



Reactive Sealant Technology as an Alternative Route to Zonal Isolation

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February 22, 2017



Outline

- Zonal Isolation
- Why Non-Portland?
- Types of Synthetic Resin
- Kraton “Liquid-to-Solid” Reactive Sealant System

Zonal Isolation

- Preventing communication of liquids and gases between zones downhole
- Environmental safety and long-term production depend on ensuring zonal isolation over the life of the well
- A cement sheath is the primary means of zonal isolation for most wellbores
- Complexity of wellbore architecture, cyclic stresses over the lifetime of the well, and temperature fluctuations can compromise the integrity of the cement sheath
 - Loss of isolation occurs through formation of microannuli and/or stress fractures in the cement sheath
 - Such small defects are difficult to detect and repair through conventional remediation techniques

Why Non-Portland?

- “Cement was a convenient and readily available substance when first pumped in the early 1900s. We have spent the last 100 years trying to make it work.” -Don Purvis
- “Materials and techniques that successfully achieve short-term zonal isolation are not always sufficient to maintain that isolation in the longer term.” -Craig Gardner
- Most commonly measured cement property is unconfined uniaxial compressive strength - this measured property does not directly apply to the performance of a cement sheath under confined downhole conditions
- Need a wellbore isolation material that is flexible, impermeable, and durable with high tensile strength

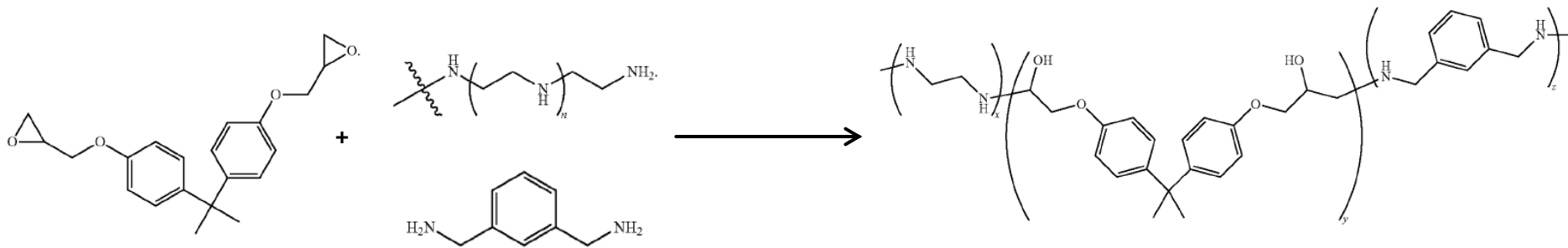
Why Non-Portland?

- Resin technologies can offer:
 - Higher compressive, tensile and shear bond strengths
 - Better tolerance to oil-based contamination
 - Solids-free solutions
 - Low viscosity; good for remediation and squeeze jobs
 - Tuneable solution state and solid state properties

Synthetic Resins

- Viscous liquids capable of hardening permanently
- Types:
 - Epoxy resin
 - Polyurethane resin
 - Melamine resin
 - Unsaturated polyester resin
 - Acrylic resin
 - Silicone resin
 - Acetal resin

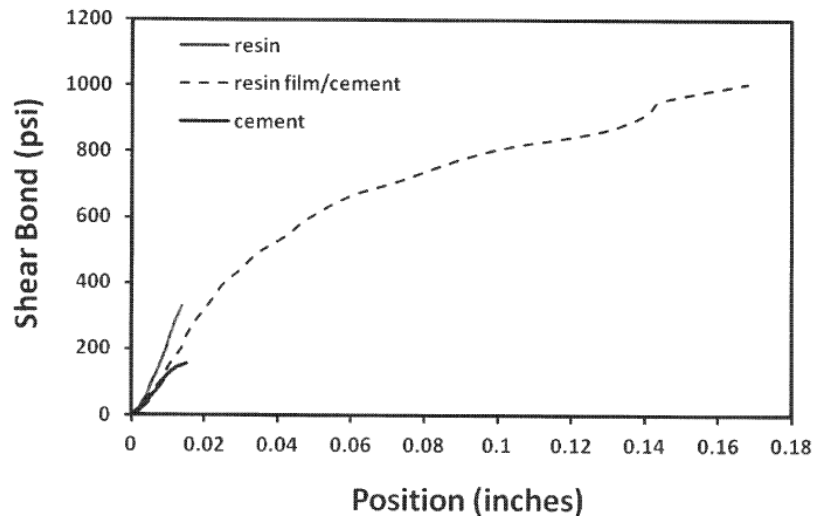
Epoxy Resin



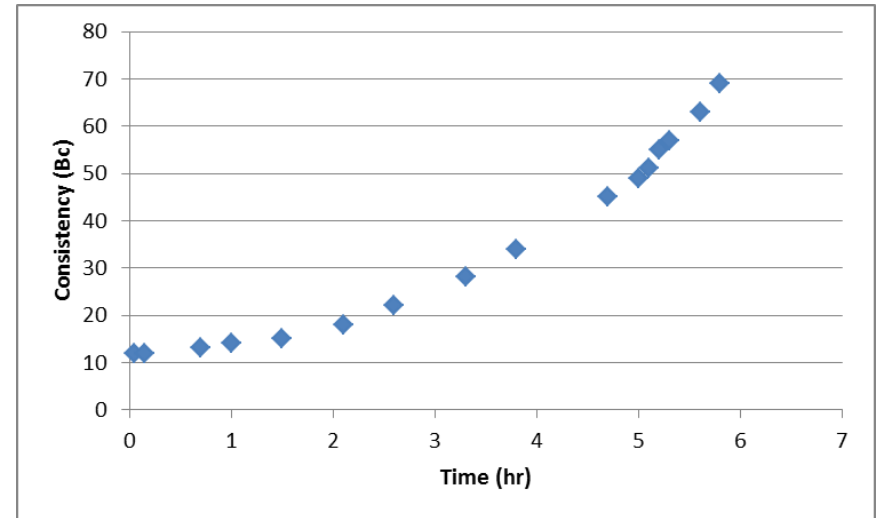
US9359547 B2

- A class of reactive polymers and prepolymers which contain epoxide functional groups
- Primarily diamines and polyamines are used as hardeners to make cross-linked networks
- Typically cured with stoichiometric or near stoichiometric amounts of hardener to achieve maximum physical properties
- Curing is an exothermic reaction
- Aliphatic epoxy resins are typically used as reactive diluents to reduce the viscosity of other epoxy resins

Epoxy Resin



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Adapted from SPE 155613

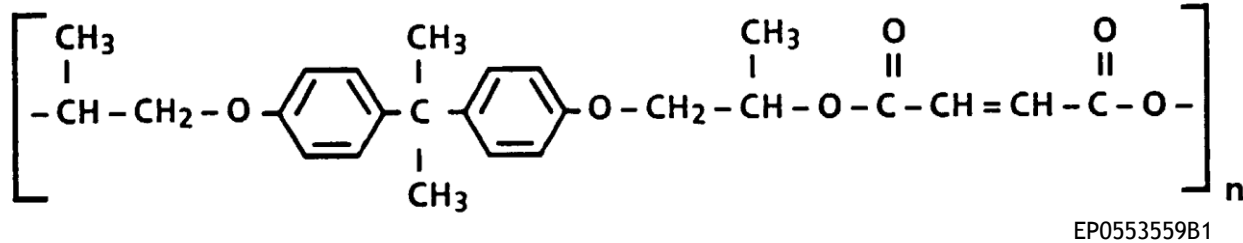
STRENGTHS

- Excellent adhesion
- Chemical and heat resistance
 - Resistant to hydrolysis
- Good-to-excellent mechanical properties

WEAKNESSES

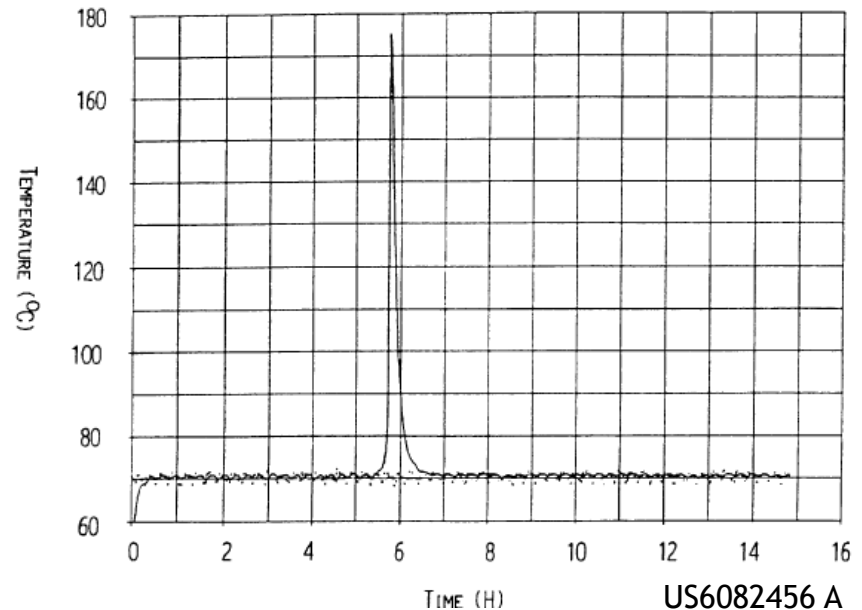
- HSE concerns related to the hardener component (primary diamines and polyamines)
- Reaction will progress step-wise, resulting in gradual increase in thickening time

Unsaturated Polyester Resin



- Thermosetting resins, can be aliphatic, semi-aromatic, or aromatic
 - Increasing aromatic content will increase glass transition temperature, melting temperature, thermal stability, chemical stability
- Copolymers are prepared by polymerizing one or more diol with saturated and unsaturated dicarboxylic acids (maleic acid, fumaric acid, etc)
- The double bond of the unsaturated polyester can then react with vinyl monomers, such as styrene, resulting in a three-dimensional cross-linked network
- This cross-linking is an exothermic free radical process, typically initiated through organic peroxides

Unsaturated Polyester Resin



STRENGTHS

- Most commonly used thermoset resin in the world; readily available
- Can be made from biorenewable resources
- Cure will be rapid once initiated

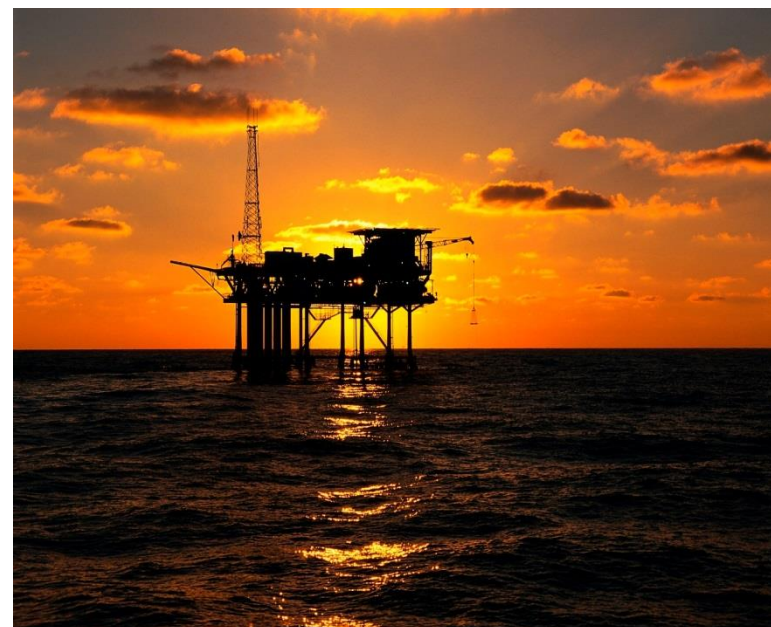
WEAKNESSES

- Polyester functionality is susceptible to hydrolysis in both acidic and basic conditions, as well as biodegradation
- Shrinkage and exotherm can be problematic

What is Liquid-to-Solid?

Liquid-to-solid reactive sealant material

- Looks/behaves like a **drilling fluid** when in the liquid state
- Can be **controllably cured** under downhole conditions
- Looks/behaves like a **cement** when in the solid state
- Benefits over existing technology:
 - Can be formulated to achieve an **extremely wide range of mechanical properties**
 - Because of tailorability, can be suitable for wide range of applications, from **zonal isolation** to **plug and abandonment**
 - Very **low solution rheology** possible, making it suitable for narrow margin wells
 - Much higher **tolerance to oil-based contamination** than Portland cement
 - **Solids-free solution** possible for remediation squeeze jobs and narrow annulus applications
 - Chemistry offers **good control over cure** and good **hydrolytic stability** as compared to other non-cement systems on the market today



Why Liquid-to-Solid (L2S)?

- Polymer network formed through **carbon-carbon bonds**, leading to greater chemical and thermal resistance than other chemistries
- **Low viscosity** fluid (30-40 cP)
- Incorporation of **elastomeric components into thermoset network** leads to lower modulus and ductility in cured material, resulting in tougher material
- Elastomeric components give ability to swell in presence of hydrocarbon — built in **self-sealing functionality**
- Good control over cure in terms of time and temperature — cure is a **right-angle set**

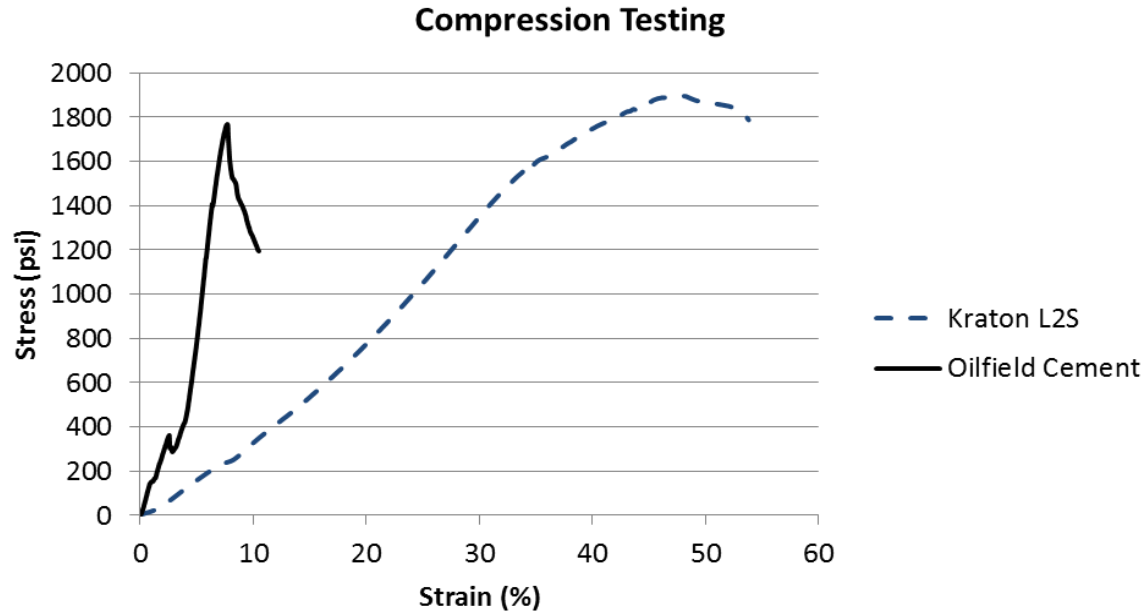
L2S for Zonal Isolation and Remediation

- *Application Requirements*
 - Zero shrinkage to ultimately form a competent seal
 - Low solution rheology for low ECD and remediation opportunities

KIC-16-050	40 °F	70 °F	150 °F
600 rpm	-	225	94
300 rpm	208	127	48
200 rpm	142	90	33
100 rpm	74	52	18
6 rpm	9	21	3
3 rpm	7	20	2
PV	-	98	46
YP	-	29	2
LSYP	5	19	1
10 sec	8	20	3
10 min	13	20	4

Weighted to 12.5 ppg with Barimite XF micronized barite.

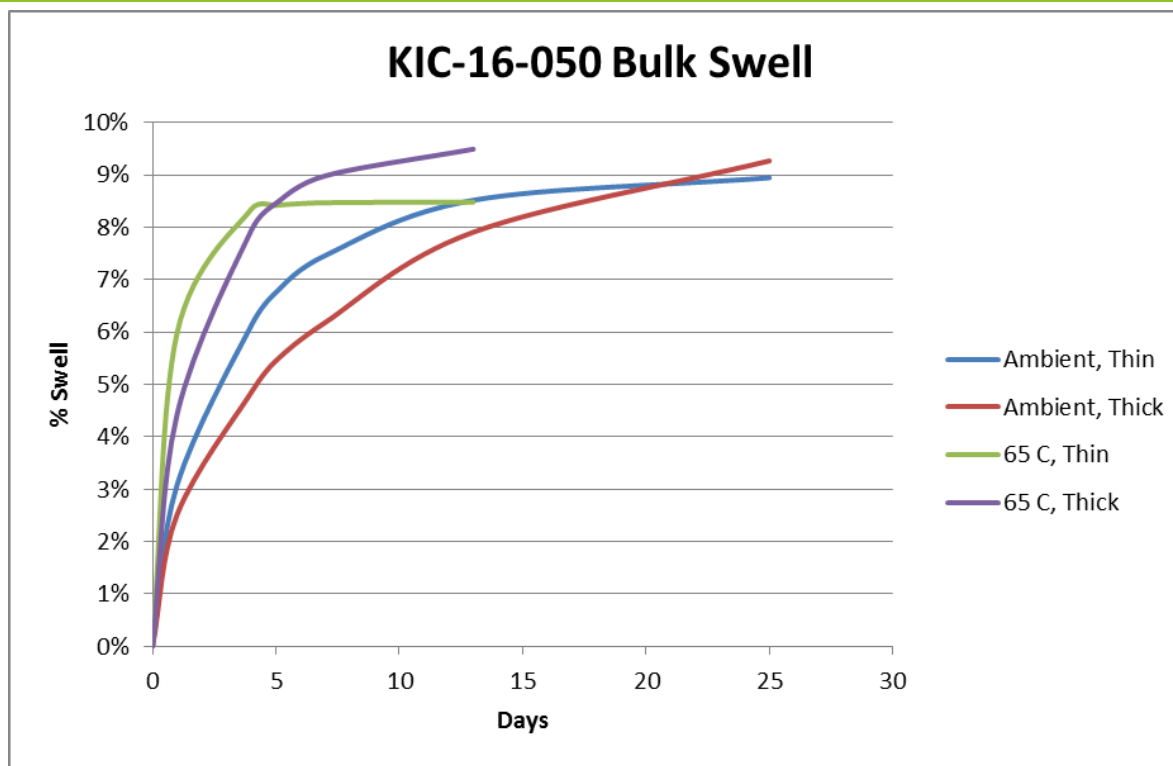
L2S: Tougher Than Cement



- **Strength:** stress a material can withstand before failure
- **Toughness:** amount of energy a material can absorb before failure
- L2S and cement may have comparable strength, but **L2S far exceeds cement in terms of toughness**
- Cement is a brittle material, failing at <10% strain
- **L2S is a ductile material**, often reaching 40-50% strain at break

Weighted to 14.0 ppg with Barimite XF micronized barite.

L2S: Ability to Swell



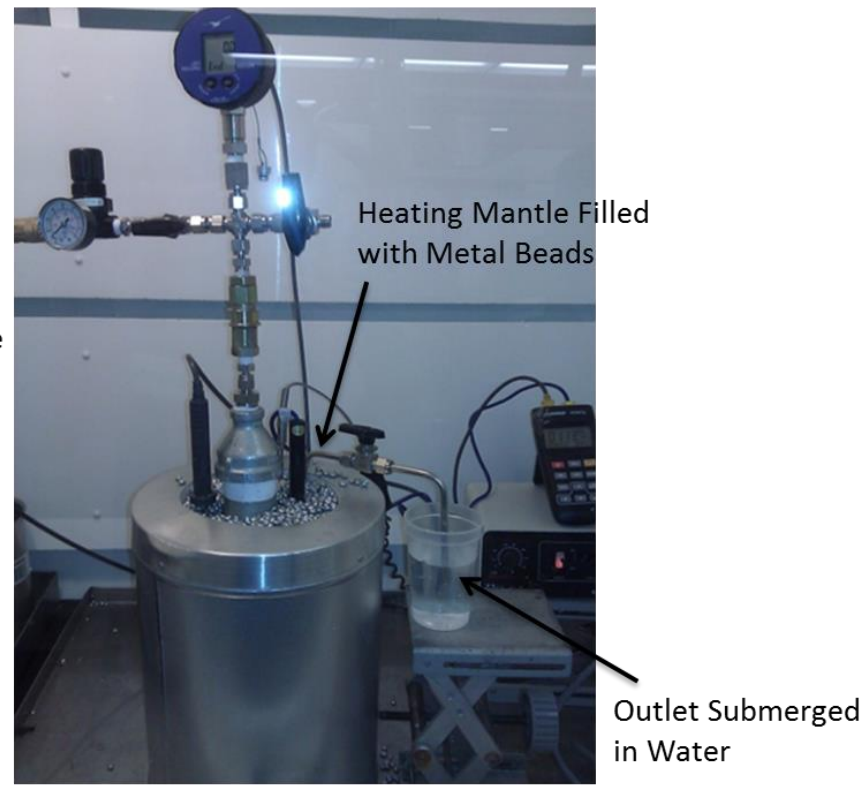
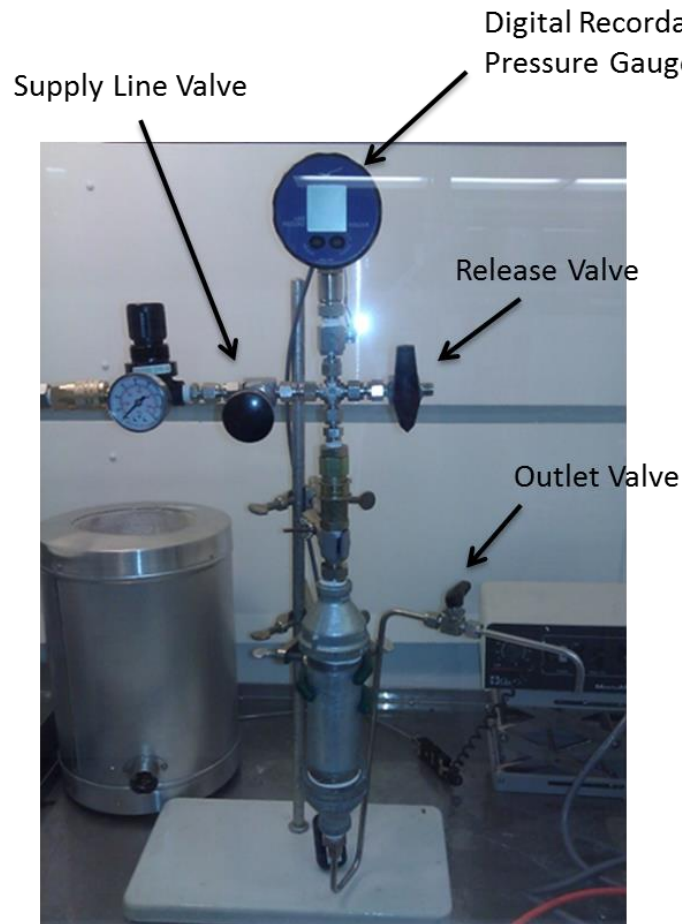
- L2S has a built-in ability to swell in the presence of hydrocarbon post-cure
- This allows for inherent self-sealing functionality

Weighted to 12.5 ppg with Barimite XF micronized barite.

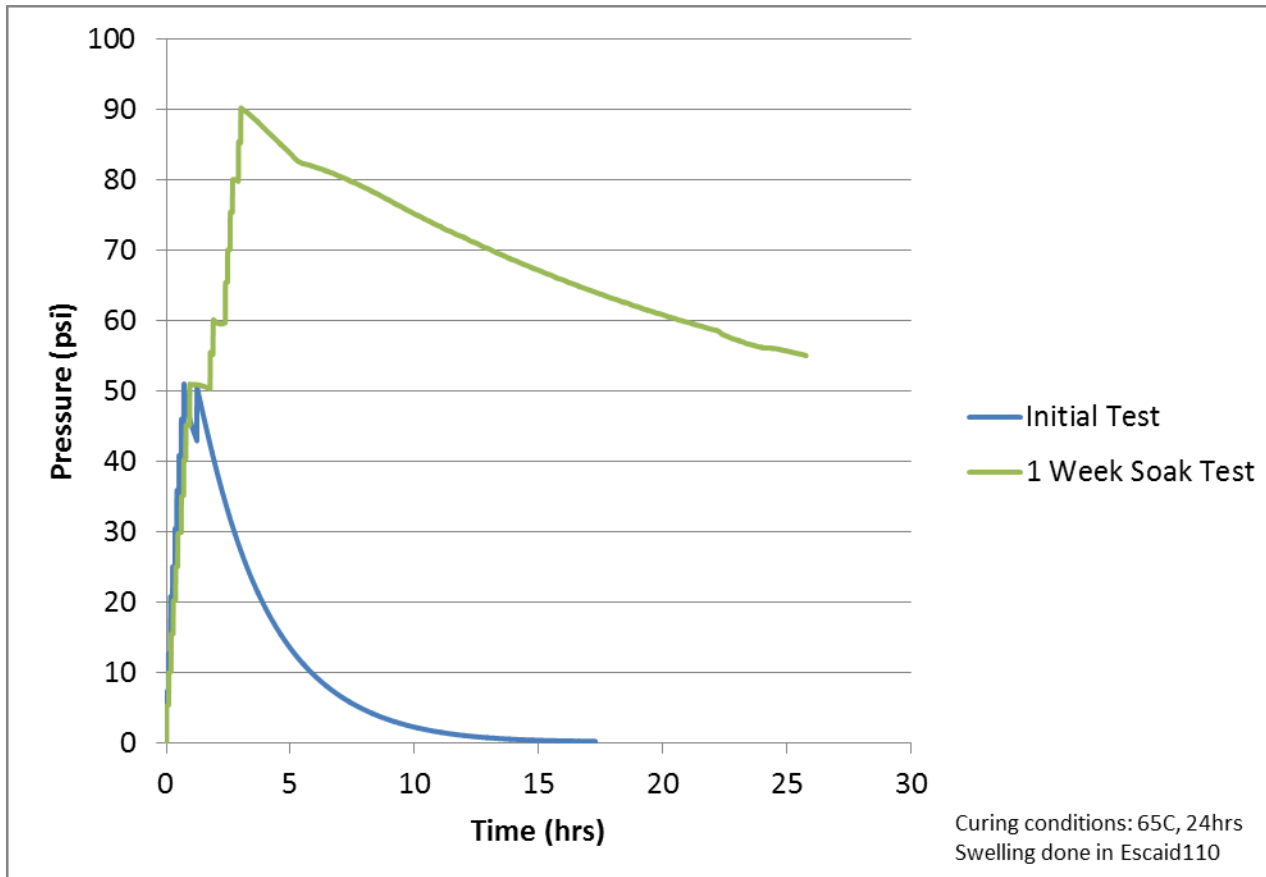
Sample had 1.3% shrinkage after curing for 24 hrs.

Pressure Testing Apparatus

- Sample cured in 6" long, 1.5" diameter galvanized pipe
- Pipe then connected to apparatus for testing



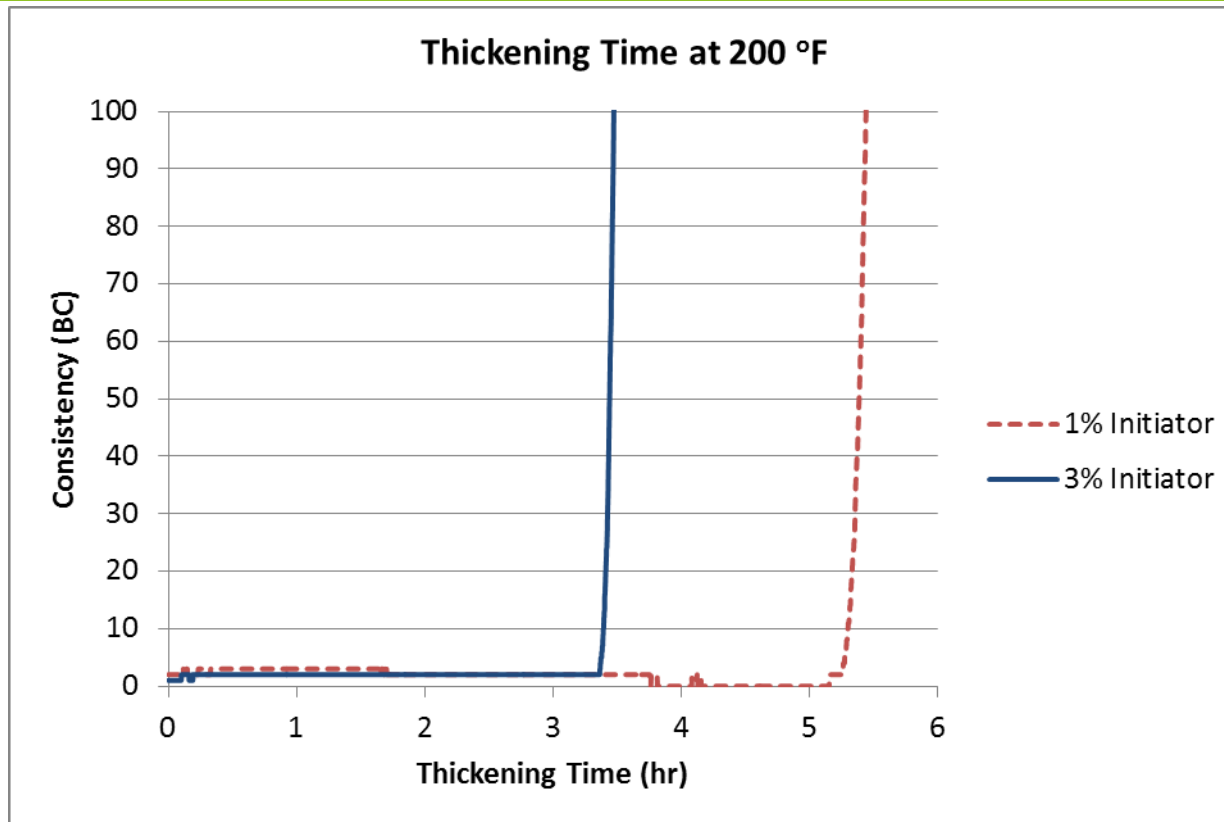
L2S: Ability to Reseal



- **Initial Test**
 - At 65 °C
 - Failed at 40 psi
 - Dropped to 0 psi after 15 hrs
- **Soaked in oil for one week at 65 °C**
- **Second Test**
 - At 65 °C
 - Failed at 90 psi
 - Dropped to 55 psi in 24 hrs
 - Sample was liquid tight
- **Ability to swell and reseal**

KIC-16-050 weighted to 12.5 ppg with Barimite XF micronized barite.

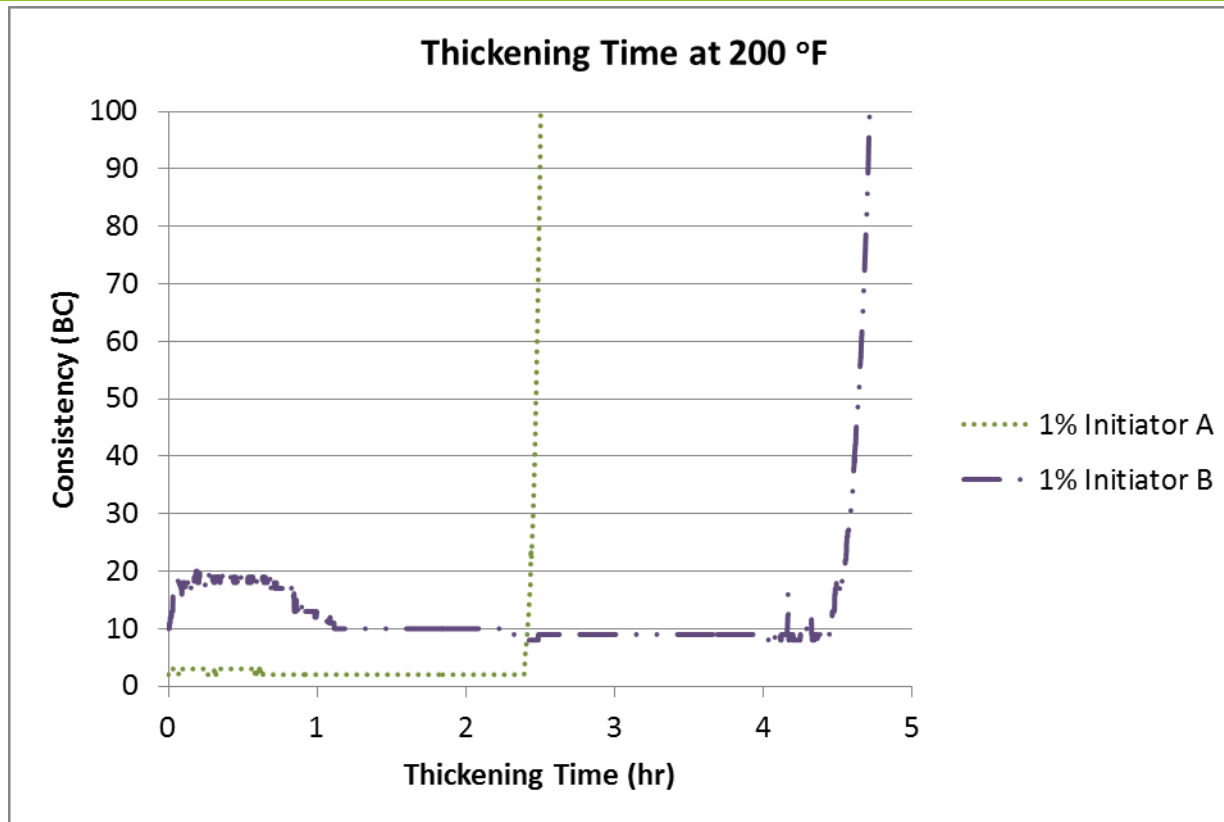
L2S: Control Over Cure



- Thickening Time can be controlled through type and amount of initiator
- Initiators chosen based on bottom hole static temperature and desired pump times

Weighted to 9.0 ppg with Barimite XF micronized barite.

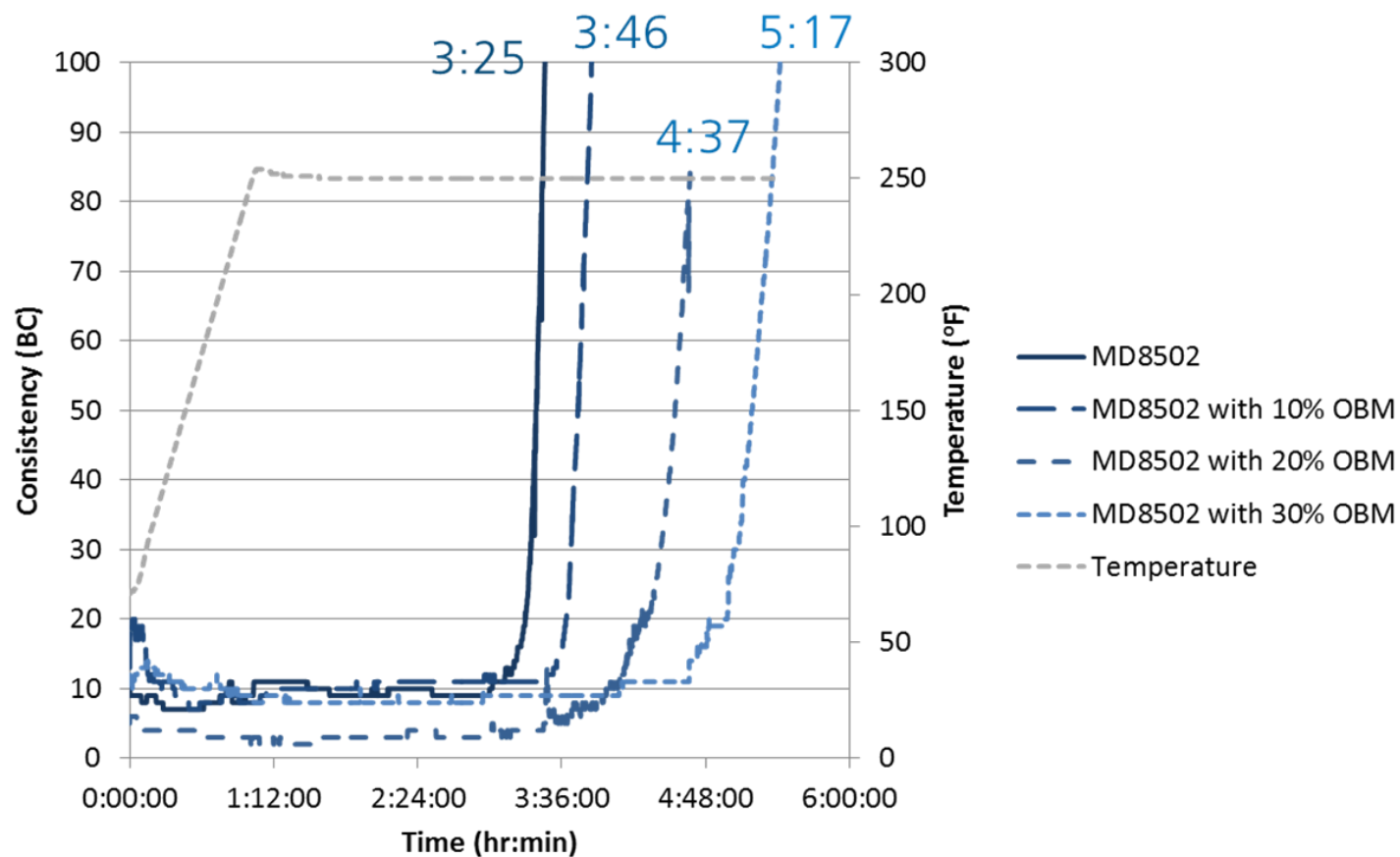
L2S: Control Over Cure



- Thickening Time can be controlled through type and amount of initiator
- Initiators chosen based on bottom hole static temperature and desired pump times

Weighted to 12.5 ppg with Barimite XF micronized barite.

L2S: Control Over Cure



Tests performed at 250 °F and 10,000 psi

MD8502 formulations all weighted to 12.5 lb/gal with BaSO₄

OBM: 14.5 lb/gal

Conclusions

- Zonal isolation over the life of a well is an ongoing challenge, one that may benefit from a non-Portland solution
- Multiple types of synthetic resin chemistries are available
- Synthetic resin technologies offer many advantages, including:
 - Wide formulating window for tuneable mechanical properties
 - Improved mechanical properties better suited to withstand temperature and pressure cycling
 - Superior chemical resistance
 - Solids-free solution for squeeze and remedial operations

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