

High Temperature Acid Precursor as Filter Cake Clean-up Fluid

Tint Htoo Aung, Clotaire-Marie Eyaa Allogo, Bala Gadiyar, Ray Ravitz, Solomon King'ori, M-I SWACO, A Schlumberger Company

Copyright 20209, AADE

This paper was prepared for presentation at the 2020 AADE Fluids Technical Conference and Exhibition held at the Marriott Marquis, Houston, Texas, April 14-15, 2020. This conference is sponsored by the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individual(s) listed as author(s) of this work.

Abstract

In open hole completions, maximizing the productivity or injectivity requires a partial or a complete removal of the filter cake. Development of filter cake breakers is based on slow reacting chemistries such as esters, chelants and/or enzymes to avoid losses before the open hole can be isolated by mechanical means, to minimize corrosion of lower completion hardware and to allow a uniform removal of the filter cake across the open hole interval. At elevated temperature above 220°F (104°C) the filter cake breaker design with existing chemistries is extremely challenging due to some being unstable and/or undergoing hydrolysis at a faster rate than desired.

The main challenge in designing breakers is to balance the delay time and clean-up efficiency. Delay time requirement varies from hours to days depending on the completion operations, breaker spotting technique, and possibly production schedule. In many areas, acid precursor-based breakers are used for their relatively slow hydrolysis rate and high calcium carbonate dissolution capacity. However, controlling the hydrolysis reaction at high temperature (>220°F or 104°C) to deliver a delay time long enough for completion operation becomes a challenge or may be impossible with the actual design concept as proven in many field applications worldwide.

Potential acid precursor chemistries were selected and evaluated in the laboratory as a high temperature filter cake breaker for water-based and non-aqueous drill-in fluid. The evaluation procedures include building the filter cake on a simulated formation to simulate the drilling operation, and then spotting the various acid precursor-based breakers to assess the delay mechanism. The cleaning efficiency of the filter cake breakers was quantified with a flowback tester.

After detailed lab studies, the specific acid precursor was finalized to achieve the desired delay at temperatures above 220°F (104°C) for water-based and non-aqueous systems. The hydrolysis rate of the new acid precursor was significantly lower than the conventional low molecular weight acid precursor and was also effective in filter cake removal. The selected acid precursor is compatible with both monovalent and divalent brines. The paper outlines the evaluation process of the new acid precursor, discussion of laboratory testing and the operational window of the new acid precursor.

Introduction

Reservoir drill-in fluids (RDFs) have been the preferred option for drilling the reservoirs when the open-hole completions are installed to enhance the productivity and injectivity of the wells. When tailored to a specific reservoir, the RDFs can minimize the filtrate invasion into the formation matrix through an ultra-low permeability filter cake. If filter cake removal is needed, then it can be facilitated by means of acid treatments or less aggressive filter cake breaker treatments during completion operations.

Filter cake breakers are preferred over acid treatments in most scenarios because they can be included as part of the completion process and provide a more uniform destruction of the filter cake. Acids also tend to cause higher corrosion rates compared to well-designed filter cake breakers.

The filter cake breakers are engineered not only to destroy the filter cake but also to act in a slow enough timeframe such that the open hole can be isolated before losses are induced by the breaker. Premature breaker fluid leak-off results in a poor removal and leaves undispersed and undissolved filter cake residues. These residues can plug the completion screens and reduce the permeability of a gravel pack.

However, it becomes extremely challenging to avoid premature breakthrough for applications when the bottom hole temperatures exceed 220°F (104°C) because of the fast reaction kinematics with the filter cake. This issue has been identified both in the laboratory and field applications. The time required to delay reaction kinematics can vary from hours to days depending on the completion design, reservoir length and breaker spotting technique. In most cases, breakers are spotted during a post-completion operation via inner string (washpipe) and it takes a few hours (4-8 hours) to pull the washpipe above the mechanical fluid loss control device.

The authors initiated a study to evaluate specific acid precursor chemistry for high temperature applications beyond 220°F (104°C). This paper reviews the current breaker chemistries, the steps taken to evaluate the new high temperature (HT) acid precursor at various laboratory settings and defines the operational window of the new acid precursor.

Review of Filter Cake Breaker Chemistries

During overbalance drilling with a well-designed RDF, an ultra-low permeability filter cake is laid down across the permeable wellbore to prevent whole fluid invasion into the reservoir matrices and minimizing the depth of invasion. However, just after the open hole completion phase, the filter cake is no longer required as to lower the risk of residual skin and to prevent plugging the sand control screens. Therefore, filter cake breakers have been developed using innovative chemistries to degrade the integrity of the filter cake. Filter cake breakers are designed to serve the following purposes, but not limited to;

- Maximize the productivity or injectivity of the wells
- Minimize the damage of the completion hardware
- Prevent the plugging of the completion screens

The benefits of the breaker application can only be fully realized when the breaker acts on the filter cake in a slow timeframe to allow even removal of the filter cake. Fast-acting breakers will cause the unwanted premature disturbance to the filter cake at the point of contact which can result in losses of the filter cake breaker itself and completion brine into the formation, bypassing most of the filter cake on the wellbore and introducing further damage to the formation. When the filter cake is removed in only a portion of the well, uneven or isolated production may occur. In many scenarios, this may lead to premature water breakthrough, lost production and completion screen collapse. For this reason, breakers are normally engineered with non-aggressive and slow reacting chemistries to delay the reaction with the filter cake for at least the period of time elapsed between the moment the breaker is spotted in the open-hole section and the time the fluid loss control valve is closed to allow even removal of the filter cake.

The breaker chemistry selection is primarily dictated by the composition and nature of the filter cake which varies largely with the constituents of the RDFs. Bio-polymer, starch and calcium carbonate are the typical components in water-based filter cake whereas the non-aqueous (NAF) filter cake composition is completely different with the inclusion of emulsifiers, brine droplets and calcium carbonate. In addition, drilled solids accumulated during drilling also become part of the filter cake and can significantly impact the performance of the breaker fluid. **Table 1** lists common breaker chemistries for specific filter cake components. The breaker formulation can consist of one of the following chemistries or a combination of at least two to achieve both delay and filter cake removal.

Table 1 Breaker Chemistries for Specific Filter Cake Components

Breaker Chemistries	Filter Cake Components	Filter Cake Type
Enzymes	Starch	WB FC
Chelating Agents	Calcium Carbonate	WB FC/NAF FC
Oxidizers	Biopolymer	WB FC
Acid Precursor	Calcium Carbonate	WB FC/NAF FC
Surfactant / Solvent	Emulsifier/Wetting Agent	NAF FC

Enzymes: Enzymes are primarily used to break down the starch component in the water-based filter cake. They are slow reacting and do not get consumed during the process. Once all the starch is degraded, the filter cake loses its structural integrity and can easily be flowed back with production. However, their application is limited by high temperature (>212°F or 100°C) and by a narrow pH window. Various enzymes have their optimum pH window and must be carefully selected to be effective.

Chelating Agents: Chelants are used to dissolve calcium carbonate by binding the calcium ions in the solution. They find their applications for both water-based and non-aqueous filter cakes. Unlike acids, they are relatively less corrosive and slow reacting but sensitive to salinity, pH and divalent ions. Incompatibility between the base brine and the chelant can generate serious precipitates and need to be carefully selected for specific applications. With increasing temperature, the reaction kinetics increases significantly especially for temperature above 200°F (93°C).

Oxidizers: Oxidizers act on starch and biopolymer by converting organic molecules into carbon dioxide and get consumed in the process. A major disadvantage is that they tend to attack indiscriminately and aggressively on downhole hardware, formation fluids and filter cake. An innovative way of using coated solid oxidizers is making them part of the RDF during drilling to ensure the oxidizers attack only the filter cake components as they become embedded in the filter cake. The internal oxidizer is activated during the completion operations with an acidic solution such as the breaker fluid, but the application is limited for temperatures higher than 200°F (93°C) due to the short allowable exposure time.

Acid Precursor: Acid precursor is one of the most common breaker chemistries for both water-based and non-aqueous filter cakes. Acid precursors convert to organic acids in aqueous solution with time and temperature in a process called hydrolysis. The hydrolysis rate is relatively slow, and the generated organic acid is consumed by the acid soluble portion of the filter cake. Therefore, it results in more even dissolution of the filter cake and reduced corrosion rate compared to acid treatments. However, the hydrolysis rate is accelerated with increasing temperature and can result in instant reaction with the filter cake. In such cases, delay is compromised and so is the removal of the filter cake.

Surfactant/Solvent: Surfactant and solvent play a key role in breaker fluids for non-aqueous filter cake. Solvents help penetrate non-aqueous filter cake while surfactants allow breaker chemistries such as chelating agents and acid precursors to react with the oil-wet solids by changing the wettability to a water-wet state.

Viscosifier: Hydroxyethyl Cellulose (HEC) (known for its reservoir friendliness) is used to temporarily delay the reaction

kinematics by thickening the breaker fluids at elevated temperatures. However, HEC starts breaking down and the viscosity diminishes quickly at temperatures above 200°F (93°C) and it becomes no longer effective in extending the delay timeframe for the breaker fluid.

Problem Statement

As stated above in the breaker chemistry review, some of the breaker chemistries are not stable and few chemistries undergo fast hydrolysis at temperature exceeding 220°F (104°C). This has been proven both in the laboratory setting and field. For example, in a multi-well campaign in Middle East, the combination of acid precursor and chelant viscosified with HEC polymer was used for wells with the bottom hole temperature of 220-240°F (104-116°C). When placing the filter cake breaker, the operator constantly faced early breakthrough which led to the heavy losses of completion brine and partial production from the pay zone due to the filter cake residue. The underlying cause was identified as the fast hydrolysis of the acid precursor at the elevated temperatures and an alternative chemistry was needed to address the issue. Therefore, a potential high temperature (HT) acid precursor was evaluated for filter cake breaker applications exceeding 220°F(104°C).

Development of High Temperature Acid Precursor

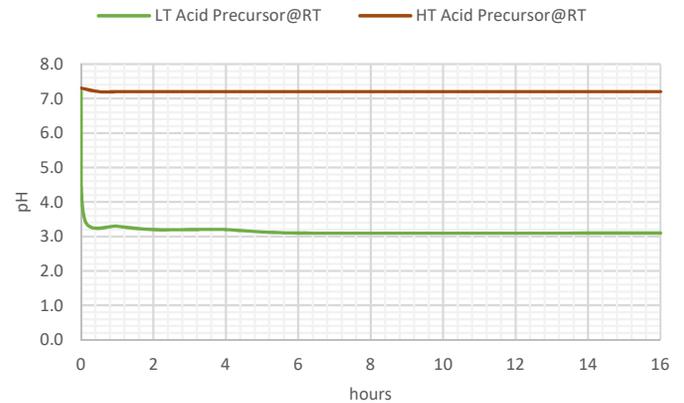
The HT acid precursor was evaluated in the following areas to qualify as a breaker chemistry;

- Hydrolysis at increasing temperatures
- Compatibility with oilfield brines
- Filter cake dissolution, delay
- Compatibility with supplementary breaker chemistries

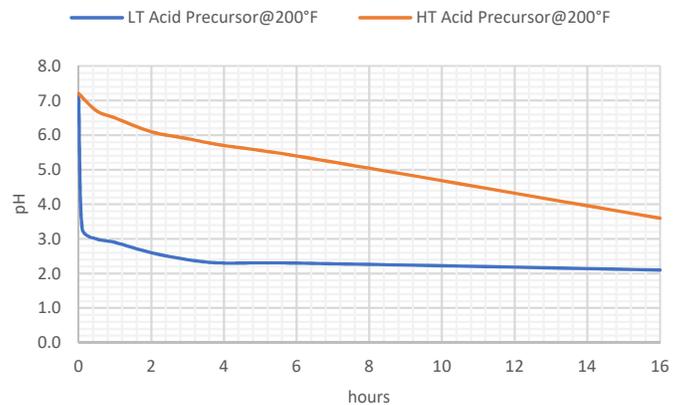
Hydrolysis Rate

The hydrolysis rate of the HT acid precursor was measured in water at ambient temperature (room temperature) and at 200°F(93°C) and compared with a low temperature (LT) acid precursor. The pH at time zero is the pH of the base fluid. For high temperature comparison, the pH readings were taken at only 200°F(93°C) due to the equipment and oven limitation and the necessity to take frequent readings at short intervals.

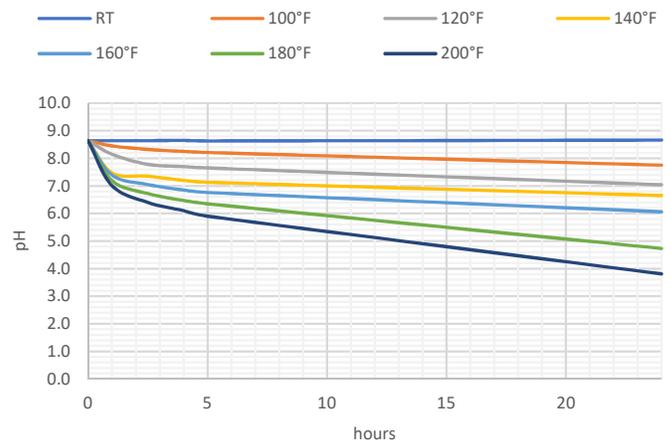
The HT acid precursor showed much lower hydrolysis rate and did not hydrolyze at ambient temperature (**Graph 1**). The conventional acid precursor starts hydrolyzing even at ambient temperature in the presence of free water (**Graph 1**) and the process is expedited by the temperature (**Graph 2**) meaning the breaker system has to be prepared as close as possible to placement time to reduce the amount of released organic acid. This sometimes makes operations complicated when the large volume is required, or pit space is limited. In contrast, the high temperature acid precursor can be mixed ahead of time and be ready for pumping due to negligible hydrolysis at ambient temperature as described in **Graph 1**.



Graph 1 Hydrolysis Rate of LT Vs HT Acid Precursor at room temperature (RT)



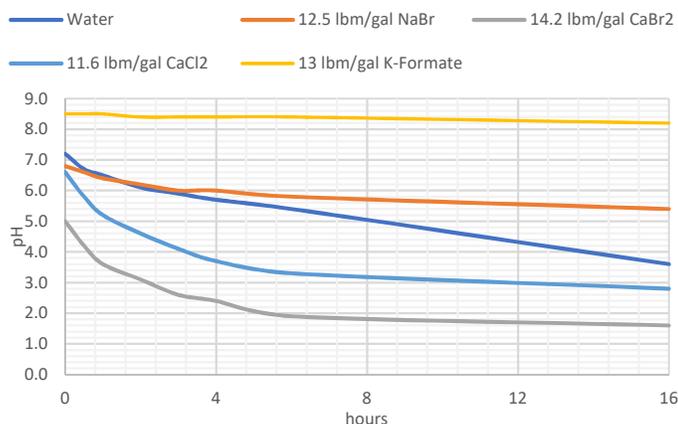
Graph 2 Hydrolysis Rate of LT Vs HT Acid Precursor at 200°F



Graph 3 Hydrolysis Rate of HT Temperature with Increasing Temperature

Compatibility with Oilfield Brines

Filter cake breaker density can vary across a wide spectrum based on well parameters and completion operation. Some acid precursors are immiscible at high salinity (Fig.1) and limited by their compatibility with specific brine. Therefore, it is critical to define the operation window for a given breaker chemistry. Unlike conventional acid precursor, the high temperature acid precursor is in a solid form and can easily be suspended by HEC viscosifier. The high temperature acid precursor was evaluated in various oilfield brines and found compatible with all of them even at high salinity (**Graph 4**).



Graph 4 Hydrolysis of HT Acid Precursor in Various Brines at 200°F



Figure 1 A LT Acid Precursor Showing Immiscibility in 14.2 lb/gal CaBr₂ and Miscibility in 19.2 lb/gal Zn/CaBr₂

Filter Cake Dissolution, Delay and Compatibility with Supplementary Breaker Chemistries

When evaluating the breaker chemistry, filter cake dissolution and delay are the two primary parameters for benchmarking its performance. For that, laboratory-scale breaker tests were set up. Common oilfield brines were utilized with supplementary breaker chemistries to evaluate any incompatibility issues during the dissolution process. The targets were set at minimum of 4 hours for the delay and 80% (production) or 50% (injection) for filter cake dissolution based

on return flow tester without any foreign materials at the end of the soaking period. The delay timeframe comes from the time to extract the washpipe above the mechanical fluid loss device after spotting the breaker in the open hole. In most cases, 4 hours is sufficient for the operation. The following testing protocol was adopted for the breaker testing;

1. The RDF system was selected – water-based or non-aqueous system - for the test.
2. A relevant formation disc was selected and initial flow rate at progressive pressures were measured as the baseline with a flowback tester.
3. Then the filter cake was deposited on a simulated formation disc for 4 hours under predetermined temperature and pressure using modified HTHP cell.
4. The RDF effluent was decanted, and the filter cake breaker was carefully spotted to not disturb the filter cake. The volume of the filter cake breaker was correlated with the volume to surface area ratio of the 8.5" open hole size with standalone completion screen.
5. Breakthrough was monitored until an uncontrollable leak-off was observed or the desired delay time was achieved.
6. The cell was then shut in and the breaker was soaked for the preset period of time. The soak time varies with the temperature and breaker chemistry (Manzolelua et al. 2016).
7. The return to flow test was performed to quantify breaker performance. The final flow rate was compared with the baseline to calculate the return to flow percentage.

$$\text{Return Flow \%} = 100 \times \frac{\text{Initial Flow Rate (mL/sec)}}{\text{Final Flow Rate (mL/sec)}}$$

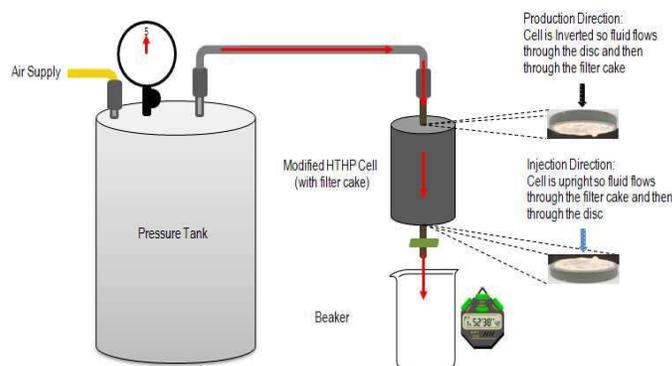


Figure 2 Schematic of a Flowback Tester

Discussion and Results

Table 2 is the summary of the outstanding filter cake breaker tests performed during the evaluation of the new high temperature acid precursor. The HT acid precursor was tested against both non-aqueous (Tests#1-9) and water-based (Tests#10-11) filter cakes from 220 - 270°F (104 -132°C) in

Table 2 The Summary of Outstanding HT Acid Precursor Evaluation Tests

Formulations	1	2	3	4	5	6	7	8	9	10	11
Testing Parameters											
Filter Cake Type	NAF FC	NAF FC	NAF FC	NAF FC	NAF FC	NAF FC	NAF FC	NAF FC	NAF FC	WB FC	WB FC
Test Temperature (°F)	230	230	230	230	230	230	260	270	270	220	200
Well Type	Producer	Producer	Producer	Producer	Producer	Producer	Producer	Injector	Producer	Producer	Producer
Brine Type	NaBr	NaBr	NaBr	NaBr	NaBr	NaBr	CaBr ₂	NaBr	NaBr	CaBr ₂	CaBr ₂
Brine Density(lbm/gal)	10.8	10.8	10.8	10.8	10.8	10.8	13.1	12.5	12.5	14.5	14.5
Breaker Density(lbm/gal)	10.7	10.7	10.7	10.7	10.7	10.7	12.5	10.6	11.0	14.2	14.2
Drilled Solids (Y/N)	No	No	No	No	No	No	Yes	No	No	No	No
Products	lb/bbl	lb/bbl	lb/bbl	lb/bbl	lb/bbl	lb/bbl	lb/bbl	lb/bbl	lb/bbl	lb/bbl	lb/bbl
HT Acid Precursor	LO	MED	OT	OT	OT	OT	OT	OT	OT	OT	OT
Chelant 1						40					
Chelant 2					45						
HEC Viscosifier	5	5	5	5	5	5	10			3	3
Surfactant	16	16	16	16	16	16	16				
Thermal Stabilizer				5							
Results											
Breaker Initial pH	6.8	6.8	6.8	11.1	2.9	7.2	4.2	-	-	6.0	6.0
Breaker Spent pH	6.0	3.2	2.6	3.5	2.8	3.2	1.3	1.7	2.2	1.2	2.4
Delay Achieved(hrs)	>4	>4	>4	>4	>4	>4	6	>6	>6	>4	>4
Soaking Period(days)	6	6	6	6	6	6	5	5	5	6	6
Removal Efficiency	Bad	Fair	Good	Good	Fair	Bad	Good	Good	Good	Good	Bad
Scales/Precipitates	No	No	No	Yes	Yes	Yes	No	No	No	No	No
Return Flow at 5 psi	N/A	72%	90%	N/A	N/A	N/A	71%	53%	85%	80%	20%

both production and injection directions. Both monovalent brine (NaBr) and divalent brine (CaBr₂) were used to formulate the breaker with salinity close to saturation in some of the formulations. In all cases, the HT acid precursor was able to meet the delay target (more than 4 hours). The compatibilities with chelant and thermal stabilizer was also assessed.

First, the optimal concentration of the HT acid precursor was determined to completely dissolve all the calcium carbonate in the filter cake (Test#1-3). The concentrations were designated as Low (LO), Medium (Med) and Optimal (OT) in **Table 2**. Once the optimal concentration was established, the same concentration was used for the rest of the testing matrix. HEC was used to viscosify the breaker solution and surfactant was used for oil-coated solids such that the released organic acid can easily react with the calcium carbonate. The return flow percentage at 5 psi with medium and optimal concentrations yielded 72% and 90% respectively.

In Test#4, a thermal stabilizer was added and resulted in

incompatibility (**Figure 3 Pic 4**). Thermal stabilizer had been used in the past to extend the lifespan of HEC viscosifier for temperature exceeding 220°F (104°C) but it was not needed for HT acid precursor due to its much lower hydrolysis rate.

Two types of chelant (Test #5&6), which have been previously used with conventional acid precursor to prevent the system upset such as precipitates during the reaction between the organic acid and calcium carbonate, were added to the HT acid precursor breaker formulation for compatibility check, but both resulted in precipitates after the end of 6 day soaking period.

In Test#7, the temperature was raised to 260°F (127°C) and 13.1 lbm/gal (1.57s.g.) calcium bromide was used to build the breaker. The breakthrough occurred at 6 hours and the return flow percentage at 5 psi was 71%. It should be noted that the residual solids on the simulated formation disc are drilled solids added to the RDF system.



Figure 3 Photos of Simulated Formation Discs after Exposure to HT Acid Precursor Breaker

Test#8 was for injector and Test#9 was producer scenario. Temperature was increased to 270°F(132°C). In both tests, the breaker was viscified by means of invert emulsion and 12.5 lbm/gal (1.5 s.g.) sodium bromide (close to saturation) was used to reach the final breaker densities of 10.6 lbm/gal (1.27 s.g.) and 11.0 lbm/gal (1.32 s.g.) respectively. The filter cake dissolution was good (**Figure 3 Pic 8**) with the return flow of 53% in injection direction and 85% in production direction. Delay was more than 6 hours and no precipitates were formed during the soaking period of 5 days.

Test#10 and 11 were the same water-based filter cake and HT breaker but one was run at 200°F (93°C) and the other at 220°F (104°C). Both breakers were soaked for 6 days. This is to determine the temperature range of the HT temperature. The 200°F (93°C) test only yielded 20% return flow at 5 psi and most of the filter cake remained while the 220°F (104°C) test showed little residues and 80% return flow at the same pressure (**Figure 3 Pics 10/11**).

Operational Window of the HT Acid Precursor

Based on the evaluation, the following operational window is defined for the HT acid precursor;

1. HT acid precursor is compatible with all common oilfield brines. The faster hydrolysis rate is observed in divalent brines such as calcium chloride and calcium bromide brine. Formate brines buffer the pH of the breaker.
2. HT acid precursor can be used with high salinity brine. Salinity has little impact on the breaker performance.
3. The temperature window of the HT acid precursor can be defined between 220°F (104°C) and 300°F (149°C). The hydrolysis rate is too slow for temperature below 200°F (93°C) and will not be practical as a breaker application unless the soaking period can be extended to months. The hydrolysis will be uncontrollable and premature breakthrough can still

- happen for applications above 300°F (149°C).
4. HT acid precursor can be mixed ahead of time with little hydrolysis under ambient condition.
 5. HT acid precursor can be used for both water-based and non-aqueous filter cake dissolution.
 6. Minimum recommended soaking timeframe for HT acid precursor is 5 days.
 7. Chelants have limited compatibility with the HT acid precursor.
 8. Amine-based thermal stabilizer should not be used with HT acid precursor.

- Technology Conference, Doha, Qatar, December 6-9, 2015
5. M. Parlar, M.E. Brady, L. Morris, A. Twynam, P. Newberry, C. Svoboda and W.E. Foxenberg. "Filtercake Removal Techniques for Openhole Water Injectors with Sand Control: Lessons from Laboratory Experiments and Recommendations for Field Practices" SPE 77449, SPE Annual Technical Conference and Exhibition, San Antonio, September 29 – October 2, 2002

Conclusions

1. The challenge to delay the filter cake breaker at temperature exceeding 220°F(104°C) can be overcome by using the new HT acid precursor without impacting the uniform filter cake dissolution.
2. HT acid precursor is compatible with common oilfield brines and can be used for a wide range of densities even with high salinity brines.
3. The temperature window for the HT acid precursor is between 220°F(104°C) and 300°F(149°C).

Acknowledgments

The authors would like to thank Cedric Manzolelua and Bala Panamarathupalayam for their contribution to this paper and acknowledge M-I SWACO, A Schlumberger Company, for its permission to publish this paper.

Nomenclature

<i>RDF</i>	= Reservoir Drill-in Fluid
<i>HT</i>	= High Temperature
<i>WB FC</i>	= Water-based Filter Cake
<i>NAF FC</i>	= Non-aqueous Filter Cake
<i>HHP</i>	= High Temperature High Pressure
<i>LO</i>	= Low Concentration of Acid Precursor
<i>MED</i>	= Medium Concentration of Acid Precursor
<i>OT</i>	= Optimal Concentration of Acid Precursor

References

1. Cedric Manzolelua, David Li, and Matt Offenbacher. "Filter Cake Breaker Evaluation Pitfalls: Lessons Learned Through Testing" AADE-16-FTCE-50, AADE Fluids Technical Conference and Exhibition, Houston, April 12-13, 2016. Available from www.aade.org
2. Clotaire-Marie Eyaa Allogo, Raymond Ravitz, Solomon King' Ori, and Tint Htoo. "Ability of a Filter Cake Breaker to Diffuse into Completion Brine and Packed Gravel" SPE-179007-MS, SPE International Conference & Exhibition on Formation Damage, Lafayette, February 24-26, 2016
3. M.R. Luyster, A.D. Patel, and S.A. Ali. "Development of a Delayed-Chelating Removal Technique for Openhole Gravel-Pack Horizontal Completions Using a Reversible Invert Emulsion Drill-In System" SPE 98242, SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, February 15-17, 2006
4. David Li and Wenwu He. "Journey into Filter Cakes: A Microstructural Study" IPTC-18246-MS, International Petroleum