

State of the Art Polymers Fulfill the Need for High Temperature Clay-free Drill-In and Completion Fluids

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Abstract

As the petroleum exploration and production industry targets increasingly deeper oil and gas reservoirs with hostile environments, the need for improved polymer performance within aqueous-based fluids has moved to the forefront of laboratory and applied research. Polymer-based reservoir drilling fluids represent a special class of fluids designed to minimize formation damage, provide effective hole cleaning, and help reduce wellbore cleanup time and cost, while allowing reservoirs to produce to the maximum of their potential. These drill-in fluids should address the wide range of difficulties frequently encountered in horizontal drilling, completion, and workover operations.

Polymeric additives are typically utilized for rheology (i.e., viscosity and suspension) and filtrate control. Polymers used for formulating reservoir drilling fluids are even more specialized as they must not render residual damage to the target production formations and must be easily removed during the well completion process. Typically polymers that are easily removed, such as hydroxyethyl cellulose, are not very thermally stable, and current commercially available thermally stable drilling fluids systems are not easily removable by conventional breakers (i.e., acid) or cleanup methods.

Through the utilization of multidisciplinary technologies, the development, testing and application of new polymeric additives have been achieved which deliver enhanced reservoir fluid performance at high subsurface temperatures. The novel polymers provide improved rheological performance, brine solubility, thermal stability, formation protection, and ease of removal from the wellbore when compared to conventional biopolymer rheology control agents such as xanthan gum, scleroglucan gum, diutan gum, and hydroxyethyl cellulose. This paper presents the laboratory results and discusses successful field application with new practical fluid preparation and maintenance procedures.

Introduction

Over the last decade, major service companies have performed extensive research towards the development of a specialized category of drilling fluids for utilization within reservoir sections.¹⁻¹³ Such work has been directed towards the need for an improved drilling fluid system that meets both

drilling and completion requirements and can be successfully applied for drilling operations in complex formations and under elevated thermal and pressure conditions.

The implementation of such fluids has become an accepted best practice within the petroleum industry. Commonly referred to as reservoir drilling fluids (RDF) or drill-in fluids, these particular formulations are specifically designed to help prevent formation damage, minimize rig time, and provide maximum production efficiency. Although aqueous- and hydrocarbon-based fluid systems exist, brine-based drill-in fluids represent the vast majority of RDFs used in field operations to date.¹⁴

Engineering a brine-based drill-in fluid system with the preferred performance characteristics for complex environments has continuously presented a host of challenges for operators and has been the subject of continued field and laboratory research. A successful reservoir fluid will ideally prevent formation damage, provide superior hole cleaning, and allow for effortless cleanup resulting in increased oil and gas production efficiency from the target reservoir. Therefore, one of the keys to the design of the fluid system and optimization of wellbore productivity by retaining the natural reservoir rock permeability is to ascertain the complex, interdependent physical interactions and chemical reactions occurring downhole between the reservoir rock fluid and minerals and the drill-in fluids utilized.¹⁵⁻¹⁹ Typical pathways of damaging a formation include pay zone invasion and plugging by fine particles, formation clay swelling, commingling of incompatible fluids, movement of dislodged formation pore-filling particles, changes in reservoir rock wettability, and formation of emulsion droplets resulting in channel blockage. If any of these damage mechanisms occur, the permeability of the reservoir is diminished and the damage is often irreversible as the original permeability is never restored.¹⁵

During deliberation of the possible pathways resulting in formation damage, numerous design criteria should be taken into consideration in order to achieve recognizable technological advancements in drill-in fluid performance. Physical and chemical characteristics of the formation (i.e., permeability, rock morphology, mineralogy, water sensitivity, temperature sensitivity, pH, etc.) effectively lead to the determination of the optimal type of filtration control and drill-in fluid required. Thus, the correct base fluid, polymeric

package, and bridging material can be subsequently chosen to minimize fluid invasion for optimal performance and wellbore producibility.

Selecting polymeric additives specifically for reservoir applications is imperative for appropriate filtration control, rheological modification, and shale stabilization.^{9,20-25} A multitude of classifications of synthetic and biological polymers can impart the desired viscosity profiles as well as aid filtration control and invasion of the drill-in fluid into the formation. However, the utilization of drill-in fluids has exposed inherent shortcomings of conventional polymeric materials formulated into commonly applied drill-in systems. Traditional polymers (e.g., xanthan, scleroglucan, diutan, acrylates, etc.) suffer from removal issues due to decreased acid solubility as compared to molecules such as starch and cellulose derivatives. However, these acid-soluble molecules suffer from decreased thermal stability. Ideally, a polymeric viscosifier would have both attributes for utilization in the well bore.

The development, testing and application of new polymeric additives have been achieved which deliver enhanced reservoir fluid performance at high subsurface temperatures. The novel polymers provide improved rheological performance, brine solubility, thermal stability, formation protection, and ease of removal from the wellbore when compared to conventional biopolymer rheology control agents such as xanthan gum, scleroglucan gum, diutan gum, and hydroxyethyl cellulose. Low polymer loading and minimal solids concentrations within the system facilitates the formation of a thin, acid-soluble filter cake that provides efficient filtration control.

Experimental

Materials

- 1) Xanthan gum (XAN)
- 2) Hydroxyethylcellulose (HEC)
- 3) Diutan gum (DIU)
- 4) Scleroglucan gum (SCL)
- 5) Rheology Modifier 1 (RM1)

*Each polymer was evaluated for solubility, thermal stability, and rheological profiles.

Methods

Sample Preparation. Each fluid sample of the evaluated polymers was mixed on the 700 ml scale (2 lab barrels) in 1000 ml glass beakers. The aqueous media of choice (either brine or freshwater) was added and placed on the paddle mixer at 550 rpms. The polymer samples were then weighed (1 wt %, 7 g) and were slowly added to prevent the formation of

local viscosified agglomerates (fish eyes). The solutions were allowed to agitate for 90 min for complete and homogeneous mixing.

Aqueous media utilized:

- 1) Freshwater
- 2) 10.0 ppg NaCl
- 3) 10.0 ppg NaBr
- 4) 10.0 ppg CaCl₂
- 5) 13.5 ppg CaBr₂ (20°F Blend)
- 6) 15.5 ppg Zn/CaBr₂ (20°F Blend)
- 7) 17.0 ppg ZnBr₂

Brine Testing. Evaluation included 10.0 ppg NaBr; 10.0 ppg NaCl; 10.0 ppg CaCl₂ brines testing for performance before and after hot roll for the various biopolymers. Also, 13.5 ppg CaBr₂ (20°F Blend) and 15.5 ppg ZnBr₂ (20°F Blend) was tested in the same manner, but not all the polymers were soluble in these fluids; performance of the successful fluids were thoroughly evaluated.

Extended Testing. Extended testing included the effect of defoamer; contamination stability (effect of defoamer, glycols, etc); and breakdown via acid hydrolysis or oxidation (to monitor if it removes as well as HEC and better than XAN)

Rheological Studies. Each polymer sample was evaluated by a series of tests on the Anton Paar Series 501 and FANN® 50 rheometers. Experiments involving shear and temperature sweeps as well as dynamic rheological studies enabled a thorough screening of the RM1 in comparison to various biopolymers as to their fluid performance in freshwater and various monovalent and divalent brines.

Results and Discussion

Aqueous Media Solubility and Rheological Studies

The solubility of the RM1 polymeric material was evaluated in the numerous aqueous media listed in the experimental section. Following the mixing procedure detailed earlier, the RM1 samples exhibited excellent solubility and viscosity response after 90 min. However, the concentrated NaCl (10.0 ppg) proved to be the only brine in which the polymer did not yield the desired properties. We can attribute this to the minimization of free water within the saturated brine as well as the possible “salting out” effects of the Na⁺ and Cl⁻ ions on the modifications located on the polymer rendering it solubility or “dispersibility” limited as the polymer adopts a very collapsed conformation.

After the mixing was complete, the samples were allowed to age at 150°F for 4 h to ensure polymer relaxation before the rheological tests were completed. The data for the shear rate sweeps at 77°F (25°C) for each solution is provided in Figure 1.

It can be seen that the RM1 provides excellent low shear viscosity response that thins at high shear rates (i.e.,

thixotropic flow properties). The indication of such elevated low shear viscosities could possibly provide evidence of increased suspension capabilities versus traditional HEC.

Once the overview of possible brine applications had been completed, the next step was to evaluate the brines individually. In doing so, a comparative analysis of other biopolymers was also performed to monitor the capabilities of the RM1 as to its rheological behavior (i.e., flow and suspension properties) and thermal stability.

Comparative Analysis of Biopolymers in Brines

10.0 ppg NaBr. The monovalent brine NaBr was the first salt solution for the comparative study. The chosen biopolymers were mixed via the previous procedure and allowed to equilibrate at 150°F for 4 h before testing. The results for the shear sweep tests are provided in Figure 2.

The low shear viscosity of the RM1 is comparable to the other biopolymers (particularly XAN) that are known to provide excellent suspension characteristics. When compared to traditional HEC, the modified polymer exhibits low shear viscosity values that are an order of magnitude higher.

The samples were also static aged at 220°F for 16 h in stainless steel aging cells. Afterwards, each were cooled and allowed to mix at 500 rpm for 10 min. RM1 exhibits excellent thermal stability in the NaBr solution as negligible thermal degradation was observed. When compared to XAN, the RM1 shows improved performance post static aging as the XAN demonstrates thermal thinning and decreased gelation behavior.

13.5 ppg CaBr₂. The solubility of the various biopolymers in the 13.5 ppg CaBr₂ was limited as the SCL yielded only minimal viscosity response and DIU would not disperse to any extent (Figure 3). However, the RM1 proved to be an excellent choice as it performed with preferred rheological properties and nominal thermal thinning.

RM1 maintained its thixotropic nature and elevated low shear viscosity values. Once again, these rheological characteristics of RM1 are indicative of increased suspension properties when compared to traditional HEC and are a result of the unique associative behavior of the polymer structure.

The CaBr₂ samples were also static-aged at 220°F for 16 h. The divalent brine managed to drive the SCL gum out of solution as the polymeric mixture phase separated due to decreased solubility parameters resulting in a collapsed conformation of the polymer structures. By contrast, the RM1 maintained its performance post static aging whereas XAN began to decrease at the elevated temperatures.

Dynamic Rheological Evaluation of the RM1 Polymer

As seen in the previous sections, the RM1 polymer seemed to provide gelation behavior that was similar to that of XAN. The ability of the new acid soluble material to provide suspension characteristics would be a vast improvement over the capabilities of conventional HEC. In order to investigate this type of behavior, dynamic rheological studies were

performed via a controlled stress rheometer to evaluate the storage (G') and loss (G'') moduli of RM1 versus XAN and HEC. XAN and HEC were excellent representatives as both are known to display both ends of the spectrum as XAN has suspension behavior and HEC does not.

The polymer samples were mixed in 10.0 ppg NaBr at 1.0 wt % polymer additive. This particular brine was chosen as all the various biopolymers were soluble within the media, and the brine provided some of the better static aging data of the various media tested. The results of the study are shown in Figure 4.

HEC exhibited a loss modulus (G'') greater than the storage modulus (G'). The rheological response had a significant viscous component but minimal elastic component which was indicative of a polymer network that does not yield favorable gel strengths and suspension properties. XAN displayed the opposite behavior than that of HEC. It had a dramatic elastic response thus providing evidence of its ability to produce preferred suspension characteristics up to 10 Pa. Stresses above 10 Pa resulted in failure of the gel and loss of suspension due to thixotropic fluid characteristics.

RM1 demonstrated behavior that is similar to XAN but superior in terms of overall performance. The storage modulus is more than double the loss modulus. The RM1 associative behavior is equivalent to a transient polymer network. Also, the gel structure is maintained over a broader stress range than that of XAN (i.e. >12 Pa). It can possibly be concluded that the RM1 exhibits improved suspension capabilities thus raising its rheological performance above conventional HEC while maintaining its preferred reservoir characteristics. Figure 5 demonstrates the improved suspension characteristics of RM1 vs. XAN.

Although the RM1 polymer and XAN have similar FANN 35 rheometer profiles, the increased low shear rheology of RM1 provides improved suspension at equivalent concentrations. Such behavior allows for efficient hole cleaning, particularly in lateral sections.

In addition to the improved suspension characteristics of the RM1 polymer, it also imparts improved stabilization and flocculation to drill solids. The unique chemistry of the polymer structure allows from inhibition of reactive shales (Figure 6).

Reservoir Performance

RM1 Removal and Acid Solubility. An important attribute to the utilization of HEC in many drill-in and completion systems is its ease of removal from the well-bore and its ability to undergo degradative processes such as oxidative or acid hydrolysis. Therefore, a final step in the evaluation of the RM1 polymer was to monitor its ability to break down in the presence of acid and heat. The same solution utilized in the previous section (i.e., 1.0 Wt % solutions of RM1 polymer in 10.0 ppg NaBr) was treated with 9.0 M HCl to lower the pH to 3.0. The solution was then placed in the FANN 50 viscometer and heated to 175°F at 100 rpms (Figure 7). In less than 1 h, the viscosity of the solution had dramatically decreased as the polymer underwent acid hydrolysis.

Permeability Testing. The acid soluble nature of the RM1 polymer allows rapid filter cake removal with treatment of acid via delayed acid breakers (Figure 8). Such characteristics are of extreme value in reservoir sections for maintaining the natural permeability of the native rock. In comparison to XAN, RMI has increased permeability numbers after acid treatment (Table 1, Figure 9).

Field Case Study

Initial application of RM1 was employment by a major operator during the drilling of a horizontal reservoir section in East Texas. Wells in this field are drilled utilizing a fresh water only system and Managed Pressure Drilling to protect the reservoir. Hole cleaning is aided through the pumping of viscous sweeps. RM1 was used to build the viscous sweeps for the horizontal lateral section. RM1 was selected as a more reservoir friendly alternative to XAN based sweeps.

RM1 was mixed in fresh water at 2 ppb concentration. Full yield of the sweep occurred within 20 minutes, and no defoamer was needed. A 15-bbl sweep achieved efficient hole cleaning (Figure 10). The slight foaming that was observed was less than that of the previous XAN sweeps (Figure 11).

The first application of RM1 in the field was rendered a success as improved hole cleaning with enhanced reservoir performance was achieved. Operator has continued use of the RM1 product.

Conclusions

The development, testing and field application of new polymeric additives has been achieved that can deliver enhanced reservoir fluid performance at high subsurface temperatures. The novel polymers can provide improved rheological performance, brine solubility, thermal stability, formation protection, and ease of removal from the wellbore when compared to conventional biopolymer rheology control agents such as xanthan gum, scleroglucan gum, diutan gum, and hydroxyethyl cellulose.

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Tables

Table 1. Return permeability studies with RM1 vs. XAN after acid clean up.

Polymer	RM1	XAN
Initial Return Perm, %	54	68
Perm after Acid Treatment, %	91.4	78

Figures

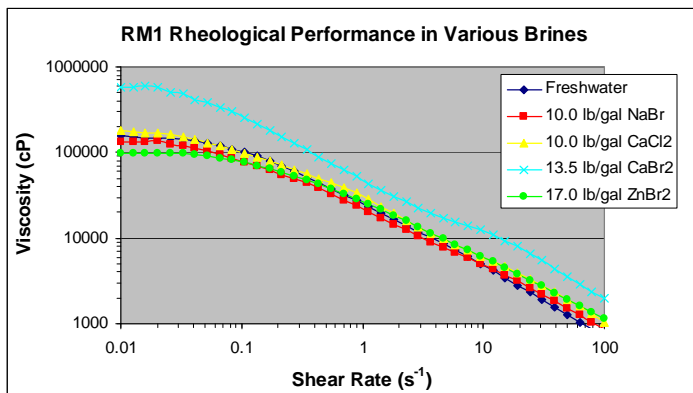


Figure 1. RM1 rheological performance in various brines at 1.0 wt % polymer.

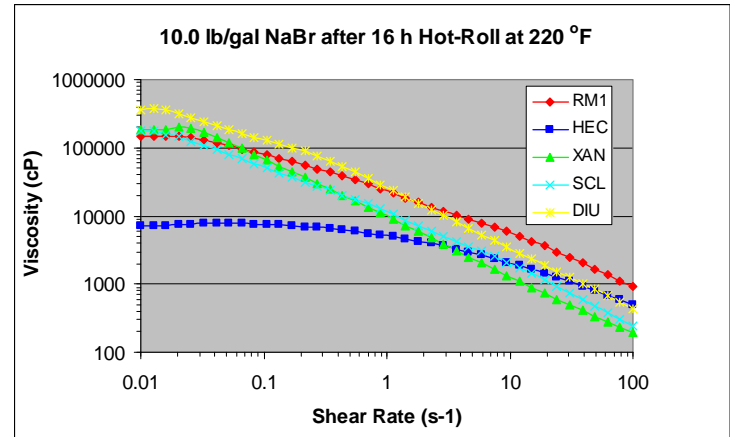
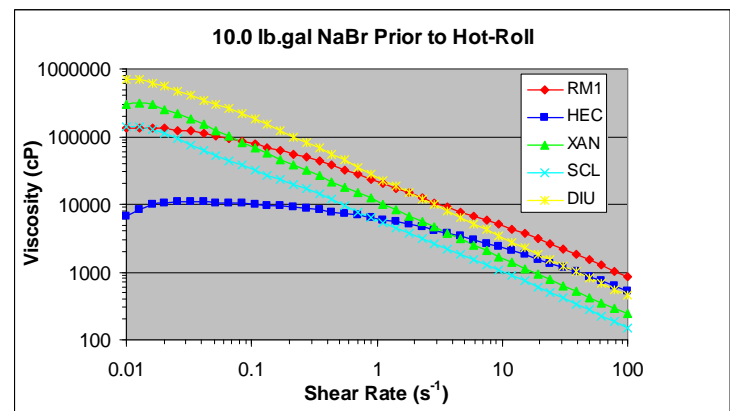


Figure 2. Rheological evaluation of 1.0 wt % various biopolymers in 10.0 ppg NaBr.

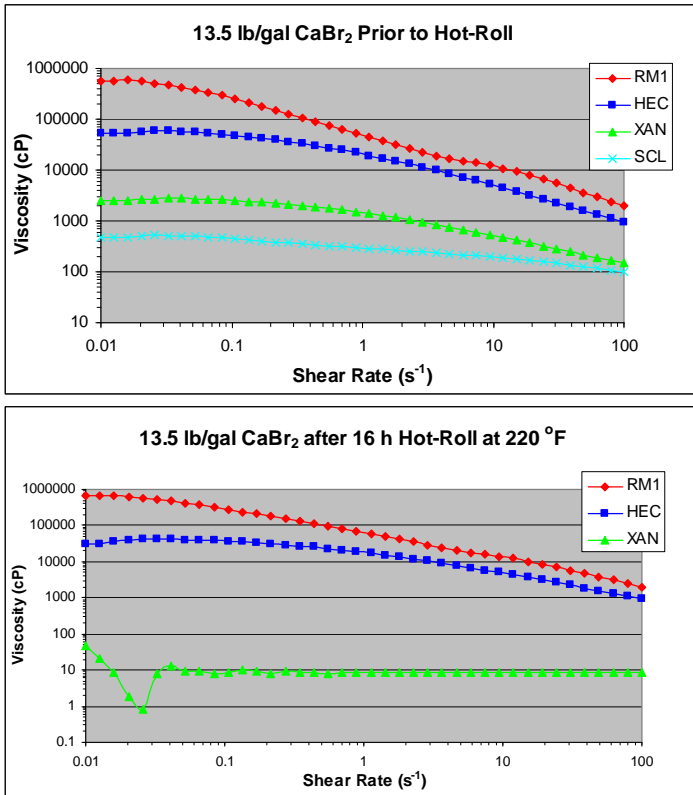


Figure 3. Rheological evaluation of 1.0 wt % various biopolymers in 13.5 ppg CaBr₂.

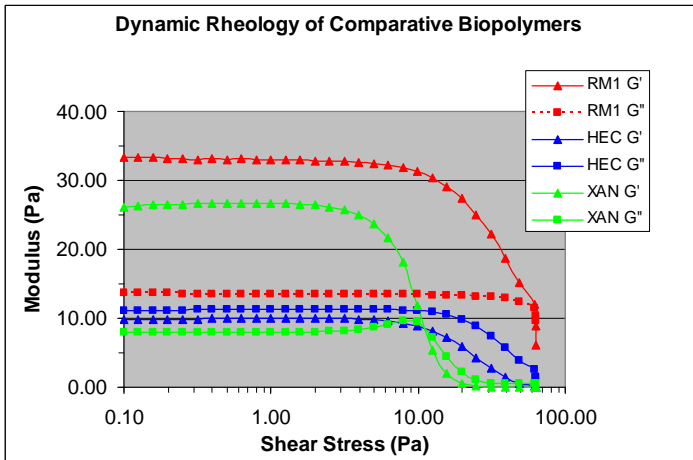


Figure 4. Analysis of RM1, HEC, and XAN via dynamic rheology.

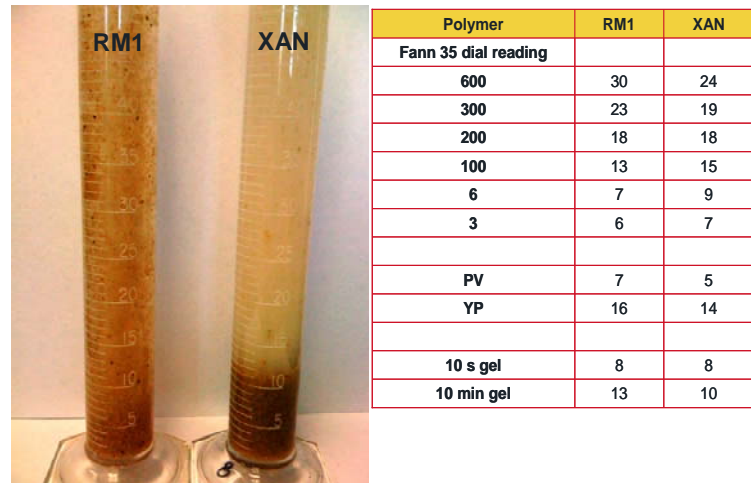


Figure 5. Static settling test of polymer fluids at 1.5 lb/bbl in freshwater for 4 hr with 80 lb/bbl 20/40 mesh sand.

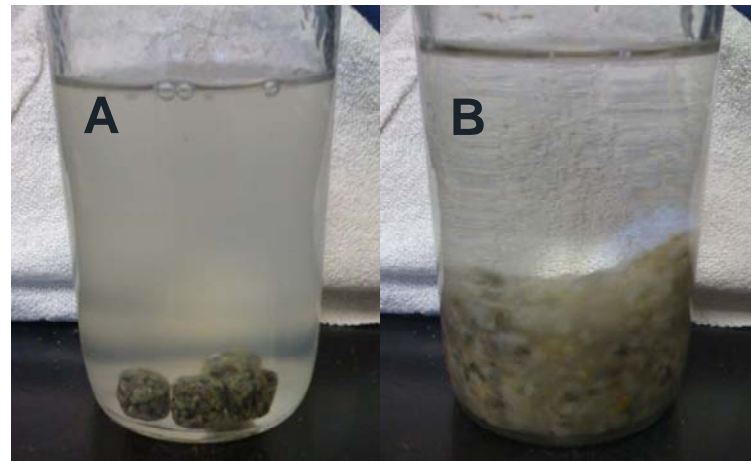


Figure 6. Bentonite stabilization studies: A) 48 h in 0.5 wt % RM1 in freshwater; B) 48 h in freshwater.

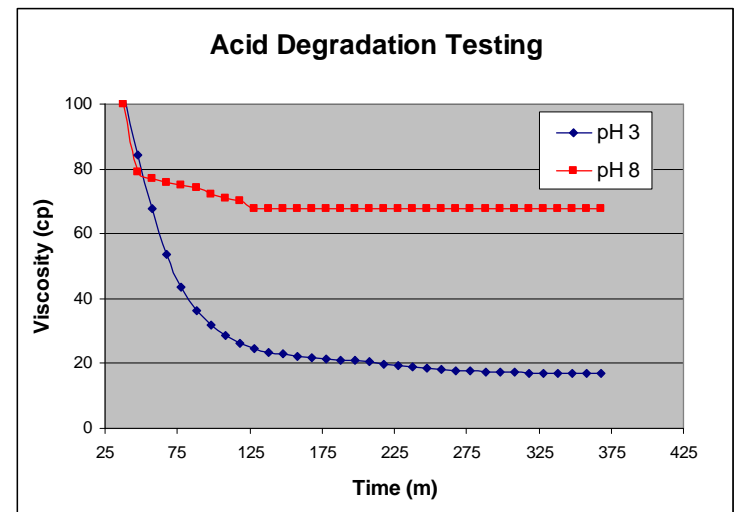


Figure 7. Acid hydrolysis curve for the degradation of RM1 at 175°F and 100 rpms.



Figure 8. 3h of treatment with formic acid (10 % vol) at 120°F.

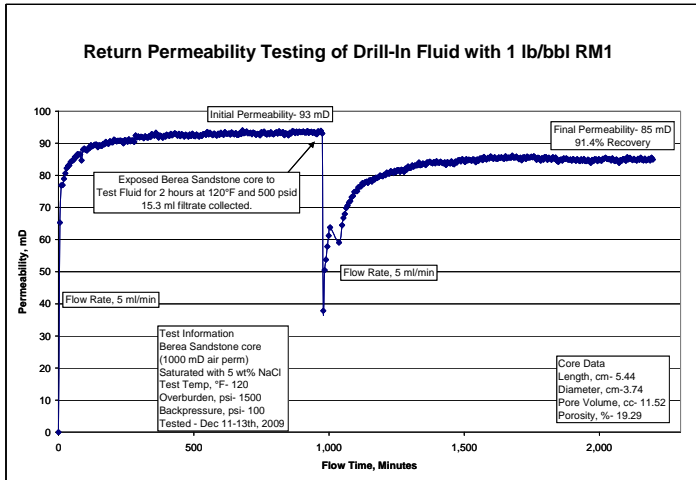


Figure 9. Return permeability of drill-in fluid with 1.0 ppb RM1 polymer with sized calcium carbonate.



Figure 11. Decreased foam was observed with the RM1 sweeps vs. XAN.



Figure 10. RM1 sweep returns at shakers during initial field application.