



Effect of elastic properties on the propagation of gelled and in-situ gelled acids in carbonate cores

Ahmed M. Gomaa^{*,1}, Hisham A. Nasr-El-Din

Petroleum Engineering Department, Texas A&M University, College Station, TX, USA

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ABSTRACT

Polymer-based acids exhibit some viscoelastic properties. Therefore, the objectives of this study are to determine the elastic and viscous properties of these acids, how these properties change as the acid reacts with carbonate formations, and their effect on the propagation of the acid inside 20-in. long carbonate cores.

Live gelled and in-situ gelled acids had weak elastic properties, while partially neutralized (pH 3.2) in-situ gelled acid had strong elastic properties. Polymer filter cake was observed for the cores that were treated with gelled acid while the cores that were treated with in-situ gelled acids did not form this filter-cake. In-situ gelled acid formed a thin layer of gel that minimized leakoff, which prevented the formation of filter cake. For gelled acid, the polymer filter cake reduced the core permeability to zero. The wormhole obtained in the case of gelled acid was nearly linear and thinner than those created by in-situ gelled acid. The strong elastic properties enhanced the ability to get the gel to remain around the wormhole, which forced the next acid stage to change its direction.

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1. Introduction

The use of chemical diversion systems has recently received increased attention. Initially, the industry concentrated on particulate systems, which have been widely used in vertical perforated wells (Schechter, 1992). Acids viscosified by polymers are probably applicable to all completion types. They are of particular benefit in horizontal, openhole, and gravel-packed wells, where many other diversion and selective placement techniques cannot be applied. The viscous fluid can be placed efficiently along the treatment interval because it can first limit fluid loss into the formation and then divert itself from regions of high to low injectivity as it was injected into the formation (Jones et al., 1996). Jones and Davies (1998) compared using a simulator between a gelled acid with a viscosity of 70 cP at a shear rate of 100 s^{-1} and conventional low-viscosity acids based on the coverage obtained over the wellbore interval. They showed that in many cases, viscosifying the fluid can significantly improve the placement over the wellbore interval.

Two types of polymer-based acids had been used in the field: (1) gelled acid for acid retardation, and (2) in-situ gelled acids for acid diversion. Gelled acids were developed primarily for fracturing but have found some applications in matrix acidizing. They are

used in acid fracturing to increase the viscosity and decrease the leakoff rate. The same principle applies to matrix acidizing conditions in fissured or vugular formations with low primary porosity. Gelled acids can also be used as a carrier fluid for ball sealers or particulate diverters. Since gelled acid is a shear-thinning (non-Newtonian) fluid, its viscosity increases further away from the wellbore, thereby blocking the following acid and diverting it to other, less permeable zones (Economides and Boney, 2000).

In-situ gelled acid is another polymer-based acid system that has been successfully used for acid diversion in carbonate formations. In-situ gelled acid consists of HCl mixed with a gelling agent and a crosslinker (Yeager and Shuchart, 1997; Conway et al., 1999). The selected polymers should be stable in acid and contain carboxyl groups that will crosslink in the presence of ferric or zirconium ions at a pH of about 2 or greater. The lower fresh acid viscosity allows penetration in wormholes and fractures until acid reaction increases the pH and causes crosslinking, thereby diverting the following acid stages to other zones. The gel breaks at a pH above 3.5 (Hill, 2005; Patil et al., 2012).

Taylor and Nasr-El-Din (2003) examined three different in-situ gelled acids and found that the viscosity of some of these systems did not behave with the pH as claimed by some vendors. Therefore, testing of in-situ gelled acids in the lab before field application is recommended. Amro (2006) noted that the viscosity of the polymer-based in-situ gelled acids depends on shear rate, salinity, temperature, and polymer concentration. Abdel Fatah et al. (2008) found that in-situ gelled acids that are based on aluminum formed

* Corresponding author. Tel.: +1 281 357 2751; fax: +1 281 351 7764.

E-mail address: ahmed.gomaa@bakerhughes.com (A.M. Gomaa).

¹ Currently with Baker Hughes.

Nomenclature

G' elastic or storage modulus (Pa)

G'' viscous or loss modulus (Pa)

J creep compliance (strain/stress) (1/Pa)

t time (s)

a gel at pH higher than that noted with iron-based crosslinkers. Goma and Nasr-El-Din (2010) showed that simple inorganic salts had an adverse effect on the viscosity buildup of in-situ gelled acids. Polymer was separated out at high salt concentrations. Therefore, this acid should be prepared using freshwater.

Gelled and in-situ gelled acids have been used extensively in the field. No previous studies have been found that examined the rheological properties of these two acid systems. Therefore, the objectives of this study are to: (1) measure elastic and viscous properties of gelled and in-situ gelled acids, and (2) examine the effect of these properties on the propagation of these acids in 20-in. long carbonate cores.

2. Experimental studies

2.1. Materials

Hydrochloric acid (ACS reagent grade) was titrated using a 1 N sodium hydroxide solution and its concentration was found to be 36.8 wt%. Calcium carbonate powder (ACS grade) was used to neutralize live acids. Pink desert limestone cores (1.5-in. diameter and 20-in. length) had the properties given in Table 1. Deionized water obtained from a water purification system that had a resistivity of 18.2 M Ω cm at room temperature. Polymer, cross-linker, and other additives were oilfield chemicals that were used without further purification.

Table 1
Summary of the coreflood experiments.

Core no.	Porosity (vol%)	Acid type	Rate (cm ³ /min)	Volume of injected acid (PV)	Permeability (md)	
					Before acidizing	After acidizing
1	32.1	Gelled	10	3.5 ^a	89	0 ^e
2	31.1	Gelled	20	3.9 ^b	80	0 ^f
3	31.7	In-situ gelled	10	4.1 ^c	82	146
4	35.0	In-situ gelled	20	3.7 ^d	88	251

^a Acid propagated only 75% of the core.

^b Acid broke through the whole core.

^c Acid propagated only 45% of the core.

^d Acid propagated only 60% of the core.

^e During flow back, the core holder inlet was plugged by polymer filter cake. The permeability was measured after removing the polymer filter cake and was found to be 251 md.

^f During flow back, the core holder inlet was plugged by polymer filter cake. The permeability was measured after removing polymer filter cake and was found to be 871 md.

Table 2
Formula of gelled and in-situ gelled acids.

Component	Gelled acid	In-situ gelled acids
Hydrochloric acid	5 wt% HCl	5 wt% HCl
Acid gelling agent: a co-polymer of polyacrylamide emulsified in hydrotreated light petroleum distillates	20 ml/l	20 ml/l
Corrosion inhibitor: methanol (30–60 wt%), Propargyl alcohol (5–10 wt%)	4 ml/l	4 ml/l
Cross-linker: Ferric chloride (37–45 wt%)	–	10 ml/l
Breaker: Sodium erythorbate (60 to 100 wt%)	–	20 lb/Mgal
Buffer: Hydroxyacetic acid (30–60 wt%)	2 ml/l	2 ml/l

2.2. Measurements

The elastic and viscous properties of gelled and in-situ gelled acids were measured using Malvern–Bohlin Rheometer CS-10. Cone (4/40)–plate assembly with a gap of 150 μ m. Coreflood setup was constructed to simulate matrix stimulation treatments. A back pressure of 1000 psi was applied. Pressure transducers were connected to a computer to monitor and record the pressure drop across the core during the experiments. A Teledyne ISCO D500 precision syringe pump, that had maximum allowable working pressure equal to 2000 psi, was used to inject the acid inside the core. pH values for the collected samples were measured using an Orion 370 PerpHecT Ross Electrode, while calcium and iron concentrations were measured using an atomic absorbance spectrometer (AAAnalyst 700-flame type). X-ray Computed Tomography (CT) was used to scan the cores before and after acid injection.

2.3. Procedures

Gelled and in-situ gelled acids were prepared using the same polymer type and concentration. Also, both acid systems had the same HCl concentration (5 wt%) and additives. The only difference between the two systems was the addition of crosslinker (Fe^{+3}) and breaker for the in-situ gelled acid. The acid formulas used in this work are given in Table 2. It is important to highlight that these are the formulas that are typically used in the field.

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