

# Tailoring Properties of Stimuli Responsive Polymers in Downhole Applications

Sunita Kadam and Rajendra Kalgaonkar, Halliburton

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## Abstract

Rapid formation and delayed dissolution of filter cake are important during drilling and completion operations to help minimize formation damage. The acid precursor chemistry is developed for the controlled and delayed reaction of treatment fluid with filter cake. During this process, organic esters slowly generate in-situ acids that dissolve filter cake over a period of time, resulting in its uniform removal. This technique is beneficial in challenging completion conditions, particularly in horizontal, multilateral, and extended reach wells. The performance of organic esters is vulnerable at high temperatures because of an increased rate of hydrolysis. This can result in early acid release, defeating the purpose of using this technique to delay filter-cake removal.

This paper addresses the shortcomings of the currently used systems and demonstrates the advancement in terms of acid precursor technology to delay dissolution of filter cake at higher temperatures using stimuli responsive polymers. Designing reversible network formations using stimuli responsive polymers is discussed. This network entraps the in-situ released acid, thus delaying dissolution of filter cake. The technique can be used to entrap organic ester. This paper documents the laboratory investigation of using stimuli responsive polymers for enhancing the scope and application of acid precursor chemistry for high-temperature applications. The new fluid system provides improved flexibility and cost management for designing high-temperature filter-cake removal treatments by broadening the in-situ chemical control mechanisms; additionally, it provides the expectation of improved production costs post filter-cake removal.

## Introduction

Water and oil-based drill-in fluids are widely used to drill reservoir sections. These fluids comprise calcium carbonates—a bridging agent—which helps form impermeable filter cake and control fluid loss to the formation while drilling. Completion operations are used to remove this impermeable filter cake formed by calcium carbonate by its dissolution to help regain permeability and increase production efficiency. Thus, the primary concern during completion operations is formation damage and decreased production rates caused by incompletely removed thick and uneven filter cake<sup>4</sup>. Additionally, costs can increase because of increased rig time and fluid chemicals.

Various approaches were applied to clean up filter cake during completion operations<sup>1</sup>. These include the use of hydrochloric acid, chelating agents, enzymes, oxidizers, and organic ester (in-situ acid generator) etc. Hydrochloric acid is effective for dissolving calcium carbonate based filter cake, but the reaction can be vigorous, uncontrolled, and lead to undesired non-uniform filter-cake removal. Chelating agents form complex with the filter cake components and dissolve the filter cake. Their rate of complexation is quick, similar to hydrochloric acid. Enzymes and oxidizer work toward degrading or dissolving the polymeric components of the filter cake and do not dissolve the carbonate particles. Therefore, some approaches involve using a combination of chelating agent and enzymes/oxidizer to dissolve calcium carbonate and polymer, respectively. In all of these approaches, the reaction between calcium carbonate and filter-cake breaker is quick, and there is no control or delay to dissolution. To overcome this, use of organic esters as filter-cake breakers has been employed for some time<sup>5-6</sup>. These esters hydrolyze in the presence of water and temperature over extended time periods to release acid that reacts with filter cake to clean it. The action of these ester based breaker systems can be retarded for several hours, depending on downhole temperatures and breaker formulations. This delayed reaction helps ensure the breaker solution is uniformly distributed throughout the completion interval before it begins working. These ester-based breaker systems generate organic acid slowly downhole, not at the surface, dissolving calcium carbonate and polymer throughout the interval. In addition, the ester breaker systems are neutral when mixed with carrier brine, and therefore help eliminate potential for injury and damage associated with handling hazardous acids at the surface. However, with all of these advantages, the high bottomhole temperature limits the use of this acid precursor chemistry. The rate of ester hydrolysis is faster at high temperatures, which results in immediate release of acid from the precursor, and thus immediate dissolution of filter-cake components. This can result in hot spots and localized, uneven removal of filter cake, thus defeating the primary purpose of imparting the delay in filter-cake dissolution using acid precursor chemistry<sup>7</sup>.

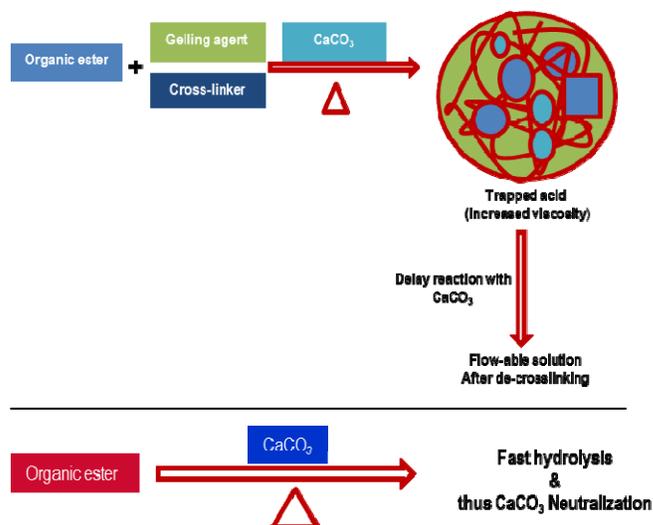
To help increase the efficiency of acid precursor chemistry, more controlled acid release and complete filter-cake removal at elevated temperatures is necessary. This methodology can be advantageous compared to current

approaches for wellbore cleanup at elevated temperatures where there can be a faster rate of hydrolysis of the ester to release the acid prematurely in the wellbore, leading to inefficient removal of the filter cake before the treatment fluid is uniformly distributed.

This paper describes laboratory evaluation of the application of stimuli responsive polymers to form reversible networks with in-situ released acid (from organic ester hydrolysis) and delay the dissolution of drill-in fluid filter cake. The goal of this laboratory study is to test an improved fluid system to control the rate of reaction of released acid with bridging agent used to build up the filter cake, thus delaying its dissolution.

### New Approach to Delay the Dissolution of Drill-In Fluid Filter Cake at High Temperatures

In the present approach, delayed dissolution of  $\text{CaCO}_3$  was attempted by means of crosslinking pH responsive polymers in the presence of organic esters. This can ultimately delay the action of released acid to react with the  $\text{CaCO}_3$  and clean up the filter cake<sup>2-3</sup>. Initially, a synthetic polymer, crosslinker and buffer were added to an organic ester based solution. The entire formulation has a low viscosity and can be easily pumped downhole. As the ester hydrolysis began, the pH of system dropped quickly to a more acidic pH. This helped ensure the acid began reacting with  $\text{CaCO}_3$  in the filter cake. As the acid spent, the pH began to rise. The crosslinker in the formulation activated under certain pH conditions and crosslinked the synthetic polymer to produce a crosslinked gel. The buffer helped retain the desired pH necessary by the crosslinker to crosslink the polymer for a longer period of time. With the formation of the crosslinked gel, the viscosity of the system increased tremendously, thereby retarding the rate of reaction of the acid with the  $\text{CaCO}_3$ . As further acid spent slowly to remove the entire filter cake, the pH of the system further increased, which lead to deactivating the crosslinker. This resulted in decrosslinking the breaker fluid that reduced the viscosity of the system, leading to easy flowback and effective wellbore cleanup. **Fig. 1** presents the scheme for crosslinking and decrosslinking of stimuli responsive polymers in the presence of  $\text{CaCO}_3$  and reaction of organic ester in the presence and absence of gelling/crosslinking.



**Fig. 1: Reversible crosslinking of stimuli responsive polymers to delay filter-cake dissolution at high temperatures. In contrast, higher rate hydrolysis of ester at high temperatures leading to faster dissolution of  $\text{CaCO}_3$ .**

### Experimental Methods

#### I. In-Situ Gelling of Stimuli Responsive Polymer and Calcium Carbonate Dissolution (Neutralization)

In-situ gelling of stimuli responsive polymers was carried out by mixing them with organic esters and  $\text{CaCO}_3$  with the appropriate quantities of crosslinkers in buffer solution and heating the test solution at the desired temperature.

Calcium carbonate dissolution was carried out to study the effect of gelling of stimuli responsive polymers on acid release and its reaction with  $\text{CaCO}_3$ . The reaction of released acid with  $\text{CaCO}_3$  was monitored by measuring the pH of the test solution. The control experiment was conducted by monitoring the  $\text{CaCO}_3$  dissolution in the absence of stimuli responsive polymer and crosslinker.

The organic ester, having a higher rate of hydrolysis at 90 to 100 °C, was selected for this study to visually monitor the rate of in-situ acid release, its reaction with  $\text{CaCO}_3$ , gelling of stimuli responsive polymer (caused by crosslinker activation) and decrosslinking of the system (increased pH of the system and crosslinker deactivation). The test solution was prepared as per the following procedure. The test components are presented in **Table 1**.

- i. Add the necessary amount of water to prepare the test fluid.
- ii. Add the appropriate amount of organic ester.
- iii. Slowly add Polymer I to help prevent the formation of polymer lumps or fish eyes.
- iv. Add buffer and then crosslinker.
- v. Hydrate the test fluid for one hour.
- vi. Heat the solution to the desired temperature.
- vii. Add  $\text{CaCO}_3$  to the above solution until it forms a gel or viscous fluid.

viii. Monitor the pH of the solution and flow (viscous/flowable) of the liquid

**Table 1: Test Solution Components**

Components	Amount
<b>Solution A (Gelled)</b>	
Ester I in water	30 + 170 mL
Polymer I	3 g
Buffer	0.4 g
Crosslinker	0.9 g
<b>Solution B (Control)</b>	
Ester I in water	30 + 170 mL
Test temperature	90°C

## II. Filter-Cake Cleanup Efficiency

This study was conducted to test the efficiency of entrapped in-situ released acid to clean up the drill-in fluid filter cake. The organic ester, having a higher rate of hydrolysis at 120 to 140 °C, was selected for this study. Testing was conducted at 150°C.

A high-temperature/high-pressure (HT/HP) (500 mL) setup was used to build up a filter cake on a 20-micron ceramic disc at 121°C and 500 psi differential nitrogen pressure. Drill-in fluid formulation used to build up filter cake is presented in **Table 2**. After formation of filter cake, the supernatant solution was carefully poured off and the respective test solution viz. in-situ gelled formulation and control fluid were added to the HT/HP cell. These HT/HP cells were hot rolled at 150 °C using a roller oven for two hours. After the test period, the cells were cooled to room temperature. The breaker solution was then poured off and the discs were removed and inspected visually for the dissolution of filter cake.

**Table 2: Drill-In Fluid Formulation for Filter-Cake Buildup**

Products	Quantity (g)
Tap water	324
Potassium chloride	10.33
A cross-linked starch (fluid-loss-control agent)	8.75
Xanthan gum polymer (viscosifier)	1.00
CaCO <sub>3</sub> particulate bridging material (various mesh sizes)	40.00
Alkaline buffer (magnesium oxide)	1.00

After mud formulation was mixed, it was placed in a pint jar and rolled at 65°C for 16 hours. The mixture was then cooled and mixed again for two minutes before being used for filter-cake formation.

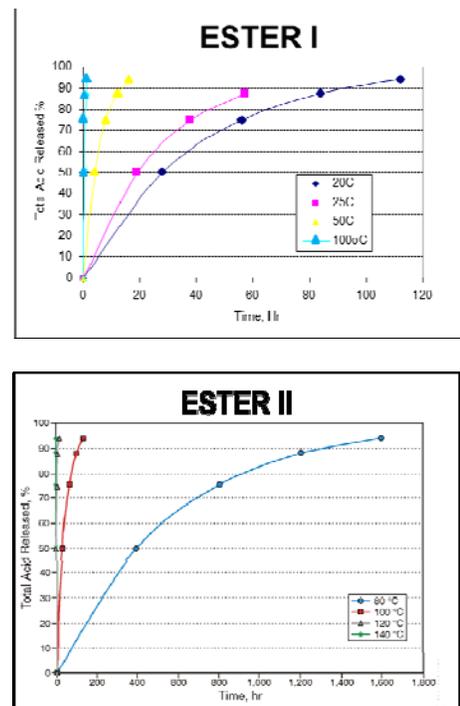
**Table 3: Test Components for Filter-Cake Dissolution**

Components	Amount
<b>Solution C (Gelled)</b>	
Ester II + water	50 + 150 mL
Polymer I	3.0 g
Buffer	0.4 g
Crosslinker	0.9 g
<b>Solution D (Control)</b>	
Ester II + water	50 + 150 mL
Test temperature	150°C

## Results and Discussion

To test the hypothesis that reversible crosslinking of stimuli responsive polymer in the presence of organic ester at high temperatures will delay the reaction of released acid (after ester hydrolysis) with the bridging material (CaCO<sub>3</sub>) and thus delay the dissolution of filter cake, two organic esters were selected—Ester I and Ester II having higher hydrolysis rates at 90 and 140°C, respectively. **Fig. 2** illustrates the rate of hydrolysis as a function of temperature and time for the selected Ester I and Ester II. As temperature increases, the rate of hydrolysis increases, resulting in the immediate release of acid. For instance, Ester I released almost all of the acid in no time at 100°C, whereas Ester II released all of the acid at 120 (also at 140°C), respectively.

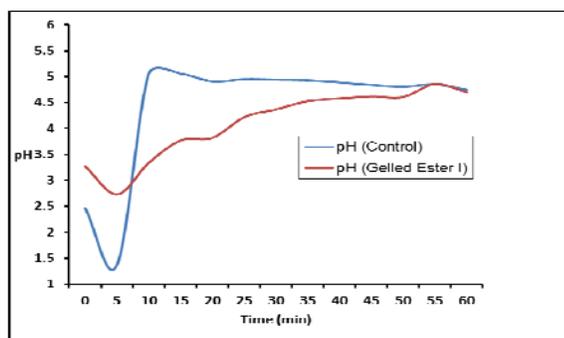
In view of this, for the current study, the performance of esters were tested at 90°C for Ester I and 150°C for Ester II.



**Fig. 2: Rate of ester hydrolysis (Ester I and Ester II) as a function of temperature and time.**

### In-Situ Gelling of Stimuli Responsive Polymer and CaCO<sub>3</sub> Dissolution

To study the effects of reversible gelling of stimuli responsive polymer in the presence of in-situ released acid and CaCO<sub>3</sub>, the organic ester (i.e., Ester I) and test ingredients were mixed together as per the test procedure and test components given in experimental methods and Table 1, respectively. Both of the solutions—Solution A (gelled ester I) and Solution B (control)—were heated to the test temperature, 90°C. CaCO<sub>3</sub> was then added to both solutions. The released acid began reacting with added CaCO<sub>3</sub>, resulting in increased pH of the system attributed to dissolution of CaCO<sub>3</sub>. Therefore, to evaluate the rate of acid reaction with CaCO<sub>3</sub>, the pH and flow (viscous vs. flowable) of the system were monitored at regular intervals. The results are depicted in **Fig. 3** and **Table 4**. The pH of Solution B, the control solution, increased immediately from 1.37 to 5.06, indicating the fast reaction of released acid with added CaCO<sub>3</sub>. Conversely, the pH of the gelled system increased only from 2.73 to 3.34 after the addition of CaCO<sub>3</sub>. This indicated the slow release of acid, and thus the slow dissolution of CaCO<sub>3</sub>. Note that the initial pH of Solution A (i.e., gelled Ester I [initial pH 3.27, after heating decreased to 2.73]) and Solution B control (initial pH 2.46, after heating decreased to 1.37) was also different in spite of using the same organic ester. This was because of the entrapping of released acid by stimuli responsive polymers, which further resulted in gelling/crosslinking with the addition of CaCO<sub>3</sub>. Thus, the stimuli responsive polymer began controlling the acid release to the solution before coming in contact with CaCO<sub>3</sub>.



**Fig. 3:** Performance testing of Ester I: Test solution pH variation with time after addition of CaCO<sub>3</sub>.

**Table 4:** Effect of Reversible Gelling of Ester I: Change in Test Solution pH Vs Time, After Addition of CaCO<sub>3</sub>

Time (min)	pH (Gelled) (Solution A)	pH (Control) (Solution B)	Temp. (°C)
0	3.27	2.46	25
5	2.73	1.37	90
10	3.34	5.06	90
15	3.77	5.06	90
20	3.82	4.91	90
25	4.22	4.95	90
30	4.37	4.94	90
35	4.53	4.93	90
40	4.58	4.89	90
45	4.62	4.84	90
50	4.61	4.81	90
55	4.86	4.85	90
60	4.70	4.75	90

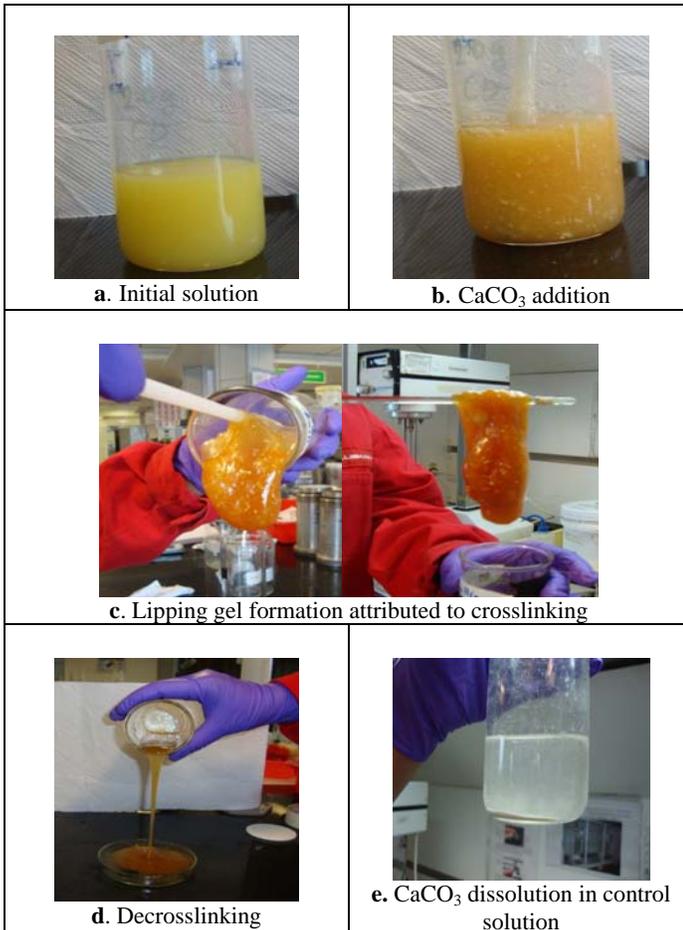
This test clearly revealed that, as the temperature increased, although the rate of ester hydrolysis increased, in the presence of a gelled Ester I system, the rate of reaction to dissolve CaCO<sub>3</sub> could be retarded. The conventional organic ester-based system (i.e., control) reached a stable pH of approximately 5 as the acid spent in 15 minutes. The gelled system required 60 minutes to reach a similar pH. Thus, the time difference of 45 minutes clearly showed that the rate of reaction of the acid with the CaCO<sub>3</sub> in the gelled system was much slower than that of a conventional system.

**Fig. 4** shows the visualization of gelling (i.e., crosslinking and decrosslinking) of the stimuli responsive polymer under testing conditions. The initial solution (Fig. 4a) was very flowable after the addition of CaCO<sub>3</sub>; the released acid began reacting to dissolve CaCO<sub>3</sub> (Fig. 4b), increasing the pH of the system, activating the crosslinker to form crosslinking (lipping gel) (Fig. 4c). Further reaction of released acid with CaCO<sub>3</sub> deactivated the crosslinker, causing decrosslinking (Fig. 4d), and resulting in flowable liquid; whereas, in Control Solution B, immediate bubbling and fast dissolution of CaCO<sub>3</sub> was observed (Fig. 4e).

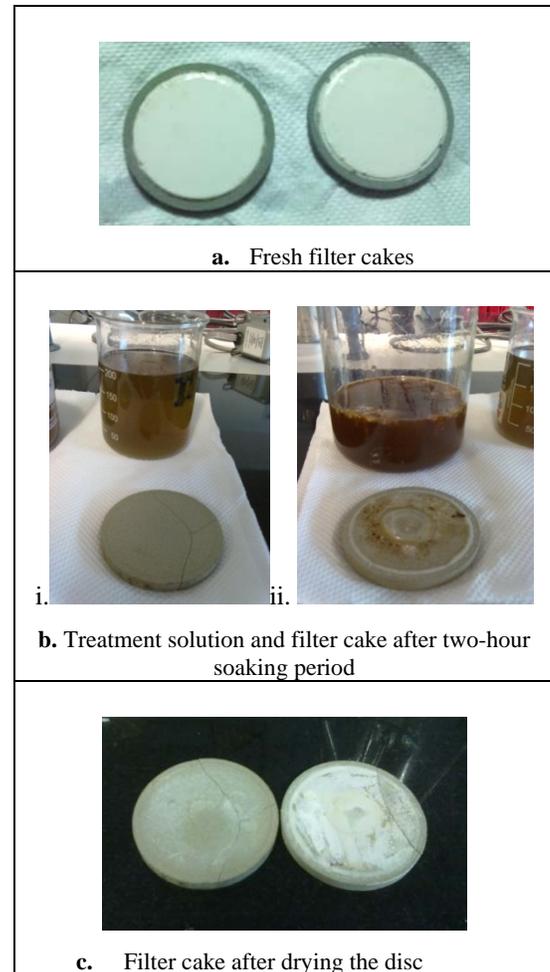
### Filter-Cake Dissolution

To test the performance of the proposed reversible crosslinking in terms of delaying the filter-cake dissolution process, water-based drill-in fluid filter cakes were prepared (Table 2, **Fig. 5a**). The filter-cake dissolution was conducted using Ester II at 150°C, a much higher temperature than its hydrolysis rate (**Fig. 1**). The test and control solutions were prepared as described in Table 3 and added to the respective filter cake in HP/HT cells and kept rolling for two hours in a rolling oven at 150°C. As presented in Fig. 5b, the complete dissolution of filter cakes was observed in the case of the

control solution, Solution D, while a white residue was observed on the filter disc of Gelled Ester II (i.e., Solution C) (Fig. 5b). This shows the delay in filter-cake dissolution with gelling of Ester II, even at higher temperatures compared to its working temperature limit. This clearly demonstrates the enhancement of acid precursor chemistry for high-temperature applications using stimuli responsive polymers.



**Fig. 4: a. initial solution; b. after addition of  $\text{CaCO}_3$ ; c. in-situ crosslinking, lipping gel formation; d. decrosslinking after dissolution of  $\text{CaCO}_3$ ; and e.  $\text{CaCO}_3$  dissolution in control solution.**



**Fig. 5: a. fresh filter cakes; b. solution and filter cakes after two hours of hot rolling, i. control solution, ii. Gelled Ester II; c. filter-cake after drying the discs.**

## Conclusions

Reversible network formation ability of stimuli responsive polymers was evaluated for the advancement of acid precursor chemistry for high-temperature wellbore cleanup applications.

- Entrapping organic ester delayed the reaction of released acid with  $\text{CaCO}_3$  because of increased viscosity and trapping of hydrolyzed acid in the gel.
- Delaying the premature reaction of acid with filter cake helped create more effective and complete filter-cake removal.
- Low pumpable viscosity on the surface helped prevent higher pumping and friction pressures.
- Controlled crosslinking can be achieved as per requirements, depending on the type of crosslinker.
- A wide choice of polymers are available to gel organic ester, varying from natural to synthetic polymers, depending on bottomhole temperature.

- A wide choice of organic esters are available to gel with stimuli responsive polymers, depending on bottomhole temperatures.

### Acknowledgments

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