

# Further Development of New, Environmentally Friendly, Salt-Free Shale Inhibitors for Water Based Drilling Fluids

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## Abstract

The shale inhibition market is trending towards more environmentally friendly materials. As such, more markets are seeking, or already mandate, lower saline or salt-free systems for reasons including environmental regulations, disposal needs and potential groundwater contamination. This paper will cover efforts to develop and evaluate new shale inhibitors in multiple chemical classes, which satisfy these requirements whilst still maintaining excellent performance relative to industry benchmarks.

Several families of novel candidate chemistries, each comprised of a homologous series, were evaluated using a variety of techniques, namely shale recovery, hardness, linear swell meter, and Slake Durability (roller cage) tests. These tests were followed by biodegradation and toxicity evaluation. This approach identified several inhibitors with improved performance across multiple parameters, both technical and environmental. Beyond discovering new shale inhibitor chemistries, it is important to understand the testing protocols used for their analysis. As part of this research, shale testing protocols, including a linear swelling method, were developed and utilized. This paper will discuss the evaluation process, the measured performance of the molecules synthesized in this study, structure/property relationships, and detailed environmental and performance analysis of the top inhibitor chemistries.

## Introduction

Shales are the most commonly encountered rock type during the drilling for oil and gas. They account for over 70% of all drilled formations, and numerous borehole problems relate back to shale instability.(1,2) Shales have been reported to cause more problems per foot drilled than any other type of formation.(3) Over the last decade, reactive shale ranked as one of the top mud-related issues affecting deepwater drilling operations. Reactive shale is also a major contributor to another frequently listed drilling concern, namely stuck drill pipe.(4,5) These statements on shale instability, while dramatic and true, should be considered with respect to the drilling fluid used and the type of shale that is encountered during drilling operations. It is the interaction of the drilling fluid and the shale type that largely determines the extent of the problem (6,7).

The reactivity of shale towards water is a much studied (8) and debated topic.(9) For years, the swelling of shale, which is due to the ingress of water and hydration of metal cations,

has been considered the “best documented” and main failure mechanism.(10) Combinations of swelling, dispersion, migration and swelling-induced migration have all received extensive attention.(11,12) Water activity, brine composition, brine concentration and pH have all been shown to play a role in shale stability.(12,13) Techniques and equipment to study these issues continue to advance as industrial knowledge and experience develops, so we should anticipate similar improvements in chemistry performance. If shale instability is not properly addressed, then the consequences can be dramatic, including complete loss of the well.

This paper will report on the further development of shale inhibitors which increase the performance of water-based muds (WBM), particularly in a salt free environment.(14) For years, the service industry has devoted significant thought and effort to bring the performance of WBM up to that of oil-based muds (OBMs). (15,16,17) To abate unwanted reactivity of certain shales towards water, WBM contain shale inhibitors that range from salts (e.g. KCl),(18,19) to simple glycols often containing or requiring salts,(20,21,22) to various amines,(23) to polymers.(24,25,26) Collaborative work by M-I Swaco and academia have put forth several different mechanisms for the polyetheramine class of shale inhibitors which is currently considered to be one of the best-in-class for low molecular weight inhibitors.(27,28) Additional studies of this nature are needed to further progress the industry’s understanding of shale inhibition.

One approach to study how molecular structure influences shale inhibitor performance is to select molecular descriptors (e.g. molecular weight, degree of branching, heteroatom content, length of hydrophilic/hydrophobic segments, number of end groups bearing certain functional groups, etc.), make different homologous series where the descriptors are systematically varied, and then conduct comparative tests. Most of the comparative testing for this work used shale recovery and hardness performance parameters (21,23) to differentiate the various candidate chemistries. While such studies generally cannot provide conclusive evidence regarding the mechanism of inhibition, they are highly informative regarding critical molecular features needed for improved performance. When structural and compositional features are identified, they can suggest reasonable assumptions regarding mode of action. The first level of screening for all materials was recovery and hardness performance on London shale samples. If a given material demonstrated outstanding inhibitory performance on this

swelling shale, then it was subjected to broader and in some respects more demanding performance tests, such as Slake Durability (roller cage) on both London and Oxford shale, and analyzed for biodegradability and toxicity, among other environmental tests.

### Test Methodology

When attempting an in-depth study of the effect of subtle changes of chemical structure can have on shale inhibition, a key initial step is to secure a large enough volume of a consistent shale material to test against. Both knowledge and consistency of the mineralogical makeup and physical-chemical nature of shales are important criteria regarding how they will behave on exposure to aqueous media.

Outcrop shales of known, characterised mineralogy have been used due to the size of this on-going study. For large, extensive and prolonged studies, this is a particularly useful approach. The advantage to such substrates is the availability of large quantities, which have similar composition and properties, and which in turn allow for better comparisons between the performance of various fluids and additives. Young and Friedheim (29) have indicated that there is a caveat to choosing outcrop shales. They describe the disadvantage of choosing such shales in that they are structurally of poorer consolidation than shales that are drilled at depth (less exposure to stress) and typically their chemical makeup is one of higher water activity. That being said it is important to balance availability against the disadvantages of using drilled cuttings that have already been exposed to mud chemistry, stresses due to drilling activity, preservation and limited availability. To compensate for the use of outcrop shale, a range of different outcrop samples was used to measure their performance at different water contents. These traverse the typical shale types that could be confronted whilst drilling, that contain clays from high montmorillonite (highly swelling) through mixed layered clays to high kaolinite (highly dispersive) formations. For shale inhibition performance, it is recognised that our laboratory testing is probably more arduous than that seen in the field because of the above influences. The out-crop shales utilized for this study are:

#### London Shale

This formation is a marine geological formation from the Lower Eocene period and is a reasonable analogue of Tertiary shale found in upper hole sections and typically contains 15-25% smectite clay.(30) The shale is plastic in nature due to its moisture content and has low bulk density. Operators and mud companies recognize this shale as representative swelling shale.

#### Oxford Shale

The Oxford shale formation is a Jurassic marine sedimentary rock formation, which is less swelling than London shale, as it contains less smectite but more illite clay. As it is dispersible and effective for hardness testing, it provides good balance to the London shale in terms of evaluating performance. Like London, Oxford is recognized as

an acceptable analogue of problems encountered during drilling and has a mixture of swelling and dispersive character.

### Shale Testing

The below shale testing procedures are described in more detail by Young and Friedheim (29) and were used to evaluate the homologous inhibiting chemistry series and benchmark comparative performance.

The standard test protocol includes:

- Bottle recovery tests
- Shale hardness test (Sometimes referred to as the BP hardness tester, 21)
- Shale moisture content change
- Slake Durability recovery (roller cage) test
- Linear swell test

### Comments on Linear Swelling Test

Shale formations have the ability to absorb fluid from a water-based fluid which can lead to wellbore stability problems such as stuck pipe, tight hole, washout and sloughing. The linear swelling test helps to determine shale hydration or dehydration by measuring the increase or decrease in size (“swelling/contraction”) of reconstituted or intact shale cores.

The premise of the test is that a pellet is placed into the test fluid, and the change in length of the pellet is then measured over time by the use of a displacement transducer. The change in length over a given time period and the constant rate of change can then be determined.

Pellets can be produced from either core material, cavings, outcrop shales or even cuttings. The common industry method is to dry a shale material, grind to a fine powder and then compress hydraulically into a pellet. The process of manufacturing these pellets artificially generates a shale pellet that has a greater tendency to imbibe water. An alternative method is to press or cut shale pellets out from a larger piece of shale sourced from an outcrop or core. This method ensures the shale structure is more representative in terms of preserving bedding planes etc. Data presented later will highlight the variations in behavior that these two approaches can bring.

Scanning electron micrographs show a significant difference in clay structure between a pellet made “cored” from out-crop (Picture 1) with bedding planes intact and a pellet reconstituted from cuttings (Picture 2). The latter shows fractures, occlusions and permeability, which would exacerbate any shale chemistry behavior. The latter is more consistent and reproducible in shale chemical testing (Figure 1).

For all other tests, the candidate inhibitor is added to a rheological controlled base fluid, the profiles of each fluid tested are designed to be similar to minimize any inaccuracies in cross-fluid comparisons. It is desired to be able to test shale inhibition character and minimize experimental artifacts. In effect, the performance efficiency of each chemistry is examined on a minimum 8 point matrix, where enhanced

performance is looked for across all data points. This then leads into toxicity and biodegradation characterization against the said same molecular changes within each homologous series.

## Results and Discussion

### ***Series 1 (quaternary amine containing molecules):***

Previous work (14) describes the initial efforts to better understand the structural properties that lead to successful shale inhibition performance. The report details the testing of a series of hydrophobically modified, quaternary amine containing molecules. After analyzing for shale recovery and hardness using London shale, an optimal hydrophobicity and molecular weight were identified. These studies provided insights that directed the design and development of future shale inhibitors.

### ***Series 2 (substituted amines with alcohol functionality):***

While new quaternary amine containing molecules can improve the shale inhibition performance of WBMs, it is preferable to use ion/salt free materials. To this end, substituted amines having alcohol functionalities provided different chemical classes and were synthesized with varying molecular weight, amine content and branching. Previous work published on these molecules (14) has been expanded, and additional materials within this class were synthesized and tested. Now over 100 compounds have been generated and analyzed, and the understanding of structure/property relationships has significantly advanced.

Similar to the studies based on quaternary amine-containing molecules, and in agreement with the conclusions of previous studies (14), it was found that the best shale inhibition performance could be obtained when an optimal amount of branching and amine content were used in combination with molecular weight. Figures 2a and 3a illustrate this trend based on shale recovery, while Figures 2b and 3b depict the relative hardness of the shale. The best molecule from this series was identified by analysis of both the shale recovery and hardness data. When plotted as seen in Figures 2a-3b, it is easy to identify the optimal chemistry as the 'hot spots' on the 3-D plots.

The optimal chemistry (Chemistry A) was then subjected to further investigations and demonstrated excellent performance relative to industry standards. Chemistry A has been commercialized and will be discussed further below. Interestingly, related materials that have the same functionalities (i.e. amines and alcohols) but different structures do not perform well, indicating that only particular substituted amines with alcohols as specific groupings generate enhanced inhibition performance. The new materials synthesized within this class have allowed further understanding of the effect of structure versus chemical performance. While trends within a series of related structures are clear, and as new inhibitors are synthesized and tested, further investigation of the effects when expanding hypotheses

to related materials will be conducted.

### ***Series 3 (primary amines with hydrophobic groups - no alcohols):***

A series of primary amines with no alcohol functionality but with hydrophobic groups was also found to demonstrate excellent performance having optimal structures. As with other materials studied, a balance exists between molecular weight and hydrophobic length that generates peak shale inhibition. The recovery of shale is also improved by increasing the hydrophobicity of the molecule, by increasing branching or by utilizing an optimal molecular weight with high hydrophobicity (Figure 4). However, hardness of the cuttings will increase with decreasing molecular weight, similar to recovery, but branching and hydrophobicity have a minimal effect. The best in class performer from this study (Chemistry B) will be further discussed below as a potential next generation shale inhibitor with superior performance relative to industry standards and with promising environmental and toxicological properties.

### ***Series 4 (polymeric quaternary materials):***

Recent studies have focused on polymeric materials with quaternary as well as tertiary and secondary amine functionalities. A set of polymers was synthesized that represented two subsets of molecular weights (high and low) as well as other chemical functionality. Due to their molecular weight, these materials are expected to utilize an alternative mechanism of shale inhibition. The first subset (Subset 1) of polymers with relatively low molecular weights yielded excellent inhibition behavior, both in recovery and hardness. It was found that the molecular weight of this subset of materials correlates well with hardness performance; lower molecular weight polymers generated better hardness in London shale than higher molecular weights (Figure 5). The effect of charge density, amine content and active functionality on these polymers is an area of active investigation.

For the second subset in this series (Subset 2), polymers with molecular weight around an order of magnitude greater than Subset 1, poor inhibition performance was measured. For these high molecular weight polymers, any effect of charge density, amine content, functional groups or branching was seemingly dominated by the overall size of the polymers; the large size limited their ability to prevent shale swelling or dispersion. Overall, polymers in this class are expected to have good environmental profiles based on modeling and comparison to existing chemistries. Further efforts are needed to identify optimal materials in this series.

## **Shale Performance Data for Shale Inhibitor Chemistries A and B**

Two chemistries in particular have come to light in this detailed investigation that had very good properties across the shale substrate testing. Candidate inhibitor Chemistry A is a commercially available material that produces very hard cuttings and good shale inhibition characteristics at

concentrations of 2-3% v/v. Its performance can be compared against industry standard amines and glycol in freshwater. Candidate inhibitor Chemistry B is a developmental material that has either equivalent, and in some tests incrementally better, shale characteristics over a broader concentration range of 1-3% but is also readily biodegradable in freshwater which advances its environmental credentials against most industry inhibitors.

The evaluation of these two shale inhibitor chemistries, both in terms of hardness and Slake Durability, is shown in Figures 6 and 7 (respectively) on London clay which is the more swelling version. Figure 6 illustrates how Chemistries A and B exhibit improved hardness performance over that of an industry leading amine reaching higher torque (i.e. hardness) with fewer turns at the same dosage. It is important to note that the fluids for Chemistries A and B are fresh water systems. The standard glycol exhibited lower hardness than Chemistries A, B, and the industry leading amine, and the former required KCl as an adjunct to perform. This feature defeated the objective of having a chloride free or freshwater drilling fluid for environmental and discharge constraints. The Slake Durability performance of Chemistry B stands out above that of all other materials tested in this study on London shale, as shown in Figure 7.

Similar to the London shale study, the same chemistries were evaluated for hardness and Slake Durability on Oxford shale. Results are shown below in Figures 8 and 9. Chemistries A, B and the industry leading amine top the hardness performance data as they develop higher torques faster than the other tested materials as illustrated in Figure 8. The Slake Durability performance of Chemistries A, B, and the industry leading amine are comparable in this study on Oxford shale, with Chemistry A showing a slight advantage as depicted in Figure 9.

## Second Generation Inhibitor

For situations where even higher performance is required and greater environmental constraints are present, a second generation inhibitor for WBMs is being developed. As detailed above, our experimental methodology has successfully identified Chemistry A as a very good shale inhibitor. These experiments also indicated another excellent performer, Chemistry B, that is from a different series. Initial results indicate that the new material has inhibition performance exceeding that of leading industry materials that do not require the addition of salts. Both recovery and hardness tests suggest high efficacy at comparable dosage levels (Figures 6 and 8) and initial Slake Durability (roller cage) studies are also very encouraging (Figures 7 and 9). This material opens up the opportunity for salt free, lower toxicity chemistry that provides very good shale inhibition.

Beyond its excellent performance attributes, several tests suggest the presence of a superior environmental profile. EPA's EPI Suite (BIOWIN models) estimated that this inhibitor would be readily biodegradable under aerobic conditions. This prediction was confirmed experimentally via a screening test based on the OECD 301F guideline (31).

According to this test, the inhibitor can be considered "readily biodegradable" since it reached 120% biodegradation at the end of the 28 day study. This result of 120% biodegradation is based on biological oxygen demand (BOD) at 28 days compared to the theoretical oxygen demand of the test material. The biodegradation percentage in this OECD 301F test may be higher than 100% due to some additional oxygen consumption other than the amount required for the bio-oxidation of the test material. Dissolved organic carbon removal was 98% after 28 days which suggests that the test material was indeed completely degraded. These results are now being validated by a more stringent GLP OECD 306 biodegradation test in seawater.

A Quantitative Structure Activity Relationship (QSAR) assessment of aquatic toxicity of the inhibitor in pure form was performed using the OECD QSAR toolbox v.3 and a relevant subset of model molecules from databases of aquatic toxicity results. According to the US EPA classification, the derived model predicted the pure compound to be moderately toxic to algae (*Pseudokirchneriella subcapitata*), slightly toxic to *Daphnia magna*, and practically non-toxic to fish. Practically speaking, aquatic species do not have a high potential for exposure to the inhibitor in pure form but rather would be far more prone to encounter drilling fluid formulations. Thus, testing for the toxicity of fully formulated drilling fluids towards aquatic species is more relevant and would often be expected to be less than that of the pure compound for each respective species as predicted above. A 96 hour definitive bioassay was conducted on a Generic 7 drilling fluid containing up to 2 wt% of the inhibitor following EPA's Drilling Fluid Toxicity Test guidelines (32). The results showed a LC50 value, the concentration at which 50% of the test organisms respond, above 50,000 ppm, thus passing the guideline minimum requirement of 30,000 ppm. This very encouraging data indicates that the second generation inhibitor may generate remarkable inhibition performance as well as have minimal environmental impact. Studies are ongoing and will be reported in due course.

## Environmental Findings

Environmental data for Chemistries A, B, and an industry leading amine that encompass toxicity and biodegradation test results, as well as partition coefficients are summarized in Table 1. It shows an evolution in improvements in toxicity and biodegradation results within the series. Chemistry A exhibits very good toxicity data but poor biodegradation, an element that Chemistry B improves upon. A high end industry leading amine, in spite of an excellent shale performance, can have very poor toxicity and biodegradation characteristics.

**Table 1.** A review of the environmental data for Chemistries A, B, and two industry standard amines.

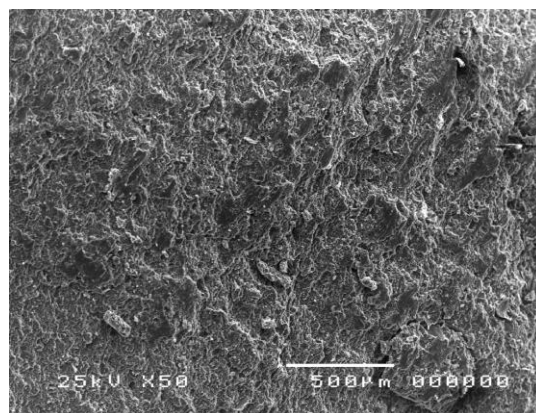
	LC50 GOM@ 2% v/v	Biodegradation tests results Freshwater	Log $P_{OW}$	Aquatic Toxicity (72hr)	Relative performance
Chemistry A	PASS	9% in OECD 301F	<3 - Pass	68.4 mg/l	2
Chemistry B	PASS	100% in OECD 301F	<3 - Pass	54.2 mg/l	1
Industry Leading Amine	PASS	0% in OECD 301F	<3 - Pass	15.0 mg/l	2
Industry Amine	PASS	100% in OECD 301F	<3 - Pass	>1000 mg/l	4

This data raises an interesting conundrum for designing and choosing chemistries that can be used in environmentally sensitive land based operations. In certain parts of the world, environmental testing is dominated by marine ecotoxicity and biodegradation testing protocols. Yet this may preclude perfectly acceptable chemistries that biodegrade in freshwater, but not necessarily as well in marine environments. A case in point is in the UK where offshore protocols are directed by CEFAS but onshore is regulated by the environment agency through the Water framework directive. However, the latter for land operations still takes worse case data which may well be marine data.

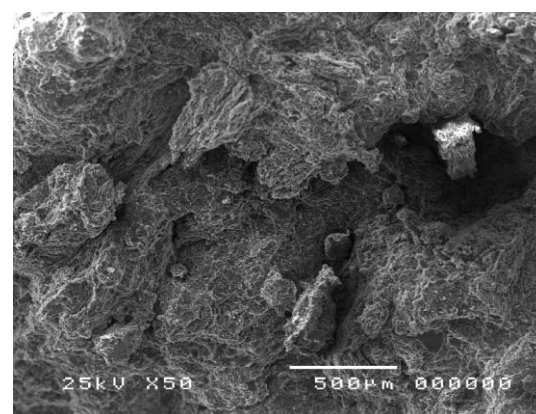
## Conclusions

The principal goal for this investigation was to identify new chemistries that have enhanced shale inhibition characteristics that could be utilized in freshwater systems which also have enhanced toxicity and biodegradation profiles. The focus of these efforts would be for land drilling in environmentally sensitive locations, e.g. the Amazon in Latin America, Europe, East Africa and the US, where environmental regulations are either already stringent, or are changing rapidly and becoming more challenging. To this end, extensive experiments were performed to identify not only new chemistries, but also structural features that contribute to excellent shale inhibition. A novel chemistry was identified and developed that shows excellent performance across economic, technical and environmental parameters (Inhibitor Chemistry A). This chemistry represents an excellent replacement for, and a significant improvement on, glycol/KCl systems. We have also identified and are further validating a next generation inhibitor (Inhibitor Chemistry B) with superior performance for the most demanding applications needing enhanced performance, toxicity, and biodegradation character. The test methodology presented allowed the development of new chemistries and an improved understanding of how molecular structure affects both shale inhibition performance and environmental impact. This knowledge will enable continued new product development and guide analytical efforts when evaluating potential shale inhibitors.

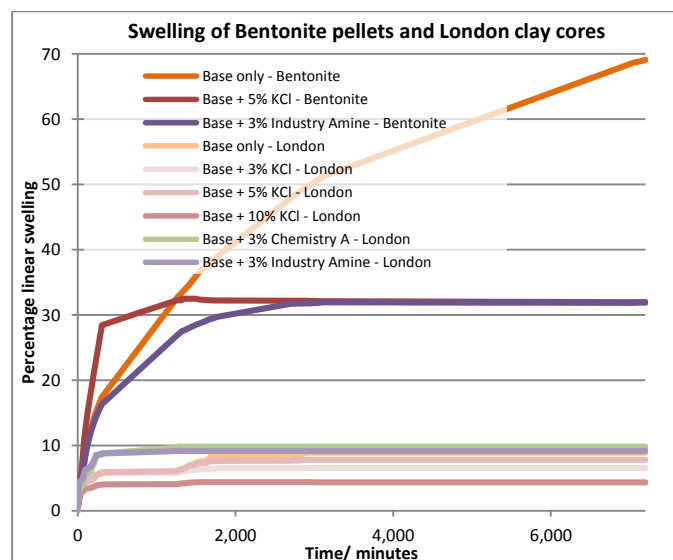
## Pictures and Figures



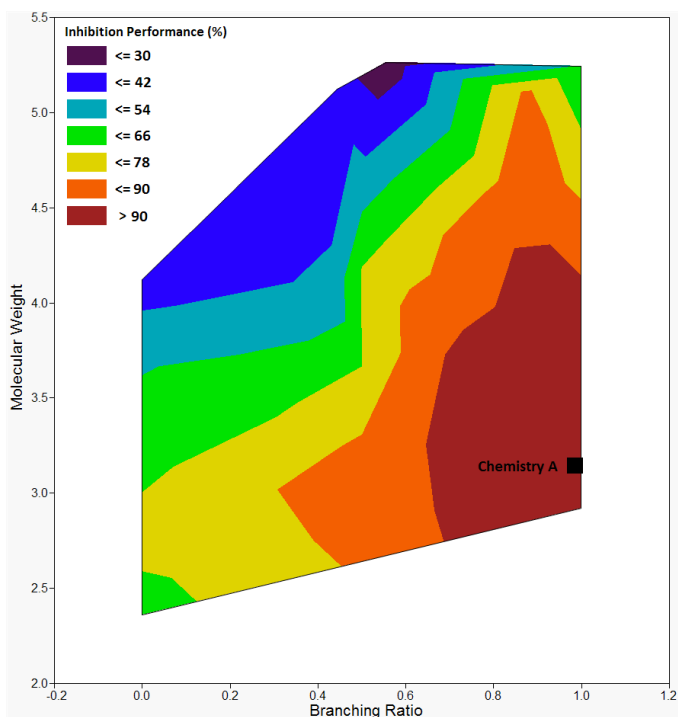
**Picture 1.** London outcrop pellet



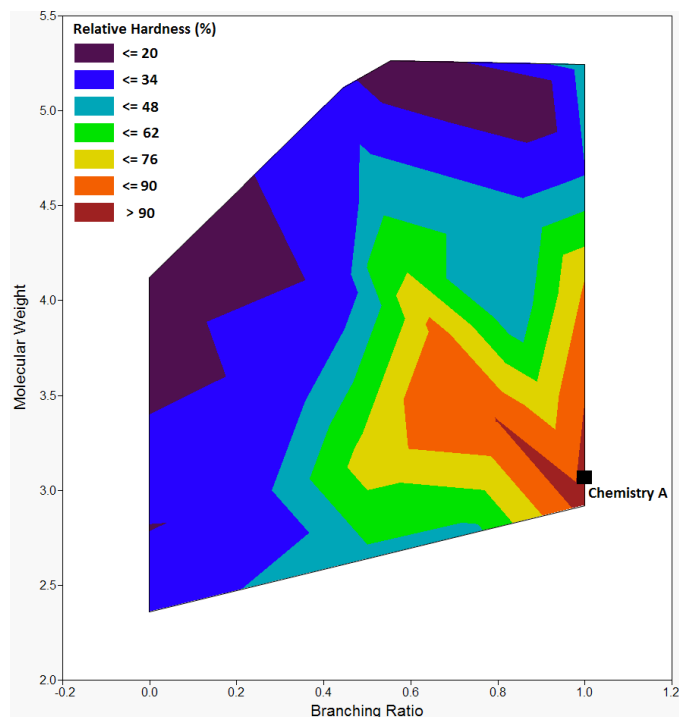
**Picture 2.** Pellet made from London cuttings



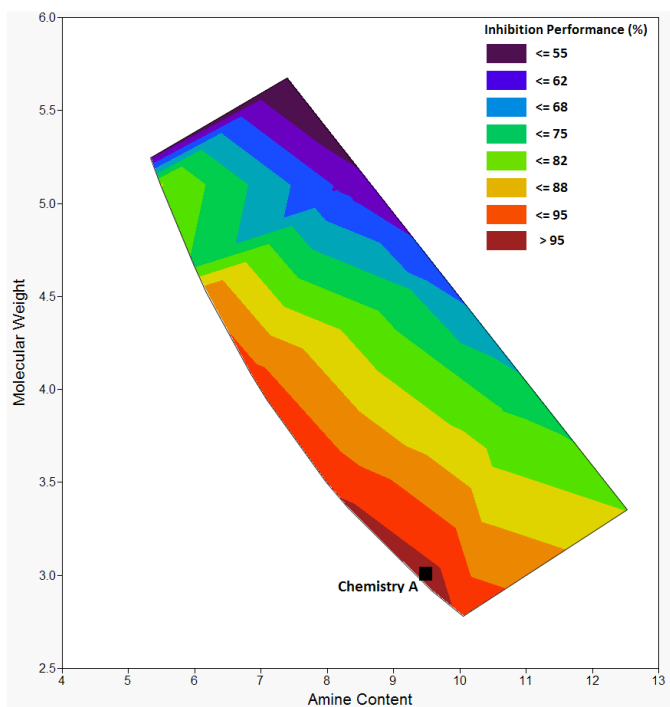
**Figure 1.** Linear swell test data on London core and Bentonite pellets to show variation in behaviour between cores and reconstituted pellets.



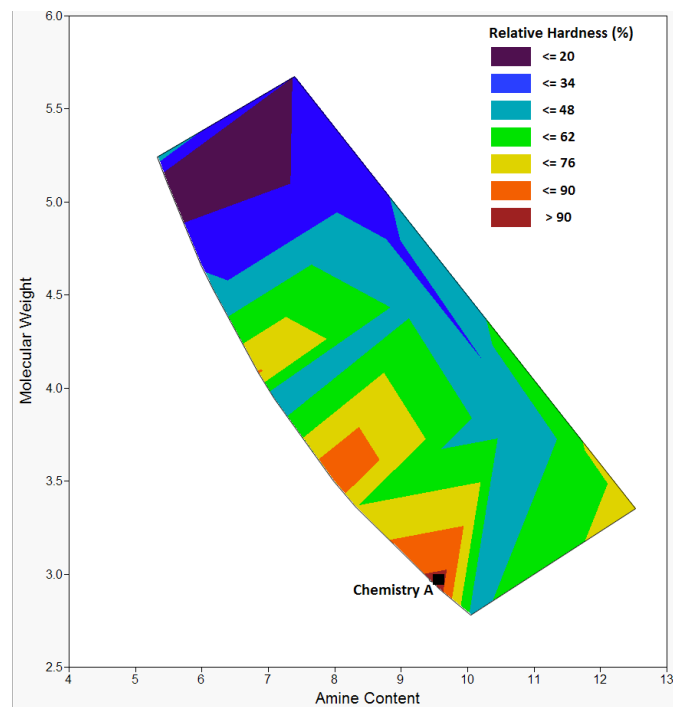
**Figure 2a.** Surface plot of shale inhibition performance based on recovery for a series of substituted amines with alcohol functionality as a function of molecular weight and branching ratio at a 4 wt% loading. The molecular weight axis indicates relative size of the molecule with higher numbers representing higher molecular weight. Similarly, the branching ratio axis indicates relative degree of branching in the molecule with one representing the maximum amount of branching possible and zero representing no branching present.



**Figure 2b.** Surface plot of shale inhibition performance based on relative hardness for a series of substituted amines with alcohol functionality as a function of molecular weight and branching ratio at a 4 wt% loading. A 100% hardness sample would be one where the sample gave equivalent performance to a benchmark industry leading sample. The molecular weight axis indicates relative size of the molecule with higher numbers representing higher molecular weight. Similarly, the branching ratio axis indicates relative degree of branching in the molecule with one representing the maximum amount of branching possible and zero representing no branching present.

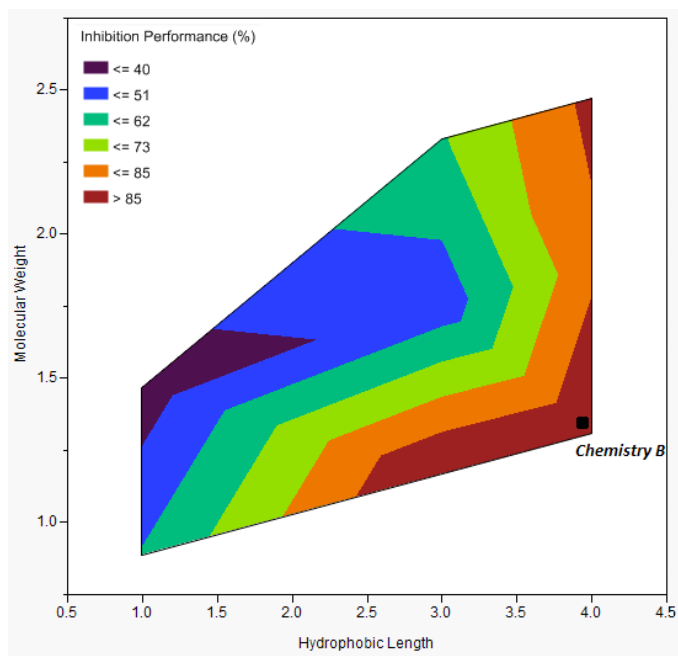


**Figure 3a.** Surface plot of shale inhibition performance based on recovery for a series of substituted amines with alcohol functionality as a function of molecular weight and amine content at a 4 wt% loading. The molecular weight axis indicates relative size of the molecule with higher numbers representing higher molecular weight. Similarly, the amine content axis indicates the relative amount of amine present in the molecule with higher numbers representing increased amine content.

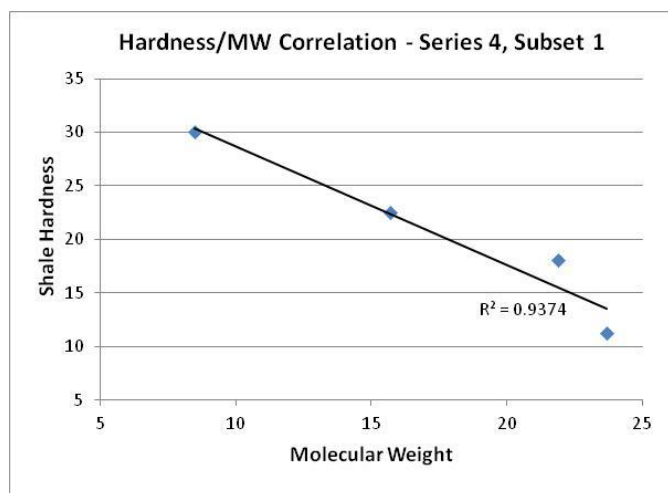


**Figure 3b.** Surface plot of shale inhibition performance based on relative hardness for a series of substituted amines with alcohol functionality as a function of molecular weight and amine content at a 4 wt% loading. A 100% hardness sample would be one where the sample gave equivalent performance to a benchmark industry leading sample. The molecular weight axis indicates the relative size of the molecule with higher numbers representing higher molecular weight. Similarly, the amine content axis indicates relative amount of amine present in the molecule with higher numbers representing increased amine content.





**Figure 4.** Surface plot of shale inhibition performance, based on recovery for a series of primary amines with no alcohol functionality; but with hydrophobic groups as a function of molecular weight and hydrophobic length. The molecular weight axis indicates the relative size of the molecule, with higher numbers representing higher molecular weight. Similarly, the hydrophobic length axis indicates relative, normalized length of the hydrophobic moiety present in the molecule with higher numbers representing increased hydrophobe length.

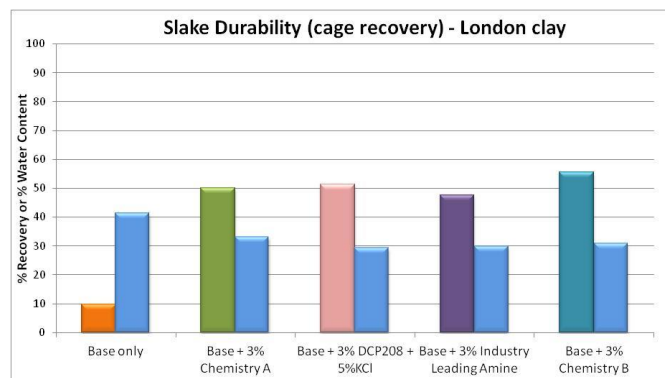


**Figure 5.** Hardness data versus polymer molecular weight using London shale for Series 4 Subset 1 quaternary polymeric materials. A high correlation ( $R = 0.94$ ) was found for the data. Hardness is represented as a dimensionless number that incorporates the overall torque measured and number of turns required to attain that torque in the hardness measurement apparatus. Thus, larger numbers represent higher shale hardness. The molecular weight axis indicates the relative

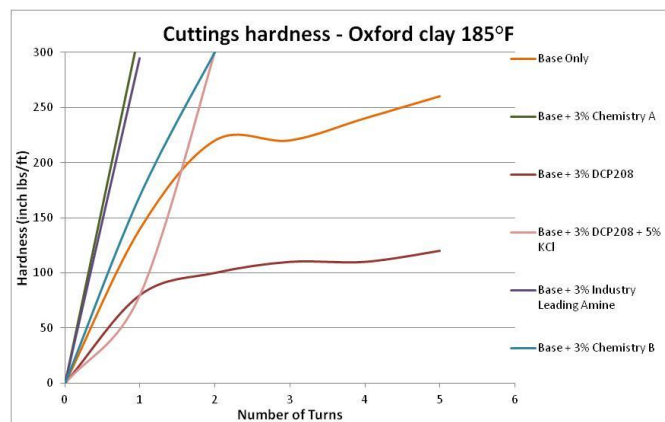
size of the molecule, with higher numbers representing higher molecular weight.



**Figure 6.** Hardness data on London shale of the two candidate materials (Chemistry A and B) versus two benchmarks KCl/poly(ethylene glycol) butyl ether (DCP 208) and an industry leading amine.

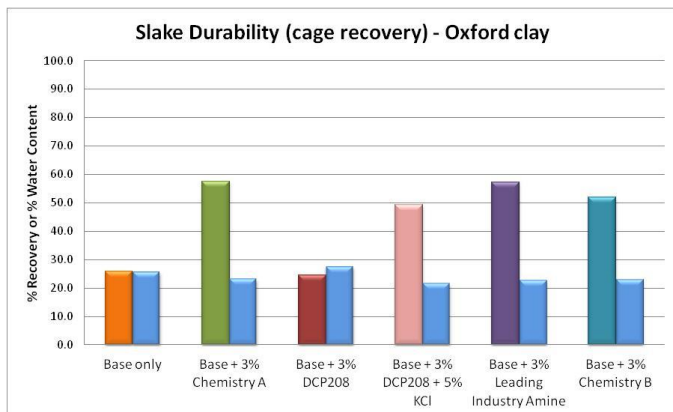


**Figure 7.** Slake Durability (cage recovery) on London shale of the two candidate materials (Chemistry A and B) versus two benchmarks KCl/ poly(ethylene glycol) butyl ether (DCP 208) and an industry leading amine.



**Figure 8.** Hardness data on Oxford shale of the two candidate materials (Chemistry A and B) versus benchmarks consisting of poly(ethylene glycol) butyl ether (DCP 208), with and without added KCl, and an industry leading amine.





**Figure 9.** Slake Durability (cage recovery) on Oxford shale of the two candidate materials (Chemistry A and B) versus benchmarks consisting of poly(ethylene glycol) butyl ether (DCP 208), with and without added KCl, and a industry leading amine.

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