed	19	failed
7	failed	20	failed
8	failed	22	na
9	failed	23	+979,337
10	16,244	27	+980,775
11	+979,337		

8.1.6 Large Scale Pressure Annular Seal

A schematic of the large-scale test fixture for pressure testing is presented in Figure 124 below. The pressure cycling test is performed by repeatedly increasing the pressure of the inner pipe to 1000 psi and then bleeding the pressure back to around ambient pressure. There are no industry standards that this test was performed in accordance with. All test fixtures were custom built for this project.

Sufficient cement, dry additives, and water were weighed to prepare approximately 25 gallons of cement slurry. Dry components were blended into the cement and the dry blend was mixed with the water using a high-shear paddle mixer. The cement was then stirred 20 minutes to ensure complete mixing. Next, the slurry was pumped into place in the fixture annulus. This cement was cured for 7 days at ambient conditions as in the small scale testing.

After curing, the annular seal competence was confirmed by application of 20 psi gas pressure at the bottom of the annulus with no pressure increase occurring at the top of the annulus during the 1-hour test duration. Then, the inner pipe was filled with water and pressure cycling started. Cycling schedule was pressurize from 0 to 1000 psi in 30 seconds, hold for 30 seconds, and release pressure allowing 1 minute for the pressure in the pipe to return to ambient conditions. This cycle was controlled automatically and repeated continuously throughout the time each day that CSI's laboratory was manned. The data acquisition system logged pressure in the inner pipe as well as pressure at both top and bottom of the annulus.

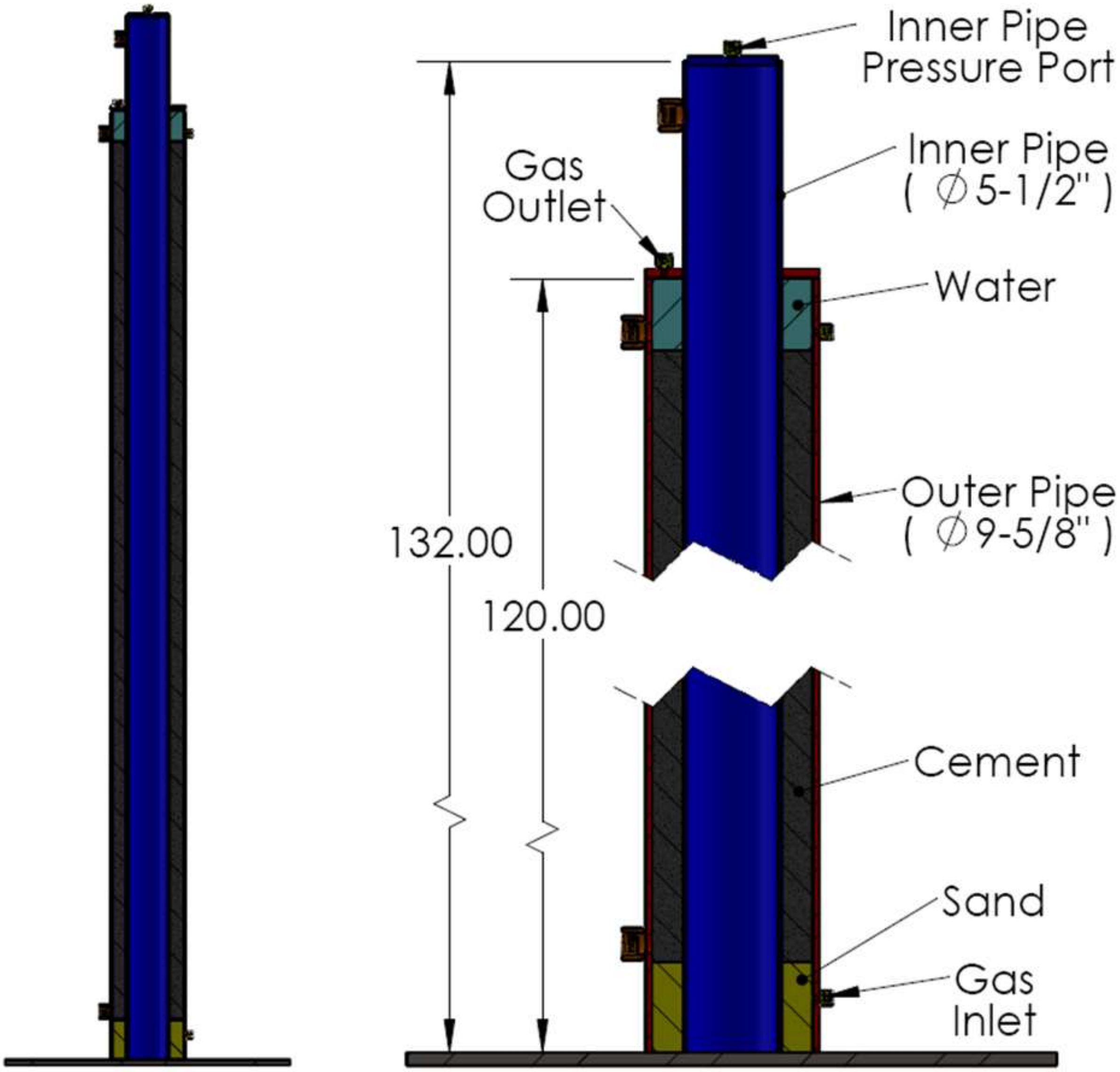


Figure 124: Large Scale Annular Seal Test Apparatus

Table 21 lists the results of the large scale annular seal results. Systems that failed small scale, failed in large scale as well. Systems that held their seal in small scale, also held their seal in large scale. Results are further discussed in Section 9.

Table 21: Large Scale Annular Seal Results for Cements and Resins

System	Joules
2	42,569,477
7	2,301,053
14	failed
23	failed
27	42,569,477

8.1.7 Cohesiveness of Resin

Cohesive nature of resin falling through a column of seawater is demonstrated by allowing resin to fall through a column of seawater and evaluating if the resin disperses or stays cohesive and sets. Figure 125 shows a picture of this fall test. All of the various categories of resin demonstrated this cohesive nature as opposed to cement which will disperse in any water or brines. Resins can be placed in a well containing seawater or brines and allowed to fall into place and provide a seal on some type of barrier that is leaking such as a leaking packer.

Figure 125: Resin Falling Through Brine

9.0 TASK 6.0 - SEAL INTEGRITY AND NUMERICAL EVALUATION OF RESIN PERFORMANCE

9.1 Summary

Finite element analysis was performed to better understand and compare how the performance of cements and resins respond to well stimulations on the annular seal of production casings in the outer continental shelf (OCS) during oil and gas operations. The scope of work for the study included:

- Laboratory testing to simulate casing-cement and casing-resin behavior in response to typical stimulation effects such as pressure.
- Development of Finite element analysis (FEA) models to analyze the cement bond and casing pressure integrity as well as the resin bond for comparison of the two types of seals.

The objective of the FEA was to examine how the well stimulation techniques affect the cement and resin bond behind the production casing and the pressure integrity of the production casing due to pressure cycling.

Initially the laboratory test results were compared to FEA models of the test arrangement to establish the best approach for the FEA. Thereafter the findings and FEA techniques were then applied to the large scale models.

A comparison of the FEA results with the small scale tests showed similar failure modes and magnitude of number of cycles to failure. There was some variance in the overall magnitudes of number of cycles. This variance in the results can be attributed to multiple factors, one of which is that a failure or failure location in the FEA may or may not translate to a leak in physical testing or in actual well conditions. In addition, some of the variance in the resin results are due to the resin not achieving a seal during the curing process.

Although there are some variations with the seal durability (no. of cycles to failure) between the FEA and lab results; there was a strong match of failure location and likely failure mode. Thus, the FEA results can indicate where the failure is likely to occur, but not precisely when. A summary of the comparisons between the lab testing and FEA modeling are shown in Section 9.4.1.

9.2 Technical Approach

Using data acquired from mechanical property tests, the ABAQUS non-linear finite element code was used to generate the required FEA models. Factors taken into consideration include cement/resin strength and the formation of a micro-annulus within the cement column. A breakdown of the subtasks is provided below.

- Data processing from information acquired from mechanical property testing conducted in earlier tasks.
- Finite Element model construction & analysis were done for the small scale tests to replicate the testing performed in the lab.
- Finite Element simulations will be performed for the large scale testing to validate the modeling approach and results.

The cement and resin sheath is subjected to damage each time it is subjected to pressure loads. Due to the material properties of Portland based cements; degradation and damage leading cracks or de-bonding at interfaces may occur below the failure stress of the material. Similar behavior of the resins is anticipated to occur however the overall behavior of the resins is expected to be much more elastic and more flexible than the cement systems.

Several failure modes were assumed to occur within the system; radial cracking in the sheath due to the tensile forces from the applied loads, de-bonding at the sheath to formation and the micro-annuli formation at the coil tubing to sheath interface. In addition, shear cracking or disking from loading may occur.

Material properties were derived from lab tests and used as inputs in the FEA. Whenever full stress-strain curves were not available generic curves were assumed.

9.3 Subtask 6.1-6.4 - Finite Element Model of Scale Systems

3D finite element models of the test setups were created using ABAQUS 2017 and solved using the Explicit solver. The explicit solver was chosen as modeling unreinforced concrete/cement materials can sometimes cause convergence problems in the Standard solver due to the extreme non-linearity caused by cracking. The Explicit solver is computationally efficient for the analysis of extremely discontinuous events such as cracking in cement. This solver can be used to perform quasi-static analyses with complicated contact conditions. Time increments in the Explicit solver are influenced by the overall event time scale, element shape and mass of the system; therefore in order to reduce solve time a combination of mass scaling and reduction of step times were used. To ensure that this method did not influence the solution, energy histories for the systems were checked and the mass scaling used was varied as required.

Geometry of the assemblies was modeled to match the lab assemblies. The small scale assembly is shown Figure 123 and the large scale assembly is shown in Figure 124. Where possible, 8 node reduced integration brick elements (C3D8R) were used. General views of the mesh used in the models are shown in Figure 126 and Figure 127. Only ¼ of the fixture was modeled to reduce the computational expense of the analysis and was done by using symmetry planes in the x and y directions on both the small and large scale models. In addition, the coil tubing was modeled to extend just slightly past the faces of the cement sheath to help with model convergence. The sand bed at the bottom of the cement was omitted as it is to allow for the placement of cement in the pipes and have some compressibility to allow movement. It is not anticipated that the exclusion of the coil tubing ends or the sand bed will have a significant effect on the analysis results.

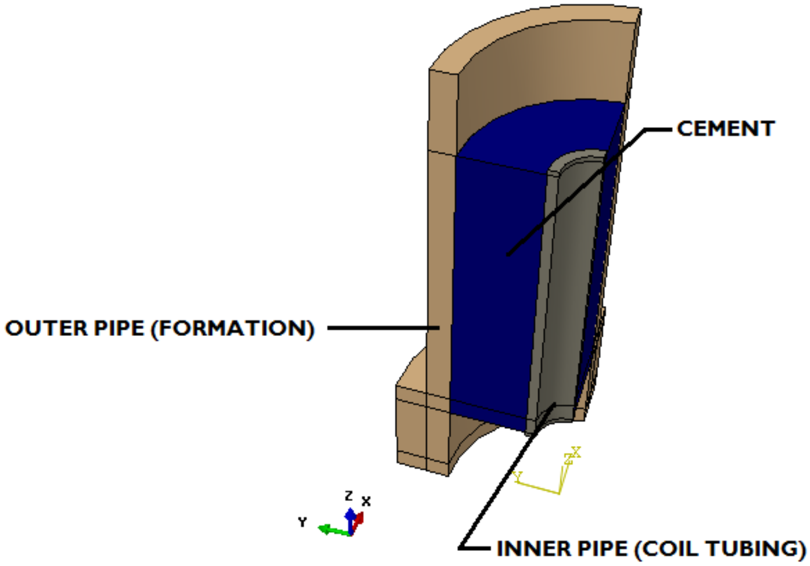


Figure 126: View of Meshing of Small Scale Model

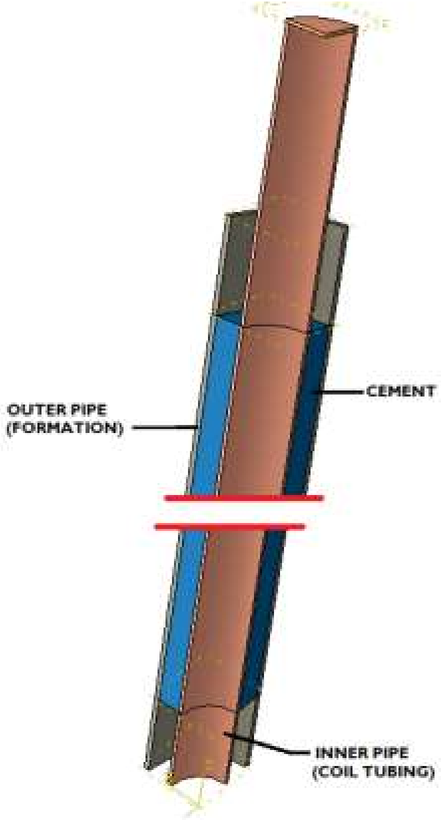


Figure 127: View of Meshing of Large Scale Model

Views of mesh used in the FEA models are shown in Figure 128 and Figure 129.

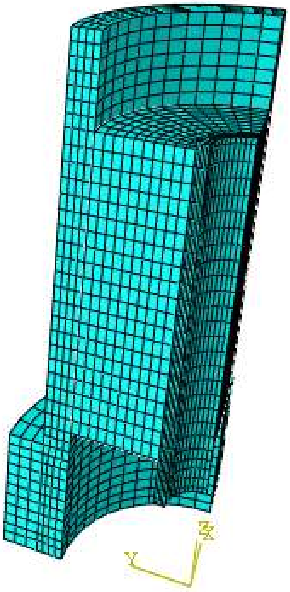


Figure 128: View of Mesh of Small Scale FEA Model

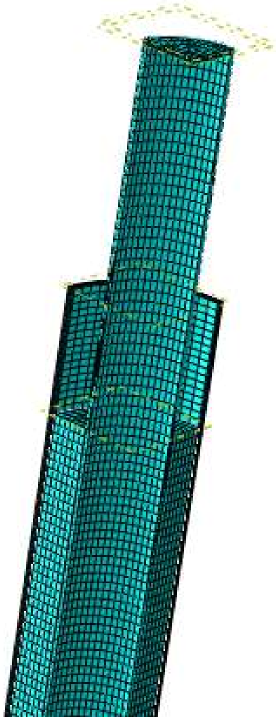


Figure 129: View of Mesh of Large Scale FEA Model

9.3.1 Boundary and Initial Conditions

The small scale and large scale models were restrained by fixing the base of the outer pipe in the vertical and horizontal directions. Symmetry planes were used in the X and Y planes. Boundary conditions for the small and large scale models are shown in Figure 130 and Figure 131 respectively.

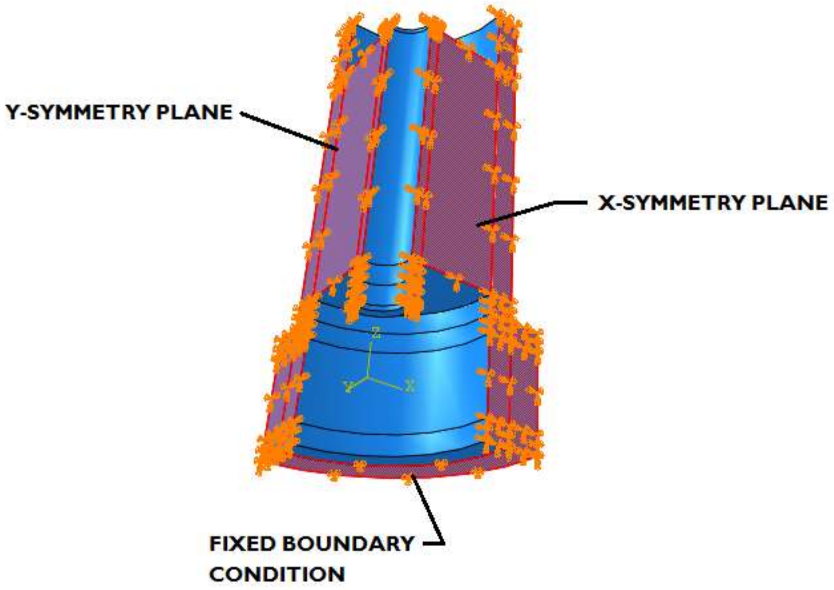


Figure 130: Small Scale Model Boundary Conditions

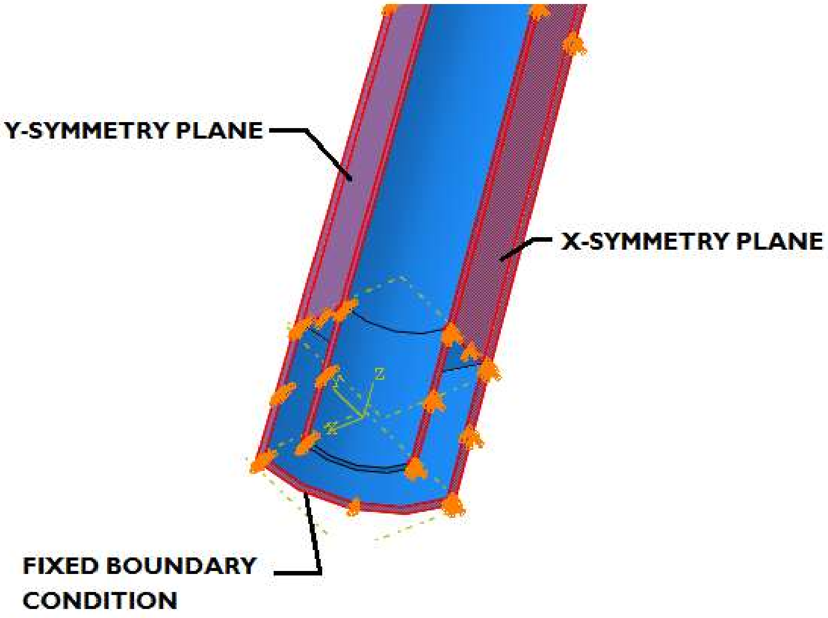


Figure 131: Large Scale Model Boundary Conditions

9.3.2 Contact Interactions

The assembly of parts used to create the test model was held in space using contact interactions true to how the parts interact in reality. Surface to surface contact definitions were defined at the cement to coil tubing interface and at the cement to formation pipe interface. The contacts were assigned a cohesive behavior utilizing a traction separation based contact enforcement method. Maximum tensile bonding strength at the interface and shear bond strength at the contact surfaces are shown in Table 9, Table 10, Table 11, Table 15, Table 16, and Table 17 in Section 8.

In order to simulate the de-bonding of the contact surfaces damage initiation was defined using the maximum nominal stress criteria interaction property. Once the contact stresses reach the tensile or shear bond strength separation is allowed to begin. After damage is initiated, damage evolution was modeled using mixed mode fracture energy with exponential softening behavior.

See Figure 132 for typical contact pairs in the small scale model. It should be noted that the large scale modeling is similar.

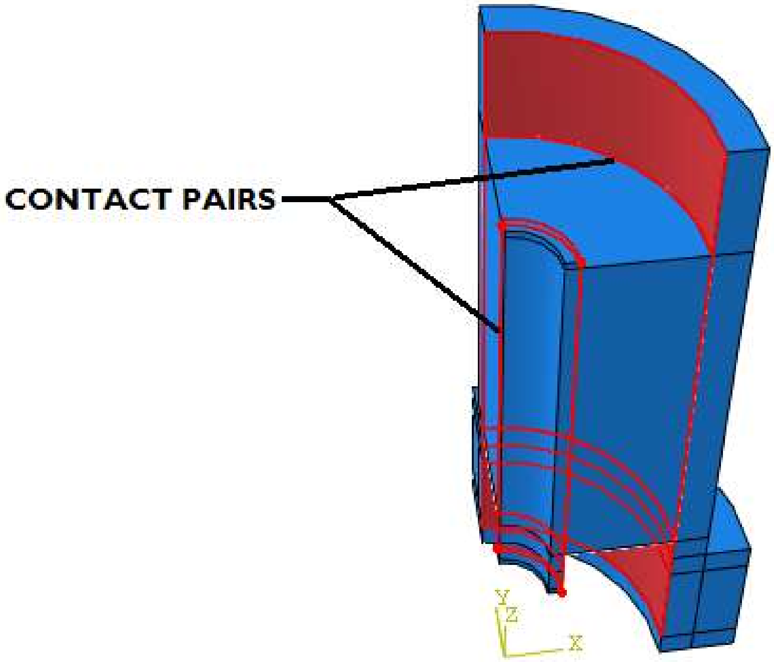


Figure 132: Typical Contact Interaction Locations

9.3.3 Damage Modeling

The sheaths were modeled using the concrete damaged plasticity model in ABAQUS. ABAQUS provides a general capability for modeling concrete and other quasi-brittle materials in all types of structures by using the concepts of elasticity in combination with tensile and compressive plasticity to represent the inelastic behavior of concrete. The resin is modeled using the same techniques as the results were validated with the laboratory scale testing.

The model is a continuum, plasticity-based, damage model for concrete and cements. It is based on the assumption that the main two failure mechanisms are tensile cracking and compressive crushing of the material. The evolution of the failure surface is controlled by two hardening variables, tensile and compressive equivalent plastic strains that are linked to failure mechanisms under tension and compression loading, respectively. The fracture energy criterion was used to model the cements behavior by using a stress-displacement relationship. The stress-strain behavior of the cement in uniaxial compression outside of the elastic range is modeled by using compression hardening and strain softening.

The concrete compression damage and concrete tension damage optional parameters were used to simulate the loss of stiffness of the cement as damage occurs. Maximum compressive stiffness reduction was set to 99% and 90% for tension. Once these values are reached a complete loss of stiffness is assumed to occur. Element deactivation was enabled to remove these elements from the stiffness matrix at complete failure.

The resin systems although considerably more elastic are currently being modeled using the same material model but with the appropriate stress-strain data from testing.

9.3.4 Pressure Loading

The models were pressurized by applying a surface pressure on the face of the interior wall of the inner tubing/pipes for all cases. For the small scale models the pressure was applied in increasing intervals of 1,000psi up to 10,000psi max. Each pressure interval up to 9,000psi was cycled 25 times; once 10,000psi was reached it was cycled up to a maximum of 650 cycles or until a failure. The maximum cycles in the FEA were limited to 650 due to time constraints; however general trends from the behavior of the sheaths can be used to evaluate anticipated performance past 650 cycles. In addition, an upward constant pressure of up to 50psi was applied to the bottom of the cement sheath. These loads are applied as shown in Figure 133. The large scale model cycled a pressure of 1,000psi max to failure or up to 200 cycles. Large scale model pressure loads are shown in Figure 134.

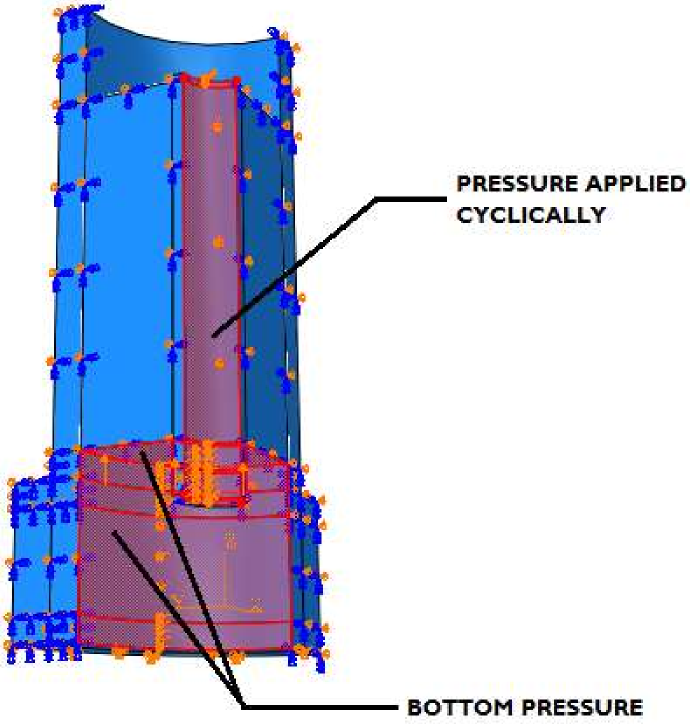


Figure 133: Small Scale Pressure Loading

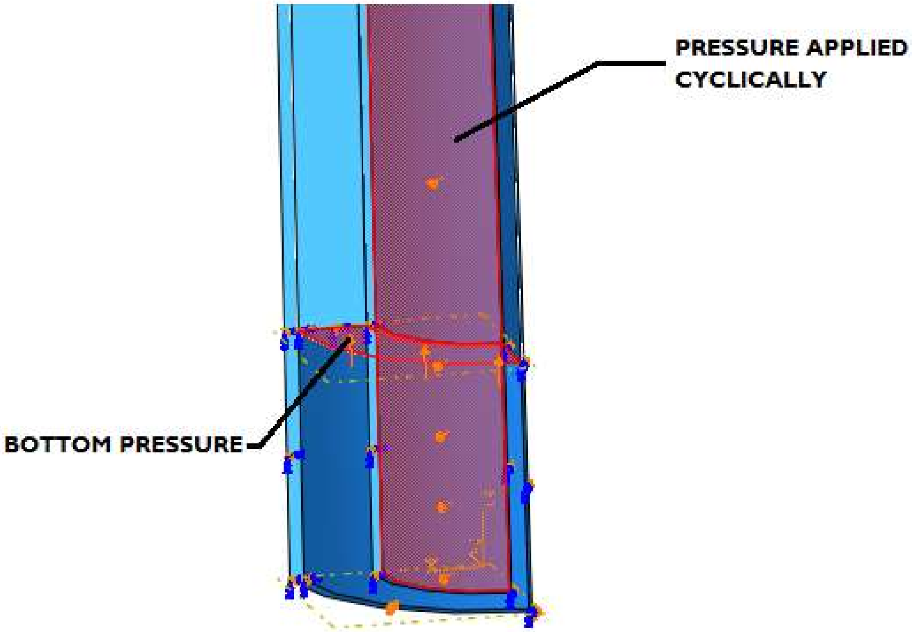


Figure 134: Large Scale Pressure Loading

9.4 Results

Using the damage modelling technique described in section 9.3.3 the damage is tracked by the variable SDEG. SDEG represents the magnitude of the damage occurring in the cement itself within each individual finite element with 0% indicating no damage and 90% indicating complete damage and loss of load carrying capabilities. Contact damage is modelled using the techniques described in section 9.3.2. CSDMG is the contact damage occurring at the bonded surfaces of the model between individual parts. CSDMG values range from 0% to 100%, once the damage reaches 100% the contact surface is allowed to separate indicating a potential leak path.

9.4.1 Small Scale Results

The results for the small scale pressure cases and a comparison to laboratory testing are shown in **Table 22**.

Table 22: Comparison of FEA Results and Lab Results for Small Scale Pressure Cycling

System	Lab results		FEA Results	
	N_{TEST}	Location	N_{FEA}	Estimated location
7	Instant Failure	Outer	20 @ 2,000psi	Outer
2	No failure	N/A	No Failure	N/A
27*	No failure	N/A	No failure	N/A
14*	40	Inner	No failure	N/A
23*	Instant Failure	Inner	No failure	N/A

N_{TEST} - No. of Cycles at 10,000psi to failure

N_{FEA} - Estimated no. of Cycles at 10,000psi to failure

*-Resin Systems

Typical damage of the cement and resin seals from the small scale tests are shown in Figure 135 to Figure 138.

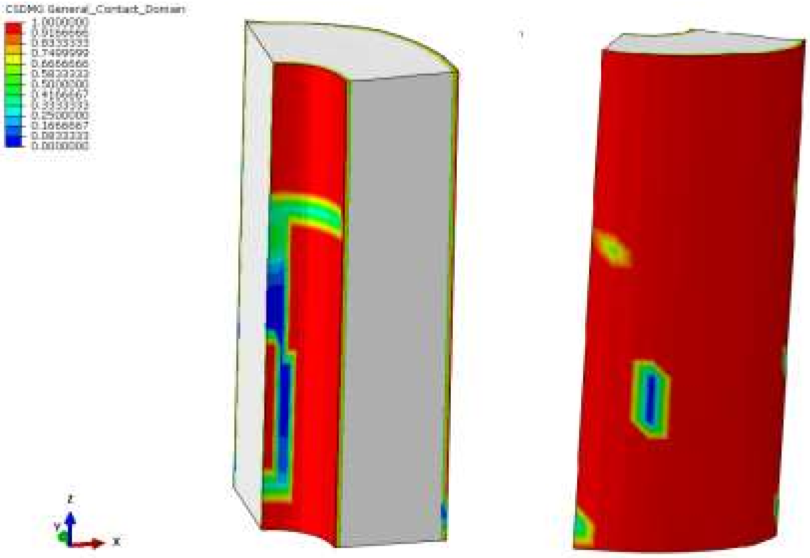


Figure 135: Contact Surface Damage (CSDMG) of #7 Cement Mix

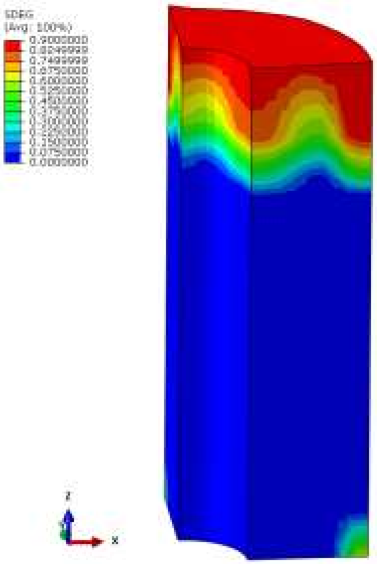


Figure 136: Element Damage (SDEG) of #7 Cement Mix

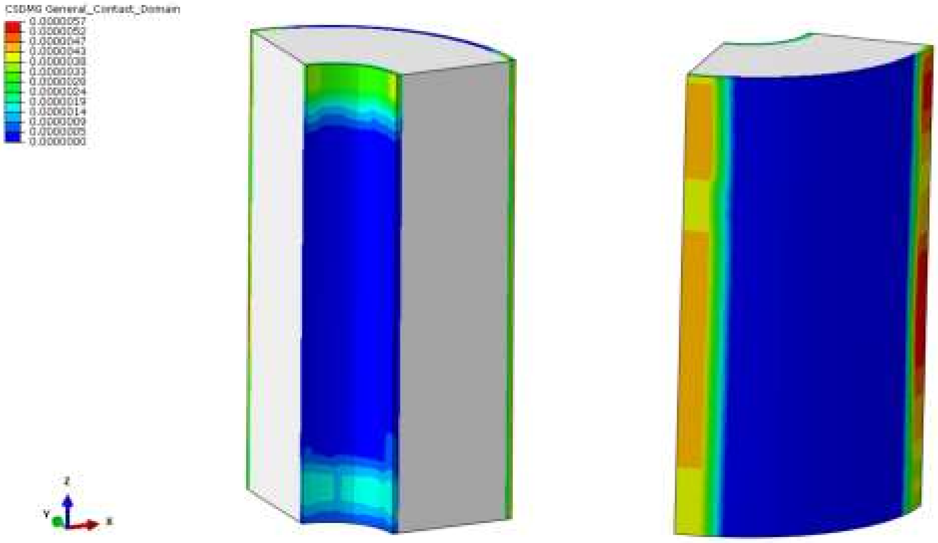


Figure 137: Contact Surface Damage (CSDMG) of #27 Resin

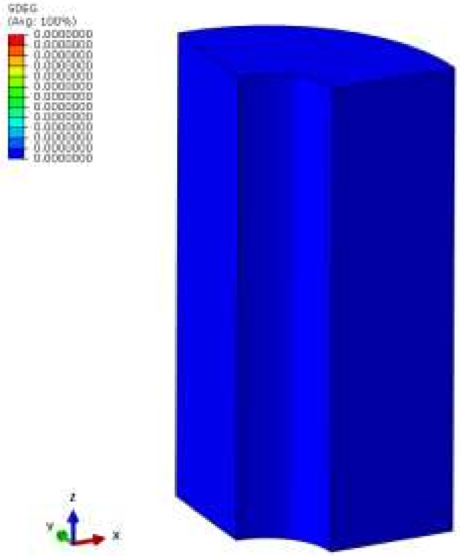


Figure 138: Element Damage (SDEG) of #27 Resin

9.4.1 Large Scale Results

The results for the pressure cases and a comparison to laboratory testing once they are complete will be shown in Table 23.

Table 23: Comparison of FEA Results and Lab Results for Small Scale Pressure Cycling

Systems	Lab results		FEA Results	
	N_{TEST}	Location	N_{FEA}	Estimated location
7	10	TBC	30	Outer
2	+185	TBC	No Failure	N/A
27*	+185	TBC	No Failure	N/A
14*	Instant Failure	TBC	No Failure	N/A
23*	Instant Failure	TBC	No Failure	N/A

N_{TEST} - No. of Cycles at 1,000psi to failure

N_{FEA} - Estimated no. of Cycles at 1,000psi to failure

*-Resin Systems

Typical damage of the cement and resin seals from the small scale tests are shown in Figure 135 to Figure 142.

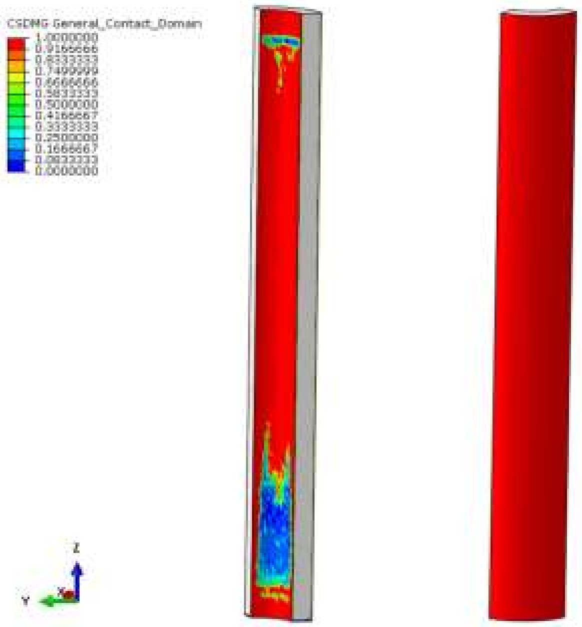


Figure 139: Contact Surface Damage (CSDMG) of #7 Cement Mix

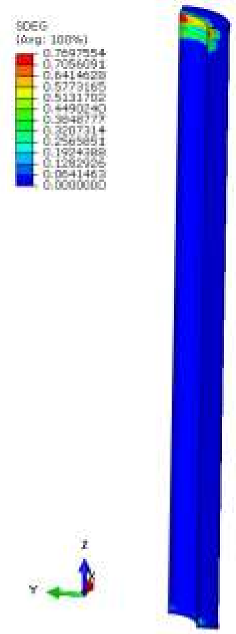


Figure 140: Element Damage (SDEG) of #7 Cement Mix

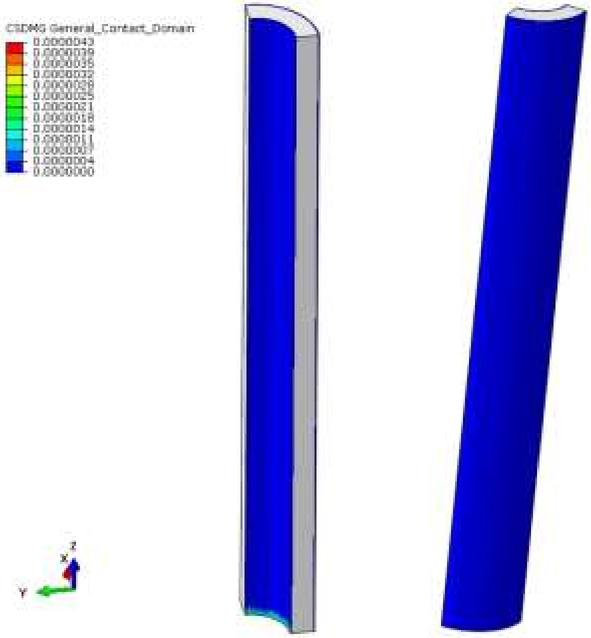


Figure 141: Contact Surface Damage (CSDMG) of #27 Resin

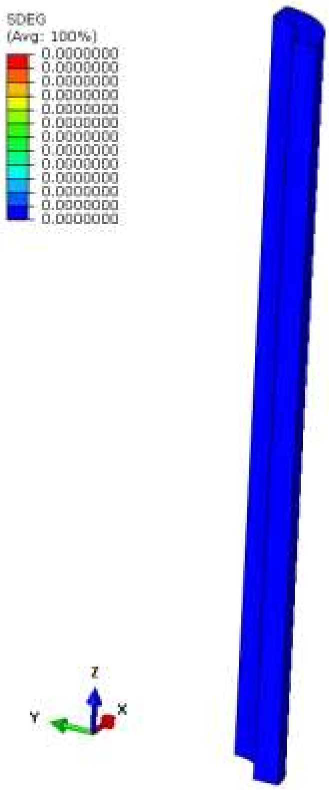


Figure 142: Element Damage (SDEG) of #27 Resin

10.0 TASK 7.0 - DEVELOP OPERATIONAL GUIDELINES

Information from the previous tasks was used to identify resin limitations, operational and supply issues, and engineering considerations including the best applications to implement this technology. HSE concerns regarding safe handling of resin materials, containment and disposal of excess resin components, spill containment, and handling exothermic reaction at surface were also analyzed and used in the development the operations guidelines.

10.1.1 Subtask 7.1 - Resin Applications

While working with the Industry Advisory Group, current problems that can be managed through the use of resin was identified based on the results in the above sections. In general the resins that were found to be applicable for OCS wells displayed the following properties:

- Lower Young's modulus
- Higher Poisson's ratio
- Higher tensile strengths
- Higher impact resistance
- Higher shear bonds and hydraulic bonds, both water and oil wet
- Ability to penetrate formations and micro-channels.
- Improved resiliently to pressure cycles
- Chemical resistance
- Higher compressive strength
- Higher tensile strength
- Improved Adhesion properties

These properties give resin the potential to provide an improved barrier for both typical and complex geometries when compared to cement. While resins could provide an improved barrier for both primary and remedial operations, the advisory group suggested resins could have the most direct and immediate impact for plug and abandonment applications. The most likely resin applications for plug and abandonments are listed below.

- Plug inside casing or open hole
- Plug inside casing x casing or formation x casing annulus
- Formation isolation
- Channel / fracture remediation

Most promising remedial applications for resin sealant are formation isolation and channel/fracture remediation as both of these needs are very challenging to successfully perform with cement. The solids in the cement slurry are too large to penetrate into the formation or small channels / fractures. This can be overcome using resins which contain only liquid reactive components and have the ability to penetrate the formation and small channels / fractures. Also resin's ability to adhere, proven with improved shear bond results, should allow for a shorter plug length to provide the same isolation compared to cement.

10.1.2 Subtask 7.2 - Operations

Field operations involving resin will vary depending on job volume, resin type, and placement method. These variables should all be considered when planning resin operations to ensure successful surface handling and barrier placement.

Job Volume: While Resin's improved mechanical properties prove smaller volumes could be used to provide improved isolation compared to cement, potential difficulties where identified mixing both large and small volumes.

For small volume applications, the main concerns are ability to accurately measure the needed chemicals and equipment availability to mix the small volumes. For some resins, changes in .05% by weight of hardener had a significant impact on the handling time and final set mechanical properties. It is recommended to identify an acceptable concentration range for all resin components and have the necessary equipment to measure all components within the acceptable range. The recommended and most likely method to mix resin during field operations will be using a cement style batch mixer. However, the common blender sizes are 50 bbls which will cause some difficulties and excessive dead volume when mixing small volume applications. The recommended blender for resin mixing would have a cone bottom to minimize the dead volume and paddles extending near the bottom with the bottom paddle below the midpoint between top of resin and bottom of the blender(when mixing 5 bbls of resin the bottom paddle should be at least at the 2.5 bbls mark).

For large volume applications the main concern is the ability to control the exothermicity reaction. Depending on the resin and activator used testing showed that some reactions can reach temperatures greater than 500°F at surface temperatures. When large a volume of resin is used the exothermicity reaction may cause the temperature of the resin to increase if it is held too long at surface. Because the resin reaction is temperature driven, this increase in temperature will accelerate the reaction rate and potentially create a chain reaction as surface. As job volume increases the total heat that can be given off during the exothermicity reaction increases increase the risk for this chain reaction. For large volume jobs it is recommended to perform lab testing to ensure the resin will not began the reaction process at surface. Also, before starting the mixing operations a plan should be put in place that identifies what to do in case the resin does start reacting a surface. The plan should include an allowable temperature increase at surface that was determined with laboratory analysis, what to do if the resin exceeds that allowable temperature increase, and a plan to monitor the temperature throughout the mixing operation.

Besides mixing no other field operations were found to vary between large and small volume applications.

Resin Type: When evaluating the resins tested during the project the major concern for field operations and placement is the *mechanism that drives the reactions process*. These *reaction drivers* are identified below:

- Temperature
- Curative
- Catalyst
- Combination

With each of the 4 *reaction drivers* identified, different field and placement operations should be followed. For temperature driven reactions the field operations will need to consider methods to control the resin temperature prior to using the product. Some resins have very low recommended storage temperatures that may necessitate refrigeration up to job time. If the resin will react with temperature only, it is recommended to identify the storage temperature needed to prevent excess aging. Develop a plan to control temperature from the manufacturing facility until the job time including transportation by truck and boat and storage on the rig. Finally, testing should be done in the laboratory to identify the expected effect of aging on resin's set mechanical properties.

For resin reactions that are driven by chemistry and concentration of curatives, the concentration needed for a complete reaction varies with curative chemistry, temperature, and desired mechanical properties of the set resin. Different curative types can be used based on application temperature or placement time needed. Curative concentrations range from 15 – 50% by weight of resin and have more flexibility in design compared to other reaction drivers.

For catalyst driven reactions, the typically concentration is less than 5% by weight of resin and testing showed large changes in handling time and final set mechanical properties with small deviations in catalyst amount. It is recommend to confirm the acceptable catalyst range via lab testing and ensure that equipment used measure the catalyst has the accuracy to be within the acceptable range.

Placement Method: It was found that the resin's fluid properties may support different placement methods compared to cement. The most dramatic difference was the resin's immiscibility in water-based fluids. When mixed with water-based fluids, such as completion brines, the resins where found to quickly separate with no visible contamination and testing the cured resin's mechanical properties showed no reduction in performance. This allows smaller treatment volume to be used without concerns about contamination during placement and minimizes the need for spacers during operations with water based wellbore fluids. Testing also showed the resins have a very low gel strength, this allows the resin to freely fall through lighter weight fluids or float above a fluid with higher density. The low gel strength means that resins will always sink or rise until they find density equilibrium or a mechanical base. This is different compared to cement, which has very high gel strength, and should considered before planning the placement method.

10.1.3 Subtask 7.3 – Resin supply for the Gulf of Mexico

Most resins are currently manufactured at a limited number of facilities and the materials are sent and stored at distribution centers throughout their marketing area. When reaching out to the manufactures for the resins that were found to be applicable for OCS wells, it was found that the potential increase in resin demand due to use in OCS wells could easily be met without additional cost or excessive delays. However, only limited number of distribution centers to store and ship the resin was found in the gulf coast area. To meet the potential resin demand it is expected that either additional resin distribution centers will need to be opened in the gulf coast area or the current companies supplying chemicals for OCS well will need to expand their inventory to include resin sealants.

10.1.4 Subtask 7.4 – Field Application Limits of Resin Placement Identified by Industry Advisory Group

Limitations and recommendations for resin placement was broken into mixing the resin and placing the resin in the wellbore. Resin volumes will be limited based on the mechanism that drives the resin reaction. For resin that use catalyst or curatives, the volumes will be limited to the available blender size since all the components need to be mixed at surface before placement downhole. For all resin types the viscosity at surface can be very high and can limit the ability to mix or pump the resin.

Several placement techniques were considered and it was determined that resin has the ability to be placed with all the current cement placement techniques when properly designed. However some difference between resin and cement for common placement techniques are identified. For coil tubing the resin viscosity could limit pump rates and potential increase pump pressure above max allowable. The main concerns is the resin viscosity's sensitive to temperature, it was found that the viscosity can have a significant increase at lower temperature which can be a concern for Deepwater wells. When placed through tubing or with a work string there are no additional concerns or recommendations when compared to cement operations. The low resin gel strength would be beneficial for dump bailer operations which would be useful for small volume applications. The main concerns using resin during dump bailer operations is the potential for settling if solids were used for weighting agents. This risk could be mitigated with stable resin designs and lab testing at down hole conditions.

10.1.5– Subtask 7.5 - HSE Concerns

HSE concerns will vary for each resin applications and resin type and a through risk analysis should always be done for each specific application. To provide some guidance and help identify some of the highest risk for resin that are different from conventional cement operations are identified below. Because some resin can give off fumes and cause skin irritation if contacted, it is recommended for everyone involved in mixing the resin to wear chemical gloves, googles, and depending on the resin respirators maybe needed. Another risk is the exothermicity created if the resin reacts at surface. Before the job a plan should be in place that includes a temperature limit and a contingency plan to handle the resin if it hits that limit. The exothermicity will also be a risk if the resin had been pumped down hole and had to be circulated back to surface and a resin handling plan should also be in place for that case. Some liquid resin components tested were found to be hazards therefore spill prevention and containment should follow current industry best practices for chemical shipment.

11.0 TASK 8 - PERFORMANCE ASSESSMENT OR RESIN COMPARED TO CEMENT

11.1 Objective

The objective of this task is first to assess the results for Tasks 5 and 6 to form an overall comparative estimate of barrier performance potential of resins and Portland cement. This assessment touches on various individual performance attributes of the sealants. These are compared and contrasted with qualitative estimate of impact on seal durability.

Then supply, operations, and cost of application of resin sealants compared to Portland cement are considered to identify pros and cons of resin sealants for well barriers.

11.2 Subtask 8.1 - Resin versus Cement Performance Comparison

All information gathered and data generated for this report is reviewed and compared broadly to develop a broad-spectrum indication of resin barrier performance and applicability compared to current Portland cement sealant.

11.2.1 Design, Mixability, and Placement

11.2.1.1 Resin Design

During the design phase of the various resin types, more linear relationships between formula modifications and performance was noted compared to Portland cement. In general, applicable designs for resin were easier and more straight-forward than for cement once the functional relationships among the components were understood.

Since resins set without added solids, design of low-density fluids was easier. However, higher density formulations were more difficult to design due to viscosity of resin base fluids.

11.2.1.2 Resin Mixability

Resin viscosity increased difficulty of achieving homogeneous mixture. At the same time, homogeneity is critical to complete crosslinking reaction forming a uniform solid. Additional shear via longer mixing times were required. Base fluid viscosity limited volumes of weighting material as stated above. Solids addition also required longer wetting and mixing time to disperse.

Large-scale mixing of resins for Task 6 testing indicated batch mixing of resins is achievable. Close attention is required to assure solids suspension to prevent settling. Extra time and energy is required compared to mixing cement. Additionally, control of crosslink reaction must consider safety factor for avoidance of premature reaction at surface with associated exothermicity.

11.2.1.3 Resin Placement

Resin viscosity is generally Newtonian when solids-free. Solids addition builds yield point. Resin rheologies are generally higher than those of Portland cement slurries. Resulting friction pressure is high limiting maximum placement rates. However, ability to extend and control set time allows for consideration of long placement times at slow pump rates.

Resins exhibited inherent fluid loss control. A positive aspect of fluid loss for resin is that the fluid lost from resin slurry to a formation or microchannel will harden and seal.

General resin compatibility with Portland cement slurry and drilling fluid support using smaller seal volumes as does the cohesiveness of resins.

11.2.2 Mechanical Properties

General mechanical property development of resin was superior to those of Portland cement.

11.2.2.1 Tensile Strength

Resin tensile strengths were significantly higher. This mechanical resistance increase is significant because tensile failure is most common failure mechanism of well sealants.

11.2.2.2 Compressive Strength

Compressive strength of resins was generally higher than for cement also.

11.2.2.3 Young's Modulus

This measure of elasticity and brittleness indicated that resins were generally less brittle than Portland cement. Young's modulus values were lower by an order of magnitude. This supports more durable, resilient seal formation.

11.2.2.4 Poisson's Ratio

Poisson's Ratio was significantly higher for resin than for Portland cement. This trend indicates more flexible resilient seal better able to prevent flow.

11.2.2.5 Impact Resistance

Resin compositions were substantially more impact resistant indicating improved durability.

11.2.2.6 Anelastic Strain

Higher anelastic strain metric for resin denotes more flexibility and ductility of the sealant.

11.2.2.7 Shear Bond

Shear bonds at all surface-wetting conditions were superior for resins.

11.2.2.8 Hydraulic Bond

Resins exhibited superior hydraulic bonds under all surface-wetting conditions as well.

11.2.3 Chemical Resistance

Chemical resistance of resins was superior to that of Portland cement.

11.2.3.1 Brines

Surprisingly, completion brines were discovered to cause deterioration of some cement compositions in a very short time. Most resin formulations remained stable under brine exposure.

11.2.3.2 Hydrocarbons

Most resins remained stable under hydrocarbon exposure as did the cements.

11.2.3.3 Thermal Stability

Fundamental thermal degradation testing indicated resin formulations are durable and thermally stable within their specified application temperature range.

Deleterious effects of resin performance above glass transition temperature were not confirmed. The practice of avoiding use of a resin sealant above its T_g is to ensure durability questioned. Application of a resin at a temperature greater than T_g does not automatically induce seal failure.

11.3 Subtask 8.2 - Seal Durability, Operations, Supply

11.3.1 Lab- and Large-Scale Seal Durability

Results of cyclic stress durability tests, both lab- and large-scale suggest superior barrier durability of resin seals exposed to stresses of well operation. Some cement compositions performed equally to resins while some resins failed, but in general, resins produced more durable barriers.

11.3.2 Operations

Laboratory experience, large-scale mixing, and Industry Advisory Group reports confirm that resin application operations are generally in line with those of Portland cement. Special consideration is required for HSE, spill prevention, exothermicity control, and clean up.

11.3.3 Supply

Discussions with chemical vendors during the course of locating and designing the resins for this project revealed that materials used for the resins are widely available. No limitations of supply or availability were mentioned. No issues with establishing a commercial supply of a resin system were uncovered.

11.4 Subtask 8.3 - Full Performance Comparison

Broadly comparing resin's potential as a well sealant to performance of Portland cement leads to the conclusion that resin can be routinely used to create more durable barriers thereby reducing risk of hydrocarbon leakage or blow out. Price of resins as compared herein is significantly higher than that of cement. Potential exists to develop lower-costs methods employing resins strategically to improve seal durability with small resin volumes thereby reducing price.

12.0 TASK 9.0 - COST-BENEFIT ANALYSIS

12.1 Objective

The objective of this task is to compare the cost of each resin system versus Portland cement as a well sealant over the range of applications and conditions. Then relative costs are compared to relative performance benefits of barriers created with each sealant as determined from previous tasks of this investigation. A general quantitative assessment of potential values or risk reduction derived from a potentially more durable flow barrier achievable using a resin sealant is presented.

APPROACH: Using the findings in Tasks 7 and 8, a cost-benefit analysis of resin versus Portland cement was conducted. This analysis considers safety, longevity and durability of seal versus relative cost of application for resin and Portland cement. It was assumed for this exercise that costs associated with mixing and placement of resin or Portland cement for a sealing operation would be similar. This assumption is supported by the operational guidelines development presented in Section 10. Similar mixing equipment, pumps, and personnel would command similar price. Thus, comparison of material price of resin material or Portland cement for seal formation is the most meaningful metric for cost analysis.

Establishing comparable costs for resin classes compared with Portland cement was not straightforward. Portland cement for well sealant applications is a well-established industry with deep technical understanding, robust product line, mature supply chain and operational protocols. This established system delivers large quantities of product to diverse, far-flung location around the world, supports customized engineering design of formulations, furnishes mixing and placement equipment, and provides personnel to conduct mixing and placement operations.

Analysis of comparative cost of resin chemical categories versus cost of Portland cement reveals that cost of resins applicable for well sealants is about 15 to 50 times that of Portland cement on a per cubic foot basis. This analysis, start with manufacturer's prices for resin and estimates appropriate markups applied along the supply chain to deliver a cubic foot of retail-priced resin sealant. These values were compared with average delivered cement cost per cubic foot as suggested from informed members of the Industry Advisory Group. Results are for material cost only. Evaluation of other cost/price comparison aspects such as transportation, blending, mixing, curing times, etc., were determined to be equivalent for resin or Portland cement.

It is concluded by the investigators conducting this work that extra cost of resin sealant is warranted in critical applications with high risk of harm to the environment from a failed barrier and no easy access to the well for containment, control, or repair. Such applications include seals for abandonment barriers in

OCS wells. This conclusion corresponds to the consensus opinion of the Industry Advisory Group in light of improved expected seal durability and associated reduction of HSE risk.

Resin sealants do not have this established history in the oilfield. Common price/cost information for the resins in this investigation consisted of chemical manufacturer's cost per unit of each resin component needed to formulate each class of resin identified for testing. From general material cost/price information for Portland cement, cost multipliers were estimated for accounting markup of chemical supply distributors to package, warehouse, and distribute the components to operations bases. Next, average cement material cost estimates were supplied by members of the Industry Advisory Group. From these data, a ratio of delivered price of a sealant to manufacturer cost was applied to manufacturer's cost data for each resin type.

12.1.1 Subtask 9.1 – Material Cost of Resin versus Portland Cement

Historical knowledge of investigators provided a basis for average cement cost per sack of cement and associated additives the service companies delivered to an operations base. This general number, determined to be \$17.50/sack, represented an average sack of cement. It is acknowledged that cement composition prices can be significantly higher than this mean if expensive, high-performance additives are required. However, for purposes of this comparison, average cost is most applicable since relative percentage of cementing operations employing expensive compositions is small. Additionally, most abandonment cement designs are relatively simple and cheap.

Assuming a yield of 1.18 ft^3/sack of cement results in an estimated fully-loaded cost of Portland cement to the service companies of \$83.20/bbl cement slurry. As noted in Table 24 below, estimated average price of a barrel of cement (per the Industry Advisory Group) is \$200.00. This establishes a markup multiplier of 2.4. Assuming that this markup would translate to commercialization of resin sealants, this factor relating material cost to retail price was applied to resin costs to calculate relative cost of each resin class compared to Portland cement. However, the resin cost data for resins used in this study were those provided by manufacturers for bulk quantities of materials. These costs do not include normal costs incurred in shipping, packaging, and warehousing materials. This additional cost was estimated to be 40% of manufacturer's price. Costs to produce a barrel of each resin formulation designed for this investigation including all resins, curatives, other additives, and fillers were calculated from the manufacturer's price data, and the markups were applied to calculate estimated commercial prices for each resin type. The estimated prices for epoxy and polyester resins were confirmed by members of the Industry Advisory Group to be in range of prices quoted to them for commercial resins of the same type. This further confirmed the validity of this price estimation method.

It should be noted that no effort was devoted to optimize designs with respect to cost. It is assumed that cost of resins can vary as much as those of Portland cement based on design, application, and additives. However, price estimates for these basic, functional compositions should provide a comparative basis for assessing relative value of resin sealants compared to Portland cement. These estimates, presented in Table 24, illustrate that resins are significantly more costly than Portland cement on a comparative volume basis: between 15 and 50 times.

Table 24: Cost Estimates for Resins and Cement

System	Estimated Price per BBL
Furan Resin	$2,500.00
Phenolic 2 Resin	$2,400.00
Polyester Resin	$2,000.00 – $5600.00
Epoxy Resin	$6,900.00
Phenolic 1 /Epoxy Combo	$9,200.00
Cement	$200.00

12.1.2 Subtask 9.2 – Cost Comparison of Resin versus Cement including Operational Costs, and Cost of Remediation

Two cost comparisons will be made between cement and resin in the following scenarios:

- Remediation after primary cement jobs in both Deepwater and Shelf
- Plug and Abandonment for lower and upper zones in both Deepwater and Shelf

Remediation after Failed Primary Job – Deepwater and Shelf

The high cost of resin prevents the practical use of resin as a sealant while drilling a well as compared to cement. The cost benefit analysis thus focused on the use of resin as a remediation after a failed primary cement job when drilling a well. For applications of resins in remedial efforts after a failed primary job the assumptions made for comparison are the following:

- Deepwater and Shelf conditions are compared.
- Deepwater rig rate is $500,000 per day.
- Shelf rig rate is $50,000 per day.
- One out of eight strings drilled in a well require remediation. This is based on information for offshore operations from discussion with industry experts and past experience.
- Nine out of ten remediations are successful for resin. This is based on potential of various resin applications and its improved sealing abilities.
- Based on Table 24 the average cost of resin is assumed to be $4800/bbl and the cost of cement is $200/bbl.
- Resin volume used is 50% less than cement. This is evidenced by the superior properties in tensile strength, bond strength, penetration ability, and sealing abilities of resin.
- One out of two remediations are successful for cement. This is based on an average for offshore operations.

The cost benefit analysis of cement and resin in Deepwater for remedial cement jobs after failed primary cement job is listed in Table 25.

Table 25: Cost Benefit Analysis of Cement and Resin in Deepwater for Remediation of Failed Primary Cement Jobs

	Material Volume	Material Cost	Days of Oper-ation	Rig Cost per day	Total Rig Cost + Material Cost	% Failure Cost	Total Cost
Deepwater Cement	75 bbl	$15,000	3	$500,000	$1,515,000	$757,500	$2,272,500
Deepwater Resin	37.5 bbl	$180,000	3	$500,000	$1,680,000	$18,000	$1,698,000

Further cost benefit analysis can be applied to the life of the well taking into account rig time and operational costs. Assumptions are made for both Deepwater and Shelf for primary remediation cases. During the drilling of this primary well, a remedial job to repair a leaking shoe or repair of flow behind pipe is required. If the remedial job using cement is assumed to be 75 bbl, the cement job will cost $15,000. The remedial job for the resin can potentially use less volume due to its superior bond performance; therefore at 37.5 bbl the cost will be $180,000. For Deepwater the rig time plus material cost are significant at $1,500,000 + $15,000 totaling $1,515,000 for cement. The cost of providing an additional cement job due to a 50% failure rate is $757,500. For Deepwater the rig time plus material cost are significant at $1,500,000 + $180,000 totaling $1,680,000 for resin. The cost of providing an additional cement job due to a 10% failure rate is $18,000. Total cement cost to repair is $2,272,500 and total resin cost to repair is $1,698,000. That is a savings of $574,500 in Deepwater to use resin instead of cement which is a 25.3% savings.

The cost benefit analysis of cement and resin in the Shelf for remediation after failed primary cement jobs is listed in Table 26.

Table 26: Cost Benefit Analysis of Cement and Resin on the Shelf for Remediation of Failed Primary Cement Jobs

	Material Volume	Material Cost	Days of Operation	Rig Cost per day	Total Rig Cost + Job Cost	% Failure Cost	Total Cost
Shelf Cement	75 bbl	$15,000	1.5	$50,000	$90,000	$45,000	$135,000
Shelf Resin	37.5 bbl	$180,000	1.5	$50,000	$255,000	$25,500	$280,500

For the specific case for the Shelf the cement volume needed is 75 bbl whereas the resin can be used at half at 37.5bbl due to its superior performance characteristics. Cost for the cement job is $15,000, cost for the resin job is $180,000. The rig time plus material cost are $75,000 + $15,000 totaling $90,000 for cement. The cost of providing an additional cement job due to a 50% failure rate is $45,000. The rig time plus material cost are $75,000 + $180,000 totaling $255,000 for resin. The cost of providing an additional resin job due to a 10% failure rate is $25,500. Total cement cost is $135,000 and total resin cost is $280,500. In this case the resin is more expensive than the cement since the rig cost on the Shelf are much lower daily rates of $50,000. The cement can provide a cost savings of 48.2% over resin.

Plug and Abandonment for Deepwater and Shelf for Lower and Upper Zones

The cost benefit analysis focused on the plug and abandonment for upper and lower zones in both Deepwater and Shelf applications for both resin and cement. For the use of resins in plug and abandonment there are applications for lower abandonment. The assumptions made for comparison are the following:

- Deepwater and Shelf conditions are compared.
- Deepwater rig rate is $500,000 per day.
- Deepwater Multipurpose Service Vessel rate is $400,000 per day.
- Shelf rig rate is $50,000 per day.
- Cement requires the use of a rig whereas resin can be placed with a lower cost options. Resin can be pumped directly down the production string into the abandonment zone, whereas cement requires to be circulated into place with coil tubing.

Cost benefit analysis for cement and resin for Deepwater in plug and abandonment of a lower zone is listed in Table 27.

Table 27: Cost Benefit Analysis for Cement and Resin for Deepwater in Plug and Abandonment of a Lower Zone

	Material Vol.	Material Cost	Days	Day Rate	Total Cost	Well Cost Savings
Deepwater Cement	40 bbl	$8,000	4	$500,000 (rig)	$2,008,000	-
Deepwater Resin	20 bbl	$96,000	2	$400,000 (MPSV)	$896,000	$1,112,000

If the P&A job is 75 bbl, the cement job will cost $8,000. The P&A job for the resin can use less volume due to its superior bond performance; therefore at 20 bbl the cost will be $96,000. For Deepwater the rig time plus material cost are $2,000,000 + $8,000 totaling $2,008,000 for cement. For Deepwater the MPSV time plus material cost are $800,000 + $96,000 totaling $896,000 for resin. That amounts to a savings of $1,112,000 for resin compared to cement which is a savings of 55.4%.

Cost benefit analysis for cement and resin for Shelf in plug and abandonment of a lower zone is listed in Table 28.

Table 28: Cost Benefit Analysis for Cement and Resin for Shelf in Plug and Abandonment of a Lower Zone

Rig	Material Vol.	Material Cost	Days	Day Rate	Total Cost	Well Cost Savings
Shelf Cement	40 bbl	$8,000	4	$50,000 (rig)	$208,000	-
Shelf Resin	20 bbl	$96,000	2	$0	$96,000	$112,000

If the P&A job is 40 bbl, the cement job will cost $8,000. The P&A job for the resin can use less volume due to its superior bond performance; therefore at 20 bbl the cost will be $96,000. The rig time plus material cost are $200,000 + $8,000 totaling $208,000 for cement. The cost for the resin is material cost only at $96,000 since when doing a resin job on the Shelf the job can be performed from the production platform and does not require an additional vessel. Total cement cost is $208,000 and total resin cost is $96,000. That amounts to savings of $112,000 for resin compared to cement which is a savings of 53.8%.

For the use of resins in plug and abandonment there are applications for upper abandonment. The assumptions made for comparison are the following:

- Deepwater and Shelf conditions are compared.
- Deepwater rig rate is $500,000 per day.
- Shelf rig rate is $50,000 per day.
- Based on Table 24 the average cost of resin is $4800/bbl and the cost of cement is $200/bbl.
- Resin volume used is 50% less than cement. This is evidenced by the superior properties in tensile strength, bond strength, penetration ability, and sealing abilities of resin.

Cost benefit analysis for cement and resin for Deepwater in plug and abandonment of an upper zone is listed in Table 29.

Table 29: Cost Benefit Analysis for Cement and Resin for Deepwater in Plug and Abandonment of an Upper Zone

Rig	Material Volume	Material Cost	Days	Rig Cost per day	Total Cost	Well Cost Savings
Deepwater Cement	32 bbl	$6,400	3	$500,000	$1,506,400	-
Deepwater Resin	16 bbl	$76,800	1	$500,000	$576,800	$929,600

Material volume is based on a 150 ft. plug in 16 in. casing for Deepwater. The material volume is based on 150 ft. plug in 13 3/8 in. casing for the Shelf. For the upper abandonment zone a cut-and-pull casing method is necessary for the cement job to take place which is a high cost operation. For a resin job there would be no need to perform a cut-and-pull. It would be replaced with a lower cost perforate-and-squeeze and section mill operation to provide the necessary barrier. If the P&A job is 32 bbl, the cement job will cost $6,400. The P&A job for the resin can use less volume due to its superior bond performance; therefore at 16 bbl the cost will be $76,800. For Deepwater the rig time plus material cost are $1,500,000 + $6,400 totaling $1,506,400 for cement. For Deepwater the rig time plus material cost are $500,000 + $76,800 totaling $576,800 for resin. Total cement cost is $1,506,400 and total resin cost is $576,800. That amounts to a savings of $929,600 for resin compared to cement which is a savings of 61.7%.

Cost benefit analysis for cement and resin for the Shelf in plug and abandonment of an upper zone is listed in Table 30.

Table 30: Cost Benefit Analysis for Cement and Resin for the Shelf in Plug and Abandonment of an Upper Zone

Rig	Material Volume	Material Cost	Days	Rig Cost per day	Total Cost	Well Cost Savings
Shelf Cement	23 bbl	$4,600	3	$50,000	$154,600	-
Shelf Resin	12 bbl	$57,600	1	$50,000	$107,600	$47,000

Material volume is based on a 150 ft. plug in 16 in. casing for Deepwater. The material volume is based on 150 ft. plug in 13 3/8 in. casing for the Shelf. For the upper abandonment zone a cut-and-pull casing method is necessary for the cement job to take place which is a high cost operation due to the extended time needed. For a resin job there would be no need to perform a cut-and-pull. It would be replaced with a lower cost perforate-and-squeeze and section mill operation to provide the necessary barrier. If the P&A job is 23 bbl, the cement job will cost $4,600. The P&A job for the resin can use less volume due to its superior bond performance; therefore at 12 bbl the cost will be $57,600. For the specific case for the Shelf in the upper abandonment the rig time plus material cost are $150,000 + $4,600 totaling $154,600 for cement. For the specific case for the Shelf in the upper abandonment the rig time plus material cost are $50,000 + $57,600 totaling $107,600 for resin. Total cement cost is $154,600 and total resin cost is $107,600. That amounts to savings of $47,000 for resin compared to cement which is a savings of 30.4%.

12.1.3 Subtask 9.2 – Barrier Performance versus Sealant Cost for the Life of the Seal

The performance data presented in Sections 8 and 9 indicate that properly-formulated resins are better well sealants. Properly-formulated resin sealants can produce durable barriers with better mechanical properties and chemical resistance. The data indicate that improved performance and cohesiveness of resins would support use of lower sealant volumes to create these more durable barriers. However, price differentials discussed above for the materials are sufficiently large to eliminate hope that resins could improve barrier performance and reduce risk of failure at the same cost as current sealants. Estimated volume reductions to achieve similar seal integrity with resin as is currently produced with Portland cement range from 50% to 25% of cement volume.

The potential for achieving price reductions of this magnitude is very small. The basic costs of components to make resin sealants are just so much more than the cost of Portland cement. However, some incremental cost reductions driven by economy of scale could be anticipated if resin sealants become widely used. One possible hybrid system not evaluated during this investigation has potential to reduce cost of barriers compared to resin. The cohesiveness of resins supports placement of small quantities of resin into a less-expensive Portland cement column during placement. Once in place, the resin sealant would seal/bond in the well to provide durable seal backed up and supported by Portland cement. Contamination tests indicated that resin fluids do not adversely affect cement performance.

In summary, potential performance benefits resulting from use of resin as a well sealant warrants its application to reduce risk of barrier failure even at significantly increased cost.

13.0 TASK 10.0 - REGULATORY ANALYSIS OF RESIN AS WELL SEALANT

13.1 Objective

The objectives of this task were to first identify any existing resin regulations presently in place for well applications. Then, determination of information and necessary steps to create meaningful regulations for OCS well resin applications would identify gaps in current resin knowledge. Finally a plan for closing those gaps and establishing regulation comparable to those currently in place for Portland cement is outlined.

Approach: The gap analysis of zonal isolation regulations was perused to identify industry standards for barriers, the requirements and regulations in the OCS, domestic onshore, international onshore and international offshore areas. This analysis compared and contrasted the regulations identified with current BSEE zonal isolation requirements and provide recommendations for improvement in well safety.

13.1.1 Subtask 10.1 – Analyze the current BSEE cementing regulations

13.1.2 Subtask 10.2 – Determine existing industry standards for well sealants

13.1.3 Subtask 10.3 – Analyze regulations from domestic onshore regulatory bodies such as the TRR, PA DEP and others

13.1.4 Subtask 10.4 – Analyze internationally recognized regulations for both onshore and offshore

13.1.5 Subtask 10.5 – Using the regulatory information gathered, develop recommendations for improvement with regards to zonal isolation requirements

13.2 Subtask 10.1-10.4 - Current Regulations, Standards, Best Practices, and Guidelines

The initial gap analysis was to review and find cement and/or resin regulations, guidelines, best practices, and standards for general well sealants both domestic and international. A summary of publications is presented in Table 31. The table identified the well cementing findings that the gap analysis was derived around. The table identified that globally there are more Standards and Guidelines internationally for resin but no Regulations. Domestically we identified there are multiple Regulations, state depended, for cement barrier isolation; however there are none for resin. A Resin Regulation would create a rule or directive, made and maintained by BSEE, to ensure proper resins (what type and application) were used to for isolation. Cement regulations could be utilized in the drafting of for Resin. A Resin Standard would not be beneficial or acceptable for all applications to create a normal or average practice, since resin can be utilized in multiple well applications.

Table 31: Regulations, Standards, Best Practices, Guidelines

Document	Type of Document	Summary
Guidelines on Qualification of Materials for the Abandonment of Wells (Oil & Gas UK) Issue 2 2015.	Guideline	This guideline includes a section on thermosetting polymers which covers all resin types. Testing requirements are listed for qualifying the thermosetting polymers. The guideline also provides testing requirements for other sealants such as cements, grouts, thermoplastic polymers, Elastomeric polymers, formation, gels, metals, and modified in-situ materials.
NORSOK Standard M-710	Standard	This standard includes sections on elastomers and thermoplastic materials which includes all resin types. Testing requirements are listed for qualifying the resins.
Well Abandonments RP-65-3 (API SC-10)	Recommended Practice	An API subcommittee is currently writing a recommended practice for well abandonments. The document will cover all sealants including resins and will provide qualification and verification of sealants for well abandonment. The document is not published with about 50% completion as of January 2018.

Cement Plug Testing: Weight vs Pressure Testing to Assess Viability of a Wellbore Seal between Zones	BSEE TAP-680AA report	Bond and seal effectiveness determined by current plug evaluation methods (pressure testing and weight testing) were evaluated in light of potential leak pathways and failure mechanisms. Conclusions were given on the effectiveness of these testing methods.
Texas Administrative Code Title 16 Chapter 3 Rule 3.13-14	Regulation	The regulations outlines the length, volume, depth, and cement type needed for primary and abandonment operations. For some application the regulation list the minimal cement performance requirements and for other just the recommended cement type.
BSEE Title 30 Chapter II Subchapter B Part 250 Subpart D and Q	Regulation	The requirements for both primary and abandonment cementing are clearly identified in table format. For primary jobs they are separated into casing type with a cement length requirement for each type. For abandonment applications they have different requirements for plug placement and length based on well geometry.
Louisiana Administrative Code Title 43 Part XIX Subpart 1 Order 29-B Chapter 1 and 3	Regulation	This regulation outlines the length and volume needed depending on the primary cementing application and exposed formations. For abandonment the critical zones were defined and the cement lengths needed to isolate those zones.

Regulations for any type of resin are nonexistent as compared to the regulations for Portland cement. The following Table 32 through Table 35 are selections from the BSEE Title 30 Chapter II Subchapter B Part 250 Subpart D and Q as they specifically pertain to cement as the barrier. These regulations are considered the most complete as compared to other onshore and offshore regulations adopted by other regulation entities. In most cases, the regulations issued by BSEE are either adopted by others or left to the operators to manage themselves.

Table 32: Gap Analysis of Regulation Title 30 Chapter II Subchapter B Part 250 Subpart D 250.415

Regulation Title 30 → Chapter II → Subchapter B → Part 250 → Subpart D → §250.415	Gap	Specific Gap for Resin Coverage
(c) Type and amount of cement (in cubic feet) planned for each casing string	Significant	Not Defined for Resin
(d) In areas containing permafrost, setting depths for conductor and surface casing based on the anticipated depth of the permafrost. Your program must provide protection from thaw subsidence and freezeback effect, proper anchorage, and well control	Significant	Not Defined for Resin

(e) A statement of how you evaluated the best practices included in API RP 65, Recommended Practice for Cementing Shallow Water Flow Zones in Deep Water Wells (as incorporated by reference in §250.198), if you drill a well in water depths greater than 500 feet and are in either of the following two areas: (1) An "area with an unknown shallow water flow potential" is a zone or geologic formation where neither the presence nor absence of potential for a shallow water flow has been confirmed. (2) An "area known to contain a shallow water flow hazard" is a zone or geologic formation for which drilling has confirmed the presence of shallow water flow; and	Significant	Not Defined for Resin
(f) A written description of how you evaluated the best practices included in API Standard 65—Part 2, Isolating Potential Flow Zones During Well Construction, Second Edition (as incorporated by reference in §250.198). Your written description must identify the mechanical barriers and cementing practices you will use for each casing string (reference API Standard 65—Part 2, Sections 4 and 5).	Significant	Not Defined for Resin

Table 33: Gap Analysis of Regulation Title 30 Chapter II Subchapter B Part 250 Subpart D 250.420

Regulation Title 30 → Chapter II → Subchapter B → Part 250 → Subpart D → §250.420	Gap	Specific Gap for Resin Coverage
You must case and cement all wells. Your casing and cementing programs must meet the applicable requirements of this subpart and of subpart G of this part. (a) *Casing and cementing program requirements.* Your casing and cementing programs must: (1) Properly control formation pressures and fluids; (2) Prevent the direct or indirect release of fluids from any stratum through the wellbore into offshore waters;	Significant	Not Defined for Resin

(3) Prevent communication between separate hydrocarbon-bearing strata; (4) Protect freshwater aquifers from contamination; (5) Support unconsolidated sediments; (6) Provide adequate centralization to ensure proper cementation; and (7)(i) Include a certification signed by a registered professional engineer that the casing and cementing design is appropriate for the purpose for which it is intended under expected wellbore conditions, and is sufficient to satisfy the tests and requirements of this section and §250.423. Submit this certification with your APD (Form BSEE-0123). (ii) You must have the registered professional engineer involved in the casing and cementing design process. (iii) The registered professional engineer must be registered in a state of the United States and have sufficient expertise and experience to perform the certification.		
(b) *Casing requirements.* (3) On all wells that use subsea BOP stacks, you must include two independent barriers, including one mechanical barrier, in each annular flow path (examples of barriers include, but are not limited to, primary cement job and seal assembly). For the final casing string (or liner if it is your final string), you must install one mechanical barrier in addition to cement to prevent flow in the event of a failure in the cement. A dual float valve, by itself, is not considered a mechanical barrier. These barriers cannot be modified prior to or during completion or abandonment operations. The BSEE District Manager may approve alternative options under §250.141. You must submit documentation of this installation to BSEE in the End-of-Operations Report (Form BSEE-0125).	Significant	Not Defined for Resin

(c) *Cementing requirements*. (1) You must design and conduct your cementing jobs so that cement composition, placement techniques, and waiting times ensure that the cement placed behind the bottom 500 feet of casing attains a minimum compressive strength of 500 psi before drilling out the casing or before commencing completion operations. (If a liner is used refer to §250.421(f)).	Significant	Not Defined for Resin

§ 250.421 What are the casing and cementing requirements by type of casing string?
The table in this section identifies specific design, setting, and cementing requirements for casing strings and liners. For the purposes of subpart D, the casing strings in order of normal installation are as follows: drive or structural, conductor, surface, intermediate, and production casings (including liners). The District Manager may approve or prescribe other casing and cementing requirements where appropriate.

Table 34: Gap Analysis of Regulation Title 30 Chapter II Subchapter B Part 250 Subpart D 250.421

Casing type	**Casing requirements**	**Cementing requirements**	**Gap**	**Specific Gap for Resin Coverage**
(a) Drive or Structural	Set by driving, jetting, or drilling to the minimum depth as approved or prescribed by the District Manager	If you drilled a portion of this hole, you must use enough cement to fill the annular space back to the mudline.	Significant	Not Defined for Resin
(b) Conductor	Design casing and select setting depths based on relevant engineering and geologic factors. These factors include the presence or absence of hydrocarbons, potential hazards, and water depths	Use enough cement to fill the calculated annular space back to the mudline. Verify annular fill by observing cement returns. If you cannot observe cement returns, use additional cement to ensure fill-back to the mudline. For drilling on an artificial island or when using a well cellar, you must discuss the cement fill level with the District Manager.	Significant	Not Defined for Resin

	Set casing immediately before drilling into formations known to contain oil or gas. If you encounter oil or gas or unexpected formation pressure before the planned casing point, you must set casing immediately and set it above the encountered zone			
(c) Surface	Design casing and select setting depths based on relevant engineering and geologic factors. These factors include the presence or absence of hydrocarbons, potential hazards, and water depths	Use enough cement to fill the calculated annular space to at least 200 feet inside the conductor casing. When geologic conditions such as near-surface fractures and faulting exist, you must use enough cement to fill the calculated annular space to the mudline.	Significant	Not Defined for Resin
(d) Intermediate	Design casing and select setting depth based on anticipated or encountered geologic characteristics	Use enough cement to cover and isolate all hydrocarbon-bearing zones and isolate abnormal pressure intervals from normal pressure intervals in the well. As a minimum, you must cement the annular space 500 feet above the casing shoe and 500 feet above each zone to be isolated.	Significant	Not Defined for Resin

	or wellbore conditions			
(e) Production	Design casing and select setting depth based on anticipated or encountered geologic characteristics or wellbore conditions	Use enough cement to cover or isolate all hydrocarbon-bearing zones above the shoe. As a minimum, you must cement the annular space at least 500 feet above the casing shoe and 500 feet above the uppermost hydrocarbon-bearing zone.	Significant	Not Defined for Resin
(f) Liners	If you use a liner as surface casing, you must set the top of the liner at least 200 feet above the previous casing/liner shoe If you use a liner as an intermediate string below a surface string or production casing below an intermediate string, you must set the top of the liner at least 100 feet above the previous casing shoe You may not use a liner as conductor casing A subsea well casing string whose top is above the	Same as cementing requirements for specific casing types. For example, a liner used as intermediate casing must be cemented according to the cementing requirements for intermediate casing. If you have a liner lap and are unable to cement 500 feet above the previous shoe, as provided by paragraphs (d) and (e) of this section, you must submit and receive approval from the District Manager on a case-by-case basis.	Significant	Not Defined for Resin

	mudline and that has been cemented back to the mudline will not be considered a liner			

§250.1715 How must I permanently plug a well?

(a) You must permanently plug wells according to the table in this section. The District Manager may require additional well plugs as necessary.

PERMANENT WELL PLUGGING REQUIREMENTS

Table 35: Gap Analysis of Regulation Title 30 Chapter II Subchapter B Part 250 Subpart D 250.1715

if you have . . .	**Then you must use . . .**	**Gap**	**Specific Gap for Resin Coverage**
(1) Zones in open hole,	Cement plug(s) set from at least 100 feet below the bottom to 100 feet above the top of oil, gas, and fresh-water zones to isolate fluids in the strata	Significant	Not Defined for Resin
(2) Open hole below casing,	(i) A cement plug, set by the displacement method, at least 100 feet above and below deepest casing shoe;	Significant	Not Defined for Resin
	(ii) A cement retainer with effective back-pressure control set 50 to 100 feet above the casing shoe, and a cement plug that extends at least 100 feet below the casing shoe and at least 50 feet above the retainer; or	Significant	Not Defined for Resin
	(iii) A bridge plug set 50 feet to 100 feet above the shoe with 50 feet of cement on top of the bridge plug, for expected or known lost circulation conditions	Significant	Not Defined for Resin
(3) A perforated zone that is currently open and not previously squeezed or isolated,	(i) A method to squeeze cement to all perforations; (ii) A cement plug set by the displacement method, at least 100 feet above to 100 feet below the perforated interval, or down to a casing plug, whichever is less; or (iii) If the perforated zones are isolated from the hole below, you may use any of the plugs specified in paragraphs (a)(3)(iii)(A)	Significant	Not Defined for Resin

	through (E) of this section instead of those specified in paragraphs (a)(3)(i) and (a)(3)(ii) of this section.		
	(A) A cement retainer with effective back-pressure control set 50 to 100 feet above the top of the perforated interval, and a cement plug that extends at least 100 feet below the bottom of the perforated interval with at least 50 feet of cement above the retainer;	Significant	Not Defined for Resin
	(B) A casing bridge plug set 50 to 100 feet above the top of the perforated interval and at least 50 feet of cement on top of the bridge plug;	Significant	Not Defined for Resin
	(C) A cement plug at least 200 feet in length, set by the displacement method, with the bottom of the plug no more than 100 feet above the perforated interval;	Significant	Not Defined for Resin
	(D) A through-tubing basket plug set no more than 100 feet above the perforated interval with at least 50 feet of cement on top of the basket plug; or	Significant	Not Defined for Resin
	(E) A tubing plug set no more than 100 feet above the perforated interval topped with a sufficient volume of cement so as to extend at least 100 feet above the uppermost packer in the wellbore and at least 300 feet of cement in the casing annulus immediately above the packer.	Significant	Not Defined for Resin
(4) A casing stub where the stub end is within the casing,	(i) A cement plug set at least 100 feet above and below the stub end;	Significant	Not Defined for Resin
	(ii) A cement retainer or bridge plug set at least 50 to 100 feet above the stub end with at least 50 feet of cement on top of the retainer or bridge plug; or	Significant	Not Defined for Resin
	(iii) A cement plug at least 200 feet long with the bottom of the plug set no more than 100 feet above the stub end.	Significant	Not Defined for Resin
(5) A casing stub where the stub end is below the casing,	A plug as specified in paragraph (a)(1) or (a)(2) of this section, as applicable.	Significant	Not Defined for Resin
(6) An annular space that communicates with open hole and extends to the mud line,	A cement plug at least 200 feet long set in the annular space. For a well completed above the ocean surface, you must pressure test each casing annulus to verify isolation.	Significant	Not Defined for Resin

(7) A subsea well with unsealed annulus,	A cutter to sever the casing, and you must set a stub plug as specified in paragraphs (a)(4) and (a)(5) of this section.	Significant	Not Defined for Resin
(8) A well with casing,	A cement surface plug at least 150 feet long set in the smallest casing that extends to the mud line with the top of the plug no more than 150 feet below the mud line.	Significant	Not Defined for Resin
(9) Fluid left in the hole,	A fluid in the intervals between the plugs that is dense enough to exert a hydrostatic pressure that is greater than the formation pressures in the intervals.	Significant	Not Defined for Resin
(10) Permafrost areas,	(i) A fluid to be left in the hole that has a freezing point below the temperature of the permafrost, and a treatment to inhibit corrosion; and	Significant	Not Defined for Resin
	(ii) Cement plugs designed to set before freezing and have a low heat of hydration.	Significant	Not Defined for Resin
(11) Removed the barriers required in §250.420(b)(3) for the well to be completed	Two independent barriers, one of which must be a mechanical barrier, in the center wellbore as described in §250.420(b)(3) once the well is to be placed in a permanent or temporary abandonment.	Significant	Not Defined for Resin

(b) You must test the first plug below the surface plug and all plugs in lost circulation areas that are in open hole. The plug must pass one of the following tests to verify plug integrity:

(1) A pipe weight of at least 15,000 pounds on the plug; or

(2) A pump pressure of at least 1,000 pounds per square inch. Ensure that the pressure does not drop more than 10 percent in 15 minutes. The District Manager may require you to tests other plug(s).

Table 36 lists the qualification requirements for thermoplastic (resin) material taken from Norsok Standard M-710, Edition 3, September 2014. These are the properties that are used to qualify the use of resin as a barrier.

Table 36: Qualification requirements for thermoplastic (resin) material from Norsok Standard M-710, Edition 3, September 2014.

Property	Test
Density	ASTM D792, ISO 1183-1/-2
Hardness	ISO 868, ASTM D2240, Shore D, ISO 2039
Tensile properties	ISO 527-1/-2
Compression properties	ASTM D695, ISO 604
Impact strength	ISO 179-1

Measurement of glass transition temperature	DSC or MDSC
Ageing characteristics	Annex A
Softening point	ISO 306, ASTM D1525
Resistance to creep under permanent tensile and compression loads	ASTM D2990

The main characteristics of barrier materials should be as follows based on the Guidelines on Qualification of Materials for the Abandonment of Wells (Oil & Gas UK) Issue 2 2015:

- Very low permeability – to prevent flow of fluids through the bulk material.
- Provide an interface seal – to prevent flow of fluids around the barrier; the material provides a seal along the interface with adjacent materials such as steel pipe or rock; risks of shrinkage and de-bonding are to be considered.
- The barrier material must remain at the intended position and depth in the well.
- Long-term integrity – long-lasting isolation characteristics of the material, not deteriorating over time; risks of cracks and de-bonding over time are to be considered.
- Resistance to downhole fluids (e.g. CO2, H2S, hydrocarbons, brine) at foreseeable pressures and temperatures.
- Mechanical properties suitable to accommodate loads at foreseeable temperatures and pressures.

An experimental work plan for evaluating resins is listed in Table 37 below. For each property a "requirement" classification (1 to 3) is provided where:

1 = mandatory;
2 = recommended;
3 = not applicable.

Table 37: Experimental work plan for evaluating resins, provided by Guidelines on Qualification of Materials for the Abandonment of Wells (Oil & Gas UK) Issue 2 2015.

PROPERTY	**REQUIREMENT**	**TEST**	**AGEING REQUIRED?**	**ACCEPTANCE CRITERIA**	
				BEFORE AGEING	**AFTER AGEING**
PERMEATION TESTING					
Nitrogen permeability	3	-	-	-	-
Diffusion coefficient	1	See Section 8.2.2	Yes	See Section 7. Calculated release rate (Appendix 7) <0.03 m^3/year, but no more than 4.8x10^{-8} m^2/s	<50% increase
INTERACTION WITH FLUID					
Dry Mass	1	Measurement of masss after drying to constant mass at 105°C (221°F)	Yes	-	<3% loss in dry mass relative to that before aging*
Absorption	3	-	-	-	-
DIMENSIONAL STABILITY					
Expansion / Swelling					

During hardening	1	See Section 8.4.1	N/A	<1% linear expansion	-
Hardened	1	See Section 8.4.1	Yes	-	<2% linear expansion*
Shrinkage					
During hardening	1	See Section 8.4.2	N/A	<1% linear expansion	-
Hardened	1	See Section 8.4.2	Yes	-	0% linear expansion*
Differential thermal expansion	1	ASTM E228	No	Coefficient of thermal expansion +/- $5K^{-1}x10^{-6}$ of casing	-
Creep	1	ISO 899-1	No	<1% linear strain	-
MECHANICAL TESTING					
Triaxial Testing	3	-	-	-	-
Cohesion	3	-	-	-	-
Poisson's Ratio	3	-	-	-	-
Internal friction angle	3	-	-	-	-
Hydrostatic compressive yield	3	-	-	-	-
UCS	1	API RP 10B-2	Yes	>1.4 MPa (200 psi)	>1.4 MPa (200 psi)
Tensile strength	1	ISO 527-1	Yes	>1 MPa (145 psi)	>1 MPa (145 psi)
Elastic modulus	2	ISO 527-1	Yes	-	-
Hardness	2	See Section 8.4.2	Yes	-	-
OTHER CHARACTERISTICS					
Bond Strength					
Shear bond strength	1	See Section 8.6 Substrate rugosity should be measured using ASTM D7172	Yes	>1 MPa (145 psi)**	>1 MPa (145 psi)**
Tensile bond strength	3	-	-	-	-
Decomposition temperature	1	TGA / DTA / DSC measurement	No	No decomposition below operating temp.	-
Density	1	ISO 1183-1	Yes	-	-
Stress relaxation	3	-	-	-	-

*Priority after-ageing test.

**Minimum shear bond strength limit has been arrived at based on a calculation detailed in Appendix 11.

13.3 Subtask 10.5 - Example Regulation Structure for Resin Sealants for OCS Wells

A stated deliverable from this investigation is a model structure of potential resin sealant regulations. The model structure presented below is based on investigation results for resin performance including bonding, mechanical properties, and chemical durability. The segments of proposed regulation structure guidelines include: definitions, barrier description and intended function, resin chemical and mechanical performance properties, operational considerations (placement techniques, volumes, placement methods, hardware, etc.), and performance assessment. This framework can be applied to either primary or abandonment operations.

Any benefit derived from using resin sealants in OCS wells would come from improved barrier function. However, achievement of risk reduction from barrier improvement without significant cost increase would be an economic driver for industry adoption of resin sealants. Specific resin regulations allowing use of smaller resin volumes or streamlined procedures to create flow barriers would encourage use of resin as a potentially superior well sealant.

Note that the descriptions do not constitute sample regulations. It is assumed that any resin sealant regulations developed for OCS wells would mirror the current regulations in place for application of Portland cement. The decisions of well barrier locations and/or performance criteria are beyond the scope of this investigation, but current Portland cement regulation criteria are the suggested starting point for development. Once those judgements and rulings are done, suitable regulations to ensure the desired outcomes can be formulated within the following framework.

Additionally, the performance variability and functional chemistry differences among resin classes as well as between resins and Portland cement require that specification in reference to resin seal performance be included in any regulation. Performance specifications would be beyond the scope of any resin regulation, but referencing resin performance or design characteristics may be required. Similar examples exist in BSEE regulations for Portland cement. High-shear-bond cement is commonly used to dump-bail resin abandonment plugs. If shear-bond performance data supplied by the manufactured of this blend are referenced in the procedure (lab shear-bond tests results included in the certification document), then plug length reduction from 50 feet to 25 feet is commonly accepted and certified. Similarly, 30 CFR 250.415 (4)(e) regulating Portland cement for OCS well construction, references API RP65 and requires indication that these recommended design practices were considered during design of the cement and procedure.

13.3.1 Definitions

Concise definitions of well configuration, barrier placement location and coverage form the basis for regulation. Current BSEE regulations for well barriers are crafted concisely and in understandable language. They present a good template for clarity. Any expanded regulation criteria (e.g. bond strength, chemical durability, exothermicity magnitude) should be defined precisely with limits and performance criteria clearly specified. As discussed above, these performance criteria may not be actual regulations. Rather, they may be defined by reference to an industry specification or other performance guideline. Examples of this will be discussed further in Section 13.3.3.

Acceptable resin chemical classes require definition as do composite mixtures of resin and other sealants such as Portland cement. As above, these definitions may be drawn in by reference to industry specification or other documentation that may be developed.

13.3.2 Barrier Description and Function

Regulations developed to cover application of resin sealants as OCS well barriers will require clear, concise description regarding location, size, barrier components, spacing, and intended function of each barrier. Results of this investigation indicate that resin chemical and mechanical performance properties superior to those of Portland cement have potential to establish functional flow barriers from smaller sealant volumes. Volume requirements should be based on mechanical performance enhancements exhibited by a specific resin class. As above, this would require specification provided by industry-developed performance guidelines.

13.3.3 Resin Performance (Mechanical, Chemical)

Regulations developed to address resin seals applied using smaller volumes with specific mechanical performance criteria and associated chemical performance should be referenced in the regulation. These performance ranges will vary depending on intended barrier function. Mechanical property values (tensile strength, Young’s modulus, shear bond) vs time can be tied to barrier function and dimensional regulations. Specific performance specification ranges and barrier dimensions are beyond the scope of this project, but specific, meaningful performance ranges with appropriate safety factors can be chosen based on failure calculations, physical and numerical modeling, and field experience. This information describing resin performance is currently under development within the industry. Statement of performance demonstration to support required resin durability would guide the industry as it develops guidelines and specifications.

The exothermic crosslink reaction that is characteristic of resin curing and hardening affects resin performance. Although not specifically investigated during this project, exothermicity occurrence and potential for deleterious effects on bonding and sealing are well documented in the literature. Various chemical and physical formulation adaptations can alter exothermicity. Magnitude of temperature increase is also affected by resin volume, geometry, and ambient temperature. Range of exothermicity over application conditions including resin volume, ambient well temperature, reaction kinetics, and other resin formulation characteristics should be addressed.

Performance metrics for these regulations require definition and specification as well as range of acceptability. While documentation of actual performance testing may not be necessary, some explicit confirmation of the material's design in accordance with these regulated performance attributes should be required. Whether testing is required on a case-by-case basis or general performance confirmation is sufficient, explicit requirements for evaluation and specific procedures should be specified as with the reference citations described above for Portland cement.

13.3.4 Operational

Differences in resin sealant chemistry compared to Portland cement necessitate HSE considerations. Regulations referencing exposure, containment, surface spills or release/return to surface or sea floor should be considered.

Potentially smaller resin sealant volume requirements introduce issues of mixing, placement, and plug stability. Further, resin's hydrophobic nature, cohesiveness, and density warrant consideration of filler solids suspension and stability. The inclusion of API recommended practices review or other industry specifications as they become available should be considered for resin sealant applications. Inclusion of API recommended practices or other industry publication relating to resin sealant design and barrier placement expands the engineering basis and qualification for using the sealant without explicitly regulating that the host of engineering best practices be performed. This would streamline the regulation process while sharply focusing resin design and application.

13.3.5 Performance Assessment

Appropriate performance conformation methods should be specified in the regulations. Possible methods are similar to those specified in current BSEE regulations. Pressure isolation and tag weight support are most direct methods. Bond logs are not directly applicable to resins due to material structure differences compared to Portland cement (crosslinked polymer chains compared to crystalline lattice). Acoustic or ultrasonic methods may not indicate location of resin and barrier extrapolations.

13.4 Resin Sealant Qualification Process

Current regulations for Portland cement performance in OCS wells grew over time through a number of iterations (see 30 C.F.R. § 250.415(4) (e), 30 C.F.R. § 250.198(64), 30 C.F.R. § 250.1712, 30 C.F.R. § 250.1715, and 30 C.F.R. § 250.1716). Furthermore, a long history of barrier seals formed using Portland cement existed within the well industry provided performance basis for regulation development. Experience level for resin as a well sealant is very low compared to use of Portland cement. Thus, it is important to develop resin barrier performance database and regulation criteria simultaneously in order to form the basis of regulations.

The current state of regulations for resin well sealants on OCS appears to be hindered by contradictory conditions. Technical evidence generally supports using resin sealant to reduce risk of hazards caused by a well barrier breach. However, assurance of resin sealant performance and establishment of application protocols requires substantial demonstration of actual resin performance. Regulations stating resin sealant barrier number, locations, and dimensions cannot be imposed without basis.

One approach to interrupting this cyclic challenge involves BSEE actively encouraging OCS operators to use resin sealants in their wells and monitor sealant effectiveness over time. Active documentation and review of engineering, design application, and seal durability would accelerate demonstration database gathering and analysis. An ongoing collaboration between operators using resin sealants and BSEE to evaluate resin effectiveness would speed up application use, accelerate performance assessment, and guide BSEE toward regulation limits and controls faster than amassing performance information traditionally. This approach would also manage risk of HSE damage due to sealant failure.

This BSEE-driven simultaneous establishment of barrier performance and regulations must be iterative with participation from BSEE, industry groups, operators, service companies, resin manufacturers and academia. One possible approach to this task would start with assessment of all resin applications in OCS wells. Even though, resin is not recognized as a viable sealant in the current BSEE regulations, a significant number of resin applications have been performed in OCS wells after exceptions were granted on a case-by-case basis (estimated from Industry Advisory Group and CSI experience to be over 1000 in the past 15 years). Analysis of the results from all these resin sealant applications has not been performed. Gathering and analyzing the case histories should provide insight regarding resins utility as a barrier and identify potential issues associated with resin use.

Those results coupled with results of this investigation would provide foundation supporting initial performance ranges and boundaries. This information crafted into initial regulation structure and implemented provisionally would serve as alpha test of regulation function. Tracking results of this process would provide additional input for adjustment of parameters to produce more meaningful regulations. Finally repeat of this cyclic process one or two more times with active participation of all vested parties would fast track regulation development, verification and acceptance. With estimated sealant volumes reduced to 25% of Portland cement, resins are still significantly more expensive.

Steps of this process are depicted in a flow chart below Figure 143.

Alpha testing would require collaboration between BSEE, industry groups, operators, service companies, resin manufacturers, and academia. Operators would have to provide well that are planned for temporary abandonment with the permanent abandonment planned at a later date. Resins would be used for the temporary abandonment and the seal integrity could be confirmed before completing the permanent abandonment

Figure 143: Flow Chart for Resin Regulation Development

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APPENDIX A FUNDAMENTAL CHEMICAL EVALUATION OF RESINS

Fundamental Chemical Evaluation of Resin Stability as Sealants in OCS Wells

Project No:	E17PC00004
Date:	July 31, 2018
Version:	1.0

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1 INTRODUCTION

In order to vet candidate resins for sealing of oil wells, it is vital to determine how their physical and chemical properties are affected by oilfield conditions. An evaluation of the fundamental chemistry of resin stability and durability under conditions imposed on OCS well sealants is presented to help address the gap in understanding with regard to resin performance. The chemical and physical interactions of various resin components are discussed here along with specialized testing techniques that will be used to comparatively analyze performance and stability limits of different resin classes.

2 CHEMISTRY OF RESIN DEGRADATION MECHANISMS IN OCS WELL ENVIRONMENT

Resins are similar to Portland cement, in that they can be prepared as a liquid for placement, and once placed they harden to form a monolithic solid. The important difference is that resin hardening involves cross-linking and polymerization reactions that lead to three-dimensional covalent bonding that extends throughout the resulting monolith. As a result, the resin seal is both highly durable and non-porous and more suited to withstanding cyclic stresses encountered in a wellbore than Portland cement. Thermoset plastic resins have rigid three-dimensional structures high molecular weight, and normally decompose before melting at moderately high temperatures. Depending on their composition, degree of cross-linking and temperature, the resins can be elastomers that are soft and springy or rubbery and can be deformed and revert to their original shape on loading release or they can be glassy and undergo permanent or plastic deformation under load. Each type of thermosetting plastic has a unique set of properties. Epoxies, for example, exhibit elasticity and exceptional chemical resistance, and are relatively easy to cure. On the other hand, phenolics, while fairly simple to mold, are brittle, strong, and hard.

The higher the crosslink density and aromatic content of a thermoset polymer, the higher the resistance to heat degradation and chemical attack. Mechanical strength and hardness also improve with crosslink density, although at the expense of brittleness. Due to their wide range of tunable physical and chemical characteristics, thermosetting plastics have remarkable utility for sealing wells in a wide variety of oilfield conditions. In these applications, the thermoset resins must meet the challenges posed by thermal decomposition, attack by corrosive chemicals and mechanical stresses while providing a gas-tight seal. Thus, it is important to understand and screen the mechanical and chemical properties of potential resins for sealing of wells.

As can be seen from Table 1, the decomposition temperature of representative polymers is strongly dependent on the composition and structure of the polymers. There are actually several different types of chemical mechanisms by which polymers thermally decompose:
(1) Random-chain scission, in which chain scissions occur at random locations in the polymer chain.
(2) End-chain scission, in which individual monomer units are successively removed at the chain end.
(3) Chain-stripping in which atoms or groups that are not part of the polymer backbone are cleaved of the polymer chain.
(4) Cross-linking by which bonds are formed between polymer chains.
(5) Further curing of the polymer due to unreacted functional groups being able to interact with each other as polymer chains become more mobile at elevated temperature.

Thermal decomposition of a polymer typically involves more than one of these types of reactions. More importantly, the type of mechanism can have a profound impact on the physical properties of the degraded resin. For example cross-linking could improve physical strength while chain scission would rapidly degrade it by decreasing the molecular weight. Furthermore, resins that might be used in oilfield applications tend to not be homopolymers (i.e. are composed of more than one component) and are also cross-linked. This makes their thermal properties less predictable. Even within a class of polymers, such as epoxy resins, the components can be quite diverse and judicious selection of the reactants from which the polymers are prepared can be used to create highly thermally stable polymers. In current OCS applications, the maximum temperature to which cured resins might be exposed is under 150˚C, well below temperatures at which most polymer decomposition reactions occur unless the polymer has pendant reactive side groups that condense with each other as is the case of poly(vinylalcohol) listed in Table 1 – the alcohol groups can condense with each other to form water and an ether.

Table 1. Glass Transition and Thermal Decomposition Temperatures of Selected Polymers

Polymer	Glass Transition (˚C)	Thermal Decomposition Temperature (˚C)
Polyethylene	-105	217
Polyacetal	-82	230
Poly(vinylidene fluoride)	-35	355
Polypropylene	-20	258
Poly(vinyl chloride)	-20	140
Nylon-6	47	310
Polybutadiene	58	209
Polyisoprene	66	187
Poly(vinyl alcohol)	85	64
Polystyrene	95	163
ABS	105	167
Polytetrafluoroethylene	115	473
Poly(methyl methacrylate)	158	255

Ultimately, there is also a need to assess the properties of resins *in situ* under well-like conditions. Bosma, Cornelissen, and Schwing have described an apparatus and experimental methods for doing such testing [1]. Notably the equipment and methods are useful for all sealing materials including Portland cement, resins, and elastomer. The reported characterization system can operate at pressures up to 1500 Bar and temperatures up to 300˚C and is capable of monitoring: (a) the progress of the "setting" reaction of Oil

Well Cements and/or thermosetting resins (b) the reaction behavior of these materials from the onset of gelling to their final set and (c) measuring the softening or swelling properties of thermoplastic and thermoset resins with changing temperature of upon the chemical setting of the materials as cross-linking reactions take place. The apparatus is also capable of the determination of volume changes at constant pressure or pressure changes at constant volume during the setting of cement or resin systems. In this manner, volumetric properties such as shrinkage or expansion of cements and resins or their compressibilities can be measured with times ranging from the onset of gelling to beyond the final set of the materials. The volumetric thermal expansion coefficient of set materials can also be quantified. In this paper, the authors also provide clear examples that demonstrate that zonal isolation materials can lose their integrity as a consequence of stresses induced by changes in temperature or pressure within the wells and by external mechanical loading processes. They point out that these stresses are particularly prevalent in Deepwater wells. Further, they discuss how the conventional criterion for choice of a material for zonal isolation, the compressive strength of a sealant, is insufficient to identify which sealant is most suitable for the effective annular sealing of a well. Instead, other mechanical properties such as its Young's modulus, Poisson's ratio, Tensile Strength, Shear Strength and Bonding Strength must also be assessed. The authors indicate that it is necessary to have a ductile zonal material that is kept in a permanent compressed condition during the entire well's operational lifetime. The ratio of the Tensile Strength to Young's modulus should be as high as possible, the Young's modulus of the 'cement' should be lower than the rock and the Poison's ratio of the sealing materials should be as close to 0.5 as practically attainable. The authors point out that traditional cement formulations are not sufficient to meet these requirements in all wells leading to the requirement of novel formulations such as resins, cement rubber composites, and in-situ vulcanizing rubbers and foams

It was previously suggested that the glass transition temperature, T_g, was an important parameter for judging the thermal stability of resins for oilfield use. However, Haliburton researchers found no correlation between T_g and the decomposition of three similar epoxy resins [2]. This is a more general phenomenon as shown in Figure 1 where the decomposition temperatures of a wide range of polymers are plotted versus their glass transition temperatures. The numerical data are provided in Table 1 and are sorted by increasing T_g. There is no obvious correlation between the two parameters. A linear fit of the data returned a slope close to zero and an R^2 of only 0.002.

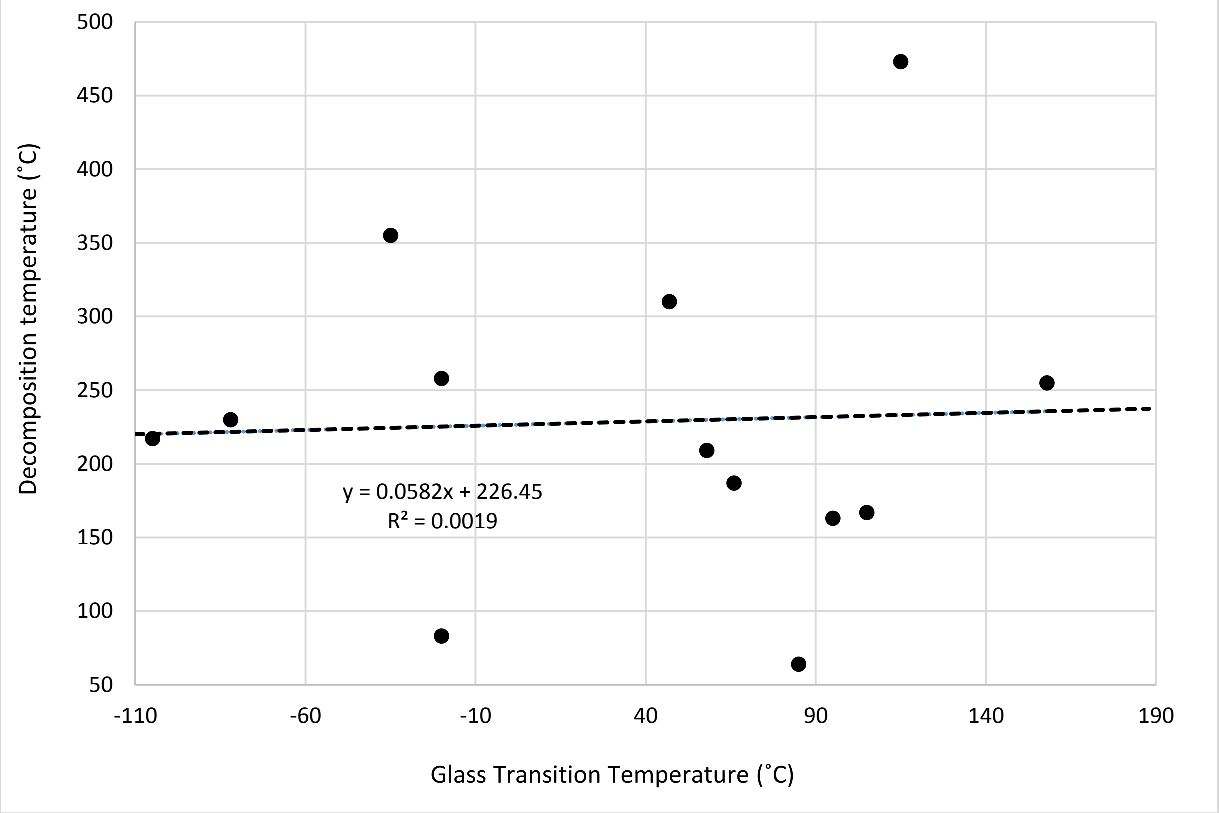

Figure 1. Correlation (or lack thereof) of Glass Transition Temperature versus Decomposition Temperature

It was conjectured that upon going through the glass transition, the polymer is more open and the expanded space leads to faster thermal decomposition. If this is the case, it would suggest that thermal decomposition would be slower at elevated pressure, but this is opposite to what is observed [2]. Instead, thermal decomposition was found to be faster under pressure. To one experienced in kinetics and reaction mechanisms, this finding would suggest that the reaction occurs by an associative process - possibly by two polymer chains approaching and interacting with each other or adjacent parts of a chain reacting with each other. Knowing which of these occurs is important since the first mechanism leads to cross-linking while the second might lead to chain scission. Thus, the changes in the physical properties of the resin will be completely different in each case. Furthermore, the thermal decomposition will depend on the type and composition of the polymer-this is discussed further below.

The glass transition temperature cannot be ignored since it is the temperature where a polymer changes from a hard, rigid or “glassy” state to a more pliable, compliant or “rubbery” state. In actuality the glass transition is not a discrete thermodynamic transition, but a temperature range over which there is a significant increase in the mobility of the polymer chains. Therefore, the physical properties of the resin are highly dependent on whether the polymer is above or below the glass transition temperature. If flexibility and sealing properties of an elastomer are necessary for an application, such as the pressure loaded elastomers described by Shell researchers for oil well sealing, the material needs to be above the glass transition [1]. Below the glass transition the materials will be glassy and more applicable to high strength applications. The glass transition should not be confused with the melting temperature of the polymer that generally occurs at much higher temperature and results in a viscous molten polymer (Figure

2). Cross-linked resins typically will not re-flow in the region between the glass transition temperature and the melting temperature. A force produced by covalent bonds within the cured resin structure will cause the more compliant resin back to its original shape when cooled back below the glass transition or when stress is released. In many cases it is advantageous to use a resin above its glass transition as the added flexibility makes the material more shock and vibration resistant. The sealing ability of a resin is much better in the rubbery state - if the temperature is dropped below the glass transition, it becomes brittle and rigid. This transition caused the Challenger disaster in 1986 because the ambient temperature prevented O-rings in the solid rocket boosters from sealing properly.

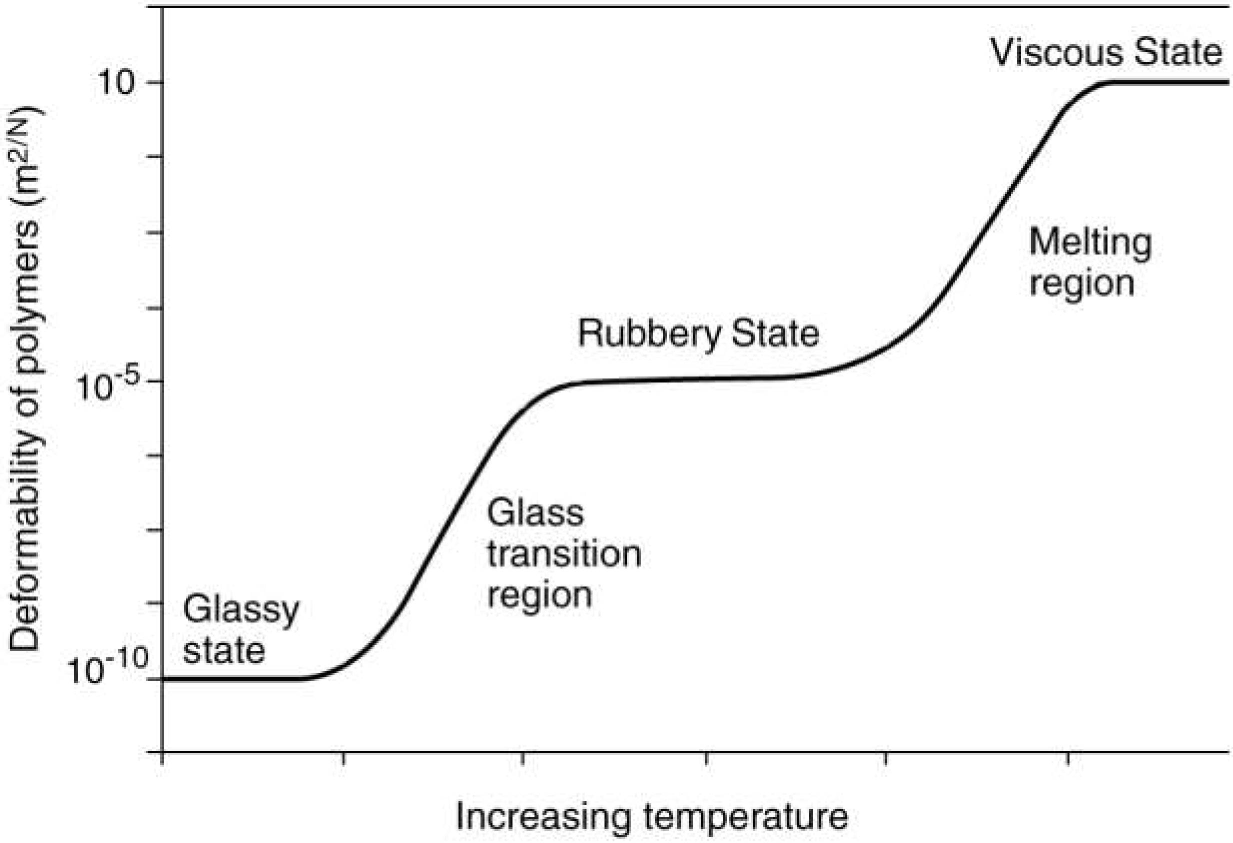

Figure 2. Temperature Response of a Polymer

The testing of three commercial epoxy adhesives used in the petroleum industry as pipeline integrity repair both onshore and offshore revealed that they were stable up to at least 220˚C [3]. One resin, Multimetall Steelceramic, was reported to have an operating range as high as 280˚C. None of the resins showed any decomposition during thermal gravimetric analysis in the temperature range that they would be exposed to in oil wells. These particular resins were based on the diglycidyl ether of bisphenol A but each utilized different amine hardeners. They had decidedly different glass transition temperatures, operational ranges, and thermal stabilities (Table 2). These results indicate that the judicious choice of resin components can result in a material with ideal sealing properties and thermal stability for oilfield applications. Note also the disconnect between maximum operating temperature as recommended by the manufacturer and the decomposition temperature. With the exception of ARC858, the maximum operating temperature is above the point at which the resin starts to lose weight. This is likely due to further curing of the resin as polymer chains become more mobile. The case of ARC858 indicates that one cannot ignore changes in physical properties (in this case adhesive strength) at elevated temperature

Table 2. Properties of Epoxy Adhesives Based on Bisphenol A with Varying Hardeners

Adhesive	Glass Transition Temperature (˚C)	Maximum Operating Temperature (˚C) [1]	Decomposition Temperature (˚C) [2]
ARC858	70	160	263
Belzona 1111	74	200	161
Multimetall Steelceramic	90	280	220

1. Reference [3]
2. As reported by the resin manufacturers
3. Determined from thermal gravimetric data in reference [3].

Beyond the intrinsic thermal behavior of the resins, the influence of extrinsic reactants that will be in contact with the resins must also be determined. For oilfield applications, this means that the hydrothermal properties of the resins in the presence of water and brine must be investigated. Resins tend to have fairly good hydrothermal stability. Hydrolysis of epoxy resin is negligible up to 200 °C and only becomes significant between 300 and 400 °C [4]. Phenolic resins are also stable to hydrolysis in water at temperatures in excess of 200˚C [5] and in brine to 300˚C. There is not a lot of information in the literature concerning hydrothermal stability of various resin systems. Again the nature of the functional groups present and the degree of cross-linking will strongly influence hydrothermal stability, making it difficult to predict performance.

3 EVALUATION OF RESIN DEGRADATION

The best method for probing thermal decomposition is thermal gravimetric analysis (TGA) whereby the weight of a material is monitored as temperature is increased. Of course, this assumes that decomposition is accompanied by loss of volatile species. Since some mechanisms might not evolve gases, the TGA is best performed in an instrument that simultaneously performs differential scanning calorimetry (DSC) so that the latter types of reactions might be detected by a heat gain or loss. For oilfield resin candidates, experiments must be performed in an inert atmosphere such as nitrogen so that intrinsic thermal stability is probed and not oxidation reactions. In the field, the materials will be exposed to anoxic environments at elevated temperature so the absence of dioxygen in the testing is important. Notably, the resin specimens to be tested will be cured in laboratory conditions (in fresh water) and under simulated well conditions such as exposure to brine or hydrocarbons. Comparison of same resin cured in water vs brine vs hydrocarbon will yield interesting and useful comparative data. The analysis by TGA will be performed according to ASTM E1131 while DSC analyses will be performed according to ASTM D 3418. This will include nonisothermal experiments where the temperature is ramped at 5˚C/minute from ambient to 250˚C. If decomposition is observed, isothermal TGA experiments will be performed at four temperatures in the weight loss step to initial rates of decomposition at each temperature so that the activation energy can be determined and used to predict worst case lifetime of a resin in the field (i.e. assuming that decomposition occurs at a calculated rate at 200˚C and is not self-limiting – see discussion below). Since

200˚C is greater than the expected maximum temperature to which the resins are currently exposed in the field, isothermal TGA experiments will be performed at this temperature for 24 hours for all candidate materials.

As noted above, the thermal decomposition of polymers can occur by a number of mechanisms and seldom by a single mechanism. Even if only a subset of these reaction types are involved in the thermal decomposition of a resin and the reaction rates are not significantly dependent on the size of the polymer chains and radicals, the kinetics describing the process will be very complex. Typically, in engineering applications, such complex reaction mechanisms are not utilized but instead simple overall kinetic expressions are employed. One of the more common assumption for polymers is that the decomposition reactions can be described by an Arrhenius expression of first order in the remaining polymer mass. Jones *et al*. used this method to study the kinetics of thermal decomposition of epoxy resins meant for oilfield use [2]. The activation energy was determined from the slope of a plot of the natural logarithm of the weight of the polymer versus the reciprocal of the Kelvin temperature.

One caveat concerning TGA experiments is that lower temperature weight losses can be simply due to loss of extraneous species present in the resins. For example, phenolic resins contain water from the condensation process by which the resins form and cure. Also, as temperature is raised, further condensation can also occur. Thus, phenolic resins lose water up to 300˚C and thermal decomposition of the polymer chains only occurs above this point [6]. Thus, it is important to determine what exactly is happening in any weight loss that is observed at or below 200˚C. This will be done by analysis of the off-gases by mass spectroscopy.

The most sensitive method for determining glass transition is Dynamic Mechanical Analysis (DMA). In this test, the sample is subjected to an oscillatory stress, and the material response is measured. The nature of this response may be used to determine the elastic and viscous properties of the material (storage modulus and loss modulus, respectively), and this can be very sensitive to T_g as the material rapidly becomes more flexible at the transition temperature. For this reason, DMA will be utilized in the investigation of the candidate resins for sealing of oil wells. It will be necessary to investigate each material in this way with the resin preferably being "cured" under conditions similar to the real world application in oil wells. This is due to the fact the glass transition temperature of a resin system includes the chemical structure of the resin components, the degree of cure, the curing temperature, and the moisture content .

In order to perform an initial fundamental assessment of degradation of the resins tested in this investigation, TGA and DMA will be performed on a series of resins samples currently under evaluation. A range of temperatures, pressures and curing media will be employed. Additionally, compositions will be modified within range of acceptable application function to vary chemistry for specific resin types. These data will be used to assess intrinsic resistance to chemical degradation as well as to detect any changes in chemistry associated with exposure conditions.

4 CONCLUSIONS AND PATH FORWARD

Resins were used to seal oil wells more than 60 years ago and there does not appear to ever be a report of their failure. Thus, it is extremely likely that solutions for sealing oil wells can be elucidated from testing of the candidate resins as described above. Furthermore, it would be extremely easy to adjust resin properties by varying the components to eliminate problematic responses to oilfield conditions.

Furthermore, it is possible to accomplish much more with a resin than can be done with cement. For example, a judicious adjustment of the glass transition temperature, it would be possible to have a better sealing and shock-absorbing rubbery material at the bottom of the well that transforms through a "graded seal" (over the range of temperature of the glass transition) to a mechanically strong glassy material in cooler sections higher in the well. Resins were mostly abandoned in the past due to cost but the added value of better performance and prevention of potentially catastrophic leaks makes novel resin technology for oil well selling highly attractive.

Therefore experiments will be performed in which the candidate materials are immersed in water, hydrocarbon, or brine for extended periods. The weight, appearance, radius and length of the specimens will be monitored with time. Physical properties will be reassessed by DMA at the end of the hydrothermal experiments. Fourier-transform infrared spectroscopy will be performed to assess chemical changes in the resin. Solid state carbon-13 NMR spectroscopy will be performed where merited. Resin formulations and curing conditions will be finalized as initial design and performance metrics are being completed this month. Exposure and analysis will continue until project completion. This testing is expected to produce comparative estimates of different resins' stability and durability as an OCS well sealant.

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APPENDIX B LITERATURE REVIEW

CSI TECHNOLOGIES

Literature Review Report
Resin Compared to Portland Cement

Project No: E17PC00004

Date: April 6, 2017

Version: 1.0

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Table of Contents

1 PURPOSE

This project evaluates performance of various resin-based compounds as sealants for petroleum wells in the OCS. This report presents results of Task 2: Review of Previous Work. A survey of publically-available literature covering resin as a well sealant identified a significant bibliography of resin-related documents. These documents have been reviewed, and information pertinent to the investigation is summarized.

2 CONCLUSIONS

The following conclusions are based on review of available literature:

1. A total of fifty-eight publications discussing use of resin as well sealants were located. Initial screening of content has been completed and catalogued. This information will provide background and establish bounds for the remainder of this work.

2. Publication topics fell into 5 general categories:
   - Commercial sales and performance bulletins
   - Chemistry of resins used as well sealants
   - Performance or application of resins used as well sealants
   - Chemistry of blends of resin and cement
   - Performance or application of resin-cement blends

Information from each category is summarized in **Discussion of Results**.

3. Four service companies currently offer resin sealants in wide-spread distribution. Literature indicates these materials are either epoxy or polyester. Range of application conditions and operational scenarios are broad. A significant number of applications are remedial well seal treatments. Another regional service company offers resin for dump bailer applications. Other commercial resin offerings had been reported, but no evidence of these was discovered in the search.

4. Two other resin products previously sold commercially are summarized.

5. Published papers reveal investigation of resin as a well sealant dating back to the 1940's. Resin-only sealants have been explored as well as combinations of resin and hydraulic cement.

6. Major categories of materials classified as resin sealants for the scope of this work include epoxy, polyester, furan, and phenolic. Selected literature describing thermoplastic polymers or elastomers as sealants are included although they provide limited potential for wide application due to low strength of difficulty in placement. These concepts and associated applications serve to bracket usage and utility range of resins. A wide variety of resin-cement mixtures have also been investigated as potential well sealants.

3 NEXT STEPS

Review of past investigations reported in the technical literature has identified specific resin types with potential petroleum well applications. The initial list of resin types will be the basis for starting the main portion of the project. The first function of the Industry Advisory Committee (first meeting is scheduled for April 5) will be to review these findings and confirm that the resin types will be studied in the project going forward. These resin types will then be evaluated according to Tasks 4 through 10 and compared to Portland cement performance. One or two resin-cement mixtures may also be evaluated.

Evaluation will include theoretical chemical evaluation of resin sealant performance, laboratory evaluation of resin performance compared to cement, and estimated seal integrity achieved with each resin type. The sizable volume of technical information amassed during this literature review will be analyzed to assemble meaningful background and support data to focus and provide backing for the projects theoretical and experimental work.

Ideally, samples of actual resins in commercial use can be obtained for comparison testing, but open-source materials will be designed as a backup. Suppliers of each class of resin chosen for investigation have committed to supply open-sourced resin systems for laboratory testing if no commercial systems are available.

4 DISCUSSION OF RESULTS

4.1 Background

The word “resin” is a general term covering a broad range of materials. For the purposes of this project, resins are defined as liquid organic compounds, either natural or synthetic, with reactive sites. Resin reacts with curing agents to transform from a liquid onto a highly-crosslinked, three-dimensional solid network. For oilfield application, resin systems are prepared as a fluid, pumped into place in a well, and then harden into a solid.

Well integrity interest within the upstream industry has been spurred in the last decade by concerns over water quality, fracturing, fugitive gas emissions, and even well control failure. This focus on well integrity and well sealants has renewed interest in sealant function. Portland cement is sealant of choice for ensuring well integrity, but Portland cement sealant performance is not ideal. Set Portland cement is brittle, subject to shrinkage, permeable, degraded by H_2S or CO_2, can form weak bonds to well surfaces, and cannot permeate small flow paths.

Thermosetting resins are potential alternative sealants to Portland cement. These materials offer improved performance properties as well as drawbacks of their own. Additionally, limited use of these sealants provides little data for direct performance comparison. Standard laboratory evaluation and design techniques for cement do not always yield meaningful comparisons from resins. If usage increases, suitable regulations for resin application will be required to ensure proper design and use of these materials. Initial development of standardized guidelines is underway but far from completely defined and vetted (Oil and Gas UK, 2012). This task of reviewing literature discussing resin as a well sealant was conducted to provide a historical basis for this project as well as provide boundaries for investigation and prevent repetition of previous research.

A total of seven resin sealants currently offered commercially were identified. Additionally, 58 technical publications describing use of resin in wells were identified. Discussion of Results groups the literature into three categories: Commercial Resin Well Sealants, Resin Sealants as Replacement for Portland Cement, and Resin Combined with Portland Cement. The latter two categories are further divided into segments discussing material chemistry and application descriptions. Discussion of findings from this review cover range of resin chemistry investigated as well sealant, past and current commercial resin sealant materials, positive and negative performance attributes, evaluation of performance properties, and any comparison of resin performance to that of Portland cement. Complete citations for each reference are presented by category in the Appendix.

4.2 Commercial Resin Well Sealants

A search of commercial sales and technical information revealed that four service companies currently offer resin sealant to the petroleum industry on a broad basis. An additional example of a regional service company offering resin is also included. Other, isolated accounts of limited, localized application of resin sealants by smaller service companies were noted, but no additional commercial sales information for these applications or products was discovered.

The five service companies offer a total of seven resin well sealants. Three of the products appear to be epoxy resin, while one is a blend of epoxy resin and cement. One is a furan resin, and the other two appear to be polyesters.

Two other products which were formerly commercially available but do not appear in current technical or sales literature are also described. One of these is an epoxy resin and the other is a mixture of synthetic resin and gypsum cement.

These findings in the literature point to a currently small but viable commercial market for resins as alternative sealants to Portland cements. Recent increase in literature citations indicates uptick in level of interest in these resin sealants. All products claim improved seal durability with chemical resistance, ability to permeate small flow channels, seal/consolidate permeable media, and gas migration control. Primary use is remedial or P&A at this time.

Descriptions found in the literature for each product are summarized below. Complete reference citations and summaries appear in the Appendix.

4.2.1 Product Name: Liquid Bridge Plug

Company: Professional Fluid Services, LLC.
Location: Lafayette, LA, USA

Professional Fluid Services has as patented resin/plastic technology called Liquid Bridge Plug. This product has been designed for gas shut off treatments but also list the follow jobs as potential applications:

- Micro Annular Gas Migration
- Mechanical Isolation Valve
- Casing Leaks
- Packer Leaks
- Wellbore Stability
- Loss Circulation

The product is listed as a two part system, "Part A" and Part "B", that are mixed on location then the mixture is used for the treatment. An injection rate with sea water threshold is identified for using the product, Liquid Bridge Plug is only recommended for applications when the injection rates are less than 0.25 bpm. The minimal treatment volume of 4 bbls is recommended for all application and at least 50 ft of product above a leak in the casing is recommended.

No temperature limitations or set mechanical properties are provided. A total of 17 case studies were referenced with most of them being application in the GoM. Although not specifically stated in this literature, patents held within this organization cover use of epoxy resin as a well sealant.

4.2.2 Product Name: ThermaSet

Company: Wellcem
Location: Orstad, Klepp, Norway

Wellcem, a company headquartered in Norway, has a patented polymer based resin called ThermaSet. The product starts in a liquid state and with time and temperature will transition into a hard set solid with mechanical properties that exceeds those of conventional cement. The fluid properties such as density, viscosity, and curing time can all be customized based on specific will conditions. Although resin type is not explicitly stated in this literature, patents assigned to Wellcem cover use of polyesters as well sealants.

Some common applications for ThermaSet are listed below:

- Competent well barrier for permanently abandoning wells
- Lost Circulation control – Treat & Drill without POOH
- Well bore strengthening
- Fast setting kick off plug – Treat & Drill without tripping
- Zonal Isolation / Water and Gas Shut off
- Primary Cementing
- Strengthening the shoe
- Weak formations and zones with low fracture gradients where low density systems are required i.e. foam cement.
- Packer Inflation material to permanently set a packer
- Consolidation of loose formations
- Plugging of control/ transmittal lines

The product has the following specifications:

- Density range from 6ppg – 20ppg
- Viscosity range from 10cp -2,000,000c$_p$
- Operating range from 16°F – 300°F (and once cured 600°F)

Over 100 treatments have been performed with ThermaSet to solve a variety of technical challenges ranging from lost circulation to sustained casing pressure.

4.2.3 Product Name: EnvoSet

Company: Wellcem
Location: Orstad, Klepp, Norway

EnvoSet is an environment friendly thermosetting resin system developed by Wellcem for plugging applications in the oil and gas wells. The produce has a low viscosity and density that can be adjusted based on treatment applications. The curing process starts when its curing initiator is mixed with EnvoSet and exposed it the design temperature. The target applications for EnvoSet are:

- P&A – Permanent well barrier
- Lost Circulation control
- Zone isolation and plugging of unwanted zones
- Plugging of Control lines
- Remedial Treatment of Sustained Casing Pressure

The product has the following specifications:

- Density range from 6ppg – 20ppg
- Operating range from 122°F – 302°F
- Flash point >230°F
- Registrations: NEMS, OCNS & CEFAS

This product is planned to become commercially available 4/2017. No indication of resin type is indicated.

4.2.4 Product Name: WellLock

Company: Halliburton

Halliburton has a patented Resin system, WellLock, designed to be used gas impermeable barrier. WellLock using a cross-linking reaction between an amine hardener and epoxides, resulting in a cured three-dimensional infinite polymer network. Some common application for WellLock are listed below:

- Secondary barrier above primary cement jobs
- High pressure squeeze jobs
- Tight casing leaks
- Remediation
- Gravel packers
- Permanent Plug and Abandonment
- Disposal wells

WellLock is a low viscosity sealant with the ability to penetrate micron-size pores then sand very high differential pressure once cured. The resin is chemically resistant to acids, bases, salts, hydrocarbons, and CO_2 and been used to storage well applications. Fluid specification include the following:

- Density range from 6.5 ppg – 16.4 ppg
- Operating range from 60F – 200°F (and once cured 225°F)
- Compressive strength up to 18,000 psi (achieved with some formulations)
- Tensile strength greater than 1,000 psi

4.2.5 Product Name: LockCEM Cement

Company: Halliburton

Halliburton has a proprietary blend of WellLock resin system and any class of Portland cement. LockCEM cement provides best of both cement and resin while overcoming the challenges of oilfield resin use. Only a small percentage of the overall blend involves the resin system (examples show 20% resin by volume).

Some of the improved mechanical properties when compared to conventional cement are:

- Increased compressive strength
- Lower Young's Modulus for ductility
- Increased Shear Bond
- Reduced Permeability
- Achieve Lower Density

Some of the recommended application for LockCEM are:

- Primary Cementing
- Remedial Cementing
- Plug and Abandon

4.2.6 Product Name: ControlSEAL Resin

Company: Wild Well Control, Inc.
Location: Houston, TX, USA

ControlSEAL is an epoxy resin sealant marketed by Wild Well Control. ControlSEAL offers and effective long-lasting barrier alternative to conventional cement. The compressive strength, tensile strength and shear bond of ControlSEAL will outperform cement while providing a noncorrosive and impermeable set solid. The solids free design allows the product to infiltrate microannuli to create barriers. The product is also able to stay intact while dropping through water, seawater, and brines then will reform at the target zone.

Some common application for ControlSEAL are listed below:

- Casing installation
- P&A operations
- Leaking production packers
- Control lines, gas leaks, valves and wellheads
- Remedial squeeze jobs
- Water flows and gravel packs
- Weak, permeable formations
- Isolation of adjacent wells

The product has the following specifications:

- Density range from 7ppg – 19ppg
- Operating range from 40°F – 275°F
- Compressive Strength ≈ 8,000psi
- Tensile Strength ≈ 3,500psi
- Young's Modulus ≈ 200 Mpsi
- Shear bond ≈ 1,800psi

4.2.6 Product Name: TexPlug

Company: Alamo Oilfield Services
Location: Lafayette, LA USA

TexPlug shuts of water production by saturation the formation matrix with custom formulated furan resin resulting in a thermally resistant, chemically inert plug. After consolidating, the plug is inert to oilfield chemicals, stale to temperature up to 700°F and is non-hazardous and non-toxic. The target applications for TexPlug are:

- Cut water production in gravel pack wells
- Casing repairs
- Reducing water coning
- Water shut off to keep wells on-line longer
- Improve injection well performance by shutting off high volume layers

The product has the following specifications:

- Density range from 10.2ppg – 11.7ppg (special order at 15+ ppg)
- Operating range from 60°F – 450°F (once set can withstand temps up to 700°F)
- Viscosity 10-12 cp

This product has been used for several dozen water shut off application in the GoM Shelf and few fluid shut off treatments internationally.

Two other resin sealants that were commercially available previously, but no longer appear in commercial sales literature are discussed below.

4.2.7 Product Name: Hydromite

Company: Halliburton

Hydromite is reported to be a combination of synthetic resin and gypsum cement. The material is designed to form a hard and durable plug with good bonding, no permeability, and post-set expansion. The composite was designed and recommended for placement by dump bailer. Squeezing of the composite can be achieved if necessary.

Application range is 60-180°F.

4.2.8 Product Name: EPSEAL^R Sealant

Company Name: Halliburton

EPSEAL sealant is described as a low-viscosity resin composition for plugging application and formation consolidation. It has high strength and chemical resistance. Application areas listed include fluid shutoff, casing repair, liner cementing, and remedial cementing. Stated application temperature range is 60°F to 245°F. This document does not specify that EPSEAL is epoxy based but that is stated in other technical literature cited in this report.

4.3 Technical Publications Discussing Resin as a Well Sealant

Fifty-eight publications discussing various aspects of resin as well sealants were chosen for this review. Various aspects of materials to replace Portland cement as a well sealant are discussed including material chemistry, application ranges, performance benefits and improvements, application methods, durability and cost. The first published account of resin used as a well sealant presented here dates back to the 1940's confirming a long history of interest in developing an improved sealant. More recent work reported by Endeavor (2015) and BSEE (2012) indicates amplified interest in resins.

The majority of materials discussed in the literature reviewed here are thermosetting polymers. However, examples of elastomeric polymers and thermoplastic polymers as well sealants are also included. Hybrid systems, including resin-cement composites, resin-elastomeric composites, and resin-thermoplastic composites, are also discussed. Chemistry, application range, performance property improvements, and case histories are presented.

4.4 Resin Sealant Replacing Portland Cement

Discussions of resin chemistry, performance enhancements, and case histories are presented. Detailed summaries of each citation appear in the Appendix. Generally, these publications describe improved performance of resin sealants over Portland cement. Several publications discuss needs to standardize or regulate resin application.

4.4.1 Chemistry and Materials

This literature category includes general survey articles discussing all categories of well sealant chemistry (Bensted, 1988) to specific sealant chemistry and performance descriptions. Epoxy formulations are covered by Cole *et al* (1978). Eilers (1985) presents chemistry and performance range of furan resin while Peavy (1991) discusses application of phenolic resin. Beharie *et al* (2015) discuss application of polyester resin as well sealant.

Chan and Griffin (1997) discuss diluents for epoxy to lower viscosity and corresponding placement pressure. Bond enhancement for epoxy resin is described by Chatterji *et al* (1999). Dahl-Jorgensen and Arne (2000) report that dehydrated bentonite powder added to diallyl phthalate reduces shrinkage and lowers reaction exotherm. Griffith et al (2002) describe adding styrene-butadiene latex and organophilic clay to epoxy resin mixtures to enhance resiliency.

This literature review establishes a suitable guide to move forward with this project focusing on performance of potential resin sealant types and formulations.

4.4.2 Properties and Applications

This literature category includes various examples of resin applications and attempts to quantify performance of resin sealants.

Oil & Gas UK (2012) is driving an industry effort to develop performance criteria and qualification metrics for resins used as well sealants for abandonment. Hefly and Cardwell (1943), Clasen (1945), and Dale (1947) describe early use of resins for well remediation although little description of sealant chemistry is provided. Bosma *et al* (2004) discloses a method of controlling exothermic reaction of resin curing by cooling the well substantially via cool fluid circulation prior to placing the resin. Onan *et al* (1999) describe foaming epoxy resin to reduce density. Cole (1979) discusses superior chemical resistance of epoxy resin over Portland cement as sealant for chemical disposal wells.

The first use of epoxy resin for abandonment of a lower producing zone in the GoM is documented in **DecomWorld** (2016). Leal et al (2016) present a method of placing epoxy sealant into a hurricane damaged well in the GoM. Resin was fed into the well and allowed to gravity displace and coalesce to seal casing and annular leaks so that abandonment of damaged well could be achieved.

Versatility of resins as well sealants was generally supported by the literature uncovered here.

4.5 Resin Combined with Portland Cement

Although numerous performance drawbacks of Portland cement have been discussed as the basis for this investigation, the industry has realized several beneficial performance attributes and potential to improve Portland cement by combination with resin. Potential of modification and improvement of Portland cement behavior by resin addition yielded several viable sealants. A major driver behind addition of resin to Portland cement is sealant cost reduction driven by using a less costly component.

4.5.1 Chemistry and Materials

Combination of Portland cement slurry and epoxy resin to provide a sealant with improved performance over Portland cement alone was described by Chatterji *et al* (2000). Kukachka, (1977) discussed utility of polymer impregnated cement (PIC) in geothermal applications. Porosity of cement was filled with monomer which was subsequently polymerized to produce impermeable, chemical resistant cement with improved strength at high temperature. Onan described adding styrene-butadine latex to cement slurry and vulcanizing the SBR to improve mechanical properties. Totten et al (1995) combined epoxy with drilling fluid and slag cement, or with micro-fine cement to produce a suitable composite well sealant.

4.5.2 Properties and Applications

Padgett (1946) documents an early application of Hydromite. This resin-gypsum cement blend was dump-bailed during plugging operations. Evaluation of resin-cement composite bond was addressed by Burkdorfer *et a*l (1983) and by Frisch *et al* (2013). Gamwell and Lewis (2016) describe compatibilizer for forming stable mixtures of resin and cement slurry over a wide range of ratios.

5 APPENDIX

5.1 Bibliography and Summaries

References are grouped into the same categories as discussed in the body of the report. Each group is arranged alphabetically by primary author's last name. In the case of commercial literature, references and summaries are arranged alphabetically by company offering them.

5.2 Commercial Resin Well Sealants

5.2.1 Product Name: Liquid Bridge Plug

Company: Professional Fluid Services, LLC.
Location: Lafayette, LA, USA

Professional Fluid Services has as patented resin/plastic technology called Liquid Bridge Plug. This product has been designed for gas shut off treatments but also list the follow jobs as potential applications:

- Micro Annular Gas Migration
- Mechanical Isolation Valve
- Casing Leaks
- Packer Leaks
- Wellbore Stability
- Loss Circulation

The product is listed as a two part system, “Part A” and Part “B”, that are mixed on location then the mixture is used for the treatment. An injection rate with sea water threshold is identified for using the product, Liquid Bridge Plug is only recommended for applications when the injection rates are less than 0.25 bpm. The minimal treatment volume of 4 bbls is recommended for all application and at least 50ft of product above a leak in the casing is recommended.

No temperature limitations or set mechanical properties are provided. A total of 17 case studies were referenced with most of them being application in the GoM.

All the Information described is based on publicly available information from the following reference: http://www.professionalfluid.com/ProductDescription.asp?ProductID=56; Accessed -23 Mar. 2017

5.2.2 Product Name: ThermaSet

Company: Wellcem
Location: Orstad, Klepp, Norway

Wellcem, a company headquartered in Norway, has a patented polymer based resin called ThermaSet. The product starts in a liquid state and with time and temperature will transition into a hard set solid with mechanical properties that exceeds those of conventional cement. The fluid properties such as density, viscosity, and curing time and all be customized based on specific will conditions. Some common applications for ThermaSet are listed below:

- Competent well barrier for permanently abandoning wells
- Lost Circulation control – Treat & Drill without POOH
- Well bore strengthening
- Fast setting kick off plug – Treat & Drill without tripping
- Zonal Isolation / Water and Gas Shut off
- Primary Cementing
- Strengthening the shoe
- Weak formations and zones with low fracture gradients where low density systems are required i.e. foam cement.
- Packer Inflation material to permanently set a packer
- Consolidation of loose formations
- Plugging of control/ transmittal lines

The product has the following specifications:

- Density range from 6ppg – 20ppg
- Viscosity range from 10c_p -2,000,000c_p
- Operating range from 16°F – 300°F (and once cured, 600°F)

Over 100 treatments have been performed with ThermaSet to solve a variety of technical challenges ranging from lost circulation to sustained casing pressure.
All the Information described is based on publicly available information from the following reference: http://www.wellcem.no/product-solutions; Accessed -23 Mar. 2017

5.2.3 Product Name: EnvoSet

Company: Wellcem
Location: Orstad, Klepp, Norway

EnvoSet is an environment friendly thermosetting resin system developed by Wellcem for plugging applications in the oil and gas wells. The produce has a low viscosity and density that can be adjusted based on treatment applications. The curing process starts when its curing initiator is mixed with EnvoSet and exposed it the design temperature. The target applications for EncoSet are:

- P&A – Permanent well barrier
- Lost Circulation control
- Zone isolation and plugging of unwanted zones
- Plugging of Control lines
- Remedial Treatment of Sustained Casing Pressure

The product has the following specifications:

- Density range from 6ppg – 20ppg
- Operating range from 122°F – 302°F
- Flash point >230°F
- Registrations: NEMS, OCNS & CEFAS

This product is planned to become commercially available 4/2017
All the Information described is based on publicly available information from the following reference: http://www.wellcem.no/product-solutions/envoset; Accessed - 23 Mar. 2017

5.2.4 Product Name: WellLock

Company: Halliburton

Halliburton has a patented resin system, WellLock, designed to be used gas impermeable barrier. WellLock using a cross-linking reaction between an amine hardener and epoxides, resulting in a cured three-dimensional infinite polymer network. Some common application for WellLock are listed below:

- Secondary barrier above primary cement jobs
- High pressure squeeze jobs
- Tight casing leaks
- Remediation
- Gravel packers
- Permanent Plug and Abandonment
- Disposal wells

WellLock is a low viscosity sealant with the ability to penetrate micron-size pores then sand very high differential pressure once cured. The resin is chemically resistant to acids, bases, salts, hydrocarbons, and CO_2 and been used to storage well applications. Fluid specification include the following:

- Density range from 6.5 ppg – 16.4 ppg

- Operating range from 600°F – 200°F (and once cured, 225°F)
- Compressive strength up to 18,000 psi (achieved with some formulations)
- Tensile strength greater than 1,000 psi

All the Information described is based on publicly available information from the following reference: http://www.halliburton.com/en-US/ps/cementing/cementing-solutions/resins/welllock-resin.page?node-id=hfqela4d; Accessed - 23 Mar. 2017

5.2.5 Product Name: LockCEM Cement

Company: Halliburton

Halliburton has a proprietary blend of WellLock resin system and any class of Portland cement. LockCEM cement provides best of both cement and resin while overcoming the challenges of oilfield resin use. Only a small percentage of the overall blend involves the resin system (examples show 20% resin by volume). Some of the improved mechanical properties when compared to conventional cement are:

- Increased compressive strength
- Lower Young's Modulus for ductility
- Increased Shear Bond
- Reduced Permeability
- Achieve Lower Density

Some of the recommended application for LockCEM are:

- Primary Cementing
- Remedial Cementing
- Plug and Abandon

All the Information described is based on publicly available information from the following references: http://www.halliburton.com/en-US/ps/cementing/cementing-solutions/slurries-cements/lockcem.page?node-id=hfqela4d#; Accessed - 23 Mar. 2017

5.2.6 Product Name: ControlSEAL Resin

Company: Wild Well Control, Inc.
Location: Houston, TX, USA

ControlSEAL is a resin sealant marketed by Wild Well Control. ControlSEAL offers an effective long-lasting barrier alternative to conventional cement. The compressive strength, tensile strength and shear bond of ControlSEAL will outperform cement while providing a noncorrosive and impermeable set solid. The solids free design allows the product to infiltrate microannuli to create barriers. The product is also able to stay intact while dropping through water, seawater, and brines then will reform at the target zone. Some common applications for ControlSEAL are listed below:

- Casing installation
- P&A operations
- Leaking production packers
- Control lines, gas leaks, valves and wellheads
- Remedial squeeze jobs
- Water flows and gravel packs
- Weak, permeable formations

- Isolation of adjacent wells

The product has the following specifications:

- Density range from 7ppg – 19ppg
- Operating range from 40°F – 275°F
- Compressive Strength ≈ 8,000psi
- Tensile Strength ≈ 3,500psi
- Young's Modulus ≈ 200 Mpsi
- Shear bond ≈ 1,800psi

All the Information described is based on publicly available information from the following references: http://www.wildwell.com/emergency-well-control/controlseal/; Accessed - 23 Mar. 2017

5.2.7 Product Name: TexPlug

Company: Alamo Oilfield Services
Location: Lafayette, LA USA

TexPlug shuts of water production by saturation the formation matrix with custom formulated furan resin resulting in a thermally resistant, chemically inert plug. After consolidating, the plug is inert to oilfield chemicals, stale to temperature up to 700F and is non-hazardous and non-toxic. The target applications for TexPlug are:

- Cut water production in gravel pack wells
- Casing repairs
- Reducing water coning
- Water shut off to keep wells on-line longer
- Improve injection well performance by shutting off high volume layers

The product has the following specifications:

- Density range from 10.2ppg – 11.7ppg (special order at 15+ ppg)
- Operating range from 60°F – 450°F (once set can withstand temps up to 700°F)
- Viscosity 10-12 cp

TexPlug furan resin is specifically claimed to be settable over a wider temperature range than phenolic resin. This product has been used for several dozen water shut off application in the GoM Shelf and a few fluid shut off treatments internationally. Although not specifically stated here, it is believed that the preferred method of placement is via dump bailer.
All the Information described is based on publicly available information from the following reference: http://www.texplug.com/index.html; Accessed - 31 Mar. 2017

Two former commercial offerings of resin materials are listed here for reference although these products are not discussed in current technical sales literature.

5.2.8 Product Name: HYDROMITE

Company Name: Halliburton

Hydromite is reported to be a combination of synthetic resin and gypsum cement. The material is designed to form a hard and durable plug with good bonding, no permeability, and post-set expansion. Hydromite is a two-phase composite. The gypsum phase sets quickly while the resin phase takes longer.

The composite was designed and recommended for placement by dump bailer. Squeezing of the composite can be achieved if necessary. When squeezed into a permeable formation, the resin phase

Application range is 60-180^{o}F.

All information presented here is available from Halliburton Cementing Technology Manual dated January, 1996. This manual is available at the following url: https>//www/scribd.com/doc/136919004/Special-Cement.

5.2.9 Product Name: EPSEAL^{R} Sealant

Company Name: Halliburton

EPSEAL sealant is described as a low-viscosity resin composition for plugging application and formation consolidation. It has high strength and chemical resistance. Application areas listed include fluid shutoff, casing repair, liner cementing, and remedial cementing. Stated application temperature range is 60^{o}F to 245^{o}F. This document does not specify that EPSEAL is epoxy based but that is stated in other technical literature cited in this report.

All information presented here is available from Halliburton Cementing Technology Manual dated January, 1996. This manual is available at the following url: https>//www/scribd.com/doc/136919004/Special-Cement.

5.3 Resin Sealant Replacing Portland Cement

5.3.1 Chemistry and Materials

Beharie, C.; Francis, S.; and Ovestad, K.H.; SPE 173852-MS, “An Alternative Barrier Solution Material”, April 22, 2015

This paper describes the resin product that Wellcem company provides. They show the comparison of cement to resin in compressive strength, flexural strength, E-modulus and permeability, all showing resin to be better. They go on to discuss the industry’s question of long term durability and show testing in Crude Oil, Methane Gas, CO_2, and H_2S all exposed to 212°F and 266°F for Initial, 1, 3, 6 and 12 month timeframes. For these aging tests only the resin is shown for testing of permeability, compressive strength and flexural strength. Results with crude show a drop off at 1 month but maintains numbers throughout the year as did H_2S. All other exposures showed little to no change over time. Two case studies were listed proving the successful use of resin.

Bensted, J.; “A Review of Novel Cement with Potential for Use in Oilwell Cementing - Chemicals in the Oil Industry”, Third Royal Society of the Chemical Industry, **Chemistry in the Oil Industry International Symposium Proceedings** Pages 37-56, 1988

Several alternatives to Portland cement are presented along with the state-of-the-art of each as of writing. They are classified into six categories.
Category 1 - Silicate and aluminate-based non-Portland cements:

- Class J and belite-silica cement (BSC), can be used in high temperature well construction where conventional oilwell cement is too reactive. Class J is 60:40 by weight dicalcium silicate:quartz sand. It has excessive free water issues due to low reactivity.
- Lime-Silica Cements have not been used in application because additive response is variable.
- Silicate cements have been used to plug highly permeable zones. They require batch mixing and the formulation must be well-matched to the well conditions be prevent early or extremely delayed set-up.
- High Alumina Cement have been used when temperatures about 914°F are expected (e.g. Fireflood, thermal recovery). Long-term permeability is considered a concern. It is not more widely used because of high permeability at lower temperatures.
- Carbo-Aluminous Cement is a newly developed cement which is not well understood above 140°F.
- Hydrogarnet Cements require very precise SiO_2: Al_2O_3 ratio control. The hydration product of this is either high in porosity or unstable about 212°F.
- Ferrite Cements have slow hydration rates. Some accelerants are known, but the long term durability is not.

Category 2 – Oxychloride, Phosphate, and related cements:

- Magnesium Oxychloride cement is a mixture of magox and magnesium chloride. They have good adhesion to salt. However, they are dimensionally instable, have poor freeze-thaw resistance and some aspects are water soluble with corrosive solutions releasing as a result.
- Some variants such as magnesium oxysulphate cement, zinc and aluminum oxychloride cement, silicophosphate and sodium hexametaphosphate cement, calcium zinc and magnesium phosphate cement, magnesia-ammonium phosphate cement, aluminosilicate cement, and ionic polymer cement, have all bene attempted with varying degrees of success.

Category 3 – Bentonite-based cementitious drilling muds

- Bentonite-Ammonium Polyphosphate-Borax systems function similar to Magnesia-phosphate type cements
- Water-Based bentonite – API Cement/Silica Flour-Borax systems use Borax to control the thickening time and are similar to API cements.
- Bentonite-Polyacrylamide systems use a polymer to delay the bentonite swelling such that it can be placed.
- Bentonite-Chrome Lignosulphonte-Crosslinking polymer slurries require radioactive exposure (from ^{60}Co typically) to induce crosslinking and become a cured solid. The end result will anywhere from 670-8630 psi compressive strength. Long-term stability of the crosslinked solid, and effects on the environment are unknown.

Category 4 – Plastic and other organic extenders

- Resin or plastic cements exist in three forms: pure resin based upon epoxides, phenols, or formaldehyde with a catalyst; mixed cements where a Portland or high alumina cement is mixed with a water-soluble resin; and Portland cement with polymers (acrylics typically) mixed in. All three are typically used for low volume squeeze applications. Large resin quantities can lead to brittleness and some have restricted temperature ranges.
- Thermoset plastics are Sulphur based polymers. They have good mechanical properties and chemical resistance to acids and oils but poor resistance to alkalis.

- High Temperatures organic extenders, such as furfuryl alcohol, have been used, but their compatibility with organic additives is unknown. The use of organosiloxane polymers has also been proposed as their use in conjunction with Portland cement results in high-strength, thermally and hydrolytically stable composites.

Category 5 – Non-Portland Slag Cements

- Slag cements of ground granulated blast-furnace slag (ggbs) have been used without Portland cement in some applications. The reaction is slow but can be tailored with alkali or sulphate materials. Variations in ggbs composition makes tailoring the slurries difficult.

Category 6 – Special Portland type Cements

- Non-calcareous and non-siliceous Portland-Style cements can be produced but raw material sources are lacking and expensive where available.
- Non-gypseous Portland cements are available but the substitutes for the gypsum (e.g. calcium lignosulphonate-sodium bicarbonate, and polyphenolsulphonate-alkali metals salts) have batch-to-batch variability which would create difficulties in widespread use.
- Alinite cements have high early strength and are different from Portland cements as the hydration products incorporate chloride. Alternatives with the incorporation of sulphide is hydraulically poor. Bromide alternatives have been investigated but hydraulic performance is unknown.
- Belinite Cement is synthesized from a calcium chloride melt containing magnesia and is hydraulically poor compared to belite.
- Belite cements have high long-term strength development in alkali environments but the large quantities of dicalcium silicate makes tailoring oilwell slurries difficult.
- High early strength cements (containing calcium fluoride and calcium sulphate) have suitable for use but may thicken too soon in the event of operational delays
- Portland polymer cements demonstrate superior flexural strength, mechanical properties, and durability. Many are attacked by strong alkalis but some give resistance to strong acids. Additionally, fibers can be used to mechanically strengthen Portland cements. Some well-known Portland polymer cements have very high flexural and compressive strength but the water ratios of them make the product impractical for oilwell use.
- Expansive cements contain agents which expand slightly during the first few days of hydration to offset normal shrinkage of Portland cement and provide up to 5% expansion. Compositions using slag and silica have bene proposed for high temperature applications but there is no indication if practical application exists in the oilfield.
- Thixotropic cements (i.e. gypsum cement) is quick setting and has a rapid gel strength development once motion ceases. It is only viable below 176°F and will impart some expansion as well as thixotropic properties.
- Arctic cements should be quick setting with low heat of hydration. Gypsum cements can be used for this application as can high alumina cement with fly ash.

Bureau of Safety and Environmental Enforcement, “Evaluation of the use of Epoxy-Based Materials in Well Abandonment: Final Report”, U. S. Department of the Interior, 2012

This report describes the use of epoxy based material for well abandonment of wells damaged by hurricanes. The report shows the benefits of resin over cement. It can be gravity fed into damaged areas at least up to 7,000 ft and coalesce into a sealant. The epoxy resins chosen for study where a Bis A and Bis F with the Bis F giving superior results. The report also noted barite as a viable form of weighting agent. Various fall rates at different angles were investigated. Also contamination with seawater, pipe dope, etc. were investigated with shear bond and adhesion tests and showed resin to perform sufficiently as a sealant in a well condition.

Chan, K. S. and Griffin, T. J. Jr.; U.S. Patent No. 5,547,027; “Low Temperature, Low Rheology Synthetic Cement”; August 8, 1996

This patent describes the invention of a low temperature low rheology epoxy resin (described as synthetic cement). In cold conditions the viscosity of epoxy resins are very high and can be unusable. This patent summarizes the use of an aromatic solvent used as a diluent in epoxy resin at temperatures below 20^{o}C. The amount of solvent can be used is in the range of 10% to 100% to achieve the desired rheology. With the addition of the solvent, the resin can be pumped into the annular space in a well with minimal friction pressure. The solvents that were mentioned in the patent were: benzene, toluene, and xylene. The effect of the solvent on the thickening time and the set time of the epoxy are summarized.

Chatterji, J.; Onan, D. D.; and Cromwell, R. S.; U.S. Patent No. 5,875,845; “Methods and Compositions for Sealing Pipe Strings in Well Bores”; March 2, 1999

This invention describes epoxy resin, a hardener, silane, as a well sealant. Sealant properties are superior to those of Portland cement. A range of epoxies, hardeners, and weighting agents is compiled.

Cole, R. C.; Koch, R. K.; Ramos, J.; US patent 4,072,194; “Pumpable Epoxy Resin Composition”; February 7, 1978

An epoxy resin composition curable to a hard impermeable solid which contains a liquid aromatic diluent having the formula C6(R1)6 where in the R1 is hydrogen, a straight or branched chain alkyl radical, a cyclopariffin, radical or a mixture there of. Many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and it is not intended to be limited except as indicated in the appended claims.
A method of completing a wellbore with an epoxy composition containing 20-40 parts by vol of an aromatic diluent composition wherein said aromatic diluent is selected to prevent premature setting by absorbing heat to provide a cured epoxy resin composition. Many compositions should be considered.

Dahl-Jorgensen, E. and Arne, B.; U.S. Patent 6,082,456 A; “Means and Method for the Preparation of Sealings in Oil and Gas Wells” July 4, 2000.

This patent describes the use of a polymer-based cementing agent called diallyl phthalate (DAP) with a filler material to reduce shrinkage (pre-dried bentonite). The use is for shutting off water zones with a rapid cure material (less than 24hrs) with a temperature range of 41-248°F. The resin comprises of a monomer, initiator, inhibitor and optional filler. The patent lists details of these additives and quantities used for various formulations. They describe performing exothermic reactions and inhibitors to reduce the exothermic reaction, they mention being able to predict resin performance based on linear correlations between pot life and temperature. The patent finishes with describing a polymer based composition that had an exotherm to 248°F, had instantaneous strength, and practically no shrinkage

Eilers, L. H., U. S. Patent 4,556,109, Process for Cementing Geothermal Wells", Dec. 3, 1985

This patent discloses Furfuryl alcohol mixed with a low-molecular-weight of furfuryl alcohol and/or furfural combined with crushed coal into a pumpable slurry and used as primary cement for a geothermal well. Crushed coal provides improved heat capacity over carbon black to mitigate reaction exotherm, and particle size is larger allowing addition of more filler without exceeding highly rheology. A polymerization catalyst may also be incorporated.

Griffith, J. E.; Cox, R. A.; Chatterji, J.; King, B. J.; Cromwell, R. S.; Dennis Jr., J. L.; U. S. Patent Application US2002/0022579 A1; "Sealing Subterranean Zones"; February 21, 2002

This patent application discloses a composite material for well sealing. The composite contains an aqueous solution of styrene-butadiene latex, a latex-stabilizing surfactant, epoxy resin, and hardener. An organophilic clay and silane may be added also. Primary function of the composite sealant is to plug weak formations into which lost circulation is occurring. The composite is pumped into the well and into the weak zone. Once there the composite comes into contact with brine or hydrocarbon fluids lost into the formation. The composite interacts with these fluids causing the latex to coagulate (brine) or the clay to swell (hydrocarbon) creating a gelatinous mass blocking further fluid movement. The epoxy and hardener then react to solidify the barrier.

Hundt, G.; Karcher, J. D.; and Jones, P. J.; World Patent Application Publication WO 2015/034474 A1; "Heavy-Atom Resin Formulation for Use in Subterranean Wells", March 12, 2015

This patent describes the use of a resin and hardener that comprises a molecule having at least one heavy atom such as halogen atoms like fluorine, bromine and iodine. These heavy atoms provide higher densities to the resin without having to add solids. The patent lists liquid hardenable resins to include: epoxy resins, novolac resins, furan/furfuryl alcohol resins, urethane resins, glycidyl ether resins, polyester bisphenol A-epichlorohydrin resins, bisphenol F-epichlorohydrin resins, bisphenol AF-epichlorohydrin resins, and tetrabromobisphenol A-epichlorohydrin resins. It also lists all types of diluents, hardeners, silanes, and accelerators. Hardeners mentioned are Ethacure 100 as a slow setting hardener, and Jeffamine D-230 as a fast setting hardener. All types of solids are listed, about 60, and fibers. The patent gives examples of Epon 828 mixed with DETDA will have a cured density of 9.79 lb/gal whereas a halogenated resin DER 560 mixed with DETDA will have a cured density of 14.17 lb/gal. The DER 560 has to be heated as it is a solid at ambient.

Justnes, H. and Dahl-Jorgensen, E, CPCT/NO93/00173 "Alternative Cementing Materials for Completion of Deep, Hot Oil-Wells", November 20, 1993

For use in the 120-200°C range, a resin of ortho, meta-, or para-diallyl phthalates, oligomers thereof, and prepolymers thereof, is mixed with an organic peroxide curing agent to develop free radicals, an inhibitor (e.g. para-benzoquinone)for stabilizer those free radicals to allow placement, and optionally weighting agents, extenders (e.g. calcite, silica flour, or silica fume) to control consistency, and materials to compensate for shrinkage (e.g. bentonite predried at a temperature just below BHCT).

Kennedy, H. J.; Jones, P. J.; and Albrighton, L. D.; International Patent Application Publication Number WO 2016/048332 A!; "Composition Including a Curable Resin and Organophilically-Modified Clay for Subterranean Oil Well Applications"; March 31, 2016.

This international patent application describes treating well or subterranean formation using a curable resin and/or a thermosetting polymer to which an organophilically-modified clay is added. The clay acts as a suspending aid; increasing the fluid's yield point to improve larger particle suspension. It is necessary to add solids to curable resin or thermosetting polymer sealants for oil wells in order to prevent sealant buoyancy from disrupting fluid placement or to maintain proper hydrostatic pressure of the fluid column for well control. Solids added to the fluid sealant must be suspended to form a stable slurry. The fine particulate clay aids in particle suspension while the organophilic surface treatment of the clay provides improved wettability and dispersability.

The application lists numerous resins and thermosetting polymers and combinations including all major classes described in this report. Clay treatments involve addition of fatty acid salts to a clay (kaolinite, montomorillonite, illite, or chlorite with montmorillonite preferred). A vast array of weighting materials is listed. Uses listed include any application for creating or remediating a well seal; either primary or remedial operations.

Lane, J. M. and Bowditch, M. R., "The Development of Resin Systems and Processes for Underwater Bonding and Sealing", **Proceedings of the Annual Meeting of the Adhesion Society**, Volume 24, Pages 471-473, 2001

The development of epoxy based-systems for underwater bonding, sealing and composite repair is reported. The technology is a cold-curing epoxy resin with suitable rheological properties is impregnated into a porous flexible reticulated foam. This is applied to leaking pipes where it hardens and seals. The resin/foam sealant was used for the underwater repair of the damaged outer sheath of a riser and emergency repairing of subsea pipelines. A detailed screening program is described that includes durability in seawater but none of the results are reported

Peavy, M.A.; SPE 22778, "Successful Water Control in Openhole Gravel-Packed Completions Within a TEOR Environment", Sixty-Sixth Annual SPE Conference, October 6-9, 1991

A phenolic resin plug back technique was developed and successfully employed on thirty-two wellbores with open hole gravel packed completions in the Midway-Sunset field during 1987. Resulted in sustained water production decrease of 5850 BWPD and an oil production increase of 256BOPD. Total revenue and savings from wellbore plugback project est at $970,790 per year. Successful placement temp range was 100-200°F. During in-field development of the Victory properties in 1986, high water production was encountered across two adjoining leases. It was theorized that a water channel existed within the reservoir previously thought to be oil productive. These had gravel packed completions. Conventional class G cementing for water shutoff was only marginal.

Research was initiated to find a water shut off technique that was low cost and provided good penetration through the liner and gravel pack into the formation. Class G and phenolic resin were reviewed. A field model was used for testing consisting of sand within the liner/conductor annulus, the annulus was filled with water and closed. Two ports were opened to allow circulation. Class G was tested first and after

7days WOC the sample was inspected. The cement had low compressive strength and was crushable by hand. Poor penetration and poor properties overall.

The first documented use of resin for water control was in 1902 in Kern River field. For this project, phenolic resin was tested across a temperature range from 135°F to 451°F simulated reservoir temperature, for up to 140hr in dry and wet conditions. This testing showed the resin is sensitive to temps above 400°F. Acid solubility testing showed 8.6% of the resin will be dissolved at 15%HCL system where 26% would dissolve with a 12/3 HCL/HF acid.

For the actual shutoff procedure, three major problems were encountered – low bottomhole temperature (105°F instead of 135°F), breakage of parts on the dump bailer, Third was movement of resin to the gravel pack. Once they rectified these issues, benefits from the project were around $970,790/yr. Control of water is possible using phenolic resin, long term economic benefits have been derived with the use of the resin cement water shutoff technique, and these phenolic resin plugs can be successfully catalyzed in wellbore environments with temps from 100-200°F.

Tcherbi-Narteh, A; Hosur, M.; and Jeelani, S.; "Effects of Different Montmorillonite Nanoclay Loading on Cure Behavior and Properties of Diglycidyl Ether of Bisphenol A Epoxy"; **Journal of Nanomaterials**; Volume 2016, Article ID 3840348

This paper discusses benefits of adding nanoclay as a filler for reinforcement of epoxy. Nanoclays exhibit significant benefits due to cost and availability. Additionally the high aspect ratio and platelet structure allow increased interaction (with aid from surfactants) with epoxy to form an intercalated microstructure which improves mechanical properties. Relatively small concentrations of nanoclay (1-3 wt%) were incorporated.

5.3.2 Properties and Applications

Bosma, M. G. R.; Cornelissen, E. K.; and Schwing, A.; U.S. Patent No. 6,802,375 B2; "Method for Plugging a Well with a Resin"; October 12, 2004

This invention covers a method controlling thermal effects of resin curing or elastomer vulcanization when setting a plug in a well. The exothermic reaction increases the temperature of the resin plug and its surroundings during curing. When the mass cools down to normal well temperature, the higher coefficient of thermal expansion of resin compared to the surrounding materials results in sealant volume reduction greater than that of the surroundings. This induces stress internally in the resin as well as at the resin-well interface. The stress can induce material or bond failure resulting in failed seal.

The invention calls for cooling the area of the well into which the sealant will be placed prior to placement. Cooling is achieved by circulation of cool fluids, and desired temperature decrease is around 100°C. Then, a sealant properly designed to set at the cooled condition is placed in the well and sets at temperature below the static well temperature. After sealant sets, the temperature of the well returns to normal static conditions. The cured resin seal expands on heating thereby alleviating the stresses and bond failure resulting from shrinkage.

Boughton, L. D.; Dellinger, T. B.; "New Cementing Process for Big Pipe in a Salt Plug"; **World Oil**, January, 1965

This paper describes a method used to successfully cement a 20-inch casing by 28-in hole in a salt plug using expanding cement and a chemical sealant. Additionally, operational techniques were deployed to prevent channeling during slurry placement such as coating the casing with an epoxy-sand for bonding, use of centralizers, scratchers, pipe reciprocation and staging tools. To counteract expansion and contractions of the casing due to temperature and pressure, a circulation system using a 4.5 ppg cooled fluid used to control the internal hydrostatic pressure and pipe temperature. Operational success was achieved after a three stage approach involving pumping expanding cement, WOC 24hrs then pumping a chemical seal ring, WO chemical seal to set and then pumping filler cement to surface.

The paper also reports test data for the expanding cement and chemical sealant. The expanding cement was evaluated against neat class A cement using volumetric expansion tests. Both the Expanding salt saturated and neat (not salt saturated) cement systems expanded slightly while setting whereas the Class A salt saturated and neat cement systems contracted. Hydraulic bond tests performed by cementing salt cores in pipe using the expanding salt saturated and neat cement systems resulted in failure at the at the cement salt contact below 400 psi hydraulic pressure. A chemical seal composed of a hydromorphic polymeric material was tested for thickening time and hydraulic bond. The addition of 1 in fill of chemical sealant above the previously failed cement hydraulic bond test specimens increased the amount of pressure withheld to 1700 psi. A large scale HB test was performed on a 2-3/8” by 5-1/2” annular plug created with the chemical seal and successfully tested to 6000 psi without failure.

Chivvis, R.W.; Julian, J.Y.; and Cary, D. N.; SPE 120978, “Pressure-Activated Sealant Economically Repairs Casing Leaks on Prudhoe Bay Wells” Society of Petroleum Engineers Western Regional Meeting, March 24-26, 2009

This paper discusses the successful repair of production casing leaks in 2 wells located in Prudhoe Bay using a pressure activated sealant. The authors discourses the leak diagnostic techniques, job screening criteria utilized, and improvements in treatment planning and execution that led to the proper selection and repair on two of the three reviewed candidates. The lower cost of remediating a well without a rig workover units and the provided flexibility for future workovers and operations involving the A annulus are listed as advantages of the pressure activated sealant repair method that does not involve pulling tubing or setting a solid plug in the A annulus. The pressure activated sealant is described as an oil or water-based fluid designed for specific job conditions that polymerizes into a flexible solid at the point of differential pressure. As the polymerizations reaction proceeds the material hardens from the edges outward bridging off the leak until completely sealed. The SG and viscosity of the sealant is adjusted to ensure the exact placement of sealant. The authors deploys a casing repair procedure with three steps:

Step 1: Pre-job diagnostics involving the size and location of the leak either by performing an injection test on the tubing by production casing “A” annulus or deploying a leak detection log down the tubing. An ultrasonic log is recommended over temperature or noise logs.

Step 2: Determine if the well meets the following 6 screening criteria which are in place to ensure a high likelihood of success.

1. The exact location of leak is known. Pressure and temperature must be within unspecified values.

2. Liquid leak rate measured and below max of 8 gal/min. Geometry is also important. High surface area and low cross sectional area leaks have higher likelihood of success. Data used to design sealant with optimize viscosity, weight and polymerization.
3. The existing well fluids are known and means for displacing fluids down the A annulus below the leak is required. Compressibility of various fluids effects fluid levels. Density hierarchy ensures no loss of depth control due to gravity. Reaction to pressure eliminates ability to bullhead.
4. Pressure rating of equipment must accept pressure requirement for sealant activation.
5. Additional leaks may not be present in the system. Squeeze pressure can be lost to the “thief” leak preventing activation.
6. Positive pressure can be maintained indefinitely after treatment.

Step 3: Prepare the well, pump sealant, and activate. Well preparation may involve setting plug in tubing, opening gas lift mandrels or punching tubing to establish circulation path below the leak, circulating heavier weight fluid in hole to prevent swapping of fluids once placed. Pumping the sealant involves floating the sealant on brine and displacing with a lighter weight fluid such as diesel. Once in place the sealant is squeezed into leak creating a pressure drop and activating the sealant. The sealant is allow to cure under pressure for 3 days.

The two successful well repairs ran an ultrasonic log to accurately locate the leak and met all 6 of the screening criteria requirements in step 2. The third well reviewed did not meet criteria 6. The third well operates with gas lift and a positive pressure differential would not be possible due a lower expected pressure in the A annulus than on the leak side. One of the two successful case histories uniquely sealed 4 leaks in one application. The leaks were treated from the top down by squeezing part of a sealant slug and holding pressure for 12 hrs prior to bleeding off tubing pressure and displacing the slug down to the following leak and repeating the process

Clason, C. E., “Cement Substitutes for Elimination of Water”, **The Oil Weekly**, December 10, 1945, Pages 54-57

This paper reports the advent of Resinite Seal products for elimination of water. One of these was reported to be particularly suitable for sandstone formations with bottom hole temperatures between 70˚F and 120˚F. It was successfully used in East Texas Woodbine sand and Talco-Paluxy sand as well as in wells in Pennsylvania, Oklahoma, West Texas, and Illinois. This resin sets to a compressive strength of 12,000 to 15,000 psi and a tensile strength from 5000 to 9000 psi. The setting time was easily adjusted by variation of the amount of liquid accelerator. It was found that some wells could be treated with a pure liquid resin but others benefited by addition of a finely ground material that prevented excessive penetration of the resin.

A second resin system for use in both limestone and sandstone was reported that is a mixture of two resins. This resin mixture sets to a much lower compressive strength of 1900 psi.

Cole, R. C., SPE 7674, “ Epoxy Sealant for Combating Well Corrosion”, 1979 SPE Oilfield and Geothermal Chemical Symposium:

This paper describes an epoxy sealant for combatting well corrosion which has adhesion, compressive strength, and chemical resistance superior to Portland and modified Portland cements. The epoxy sealant consists of bisphenol A type epoxy resin, a non-reactive diluent for viscosity reduction and to reduce reactivity, inert solids for density control and for minimizing "mass effect", and a hardener system comprising a primary hardener and an accelerator. The accelerator acts catalytically with the hardener compound by accelerating its reaction with the resin and it also reacts with the resin itself as a tertiary amine.

The paper also reports chemical resistance test results of the epoxy sealant. The chemical resistance tests were conducted at 60 °C for 485 days in various chemical reagents. The testing showed the epoxy sealant provided suitable protection from oilfield brines, hydrochloric acid, sulfuric acid, formalin, ammonium hydroxide, and nitric acid solutions. It also showed that the epoxy sealant provided limited protection from sodium hydroxide, sodium hypochlorite, and chromic acid solutions. Finally, the results indicated that the epoxy sealant provided very limited protection from acetic acid, chlorinated hydrocarbon, and toluene solutions.

The paper also describes three general types of field applications where the epoxy sealant had been used with success including casing cementing, casing leak repair, and repairing long sections of corroded casing. In casing cementing with the epoxy system, the paper outlined some important issues. These included temperature information, mud removal, good centralization, and removal of water and water-based muds. Water and mud removal was addressed by using gelled diesel pre flush. For sealing casing leaks, determining leak location and temperature is important first step. Additionally, the magnitude of the leak is required to determine volume and amount of filler in the epoxy sealant. A retrievable bridge plug is placed 8 m below the leak and then covered with 2 m of sand. Then, the epoxy sealant is placed through a packer with a gelled diesel pre flush to remove water / water-based fluids. For repairing long sections of corroded casing, the paper introduced a technique of filling section with resin and drilling it out to essentially end up with an epoxy resin liner (instead of running conventional liner).

Dahl-Jorgensen, E. and Justnes, H., "Well Cementing Materials based on Thermosetting Polymers", 2nd Annual IADC European Well Construction Conference, June 11-13, 1991

This article summarizes the benefits of using a polymer over cement. Cementing is arguably the most important operation performed on a well. Primary goal being to achieve zonal isolation. Long term mechanical and chemical durability is also essential. Sometimes the needs of the well exceed the properties of the cement. Materials based on liquid monomers have been developed to meet these needs. Major differences between the monomer systems and cement – 1. The liquid portion of a mix cures to a strong, impermeable binding material, while the liquid phase of cement is water. 2. The monomer based material hardens quickly once curing is initiated reducing the changes of gas migration and lowering WOC. 3. The final material has far better compressive and shear bond strength and durability than cement. State of the art monomer based cementing system can be designed to cure at a range of 40°F-340°F.
In most cases, primary cementing is carried out satisfactorily using ordinary oil well cement, and there is no reason to replace it with expensive thermoset polymers. In three projects, the cost-effectiveness of these materials is being investigated.

1 – Cementing the conductor pipe in the upper part of the well with low temps (40-45°F)
2 – Regulating set time in deep wells with high temps (265-375°F)
3 – Development of materials for zonal isolation to reduce the influx of water in the well. This also includes development of a monomer system to be used in the static bottom hole temperature range of 160-265°F.

Also, primary cementing can be difficult in deviated wells where cement solids may settle out of the slurry leading to channels. Even if the solids in a monomer system settle, a channel would not be formed. Many areas require deviated and horizontal drilling to be economical. Also monomers may be useful in secondary cementing or squeeze operations to repair a micorannulus, correct a defective primary job, isolation abandoned pay zones, or temporarily isolate one reservoir formation in a multiple production zone well. A cement slurry may dehydrate during squeeze operations, the liquid in a monomer system can provide the necessary seal.

Overall – these projects represent novel areas of application of thermosetting, filled and unfilled resin materials. Polymer based materials are not expected to replace ordinary oil well cements as a bulk material, but may find applications in situations where better properties are required and where they prove to be cost effective.

Dale, Orie; "Cementing with Plastic Resins in California Oil Fields"; **California Oil World**, Volume 40, Issue 4, February, 1947; pp 3-8.

The author provides a report on cementing with plastic resins in California oilfields. Specifically, he finds that thermosetting plastic resins have inherent properties that are useful for specialized phases of oil well cementing. Plastics are recommended for jobs where Portland cement is inadequate. At the time this paper was published, three particular plastic were available, e to cover the heat range from 70˚F to 300˚F. Setting times could be varied from 30 minutes to sixteen hours. The plastic resins were homogeneous fluids that were immiscible with brines and oils in the well and were chemically inert once they cured. The resins had a specific gravity near 1.2 at 60˚F and a viscosity comparable to that of S.A.E. 30 motor oil. Their fluidity allows the resin to enter sands or run through perforations in pipe and minimizes squeeze pressure

It was found that water-based colloidal drilling muds had a major negative impact on the liquid plastic because it was unable to penetrate or bond to the filter cake. For this reason, mud must be cleaned from the area to be sealed as well from adjacent sites from which it could migrate and spoil the job. Oil-based muds, water, and brine had no deleterious effect. It was also discovered that placement at the source of water entry was vital since the plastic would seal a productive sand if misapplied.

The plastic resins could be placed by means of a positive displacement dump bailer or by pumping and displacing through tubing. Controlled penetration of the plastics into sand of a given permeability can be effected by the addition of fillers.

While the material has good bonding properties and strength, its entry into sands to form an impervious solid means that a plugging job need not depend on bonding alone.

The paper provides no clues as to the chemistry of these "liquid plastics".

Dartez, T. R. and Jones, R. K., U.S. Patent No. 5,314,023; "Method for Selectively Treating Wells with a Low Viscosity Epoxy Resin-Forming Composition"; May 24, 1994

This patent describes using epoxy resin to selectively remediate wells; e.g. plugging permeability, shutting off water, plugging gravel packs, or repairing casing leaks. The resin has long pot life, is thin, and is immiscible with aqueous well fluids. The patent describes placement methods using dump bailers or pumping through jointed or coiled tubing.

Decomworld, “Resin Makes GoM Debut with Permitted Lower Abandonment”, March 30, 2016

This article reports use of an epoxy resin to seal a lower producing zone in a Gulf of Mexico well. A downhole obstruction prevented traditional placement and squeezing of cement. Resin would not bridge or dehydrate during placement through the restricted flow area. Thirty-five barrels of resin was pumped into the well and displaced to the lower zone depth. The fluid was then squeezed into the formation and allowed to set. The abandonment was successful.

Degouy, D. and Martin, M., SPE 20904, “Characterization of the Evolution of Cementing Materials after Aging under Severe Bottomhole Conditions”, SPE EUROPEC 1990, October, 21-24, 1990

Characterization of the Evolution of Cementing materials After Aging under Severe Bottomhole Conditions –This paper describes the characterization of commonly used cementing materials such as cement as well as potentially useable, such as thermosetting resins as they cure and age over long periods of time under high temperatures and pressure. Primarily, effects to compressive strength, permeability, and physical structure were studied. The resins studied in this paper were organic phenolic-resin-based compositions. The first resin was a phenol/formol composition and the second resin was a phenol/formol/furan composition. These systems are deemed useable from less than 160°C and from 140-200°C, respectively. At 200°C, the resin systems performed well, showing to maintain a low permeability even after a year of exposure. However, there were large fissures noticed internally in the resin and with prolonged exposure, communication could ensue. Overall the organic resins maintained more satisfactory compressive strength and permeability characteristics than conventional cements, at least up to 200°C.

Edgely, K.; Sabins, F. L.; and Watters, L. T.; DOE Technical Report, “Supercement for Annular Seal and Long-Term Integrity in Deep Hot Wells “DeepTrek”; DOE Award Number DE-FC26-02NT41836, August 31, 2005

The purpose of this project is to formulate a “Supercement” designed for improving the long-term sealing integrity in HPHT wells. Phase I concentrated on chemistry studies and screening tests to design and evaluate Portland-based, hybrid Portland, and non-Portland-based cement systems suitable for further scale-up testing. Phase II work concentrated on additional lab and field testing to reduce the candidate materials list to two systems, as well as scaleup activities aimed at verifying performance at the field scale. Phase II was extended thorough a proposal to develop additional testing capabilities aimed at quantifying cementing material properties and performance that were previously not possible. Phase III focused on bringing the material(s) developed in previous Phases to commercialization, through Field Trials, Cost/Benefit Analysis, and Technology Transfer.

Extensive development and testing work throughout the project led to Phase III commercialization of two very different materials:

- Highly-expansive cement (Portland-based), patent pending as “PRESTRESSED CEMENT”.
- Epoxy Resin (non-Portland-based), patent pending. Trade name is Ultra Seal-R.

In Phase III, work concentrated on application of the Supercement materials in various increasingly-challenging wells. Previous testing revealed that PRESTRESSED CEMENT, when applied in weak or unconsolidated formations, tends to expand away from the central pipe, restricting the applicability of this material to competent formations. Tests were devised to quantify this effect so the material could be applied in appropriate wells. Additionally, the testing was needed because of industry resistance to expansive cements, due to previous marketing attempts with other materials that were less than successful. Field trials with the Epoxy Resin currently numbers in the hundreds of jobs at up to 295 deg F, with a large percentage being completely successful.

Both the PRESTRESSED CEMENT as well as the Ultra Seal-R represent materials fulfilling the objectives of the DeepTrek project.

Endeavor Management, JIP invitation, "Subsea Decommissioning Joint Industry Project" www.endeavormgmt.com, 2015

Endeavor has initiated a joint industry project addressing subsea decommissioning. One issue covered in the work is use of resin to replace cement in plugging and abandonment operations. Noting that resins are costly, a stated project goal is to assess resin cost and performance compared to cement and to determine true cost of resin considering performance benefits.

Foianini, I., Frisch, G., and Jones, P.; "Successful Identification and Bond Assessment of Epoxy-Based Resin Cement Behind Production Casing: Integrating Cementing Technology with New Log Interpretation Methodology to Provide an Innovative Well Integrity Solution"; 55th annual SPWLA Logging Symposium; May 18-22, 2014

This article discusses a case study were 11.5 ppg epoxy resin was used to cement the first stage of a two stage job for a disposal well's production casing. The paper highlights epoxy resin cement (they call resin a "cement" but seems to be just resin with inert weighting agents) benefits to mechanical properties, chemical resistance, and immiscibility. It does reference one test that it shows the shear bond of cement was increased 6x by adding a resin coating to the interface. The paper then goes into detail about the 240 bbl resin cement job then the effort involved with trying to confirm resin placement with cement evaluation tools. To evaluate the resin they ran both a CBL and ultrasonic scanner. The CBL showed largely conflicting results and no real conclusions could be drawn from the log. The ultrasonic scanner identified the resin's acoustic impedance was between 3-4 MRayls and the author was able to develop specialized interpretation methods to identify flags that show the presence of resin in the annulus

Fraser, W. M., U.S. Patent 4,415,269; "Device for Providing a Reinforced Foam Lining for Well Bore Holes", November 15, 1983

This patent describes the device and method for providing a reinforced foamed resin lining for wellbores. The device consists of and upper and lower housing. The upper housing consists of an electric motor and the electronic components necessary. The lower housing consists of chambers housing the resin components and mixer. The method involves placing a length of perforated pipe at a desired depth in a wellbore. Then, the downhole foam generating device described by the patent is lowered inside this perforated pipe. The foam generating device is activated and the components are mixed downhole under pressure. The foamed resin is then dispensed into the perforated lining, filling the voids between the perforated pipe and the side of the wall. The device is removed, and the resin is allowed to expand and set. A drill is then paced through the section, leaving a hollowed cylinder of hardened resin foam.

Gunnarsson, B.; Tonnesen, S. H.; Olsen, E; and Leong, Y.; "New Tool and Sealant Technology Expedites Annular Isolation Tasks"; **Journal of Petroleum Technology**; July, 2016; pages 20-21

This paper reports a successful application of a tool to precisely place a proprietary epoxy sealant into an annulus. This precise placement can address issues such as thief zones, high water cuts, or failed well barriers thereby postponing or eliminating need for recompletion. The tool perforates the casing and injects small epoxy sealant volumes (70 liters was noted in the example) into the annulus to create a seal. Tool can be deployed using electrical wireline or electrical coiled tubing. During the operation, the tool locates exact point specified for plug placement, perforates the casing, and injects premixed sealant while monitoring injection rate and pressure. Injection rate for the subject treatment was 0.5 l/min.

The epoxy sealant's rheology enables injection into a gravel pack or a cement matrix. It is reported to function in applications with possible water cross flow.

Three successful plugs were set during the field trial with total placement time of 24 hours per plug.

Hefly, D. G. and Cardwell, P. H., "Use of Plastics in Water Control" Petroleum Management, Volume 15, Issue 3, Pages 51-54, 1943

This paper is a very early review of the use of plastics in water control. Examples of liquid plastics that were cited included unpolymerized styrene, vinylidine chloride, partially condensed phenol-formaldehyde, vinyl esters, and the ester of maleic acid with diethylene glycol. The authors also report that the usable range of many of the liquid plastics is only 30˚F but this can be adjusted chemically. This was demonstrated with reference to an unidentified plastic used in a well in the East Texan field. It was also reported that over 225 such treatments were made in that area prior to November 1, 1943. A review of data from 100 wells found that 65 had complete water shutoff, 18 had the water production reduced by 50% while in only 17 wells was the water reduction less than 50%.

The procedure for applying the liquid plastic involved determining the distance that the well needs to be plugged back from well data and then calculating the quantity of liquid plastic necessary. This quantity of liquid plastic is then applied with a pump bailer and allowed to harden. A measuring line is run to determine the fill up level. If it is less than desired, the procedure is then repeated. It was found that, on average, the East Texas Field required about 25 gallons of plastic.

Jones, P. J.; Hundt, G.; Karcher, J. D.; and Guillory, B. N.; World Patent Application Publication No. 2015/034,473 A1; "Epoxy resin formulations containing an impact modifier fur use in subterranean wells"; September 4, 2013

The impact modifier is to keep a resin from becoming fractured when struck by a force, such as a hammer at low (50-80°F) temperatures. The resin formulation includes a liquid hardenable resin, a liquid hardening agent component and the impact modifier. The liquid hardenable resin may include diluents (reactive or not), solvents, and may be emulsified in an aqueous state. The liquid hardening agent may also include accelerators, silane bonding agents, and solvents or diluents. The impact modifier is selected from a group of polyethyleneglycol or polypropyleneglycol having a functionality selected from the group consisting of: glycidyl ether, epoxide, carboxylic acid, and anhydride. The polyetheleneglycol has 2-1,000 monomeric units. For example, the incorporation of polyethylenelgycol diglycidyl ether ("PEGDGE") into epoxy resin formulations has resulted in substantial improvements in impact resistance

Knudsen, K.; Leon, G. A.; Sanabria, A. E.; Ansari, A.; Pino, R. M.; SPE 177430, “First Application of Thermal Activated Resin as Unconventional LCM in the Middle East”, SPE Abu Dhabi International Petroleum Conference, November 9-12, 2015

This paper describes thermal activated resin as a particle free, multicomponent polymer resin based liquid plugging material with a curing process activated by temperature. Thermal activated resin has a low (adjustable) viscosity and set mechanical properties which far exceed that of traditional cements, and ageing tests indicate that mechanical properties do not diminish over time. Some properties of the thermal activated resin are: Specific gravity 1.03-1.05, density 0.75-2.5 g/cc, viscosity 10-2000 cP, set time 3 min – as long as required, temperature range 48-275 °F, temperature resistant to 896 °F. Thermal activated resin has wide range of applications such as: loss circulation material, casing leak repairs, elimination of pressure build up in casing-casing annulus, plugs for P&A, fast setting kick off plug, zonal isolation, casing cementing, control line plugging and inflatable packer fluid, sand consolidation, and multilateral strengthening. The paper also compares thermal activated resin to traditional cement in table below.

Properties	Thermal Activated Resin	Traditional Cement
Water Permeability, mD	< 0.5	1,600
Compressive Strength, MPa	77	58
Flexural Strength, MPa	43	10
Failure Flexural Strain, %	1.9	0.32
E-Modulus, MPa	2,240	3,700
Tensile Strength, MPa	60	1
Density, S.G	0.75-2.5	1.5+
Right Angle Setting	Yes	No

The paper also describes a case history of the fast-setting polymer-based, thermal activated resin for successful treatment of heavy mud losses to the formation in wells located in offshore gas fields in the Kingdom of Saudi Aramco. Total downhole losses were encountered while drilling 12 ½ inch open hole at 10,714 ft, showed more than 300 BPH losses. Several conventional LCM and cement plugs were pumped without success. The BHT was 194 °F and the mud weight was 152 pcf. 50 BBL of thermal activated resin slurry was prepared in a batch mixer with a set time of 10-15 minutes at 194 °F. The resin plug was spotted through drill pipe at 500 ft above the loss zone at 4-4.5 BPM with a cement unit, followed by 10 BBL of 152 pfc mud. When the resin slurry reached 50 ft above the BHA, the pump rate was reduced to 2 BPM. Then, they displaced out thermal activated resin slurry plus safety factor margin mud volume with dynamic losses rate. Pumping was stopped when the resin slurry reached the loss zone and allowed to cure. Full returns were confirmed and the thermal activated resin plug was tagged with 10,000 lb on the bit and then drilled out at 100 ft/hr.

Kyu-Seok, Y., “Polymer Concrete as Construction Materials”, Int. J. Soc. Mater. Eng. Resour. Japan. August 25, 2010.

This report describes several important aspects of polymer concrete (PC) in comparison to cement concrete, primarily with respect to construction materials. PC mixture composed of aggregate, filler, and polymeric binder. It is made by fully replacing hydraulic cement in conventional concrete with polymeric binders such as liquid resins. Examples of the resins listed were polyester, epoxy, PMMA, and polyurethane. The report listed generic data comparing Portland cement concrete to PC. PC had far superior mechanical properties including compressive strength, flexural strength, tensile strength and elasticity. The report showed a chart demonstrating the effects of temperature on the compressive strength of PC. The compressive strength reduced significantly with temperatures above 40°C. The report also had a table of chemical resistance of the various types of PC; it showed epoxy resin PC was the best and polyester PC was the worst (furan and acrylic were in the middle); while all types of PC were superior to Portland cement concrete.

Leal, J.; Brown, D. D.; Watters, J. T.; McDaniel, C.; and Meade, C.; "Packer Isolation in Hurricane-Damaged Well Sealed Using Innovative Resin Application"; AADE-16-FTCE-64; 2016 AADE Fluids Technical Conference and Exhibition; Houston, TX, April 12-13, 2016.

This paper describes application of an epoxy sealant to seal a damaged offshore well. The well casings were sheared off below the mud line (210 feet water depth) by a hurricane leaving no direct access to inject into the well. Three separate barriers were set in the well using the epoxy. With no way to inject or displace fluid into the well, the sealant was fed into the appropriate well annulus and allowed to fall to the lowest point. Since the resin was cohesive and not altered by surrounding water, fluid resin of higher density than the well fluid, when introduced into the desired annulus, would fall through the bine present in the annulus, settle to the bottom of the annulus where the plug was desired, reform into a contiguous fluid plug, and set to form a barrier. This operation was successfully applied in three different well points of the well in order to establish control and resume normal abandonment operations. Resin hardner concentration was adjusted to provide ample time for falling through brine to the desired depth and then setting quickly once in place.

Oil&Gas UK, "Guidelines on Qualification of Materials for the Suspension and Abandonment of Wells", Issue1, July 2012.

This first issue of Oil&Gas UK lists presents functional requirements for permanent well barriers and discusses potential barrier failures and their causes. Additionally, the document defines types of materials considered to be well sealants and outlines a pathway for developing barrier performance criteria. Three types of polymer materials are discussed as barriers:

- Thermosetting polymers (resins)
- Thermoplastic polymers
- Elastomeric polymers

Experimental work plans for assessing each material class's barrier performance are presented.

Onan, D. D.; Chatterji, J.; and Cromwell, R. S.; US Patent 6,006,835; "Methods for Sealing Subterranean Zones using Foamed Resin"; December 28, 1999

The patent describes an improved hardenable corrosion resistant sealant composition having improved elasticity and ductility properties. Methods of utilizing these compositions are also discussed. The sealant is described as an epoxy resin comprised of a product of the condensation reaction of epichlorohydrin and bisphenol A, an aromatic hydrocarbon diluent, a plastic fixer (silane family), a hardening agent, a foaming agent, and a compressible gas. Essentially, the patent describes the process of designing and making a foamed epoxy resin for the purpose of providing a sealant with enhanced ductility and elasticity. The resin component is a bisphenol A that has a molecular weight between 200 and 1000, preferably around 340. The liquid diluent is an aromatic hydrocarbon that has the sole purpose of reducing the viscosity of the resin and make it pumpable. The diluent is usually added in at around 25% to 50% by weight of epoxy resin, preferably at 27%. The plastic fixer is used for enhancing the bonding strength of the epoxy resin. It is of the trimethoxysilane family and is utilized in the 0.01% to 5% by weight of epoxy resin, preferably at about 0.65%. The hardening agents described are from the amine, imidazole, and anhydride family. The preferred hardening agent is 2-ethyl-4-methyl imidazole and is used at about 57% to 60% by weight of epoxy resin, preferably at 58%. The foaming agent is a fluorocarbon surfactant. Fluorocarbon surfactants are used because they do not adversely react with the epoxy resin, as shown by the data table in the patent. The foaming agent is used from 1% to 12%, depending on the foam quality desired. This patent covers densities ranging from 6 ppg to 16 ppg. Higher densities are obtained using filler materials, usually from the crystalline silica group and having a particle size distribution from 10 to 20 microns. The filler is typically used in a range of 10% to 200% by weight of epoxy resin, preferably around 150%.

Ostroot, G. W. and Donaldson, A. L., “Sub-Surface Disposal of Acidic Effluents”, SPE 3201, 1970 Evangeline Section Regional Meeting of SPE, Lafayette, LA, Nov. 9-10, 1970

This paper presents design protocols for chemical disposal wells. Well sealants are considered critical since many chemical effluent streams are corrosive to Portland cement. The paper recommends a resin-gypsum cement (assumed to be Hydromite) or an epoxy resin (assumed to be EPSEAL Sealant) to provide durable sealants when exposed to acids.

Rahal, A, S, and Havens, J. H.; “Low Void Concrete Mixtures”, **Cement, Concrete, and Aggregates**, Volume 1, Issue 1, Pages 25-37, 1979

The authors report a study to modify concrete mix-design formulas to supplant all water over and above that needed for hydration with a non-evaporable liquid material. Several polymeric materials, were used, Success was achieved with two latex resins and one epoxy resin. The use of these materials in concrete resulted in improved strength, reduction of air voids and permeability, and enhancement of resistance to corrosive chloride salts.

The following characteristics were described as necessary to achieve successful water replacement:

1. The materials should be a liquid soluble that is soluble or emulsifiable with water and have a viscosity similar to water or light oil. In all cases water should be the continuous phase and the disperse phase should remain dispersed throughout the concrete-mixing process.
2. Be a liquid which would eventually solidify: for example, a latex, epoxy, or a similar material. 3. Solidification should take place within a reasonable time after mixing and the material should not weaken the strength of the hardened concrete.

Three latex polymers were tested but only two, Dow Latex Modifiers A (styrene-butadiene) and B (75% Saran 25% Styrene-Butadiene), were considered successful. Note that the latexes were stabilized with a polydimethylsiloxane-based non-ionic surfactant A DuPont chloroprene latex was unsuccessful because it hardened too fast making placement of the concrete very difficult and the hardened concrete exhibited low strength. The epoxy-type polymer that was successful was a special formulation developed by Celanese Coatings Company of Louisville, Kentucky. This EPI-TOP, PC-10 Epoxy was a Liquid, Bisphenol A Epoxy Resin stabilized with water-dispersible surfactants.

The latex and epoxy concretes had significantly higher flexural and compressive strengths than the control mix. The Dow Latex Modifier B had the highest strength. The latex mixtures
had the lowest permeability (measured zero for all specimens). Although more permeable than the latexes, the epoxy had half the permeability of the control mixture (Class A cement).

Sabins, F. L. and Watters, L. T, "Cement Alternative Has Unique Properties", E & P Magazine, June 4, 2007

This article compares performance of epoxy resin sealant to that of Portland cement. Epoxy advantages include:

- Cohesive—can be gravity displaced through lighter aqueous fluids
- No gel strength—prevents gas flow
- Permeates gravel packs
- Mechanical properties

5.3.3 Application examples from GoM wells illustrate the sealant's utility.

Singhal, R.K.; Bahuguna, V. K.; Kumar, R.; Katiyar, A. K.; Kumar, A.; Prasad, U. S.; and Lal, C.; PETROTECH-2007 Paper No. 3-2-239; "Selective Water Shut-off Treatment By Resin-Polymer Technology First Ever in Mature Sandstone Reservoirs Of Geleki Wells of Assam Assett: A Successful Case Study", Seventh Oil and Natural Gas Corporation LTD International Oil and Gas Conference, January 15-19, 2007

The oil industry is facing major problems of water production from most of the oil producing wells, producing 3 bbls of water for every 1 bbl of oil in depleted reservoirs. The best solution according to this research is water soluble resin polymers forming in-situ strong hard stable gelled masses. They are simple to apply, versatile, and widely available. This paper describes the outcome of lab findings and case history of 2 successful water shutoff applications in the wells of Geleki oilfield.

Excessive water production can lead to premature abandonment of a well if not corrected. This compromises the reservoir recovery and causes an increase in field development and expenditure because of the need to drill new wells for access and for handling of produced water. Conventional solutions include cement squeezes, sodium silicate gel placement, and polymer gel treatment; these techniques are met with varying success. The technology needed can withstand high extrusion rates, and a phenol-formaldehyde resin system has been developed that has been successful in water shutoff. This paper discusses a new thermosetting chemical comprising indigenous resin polymer and in-house developed catalyst. The application temperature is 70°C.

Case history 1: Well was drilled in 1991, it was non-flowing by 1999 due to high water cut. The water interval was identified as the bottom most interval associated with the coning/channel. The job was planned with a work over rig. Prior to execution, cement retainer was set for selective gel placement. Job was executed Dec 2005. 6m3 of polymer solution was followed by cement tail-in and kept the well for shutting in under pressure. After shut in period, well was opened and perforated the interval. On activation, the well produced oil with 47% water cut, which decreased to 0.4%. Water oil ratio was decreased, oil production was increased to 70m3 per day…prior to this, the well was not producing.
Case History 2: Well was producing with 90% water cut in august 2004, and has been non-flowing since Feb 05. Source of water was identified as bottom most interval. Job was planned with a workover rig, and utilized a cement retainer for selective gel placement. 7.2m3 of polymer followed by cement tail-in

and then the well was shut in. Economic analysis says the total chemical cost is $25K, paid back by 3-4 days of production. Additional oil gained after treatment is around 69,000bbl in 6 mo. Sustained production rate is continued.
The results indicate resin polymer system is effective as water seal off agent and compatible with sandstone reservoir. Technology is simple; treatment is effective and long lasting.

Urdaneta, J. A.; Arroyave, J. M.; Jones, P.; Amaya, J. L.; Coral, A.; and Hernandez, H.; "Novel Gas Shutoff Resin System for Well Abandonment Applications in Colombia: a Case History"; SPE-169400-MS; SPE Latin American and Caribbean Petroleum Engineering Conference; May 21-23, 2014.

This case study documents using epoxy resin to squeeze a micro annulus behind production casing. Permanent abandonment of the well was underway and the source of the gas leakage was determined to be the upper producing zone with leak path through a micro-annulus.. Wishing to effectively stop the leak at the source, the operator wished to apply a sealant better suited than Portland cement to penetration of small flow channels. A solids-free epoxy sealant was chosen for the squeeze fluid. The fluid does not build filtercake during squeeze placement, nor does it require filtercake to set to form the desired flow barrier. Rather, the fluid squeezed into the small flow channels sets to create the seal. Additionally, lab-scale testing that the fluid placed in underbalanced conditions would arrest gas percolation and set to form a barrier seal with no open residual flow path remaining. Five bbl of the epoxy was squeezed into perforations at roughly 6000 feet followed by a squeeze stage of Portland cement slurry. The annular pressure at the surface was eliminated.

5.4 Resin Combined with Portland Cement

5.4.1 Chemistry and Materials

Chatterji, J.; Kuhlman, R. D.; Cromwell, R. S.; and King, B. J.; EP 1 028 096 A2; "Cementing pipe strings in well bores"; August 16, 2000

Cements need to have the ability to isolate flows from below from reaching the wellhead throughout the life of activities of the well, including continued drilling and pressure and temperature cycles or changes. The novel cement is a mixture of hydraulic cement, an epoxy resin, a hardening agent for said resin, and water.

The resin is included 5-20% BWOC, preferably 8-10%. The resin is preferred to be a condensation product of epichchlorohydrin and bisphenol A – available from Shell as EPON Resin 828. This is preferred to be dispersed in an aqueous fluid. Many hardeners can be used, in ranges of about 0.01% to 0.02% BWOC. The product can be foamed if needed

Chappell, R. G. and Duncan, F. J.; U. S. Patent 3,850,651, "Cementing Compositions and Concretes and Mortars Derived Therefrom", November 26, 1974

Concretes and mortars having improved mechanical properties and resistance to chemicals are obtained by incorporating vinyl polymers or copolymers into cementing compositions and effecting curing at an elevated temperature. This invention relates to concretes and mortars derived from cementing compositions and incorporating polymers and copolymers derived from polymerizable vinyl compounds. We have found that concretes and mortars having improved mechanical properties and resistance to chemicals as well as good weathering properties may be obtained by incorporating vinyl polymers and copolymers in cementing compositions provided that the curing of the cementing composition is carried out at an elevated temperature, at least 40°C. Suitable polymers include those derived from acrylic esters, methacrylic esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, acrylonitrile, butadine and vinyl esters of long chain carboxylic acids. It is preferred to use alkyl acrylate/alkyl methacrylate copolymers.

The cementing composition may comprise materials conventionally used in the production of concrete and mortar such as hydraulic cements and aggregates. Reinforcing materials may also be included. The amount of polymer or copolymer is 5-50%, typically 15-35% by weight of the cement component. When tested all polymer containing blocks were resistance to freeze thaw cycles

A method of preparation of a concrete or mortar which comprises curing a cement composition of inoraganic cement, aqueous dispersion of a copolymer, cured at 40°C or hotter and at least 12 hr. can use various cements and polymers.

Kukacka, L. E.; Colombo, P.; Manowitz, B.; Steinberg, M.; “Concrete-Polymer Composites” Journal of the Structural Division Proceedings of the American Society of Civil Engineers. September, 1971.

This paper summarizes some work performed by Brookhaven National Laboratory. The authors summarizes a method to improve the performance of concrete set compositions with the impregnation of a monomer into the set concrete and then polymerizing the monomer with one of two methods. The first method is to use 60 gamma radiation. The second method is with chemical initiators. The advantages of this process over conventional concrete are numerous. Mechanical properties of the Concrete-Polymer Composite are greatly improved. Authors list improvements in compressive strength, tensile strength, flexural modules, modules of elasticity and others. In addition the chemical resistance of the composite is improved. There were four different types of monomers presented: methacrylate, styrene, polyester resin and epoxy resin. All the types of monomers indicated improvement in mechanical property.

Kukacka, L. E.; SPE 6611, “The Applicability of Concrete Polymer Materials for use in in Geothermal Environments”, 1977 SPE Oilfield and Geothermal Chemistry Symposium

This article discusses the feasibility to use 3 different types of concrete polymers to resist the material degradation in Portland cement when used in high temp geothermal wells. The first type was polymer impregnated concrete (PIC), this is basically using polymer to fill the void spaces of the cement. The second was Polymer concrete (PC) aggregate mixed with resin, and the third is similar to type one (PIC) but the polymer is only impregnated at the contact surface. The paper says polymer concretes have been used since the 1970s at temps up to 240C. The article then discusses how to make each of the polymer concerts and which different polymers have seen the best results. They mention 60% styrene, 40% trimethyoloropane trimethacrylate(TMPTMA); 50% styrene, 33 acrylonitrile, 17% TMPTMA. The article references some long term testing done at 220°C and shows that samples loss about half its compressive strength but starts to level off. Testing was also done of the resistance to strong acids and no deterioration was apparent

Lesage, Jean; U.K. Patent 1,506,223; “Hydraulic Cement Slurry, Concrete, and Mortar”; April 5, 1978.

This patent covers a composite material of cement slurry or concrete, an epoxy resin and hardener and a melamine-formaldehyde resin. The basis for this composite is cement and aggregate if used mixed with enough water to achieve hydration. With this water ratio, the cement is not fluid or pumpable. The paste is fluidized by an aqueous emulsion of epoxy resin and hardener and an aqueous emulsion of melamine-formaldehyde resin. Additionally, including a styrene-butadiene latex to the composite further improves performance. Properly formulated composite slurries required less liquid to reach a fluid state. Set property improvements included substantial increase in compressive strength, reduction in dimensional shrinkage and significant reduction in permeability.

Onan, D. D., U. S. Patent 5,738,463, "Elastomeric Grouting of Subsurface Condiuts", April 14, 1998

This patent provides a method for grouting an underground pipeline with a more flexible, stress-resistant cement system. The elastomeric properties of the grout system contain aqueous latex (SBR), a vulcanizing agent, and a vulcanizing activator. The system has a low initial viscosity so it can be pumped and then improved set mechanical properties to resist stresses post set. This patent covers grout compositions comprising the following: aqueous styrene/butadiene rubber latex, a sulfur vulcanizing agent, a zinc oxide vulcanizing activator, a sodium lauryl sulfate latex stabilizing surfactant, a dithiocarbamate compound vulcanization accelerator, a calcined clay extender and a polydimethylsiloxane defoaming agent.

Shearing, H. J.; U. S. Patent 3,977,889, "Cement Compositions", August 31 1976

Cement compositions setting readily below 0°C are disclosed which are prepared by mixing together and allowing to cure a hydraulic cement, an inert filler and an organic polyisocyanate, water and coal tar. The polyisocyanate is used in an amount to provide an excess of isocyanate groups over the tar itself. The weight of the tar and polyisocyanate together is at least equal to the water weight. This system shows advantages over conventional cement, known urethane, epoxy and polyester resin containing concretes. This patent relates to cement compositions that are isocyanate based and have improved low temperature setting properties.

This invention is a composition which is the product obtained by mixing together and allowing to cure a hydraulic cement, an inert filler, an organic polyisocyanate, water and coal tar. Hydraulic cement includes the class of structural materials which are applied in admixture with water and which harden or set as a result of physical and or chemical changes which consume the water present. An example of the cement is Portland cement, the inert fillers may include sand, gravel and other aggregate having low clay content, and others. Examples of organic polyisocyanates may include aliphatic diisocynates such as tetramethylene diisocyanate, hexamethylene diisocyanate and others. Various compositions showed advantages in providing flooring surfaces and pipeline coatings.

Shearing, H. J.; Australian Patent 459,245; "New Cement Compositions"; March 4, 1975.

The invention described here is a mix of Portland cement, silica, water, an isocyanate compound and one or more long chain hydrocarbons including polyesters and polyethers. This composite, which is optimally around 50:50 cement slurry to resin is fluid and self-leveling, but hardens quickly into a high-strength material with improved flexibility. Preferred resin is described as a reaction product of castor oil heated with a "hard resin". Example of "hard resin" is phenol formaldehyde. Resin is reacted with poly-functional isocyanates such as toluene di-isocyanate.

Totten, P. L.; King, B. J.; and Chatterji, J.; U. S. Patent No. 5,458,195; "Cementitious Compositions and Methods" October 17, 1995

The patent describes a method of creating cementing composite comprising conventional cement, a hardenable resinous material and up to 70% of drilling fluid. The cement material can be from the list of Portland cement, high alumina cement, slag, flyash, condensed silica fume with lime, micro fine cement and gypsum cement. The resin material is listed at phenolic resin or acrylic resin. The drilling fluid can be of a multiple variety of types. This invention will save the disposal cost of the drilling fluid in offshore drilling operations.

5.4.2 Properties and Applications

Bruckdorfer, R. A.; Jacobs, W. R.; Masson, J. P.; SPE 11980, "CBL Evaluation of Foam-Cemented and Synthetic-Cemented Casings". Society of Petroleum Engineers, 1983

This paper discusses the development of a short sonic sonde that can log 3 ft long sections of 4.5" diameter cemented casing, the successful use of the logging tool to evaluate 6 to 12 ppg foam cement and 9.5 to 13.1 ppg synthetic epoxy-based slurry, and a method to derive CBL interpretation charts for foamed and synthetic cement systems for accurate field interpretation of cement bond logs.

The experimental setup consisted of centralizing and cementing an 8" cardboard or PVC outer pipe outside a 4.5", 10.5 ppf casing using foamed Class G cement or an epoxy based synthetic cement weighted up with silica flour. The density was varied in each respective system by foaming varied volumes of base class G cement to a set volume or modifying the amount of weighting material added to the synthetic cement system. Compressive test samples for each system were poured at similar ambient conditions as the pipes and crushed to compare with measured attenuation rates and standard CBL interpretation charts. The cementing interpretation chart was then adjusted to reflect reasonable compressive strength values for the tested media.

The sonde, consisting of a transmitter and receiver mounted on a support rod, measures the attenuation of the E1 peak casing-borne signal. This signal was verified to be in agreement with reading provided from a standard logging tool used to log 10 ft sections cemented sections. Additionally, the 3 ft sonde showed good agreement with readings provided by a conventional cement system and measured compressive strengths of that system.

Evans, V.; "Corrosion Resistant Cements", **Anti-Corrosion Journal**, Volume 18, Number 12, Pages 15-17, December 1971

Paper gives general descriptions of industry challenges and needs for corrosion resistant cements. (It does not reference oilfield cements or cementing needs)

- Hydraulic Cements (mild corrosion resistance)
  - Portland / Cement Fondu / Supersulphated
- Latex Cements (mild corrosion resistance)
  - Add latex (either natural rubber/ synthetic resin latex / etc.)
- Silicate Cements
  - Complete acid resistance (exp hydrofluoric)

  - Resistant to strong oxidizing acids
- Sulphur Cements
  - Used in molten condition
  - Improve resistance to molten shock
  - Acid resistance (Up to 40% nitric acid)
  - Not suitable for use with solvents
- Resinous Cements
  - Most Advanced!!
  - Resinous Cement Types (Phenolic / Furan / CNSL resin / Polyester / Epoxide)
  - Gives a table of properties of each and their associated resistance.
  - Does speak about a departure from silica fillers to carbon fillers which improve mechanical properties.

Frisch, G. J.; Jones, P.; and Foianini, I.; PCT/US2013/078148, "Cementing Job Evaluation Systems and Methods for Use with Novel Cement Compositions Including Resin Cement",
December 28, 2013

A new logging processing unit has been developed that, combined with collected acoustic measurements from a logging tool, receives an indication of cementing regions and processes a cement log that is displayed to the user as a map of annular coverage. In this set-up, the cemented region may contain resin cement. The logging tools must contain a CBL and an ultrasonic logging tool for the processing to work correctly.

Gamwell, C. R. and Lewis, S.; International Patent Application Publication Number WO 2016,048303 A1; "Compatibilized Resin-Cement Composite Compositions"; March 31, 2016.

This patent application describes formation of a resin-cement composite to treat a well. The composite consists of resin, a cement, and a substituted or unsubstituted poly(alkylamine) compatibilizer. A preferred composite is 20 to 80 wt% curable epoxy, 80 to 20 wt% cement and 1 to 15% polyethylene imine. It is claimed that this composite forms a mixture that is stable and resistant to phase separation. The composite is said to be less expensive than resin but retains the properties of resin. Multiple uses of the composite as a sealant are disclosed including primary and various remedial applications.

Although epoxy resin is preferred, extensive classes of resin and thermoset polymers are disclosed. Portland cement is preferred, but multiple classes of hydraulic cement are disclosed. The application also states that drilling fluid, either aqueous or non-aqueous, can be incorporated into the mixture. Tensile strength of various compositions is presented as a performance metric. These data indicate significant increase in tensile strength with 30% PEI solution added to a 50:50 blend of resin and cement.

Gebauer, J. and Coughlin, R. W.; "Preparation, Properties and Corrosion Resistance of Composites of Cement Mortar and Organic Polymers" Cement and Concrete Research, Volume 1, No. 2, pages 187-210, 1971

The paper presents the summary of findings investigating the polymer impregnated concrete. The main emphasis of this paper was to present the corrosion resistance the Concrete-Polymer Composite. Various composites were tested in the following corrosion areas: freeze thaw cycling, water absorption over time, sea water exposure, sulfate solution exposure, dilute HCL exposure and hot air exposure at 200 F. The following monomers were tested: methymethacrylate, styrene and some derivatives of these monomers. The concrete was designed with various grades of Ottawa sand from Illinois. All of the various combinations of monomers with concrete performed better than the concrete by itself. Some polymers performed better than others and are summarized in the paper

Huerta, H. M.; Ramirez Lara, R. R.; Marin, M.; Kowaski, R.; Franco, E.; Ortega, R.; Ponce, G.; Hernandez, D.; and Ramos, J.; SPE 168223, “First Offshore Coiled Tubing Intervention Using a Catenary System in the Gulf of Mexico”, Society of Petroleum Engineers Coiled Tubing and Well Intervention Conference, March 25-26, 2014

This paper describes the analysis, execution and evaluation of a first-of-its-kind well intervention case where coil tubing operation were conducted utilizing a floating anchored vessel for auxiliary services in the Gulf of Mexico. A review of conventional CT interventions and rigless interventions in an 8 legged structure is provided and the limitations and disadvantages are discussed. The CT intervention using a catenary system addresses crane limitations and deck loading constraints that could not be addressed with jack-ups or semisubmersible platforms. The case history reviewed showed the successful deployment and execution of this system resulting in a well reassuming production of 3 kbopd after being shut in for 9 months.

Padgett, John C.; “New-Type Plug-Back Material Tried in Oil Wells”; **The Oil Weekly**, April 1, 1946; pp 30-31.

This paper provides an early report of field tests the application of a waterproof plastic cement as a plug-back material in oil wells. The author points out that the full significance of these tests would not be determined until several years of aging had passed. The plastic cement, known as oil well hydromite, is a mixture of a pulverized cementitious material and a powdered resin. This mixture is activated by addition of an accelerator and made into a slurry with water and applied using the dump bailer method. The setting time can readily be adjusted by the amount and type of accelerator used. Within 10 to 15 minutes after the initial set of the resin the compressive strength reaches 1500 psi. With time, this increases to 4000 psi. There is an expansion of 0.3% during the initial set that leads to tight bonding.

Field and laboratory tests demonstrated that the liquid penetrates porous and permeable zones and seals them off. The cementitious material restricts the penetration of the liquid phase to about 12% by volume.

The permeability of cores taken from solidified hydromite was found to be negligible within the limits of the test apparatus. They solidified material was also unreactive with substances ordinarily found in an oil well.

Halliburton has offered a product with the trade name Hydromite (not to be confused by an explosive of the same name!) that consists of calcined gypsum and urea formaldehyde resin. Several different accelerators are also available.

6 ACRONYMS AND ABBREVIATIONS

Al_2O_3: Aluminum Oxide
API: American Petroleum Institute
Bbls: Barrels
BHCT: Bottom hole circulating temperature (°F)
BHP: Bottomhole pressure (lb_f/in^2)
BHST: Bottomhole static temperature (°F)
BHT: Bottomhole temperature (°F)
Bis A: Bisphenol A resin
Bis F: Bisphenol F resin
BOPD: Barrels of Oil per Day
BPH: Barrels per Hour
BPD: Barrels per Day
BWPD: Barrels of Water per Day
CBL: Cement Bond Log
CEFAS: Center for Environment, Fisheries, and Agriculture Science
CO_2: Carbon Dioxide
cp: Centipoise
°C: Degrees Celcius
°F: Degrees Fahrenheit
ft: feet
ft/hr: feet per hour
ggbs: ground granulated blast-furnaced slag
g/cc: grams per cubic centimeters
gal/sk: Gallons per sack
H2S: Hydrogen Sulfide
HCL/HF:Hydrochloric acid/Hydrofluoric acid
HTHP: High Temperature High Pressure
hr: hour
l/min: Liters per minute
MD: Measured depth (ft)
Mpsi: Mega pounds per square inch
MRayls:Mega Rayls
OCNS: Offshore Chemical Notification Scheme
OCS: Outer Continental Shelf
OH: Open Hole
P: Pressure
P&A: Plug and Abandonment
PC: Polymer Concrete
PIC: Polymer Impregnated Cement
PMMA: Polymethylmethacrylate
POOH: Pull Out of Hole
ppg: Pounds per gallon
psi: Pounds per square inch

sg:	Specific Gravity
SiO_2:	Silicon Dioxide
vol:	Volume
WO:	Waiting On
WOC:	Waiting On Cement
TVD:	Total vertical depth (ft)

Supplemental Literature Review Report
Resin Compared to Portland Cement

Project No: E17PC00004

Date: June 13, 2017
Version: 1.0

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Table of Contents

1 PURPOSE

This project evaluates performance of various resin-based compounds as sealants for petroleum wells in the OCS. A report presenting results of Task 2: Review of Previous Work was submitted on April 6. The report identified and summarized a significant bibliography of publically-available documents concerning resin as well sealant. During May, additional pertinent publications were discovered and literature from resin suppliers was acquired. This supplemental report presents the additional information discovered along with summaries detailing relevance to this project.

2 CONCLUSIONS

The following conclusions are based on review of additional literature discovered after the original report was completed:

1. A total of 18 additional publications discussing resins related to well sealant applications are listed and summarized here.

2. Several publications focused on fundamental long-term well sealant performance and characterization of sealant durability. Not all of these publications were directed to resin sealants. Rather, they addressed general sealant performance.

3. Several more described general evaluation of resin compared to Portland cement as a well sealant. These evaluations were comprehensive including placement, stability and reaction to stress application over the life of the well.

4. 3 publications presented comprehensive performance screening (and in some cases cost/performance benefit analysis) of resins as alternatives to Portland cement well sealant. These comprehensive evaluations expanded beyond compressive strength and handling time to include additional sealant mechanical properties and assessment of the well components (casing, sealant, and formation) as a system.

5. Three papers describe evaluation of resin materials for applications other than well sealant. These papers describe adhesion testing and bond durability that may be relatable to well sealant evaluation.

6. The fundamental long-term sealant performance studies emphasize the lack of complete understanding of seal failure mechanisms and properties required to ensure seal durability. Lab evaluations of resins emphasize functional knowledge gaps created by the major differences between resins and Portland cement. Mechanical property comparisons illustrate resin's superiority, but other mechanical, thermal, and chemical issues arise that are outside the industry's normal focus. Additional testing, design, and performance criteria must be developed to ensure optimum sealant performance.

7. Two commercial websites listing resin sealants for well application were included. Few chemical suppliers and vendors list resin compositions specifically for well sealant application although they are noted as construction materials for high performance components or corrosion resistance.

3 DISCUSSION OF ADDITIONAL PUBLICATIONS

Classification and overview of the 18 additional technical publications chosen for this supplemental review is presented below. Complete citations and detailed summaries are presented in the **Bibliography and Summaries** Section immediately after this discussion.

3.1 Fundamental Sealant Performance

Bosma *et al* (1999 and 2000) present results of comprehensive, life-of-the-well analyses for sealant selection. The first study presents a detailed fundamental method of assessing stresses a sealant must withstand over the operating life of the well and engineering sealant design to withstand those stresses. This method does not address resins explicitly. However, the progression of the method leads to assessment of economic impact of sealant performance in terms of seal failure, remediation cost, and environmental impact. Similar logic is being employed in this project. The second paper builds on the first while expanding sealant materials to resins and elastomers. A laboratory test apparatus designed to measure early sealant gelation, reaction rates, and volume changes of sealant is introduced. Results of the second study indicate high-Poisson's ratio sealants are more durable.

Jones et al (2017) describe studying decomposition of epoxy resins via isothermal gravimetric analysis quantified using the Arrhenius equation. Analytical results were varied. No correlation between glass transition temperature and decomposition rate was evident. Increased pressure resulted in increased decomposition rate. Resin formulation durability did depend on chemical composition. Expected seal lifetime was estimated to be in excess of 100 years.

Sobolik *et al* (2015) describe another comprehensive fundamental study that addresses seal repair material durability for CO_2 injection wells. This detailed approach includes numerical models to simulate seal failure mechanisms and stresses caused by injection field operation. Broad ranging mechanical property correlation, failure mechanisms, and sealant composition is planned. No applicable information was presented in this paper, but the completed investigation should help characterize resin sealants for remedial applications.

3.2 Comprehensive Resin/Sealant Economic/Performance Evaluations

Morris *et al* (2012) assessed epoxy resins as alternative sealants to Portland cement in deepwater applications. Key resin benefits were identified for deepwater were density design and control, low rheology, and compatibility with synthetic based drilling fluid. While no quantitative cost comparison was performed, the authors did recognize that the high cost of resin was disadvantageous. They recommended using resin only in applications in which Portland cement had been proven an ineffective sealant.

Two extensive studies by Jimenez *et al* (2016 and 2017) cover life-of-the-well sealant evaluation methods described by Bosma *et al* (1999) with expanded consideration for resin sealants. The first paper describes utility of analytical tools (e.g. bond logs) diagnostics, modeling, and expanded design methods to optimize sealant performance. Resins are noted for improved mechanical properties and chemical resistance. Long-term monitoring of well integrity, even after abandonment, is recommended to drive continued sealant research. The second paper presents successful application of the previously-described method for an unconventional field drilling program. The design approach indicated use of an elastic cement (Portland cement modified with elastomers and fibers). Use of this sealant resulted in significant cost reduction for the field.

Shanbhag (2013) and Shanbhag *et al* (2015) describe performance of a thermosetting polymer based flexible synthetic cement. The sealant is comprised of one or more resins and crosslinking agents along with engineered reactive and inert particulates. Improved performance properties (flexural strength, compressive strength, tensile strength, fracture toughness, durability, and flex fatigue resistance) over those of Portland cement are reported. A successful field scale mixing test demonstrated the material's oil field potential.

3.3 Case Studies

Jones *et al* (2013 and 2014) and Ali *et al* (2016) describe three uses of epoxy resin in remedial work. The case studies cover a wide range of leak paths and placement methods. Detailed description of design and operational procedure are described. In all cases, the epoxy resin was successful.

Yami *et al* (2017) present a case study employing a resin-Portland cement mixture as one component of a two-stage primary cement application. This extremely high density cement fluid was used to increase the chance of achieving a barrier to gas flow following cementing in a field that experienced this issue routinely. A stage of the composite mixture containing around 6 vol% resin was pumped on two wells. Neither well experienced gas flow following cementing and drilling continued without incident.

3.4 Laboratory Measurements

Adhesion strength has been identified (Bosma *et al*, 1999) as a key mechanical property governing seal failure. However, little testing is performed with cement sealants to quantify a sealant's adhesiveness *in situ*. Saydam and Docrat (2007) describe a simple laboratory adhesion test for evaluating resin coatings to exposed rock substrate in mining applications. The method appeared to provide comparative data for adhesion of coatings, and it's utility for application to well sealants will be assessed. Centeno *et al* (2014) assessed epoxy coatings for the exterior of petroleum pipelines operating at high temperature (150°C). Durability of the thin films was evaluated after long-term exposure. None of the commercial coatings tested satisfactorily survived the exposure. Two test methods were employed that may be adaptable to well sealant evaluation. An adhesion test and a disbondment test measured each coating's ability to adhere to the pipe. These two ASTM test methods will be examined for adaptation to measure sealant adhesion and durability.

Recent work reported by van Eijden *et al* (2017) presents a suite of laboratory testing apparatus to evaluate sealant performance under simulated well conditions. This elaborate test suite includes measurement of sealant volume change with setting, and various scales of seal function tests performed under realistically-simulated well conditions. Results from these tests along with other mechanical property measurements can provide comparative performance evaluation for various well sealants. All example data were from Portland cement, but the authors envision testing other sealant varieties including resin.

3.5 Commercial Descriptions

Two web addresses included in this review list resin usage as oilfield sealant. One vendor, sbhpp, is a chemical company while the other, CannSeal^{TM} uses resin placed via a special tool to repair leaking well barriers.

The lack of resin suppliers listing commercial well sealants emphasized the fact that this application is not geared to off-the-shelf products. Rather, these materials are offered by service companies as components of a service package of sealant formulation and placement to affect a well barrier. Several chemical vendors contacted to provide resins for testing under this project reported that a significant number of commercially-offered resin well sealants are blends of two or more resin types. This further supports the observation that proprietary resin sealant formulas are protected by service companies.

4 BIBLIOGRAPHY AND SUMMARIES

4.1 Technical Papers

Ali, A.; Morsey, A.; Bhaisora, D.; and Ahmed, M.; SPE 183295-MS, "Resin Sealant System Solved Liner Hanger Assembly Leakage and Restored Well Integrity: Case History form Western Desert", SPE Abu Dhabi International Petroleum Exhibition and Conference, November 7-10, 2016.

This case study presents application of solids-free epoxy resin sealant to repair a leaking liner-top packer. The resin used consisted of epoxy resin and hardener. Handling time was around 3 hours at BHCT of 188°F. Twelve bbl resin was mixed and placed across the leak site. A total of 3.5 bbl resin was injected into the leak before maximum injection pressure was reached. The treatment was successful in repairing the leak. It was concluded that significant cost was saved since the only alternative to using resin was sidetracking the well.

Bosma, M.; Ravi, K.; van Driel, W; and Schreppers, G. J.; SPE 56536, "Design Approach to Sealant Selection for the Life of the Well", 1999 SPE Annual Technical Conference and Exhibition, October 3-6, 1999.

This paper presents a detailed fundamental method of assessing stress magnitude that a well sealant must resist over its operating life. The traditional method of quantifying sealant competency based on short-term compressive strength development. This method relies on modeling and diagnostics with operational assessment of well stresses over the operating life of the structure to quantify the stability of the well bore and the integrity of the sealant. The engineered sealant performance design method establishes a performance envelope for the sealant in the well. The performance criteria include mechanical properties, adhesion, shrinkage/expansion, and magnitude of stress application under *in situ* well conditions (HTHP).

This work does not discuss resin performance, but it does discuss potential need for alternative sealants with improved properties compared to Portland cement. The paper was included here since it outlines a comprehensive approach to assessment of well sealants relating properties to performance. This logic can be followed to the outcome of economic impact of sealant performance in terms of seal failure, remediation cost and environmental impact. This logic path will be followed during Tasks 6 and 8 of the project.

Bosma, M. G. R.; Cornelissen, E. K.; and Schwing A.; SPE 64395, “Improved Experimental Characterization of Cement/Rubber Zonal Isolation Materials”, SPE Asia-Pacific Oil and Gas Conference and Exhibition, October 16-18, 2000.

The authors report cement/rubber materials for use as zonal isolation materials (a thermally pre-stressed ‘rubber’ abandonment plug) and an apparatus and improved experimental methods for their testing. Notably the equipment and methods are useful for all sealing materials including Portland cement, resins, and elastomer. The reported characterization system can operate at pressures up to 1500 Bar and temperatures up to 300˚C and is capable of monitoring: (a) the progress of the ‘setting’ reaction of Oil Well Cements and/or thermosetting resins (b) the reaction behavior of these materials from the onset of gelling to their final set and (c) measuring the softening or swelling properties of thermoplastic and thermoset resins with changing temperature of upon the chemical setting of the materials as cross-linking reactions take place. The apparatus is also capable of the determination of volume changes at constant pressure or pressure changes at constant volume during the setting of cement or resin systems. In this manner, volumetric properties such as shrinkage or expansion of cements and resins or their compressibilities can be measured with times ranging from the onset of gelling to beyond the final set of the materials. The volumetric thermal expansion coefficient of set materials can also be quantified.

The authors provide clear examples that demonstrate that zonal isolation materials can lose their integrity as a consequence of stresses induced by changes in temperature or pressure within the wells and by external mechanical loading processes. They point out that these stresses are particularly prevalent in deepwater wells. Further, they discuss how the conventional criterion for choice of a material for zonal isolation, the compressive strength of a sealant, is insufficient to identify which sealant is most suitable for the effective annular sealing of a well. Instead, other mechanical properties such as its Young’s modulus, Poisson’s ratio, Tensile Strength, Shear Strength and Bonding Strength must also be assessed. The authors indicate that it is necessary to have a ductile zonal material that is kept in a permanent compressed condition during the entire well’s operational lifetime. The ratio of the Tensile Strength to Young’s modulus should be as high as possible, the Young’s modulus of the ‘cement’ should be lower than the rock and the Poison’s ratio of the sealing materials should be as close to 0.5 as practically attainable. The authors point out that traditional cement formulations are not sufficient to meet these requirements in all wells leading to the requirement of novel formulations such as resins, cement rubber composites, and in-situ vulcanizing rubbers and foams

Shell International‘s efforts to develop alternative materials for well abandonment are discussed. These are pumpable durable fluorosilicones and perfluoro-ether silicone elastomers. These are injected into a well after it has cooled to a suitable temperature. After the elastomer is pumped and allowed to set, the immediate vicinity of the borehole is allowed to heat up again to the normal bottom hole temperature (in the order of days). Due to the much larger thermal expansion of the elastomer plug compared to the rest of the completion (steel casing, primary cement sheath), the plug expands significantly more than the rest of the well, providing a superior seal. Experimentally, it was demonstrated by Shell that a 0.5 m long elastomer plug backed up by cement could withstand pressure differentials of at least 20 MPa (200 Bar) without any gas leakage.

Centeno, O.; Arellano, M.; Salazar, E,; and Fernandez, C.; NACE Paper No. 3650, “Degradation of Liquid Epoxy Resins at High Temperatures”, NACE Corrosion 2014, March 9-13, 2014.

This research focused on external epoxy coatings for petroleum pipelines operating at 150˚C. Commercial epoxy coatings are recommended to exhibit corrosion protection at this elevated temperature, but field results do not always support that recommendation. This laboratory study was conducted to assess epoxy film durability after long term exposure. None of the materials endured the testing. Significant oxidation contributed to failure of all samples (2 phenolics, 2 Novolacs and 1 epoxy resin-polyamide curative).

No direct comparisons to down-hole applications apply since the specimens were thin films heated in air. However, several test methods beyond the normal analytical techniques were employed to evaluate bonding. These techniques measured adhesion (ASTM D4541) and cathodic disbondment (ASTM G 42-11). These methods are being evaluated for potential adaption to resin performance in wells.

Jimenez, W. C.; Urdaneta, J. A.; Pang, X.; Garzon, J. R.; Nucci, G.; and Arias, H.; SPE 180041, "Innovation of Annular Sealants During the Past Decades and Their Direct Relationship to On/Offshore Wellbore Economics", SPE Bergen One Day Seminar, April 20, 2016.

This wide-ranging paper discusses the importance of achieving well integrity, the evolution of well sealants, the importance of diagnostics and design in producing durable seals, and the qualitative economic impact resulting from reducing well integrity failures. An evaluation of historical well integrity issues occurrence supports the need for investigation of alternative sealants. The work presents evolution of Portland cement as the predominant well sealant along with the mechanical and chemical performance issues Portland cement presents. A chronology of sealant improvements is discussed next including use of resins. Resins are noted as delivering improved mechanical properties and chemical resistance. The main thesis of the paper is successful use of analytical tools, diagnostics, and expanded design methods to optimize sealant properties. Several of these "life of the well" methods are cited.

The paper concludes that the documented issues of well integrity are costly and improvements can be achieved through the expanded design methods and optimized sealants. General, qualitative evidence of reduced well integrity issues and reduced remedial cost is stated. Long term monitoring and documentation of well integrity issues in both producing and abandoned wells is recommended to provide the basis for driving continued research to reduce well construction risks and improve production economics.

Jimenez, W. C.; Pereia, J.; and Matzar, L.; SPE188112, "Improving Wellbore Economics and Long Term Integrity by Optimizing the Design and Evaluation of Annular Sealants for Hydraulically Fractured Wells: A Case Study", SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition, Aprio 24-27, 2017.

This paper describes a field application of the method discussed in the paper summarized immediately above (Jimenez *et al*, 2016). While no specific discussion of resin as a well sealant, the paper does qualify the well integrity benefits of designing and correctly applying a sealant with improved properties for an unconventional field (multiple fracs and long horizontal sections). In the case study, use of an "elastic cement" (Portland cement modified with elastomers and fibers) as part of the engineering and design method delivered improved seal integrity. The paper describes the steps of the process and cites underlying theory. Quantified risk of seal failure with candidate sealants are compared over a broad operational range of well conditions providing a direct indication of sealant capability.

The paper concludes that the “life of the well” approach delivered significant cost reduction due to fracturing procedure modifications based on predicted well durability and the absence of seal failure occurrence requiring remediation.

Jones, P. J.; London, B. A.; Tennison, L. B.; and Karcher, J. D.; SPE 165669, “Unconventional Remediation in the Utica Shale Using Advanced Resin Technologies”, SPE Eastern Regional Meeting, August 20-22, 2013.

Application of epoxy resin sealant to repair failed cement seals in shale wells that exhibit gas migration. The flow channels to be repaired are very small, and Portland cement will not penetrate and seal the space. A solids-free resin system was developed for the process. The resin formulation contained resin, hardener, and accelerator in a newly-developed system that is compatible with water. Absence of solids promotes penetration of the resin into the flow channels to restore the seal.

The resin fluid was injected into perforations followed by cement slurry. The cement slurry bridged on entry into the perforations thereby ending the squeeze and blocking the resin in the annulus. Fluid volumes used in each squeeze operation were 10 bbl resin and 20 bbl cement.

Jones, P. J.; Karcher, J. D.; Ruch, A.; Beamer, A.; Smit, P.; Hines, S.; Olson, M. R.; and Day, D.; SPE 167759, “Riggless Operation to Restore Wellbore Integrity using Synthetic-based Resin Sealants”, SPE/EAGE European UnconventionalConference and Exhibition, February 25-27, 2014.

This paper documents application resin through coiled tubing to repair a breached packer in a well to be fraced after remediation. The epoxy resin was designed with appropriate density, viscosity, handling time, and mechanical properties to allow placement and seal of the packer breach. The resin was formulated without solids.

The resin was successfully placed through the coiled tubing into the packer breach. After setting, excess resin was drilled out from the casing using a coiled tubing drill. The remediation was pressure tested and fraced. Fracturing operation and subsequent flow test were successful with no indication of seal failure.

Jones, P.; Boontheung, C.; and Hundt, G.; SPE 184557-MS, “Émploying an Arrhenius Rate Law to Predict the Lifetime of Oilfield Resins”, SPE International Conference on Oilfield Chemistry, April 3-5, 2017.

The authors report using isothermal gravimetric analysis to study the temperature dependence of thermal decomposition of three epoxy resin mixtures. The employed resins and hardeners were not identified making the investigation irreproducible. Weight loss at a variety of temperatures were roughly first order with some deviations. Activation energies were determined according to the Arrhenius equation. The expectation that there should be a correlation between the glass transition was promulgated but the data from the three resin systems showed no such correlation. Further, counter to the authors’ model, increased pressure (450 psi) led to faster thermal decomposition as compared to unpressurized reactions. The authors concluded that the data must be suspect although it appeared quite reproducible, was collected for multiple points, and could reliably predict the decomposition rates at other temperatures. Finally, the paper concluded that, not surprisingly, the choice of resin components and compositions affect the decomposition temperature. The paper does indicate that it is possible to predict the effect of thermal decomposition in the absence of water, oxygen, or other reactive species on the lifetime of a resin plug in an oilfield.

Morris, K. A.; Deville, J. P.; and Jones, P.; SPE 155613, “Resin-Based Cement Alternatives for Deepwater Well Construction”, SPE Deepwater Drilling and Completions Conference, June 20-21, 2012.

Epoxy resins were assessed as cement alternatives for deepwater applications in this study. Resin performance was tested over temperature range from 90˚F to 225˚F and density range from 9.0 to 14.0 lb/gal. The resin’s benefits identified for deepwater application were density control, low rheology (similar to synthetic based drilling fluid) and compatibility with synthetic based drilling fluid. Solid suspension of the thermally thinning fluid was demonstrated with several weighting agents.

Dimensional shrinkage of set resin was noted, but the shrinkage did not seem to disrupt the bond between sealant and pipe wall. Resin was demonstrated to be compatible with up to 20% synthetic based fluid contamination.

Cost of resin compared unfavorable with cement. A possible remedy for this economic obstacle was to use resin technology judiciously only in applications in which Portland cement would not provide a reliable seal.

Saydam, S. and Docrat, Y. S., “Evaluating the adhesion strength of different sealants on kimberlite”, 11th Congress of the International Society for Rock Mechanics, 2007.

Adhesion of sealants used as “liners” in the mining industry to coat and seal the surfaces of mining excavations was evaluated using a simple adhesion test. Sealants included proprietary cement blends, cement-polymer blend, copolymers and epoxy resin. Results from this straight-forward, comparative test method showed promise for qualifying sealants. This technique will be compared to ASTM test methods mentioned above for evaluating adhesion strength of well sealants.

Shanbhag, R.; Melrose, Z.; Nutt, S.; Cleveland, M.; and Keese, R.; SPE-178454-MS, “Thermosetting Polymer Based Flexible Synthetic Cement for Successful Zonal Isolation in Thermal Wells-A New Approach”, SPE Thermal Well Integrity and Design Symposium, November 23-25, 2015.

Performance of a thermosetting polymer-based sealant designed for thermal and other high-stress-gradient wells is presented. The system consists of reactive and inert particulate fillers in a blend of thermosetting polymers. The paper references U. S. Patent 8,387,695, discussed below, which claims a wide range of materials and blends. Favorable placement design parameters and characteristics of the set composite are presented as illustration of the resin’s improved well sealant performance compared to Portland cement. Successful full-scale mixing demonstration using typical oilfield equipment confirms the sealant can be prepared in typical fashion. Well trials are being planned for this formulation.

Sobolik, S. R.; Gomez, S. P.; Matteo, E. N.; Dewers, T. A.; Newell, P.; Stormont, J. C.; and Reda Taha, M. M.; ARMA 15-290, “Geomechanical Modeling to Predict Wellbore Stresses and Strains for the Design of Wellbore Seal Repair Materials for Use at a CO_2 Injection Site”, 49th US Rock Mechanics/Geomechanics Symposium, June 28 through July 1, 2015.

This paper reports progress of a four-part experimental and numerical modeling study of CO_2 injection wellbore system stresses, seal failures and properties of remedial sealants to optimize seal repair. The study consists of four distinct elements: bench-top experimental model, bench-top numerical model, field-scale numerical model, and a wellbore scale model.

This extensive project plan employs the three numerical models, bench, field, and wellbore, to assess stresses produced on well sealants as a result of CO_2 injection. The experimental model and the bench scale numerical model coupled to it are describing sealant failure mechanisms and sealant mechanical properties governing seal durability. This modeling has produced failure mechanisms and defined leak paths requiring remedial sealant. The field scale model is shedding light on stress generation resulting from CO_2 injection. The wellbore model is designed to confirm sealant durability and failure in active wellbore. Additionally, the modeling suite is aimed at evaluation of nanoparticulate resin or polymer sealants to remediate failed annular seals.

The sealants of interest for repair materials include novolac epoxy, poly-sulfide-siloxane epoxy, and SBR latex. Nanoparticles to be studied include multiwall carbon nanotubes, nanoclay, nanosilica, and nanoalumina.

No direct information concerning resin performance was contained in this progress report. The results promised do have potential to add to the characterization of resins used as well sealants.

van Eijden, J.; Cornelissen, E.; Ruckert, F.;,and Wolterbeek, T.; SPE/IADC 184640-MS, “Development of Experimental Equipment and Porcedures to Evaluate Zonal Isolation and Well Abandonment Materials”, SPE/IADC Drilling Conference and Exhibition, March 14-16, 2017.

While this paper does not specifically address resin sealants, it does describe a suite of lab testing apparatus to evaluate sealant performance under well conditions. Examples of test results and interpretation are from Portland cement testing, but subsequent discussions with the authors confirmed plans to test resin sealants as well.

Expansion/shrinkage test apparatus addresses sealant volume changes in terms of pore volume, dimensional changes, pore pressure changes, and internal stresses. This comprehensive test device independently control and measure effects of both pore pressure and confining pressure on a sealant. The method quantifies bulk volume change, total volume change, pressure behavior and internal stress profile as the sealant sets and develops strength.

A series of other experimental set-ups are designed to measure a sealant’s function under simulated well conditions. The set ups cover range in diameter from 2 to 10 inches with both annulus and plug configurations. Test pressures range to 1500 psi and temperature maximum is from 210˚F to 325˚F. Sealant fluids are introduced into cylindrical test chambers, heated, and pressurized. Differential gas pressure gradient is applied after curing, and pressure/flow monitored across the sealant sample.

The authors’ stated intention of the paper was to announce the experimental facilities for evaluating commercially available sealants for P&A and zone isolation. Correlation of test results to field observation is anticipated as data is gathered.

Yami, A.; Buwaidi, H.; Al-Herz, A.; Mukherjee, T. S.; Bedford, D.; Viso, R.; and Hugentoblar, K.; SPE 185337-MS, “Application of Heavy Weight Cement-Resin Blend System to Prevent CCA Pressure in Saudi Arabia Deep Gas Fields”, SPE Oil and Gas India Conference and Exhibition, April 4-6, 2017.

The authors detail application of a resin-Portland cement blend as a component of primary cementing wells that exhibit sustained casing pressure after cementing. Epoxy resin and aromatic amine hardener comprised the resin which was mixed with cement slurry mixed at extremely high density (over 20 lb/gal). Resin:cement slurry ratio was approximately 6 vol%. Beneficial attributes expected from adding resin to cement included:

- Reduced permeability
- Reduced Young's Modulus
- Increased compressive strength
- Improved bonding.

These performance attributes were demonstrated via lab testing results.

Casings of two wells were cemented using the cement-resin blend. The blend was placed as one of two or three formulations placed in the second stage of a two-stage placement procedure. Cement was placed successfully and no post-job pressure was observed on either well.

4.2 Patents

Shanbhag, R. M.; U. S. Patent 8,387,695, "Compositions and processes for downhole cementing operations", March 5, 2013.

This patent claims a composite of a thermosetting resin and filler mixture as alternative to Portland cement in well cementing. The invention is reported to produce improved compressive strength, flexural strength, fracture toughness, tensile strength, flex fatigue resistance, and durability. Filler material can include a variety of organic and inorganic materials with a graded PSD. Resin materials listed range from epoxy to polyester, to phenolic and furan. Initiators and crosslinking agents are also disclosed. Specific properties of the sealant can be tailored controlling resin chemistry and filler type, loading and particle size. Fibers and nanoclays are also specified

Example performance is illustrated using unsaturated polyester resin, calcium carbonate filler, and chopped glass fiber. Another example composition is epoxy resin and sand.

Commercial Material Literature

https://www.sbhpp.com/products-applications/oil-gas, sbhpp web site.

This chemical company offers a wide range of polymers for oilfield application. Of particular interest is application of sbhpp resins as cement additives to improve adhesion, chemical resistance, and mechanical properties. Additionally, the description presents unspecified sbhpp resin as a cement alternative.

http://cannseal.com/products-and-services/, CannSeal^{tm} web site.

This website describes application of a tailored sealant precisely placed in the well using a wireline tool to locate, isolate, and establish injection path. No specific sealant chemistry is described, but the site reports that the sealant rheology and density can be designed for any well application. Examples of sealant application into cemented annulus, packer leak, gravel pack, etc. are listed.

5 ACRONYMS AND ABBREVIATIONS

ASTM: American Society for Testing and Materials
Bar: Unit of Pressure
Bbls: Barrels
BHCT: Bottom hole circulating temperature
CO_2: Carbon Dioxide
°C: Degrees Celcius
°F: Degrees Fahrenheit
HTHP: High Temperature High Pressure
Lb/gal: Pound per gallon
m: Meter
MPa: Megapascal
OCS: Outer Continental Shelf
P&A: Plug and Abandonment
psi: Pounds per square inch
SPE: Society of Petroleum Engineers
vol: Volume